BEFORE THE ILLINOIS POLLUTION CONTROL BOARD

DYNEGY MIDWEST GENERATION, LLC,	)	
Petitioner,	)	
v.	)	**PCB 2024-053** (Petition for Review – Alternative Source Demonstration)
ILLINOIS ENVIRONMENTAL PROTECTION AGENCY,	)	
Respondent.	)	

NOTICE OF FILING

To: See Attached Service List (Via Electronic Filing)

PLEASE TAKE NOTICE that the undersigned filed today with the Office of the Clerk of the Illinois Pollution Control Board by electronic filing the following NOTICE OF FILING, CERTIFICATE OF SERVICE, CERTIFICATE OF RECORD ON APPEAL, and RECORD ON APPEAL, copies of which are attached hereto and hereby served upon you.

Respectfully submitted,

ILLINOIS ENVIRONMENTAL PROTECTION AGENCY

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Dated: July 25, 2024

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CERTIFICATE OF SERVICE

The undersigned hereby certifies that on July 25, 2024, before 5:00 PM, she caused to be served by electronic mail, a true and correct copy of the following instruments entitled Notice of Filing and Record on Appeal to:

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This email transmission contains 835 pages.

/s/ Mallory Meade
Assistant Attorney General
Environmental Bureau

Under penalties as provided by law pursuant to Section 1-109 of the Code of Civil Procedure, the undersigned certifies that the statements set forth in this Certificate of Service are true and correct, except as to matters therein stated to be on information and belief and as to such matters the undersigned certifies as aforesaid that she verily believes the same to be true.

/s/ Mallory Meade
Assistant Attorney General
Environmental Bureau

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	)	**(Alternative Source Demonstration**
	)	**– Petition for Review)**
ILLINOIS ENVIRONMENTAL PROTECTION AGENCY,	)	
	)	
	)	
Respondent.	)	

CERTIFICATE OF RECORD ON APPEAL

Respondent, ILLINOIS ENVIRONMENTAL PROTECTION AGENCY ("Illinois EPA"), in accordance with the procedural rules of the Illinois Pollution Control Board ("Illinois PCB") as set forth in 35 Ill. Adm. Code 105.212 and 105.116, files as its Record in this cause the Illinois EPA's record of non-concurrence of the Vermilion Power Plant New East Ash Pond Alternative Source Demonstration ("ASD") which is attached and consists of the following documents:

Document #	Description	Date	Pages
1	Pages from Drever, James 1997 Geochem of Natural Waters Elements and Modeling	12/31/1997	R000002 - R000011
2	Pages from Faybishenko, Boris Dynamics of Fluids in Fractured Rock Chapter on Fracture Connections	12/31/2000	R000013 - R000022
3	US EPA SW846 Disclaimer	7/31/2017	R000024 - R000024
4	US EPA SW846 Chapter 1	7/31/2017	R000026 - R000050
5	US EPA SW846 Chapter 2	9/19/2017	R000052 - R000141
6	US EPA SW846 Method 1315	7/31/2017	R000143 - R000179

Document #	Description	Date	Pages
7	US EPA SW846 Method 1316	7/31/2017	R000181 - R000200
8	USEPA GW Guide 2017	9/19/2017	R000202 - R000231
9	Pages from Contaminant Hydrology by Fetter et al 2017	12/31/2017	R000233 - R000500
10	TITLE 35: Environmental Protection, PART 845: Standards for the Disposal of Coal Combustion Residuals in Surface Impoundments	4/21/2021	R000502 - R000641
11	Region 4 USEPA Laboratory Services & Applied Science Division: Operating Procedure - Pore Water Sampling	4/22/2023	R000643 - R000657
12	Email from Lynn Dunaway to Stefanie Diers, Sara Terranova and IEPA staff RE: Joppa AS	11/1/2023	R000659 - R000660
13	Email thread Michael Summers, Lauren Hunt, Lynn Dunaway and IEPA staff RE: Joppa West Adjusted Standard Recommendation meeting follow up	11/1/2023	R000662 - R000665
14	Email from Brian Voelker to EPA.CCR.Part845 RE: Vermilion Power Plant NEAP ASD submittal notice	12/1/2023	R000667 - R000667
15	Email from Josiah Seif to IEPA Staff RE: Vermilion Power Plant New East Ash Pond received on 12/1/2023	12/1/2023	R000669 - R000669
16	Vermilion Power Plant New East Ash Pond ASD Submittal	12/1/2023	R000671 - R000789
17	Email from Rhys Fuller to Keegan MacDonna, 12:15 PM [External] RE: Groundwater Monitoring at Vermilion Power Plant – NPDES Permit IL0004057	12/5/2023	R000791 - R000792

Document #	Description	Date	Pages
18	Email from Rhys Fuller to Keegan MacDonna, 3:01 PM [External] RE: Groundwater Monitoring at Vermilion Power Plant – NPDES Permit IL0004057	12/5/2023	R000794 - R000795
19	Email from Lauren Hunt to Josiah Seif RE: Vermilion Power Plant New East Ash Pond received on 12/1/2023	12/5/2023	R000797 - R000798
20	Email from Earth Justice to IEPA Staff RE: PRN comments on ASD for Vermilion	12/19/2023	R000800 - R000816
21	Email from Justin Bierwagon to Lynn Dunaway, Lauren Hunt RE: Draft ASD Vermilion Letter	12/20/2023	R000818 - R000820
22	Email from Justin Bierwagon to Lynn Dunaway, Lauren Hunt RE: Draft ASD Vermilion Letter	12/28/2023	R000822 - R000825
23	Vermilion Power Plant New East Ash Pond ASD Nonconcurrence Letter	12/28/2023	R000827 - R000828

I, Lynn Dunaway, of the Illinois EPA, hereby certify that the documents of the Record on Appeal filed in the above reference matter and summarized in the above Index are complete to the best of my knowledge, information, and belief.

BY: Lynn Dunaway

Lynn Dunaway
Former Environmental Protection Specialist IV; Current Contract Employee
Illinois Environmental Protection Agency

Respectfully submitted,

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Attorney General of the
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Dated: Wednesday, July 24, 2024

DOCUMENT

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by organisms (nitrogen, phosphorus, sometimes carbon, potassium, and silica), biological processes are often the dominant control in surface waters. For elements utilized in only trace amounts (e.g., Mn, Cu, Ni, Mo, and Se), uptake by organisms in open waters such as lakes probably affects dissolved concentrations significantly only in environments where concentrations are low in general. In environments where concentrations are high as, for example, in polluted waters, the amounts taken up by organisms are likely to be small compared to the amounts in solution or to the amounts removed by adsorption processes.

In terrestrial systems uptake by plants can have a major influence on both heavy metals and organic compounds. One method of water treatment is to route a contaminated water through an artificially constructed wetland—a swamp with abundant plants (e.g., Wieder, 1993). Contaminants are removed by direct plant uptake, by adsorption on solid organic matter, and by precipitation as sulfides where the environment is anaerobic. One problem with artificial wetlands is that their lifetime is generally finite (a decade or so), and then the material that makes up the wetland must be disposed of.

:HAVIOR OF SPECIFIC ELEMENTS

Several specific elements are discussed here to provide an overview of their behavior and to illustrate patterns of behavior that are common to many other elements.

Copper, Zinc, Cadmium, and Lead

These elements have several features in common. The dominant species in solution is a divalent cation (free or complexed). Under oxidizing conditions, they are soluble under acid conditions and their solubilities at higher pH are limited by the solubility of a carbonate or oxide/hydroxide (Figs. 9-12 to 9-16; these and subsequent figures have been simplified by omission of some possible complexes in solution involving sulfate, sulfide species, carbonate species, and OH^-. These omissions do not significantly change the diagrams for the conditions commonly encountered in fresh waters). Under reducing conditions, in the presence of sulfur all form relatively insoluble sulfides. In the absence of sulfur, copper is insoluble as the native metal (Fig. 9-16). The others behave as they do in oxidizing environments: they are relatively soluble at low pH and insoluble as carbonates/oxides/hydroxides at high pH. Copper, zinc, and cadmium form anionic species at high pH. It is rare, however, for pH values in nature to be sufficiently high for such species to be important. The response of these elements to a change in redox conditions is determined less by redox reactions involving the elements themselves than by changes occurring in sulfur species, and in Fe and Mn oxyhydroxides, which are important substrates for adsorption.

All members of the group are complexed by natural organic matter. Some binding constants for complexing of the M^{2+} ion with humic substances are shown in Table 9-2. These constants give a general indication of the strength of interaction between the metal and dissolved organic matter. The constant for calcium is included for comparison. In general, copper is the most strongly complexed member of the group and is very commonly influenced by organic complexation. Lead is next, followed by zinc and cadmium. Complexing of zinc and cadmium by organic solutes is, generally speaking, important only where concentrations of dissolved organic carbon are relatively high.

All members of the group are potentially affected by adsorption on iron and manganese oxyhydroxides (Fig. 9-17), and Cd is potentially affected by adsorption on calcite. As discussed in Chapter 5, adsorption is pH dependent. Lead adsorbs at the lowest pH, followed by Cu, Zn, and Cd. The curves shown in Fig. 9-17 illustrate the results of experiments conducted under a specific set of conditions and should not be overgeneralized.

The expected behavior of these metals in the environment can be summarized as follows: under oxidizing conditions at low pH, they are all soluble and mobile. As the pH rises, their concentrations tend to decrease, first because of adsorption (particularly for Pb and Cu), and then because of the limited solubility of carbonates and oxides/hydroxides. Under reducing conditions, if sulfur is present, all should be immobilized as sulfides. If sulfur is absent, for Zn, Cd, and Pb the solubility control will be the same as under oxidizing conditions; Cu should be insoluble at all pH values. Adsorption is generally less important under reducing conditions because the most important substrates for adsorption, Fe and Mn oxyhydroxides, tend themselves to dissolve.

Arsenic and Selenium

Arsenic and selenium differ strongly from the previous examples in that both elements undergo important changes in oxidation state themselves, and both occur in solution as anions or as neutral species rather than as cations. *pe*-pH diagrams are shown in Figs. 9-18 and 9-19. Under oxidizing conditions, the dominant form of arsenic is the +V oxidation state, which is present as arsenic acid and its anions (arsenate), corresponding closely to phosphoric acid and phosphate species. For selenium, the dominant form under oxidizing conditions is selenate, which is closely analogous to sulfate. As conditions become reducing, As(V) is reduced to As(III)—arsenious acid and arsenite anions. When sulfate reduction occurs, As precipitates as a sulfide; if sulfur is absent, it remains in solution as arsenious acid or an arsenite. Elemental arsenic should be a stable species under highly reducing conditions, but it does not occur commonly in nature. For selenium, selenite species (analogous to sulfite) occur at intermediate redox levels, followed by elemental selenium and hydrogen selenide (analogous to hydrogen sulfide) species under strongly reducing conditions. Both

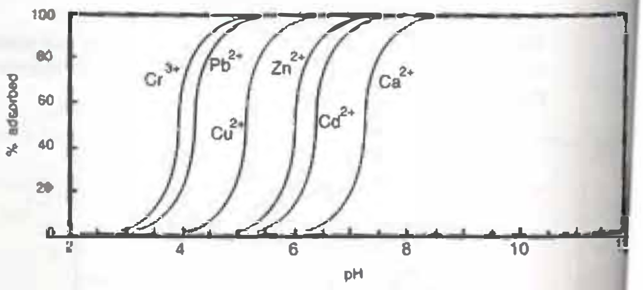

FIGURE 9-17 Adsorption of Cu^{2+}, Cd^{2+}, Zn^{2+}, Pb^{2+}, Cr^{3+}, and Ca^{2+} (for comparison) on hydrous ferric oxide as a function of pH. Each metal shows an adsorption "edge"; at pH values below the edge, the ion is not adsorbed or very weakly adsorbed. At pH values above the edge, the ion is strongly adsorbed. Conditions correspond to a high ratio of hydrous ferric oxide to adsorbing cation and an ionic strength of 0.1 m. The edges move towards higher pH as the ratio adsorbing cation:hydrous ferric oxide increases. From data in Dzombak and Morel (1990).

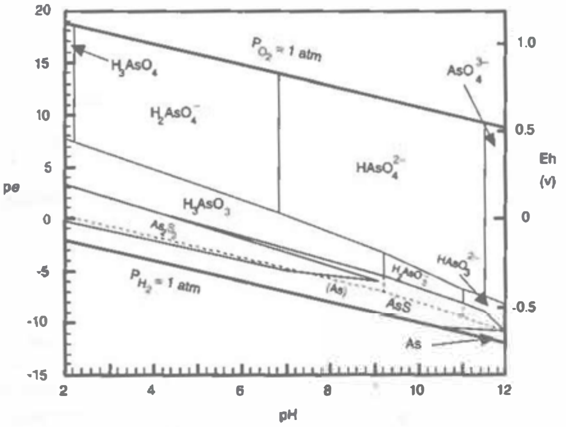

FIGURE 9-18 Simplified pe–pH diagram for the system As–O–H_2O at 25°C and one atm. Total activity of sulfur species = 10^{-2}. Light lines are boundaries involving dissolved species only. Dashed line is field of solid elemental arsenic in the absence of sulfur. Solubility is defined as a dissolved As species activity of 10^{-6}.

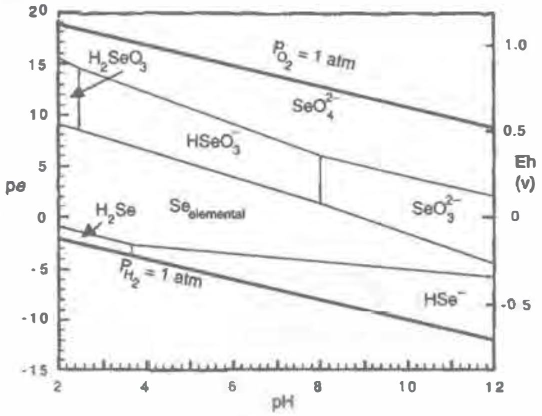

FIGURE 9-19 Simplified pe–pH diagram for the system Se–O–H_2O at 25°C and one atmosphere. Solubility is defined as a dissolved Se activity of 10^{-6}. Data are from Cowan (1988).

arsenic and selenium may be incorporated into iron sulfides under reducing conditions. The kinetics of redox transformations involving arsenic and selenium are slow, so disequilibrium is common (Kent et al., 1994; Runnells and Lindberg, 1990).

Arsenate species form inner-sphere complexes at the iron oxyhydroxide surface and are strongly adsorbed at near-neutral pH (Fig. 9-20). At high pH the strong negative charge on the oxide surface decreases adsorption of anions. As(III) apparently does not form inner-sphere complexes at the oxide surface. It is not strongly adsorbed at any pH value. For selenium, the adsorption picture is reversed. The oxidized form is only weakly adsorbed (similar to sulfate), whereas Se(IV) is strongly adsorbed under near-neutral conditions.

Organoarsenic compounds occur in nature but do not appear to be particularly important in the overall cycle of arsenic. Organic forms of selenium are more important, particularly in plants that accumulate selenium. Certain plants, notably vetches of the genus *Astragalus*, can accumulate high concentrations of selenium and may cause toxicity problems for livestock.

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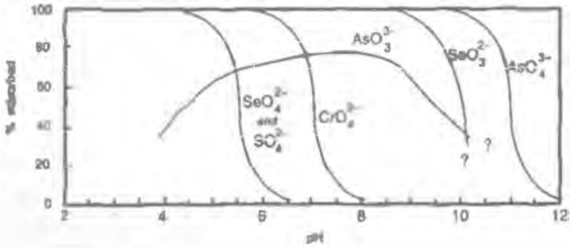
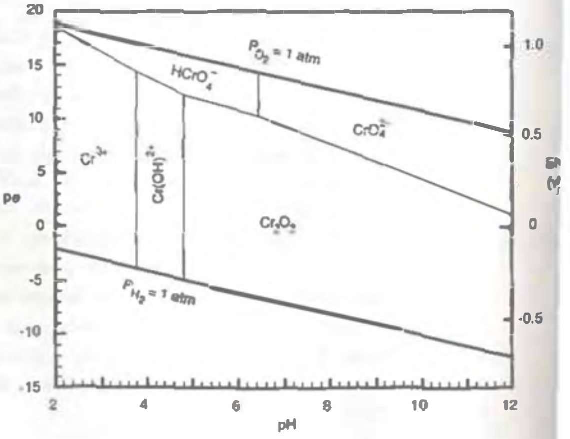


FIGURE 9-20 Adsorption of arsenate, arsenite, selenate, selenite, chromate, and sulfate (for comparison) on hydrous ferric oxide as a function of pH. Most of the anions show an adsorption "edge"; at pH values above the edge (for anions), the ion is not adsorbed or very weakly adsorbed. At pH values below the edge, the ion is strongly adsorbed. The anomalous behavior of arsenite is related to the fact that AsO_3^{3-} is fully protonated to H_3AsO_3 below pH 9 (Fig. 9-18); the symbol AsO_3^{3-} is used for all As in the +III oxidation state. Conditions correspond to a high ratio of hydrous ferric oxide to adsorbing cation and an ionic strength of 0.1 m. The edges move towards lower pH as the ratio adsorbing anion:hydrous ferric oxide increases. From data in Dzombak and Morel (1990).

Chromium

Chromium (Fig. 9-21) shows some similarities to both of the groups of elements discusse above. Under highly oxidizing conditions, the hexavalent form (chromate) is stable as a anion. It is not strongly adsorbed (adsorption edge at about pH 7, Fig. 9-20) and is therefor mobile in the environment. Under intermediate and reducing conditions, Cr(III) is the stabl oxidation state. It is insoluble in the neutral and alkaline pH ranges. It is soluble (largely a $Cr(OH)^{2+}$) under acid conditions. In general, Cr(III) species are strongly adsorbed (Fig. 9-17 Where dissolved chromium pollution occurs, the problem form is generally Cr(VI).

FIGURE 9-21 pe–pH diagram for the system Cr–O–H_2O at 25°C and one atm. Solubility is defined as a dissolved Cr activity of 10^{-6}. Data from Brookins (1988).



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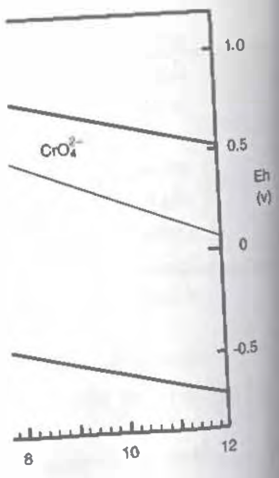


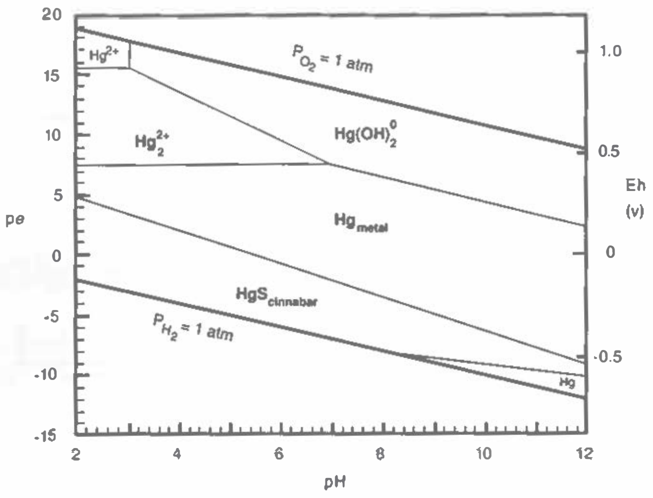


FIGURE 9-22 pe–pH diagram for the system Hg–S–O–H_2O at 25°C and one atm. Solubility is defined as a dissolved Hg activity of 10^{-6}. Total activity of sulfur species = 10^{-2}. The diagram is the same in the absence of S species, with the HgS (cinnabar) field replaced by Hg (metal). In the presence of chloride, the Hg_2^{2+} may be replaced by the insoluble mercurous chloride (calomel). Data are consistent with Allison et al. (1991).

Mercury

The chemistry of mercury in the environment is highly complex. The thermodynamically stable forms are shown in Fig. 9-22. The common soluble form is the oxidized (mercuric) Hg^{2+} ion and its hydrolysis product $Hg(OH)_2^0$, with the reduced (mercurous) Hg_2^{2+} ion being less important. Elemental mercury has a large stability field. The elemental form is volatile and slightly soluble in water. The global cycle of mercury is dominated by vapor-phase transport of Hg^0 through the atmosphere (Mason et al., 1994). Mercury is transformed by microorganisms into organic forms, notably monomethyl mercury (CH_3Hg) and dimethyl mercury [$(CH_3)_2Hg$]. These organic forms, in addition to being highly toxic, are volatile and tend to accumulate in the food chain. High concentrations of Hg in fish, which are common in polluted waters, generally result from accumulation of organomercury species. Pollutant Hg in sediments is partly transformed to organomercury species and partly to the sulfide.

Most of the metals discussed above—Cu, Zn, Cd, Pb, As, Hg, and, to a lesser extent, Se—are transformed to sulfides in anaerobic sediments. So long as conditions remain anaerobic and sulfur is available, they are relatively immobile. However, any disturbance, such as dredging, that brings the sediment into contact with oxygen will cause oxidation of the sulfides and release of the metals into solution. Cleaning up or moving contaminated sediments is a difficult problem because it may lead to oxidation and mobilization of these metals.

SUMMARY

1. To understand the behavior of any trace element in natural waters, it is essential to know the chemical form of the element in the water of interest. Anomalously high concentrations are often related to the presence of stable complexes in solution.

2. The solubility of phases containing the element as a major constituent (commonly an oxide/hydroxide, carbonate, or sulfide) provides a general upper limit to the concentration of a specific element.

This is exactly the expression we had for a non-adsorbed solute (Eq. 16–9), but with D/R substituted for D (which could be either a dispersion coefficient or a diffusion coefficient). Thus spreading by diffusion or dispersion is retarded in an analogous manner to advection. Provided dispersion is much greater than diffusion, the geometry of movement and spreading of an adsorbed solute as it moves through an aquifer will be exactly the same as that of an unadsorbed solute, but the time taken to reach a particular position and "width" will be a factor of R longer.

Adsorption affects only non-steady-state diffusion. At steady state (e.g., a constant concentration gradient between a constant source and a constant sink), there is no net uptake or release by adsorption, so adsorption has no effect on diffusion. The diffusional flux will be given by Fick's first law with no correction for adsorption.

The above discussion applies only to the limiting case of rapid, reversible, linear adsorption. Because of its mathematical convenience, the retardation equation based on the linear K_d is often used as an approximation even where these conditions do not hold. It should also be remembered that, in general, the numerical value of K_d is specific to the solute, the substrate, and the composition of the groundwater. It is not readily transferred from one experiment or situation to another.

Example 3

Suppose the pollutant in Example 2 above is adsorbed by the sediment, and the adsorption can be described by a constant K_d of 5 ℓ/kg. How long will it now take for the pollutant to reach a depth of 50 cm?

If we assume a grain density of 2.6 g/cm^3, the redardation factor, R, is

$$\left(1+\frac{0.3}{0.7}\times 2.6\times 5\right)=6.57$$

The times calculated in Example 2 will be multiplied by this number. The time for 1 percent of the initial concentration to reach 50 cm will thus be 10.97 y rather than 1.67 y. Note that, for a given K_d, the retardation factor increases as the porosity decreases as a result of the factor $(1-\phi)/\phi$. If, in this example, the porosity had been 10 percent rather than 70 percent, the retardation factor would have been 118 rather than 6.57.

REACTION PATH MODELING

Reaction path calculations, or *mass-transfer* codes, give us the successive compositions of a solution as a mineral (or several minerals) reacts with a solution or as some other process, such as evaporation of the solution, proceeds. The mass of each solid phase or gas produced or consumed is calculated. Such codes do not, in general, contain any kinetic information: They calculate changes as a function of the amount of reaction that has taken place but do not say anything about how long the reaction should take. The most widely available and widely used codes are PHREEQE (Parkhurst et al., 1980), EQ3/6 (Wolery, 1979), SOLMINEQ.88 (Kharaka et al., 1988), and MINTEQA2 (Allison et al., 1991). PHRQPITZ (Plummer et al., 1988) is a version of PHREEQE modified to include Pitzer's equations for calculations at high ionic strength (see Chapter 2); PHREEQC (Parkhurst, 1995) is an updated version of PHREEQE that includes inverse modeling analogous to NETPATH (see Chapter 12 and later in this chapter). Each of these codes was developed for a slightly different purpose, which gives them advantages and disadvantages for particular applications. PHREEQE is a relatively versatile code that can model many different types of reaction at a fixed temperature. However, the database supplied is fairly limited, particularly for trace elements, so the user may have to enter all the information for particular elements/reactions him/herself. It is not a particularly easy code for a beginner to use. MINTEQA2 is in a sense the reverse: it has an extensive database and is quite "user friendly," but the range of calculations it can perform is more limited. EQ3/6 is a large, complex, and versatile program, currently geared towards simulations associated with radioactive waste disposal. It can simulate reactions with changing temperature as well as reactions at a fixed temperature. SOLMINEQ.88 was designed particularly to simulate processes associated with petroleum basins, which implies moderately elevated temperatures and the presence of several organic species.

As an example of a reaction path calculation, let us consider the case of a mineral reacting with water. The general approach is:

1. A small increment of the mineral is dissolved.
2. A speciation-saturation program (Chapter 2) tests if the solution is supersaturated with respect to any solid phase. (The speciation–saturation program is part of the mass-transfer code. Thus each of these codes can be used for speciation–saturation calculations.)
3. If the solution is supersaturated with respect to any phase (or to specific phases specified by the user), an amount of that phase is precipitated sufficient to bring the solution into equilibrium with that phase. If the solution becomes undersaturated with respect to a previously precipitated phase, that phase redissolves to establish equilibrium.
4. An iteration procedure ensures that the solution is in equilibrium with all solid reaction products before another increment of the original mineral is dissolved.

The procedure for simulating evaporation is the same, except that increments of water are removed instead of increments of mineral being added. The calculated composition of a solution reacting with K-feldspar is shown in Figs. 16-10 and 16-11.

Although mass transfer programs in the strict sense calculate only the path that the solution composition will follow and do not contain any rate expressions to relate reaction progress to time, it is possible to combine a mass-transfer model with a kinetic model to predict solution composition as a function of time. Examples include KINDIS (Madé et al., 1990) and PHREEQM (Appelo and Postma, 1993). There is some question as to whether our understanding of kinetics at low temperatures is sufficient for this approach to be realistic.

Example 4

A mining company proposes to dig a pit, which will be left to form a lake at the end of mining operations. The composition of the groundwater that will flow into the pit is shown in Table 16-2. The bedrock is altered granite containing calcite as the only reactive mineral. Use MINTEQA2 to predict the composition of the final lake.

In order to solve this problem, we need to make some simplifying assumptions. Some of these are:

1. A chemical equilibrium model is a suitable approximation.
2. The final lake will be in equilibrium with atmospheric oxygen and CO_2.

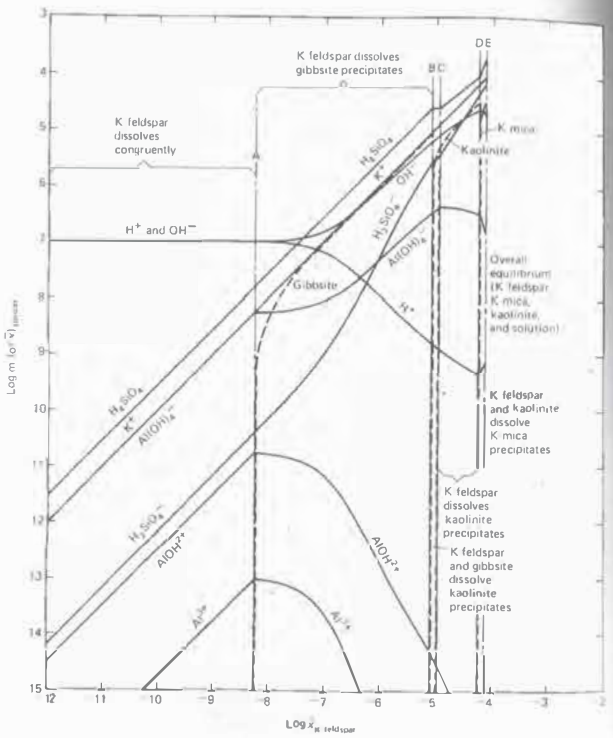
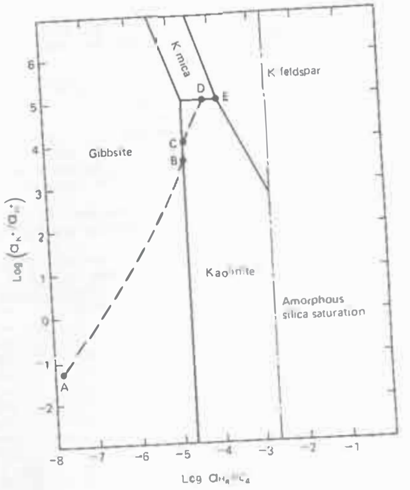


FIGURE 16-10 Concentration (m) of species in the aqueous phase (solid lines) and amounts (mol/kg H_2O) of minerals produced and destroyed (dashed lines) as K-feldspar reacts with water at 25°C and 1 atm pressure. The abscissa represents the number of moles of K-feldspar destroyed per kg H_2O. The letters correspond to the points on the reaction path shown in Fig. 16-11 (Helgeson et al., 1969).

3. Reactions involving silicates can be ignored. The justification for this assumption is that the groundwater has been in contact with the silicate minerals surrounding the pit for a long time and should be close to equilibrium or at least steady state.
4. Our time span and flow rate are such that evaporation and dilution by rainfall can be neglected. In reality these would be incorporated into the model. They are omitted here for the sake of simplicity.

FIGURE 16-11 Path of solution composition (ABCDE) as K-feldspar reacts with water, plotted on a mineral stability diagram (after Helgeson et al., 1969).



The first step is to use MINTEQA2 as a speciation-saturation program only, with the water of Table 16-2 as the input. This has two purposes: (1) To see which phases are supersaturated and hence are likely to precipitate, and (2) To convert the alkalinity input into total concentration of carbonate species and concentration of the component H^+. MINTEQA2 requires the input to be in this form for further calculations. At this stage we also have to decide on an oxidation state for the Fe in the analysis. We can either input it as Fe^{2+} (which is probably the actual form), or we can input it as the oxidized species, Fe^{3+}, with the justification that the final water will be in equilibrium with atmospheric oxygen. If iron is input as Fe^{3+}, MINTEQA2 does not have to perform any redox calculations, as all the inputs are in their oxidized form. There are often advantages to minimizing the number of different reactions that the reaction path code has to consider simultaneously. The concentration of Fe is sufficiently low that the choice of oxidation state does not affect the cation–anion balance significantly. Part of the output from this first run is shown in Table 16-3.

TABLE 16–2 Composition of Inflow Water for Example 4

Na	64.2	ppm	As	0.05	ppm
K	17	ppm	Cu	0.014	ppm
Ca	151.4	ppm	Zn	1.1	ppm
Mg	54.6	ppm			
Cl	23.8	ppm	pH	7.51	
SO_4	104	ppm			
Alkalinity	12.54	meq/ℓ	T	20°C	

We can see from Table 16-3 that the water is supersaturated with respect to various phases, including calcite, dolomite, magnesite, and a range of compounds containing ferric iron (ferrihydrite, goethite, hematite, jarosite, etc.) the high saturation indices for these phases is a consequence of our decision to specify the total Fe as Fe^{3+}. The next step is to choose which phases will precipitate. We shall choose ferrihydrite as the iron compound, as it is the phase most likely to precipitate. We shall also choose calcite as a phase likely to precipitate in a natural system, but we shall not allow dolomite (or other Mg-carbonate phases) to precipitate because the kinetics of precipitation of these phases are generally slow (Chapter 3). Note that no phases containing the trace elements Cu, Zn, or As are supersaturated.

With these choices, we can now perform a second MINTEQA2 run in which we:

1. Do not specify the input pH, instead allowing MINTEQA2 to calculate the pH.
2. Specify equilibrium with a CO_2 gas phase at a pressure of 3.16×10^{-4} atm (atmospheric CO_2 pressure). We could also list O_2 at a fixed pressure of 0.2 atm, but this is unnecessary if our input does not contain any reduced species.
3. Specify calcite and ferrihydrite as *possible solids*. A possible solid is one that is allowed to precipitate if the solution is supersaturated with respect to it. Phases that are not listed in this way (or in an analogous way) will not be considered in the calculations.

Part of the output from this run is shown in Table 16-4. The solution is in equilibrium with calcite and ferrihydrite, and has a final pH of 8.88. This output would constitute our prediction for the major ions in solution. Note that the solution is still supersaturated with respect to ferric (hydr)oxides more stable than ferrihydrite (Chapter 7), and with respect to Mg-containing carbonates. 99.9 percent of the iron has been precipitated as ferrihydrite, and 98.6 percent of the calcium as calcite. The presence or absence of calcite in the bedrock would make no difference to the calculation, as calcite is precipitating and not dissolving. The main reason why so much calcite precipitated is the drop in P_{CO_2} from a value of $10^{-1.7}$ in the inflow water to $10^{-3.5}$ in the equilibrated pit lake.

So far, the only process we have considered is precipitation of supersaturated phases. Adsorption is also likely to be a significant control on trace element concentrations, particularly As, Cu, and Zn in our example (Table 16-2). As discussed in Chapter 5, adsorption can also be modeled by use of MINTEQA2. This calculation is performed after the major element chemistry has been calculated. It is necessary to specify the amount and properties of the adsorption substrate, which requires further assumptions. The details of these calculations are not presented here. A reasonable set of assumptions would be that ferrihydrite is the adsorbing phase, the amount present is equal to the amount precipitated in the previous modeling step, and its properties are the same as those of ferrihydrite used in laboratory experiments by Dzombak and Morel (1990). The Dzombak and Morel numbers are supplied as a data file with MINTEQA2. Calculations based on these assumptions indicate that adsorption should greatly reduce the concentrations of arsenic, copper, and zinc.

Application to Contaminant Transport in Groundwater

It has become recognized in recent years that human activities are introducing contaminants into groundwater systems on an enormous scale. Examples include leaching from municipal landfills, hazardous waste burial sites, mine tailings, and various spills, both deliberate and accidental. Agriculture itself often causes contamination of groundwater by fertilizers (notably nitrate) and pesticides. A great deal of effort is currently being put into modeling the

TABLE 16-4 Output from the MINTEQA2 Equilibration Calculation for Example 4 (The output file has been greatly condensed.)

```
_____________________ PART 1 of OUTPUT FILE________________________
Example 4: Equilibration with atmosphere and solid phases


-------------------------------------------------------------------
  Temperature (Celsius):  20.00
  Units of concentration: MG/L
  Ionic strength to be computed.
  If specified, carbonate concentration represents total inorganic carbon.
  Do not automatically terminate if charge imbalance exceeds 30%
  Precipitation is allowed only for those solids specified as ALLOWED
    in the input file (if any).
  The maximum number of iterations is:  40
  The method used to compute activity coefficients is: Davies equation
  Intermediate output file
-------------------------------------------------------------------
INPUT DATA BEFORE TYPE MODIFICATIONS
   ID        NAME        ACTIVITY GUESS     LOG GUESS   ANAL TOTAL
   330  H+1                 1.000E-07         -7.000    1.370E+01
    61  H3AsO4              3.548E-07         -6.450    5.000E-02
   150  Ca+2                3.802E-03         -2.420    1.514E+02
   180  Cl-1                6.761E-04         -3.170    2.380E+01
   231  Cu+2                2.188E-07         -6.660    1.400E-02
   281  Fe+3                2.291E-05         -4.640    1.270E+00
   460  Mg+2                2.239E-03         -2.650    5.460E+01
   410  K+1                 4.365E-04         -3.360    1.700E+01
   500  Na+1                2.818E-03         -2.550    6.420E+01
   732  SO4-2               1.072E-03         -2.970    1.040E+02
   950  Zn+2                1.698E-05         -4.770    1.100E+00
   140  CO3-2               9.333E-05         -4.030    7.859E+02
     2  H2O                 1.000E+00           .000    0.000E-01

      Charge Balance: UNSPECIATED
        Sum of CATIONS=  2.900E-02 Sum of ANIONS =  2.906E-02
        PERCENT DIFFERENCE =  1.065E-01  (ANIONS - CATIONS)/(ANIONS + CATIONS)

  Type V - POSSIBLE SOLIDS
    ID        NAME         CALC MOL       LOG MOL   NEW LOGK      DH
  5015001  CALCITE         1.937E+02      2.287      8.446      2.585
  2028100  FERRIHYDRITE    6.817E+02      2.834     -4.891       .000
___________________________________________________________________
______________________ PART 5 of OUTPUT FILE ______________________

                 --------------------------------------------
                 -------EQUILIBRATED MASS DISTRIBUTION-------

                           DISSOLVED             SORBED              PRECIPITATED
 IDX     NAME          MOL/KG    PERCENT    MOL/KG    PERCENT     MOL/KG     PER-
 CENT

 330   H+1           4.365E-03    100.0    0.000E-01      .0     0.000E-01      .0
  61   H3AsO4        3.527E-07    100.0    0.000E-01      .0     0.000E-01      .0
 950   Zn+2          1.685E-05    100.0    0.000E-01      .0     0.000E-01      .0
 180   Cl-1          6.721E-04    100.0    0.000E-01      .0     0.000E-01      .0
 231   Cu+2          2.206E-07    100.0    0.000E-01      .0     0.000E-01      .0
 732   SO4-2         1.084E-03    100.0    0.000E-01      .0     0.000E-01      .0
 460   Mg+2          2.248E-03    100.0    0.000E-01      .0     0.000E-01      .0
```

(Continued)

```
410  K+1            4.353E-04   100.0   0.000E-01      .0   0.000E-01     .0
500  Na+1           2.796E-03   100.0   0.000E-01      .0   0.000E 01     .0
281  Fe+3           1.853E-08      .1   0.000E-01      .0   2.275E-05   99.9
150  Ca+2           5.213E-05     1.4   0.000E-01      .0   3.730E-03   98.6
140  CO3-2          4.727E-03    55.9   0.000E-01      .0   3.730E-03   44.1
  2  H2O            9.297E-06   100.0   0.000E-01      .0   0.000E-01     .0

     Charge Balance: SPECIATED
       Sum of CATIONS =  7.178E-03 Sum of ANIONS   7.239E-03
       PERCENT DIFFERENCE =  4.291E-01  (ANIONS - CATIONS)/(ANIONS + CATIONS)
     EQUILIBRIUM IONIC STRENGTH (m) =   1.029E-02
     EQUILIBRIUM pH                 =   8.879

_______________________________PART 6 of OUTPUT FILE ___________________________
Saturation indices and stoichiometry of all minerals
    ID #      NAME       Sat. Index        Stoichiometry in [brackets]
 5015000 ARAGONITE          .154     [  1.000] 150  [  1.000] 140
 5015001 CALCITE            .000     [  1.000] 150  [  1.000] 140
 5015002 DOLOMITE          1.654     [  1.000] 150  [  1.000] 460  [  2.000] 140
 2028100 FERRIHYDRITE      0.000     [ -3.000] 330  [  1.000] 281  [  3.000]   2
 2028102 GOETHITE          4.210     [ -3.000] 330  [  1.000] 281  [  2.000]   2
 6015001 GYPSUM           -2.897     [  1.000] 150  [  1.000] 732  [  2.000]   2
 3028100 HEMATITE         13.405     [ -6.000] 330  [  2.000] 281  [  3.000]   2
 5015003 HUNTITE            .812     [  3.000] 460  [  1.000] 150  [  4.000] 140
 6041002 JAROSITE K       -7.386     [ -6.000] 330  [  1.000] 410  [  3.000] 281
                                     [  2.000] 732  [  6.000]   2
 3028101 MAGHEMITE         3.397     [ -6.000] 330  [  2.000] 281  [  3.000]   2
 5046002 MAGNESITE         1.156     [  1.000] 460  [  1.000] 140
 2023101 TENORITE          -.815     [ -2.000] 330  [  1.000] 231  [  1.000]   2
 5095000 SMITHSONITE       -.861     [  1.000] 950  [  1.000] 140
 5095001 ZNCO3, 1H2O       -.546     [  1.000] 950  [  1.000] 140  [  1.000]   2
 2095005 ZNO(ACTIVE)       -.449     [ -2.000] 330  [  1.000] 950  [  1.000]   2
 2095006 ZINCITE           -.552     [ -2.000] 330  [  1.000] 950  [  1.000]   2
 5023101 MALACHITE        -2.691     [  2.000] 231  [  2.000]   2  [  1.000] 140
                                     [ -2.000] 330
 3028102 LEPIDOCROCIT      3.520     [ -3.000] 330  [  1.000] 281  [  2.000]   2
________________________________________________________________________________
```

behavior of contaminants in the subsurface, both for predicting the fate of and designing remediation strategies for existing contaminants and for designing and locating disposal sites for future waste, particularly high-level radioactive waste.

Before any detailed geochemical modeling can be attempted, the hydrology of the area in question, particularly groundwater flow paths and velocities, must be established. This is by no means a trivial requirement; the information required for an adequate hydrologic model may be greater than that required for a chemical model, and the mathematical formulation of the hydrologic model may be extremely complex.

For modeling purposes, it is often convenient to divide the region to be studied into a source, a mixing zone (*near field,* in the terminology of radioactive waste disposal), and a relatively undisturbed aquifer or aquifers (*far field*). This is illustrated conceptually in Fig. 16-12 for a mill tailings pile. A real example of modeling applied to a uranium mill tailings pile is given by White et al. (1984) and Narasimhan et al. (1986). The source is the downward movement of solutions from the tailings pile. These solutions are oxygenated and highly acidic from the processing used in the mill and contain high concentrations of iron and several trace elements such as uranium, molybdenum, and selenium.

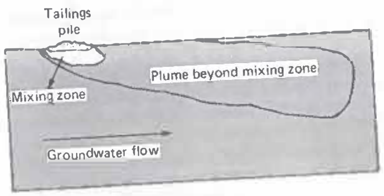


FIGURE 16-12 Schematic illustration of migration of contaminants from a uranium mill tailings pile.

Groundwaters are typically mildly alkaline and may be oxidizing or reducing. When the acid tailings solution enters the aquifer, it reacts chemically with the groundwater and with the minerals of the aquifer. Calcite dissolves, gypsum may precipitate, and iron and aluminum hydroxides precipitate, coprecipitating trace metals with them. Chemical reactions such as these can be modeled successfully by a program such as PHREEQE, MINTEQ, or EQ3/6. The mixing zone, where the major chemical reactions take place, is commonly a relatively small volume, and the hydrology of such a small volume can be modeled in a relatively simple way.

Beyond the mixing zone, the groundwater is more or less in equilibrium with the minerals of the aquifer. Dissolution and precipitation are no longer major processes, and modeling focuses on hydrology/water movement plus hydrodynamic dispersion and on relatively simple chemical processes such as adsorption, radioactive decay, and, for some organic compounds, biodegradation.

An additional problem with modeling of contaminant transport is the question of how to treat uncertainty. One can never know with certainty the porosity, permeability, and dispersivity, for example, at all points in an aquifer. One can make estimates for the regions in which data are missing and, using them, calculate, for example, a travel time for a particular solute between two locations. For problems such as disposal of high-level radioactive waste, it is important to know the uncertainty associated with the travel time as well as the "best estimate." Increasingly, *stochastic modeling* is being used to assess uncertainty. Instead of single values being assigned to the properties of each location in the aquifer, a statistical distribution of properties is assigned, and the model generates a statistical distribution of travel times or whatever other output is required.

CHEMICAL EVOLUTION OF GROUNDWATER

The reaction path modeling discussed above has been "forward" modeling in that we posed the problem in the form: "Suppose we have water A and allow it to react with minerals B and C, what will be the final composition of the water?" For understanding the chemical composition of groundwater, we are generally presented by the "inverse" problem (Plummer, 1992): we know the composition of the final water, the problem is to deduce the reactions that gave rise to it. One approach is simply to solve the forward problem repeatedly, changing the identity and amount of the minerals reacting until a "match" is achieved. Alternatively, one can use the code NETPATH (Plummer et al., 1991) or PHREEQC (Parkhurst, 1995) to solve the inverse problem directly. The use of NETPATH to solve a mass balance problem was discussed in Chapter 12. The input is an initial water composition, a final water composition, and a list of phases that may dissolve, precipitate, or both. The output is a list of all the possible reactions involving the listed minerals that satisfy the mass balance constraints. NETPATH also considers isotopic balance for ^{13}C, ^{14}C, ^{34}S, D, T, ^{18}O and ^{87}Sr, and includes WATEQ4F as a subroutine to test whether the reactions deduced from mass balance are chemically reasonable. It would not be reasonable, for example, to postulate that gypsum precipitates from a solution that is undersaturated with respect to gypsum.

An excellent example of this type of modeling is the study by Plummer et al. (1990) of the chemical evolution of groundwater in the Madison aquifer as it moves several hundred km eastward from recharge areas in Montana and Wyoming. The chemical evolution of the water was consistent with dissolution of gypsum and dolomite, precipitation of calcite, and oxidation of organic matter. That set of reactions explained not only the major element chemistry, but also the isotopes of carbon and sulfur.

A major problem with NETPATH-type modeling, particularly of silicate weathering reactions, is that solutions are rarely unique. Several different sets of minerals can usually be found that satisfy the constraints. Also, depending on the number of solid phases chosen, there may be no solution or an indeterminately large number of solutions. The code is thus a tool to be used in conjunction with geologic insight and judgment: it does not provide simple, unique answers. The inclusion of isotopes may greatly constrain the number of possible answers, provided sufficient isotopic data are available.

REVIEW QUESTIONS

1. Suppose you had a 1 mm wide fracture in an igneous rock, and the concentration of a contaminant in the fracture were kept at a constant value (say by rapid flushing). How long would it take for a mass of contaminant equal to the mass present in the fracture at any instant to diffuse into the rock matrix? Assume a porosity for the matrix of 0.01 and an effective diffusion coefficient of 1×10^{-7} $cm^2 s^{-1}$.
2. Suppose you assume instead (Problem 1) that the fluid in the fracture were not moving. Estimate how long it would take for half the material in the fracture to diffuse into the rock matrix. How long would it take if the fracture width were 0.1 mm?

   Note: The analytical solution to this problem is by no means simple. You could (a) make an educated guess based on example 1 above; (b) construct a simple numerical model; or (c) (if you have the background) construct a finite difference model.
3. The following analyses (from Plummer et al., 1990) represent two wells from the Madison aquifer in Montana that lie approximately along a flowline. The aquifer contains limestone, dolomite, and occasional evaporites. Use NETPATH to come up with a set (or more than one set) of reactions that could account for the difference. Do you think the reactions are plausible?

	T(°C)	pH	Ca	Mg	Na	K	Cl	SO_4	ΣCO
Well 1	11	7.58	1.87	1.15	0.10	0.02	0.05	1.46	3.31
Well 2	32	7.08	6.50	3.96	3.44	0.31	1.89	10.32	3.72

4. In Example 4 above, suppose the pit lake were to stratify, forming an anoxic hypolimnion (Chapter 8). Predict the chemical composition of the anoxic waters. Make your assumptions clear, and discuss how reasonable these assumptions are.

SUGGESTED READING

ALBARÈDE, F. (1995). *Introduction to Geochemical Modeling.* Cambridge, England: Cambridge University Press.

ANDERSON, M. P. (1979). Using models to simulate the movement of contaminants through groundwater flow systems. *CREC Critical Reviews in Environmental Control* (pp. 97–156). Boca Raton, FL: CREC Press.

ANDERSON, M. P., and W. W. WOESSNER. (1992). *Applied Groundwater Modeling: Simulation of Flow and Advective Transport.* San Diego, CA: Academic Press, Inc.

APPELO, C. A. J., and D. POSTMA. (1993). *Geochemistry, Groundwater, and Pollution.* Rotterdam, Germany: Balkema.

FETTER, C. W. (1994). *Applied Hydrogeology,* (3rd ed.). New York: Macmillan.

FREEZE, R. A., and J. A. CHERRY. (1979). *Groundwater.* Englewood Cliff's, NJ: Prentice-Hall. Chapters 7 (Chemical Evolution of Natural Groundwater) and 9 (Groundwater Contamination).

LICHTNER, P. C.; C. I. STEEFEL; and E. H. OELKERS, (Eds.) (1996). Reactive transport in porous media. *Reviews in Mineralogy,* (v. 34). Washington, DC: Mineralogical Society of America.

DOCUMENT
2

Predicting Hydrology of Fractured Rock Masses from Geology

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Fracture network connectivity often dominates movement rate, flow volume, and mass transport through rock masses. These networks influence the effectiveness of petroleum reservoir development, safe disposal of nuclear waste, delineation of water supply or establishment of well-head protection plans, recovery from geothermal reservoirs, solution mining, construction of underground openings, and the remediation of contaminated rock. Well tests can provide a great deal of useful information on the hydraulic properties of fracture systems, but they are often expensive or logistically infeasible. These tests also may not provide an accurate description of the hydrologic properties of the rock volume under consideration. Methods to model fractured rock can be improved by quantifying the relation between geologic parameters and the hydrologically conductive fractures. This study illustrates the application of four statistical and pattern recognition methods—evaluation of correlation coefficients, contingency table analysis, multivariate regression, and neural net analysis. The data for the study consist of borehole and well-test information from eight boreholes used for characterizing a proposed low-level radioactive waste repository in Wake County, North Carolina. The analyses show that high localized flow rates are related to the presence of increased fracture intensity, and that this intensity is controlled by a complex interplay of structural geology and lithology. Some of the initial hypotheses concerning the relation of geology to hydrology were not substantiated by the data, leading to a refined conceptual model that differed in significant ways from the initial model. Although the techniques used are of general applicability, the precise nature of the correlation between geology and hydrology is site dependent.

1. INTRODUCTION

1.1 Overview

Fractures are geologic features that form networks capable of transporting fluids through rock over long distances. The rate of movement, the volume of flow, the amount of mass transport through the system interconnected fractures affect petroleum reser development, safe disposal of nuclear waste, delineatio water supply or establishment of well-head protec plans, recovery from geothermal reservoirs, the efficie of solution mining, the construction of undergro openings, and the remediation of contaminated rock.

It is common for engineers and hydrologists to em hydrologic testing to directly characterize fracture netw flow parameters. However, well tests are often expen

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or logistically infeasible. For example, the number and spatial reach of wells drilled from an offshore oil platform are very much restricted. This may cause direct hydrologic test results to be very sparse for the volume of rock under consideration. It also presents a problem because hydrologic heterogeneity is often quite significant, so that and, therefore, a few tests may not provide an accurate description of the hydrologic properties of the large volume of rock under consideration. Such a situation makes it necessary to infer parameters from the well or boreholes to a much larger volume of rock.

There are two broad approaches to modeling flow and transport in fractured rock [*National Research Council*, 1996]: the Discrete Fracture Network (DFN) approach and the Stochastic Continuum (SC) approach. Both methods have advantages and disadvantages.

DFN models require the specification of the geometry, location, and hydraulic properties of the fractures that play a significant role in the rock permeability.

SC models need permeability and porosity values that reflect the local matrix and fracture systems' effective properties at the scale and shape of the numerical grid. SC models incorporate geology to delineate large-scale statistically homogeneous regions, often referred to as *domains* or *zones*. Parameter values within these domains can be assigned according to statistical distributions or conditioned to geologic parameters. Often, the relation between mappable geology and values of effective permeability is not well understood. Parameter assignment within each domain is carried out using a spatial statistical model or an inversion that matches known well test results, but is constrained elsewhere to statistical parameters only [*Zimmerman et al., 1998*]. Better geologic conditioning of the parameter values within zones and better definition of zones can greatly improve model accuracy [*La Pointe et al.*, 1996; *National Research Council*, 1996].

Over the past decade, DFN models [*Hudson and La Pointe*, 1980; *Long et al.*, 1982; *Dershowitz*, 1984; *Endo et al., 1984; Robinson*, 1984; *Smith and Schwartz, 1984*] have evolved to successfully address problems of regional fracture network connectivity [*Cacas et al.*, 1990a,b; *Dershowitz et al.*, 1992; *Swaby and Rawnsley*, 1996]. The models represent fractures as polygons with flow and transport properties. However, the specification of these models relies upon accurately describing the geologic context of the subset of fractures that contribute to large-scale flow. This subset of fractures constitutes the network of *conductive* fractures. As detailed surveys of wellbores prove, only a portion, often less than 10% [*National Research Council*, 1996] play a role in flow at the scale of contaminant dispersal, energy production, or containment of nuclear waste. It is the intensity, geometry, and fluid-flow properties of this conductive subset that control the important behavior of fracture-dominated flow systems.

Thus, better understanding of the geologic habitat of conductive fractures could lead to improved DFN modeling, as well as a better understanding of why some fractures play a significant role in regional flow, while others play a limited, or insignificant role.

The attractiveness of geologically conditioning DFN or SC models rests on the presumption that hydrology relates to geology. By understanding the geologic characteristics that are associated with hydrologic variability, it is possible to describe the conductive fracture network or assign values of permeability (or other properties) at unsampled locations based upon the geologic characteristics.

The geologic approach is very appealing, since it is much more flexible in handling hydrologic variability as a result of variability in underlying geology than any zonal statistical model. This is because the geologic approach need not conform to overly simplistic statistical models. Moreover, a demonstrated connection between mappable geology and flow modeling is important in many licensing applications for proposed waste repositories or other facilities. Another advantage is that the geology is often known with reasonably high accuracy and resolution throughout the site.

However, the attempt to relate flow in fractured rock masses to underlying geology has proven challenging, particularly in fracture-dominated flow systems. Fracture network connectivity often controls flow and transport. This means that local geologic conditions might be affected by the properties of individual fractures and may not correlate to the larger-scale fracture network connectivity.

The current study attempts to understand the geologic habitat of fractures that play an important role in regional flow and mass transport. The focus of the study is a preliminary site investigation of a proposed low-level nuclear waste repository in Wake County, North Carolina. Licensing of the site requires modeling of possible movement of radionuclides through the rock and soil.

The goal of this work was to investigate the interrelation of hydrologic behavior and geologic characteristics by using multivariate analysis or other techniques, as appropriate, to help prepare the initial site conceptual model and support the development of the preliminary groundwater flow simulations. The identification of key geologic parameters was also important. These parameters needed to be measured in a manner sufficient for subsequent hydrologic modeling and so as to identify how data collection protocols might be altered in order to obtain the necessary data.

The problem of relating geology to hydrology is one of pattern recognition. Powerful and sophisticated tools to recognize patterns and correctly classify new data into proper groups are in common use in many disciplines. These tools differ in mathematical assumptions and outcomes, but all share the ability to classify data into categories. Section 1.4 below describes the methodology employed in this study in greater detail.

1.2 Data

A thorough data set was obtained for this study from geochemical surveys, hydrophysical logging, packer tests, and geologic logging. The data came from a series of eight wells, aligned from west to east. The line formed by these wells transects a prominent fault north-striking a normal fault (Figure 1). Wells W206 through W208 lie to the east of the fault in the footwall of the normal fault. Wells W201 through W205 lie in the hanging wall. As shown in Figure 1, well W205 cuts through the fault plane. Each of these boreholes was carefully logged to record both the lithologic characteristics and the attributes of any fractures present. Subsequently, the core and the borehole imagery was interpreted to create a data set in which fractures were identified, and their measured depths, orientations, apertures, and types recorded. Lithologic information was also recorded. This included grain-size classification, ranging from conglomerate to claystone, as well as the orientation and measured depth of contacts separating strata of contrasting lithology.

Hydrophysical anomalies were identified as part of the testing and logging program carried out in the eight wells. Such anomalies were determined as follows. First, a borehole was filled with deionized water and a logging tool to measure electrical conductivity is placed in the borehole. Next, the nonconductive deionized water was slowly pumped out, which allowed the conductive groundwater to flow through fractures or other permeable pathways into the borehole and be sensed by the logging tool. Continuous recording of the conductivity made it possible to identify locations and rate of groundwater flow into the borehole. The term "strength," as used in this study, refers to the magnitude of the conductivity change between the nonconductive, deionized water and the inflowing groundwater. The magnitude of the anomaly is a function of flow rate, and is used as a surrogate for fracture transmissivity or local wellbore permeability. The tool used in this study has a 1 ft (0.3 m) resolution. Together with image logs, it is possible to relate hydrophysical anomalies to fractures or other geologic features within the 1 ft intervals. Figure 2 summarizes the interpreted lithology, and shows the location and geometric aperture of detected fractures, as well as the location and magnitude of flow for hydrophysical anomalies. Figure 3 and Table 1 show the directly measured and derived geologic parameters used in this study. Parameters related to the four nearest fractures were included to account for the 1 ft resolution of the hydrophysical logs, and for any small misregistration among the hydrophysical logs, the borehole imagery, and the core.

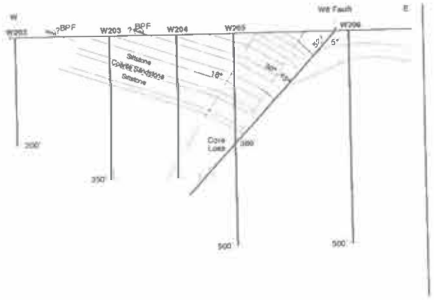

Figure 1. Geologic cross section along trench GM-1. Trench is oriented along an east-west axis. The normal fault, denoted as W8, strikes approximately north-south.

1.3 Initial Hypotheses

A preliminary focus of efforts at the Wake County site was to clarify the role of jointing and faulting in the site-scale hydrology. It was thought that fracture intensity at the site might be related to depth, weathering, structural deformation, and structural position. Thus, the study focused on evaluating some initial hypotheses concerning the relations between site geology and conductive flow features. These hypotheses are:

1. Hydrophysical anomalies are caused by fracture flow.
2. Fracture intensity is greater in the hanging-wall deformation zone.
3. Proximity to contacts between strongly contrasting lithological units leads to an increase in fracturing.
4. Fracture intensity relates to lithology.
5. Fracture intensity changes with depth/elevation because of weathering or lithostatic effects.
6. None of the above.

1.4 Methodology

A number of statistical and pattern-recognition techniques were applied to the data in order to investigate possible relations between geologic parameters and fracture flow. These studies were designed not only to test existing hypotheses, but also to uncover other unsuspected relations between geologic parameters and the

Table 1. Directly measured and derived geologic parameters.

Directly Measured Parameters	Symbol	Dimensions
Fracture Parameters		
Measured depth to fracture	MDF	Feet
Fracture dip and dip direction	DIP,DPDIR	Degrees
Fracture type: Shear or bedding	TYPE	
Fracture Aperture	AP	Inches
Lithologic Parameters		
Lithologic classification, based on grain size, gradated from 1 to 9 (1 being coarsest; 9 being finest): Conglomerate (Cnglom) = 1 Very coarse sandstone (VCrsSS) = 2 Coarse sandstone (CrsSS) = 3 Medium sandstone (MedSS)= 4 Fine sandstone (FineSS)= 5 Very fine sandstone (VFineSS)= 6 Siltstone (SiltS) = 7 Mudstone (MudStone) = 8 Claystone (Claystone) = 9	LITH	Grain size
Measured depth to contact between lithologic units	MDCON	Feet
Orientation of contact between lithologic units	CONDIP, CONDPDIR	Degrees
Layer (lithologic unit) thickness , distance measured vertically	UTHICK	Feet
Dip of contact above anomaly	DIP_A	Degrees
Dip of contact below anomaly	DIP_B	Degrees

hydrophysical anomalies. The following statistical techniques were used:

1. Evaluation of correlation coefficients among all parameters.
2. Contingency table analysis.
3. Multivariate regression.
4. Neural net analysis.

Correlation coefficients are very useful in examining the first-order relations between continuous variables such as the strength of the hydrophysical anomaly and its proximity to the boundary of a contrasting lithologic unit, or between the depth of a fracture and its aperture. These coefficients are also important in gaining an understanding of which variables may be redundant. Identifying redundant variables is important when data are sparse. When there are more variables—degrees of freedom—than hydrophysical anomalies, it is possible to predict the anomalies with a good degree of accuracy without actually determining any significant relations among the parameters.

Two-way contingency table analysis is a method for looking at the correlation among class or ordinal variables. It is also useful for examining relations between a parameter-like lithologic unit and a hydrophysical anomaly.

Contingency table analysis and correlation coefficients examine relations between pairs of variables. Multiple regression takes into account the combined relations among many variables. Multiple regression assumes that the dependent variable is a linear combination of independent (uncorrelated) variables.

Neural nets are the most complex of the methods used to investigate the relations among dependent variables and hydrophysical anomalies. This approach does not assume a simple or hypothesized model among the variables, nor does it require linear independence. Unlike multiple regression, it can also include class or ordinal variables such as lithologic type. Since the variable of interest, i.e., the hydrophysical anomaly flux rate, is a continuous variable, a Generalized Regression Neural Network (GRNN), was employed. This type of network architecture has proven very useful for this type of application [*Ward*, 1996].

Table 1(continued).

Derived Parameters		
Distance from hydrophysical anomaly to four nearest fractures	D1, D2, D3, D4	Feet
Apertures of four fractures nearest to a hydrophysical anomaly	W1, W2, W3, W4	Inches
Lithology of four nearest fractures (ranging from conglomerate to mudstone, 1 to 8)	L1, L2, L3, L4	Grain size
Depth of four nearest fractures	MD1, MD2, MD3, MD4	Feet
Lithology contrast between layer containing hydrophysical anomaly lithology and layer above; grain-size class of layer above used for computation	LCA	Dimensionless
Lithology contrast between layer containing hydrophysical anomaly lithology and layer below; grain-size class of layer above below for computation	LCB	Dimensionless
Absolute contrast above; computed as ABS(LCA)	ALCA	Dimensionless
Absolute contrast below; computed as ABS(LCB)	ALCB	Dimensionless
Total contrast between lithological unit containing anomaly and units above and below; computed as LCA+LCB	TC	Dimensionless
Total absolute contrast between lithological unit containing anomaly and units above and below; computed as ALCA+ALCB	ATC	Dimensionless
Distance from anomaly to nearest upper contact; computed as distance perpendicular to contact interface	CDA	Feet
Distance from anomaly to nearest lower contact; computed as distance perpendicular to contact interface	CDB	Feet
Minimum distance to contact; computed as MIN(CDA, CDB	CMIN	Feet
Grain size contrast with nearest unit	C_NEAR	Dimensionless
Apparent distance to upper contact	APCDA	Feet
Apparent distance to upper contact	TDIST_MIN	Feet
Apparent distance to lower contact	APCDB	Feet
Angular difference between upper and lower contact; computed as DIP_B - DIP_A	UNCONF	Degrees
Absolute value of UNCONF	ABS(UNCF)	Degrees
Bed thickness	THICK	Feet

2. RESULTS

2.1 Correlation Coefficients

Table 2 shows the correlation coefficients for all of the independent variables with hydrophysical anomaly strength. This strength has been expressed in two ways: the arithmetic strength, which is the actual measured value, and the base-ten logarithm of the measured strength. The logarithmic transformation of a variable reduces the impact of extreme values, which may be outliers or spurious measurements.

Correlation coefficients vary between -1.0 (perfect anticorrelation) and +1.0 (perfect correlation). The statistically significant correlations at the 95% level in Table 2 are those in which the absolute value of the

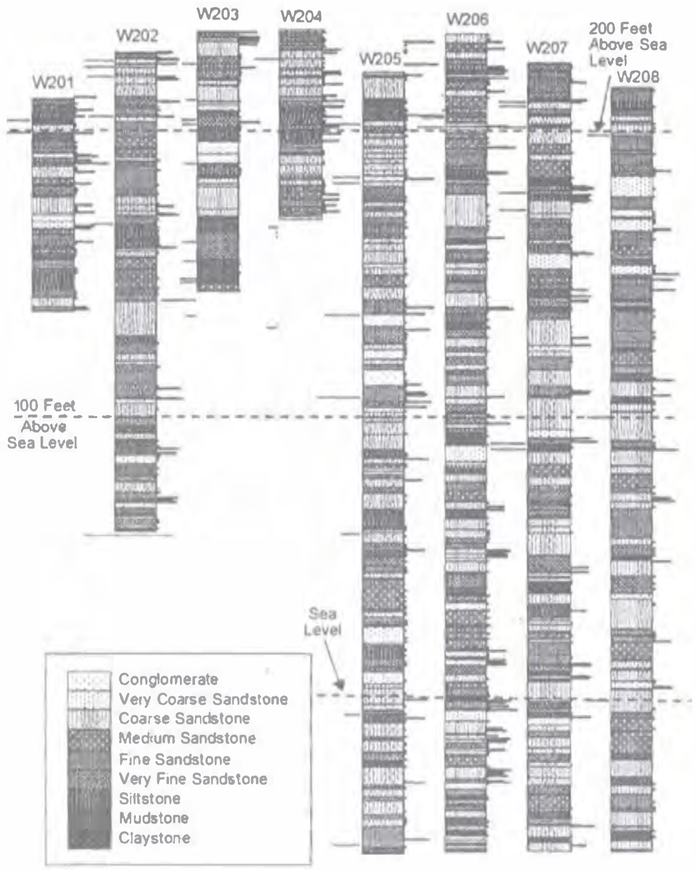

Figure 2. Summary of lithology, fractures, and hydrophysical anomalies. For each borehole, the location of hydrophysical anomalies and fractures are shown by horizontal lines. The length of the line to the left of the borehole is proportional to the logarithm of the hydrophysical anomaly magnitude, while the length of the line to the right of the borehole is proportional to the logarithm of the fracture aperture. In both cases the lines represent relative, not absolute lengths.

correlation coefficient is greater than or equal to 0.35.

This table shows that the anomaly strength and the log of the anomaly strength are positively correlated with the fracture width (aperture), the lithology of the unit in which the hydrophysical anomaly occurs, and the surrounding lithologic units, their contrast, and the dip of the contact between lithologic units. The positive correlation with lithology means that finer-grained lithological units have stronger anomalies. The positive correlation with the absolute total contrast (ATC) implies that stronger anomalies tend to be in lithologies, unlike the units immediately above and below. The correlation with contact dip may reflect structural disruption in the hanging wall of the fault, but other explanations may also be possible. The log of the anomaly strength is negatively correlated with the distance to the nearest fractures (in other words, the closer the fractures to the anomaly and the more there are of them, the stronger the anomaly).

Table 2. Correlation coefficients for flow anomaly and $\log_{10}$(anomaly) with geological parameters. Absolute values of the coefficient equal to 0.35 or greater are significant at the 95% level.

Variable	Anomaly	Log_{10} (anomaly)
W2	0.36	0.53
ALCA	0.31	0.48
ATC	0.20	0.47
W3	0.40	0.40
LITH	0.08	0.31
CONDIPB	0.47	0.27
CNEAR	−0.02	0.27
ALCB	0.00	0.23
W1	0.00	0.19
W4	−0.03	0.18
LCB	0.15	0.16
LCA	−0.25	0.15
LITHA	0.38	0.14
LITHB	−0.11	0.13
MDF	0.19	0.08
CONDIPA	0.23	0.01
APCDB	−0.01	0.00
CDB	−0.04	−0.02
CDA	0.17	−0.12
APCDA	0.19	−0.13
CMIN	0.08	−0.25
D1	−0.12	−0.34
D4	−0.15	−0.39
D3	−0.18	−0.40
D2	−0.18	−0.45

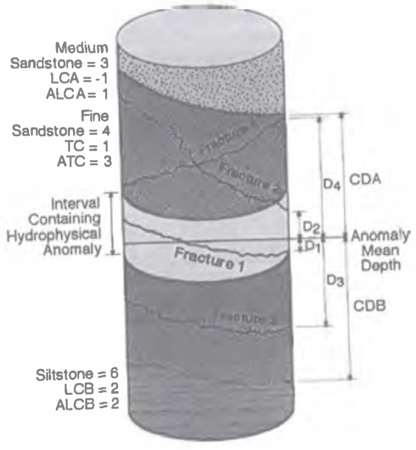

Figure 3. Derived parameters used in the statistical analyses Table 1 provides additional explanation of these and other parameters.

2.2 Contingency Tables

Contingency tables were computed for various combinations of variables. This type of analysis is useful for determining whether a variable of interest shows up with unusually high or low frequency in some other variable class. For example, do siltstones have an unusually high frequency of fractures or hydrophysical anomalies that is out of proportion to their stratigraphic percentage?

Tables 3, 4, and 5 provide overall lithology and fracture intensity data for the eight wells. Table 3 shows how lithology varies among the eight wells. This Table illustrates that fine-grained lithological layers, particularly siltstone, increase eastward from W201 to W205, where such layers reach upwards of 45% of the total amount. They decrease abruptly in the three wells to the east of W205.

Tables 4 and 5 summarize the fracture intensity by lithology and well. These tables show that fractures in the western wells (W201 through W203) tend to reside in the coarse sandstone, while in the wells nearer to the fault, the fractures tend to occur in the siltstones. However, the

Table 3. Lithology statistics by well.

Total Thickness (inches) of Lithological Layers Within Wells										
	Lithology									
Well No.	1 Cnglom	2 VCrsSS	3 CrsSS	4 MedSS	5 FineSS	6 VFineSS	7 SiltSt	8 MudStone	9 ClayStone	Total
W201		50.25	146.74	218.29	108.29	74.42	177.11	79.44		854.54
W202			188.71	432.06	420.76	209.13	550.51	147.26		1948.43
W203		72.8	175.94	351.29	9.41	34.18	354.3	88.82		1086.74
W204		4.43	117.38	107.36	63.42	74.03	326.4	29.17		722.19
W205	30.71	220.76	479.08	1388.54	590.14	299.59	3403.86	648.01	70.87	7131.56
W206	66.35	186.64	304.61	912.62	484.35	611.72	1286.1	349.94	46.55	4248.88
W207	266.82	194.12	349.49	814.3	434.02	546.04	1814.42	402.63		4821.84
W208	110.12	67.26	189.86	474.12	1822.33	759.82	1584.26	429	43.26	5480.03
Total	474	796.26	1951.81	4698.58	3932.72	2608.93	9496.96	2174.27	160.68	26294.21
Percent of Thickness of Lithological Layers Within Wells										
	Cnglom	VCrsSS	CrsSS	MedSS	FineSS	VFineSS	SiltSt	MudStone	ClayStone	
W201		5.88	17.17	25.54	12.67	8.71	20.73	9.30		
W202			9.69	22.17	21.59	10.73	28.25	7.56		
W203		6.70	16.19	32.33	0.87	3.15	32.60	8.17		
W204		0.61	16.25	14.87	8.78	10.25	45.20	4.04		
W205	0.43	3.10	6.72	19.47	8.28	4.20	47.73	9.09	0.99	
W206	1.56	4.39	7.17	21.48	11.40	14.40	30.27	8.24	1.10	
W207	5.53	4.03	7.25	16.89	9.00	11.32	37.63	8.35		
W208	2.01	1.23	3.46	8.65	33.25	13.87	28.91	7.83	0.79	

greater number of fractures in siltstones near the faults may be due to a higher proportion of siltstone in these wells than in the western wells (Table 3), rather than a greater fracture intensity in siltstones near the faults.

Two series of questions have been formulated to specifically address fracture variability and hydrophysical anomalies among the wells. The first series of questions focuses on the fracturing itself. The correlation between hydrophysical anomaly strength and the number of fractures and their closeness to the anomaly indicates that the existence of multiple fractures could mean the presence of a strong hydrophysical anomaly.

Table 4 Total number of fractures by lithology within wells, independent of aperture.

Total No. of Fractures by Lithology within Wells										
	Lithology									
Well No.	1 Cnglom	2 VCrsSS	3 CrsSS	4 MedSS	5 FineSS	6 VFineSS	7 SiltSt	8 MudStone	9 ClayStone	Total
W201		7	6	32	5	3	16	16		85
W202			22	30	9	2	19	10		92
W203		1	4	36	0	1	10	1		53
W204		0	16	19	11	16	37	2		101
W205	3	36	57	124	60	22	203	82	5	592
W206	2	10	24	54	19	17	82	54	7	269
W207	13	13	27	66	34	14	55	41		263
W208	5	3	7	37	46	40	69	43	13	263
Total	23	70	163	398	184	115	491	249	25	1718
Percent of Total Fractures by Lithology within Wells										
	Cnglom	VCrsSS	CrsSS	MedSS	FineSS	VFineSS	SiltSt	MudStone	ClayStone	
W201		8.24	7.06	37.65	5.88	3.53	18.82	18.82		
W202			23.91	32.61	9.78	2.17	20.65	10.87		
W203		1.89	7.55	67.92	0.00	1.89	18.87	1.89		
W204		0.00	15.84	18.81	10.89	15.84	36.63	1.98		
W205	0.51	6.08	9.63	20.95	10.14	3.72	34.29	13.85	0.84	
W206	0.74	3.72	8.92	20.07	7.06	6.32	30.48	20.07	2.60	
W207	4.94	4.94	10.27	25.10	12.93	5.32	20.91	15.59		
W208	1.90	1.14	2.66	14.07	17.49	15.21	26.24	16.35	4.94	

Table 5. Total number of fractures by lithology within wells for apertures > 0.03 in

Total No. of Fractures > 0.03 in. by Lithology within Wells										
	Lithology									
Well No.	1 Cnglom	2 VCrsSS	3 CrsSS	4 MedSS	5 FineSS	6 VFineSS	7 SiltSt	8 MudStone	9 ClayStone	Total
W201		2	2	4	2	0	2	6		18
W202			4	8	1	0	10	1		24
W203		0	0	5	0	0	4	0		9
W204		0	4	5	2	2	8	0		21
W205	0	3	3	9	6	1	27	9	1	59
W206	0	3	3	11	5	3	20	22	4	71
W207	4	3	7	20	9	2	7	18		70
W208	0	1	0	6	7	7	9	7	1	38
Total	4	12	23	68	32	15	87	63	6	310
Percent of Total Fractures > 0.03 in. by Lithology within Wells										
	Cnglom	VCrsSS	CrsSS	MedSS	FineSS	VFineSS	SiltSt	MudStone	ClayStone	
W201		11.11	11.11	22.22	11.11	0.00	11.11	33.33		
W202			16.67	33.33	4.17	0.00	41.67	4.17		
W203		0.00	0.00	55.56	0.00	0.00	44.44	0.00		
W204		0.00	19.05	23.81	9.52	9.52	38.10	0.00		
W205	0.00	5.08	5.08	15.25	10.17	1.69	45.76	15.25	1.69	
W206	0.00	4.23	4.23	15.49	7.04	4.23	28.17	30.99	5.63	
W207	5.71	4.29	10.00	28.57	12.86	2.86	10.00	25.71		
W208	0.00	2.63	0.00	15.79	18.42	18.42	23.68	18.42	2.63	

If fractures are correlated with hydrophysical anomalies, then it is important to determine how fractures vary throughout the site, and what factors influence variations in fracture intensity. Tables 6 through 9 address the following four questions regarding fracture intensity and whether it varies among the wells or lithologic groups:

1. Are fractures distributed uniformly within all logged lithologic layers? If this is true, then it may imply that fracturing is relatively independent of lithological controls or structural position.
2. Are fractures distributed uniformly within each lithological layer in each well? If so, then fracture intensity may be controlled by lithology, and be relatively unaffected by structural position.
3. Are fractures with an aperture of >0.03 in. (0.76 cm) distributed uniformly within all lithologic layers? This question is similar to the first, except the emphasis here is on fractures with the largest geometric apertures. Such fractures may represent only a small subset of the most conductive fractures in a well, which may account for most of the flow.
4. Are fractures with an aperture of >0.03 in. distributed uniformly within each lithological layer within each well? This question is similar to the second, except it focuses on the fractures with the largest geometric apertures, which might in turn represent the most conductive fractures.

Table 6 shows that the p-value (the probability of observing the calculated Chi-Square statistic given that the null hypothesis is true) is essentially 0.0, implying that fracture intensity is not uniform among the wells. Wells W204, W205, and W208 are the most anomalous in terms of fracture intensity, as shown by their high Chi-Square values. Table 7 demonstrates that the frequency of fracture variation from well to well is influenced by lithology. The high Chi-Square value for siltstone and mudstone in well W205 shows that the fracture frequency is anomalous in these fine-grained lithologies in the well. The higher values for the coarser-grained layers in wells W202 and W203 confirm that fracturing is anomalous in these units. The p-values show that fracture intensity varies with lithology within individual wells. Tables 8 and 9 show similar results for fractures with apertures greater than 0.03 in. In summary, these tables indicate that fracture intensity varies among wells, and this variation is due not only to differences in the proportion of different lithologies. For example, siltstones in well W205 have a different frequency than siltstones in well W202.

With regards to the hydrophysical anomalies themselves, several questions arise:

1. Does the strength of the conductivity anomaly or number of anomalies vary by well?
2. Does the strength of an anomaly depend upon being located in a particular lithology?
3. Is the strength of an anomaly influenced by the thickness of the unit in which it occurs?
4. Is the strength of an anomaly influenced by the

Table 6. Evaluation of the degree to which fractures are distributed uniformly among the wells, using Chi Square criteria.

Well	Total Thickness of Layer (inches)	Total No. of Fractures	Expected No. of Fractures	Chi Square	p-value
W201	854.54	85	55.8	15.24	
W202	1948.43	92	127.3	9.79	
W203	1086.74	53	71.0	4.57	
W204	722.19	101	47.2	61.37	
W205	7131.56	592	466.0	34.09	
W206	4248.88	269	277.6	0.27	
W207	4821.84	263	315.0	8.60	
W208	5480.03	263	358.1	25.23	
Total	26294.21	1718	1718.0	159.16	4.82E-31

proximity to a contact with another lithologic unit?

5. Is the strength of an anomaly correlated to a sharp contrast in the lithologies of units immediately above and below the unit?

Figure 4 shows the percent of hydrophysical anomalies by lithology within each well. There is insufficient information to carry out meaningful contingency table analyses on these data, but the figure clearly illustrates that the anomalies occur in different lithologies in a manner that is not in proportion to the relative net thickness of the lithologic layers in the wells

Figure 5 illustrates the relation of the thickness of a unit containing a hydrophysical anomaly to the thickness of all units found in the eight wells. There is no obvious visual difference.

The hypothesis that lithologic contrasts are related to anomalies was tested by comparing the anomaly strength to:

1. The absolute strength of the contrast (parameter ATC).
2. The contrast with the nearest adjacent lithology (parameter C_NEAR).
3. The distance to the nearest adjacent lithology.
4. Whether anomalies are predisposed to occur more closely to lithologic unit contacts.

Figure 6 shows the relation between both total contrast (TC) and ATC with the strength of the anomaly. The figure illustrates that there is a weak trend between increasing ATC and anomaly strength, but none between TC and anomaly strength. Figure 6 also compares anomaly strength to the contrast of the unit above (ALCA) and the unit below (ALCB). There is no obvious visual trend between these parameters and anomaly strength.

Table 7 Evaluation of the degree to which fractures are distributed uniformly with lithologic layer in individual wells.

Expected Number of Fractures											
Well No.	1 Cnglom	2 VCrsSS	3 CrsSS	4 MedSS	5 FineSS	6 VFineSS	7 SiltSt	8 MudStone	9 ClayStone	Total	
W201		5.00	14.60	21.71	10.77	7.40	17.62	7.90		85	
W202			8.91	20.40	19.87	9.87	25.99	6.95		92	
W203		3.55	8.58	17.13	0.46	1.67	17.28	4.33		53	
W204		0.62	16.42	15.01	8.87	10.35	45.65	4.08		101	
W205	2.55	18.33	39.77	115.26	48.99	24.87	282.56	53.79	5.88	592	
W206	4.20	11.82	19.29	57.78	30.66	38.73	81.42	22.15	2.95	269	
W207	14.55	10.59	19.06	44.41	23.67	29.78	98.96	21.96		263	
W208	5.28	3.23	9.11	22.75	87.46	36.47	76.03	20.59	2.08	263	
Total	26.59	53.13	135.73	314.47	230.75	159.14	645.52	141.76	10.91	1718	
Chi-Square Analysis											
	Cnglom	VCrsSS	CrsSS	MedSS	FineSS	VFineSS	SiltSt	MudStone	ClayStone	Total	p-Value
W201		0.80	5.06	4.87	3.09	2.62	0.15	8.30		24.90	0.00036
W202			19.23	4.52	5.94	6.28	1.88	1.34		39.19	2.18E-07
W203		1.83	2.45	20.78	0.46	0.27	3.07	2.56		31.41	0.00002
W204		0.62	0.01	1.06	0.51	3.08	1.64	1.06		7.98	0.23973
W205	0.08	17.05	7.47	0.66	2.48	0.33	22.40	14.79	0.13	65.39	4.05E-11
W206	1.15	0.28	1.15	0.25	4.44	12.19	0.00	45.77	5.57	70.81	3.39E-12
W207	0.17	0.55	3.31	10.49	4.51	8.36	19.53	16.51		63.42	3.13E-11
W208	0.02	0.02	0.49	8.92	19.65	0.34	0.65	24.40	57.48	111.96	1.51E-20

In addition, Figure 6 shows two parameters relating the anomaly strength to the contrast between the unit containing the anomaly (C_NEAR) and the distance to the nearest adjacent unit (CMIN). These data suggest no obvious trend.

The data shown in Figure 6 were tested to determine if hydrogeologic anomalies tend to be within 1 ft of the nearest contact. Does this imply that hydrophysical anomalies tend to occur close to lithology changes? This proposition was tested by selecting a random point in each unit penetrated by the eight wells and then computing the distance to the nearest contact. Figure 7 summarizes the result. Visually these two distributions appear very similar. A Chi-Square test does not reject this hypothesis, showing with an approximate 86% significance that these distributions are the same. This implies that anomalies do not appear to be preferentially located near major changes in lithology, although lithology contrasts have some importance.

The location and relative strength of each hydrophysical anomaly identified in the eight boreholes are indicated in Figure 2 by a line on the left-hand side of the borehole log. The length denotes the log of the flow rate. The figure indicates that the strongest hydrophysical anomalies are in W205, which intersects the fault.

2.3 *Multiple Regressions*

A series of step-wise multiple regressions was carried out using a data-mining application, SAS™. The results are summarized in Table 10. This table contains the results for the six multiple regressions with the highest R-square value for different numbers of independent variables.

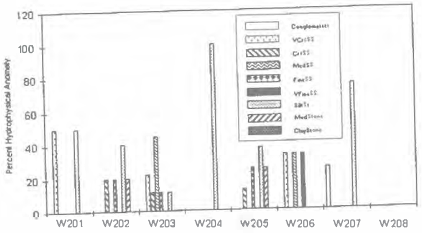

Figure 4. Percent of hydrophysical anomalies by lithology for individual wells. The height of the bars represents the percent of the logged interval of the well comprised by each lithology. Missing bars indicate the absence of a particular lithology in a well.

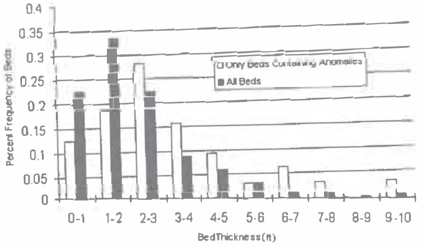

Figure 5. Bed thickness histograms. Open bars represent the histogram of bed thickness for all beds encountered by the wells. Black bars represent the histogram of bed thickness for only those beds containing hydrophysical anomalies. The vertical axis represents the percent of the beds belonging to a particular bed thickness class.

Improvement in R-square decreased significantly after seven variables. Those variables that produced the best R-square values for a given number of parameters are shown in the table and marked by an "X." The table demonstrates that certain variables explain much of the variance in anomaly strength. These variables include the distance to the nearest fractures (D1, D2, D3), the aperture, or width of the fractures (W3), the absolute lithologic contrast (ATC), the dip of the unit below the anomaly (CONDIPB), and the contrast with the unit above (ALCA).

Thus, the multiple regression results suggest that the distances to the three nearest fractures are important, as well as the data on a strong lithology contrast and wider fracture apertures. These variables account for approximately 80% of the variability in anomaly strength.

2.4 *Neural Net Analyses*

All neural net analyses were carried out using NeuroShell II™ Version 3.0 [*Ward*, 1996]. A genetic adaptive GRNN architecture was used [*Specht*, 1991]. GRNNs are designed to predict a continuous variable. They are memory-based feed-forward networks based on the estimation of probability density functions. The classic GRNN contains only one adjustable parameter, termed the *smoothing factor*. The smoothing factor allows the GRNN to interpolate between patterns in the training data set. The genetic adaptive GRNN differs in that it has smoothing factors for each input parameter as well as a conventional overall smoothing factor. These smoothing factors are

Table 8. Fractures > 0.03 in. are distributed uniformly with lithologic layer.

Well	Total Thickness (inches)	Total Fractures	Expected Fractures	Chi Square	p-value
W201	854.54	18	10.1	6.23	
W202	1948.43	24	23.0	0.05	
W203	1086.74	9	12.8	1.13	
W204	722.19	21	8.5	18.31	
W205	7131.56	59	84.1	7.48	
W206	4248.88	71	50.1	8.73	
W207	4821.84	70	56.8	3.04	
W208	5480.03	38	64.6	10.96	
Total	26294.21	310	310.0	55.93	9.75E-10

optimized by iterative changes in the factors based on cross-validation to minimize the mean squared error of the outputs over the entire test set. The genetic adaptive GRNN is much more robust against noisy data and redundant parameters than traditional GRNNs, and is particularly well suited when the input parameters are of different types, and some may have markedly more impact on predicting the output variable than others.

When an observation, which consists of parameter values for all input parameters under consideration, is presented to the GRNN, it is compared to all of the patterns in the training set to determine how closely this observation corresponds to those patterns. The GRNN essentially computes a weighting factor for each training data-set observation, and then computes an overall output value based upon these weights and the input training set parameter values.

Application of a neural net to the hydrophysical anomaly dataset would be improved if the data set were larger. This is because a small training set and a small test set increase the variability in the results. Also, with a very small training set, it is possible that the training data would not span the n-dimensional parameter space and would thereby have difficulty interpolating to new observations with characteristics outside of the data training subspaces. Likewise, it is important to have fewer degrees of freedom (i.e., input variables) in the network than training cases; otherwise, the net "memorizes" the training set without uncovering useful relations.

Table 9. Evaluation of the degree to which fractures > 0.03 in. are distributed uniformly with lithologic layer in individual wells.

All Fractures >.0.03 in. by Lithology within Wells										
Expected Number of Fractures										
	Cnglom	VCrsSS	CrsSS	MedSS	FineSS	VFineSS	SiltSt	MudStone	ClayStone	Total
W201		1.06	3.09	4.60	2.28	1.57	3.73	1.67		14.89
W202			2.32	5.32	5.18	2.58	6.78	1.81		10.40
W203		0.60	1.46	2.91	0.08	0.28	2.93	0.74		5.05
W204		0.13	3.41	3.12	1.84	2.15	9.49	0.85		2.47
W205	0.25	1.83	3.96	11.49	4.88	2.48	28.16	5.36	0.59	5.73
W206	1.11	3.12	5.09	15.25	8.09	10.22	21.49	5.85	0.78	67.51
W207	3.87	2.82	5.07	11.82	6.30	7.93	26.34	5.85		51.47
W208	0.76	0.47	1.32	3.29	12.64	5.27	10.99	2.97	0.30	15.45
Total	6.00	10.02	25.73	57.80	41.30	32.48	109.91	25.10	1.66	172.96
			Chi-Square Analysis							
	Cnglom	VCrsSS	CrsSS	MedSS	FineSS	VFineSS	SiltSt	MudStone	ClayStone	Total	p Value
W201		0.84	0.39	0.08	0.03	1.57	0.80	11.19		14.89	0.02111
W202			1.21	1.35	3.38	2.58	1.53	0.37		10.40	6.47E-02
W203		0.60	1.46	1.50	0.08	0.28	0.39	0.74		5.05	0.53790
W204		0.13	0.10	1.13	0.01	0.01	0.23	0.85		2.47	0.87224
W205	0.25	0.75	0.23	0.54	0.26	0.88	0.05	2.47	0.29	5.73	6.78E-01
W206	1.11	0.00	0.86	1.18	1.18	5.10	0.10	44.62	13.35	67.51	1.54E-11
W207	0.00	0.01	0.73	5.66	1.16	4.43	14.20	25.28		51.47	7.42E-09
W208	0.76	0.61	1.32	2.24	2.51	0.57	0.36	5.45	1.63	15.45	5.10E-02

The performance of a neural net is determined by how well it predicts the strength of the anomaly of a test set as quantified by R and R-square statistics. These statistics vary from 0.0 to 1.0; a perfect prediction has an R and R-square statistic of 1.0. The importance of an input parameter is quantified by its smoothing factor, which can vary from 0.0 (no importance) to 3.0 (very important).

Because of the small (approximately 30) number of hydrophysical anomalies available for use as training and test patterns, the results are sensitive to the random subset selected as the training pattern. For this reason, several random subsets were selected and processed.

Correlation shows up in the smoothing factors as a substitution of one correlated variable in random samples. For example, in one run, the distance to the third nearest fracture might be important. In a subsequent run, this distance might have little importance but the distance to the second nearest fracture would now be important. Highly correlated variables can substitute for one another since virtually all of the information in all of the variables can be contained in any one of the variables.

Neural net regression was much more successful for the logarithm of the anomaly than for the anomaly itself. A series of preliminary neural nets was constructed to look at different components of the data—in particular, fracture-related parameters and lithological parameters. In the preliminary processing that focused on fractures, several parameters played an important role. These included depth of the fractures, width of the fractures, distance from the anomaly to the nearest fractures, and the lithology of the nearest fractures. Depth was probably an artifact of the available dataset, however. Well W205, the deepest well, had the strongest anomalies. The other wells either were not drilled to the depth of W205, or else did not have all of the necessary parameters for the deeper portions of the borehole.

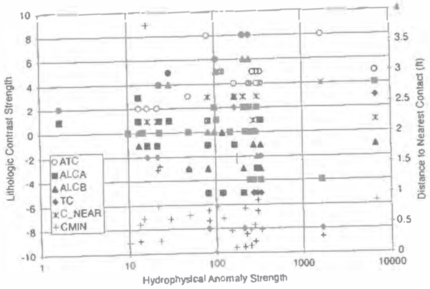

Figure 6. Anomaly strength vs. lithological contrast parameters. The vertical scale on the left-hand side of the graph pertains to the contrast parameters ATC, ALCA, ALCB, TC, and C_NEAR. The vertical scale on the right-hand side indicates the value of the distance parameter CMIN.

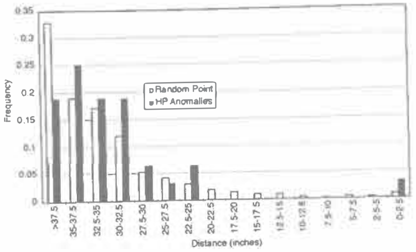

Figure 7. Percent frequency histogram of distance to nearest lithology change. Open bars represent distances between a location randomly assigned in the wells and the nearest contact. Black bars represent the distance from the locations of all hydrophysical anomalies to the nearest contact. The frequencies have been normalized to percentages in order to facilitate visual comparison.

The lithologies above and below the hydrophysical unit did not appear to explain the hydrophysical anomaly. However, the lithologies of the four nearest fractures were quite informative. Although these lithologies correlated very strongly, surprisingly, at least three of them always seemed to have significant smoothing factors. This is reminiscent of the results from the step-wise regression, which showed that the distance to at least three of the four nearest fractures was important. If the information content in any one of these parameters were a good representation of the information content in any other, then it would be expected that only one of the lithology, depth, or aperture parameters would have a significant smoothing factor. The fact that more than one lithology parameter has a significant smoothing factor might be evidence that hydrophysical anomalies are in some way enhanced by the presence of multiple fractures near the anomaly, whether or not these fractures actually have an anomaly associated with them.

These preliminary runs guided the final runs in which redundant variables and depth measures had been eliminated. Tables 11 and 12 summarize those results.

Table 11 shows the mean of the smoothing factors for five randomly drawn training and test sets. The lithology of the fractures (L1 and L2), fracture width (W1 and W2), and proximity (D1 and D2) to fractures to the anomaly are

Table 10. Results of step-wise regression.

No. of Variables	R-square	ALCA	ATC	CDA	CONDIPA	CONDIPB	D	D2	D3	D4	LCA	LITH	Log(W1)	Log(W2)	Log(W3)	W1	W2	W3
2	0.477	X												X				
2	0.438		X											X				
2	0.419	X															X	
2	0.402							X						X				
2	0.387							X									X	
2	0.383		X														X	
3	0.527	X						X						X				
3	0.513		X			X		X										
3	0.511	X											X	X				
3	0.508	X								X				X				
3	0.507		X					X						X				
3	0.506	X				X								X				
4	0.622						X	X	X									X
4	0.596		X					X	X						X			
4	0.591						X	X	X						X			
4	0.581	X						X	X					X				
4	0.580		X			X	X	X										
4	0.571	X				X							X	X				
5	0.717		X				X	X	X						X			
5	0.711		X				X	X	X									X
5	0.687						X	X	X							X		X
5	0.684						X	X	X					X				X
5	0.679	X					X	X	X									X
5	0.677		X			X	X	X	X									
6	0.802		X			X	X	X	X									X
6	0.783		X			X	X	X	X						X			
6	0.765		X				X	X	X					X				X
6	0.753	X					X	X	X					X				X
6	0.751		X				X	X	X					X	X			
6	0.750		X				X	X	X							X		X
7	0.828		X	X		X	X	X	X									X
7	0.823		X			X	X	X	X					X				X
7	0.820		X			X	X	X	X							X		X
7	0.817		X		X	X	X	X	X									X
7	0.816		X			X	X	X	X		X							X
7	0.815		X			X	X	X	X			X						X

always important. In particular, the distance to the second closest fracture is much more important than the distance to the closest fracture. Two other parameters, used only in the neural net analysis, also were important—UNCONF and ABS(UNCF). These variables were introduced to assess structural or stratigraphic disruption, an area also important in the neural net analyses. Absolute lithology contrast (ATC), lithology of the anomaly (LITH), and distance to the nearest contact (CMIN), have a moderate impact. Bed thickness (BED_TH) and the contrast between the anomaly unit and the nearest adjacent unit (C_NEAR) play very minor roles.

Table 12 shows the R-square and r-square statistics for both the training and test sets. R-square is the coefficient of multiple determination, whereas r-square is the more familiar coefficient of determination [*Ward*, 1996], which is the square of the correlation coefficient. The R-square value for the training sets averages nearly 92%, with a variation of 81% to 100%. The R-square value for the test sets averages nearly 77%, with a variation of 50% to 97%. Note that the lowest R-square for the test set comes from realization 2, which conversely has the highest value (1.0) for the training sets. The smoothing factors for this realization are also somewhat anomalous. The R-square values for both the training and test sets are higher than for the multivariate regression. This suggests that some of the input parameters have a nonlinear relation with anomaly strength. In general, the GRNN achieves about a 20% improvement over the multivariate regression in terms of R-square values.

Table 13 shows the predictions made by the neural net method for the ten test sets of observations. In general, the predictions are reasonably accurate, the average error being -0.0250 and the standardized mean squared error 0.34.

Thus, the neural net analysis confirms the results of the simpler statistical techniques and suggests that a GRNN offers greater accuracy than multivariate regression.

3. CONCLUSIONS

The statistical results for the Wake Co. site support the following conclusions:

1. There are statistically significant correlations between the geologic variables directly measured or derived from core data or borehole imagery and the strength of hydrophysical anomalies.
2. Hydrophysical anomalies do not appear to be located preferentially in particular lithologies for all eight wells. The frequency histograms and associated statistical test results show that hydrophysical anomalies are located in randomly selected subsets of all of the lithologic units.
3. Hydrophysical anomalies are not preferentially located near to boundaries between contrasting lithologic units. Frequency histograms of the proximity of anomalies to the nearest lithologic boundary are statistically indistinguishable from the distance from a random point located in every unit to its nearest boundary.
4. There is a weak trend between the magnitude of a hydrophysical anomaly and the strength of the contrast between the lithologic unit containing the anomaly and the units above and below it.
5. The trend noted in the conclusion above is independent of whether the anomaly occurs in a fine-grained unit surrounded by coarse-grained units or a coarse-grained unit surrounded by fine-grained units.
6. There is no correlation between the strength of the hydrophysical anomaly and the strength of the contrast with the lithologic unit above or below.
7. There is no correlation between the strength of the hydrophysical anomaly and the distance to either the upper or lower contact with the adjacent lithologic units.
8. The strongest hydrophysical anomalies occur in the fine-grained lithologies in Well W205, which intersected the fault and was drilled and logged deeper than most of the other wells. The anomalies in well W205 have three unique characteristics: they occur preferentially in siltstone or mudstone lithologies,

Table 11. Average smoothing factors for neural net analyses.

Average of 5 Realizations	Smoothing Factor [0 to 3.0]
Lithology to 1st Nearest Fracture	2.37
Distance to 2nd Nearest Fracture	2.24
Lithology to 2nd Nearest Fracture	2.09
Aperture of 1st Nearest Fracture	1.97
Absolute Value of Angular Difference between Upper and Lower Contacts	1.86
Difference between Upper and lower Contacts	1.59
Distance to Nearest Contact	1.28
Aperture of 2nd Nearest Fracture	1.21
Absolute Grain Size Contrast	1.15
Grain Size of Unit Containing Anomaly	1.12
Distance to 1st Nearest Fracture	1.08
Minimum Apparent Distance to Nearest Contact	0.76
Bedding Thickness	0.60
Dip of Contact with Unit Above	0.47
Grain Size Contrast with Nearest Unit	0.29

Table 12. Statistics for GRNN prediction of hydrophysical anomaly strength.

Training Set	#1	#2	#3	#4	#5	Average
R squared	0.91	1.00	0.99	0.81	0.88	0.92
r squared	0.94	1.00	0.99	0.90	0.88	0.94
Mean squared error	0.05	0.00	0.01	0.12	0.06	0.05
Mean absolute error	0.15	0.00	0.06	0.24	0.07	0.10
Min. Absolute error	0.00	0.00	0.00	0.00	0.00	0.00
Max. Absolute error	0.80	0.00	0.25	1.04	1.35	0.69
Correlation coefficient r	0.97	1.00	0.99	0.95	0.94	0.97
Percent within 5%	45.46%	100.00%	77.27%	27.27%	87.50%	67.50%
Percent within 5% to 10%	36.36%	0.00%	13.64%	22.73%	3.13%	15.17%
Percent within 10% to 20%	13.64%	0.00%	9.09%	31.82%	6.25%	12.16%
Percent within 20% to 30%	0.00%	0.00%	0.00%	9.09%	0.00%	1.82%
Percent over 30%	4.55%	0.00%	0.00%	9.09%	3.13%	3.35%
Test Set	#1	#2	#3	#4	#5	Average
R squared	0.86	0.50	0.97	0.85	0.67	0.77
r squared	0.96	0.53	0.98	0.87	0.73	0.81
Mean squared error	0.04	0.34	0.01	0.02	0.19	0.12
Mean absolute error	0.15	0.29	0.08	0.11	0.20	0.17
Min. Absolute error	0.00	0.00	0.00	0.03	0.00	0.01
Max. Absolute error	0.37	1.70	0.14	0.36	1.35	0.78
Correlation coefficient r	0.98	0.73	0.99	0.93	0.85	0.90
Percent within 5%	50.00%	60.00%	50.00%	80.00%	60.00%	60.00%
Percent within 5% to 10%	10.00%	0.00%	40.00%	0.00%	10.00%	12.00%
Percent within 10% to 20%	10.00%	30.00%	10.00%	10.00%	20.00%	16.00%
Percent within 20% to 30%	20.00%	0.00%	0.00%	0.00%	0.00%	4.00%
Percent over 30%	10.00%	10.00%	0.00%	10.00%	10.00%	8.00%

which is not true for anomalies in other wells; they occur at a greater depth than in the other wells; and the fractures nearest the anomalies have greater apertures than the fractures near anomalies in other wells. The depth correlation is probably an artifact.

Away from faults, hydrophysical anomalies are smaller on average and not as strongly associated with siltstone and mudstone. Near faults in the hanging wall, the strength of the anomalies is greater and they are correlated with fractures with larger aperture.

The results of our analyses confirm that a fault-related deformation produces new fractures or enhances the aperture of existing fractures in lithological units with lower resistance to shear—mudstones and siltstones—and thereby increases the strength of hydrophysical anomalies.

4. RECOMMENDATIONS

This section offers recommendations for using the results of this study to construct site-scale DFN and SC flow models. The results confirm that it is not correct to assign permeability values to grid cells or flow properties to fractures based on lithologic type alone. The boundaries between contrasting lithologic types do not focus strain. If they did, then the DFN model could have reproduced this effect by having large, bedding-parallel fractures at these interfaces with enhanced transmissivity values. SC models could have approximated this effect by having bedding-parallel layers of grid cells with enhanced subhorizontal permeability. While there is some correlation between lithological contrasts, the correlation is second order and should probably be ignored in preliminary flow models.

Table 13. Comparison of measured hydrophysical anomaly strength with strength predicted by GRNN for ten randomly selected anomalies not used in the GRNN calibration.[a]

#1		#2		#3		#4		#5	
Actual	GRNN	Actual	GRNN	Actual	GRNN	Actual	GRNN	Actual	GRNN
2.52	2.52	3.22	2.62	2.44	2.46	2.52	2.48	3.82	2.48
2.48	2.45	2.52	2.52	2.34	2.29	2.48	2.54	2.52	2.52
2.48	2.39	2.52	2.44	2.32	2.41	2.40	2.35	2.48	2.44
2.22	2.19	2.22	1.92	2.18	2.17	2.35	2.10	2.45	2.39
2.09	2.28	2.09	2.09	1.92	2.03	2.34	2.27	2.40	2.22
2.02	1.99	1.48	1.46	1.48	1.60	2.32	2.43	2.09	2.35
1.99	2.23	1.37	1.37	1.37	1.28	2.18	2.21	1.48	1.47
1.48	1.78	1.34	1.34	1.37	1.32	2.02	1.99	1.37	1.37
1.12	1.37	1.18	1.34	1.12	1.26	1.92	1.83	1.34	1.34
1.00	1.37	0.22	1.92	1.12	1.21	1.12	1.49	1.18	1.34

[a] The ten rows, corresponding to the randomly selected anomalies for each of the five test sets, were sorted by anomaly, from largest anomaly to smallest, to illustrate that the GRNN tends to overpredict the strength of small anomalies (calculations were carried out for five runs).

Fault proximity is a first-order control in and of itself, and lithology plays a significant role near faults. Deformation is greatest in the hanging-wall siltstones and mudstones within the deformation zone that extends from the fault eastward to the fold hinge that intersects the bottom of W204. This implies that fractures in these lithologies and structural positions should have larger aperatures, resulting in higher transmissivity. Alternatively, the grid cells within this region of a SC model would have higher layer-parallel permeability. Based on the data obtained, the footwall appears to be similar to the rock outside of the hanging-wall deformation zone.

The fact that anomalies do exist outside of the hanging-wall zone, but are smaller and not as strongly correlated with lithology, suggests simple "background" fracture and permeability models for the remainder of the rock mass. At least for the preliminary model, the background fracturing would be homogeneous throughout the model. This means that the discrete fractures in the DFN model would be distributed with the same size and orientation distributions, the same transmissivity and transport properties, and the same average intensity independent of depth, lithology, or location. In the SC model, the permeability, porosity, and transport parameter values would be assigned as random (Monte Carlo) draws from a single parent distribution for each parameter. Only in the vicinity of the hanging-wall deformation zone would properties be changed as previously described.

The next stage in refining these DFN or SC models would be to simulate field flow or transport experiments in order to assess whether the models are reproducing the first-order effects, and if so, whether certain second-order effects should be included to improve the modeling forecasts. There is considerable freedom in assigning transmissivity and transport properties either to the fractures themselves in the DFN formulation or as effective properties to the stochastic continuum models. Iterative refinement of these properties to match the field-flow or transport results is usually an important step in the evolution of models that will be used subsequently for forecast or design.

Acknowledgments. Portions of this work were performed under contract to Harding-Lawson Associates, whose support is gratefully acknowledged. The opinions expressed in this paper, however, remain those of the author and do not necessarily coincide with those of Harding-Lawson Associates or any other party involved in the North Carolina LLRW Facility Project.

REFERENCES

Cacas, M. C., E. Ledoux, G De Marsily, B. Tillie, A. Barbreau, E. Durand, B. Feuaga, and P. Peaudecerf, Modeling fracture flow with a discrete fracture network: calibration and validation 1, the flow model, *Water Resour. Res.*, 26(3), 479–489, 1990a.

Cacas, M. C., E. Ledoux, G. De Marsily, A. Barbreau, P. Calmesl, B. Gaillard, and R. Margritta, Modeling fracture flow with a discrete fracture network: calibration and validation 2, the transport model, *Water Resour. Res.*, 26(3), 491–500, 1990b.

Dershowitz, W. S., *Rock Joint Systems*, Ph.D. thesis, Massachusetts Institute of Technology, Cambridge, Mass., 1984.

Dershowitz, W. S.N. Hurley, and K. Been, Stochastic discrete fracture modeling of heterogeneous and fractured reservoirs, in *Proceedings of the Third International Conference on the Mathematics of Oil Recovery*, Delft University Press, Delft, Holland, 1992.

Endo, H. K., J. C. S. Long, C. K. Wilson, and P. A. Witherspoon, ɜl for investigating mechanical transport in fractured *Water Resour. Res.*, *20*(10), 1390–1400, 1984.

. A., and P. R. La Pointe, Printed circuits for studying ass permeability, *Int. J. Rock Mechanics and Mining and Geomechanics Abstracts*, *17*, 297–301, 1980.

, P. R., P. C. Wallmann, and S. Follin, Continuum ıg of rock masses: Is it useful?, *Proceedings of the Int. of Rock Mechanics Symposium on Prediction and ıance in Rock Mechanics and Rock Engineering—K '96*, pp. 343–350, Balkema, Rotterdam, 1996.

. S., J. S. Remer, C. R. Wilson and P. A. Witherspoon, media equivalents for networks of discontinuous s, *Water Resour. Res.*, *18*(3), 645–658, 1982.

Research Council, Committee on Fracture erization and Fluid Flow, *Rock Fractures and Fluid* Chap. 6, pp. 307–404, National Academy Press, gton, D.C., 1996.

P., *Connectivity, flow and transport in network models ured media*, Ph.D. thesis, Oxford University, UK, 1984.

, and F. W. Schwartz, An analysis of the influence of geometry on mass transport in fractured media, *Water Res.*, *20*(9), 1241–1252, 1984.

Specht, D. F., A generalized regression neural network, *IEEE Trans. on Neural Networks*, *2*, 568–576, 1991.

Swaby, P. A., and K. D. Rawnsley, An interactive 3D fracture modelling environment, *Proceedings of the Petroleum Computer Conference, SPE 36004*, Society of Petroleum Engineers, Dallas, Tex., 1996.

Ward, Inc., *NeuroShell 2 User's Manual*, Ward Systems Group, Inc., Frederick, Md., 1996.

Zimmerman, D. A., G. De Marsily, C. A. Gotway, M. G. Marietta, C. L. Axness, R. L. Beauheim, R. Bras, J. Carrera, G. Dagan, P. B. Davies, D. P. Gallegos, A. Galli, J. Gómez-Hernández, S.M. Gorelick, P. Grindrod, A. L. Gutjahr, P. K. Kitanidis, A. M. Lavenue, D. McLaughlin, S. P. Neuman, B. S. Rama Rao, C. Ravenne, and Y. Rubin, A comparison of seven geostatistically-based inverse approaches to estimate transmissivities for modeling advective transport by groundwater flow, *Water Resour. Res.*, *34*(6), 1373–1413, 1998.

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DISCLAIMER

The U.S. Environmental Protection Agency's Office of Solid Waste (EPA or the Agency) has compiled this methods manual in order to provide comprehensive guidance to analysts, data users, and other interested parties regarding test methods that may be employed for the evaluation of solid waste and other testing specified in regulations issued under the Resource Conservation and Recovery Act (RCRA). Except where explicitly specified in a regulation, the use of SW-846 methods is not mandatory in response to Federal testing requirements.

The Agency does not intend to restrict the use of new analytical techniques. Advances in technologies applicable to the sampling and analysis of environmental media and hazardous wastes outpace the ability of the Agency to promulgate revisions to this manual. In addition, given the large number of manufacturers and vendors of scientific equipment, glassware, reagents, and supplies, it is not feasible to cite all possible sources for these materials. Thus, the mention of trade names or commercial products in this manual is for illustrative purposes only, and does not constitute an endorsement or exclusive recommendation for use by EPA. The products and instrument settings cited in SW-846 methods represent those products and settings used during method development or subsequently evaluated by the Agency. Glassware, reagents, supplies, equipment, and settings other than those listed in this manual may be employed provided that method performance appropriate for the intended RCRA application has been documented as described in Chapter Two (see Sec. 2.1).

EPA generally does not intend these methods to be overly prescriptive. The words "shall," "must," or "require" are used to indicate aspects of the method that are considered essential to its performance, based on sound analytical practices (e.g., an instrument must be calibrated before use). In contrast, the words "should," "may," or "recommend" are used to provide guidance on aspects of the method that are useful but not essential. This flexibility does not apply to those method-defined parameters where the analytical result is wholly dependent on the process used to make the measurement.

EPA emphasizes that the ultimate responsibility for producing reliable analytical results lies with the entity subject to the Federal, State, or local regulation. Thus, members of the regulated community are advised to refer to the information in Chapter Two and to consult with knowledgeable laboratory personnel when choosing the most appropriate suite of analytical methods. The regulated community is further advised that the methods here or from other sources need only be used for those specific analytes of concern that are subject to regulation or other monitoring requirements.

Many of the methods include performance data that are intended as guidance on the performance that may be achieved in typical matrices and may be used by the analyst to select the appropriate method for the intended application. These performance data are not intended to be used as absolute QC acceptance criteria. Rather, each laboratory should develop performance criteria as described in Chapter Two and elsewhere in the manual.

In summary, the methods included here provide guidance to the analyst and the regulated community in making judgments necessary to generate data that meet the data quality objectives for the intended use of the results.

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CHAPTER ONE
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CHAPTER ONE

Project Quality Assurance and Quality Control

For a summary of changes in this version from the previously published Chapter One, please see Appendix A at the end of this document.

1.0 INTRODUCTION

The goal of this chapter is to provide an understanding of environmental data and the need for quality. EPA has developed numerous guidance documents on quality assurance. This chapter is not intended to summarize the previously developed EPA guidance. Instead, this chapter will provide familiarity with regulations and guidance relating to QA and where to find them.

Regulations promulgated under the Resource Conservation and Recovery Act (RCRA) of 1976, as amended; require the collection and use of environmental data by regulated entities. In addition, organizations often collect and use environmental data for decision making. Given the significant decisions to be made based on environmental data, it is critical that the data are of sufficient quantity and quality for their intended use and can support decision-making based on sound science.

In response to the need for quality data, it is recommended that all parties follow a structured system of data quality assurance and quality control (QA/QC). In addition, some of the RCRA regulations include specific requirements for ensuring data quality.

This chapter provides general guidance intended to ensure data are of sufficient quality for their intended use. Its intended audience is any entity, government or private party that may be collecting environmental data. It is designed to support the efforts of those responsible for preparing and reviewing project planning documents such as Quality Assurance Project Plans (QAPPs), those involved in implementing and assessing data collection and generation activities in the field or laboratory, and those who use the data for decision-making.

Due to the diversity of data collection efforts, it is not possible to provide all details necessary to meet the needs of all members of the intended audience. However, EPA has developed a variety of detailed QA guidance documents that are incorporated into this Chapter by reference. This series of quality systems documents can be accessed on the EPA's Quality web site at: http://www.epa.gov/quality. These documents describe in detail EPA policies and procedures for planning, implementing and assessing the effectiveness of quality systems.

EPA's quality system comprises three structural levels: policy, organization/program, and project. This document addresses quality at the project level of the system, including technical aspects of analytical method quality assurance (QA) and quality control (QC). Entities which desire guidance on the other two structural levels (policy and organization/program levels) can access such guidance at the aforementioned EPA quality web site.

A project's life cycle under EPA's quality system has three phases: planning, implementation, and assessment. This chapter is organized into these three phases. Additionally, Figure 1 is provided, and illustrates this process.

Additionally, this chapter contains general project QC guidance to be used with the subsequent chapters and methods in this manual. It should be noted that several methods (e.g., Method 8000) also contain general QC criteria and guidance that pertain to the individual methods referenced therein (e.g., Methods 8081, 8082, 8260 and 8270). Individual methods may also contain QC criteria specific only to that method. The QC criteria in the general methods take precedence over chapter QC criteria. Method-specific QC criteria take precedence over general method QC criteria.

1.1 PLANNING

Planning, the first phase of a project's life cycle, involves the development of project objectives and acceptance or performance criteria using a systematic process. Data quality objectives (DQOs) and a sampling and analysis design are established to generate data of an appropriate type, quality and quantity to meet project objectives. The final output of this phase is a planning document, such as a QAPP, and/or a sampling and analysis plan (SAP) or a waste analysis plan (WAP).

This section provides guidance on activities and concepts that EPA recommends to be used or considered during the planning phase, when appropriate to a specific project.

1.1.1 Systematic Planning

Systematic planning is a process designed to ensure that the level of detail in planning is commensurate with the importance and intended use of the work and the availability of resources to accomplish it. The ultimate goal of systematic planning is to ensure collection of the appropriate type, quantity, and quality of data to support decisions with acceptable confidence. Following is a summary of EPA's Agency-wide guidance on systematic planning. More detail can be found in the *EPA Quality Manual for Environmental Programs (CIO-2105-P-01-0).*

The systematic planning process generally involves the following elements:

- Identification and involvement of data generators and users.

- Identification of project schedule, milestones, resources (including budget), and any applicable requirements.

- Description of the project goals and objectives (i.e., what is trying to be accomplished by performing this project)

- Identification of the type (e.g., individual data points to be used to estimate risk at a site, multi-point composites to be used to evaluate the average concentration in a decision unit), quantity and quality (e.g., screening for the presence/absence of an analyte, definitive data supported by all method specific QC results) of data needed. Be specific on what kind of analytical result will be needed to make a decision, whether the collected results need to be comprehensive and meet well defined DQOs or are merely for screening purposes to make a presence/absence decision?

- Specification of acceptance or performance criteria for ensuring the data collected meets the needs of the project.

- Description of how, when, and where the data will be obtained, and identification of any constraints on data collection.

- Specification of QA and QC activities needed to assess quality performance criteria (e.g., QC samples for the field and laboratory, audits, technical assessments, performance evaluations, etc.).

- Description of how acquired data will be analyzed (i.e., field and/or laboratory), evaluated, and assessed against performance criteria. If statistical assumptions are made as part of the planning process, the assessment must discuss how the assumptions will be verified as accurate, and what actions will be taken if the statistical assumptions are not supported by the data.

Planners should also recognize that existing data (i.e., secondary data) can be useful in supporting decision making. Secondary data can provide valuable information to help design a plan for collecting new data, while also lowering the cost of future data collection efforts. However, the limitations on using any secondary data must be clearly understood and documented. For example, secondary data must be examined to ensure that their quality is acceptable for a given application. Combining secondary data with current data can be a complex operation and should be undertaken with care. Sometimes, statistical expertise is necessary to evaluate both data sets before they can be combined. If combining data sets, make sure historical data use is appropriate in type and quality to the current project.

1.1.2 DQOs

The DQO process, discussed in detail in the *Guidance on Systematic Planning Using the Data Quality Objectives Process, EPA QA/G-4*, is designed to produce scientific and resource-effective data collection designs that will support decision making with a defined level of confidence.

The DQO process can be applied to any study, regardless of its size. While there is no regulatory obligation to use the DQO process, it is the recommended planning approach for most EPA data collection activities. The depth and detail of DQO development will depend on the study objectives. The DQO process is particularly applicable to a study in which multiple decisions must be reached. By using the DQO process, the planning team can clearly separate and delineate data requirements for each decision to be made or question to be answered. It consists of seven planning steps that are summarized below.

1.1.2.1 Step 1: State the Problem

The purpose of Step 1 is to clearly define the problem that has created the need for the study. In describing the problem, especially for more complex sites, it is often useful to include a conceptual site model (CSM). The CSM is a three-dimensional "picture" of site conditions at a discrete point in time that conveys what is known or suspected about the facility, including releases, release mechanisms, contaminant fate and transport, exposure pathways, potential receptors, and risks.

1.1.2.2 Step 2: Identify the Goals of the Study

The purpose of Step 2 of the DQO process is to identify the key questions that need to be answered in order to resolve the problem(s) identified in Step 1. Step 2 should also identify any actions that may be taken based on study results. The goals of the study and the alternative actions are then combined to form decision statement(s) that will resolve the problem. A decision statement defines which of the identified alternative actions will be pursued depending on the outcomes of the study.

1.1.2.3 Step 3: Identify the Information Inputs

The purpose of Step 3 of the DQO process is to identify the information needed to resolve the decision statement. This may include, but is not limited to:

- Primary data, including sampling and analysis methods
- Secondary data, including the necessary information to ensure the data is of known and documented quality (e.g., sampling and analysis methods used as well as sufficient information to evaluate the quality of the data)
- Action limits to be considered
- Background information about the site or process, including known or anticipated variability of the study parameters that may help the planning team identify critical sampling locations

1.1.2.4 Step 4: Define the Boundaries of the Study

The purpose of Step 4 of the DQO process is to define the spatial and temporal boundaries for the data collection design, including where samples will be collected. Spatial boundaries describe the physical area (i.e., horizontal and vertical boundaries) of the study. They can include geographic area or volume of material. Temporal boundaries include both the period of time the data collection effort will represent and the timeframe to which the decision will apply.

1.1.2.5 Step 5: Develop the Analytic Approach

The purpose of Step 5 of the DQO process is to consider the outputs from Steps 1-4 and develop “If..., then... else” decision rules that unambiguously state which of the alternative actions identified in Step 2 will be pursued. These if/then/else decisions should be formulated to be dependent on how the results of the study compare to an established action level.

1.1.2.6 Step 6: Specify Performance or Acceptance Criteria

The purpose of Step 6 of the DQO process is to set limits on decision errors, and to document those limits. For judgmental and random samples, Step 6 should examine consequences of making incorrect decisions, and place acceptable limits on the likelihood of making decision errors. For random samples, Step 6 should specify any statistical hypothesis to be considered and all applicable statistical tests that will be used to assess the data.

1.1.2.7 Step 7: Develop the Plan for Obtaining Data

The purpose of Step 7 of the DQO process is to develop the data collection plan that will satisfy the objectives presented in Steps 1 through 6. *RCRA Waste Sampling Draft Technical Guidance*, dated August 2002, provides guidance that may be used during sampling design development. EPA also developed a guidance document called *Guidance for Choosing a Sampling Design for Environmental Data Collection (QA/G-5S)*, to specifically provide the information needed to carry out step 7 and develop a sampling design.

The proposed plan should be the most resource-effective data collection design that meets the previously identified performance or acceptance criteria. The plan for obtaining data is documented in detail by developing a project QAPP as per *EPA Requirements for*

Quality Assurance Project Plans (QA/R-5), which presents the requirements for QAPPs, and its companion document, *EPA Guidance for Quality Assurance Project Plans (QA/G-5)*.

1.1.3 Development of QAPPs, Waste Analysis Plans (WAPs) and Sampling and Analysis Plans (SAPs)

Documentation of planning processes and outcomes are critical to the:

- effective communication of planned activities to all participants in the process,
- reconstruction of completed events, and
- reconciliation of the analytical data with the project plans.

Two types of planning documents are discussed in this section. Section 1.1.3.1 discusses QAPPs, which are a key output of the systematic planning process. Section 1.1.3.2 discusses WAPs and SAPs.

1.1.3.1 QAPPs

All environmental data collection efforts performed by or funded by EPA (e.g., through an EPA contractor) must be supported by an approved QAPP. EPA also recommends the use of QAPPs for environmental data collection efforts by other entities (e.g., by other regulated entities in compliance with the RCRA regulations). EPA has issued several documents to aid in preparing QAPPs, including the documents noted in Section 1.1.2.7. These documents provide suggestions for both EPA and non-EPA organizations on preparing, reviewing, and implementing QAPPs.

The primary purpose of the QAPP is to present the data collection activities to be implemented, including all necessary QA and QC, to ensure that all data produced are of known and documented quality, and that the data will satisfy the stated performance criteria.

QAPPs, and any accompanying WAPs or SAPs, should be accessible to all participants throughout the life of the project. They should provide understandable instructions to those who must implement the QAPP, such as the field sampling team, the analytical laboratory, modelers, and the data reviewers.

When preparing a QAPP, a graded approach should be used to determine the level of detail needed. This will ensure that the level of information presented is consistent with the intended use of the results and the degree of confidence needed in the quality of the results. The QAPP should be detailed enough to provide a clear description of every aspect of the project, from site history through assessment of the planned data collection. At a minimum, the QAPP should provide sufficient detail to demonstrate that:

- the project technical and quality objectives are identified and agreed upon;
- the intended measurements and data generation or data acquisition methods are appropriate for achieving project objectives;
- assessment procedures are sufficient for confirming that data of the type and quality needed and expected are obtained; and
- any limitations on the use of the data can be identified and documented.

As described in QA/R-5 and QA/G-5, the QAPP should be composed of standardized, recognizable elements covering the entire project from planning through assessment. These elements may be divided into the following four general groups:

- Project Management - The elements in this group address project organization and management; site background and history; and project objectives. These elements ensure that project goals are clearly defined, that the participants understand the goals and the approach to be used, and that the planning process is documented.

- Data Generation and Acquisition - The elements in this group address all aspects of project design and implementation, including the numbers, types, and locations of all samples to be collected; the rationale for why the proposed data collection effort will be sufficient to address the study objectives; all sampling, subsampling and analytical procedures to be followed (i.e., both sample preparation as well as determinative procedures); QC requirements for all applicable field and laboratory procedures including the data quality indicators (DQIs) discussed below in Section 1.1.4; instrument calibration and maintenance for both field and laboratory equipment; use of secondary data; and data management. Implementation of these elements ensures that appropriate methods for sampling, analysis, data handling, and QC activities are employed and properly documented.

- Assessment and Oversight - The elements in this group address the activities for assessing the effectiveness of project implementation and associated QA and QC activities. The purpose of assessment is to ensure that the QA Project Plan is properly implemented as prescribed.

- Data Validation and Usability - The elements in this group address the QA activities that occur after data collection or generation is completed. These elements address how data will be reviewed, verified and validated as well as how data will be assessed and reconciled with the project objectives.

While most QAPPs will describe project- or task- specific activities, there may be occasions when a *generic* QAPP may be more appropriate. A generic QAPP addresses the general, common activities of a program that are to be conducted at multiple locations or over a long period of time. For example, a generic QAPP may be useful for a large monitoring program that uses the same methodology at different locations. A generic QAPP describes, in a single document, the information that is not site or time-specific but applies throughout the program. Application-specific information is then added to the approved QAPP, either in the form of a site-specific QAPP, QAPP Addendum, or SAP.

1.1.3.2 WAPs and SAPs

In certain cases, WAPs or SAPs are required by a RCRA regulation. For example, WAPs are required as part of a permit application. Where WAPs or SAPs are required by regulation, the applicable regulations should be reviewed to ensure that the content and format requirements for the WAP or SAP are understood. Additionally, it should be noted that EPA has prepared various guidance documents to assist in preparing WAPs and SAPs that meet various regulatory requirements. Examples of these guidance documents include the following:

- EPA guidance on the preparation of WAPs can be found in the document entitled *Waste Analysis at Facilities that Generate, Treat, Store and Dispose of Hazardous Wastes* (ECDIC 2002-011), dated April 1994.
- EPA guidance on SAPs for delisting petitions can be found in the document entitled *EPA RCRA Delisting Program Guidance Manual for the Petitioner*, dated March 2000.
- General SAP guidance can be found in EPA's *RCRA Waste Sampling Draft Technical Guidance*, dated August 2002.
- Chapter 9 of this document (*Test Methods for Evaluating Solid Waste, Physical/Chemical Methods - SW-846*) presents additional discussion on sampling plans.

A QAPP may also be prepared, and required, as a supplement to any WAP or SAP. It should also be noted that if a WAP or SAP is not required by regulation, QAPPs can be prepared such that they present sufficient detail to cover both the QAPP and WAP or SAP in a single document. If a WAP or SAP is prepared along with a QAPP, it is common for these documents to reference one another for necessary information. To enhance the usability of QAPPs and WAPs/SAPs, references between the documents should be specific, providing the full document name, section number, subsection, and page number.

1.1.4 Data Quality Indicators

As part of systematic planning, measurement performance criteria for DQIs must be established and documented for each data collection effort. DQIs apply to both laboratory and field activities. At a minimum, DQIs should include precision, accuracy, representativeness, comparability, and completeness (PARCC). The following presents a discussion of PARCC and other DQIs.

1.1.4.1 Precision

Precision measures the agreement among a set of replicate measurements. Field precision is assessed through the collection and analysis of field duplicates. Analytical precision is estimated by duplicate/replicate analyses, usually on laboratory control samples, spiked samples and/or field samples. The most commonly used estimates of precision are the relative standard deviation (RSD) and, when only two samples are available, the relative percent difference (RPD).

1.1.4.2 Accuracy

Accuracy is the closeness of a measured result to an accepted reference value. Accuracy is usually measured as a percent recovery. QC analyses used to measure accuracy include standard recoveries, laboratory control samples, spiked samples, and surrogates.

1.1.4.3 Representativeness

Sample representativeness expresses the degree to which data accurately and precisely represents a characteristic of a population, parameter variations at a sampling point, a process condition, or an environmental condition. It is dependent on the proper design of the sampling program and will be satisfied by ensuring the approved plans were followed during sampling and analysis.

1.1.4.4 Comparability

Comparability expresses the degree of confidence with which one data set can be compared to another. It is dependent upon the proper design of the sampling program and will be satisfied by ensuring that the approved plans are followed and that proper sampling and analysis techniques are applied. Further, when assessing comparability, data sets should be of known and documented quality.

1.1.4.5 Completeness

Completeness is a measure of the amount of valid data collected compared to the amount planned. Measurements are considered to be valid if they are unqualified or qualified as estimated data during validation. Field completeness is a measure of the number of samples collected versus the number of samples planned. Laboratory completeness is a measure of the number of valid measurements compared to the total number of measurements planned.

1.1.4.6 Bias

Bias is the systematic or persistent distortion of a measurement process that causes error in one direction (e.g., the sample measurement is consistently lower than the sample's true value). Bias can be introduced during sampling, analysis, and data evaluation. Sampling bias is best addressed through the proper selection and use of sampling tools, uses of correct sampling and subsampling procedures to limit preferential selection or loss of sample media, use of random sampling designs, and use of sample handling procedures that limit the loss or gain of constituents to the sample media. Analytical bias refers to deviation in one direction (i.e., high, low or unknown) of the measured value from a known spiked amount. Analytical bias can be assessed by comparing a measured value in a sample of known concentration to an accepted reference value or by determining the recovery of a known amount of contaminant spiked into a sample (matrix spike). The planning team should specify qualitative criteria for sampling bias and quantitative criteria for analytical bias, typically expressed as "percent recovery."

1.1.4.7 Reproducibility

Analytical reproducibility is a quantitative indicator that is used when referring to the uncertainty associated with the use of multiple laboratories for a specific study. The ability of multiple laboratories to generate the same result for splits of the same sample can be expressed as a measure of interlaboratory precision and bias. Specific indicators of precision and bias (such as range or variance) are generated using data from replicate samples sent to multiple laboratories.

1.1.4.8 Repeatability

Repeatability is a quantitative indicator that in used within a single laboratory (i.e., intralaboratory precision). It is determined when the laboratory, analyst, test method and equipment remain constant and random aliquots of the same sample are analyzed within a short period of time.

1.1.4.9 Sensitivity

Sensitivity is an instrument's or method's minimum concentration that can be reliably measured or reported (i.e., or lower limit of quantitation [LLOQ]).

Please note the glossary section to this chapter includes further discussion of the DQIs.

1.2 IMPLEMENTATION

Implementation is the second phase of the project life cycle. The implementation phase includes the following steps:

1.2.1 Standard Operating Procedures (SOPs)

SOPs are written documents that describe, in detail, the routine procedures to be followed for a specific operation, analysis, or action. Please note, in most cases, referencing a given method or method number is not sufficient, unless the method is performed exactly as written (e.g., a method-defined parameter). Laboratories must have an SOP to demonstrate that their procedure meets the conditions of the referenced method. Information on how to prepare SOPs can be found in EPA's *Guidance for the Preparation of Standard Operating Procedures (QA/G-6)*, dated April 2007.

SOPs enable tasks to be accomplished reproducibly, even if there are changes in the personnel performing them. Consistent use of an approved SOP ensures conformance with organizational practices, reduction in the frequency of errors, and improved data comparability and defensibility. SOPs also serve as resources for training and for ready reference and documentation of proper procedures.

The SOPs, and/or procedures described in the QAPP, must be followed for all project activities from sample collection to validation. If project-specific modifications to SOPs are needed, they must also be presented in the QAPP. Field and laboratory SOPs should be provided for the areas discussed below, as applicable:

- Sample Custody SOPs that describe sample receipt and handling; sample storage; sample security and tracking; and holding times
- Sample collection
- Analytical Method SOPs, including subsampling, sample preparation/clean-up, calibration, QC, and analysis
- Reagent/Standard Preparation and Traceability SOPs
- Equipment Calibration and Maintenance SOPs
- Corrective Action SOPs
- Data Reduction SOPs
- Data Reporting SOPs
- Records Management SOPs
- Waste Disposal SOPs

As indicated above, the QC associated with each method may be provided in appropriate SOPs. The types of QC parameters to include in the SOPs and QAPP are defined in the glossary of this chapter. Since the QC acceptance limits are frequently adjusted more often than SOPs are revised, it may be impractical to update SOPs as these limits change. Therefore, field and laboratory QC limits may need to be presented in QAPP tables rather than SOPs.

1.2.2 Conducting the Study/Experiment

The data collection effort is performed in accordance with approved plans (e.g., QAPP). The QAPP will present all proposed methods (i.e., including sampling, subsampling, preservation, preparation, clean-up and determinative methods), as well as a rationale for why the proposed methods are sufficient to meet the project DQOs.

The QAPP should also indicate whether the proposed analyses include method-defined parameters and/or whether the flexible approach to methods will be utilized. For the flexible approach, the QAPP must also demonstrate that the proposed methods are adequate to reach the study goals outlined in the DQOs.

1.2.2.1 Method-defined parameters

Method-defined parameters (MDP), such as the Toxicity Characteristic Leaching Procedure (TCLP), have been written into regulations, the methods should be followed without deviation, and should not to be modified on a project basis. For a list of method-defined parameters, see Vol 40 CFR 260.11 references or the Methods Innovation Rule (MIR), in Volume 70, Number 113 of the Federal Register (70 FR 34537 Table 3). Some method-defined parameters are discussed in Chapter 8 of this manual.

1.2.2.2 Flexible Approach to Environmental Measurements

The Flexible Approach to Environmental Measurement was finalized in 2008 as EPA’s preferred approach for environmental monitoring except in cases where methods are required by regulation.

The goals of the flexible approach are to:

- Provide method users flexibility when choosing sampling and analytical approaches to meet regulatory requirements for measurements
- Develop processes for validation to confirm measurements meeting quality requirements
- Increase collaboration with stakeholders to develop validation processes for new measurement technology
- Ensure timely assessment of new or modified technologies, methods, and procedures.

Chapter Two of this manual entitled, "Choosing the Correct Procedure” provides additional guidance regarding the selection of appropriate methods and method flexibility.

1.2.3 Technical Assessments

Technical Assessments (otherwise known as audits) are systematic and objective examinations of a program or project to determine whether environmental data generation activities and related results comply with planning documents. Technical assessments can be performed to evaluate all phases of a project including field sampling, laboratory analysis, validation and data handling/management.

The QAPP should identify all personnel responsible for performing technical assessments, the authority of the auditor (e.g., do they have the authority to stop work if significant deviations from planning documents are found), and the planned audit frequency. Additionally, if technical assessments are planned or required as part of a project, the QAPP should provide the applicable technical assessment checklists. These checklists establish and document the scope of all proposed technical assessments. The development of these technical assessment checklists should overseen by an independent party (i.e., someone not involved in the day to day operations of a project), such as the organization's QA personnel. Further, the QAPP should establish a process for correcting technical assessment findings and confirming implementation of any corrective actions taken as a result of the findings.

While most technical assessments will be scheduled in advance with an organization, there may be occasions when unannounced technical assessments are needed. However, an unannounced audit may not reveal a representative picture of project activities if it occurs when the project is not active, or activities that are not within the scope of the technical assessment are occurring.

Technical assessments may be planned as part of the pre-award activities, or throughout the life of a project. For example, pre-award audits, including performance evaluation (PE) samples, are useful tools in determining the ability of a laboratory to perform the proposed analytical work. Additionally, technical assessments may also be used as an investigative tool where problems may be suspected. The EPA document Guidance on Technical Audits and Related Assessments for Environmental Data Operations (QA/G-7), dated January 2000, provides detailed information on various types of technical audits and includes an example checklist for a technical systems audit of a laboratory measurement system.

1.3 ASSESSMENT

Following planning (Sec. 1.1) and implementation (Sec. 1.2), assessment is the third and final phase of the project data generation life cycle. The purpose of this phase is to evaluate whether the data are of the type, quantity and quality needed to meet project DQOs. Assessment can involve many different complex activities, including the use of statistical tools. This section provides an introduction and overview of these data assessment activities.

1.3.1 Data Verification and Validation

Data verification and/or validation is the first step in the assessment process. Validation and verification are defined in the EPA Guidance on Environmental Data Verification and Data Validation (QA/G-8), dated November 2002. According to QA/G-8, verification is the process of evaluating the completeness, correctness, and conformance/compliance of a data set against a specified set of requirements. QA/G-8 defines validation as an analyte and sample specific process that extends the evaluation of data beyond data verification to determine its analytical quality. For the purposes of this chapter, it should be noted that the meaning of verification and validation is often program, organization and/or system specific. Further, these terms are used interchangeably at times, and in other cases have very different meanings. Therefore, it is critical that the procedures for verification and/or validation be clearly documented in the approved QAPP.

In general, data verification/validation involves the examination and review of project data (e.g., field and laboratory data for all applicable QC measurements) to confirm that the sampling and analysis protocols specified in the QAPP (and any other planning or contractual documents) were followed. Data verification/validation also involves examining whether the data met the method performance and acceptance criteria established in the project QAPP. When these criteria are not met, data verification/validation procedures should include qualification of the data (e.g., the *J* qualifier is commonly used to indicate *estimated* data and the *R* qualifier is commonly used to indicate *rejected* data). The reasons for any failure to meet performance criteria also need to be documented during this phase of assessment (e.g., in a data verification/validation report).

In addition to QA/G-8, EPA has published several references which provide more detailed information on what should be included in data verification and validation procedures. These include EPA regional and programmatic validation guidance documents that may apply to particular projects. It is also common for EPA guidance from one program or region to be modified for use in another area. While this may be acceptable, any modifications or changes to the established validation procedures should be included in the approved QAPP.

Data verification/validation may be performed at various phases throughout a project. As such, the procedures for verifying and/or validating data may need to be described in laboratory SOPs and/or QA Plans, in addition to the project documents like the QAPP. Corrective action based on verification/validation findings may also need to be described in these documents.

Data verification/validation activities may be performed internally (e.g., when the laboratory or data collector review their own data), or externally by an independent entity (i.e., a party that is not associated with the data collection effort). Internal and external data verification/validation procedures should be defined in the QAPP or other project documents.

A data verification/validation report should be generated to document the procedures followed as well as the findings and qualifications applied during data verification/validation. The report should include a list of the samples collected, field information about how the samples were collected, the analyses performed on the samples, the results of the analysis and the quality of the reported data, at a minimum. The usability of this report can be enhanced by listing the samples and analytes affected by each QC criteria exceedance, as well as the extent of the exceedance, and any qualifiers applied. Any other observations noted by the data reviewer that may impact the usability of the data should also be documented.

1.3.2 Data Quality Assessment

Data quality assessment (DQA) is the second step in the assessment process. DQA is often needed because data verification/validation alone is generally not sufficient to determine whether a data set can be used for its intended purpose. Typically, the DQA follows the data verification and/or validation step.

In general, the DQA should include an evaluation of overall trends or biases in the data and associated QC results, as well as how the data may be affected. For random data sets, the DQA should evaluate the validity of any statistical assumptions made during the planning phase. If the statistical assumptions made during the planning phase are not supported by the data, recommendations for corrective action should be presented. All DQA findings should be summarized in a report.

Guidance documents available from EPA that discuss the DQA process include *Data Quality Assessment: A Reviewer's Guide* (QA/G-9R), dated February 2006, and *Data Quality Assessment: Statistical Tools for Practitioners* (QA/G-9S), dated February 2006.

The DQA process described in this guidance is a five-step process.

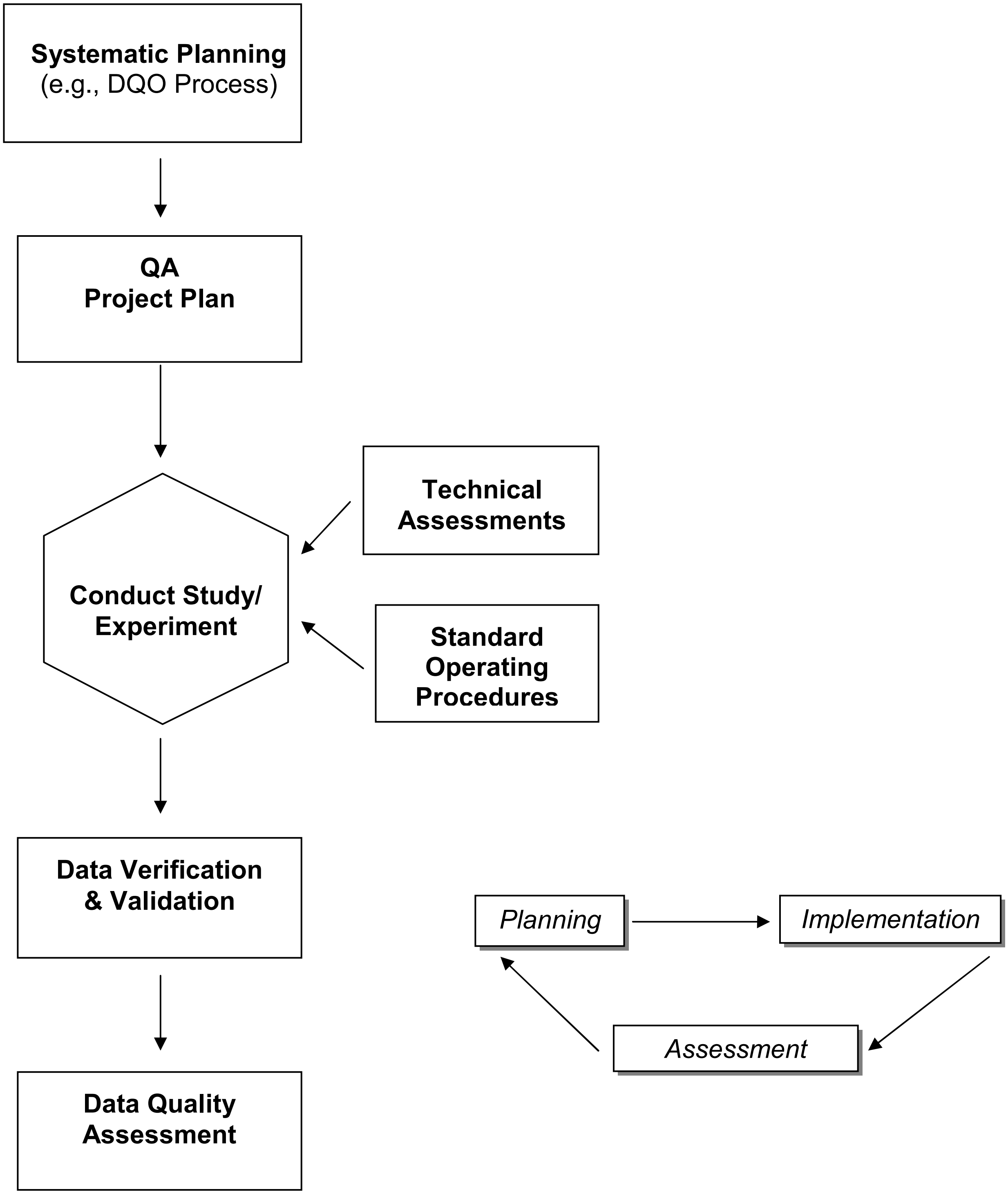
Step 1: Review the Data Quality Objectives and Sampling Design
Step 2: Conduct a Preliminary Data Review
Step 3: Select the Statistical Method
Step 4: Verify the Assumptions of the Statistical Method

It is recommended that the data user refer to these guidance documents, because they provide extensive information about DQA and the statistical tools that can be employed.

Although the DQA process described in QA/G-9R and QA/G-9S includes a significant amount of statistical procedures, it should be noted that the DQA process is not only applicable to random data sets, where statistics can be used to assess the data. A DQA should also be performed on judgmental, or biased, data sets. The process for how any data set will be assessed should be determined during the planning phase, and documented in the QAPP or other site documents.

FIGURE 1-1

PROJECT LEVEL EPA QA SYSTEM



1.4. REFERENCES AND SOURCES FOR ADDITIONAL QA/QC INFORMATION

1. USEPA. *Guidance on Systematic Planning Using the Data Quality Objectives Process, EPA QA/G-4*. Quality Staff, Office of Environmental Information, United States Environmental Protection Agency, Washington, D.C. February 2006.

2. USEPA. *EPA Quality Manual for Environmental Programs CIO 2105-P-01-0*. Office of Environmental Information Quality Staff, United States Environmental Protection Agency, Washington, D.C. May 5, 2000.

3. USEPA. *Guidance on Choosing a Sampling Design for Environmental Data Collection,* EPA QA/G-5S. Quality Staff, Office of Environmental Information, United States Environmental Protection Agency, Washington, D.C. December 2002.

4. USEPA. *Guidance on Environmental Data Verification and Data Validation*, EPA QA/G-8. Quality Staff, Office of Environmental Information, United States Environmental Protection Agency, Washington, D.C. November 2002.

5. USEPA. *Data Quality Assessment: A Reviewer's Guide*, QA/G-9R. Quality Staff, Office of Environmental Information, United States Environmental Protection Agency, Washington, D.C. February 2006.

6. USEPA. *Data Quality Assessment: Statistical Tools for Practitioners*, QA/G-9S. Quality Staff, Office of Environmental Information, United States Environmental Protection Agency, Washington, D.C. February 2006.

7. USEPA. *Guidance for Preparing Standard Operating Procedures*, EPA QA/G-6. Quality Staff, Office of Environmental Information, United States Environmental Protection Agency, Washington, D.C. April 2007.

8. USEPA. *RCRA Waste Sampling Draft Technical Guidance.* Office of Solid Waste, United States Environmental Protection Agency, Washington, D.C. August 2002.

9. USPEA. *Guidance for Quality Assurance Project Plans*, EPA QA/G-5. Quality Staff, Office of Environmental Information, United States Environmental Protection Agency, Washington, D.C. December 2002.

10. USEPA. *EPA Requirements for Quality Assurance Project Plans*, EPA QA/R-5. Quality Staff, Office of Environmental Information. United States Environmental Protection Agency, Washington, D.C. March 2001.

11. USEPA. *RCRA Delisting Program Guidance Manual for the Petitioner*. United States Environmental Protection Agency, March 23, 2000.

12. USEPA. *Waste Analysis at Facilities That Generate, Treat, Store and Dispose of Hazardous Wastes*, ECDIC 2002-011. Office of Waste Programs Enforcement, United States Environmental Protection Agency. April 1994.

13. USEPA. *Guidance on Technical Audits and Related Assessments for Environmental Data Operations*, QA/G-7. Quality Staff, Office of Environmental Information, United States Environmental Protection Agency, Washington, D.C. January 2000.

1.5. GLOSSARY

Also see the following for a glossary of quality-related terms developed by EPA:

http://www.epa.gov/fem/pdfs/Env_Measurement_Glossary_Final_Jan_2010.pdf

ACCURACY	The degree of agreement between an observed value and an accepted reference value. When applied to a set of observed values, accuracy includes a combination of a random error (precision) and systematic error (bias) components.
ANALYTICAL BATCH	A group of samples, including quality control samples, which are processed together using the same method, the same lots of reagents, and at the same time or in continuous, sequential time periods. Samples in each batch should be of similar composition and share common internal quality control standards. For QC purposes, if the number of samples in a batch is limited to 20; laboratory QC samples are not included in the batch count. Each batch should be uniquely identified within the laboratory for tracking purposes. Samples collected from the same site would normally be grouped together for batching purposes within the constraints imposed by the method holding times and batch size. Samples prepared in the same batch would normally be analyzed together on a single instrument. However, laboratories may find it necessary to group multiple clients' samples into a single batch. Under these circumstances, additional matrix QC samples (*i.e.*, duplicates, matrix spikes) may be needed to evaluate the effect of the matrix from each site on method performance.
BIAS	The constant or systematic distortion of a measurement process, different from random error, which manifests itself as a persistent positive or negative deviation from the known or true value. This can result from improper data collection, poorly calibrated analytical or sampling equipment, or limitations or errors in analytical methods and techniques. Bias can be assessed by comparing a measured value to an accepted reference value in a sample of known concentration or by determining the recovery of a known amount of contaminant spiked into a sample (matrix spike). Thus, the bias (B) due to matrix effects based on a matrix spike is calculated as: $B = (x_s - x_u) - K$ where: x_s = measured value for spiked sample, x_u = measured value for unspiked sample, and K = known value of the spike in the sample. Using the following equation yields the percent recovery (%R). $\%R = 100\,(x_s - x_u)/K$

BLANK	Blanks are generally considered to be acceptable if target analyte concentrations are less than ½ the LLOQ or are less than project-specific requirements. Blanks may contain analyte concentrations greater than acceptance limits if the associated samples in the batch are unaffected (i.e. targets are not present in samples or sample concentrations are ≥10X the blank). Other criteria may be used depending on the needs of the project. For method specific details see methods 6010, 6020 for inorganics and Method 8000 for organics). See also Calibration Blank, Equipment Blank, Method Blank, Reagent Blank and Trip Blank.
CALIBRATION BLANK	A calibration blank is a sample of analyte-free media that can be used along with prepared standards to calibrate the instrument. A calibration blank may also be used to verify absence of instrument contamination (e.g., initial calibration blank and continuing calibration blank).
CALIBRATION CHECKS	Calibration check analyses are used to assess calibration drift and memory effects over time for each analytical system. These analyses may include zero, span (low and high) to cover the full calibration range, and mid-range checks, depending on the method.
CALIBRATION CURVE	A plot of instrument response to an analyte versus known concentrations or amounts of analyte standards. Calibration standards are prepared by successively diluting a standard solution to produce working standards which cover the working range of the instrument. Standards should be prepared at the frequency specified in the appropriate method. The calibration standards should be prepared using the same type of acid or solvent and at the same concentration as the samples following sample preparation. This is applicable to organic and inorganic chemical analyses.
CO-LOCATED SAMPLES	A type of field duplicate where independent samples are collected as close as possible to the same point in space and time. They are two separate samples taken from the same source, stored in separate containers, and analyzed independently by the same method and laboratory. These duplicates are useful in documenting the precision of the sampling process.
COMPARABILITY	The degree to which different methods or data agree or can be represented as similar. Comparability describes the confidence that two data sets can contribute to a common analysis and interpolation.
COMPLETENESS	A measure of the amount of valid data obtained from a measurement system compared with the amount that was expected to be obtained under correct, normal conditions. Percent completeness is calculated as: $\% \text{ Completeness} = \frac{x}{y} \times 100$ where:

x = amount of valid data obtained
y = amount of data expected to be obtained

DATA QUALITY INDICATORS (DQIs)	The quantitative statistics and qualitative descriptors that are used to interpret the degree of acceptability or utility of data to the user. The principal indicators of data quality are precision, bias, accuracy, representativeness, comparability, completeness, and sensitivity.
DATA QUALITY OBJECTIVES (DQOs)	Qualitative and quantitative statements derived from the DQO Planning Process that clarify the purpose of the study, define the most appropriate type of information to collect, determine the most appropriate conditions from which to collect that information, and specify tolerable levels of potential decision errors.
DATA VALIDATION	The process of evaluating the available data against the project DQOs to make sure that the objectives are met. Data validation may be very rigorous, or cursory, depending on project DQOs. The available data reviewed will include analytical results, field QC data, laboratory QC data, and may also include field records.
DUPLICATE	See Co-located Samples, Laboratory Duplicate, Field Duplicate, Field Split Samples, and Matrix Spike Duplicate.
EQUIPMENT BLANK	A sample of analyte-free media which has been used to rinse the sampling equipment. It is collected after completion of decontamination and prior to sampling at a location. This blank is useful in documenting adequate decontamination of sampling equipment.
EQUIPMENT RINSATE	See Equipment Blank.
FIELD BLANK	Field blanks include any sample submitted from the field that is identified as a blank. These include trip blanks, rinsates, equipment blanks, etc. Field blanks may also be obtained by the sampling organization to measure ambient contamination in the field. If this type of field blank is requested, a container of reagent water or a solid blank material is opened in the field for a predefined period of time. The sample is then sent to the laboratory for analysis.
FIELD DUPLICATES	Field duplicates are useful in documenting the precision of the sampling process. Field duplicates are used to assess improper homogenization of the samples in the field; reproducibility of sample preparation and analysis; and, heterogeneity of the matrix. See also Co-located Samples and Field Split Samples.
FIELD SPLIT SAMPLES	A type of field duplicate where the sample is homogenized and then divided into two or more aliquots so that variability can be evaluated, (i.e., often between laboratories or methods). Homogenization may have an impact on sample integrity for some sample types (e.g., VOCs

	in soil), and in these cases co-located samples may be more appropriate.
INITIAL DEMONSTRATION of PROFICIENCY (IDP)	Prior to the analysis of samples an initial demonstration of method proficiency is accomplished through the successful calibration of method-specific instruments according to project requirements and criteria set forth in the applicable analytical methodology. This initial demonstration should be performed prior to independently running an analytical method, and should be repeated if other changes occur (e.g., instrument repair, significant change in procedure). Please see individual methods for additional guidance on IDP.
INTERNAL STANDARD	Internal standards may be spiked into prepared field samples and QC samples (or sample extracts). Their recovery is generally used to demonstrate the lack of severe matrix effect in the instrumental analysis by setting criteria for the internal standard response in comparison to a response in a sample with a known lack of matrix effect (*i.e.*, a standard). Internal standards are also used to account for matrix effects and/or variability in instrument response by normalizing the response of the target analytes and surrogates, thereby decreasing measurement bias to the extent that their behavior mimics that of the target analytes.
LABORATORY CONTROL SAMPLE	The Laboratory Control Sample (LCS) is analyzed to assess general method performance based on the ability of the laboratory to successfully recover target analytes from a control matrix. The LCS is similar in composition to the method blank in that it is an aliquot of analyte-free water or analyte-free solid (e.g., Ottawa sand, anhydrous sodium sulfate, or other purified solid) to which known amounts of the method analytes are added. LCS analyses help determine if the system is running properly (i.e., within pre-defined limits). Although the frequency of LCS analysis should be determined by the needs of a project, typically one LCS is prepared and analyzed for every analytical batch. The LCS sample is prepared and analyzed in the same analytical batch and in exactly the same manner as the other routine samples. The recovery of the target analytes in the LCS analysis demonstrates whether the methodology is in control and the laboratory is capable of making unbiased measurements. The results of the LCS are evaluated in conjunction with other QC information to determine the acceptability of the data generated for that batch of samples. Acceptance criteria for LCS recovery are calculated based on statistical treatment of historical LCS recovery data through the use of control charts.
LABORATORY DUPLICATE	The analysis or measurements of the variable of interest performed identically on two sub-samples of the same sample, usually taken from the same container. The results from duplicate analyses are used to evaluate analytical or measurement precision and include variability associated with sub-sampling and the matrix, but not the precision of field sampling, preservation, or storage internal to the laboratory. Laboratory duplicate analysis entails removing two aliquots from the

	same sample and taking them through the same preparative and analytical procedures to evaluate analytical precision. Laboratory duplicates are more commonly used to assess precision for inorganic and radiological constituents, while precision for organic analyses is usually assessed by determining the RPD between matrix spike and matrix spike duplicates. The frequency of laboratory duplicate analysis will depend on project requirements.
LOWER LIMIT OF QUANTITATION (LLOQ)	The lowest point of quantitation which, in most cases, is the lowest concentration in the calibration curve. The LLOQ is initially verified by spiking a clean control material (e.g., reagent water, method blanks, Ottawa sand, diatomaceous earth, etc.) at the LLOQ and processing through all preparation and determinative steps of the method. Laboratory-specific recovery limits should be established when sufficient data points exist. Individual methods may recommend procedures for verifying the LLOQ and acceptance limits for use until the laboratory has sufficient data to determine acceptance limits. LLOQs should be determined at a frequency established by the method, laboratory's quality system, or project. Please see individual methods for additional guidance on implementing LLOQ (e.g., 8000, 6020).
MATRIX	The material of which the sample is composed or the substrate containing the analyte of interest, such as waste water, storm water and biosolids. Also called medium or media.
MATRIX SPIKE	Matrix spikes are aliquots of environmental samples to which known concentrations of certain target analytes have been added before sample preparation, cleanup, and determinative procedures have been implemented. Matrix spike analysis would normally be included with each preparation batch of samples processed. Under ideal circumstances, the original, unspiked, field sample will be analyzed first, to determine the concentration in the unspiked sample. However, if this approach is not practical, the samples may be spiked at the midpoint of the calibration range or at the same level as the LCS. The matrix spike analysis is used to assess the performance of the method by measuring the effects of interferences caused by the sample matrix and reflects the bias of the method for the particular matrix in question.
MATRIX SPIKE DUPLICATES	Matrix spike duplicates are additional replicates of matrix spike samples that are subjected to the sample preparation and analytical scheme as the original sample. A matrix spike duplicate sample would normally be included with each preparation batch of samples processed. Analysis of spiked duplicate samples ensures a positive value, allowing for estimation of analytical precision. Matrix spike duplicates are used to document the precision as well as bias of a method in a given sample matrix. When critical decisions are based on the matrix spike and matrix spike duplicate recoveries, the laboratory should maintain control charts for these samples to monitor

precision and bias for each particular matrix.

METHOD BLANK Method blanks are analyzed to assess background interference or contamination that exists in the analytical system that might lead to the reporting of elevated concentration levels or false positive data. The method blank is defined as an interference-free blank matrix, similar to the sample matrix, to which all reagents are added in the same volumes or proportions as used in sample preparation and carried through the complete sample preparation, cleanup, and determinative procedures. For aqueous analyses, analyte-free reagent water would typically be used. For soil analyses, a purified solid matrix (e.g., sand) would typically be used, except for metals analyses. Method blank results are evaluated in conjunction with other QC information to determine the acceptability of the data generated for that batch of samples. The method blank results should be below the LLOQ for the target analytes being tested; otherwise, corrective action should be taken. A method blank is included with the analysis of every analytical batch of 20 samples or less or as stated in the QAPP or method, whichever is more frequent.

ORGANIC-FREE REAGENT WATER All references to water in the methods refer to water in which an interferant is not observed at the LLOQ for the compounds of interest. Preparation of organic-free reagent water may depend on the types of interferants of concern for the analysis and may include boiling, sparging with an inert gas, reverse osmosis purification, distillation, particle filtration, activated carbon filtration, ion exchange filtration, etc.

POST-DIGESTION SPIKES Post-digestion spike samples are typically prepared for inorganic analyses when pre-digestion/pre-distillation matrix spike recoveries are outside the required control limits. They are prepared by spiking a known amount of standard to the sample digestate. The recovery data from the post digestion spike analyses are used to further assess if matrix effects may be a source of measurement bias in sample quantitation.

PRECISION The agreement among a set of replicate measurements without assumption of knowledge of the true value. Precision is estimated by means of duplicate/replicate analyses of separate aliquots of the same sample (not multiple runs of a single digestion/extraction). These samples should contain concentrations of analyte at or above the LLOQ, and may involve the use of matrix spikes. The most commonly used estimates of precision are:

Relative standard deviation (RSD), also known as the coefficient of variation (CV):

$$RSD = CV = (100)*(S/\bar{x})$$

where:

$\bar{x}$ = the arithmetic mean of the i measurements, and
S = the square root of the variance of i measurements; and,

Relative percent difference (RPD) when only two results are compared:

$$RPD = \frac{|X_1 - X_2|}{\left(\frac{X_1 + X_2}{2}\right)} * 100$$

where: x_1 and x_2 are measurements of independently prepared aliquots of the same sample or replicate samples.

PROJECT	Single or multiple data collection activities that are related through the same planning sequence.
QUALITY CONTROL SAMPLE	A sample made from standards or matrix and used to verify acceptability of the results from preparation and/or analysis of a batch of samples. Examples of laboratory quality control samples are method blanks, laboratory duplicates, and laboratory control samples; field quality control samples are field blanks, trip blanks, field duplicates, and matrix spikes.
QUALITY ASSURANCE PROJECT PLAN (QAPP)	A formal document describing in comprehensive detail the necessary quality assurance, quality control, and other technical activities that should be implemented to ensure that the results of the work performed will satisfy the stated performance criteria.
REAGENT BLANK	Reagent blanks are analyzed to assess background interference or contamination that exists in the analytical system that might lead to the reporting of elevated concentration levels or false positive data. The reagent blank is defined as an interference-free blank matrix, to which all reagents are added in the same volumes or proportions as used in sample preparation but are NOT carried through the complete sample preparation, cleanup, and determinative procedures. The purpose of a reagent blank is to gauge contamination from chemical inputs and instrumental factors only. A reagent blank is NOT run as part of a digestion or preparation method.
REAGENT GRADE	Analytical reagent (AR) grade, ACS reagent grade, and reagent grade are synonymous terms for reagents which conform to the current specifications of the Committee on Analytical Reagents of the American Chemical Society.
REAGENT WATER	Water that has been generated by any method which would achieve the performance specifications for ASTM Type II water. For organic analyses, see the definition of organic-free reagent water.
REFERENCE MATERIAL	A material containing known quantities of target analytes in solution or in a homogeneous matrix. It is used to document the bias of the analytical process.
REPEATABILITY	The degree of agreement between mutually independent test results produced by the same analyst using the same test method and equipment on random aliquots of the same sample within a short

	period of time.
REPRESENTATIVE-NESS	A measure of the degree to which data accurately represent a characteristic of a population, a parameter variation at a sampling point, a process condition, or an environmental condition.
REPRODUCIBILITY	Reproducibility is defined as the closeness of the agreement between the results of measurements of the same analyte carried out under variable conditions of measurement.
STANDARD ADDITION	The addition of a known amount of analyte to the sample in order to determine the relative response of the detector to an analyte within the sample matrix. The relative response is then used to assess either an operative matrix effect or the sample analyte concentration.
SURROGATE	Surrogates are most commonly used to monitor the performance of organic analyses using methods such as high performance liquid chromatography (HPLC), gas chromatography (GC), and gas chromatography/mass spectrometry (GC/MS). Surrogate spikes are added to field samples and QC samples for organic analyses at known amounts, and their recoveries are used to assess matrix effects and, to some extent, verify proper processing and instrument performance for each sample. The analytes used as surrogates mimic the behavior of the target analyte(s) throughout sample preparation and instrument determination. Surrogates are organic compounds which are similar to the target analytes in chemical composition and behavior in the analytical process, but are not normally found in the environmental samples. Surrogates added to LCS samples and blanks are used to assess recovery in a matrix known to be free from interference. This information can be used to determine the magnitude of matrix interference effects on environmental sample results.
TRIP BLANK	A sample of analyte-free media taken from the laboratory to the sampling site and returned to the laboratory unopened. Trip blanks should be prepared at a frequency of one per day of sampling during which samples are collected for volatile organic constituents (VOCs). Trip blanks are prepared prior to the site visit at the time sample containers are shipped to the site. The trip blank should accompany the sampling kits throughout all the sample collection and transport operations. This blank will not be opened during the sampling activities and will be used to assess sample VOC contamination originating from sample transport, shipping, or site conditions. A trip blank is used to document contamination attributable to shipping and field handling procedures.

APPENDIX A

SUMMARY OF UPDATES/CHANGES IN CHAPTER 1

1. The entire Chapter has been rewritten and reorganized to reflect changes in the EPA data quality system approach.
2. The revision number was changed to two and the date published to July 2014.
3. This appendix was added to document changes made during the editorial process.
4. The document was updated to match the current SW-846 style guidelines.
5. Figure 1 was added based on information in EPA QA/G-8, November 2002, Figure 1.

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CHOOSING THE CORRECT PROCEDURE

SW-846 is not intended to be an analytical training manual. Therefore, method procedures are written based on the assumption that they will be performed by analysts who are formally trained in at least the basic principles of chemical analysis and in the use of the subject technology.

In addition, SW-846 methods, with the exception of required method use for the analysis of method-defined parameters, are intended to be guidance methods containing general information on how to perform an analytical procedure or technique which a laboratory can use as a basic starting point for generating its own detailed Standard Operating Procedure (SOP), either for its own general use or for a specific project application. The performance data included in these methods are for guidance purposes only, and are not intended to be and must not be used as absolute quality control (QC) acceptance criteria for the purposes of laboratory accreditation.

2.0 INTRODUCTION

The purpose of this chapter is to aid the analyst in choosing the appropriate methods for sample analyses, based upon the sample matrix and the analytes to be determined. The ultimate responsibility for producing reliable analytical results lies with the entity subject to the regulation. Therefore, members of the regulated community are advised to refer to this chapter and to consult with knowledgeable laboratory personnel when choosing the most appropriate suite of analytical methods. In addition, analysts and data users are advised that, except where explicitly specified in a regulation, the use of SW-846 methods is not mandatory in response to Federal testing requirements.

SW-846 analytical methods are written as quantitative analytical methods, and specific methods may be used to demonstrate that a waste does not contain analytes of concern that cause it to be managed as a hazardous waste. SW-846 methods typically contain relatively stringent recommended QC criteria appropriate to many levels of analyses, including trace. However, if a particular application does not require data of this quality, less stringent QC criteria may and should be used.

The choice of the appropriate sequence of analytical methods depends on the information sought and on the experience of the analyst. Appropriate selection is confirmed by the usability of data (i.e., adequate for its intended use). The use of the recommended procedures, whether they are approved or mandatory, does not release the analyst from demonstrating the correct execution of the method.

Sec. 2.1 provides guidance regarding the analytical flexibility inherent to SW-846 methods and the precedence of various QC criteria. Sec. 2.2 reviews the information required to choose the correct combination of methods for an analytical procedure. Sec. 2.3 provides useful information on implementing the method selection guidance for organic analyses. Sec. 2.4 provides guidance on choosing procedures for characteristic analyses. Sec. 2.5 provides guidance on the determination of analytes in groundwater. Finally, Sec. 2.6 provides information regarding choosing procedures for inorganic analyte analyses. Tables and figures referenced in this chapter are sequentially located after the last page of chapter text.

2.1 GUIDANCE REGARDING FLEXIBILITY INHERENT TO SW-846 METHODS AND THE PRECEDENCE OF SW-846 QUALITY CONTROL CRITERIA

The specific products and instrument settings cited in SW-846 methods represent those products and settings used during method development or subsequently evaluated by the Agency for use in the method. Glassware, reagents, supplies, equipment and settings other than those listed in this manual may be employed, provided that method performance appropriate for the intended application has been documented. Such performance includes consideration of precision, accuracy (or bias), recovery, representativeness, comparability, and sensitivity (quantitation or reporting limits, now referred to as lower limit of quantitation (LLOQ)) relative to the data quality objectives (DQOs) for the intended use of the analytical results. In response to this inherent flexibility, if an alternative analytical procedure is employed, then EPA expects the laboratory to demonstrate and document that the procedure is capable of providing appropriate performance for its intended application. This demonstration must not be performed after the fact, but as part of the laboratory's initial demonstration of proficiency with the method. The documentation should be in writing, maintained in the laboratory, and available for inspection upon request by authorized representatives of the appropriate regulatory authorities. The documentation should include the performance data as well as a detailed description of the procedural steps as performed (i.e., a written standard operating procedure).

Given this allowance for flexibility, EPA wishes to emphasize that this manual also contains procedures for "method-defined parameters," where the analytical result is wholly dependent on the process used to make the measurement. Examples include: the use of the toxicity characteristic leaching procedure (TCLP) to prepare a leachate, and the flash point, pH, paint filter liquids, and corrosivity tests. In these instances, changes to the specific methods may change the end result and incorrectly identify a waste as nonhazardous. Therefore, when the measurement of such method-defined parameters is required by regulation, those methods are <u>not</u> subject to the flexibility afforded in other methods.

Analysts and data users are advised that even for those analytes that are not method-defined, different procedures may produce some difference in results. Common examples include the differences in recoveries of phenolic compounds extracted from water by separatory funnel (Method 3510) and continuous liquid-liquid (Method 3520) extraction techniques, differences in recoveries of many compounds between Soxhlet (Method 3540) and ultrasonic (Method 3550) extraction techniques, and differences resulting from the choice of acid digestion of metals (Method 3050) or microwave digestion (Method 3051). Where practical, the Agency has included guidance in the individual methods regarding known potential problems, and analysts are advised to review this information carefully in choosing or modifying analytical procedures. Chapter One describes a variety of QC procedures that may be used to evaluate the quality of the analytical results. Additional QC procedures may be described in the individual methods. The results of these QC procedures should be used by the analyst to evaluate if the analytical procedures and/or any modifications are appropriate to generate data of the quality necessary to satisfy the data quality needs of the intended application.

The performance data included in the SW-846 methods are <u>not</u> intended to be used as absolute QC acceptance criteria for method performance. The data are intended to be guidance, by providing typical method performance in typical matrices, to assist the analyst in selection of the appropriate method for the intended application. In addition, it is the responsibility of the laboratory to establish actual operating parameters and in-house QC acceptance criteria, based on its own laboratory SOPs and in-house QC program, to demonstrate appropriate performance of the methods used in that laboratory for the RCRA analytical applications for which they are intended.

The regulated community is further advised that the methods here or from other sources need only be used for those specific analytes of concern that are subject to regulation or other monitoring requirements. The fact that a method provides a long list of analytes does not mean that each of those analytes is subject to any or all regulations, or that all of those analytes must be analyzed each time the method is employed, or that all of the analytes can be analyzed using a single sample preparation procedure. It is EPA's intention that the target analyte list for any procedure includes those analytes necessary to meet the DQOs of the project (i.e., those analytes subject to monitoring requirements and set out in a RCRA permit or other applicable regulation, plus those analytes used in the methods for QC purposes, such as surrogates, internal standards, system performance check compounds, etc.). Additional analytes, not included on the analyte list of a particular method(s) but needed for a specific project, may be analyzed by that particular method(s), if appropriate performance can be demonstrated for those analytes in the matrices of concern at the levels of concern.

2.1.1 Trace analysis vs. macroanalysis

Through the choice of sample size and concentration procedures, the methods presented in SW-846 were designed to address the problem of "trace" analyses (<1000 ppm), and have been developed for an optimized working range. These methods are also applicable to "minor" (1000 ppm - 10,000 ppm) and "major" (>10,000 ppm) analyses, as well, through use of appropriate sample preparation techniques that result in analyte concentrations within that optimized range. Such sample preparation techniques include:

1. Adjustment of size of sample prepared for analysis (for homogeneous samples)
2. Adjustment of injection volumes
3. Dilution or concentration of sample
4. Eelimination of concentration steps prescribed for "trace" analyses
5. Direct injection (of samples to be analyzed for volatile constituents)

The performance data presented in each of these methods were generated from "trace" analyses, and may not be applicable to "minor" and "major" analyses. Generally, extraction efficiency improves as concentration increases.

CAUTION: Great care should be taken when performing trace analyses after the analysis of concentrated samples, given the possibility of contamination.

2.1.2 Choice of apparatus and preparation of reagents

Since many types and sizes of glassware and supplies are commercially available, and since it is possible to prepare reagents and standards in many different ways, the apparatus, reagents, and volumes included in these methods may be replaced by any similar types as long as this substitution does not affect the overall quality of the analyses.

2.1.3 Quality control criteria precedence

Chapter One contains general QC guidance for analyses using SW-846 methods. QC guidance specific to a given analytical technique (e.g., extraction, cleanup, sample introduction, or analysis) may be found in Methods 3500, 3600, 5000, 7000, and 8000. Method-specific QC criteria may be found in Sec. 8.0 of most older individual methods, in Sec. 9.0 of newer methods, or in Sec. 11.0 of some air sampling methods. When inconsistencies exist between the information in these locations, method-specific QC criteria take precedence over both technique-specific criteria and those criteria given in Chapter One, and technique-specific QC criteria take precedence over the criteria in Chapter One.

2.2 INFORMATION NECESSARY FOR CHOOSING THE CORRECT PROCEDURE

In order to choose the correct combination of methods to comprise the appropriate analytical procedure, some basic information is necessary. This includes information on:

1. The physical state of the sample
2. The analytes of interest
3. The analytical sensitivity needed
4. The analytical objective
5. Whether the purpose is quantitation or monitoring
6. What sample containers and preservation will be used and what holding times may apply

2.2.1 Physical state(s) of sample

The phase characteristics of the sample must be known. There are several general categories of phases into which the sample may be categorized, including:

Aqueous
Sludge
Solid
Oil or other Organic Liquid
Multiphase Sample
Groundwater
Stack Sampling –Volatile Organics Sampling Train (VOST) Condensate
TCLP or Extraction Procedure (EP) Extract

There may be a substantial degree of overlap between the phases listed above and it may be useful to further divide these phases in certain instances. A multiphase sample may be a combination of aqueous, organic liquid, sludge, and/or solid phases, and generally must undergo a phase separation as the first step in the analytical procedure.

2.2.2 Analytes of interest

Analytes may be divided into various classes, based on the determinative methods used to identify and quantify them. The most basic differentiation is between organic (e.g., carbon-containing) analytes and inorganic (e.g., metals and anions) analytes.

Table 2-1 is an alphabetical list of analytes cited within the SW-846 organic determinative methods (excludes immunoassay and other screening methods). These analytes have been evaluated by those methods. The methods may also be applicable to other analytes that are similar to those listed. Tables 2-2 through 2-38 list the analytes for each organic determinative method. Table 2-39 indicates which methods are applicable to inorganic analytes.

NOTE: Analysts should review the discussion in Sec. 2.1 of this chapter with regard to the presence of an analyte in a method versus the need for its analysis for a given project.

2.2.3 Sensitivity

Some regulations may require a specific sensitivity or quantitation limit (LLOQ) for an analysis, as in the determination of analytes for the Toxicity Characteristic (TC). Drinking water quantitation limits, for those specific organic and metallic analytes covered by the National Primary Drinking Water Regulations, are desired in the analysis of groundwater.

2.2.4 Analytical objective

Knowledge of the analytical objective is essential in the choice of sample preparation procedures and in the selection of a determinative method. This is especially true when the sample has more than one phase. Knowledge of the analytical objective may not be possible or desirable at all management levels, but that information should be included in the project planning document and transmitted to the analytical laboratory management to ensure that the correct techniques are used during the analytical effort. Screening methods or composite sampling may be highly beneficial for some applications in order to generate a broader view of contaminant distribution than may be possible with a more precise and more costly method. Table 2-46 identifies some screening methods appropriate for different classes of organic chemicals in certain matrices.

2.2.5 Quantitation or monitoring

The strategy for quantitation of compounds in environmental or process samples may be contrasted with the strategy for collecting monitoring data. When there is little information available about the composition of the sample source (e.g., a well or process stream), mass spectral identification of organic analytes leads to fewer false positive results. Thus, the most practical form of quantitation for organic analytes is often mass spectral identification. However, where the sensitivity requirements exceed those that can be achieved using mass spectral methods (e.g., gas chromatography/mass spectrometry (GC/MS) or high performance liquid chromatography (HPLC)/MS), it may be necessary to employ a more sensitive quantitation method (e.g., electron capture). In these instances, the risk of false positive results may be minimized by confirming the results through a second analysis with a dissimilar detector or chromatographic column. Thus, the choice of technique for organic analytes may be governed by the sensitivity requirements and potential interferants.

Similarly, the choice of technique for metals may be governed by the sensitivity requirements and potential interferants.

In contrast, monitoring samples are analyzed to confirm existing and ongoing conditions, tracking the presence or absence of known constituents in an environmental or process matrix. In well-defined matrices and under stable analytical conditions, less compound-specific quantitation modes may be used, as the risk of false positive results is less.

2.2.6 Sample preservation and holding times

Table 2-40 provides information regarding recommended sample preservation techniques, sample holding times, and other information. Similar information may be found in Table 3-1 of Chapter Three (inorganic analytes) and Table 4-1 of Chapter Four (organic analytes). Samples need to be extracted and analyzed within the recommended holding times for the results to be considered reflective of native concentrations as collected. Analytical data generated outside of the recommended holding times should typically be considered as minimum values only. Such data may be used to demonstrate that a waste is hazardous where it shows the concentration of a constituent to be above the regulatory threshold, but cannot be used to demonstrate that a waste is not hazardous. However, regarding the information in Table 2-40, a longer holding time may be appropriate if it can be demonstrated that reported concentrations are not adversely affected from preservation, storage and analyses performed outside the recommended holding times.

2.3 CHOOSING PROCEDURES FOR ORGANIC ANALYSES

Table 2-1 summarizes the organic analysis options available in SW-846.

2.3.1 Extraction and sample preparation procedures for organic analytes

SW-846 methods for preparing samples for organic analytes are shown in Table 2-41. Method 3500 and associated methods should be consulted for further details on preparing the sample for analysis.

2.3.1.1 Aqueous samples

Methods 3510, 3520, and 3535 may be used for extraction of the semivolatile organic compounds (SVOCs) from aqueous samples. The choice of a preparative method depends on the sample. Method 3510, a separatory funnel liquid-liquid extraction technique, is appropriate for samples which will not form a persistent emulsion interface between the sample and the extraction solvent. The formation of an emulsion that cannot be broken up by mechanical techniques will prevent proper extraction of the sample. Method 3520, a continuous liquid-liquid extraction technique, may be used for any aqueous sample and will minimize emulsion formation.

Method 3535 is solid-phase extraction technique that has been tested for organochlorine pesticides, phthalate esters, polychlorinated biphenyls (PCBs), organophosphorus pesticides, nitroaromatics and nitramines, and some explosive compounds, and may be applicable to other semivolatile and extractable compounds as well. The aqueous sample is passed through a solid sorbent material which traps the analytes. They are then eluted from the solid-phase sorbent with a small volume of organic solvent. This technique may be used to minimize the volumes of organic solvents that are employed, but may not be appropriate for aqueous samples with high suspended solids contents.

2.3.1.1.1 Acidic extraction of phenols and acid analytes

The solvent extract obtained by performing Method 3510, 3520, or 3535 at a pH less than or equal to 2 will contain the phenols and acid/neutral extractable organics of interest, and may contain some mildly basic compounds. The particular pH extraction conditions needs to be defined during the project planning process based on the desired target analytes and performance goals.

2.3.1.1.2 Basic or neutral extraction of semivolatile analytes

The solvent extract obtained by performing Method 3510, 3520, or 3535 at a basic pH will contain the organic bases of interest, if acid extraction is performed first. It will also contain the neutral compounds of interest, if acid extraction is not performed. Refer to Table 1 in the extraction methods (3510 and/or 3520) for guidance on the requirements for pH adjustment prior to extraction and analysis.

2.3.1.2 Solid samples

Soxhlet extraction (Methods 3540, 3541 and 3542), pressurized fluid extraction (Method 3545), microwave extraction (Method 3546) and ultrasonic extraction (Method 3550) may be used with solid samples. Consolidated samples should be ground finely enough to pass through a 1-mm sieve. In limited applications, waste dilution (Methods 3580 and 3585) may be used if the entire sample is soluble in the specified solvent.

Methods 3540, 3541, 3542, 3545, 3546 and 3550 are neutral-pH extraction techniques and therefore, depending on the analysis requirements, acid-base partition cleanup (Method 3650) may be necessary. Method 3650 will only be needed if chromatographic interferences are severe enough to prevent quantitation of the analytes of interest. This separation will be most important if a gas chromatography (GC) method is chosen for analysis of the sample. If GC/MS is used, the ion selectivity of the technique may compensate for chromatographic interferences.

There are three extraction procedures for solid samples that employ supercritical fluid extraction (SFE). Method 3560 is a technique for the extraction of petroleum hydrocarbons from various solid matrices using carbon dioxide at elevated temperature and pressure. Method 3561 may be used to selectively extract polynuclear aromatic hydrocarbons (PAHs) from solid matrices using supercritical carbon dioxide and appropriate modifiers, based on the determinative procedure to be used. Method 3562 may be used to selectively extract organochlorine pesticides or PCBs from solid matrices using supercritical carbon dioxide.

2.3.1.3 Oils and organic liquids

Method 3580, waste dilution, may be used to prepare oils and organic liquid samples for analysis of semivolatile and extractable organic analytes by GC or GC/MS. Method 3585 may be employed for the preparation of these matrices for volatiles analysis by GC or GC/MS. To avoid overloading the analytical detection system, care must be exercised to ensure that proper dilutions are made. Methods 3580 and 3585 give guidance on performing waste dilutions.

To remove interferences for semivolatiles and extractables, Method 3611 (alumina cleanup) may be performed on an oil sample directly, without prior sample preparation.

Method 3650 is the only other preparative procedure for oils and other organic liquids. This procedure is a back extraction into an aqueous phase. It is generally introduced as a cleanup procedure for extracts rather than as a preparative procedure. Oils generally have a high concentration of semivolatile compounds and, therefore, preparation by Method 3650 should be done on a relatively small aliquot of the sample. Generally, extraction of 1 mL of oil will be sufficient to obtain a saturated aqueous phase and avoid emulsions.

NOTE: The use of traditional extraction techniques (i.e., 3510, 3520, 3535, 3540, 3541, 3545, 3546, and 3550), is neither suitable nor recommended for use in these matrices due to a high potential for hydrocarbon interferences and decreased determinative method sensitivity (i.e., poor analytical performance).

2.3.1.4 Sludge samples

Determining the appropriate methods for analysis of sludges is complicated because of the lack of precise definitions of sludges with respect to the relative percent of liquid and solid components. There is no set ratio of liquid to solid that enables the analyst to determine which of the three extraction methods cited is the most appropriate. Sludges may be classified into three categories: liquid sludges, solid sludges, and emulsions, but with appreciable overlap.

If the sample is an organic sludge (solid material and organic liquid, as opposed to an aqueous sludge), the sample should be handled as a multiphase sample.

2.3.1.4.1 Liquid sludges

Method 3510 or Method 3520 may be applicable to sludges that behave like, and have the consistency of, aqueous liquids. Ultrasonic extraction (Method 3550) and Soxhlet-type (Method 3540 series) procedures will, most likely, be ineffective because of the overwhelming presence of the liquid aqueous phase.

2.3.1.4.2 Solid sludges

Soxhlet extraction (Methods 3540 and 3541), pressurized fluid extraction (Method 3545), microwave extraction (Method 3546), and ultrasonic extraction (Method 3550) will be more effective when applied to sludge samples that resemble solids. Samples may be dried or centrifuged to form solid materials for subsequent determination of semivolatile compounds.

Using Method 3650, Acid-Base Partition Cleanup, on the extract may be necessary, depending on whether chromatographic interferences prevent determination of the analytes of interest.

2.3.1.4.3 Emulsions

Attempts should be made to break up and separate the phases of an emulsion. Several techniques are effective in breaking emulsions or separating the phases of emulsions, including:

1. Freezing/thawing -- Certain emulsions will separate if exposed to temperatures below 0 °C.

2. Salting out -- Addition of a salt to make the aqueous phase of an emulsion too polar to support a less polar phase promotes separation.

3. Centrifugation -- Centrifugal force may separate emulsion components by density.

4. Addition of water or ethanol -- Emulsion polymers may be destabilized when a preponderance of the aqueous phase is added.

5. Forced filtering through glass wool -- Many emulsions can be broken by forcing the emulsion through a pad of Pyrex glass wool in a drying column using a slight amount of air pressure (using a rubber bulb usually provides sufficient pressure).

If techniques for breaking emulsions fail, use Method 3520. If the emulsion can be broken, the different phases (aqueous, solid, or organic liquid) may then be analyzed separately.

2.3.1.5 Multiphase samples

Choice of the procedure for separating multiphase samples is highly dependent on the objective of the analysis. With a sample in which some of the phases tend to separate rapidly, the percent weight or volume of each phase should be calculated and each phase should be individually analyzed for the required analytes.

An alternate approach is to obtain a homogeneous sample and attempt a single analysis on the combination of phases. This approach will give no information on the abundance of the analytes in the individual phases other than what can be implied by solubility.

A third alternative is to select phases of interest and to analyze only those selected phases. This tactic must be consistent with the sampling/analysis objectives or it will yield insufficient information for the time and resources expended. The phases selected should be compared with Figure 2-1 and Table 2-41 for further guidance.

2.3.2 Cleanup procedures

Cleanup procedure selection is determined by the analytes of interest within the extract. Each analyte type in Table 2-42, Cleanup Methods for Organic Analyte Extracts, corresponds to one or more of the possible determinative methods available in the manual. However, the necessity of performing cleanup may also depend upon the matrix from which the extract was developed. Cleanup of a sample may be done exactly as instructed in the cleanup method for some of the analytes. There are some instances when cleanup using one of the methods may only proceed after the procedure is modified to optimize recovery and separation. Several cleanup techniques may be possible for each analyte category. The information provided is not meant to imply that any or all of these methods must be used for the analysis to be acceptable. Extracts with components which interfere with spectral or chromatographic determinations are expected to be subjected to cleanup procedures.

The analyst, in consultation with the regulator, customer, and other project planning participants as necessary, must determine the necessity for cleanup procedures, as there are no clear-cut criteria for indicating their use. Method 3600 and associated methods should be consulted for further details on extract cleanup.

2.3.3 Determinative procedures

In Table 2-43, the determinative methods for organic analytes are divided into four categories, specifically: GC/MS (this category includes single quadrupole MS, triple quadrupole (MS/MS), and time-of-flight instruments); GC with electromagnetic spectrometric (ES) detectors (i.e., Fourier Transform infrared (FT-IR) or atomic emission (AES)); specific quantitation methods (i.e., GC with specific non-MS detectors); and HPLC, including any HPLC-MS methods. This division is intended to help an analyst choose which determinative method will apply. Under each analyte column, SW-846 method numbers are indicated, if appropriate, for the determination of the analyte. A blank has been left if no chromatographic determinative method is available.

Generally, the MS procedures are more specific but less sensitive than the appropriate gas chromatographic/specific quantitation or ES method.

Method 8000 gives a general description of the techniques of GC and HPLC. Method 8000 should be consulted prior to application of any of the GC or HPLC methods.

Method 8081 (organochlorine pesticides), Method 8082 (PCBs), Method 8141 (organophosphorus pesticides), and Method 8151 (chlorinated herbicides), are preferred over GC/MS because of the combination of selectivity and sensitivity of the flame photometric, nitrogen-phosphorus, and electron capture detectors.

Method 8260 is a GC/MS method for volatile analytes. A variety of sample introduction techniques may be used with Method 8260, including Methods 5021, 5030, 5031, 5035, 5041, and 3585. A GC with a selective detector is also useful for the determination of volatile organic compounds in a monitoring scenario, as described in Sec. 2.2.5.

Method 8270 is a GC/MS method for semivolatile analytes. Method 8410 is another GC method for semivolatile analytes which uses a FT-IR detector. Method 8085 is a GC method for pesticides which uses an AES detector.

Table 2-43 lists several GC and HPLC methods that apply to only a small number of analytes. Methods 8031 and 8033 are GC methods for acrolein, acrylonitrile, and acetonitrile. Methods 8315 and 8316 are HPLC methods for these three analytes. Method 8316 also addresses acrylamide, which may be analyzed by Method 8032. Method 8325 is an HPLC coupled with particle beam MS for the determination of benzidines and nitrogen-containing pesticides in water and wastewater. Method 8520 measures formaldehyde in ambient air primarily for non-occupational exposure monitoring. Method 8540 is used for field-testing of soil samples for pentachlorophenol (PCP).

HPLC methods have been developed for other types of analytes, most notably N-methyl carbamates (Method 8318); azo dyes, phenoxy acid herbicides, carbamates, and organophosphorus pesticides (Method 8321); PAHs (Method 8310); explosives (Methods 8330, 8331, and 8332); and some volatile organics (Methods 8315 and 8316).

Method 8430 utilizes a FT-IR spectrometer coupled to a gas chromatograph to determine bis(2-chloroethyl) ether and its hydrolysis products. The sample is introduced by direct aqueous injection. Method 8440 may be employed for the determination of total recoverable petroleum hydrocarbons (TRPH) in solid samples by infrared (IR) spectrophotometry. The samples may be extracted with supercritical carbon dioxide, using Method 3560.

2.4 CHOOSING PROCEDURES FOR CHARACTERISTIC ANALYSES

2.4.1 Figure 2-2 outlines a sequence for determining if a waste exhibits one or more of the characteristics of a hazardous waste.

2.4.2 SPLP, EP and TCLP extracts

The leachate obtained from using either the Synthentic Precipitation Leaching procedure (SPLP), EP (Figure 2-3A) or the TCLP (Figure 2-3B) is an aqueous sample, and therefore, requires further solvent extraction prior to the analysis of semivolatile compounds.

The SPLP or TCLP leachate is solvent extracted with methylene chloride at a pH <2 and at a pH >11 by either Method 3510 or 3520. The leachate may also be extracted as received for organochlorine pesticides and semivolatiles and at pH <1.0 for phenoxyacid herbicides using the solid phase extraction (SPE) disk option in Method 3535. The best recoveries are usually obtained using either Method 3520 or Method 3535.

The solvent extract obtained by performing either Method 3510 or 3520 at an acidic pH will contain the acid/neutral compounds of interest. Refer to the specific determinative method for guidance on the pH requirements for extraction prior to analysis. Method 5031 (azeotropic distillation) may be used as an effective preparative method for pyridine.

Due to the high concentration of acetate in the TCLP extract, it is recommended that purge-and-trap be used to introduce the volatile sample into the gas chromatograph.

The SPLP, EP and/or TCLP extracts can also be digested using acids (Method 3010, 3015, or 3020) and analyzed for metals using a 6000 or 7000 series method (Figures 2-3A and 2-3B).

2.5 CHOOSING PROCEDURES FOR GROUNDWATER ANALYSES

Appropriate analysis schemes for the determination of analytes in groundwater are presented in Figures 2-4A, 2-4B, and 2-4C. Quantitation limits (LLOQs) for the inorganic analytes should correspond to the drinking water limits, where such limits are available.

2.5.1 Special techniques for inorganic analytes

All atomic absorption (AA) analyses should employ appropriate background correction systems whenever spectral interferences could be present. Several background correction techniques are employed in modern AA spectrometers. Matrix modification can complement background correction in some cases. Since no approach to interference correction is completely effective in all cases, the analyst should attempt to verify the adequacy of correction. If the interferant is known (e.g., high concentrations of iron in the determination of selenium), accurate analyses of synthetic solutions of the interferant (with and without analyte) could establish the efficacy of the background correction. If the nature of the interferant is not established, good agreement of analytical results using two substantially different wavelengths could substantiate the adequacy of the background correction.

To reduce matrix interferences, all graphite furnace atomic absorption (GFAA) analyses should be performed using techniques which maximize an isothermal environment within the furnace cell. Data indicate that two such techniques, L'vov platform and the delayed atomization cuvette (DAC), are equivalent in this respect, and produce high quality results.

All GFAA analysis should be carried out using the best matrix modifier for the analysis. Some examples of modifiers are listed below. (See also the appropriate methods.)

Element(s)	Modifier(s)
As and Se	Nickel nitrate, palladium
Pb	Phosphoric acid, ammonium phosphate, palladium
Cd	Ammonium phosphate, palladium
Sb	Ammonium nitrate, palladium
Tl	Platinum, palladium

Inductively coupled plasma (ICP), AA, and GFAA calibration standards need to match the acid composition and strength of the acids contained in the samples. Acid strengths of the calibration standards should be stated in the raw data. When using a method which permits the use of internal standardization, and the internal standardization option is being used, matrix matching is not required.

2.6 CHOOSING PROCEDURES FOR INORGANIC ANALYSES

Methods for preparing different sample matrices for inorganic analyses are shown in Table 2-44. Guidance regarding the use of leaching and digestive methods for inorganic analysis is provided in Table 2-45.

2.7 REFERENCES

1. M. J. Barcelona, "TOC Determinations in Ground Water," Ground Water 1984, 22(1), 18-24.

2. R. Riggin, et al.; Development and Evaluation of Methods for Total Organic Halide and Purgeable Organic Halide in Wastewater; U.S. Environmental Protection Agency; Office of Research and Development; Environmental Monitoring and Support Laboratory; ORD Publication Offices of Center for Environmental Research Information; Cincinnati, OH, 1984; EPA-600/4-84-008.

3. G. McKee, et al.; Determination of Inorganic Anions in Water by Ion Chromatography (Technical addition to Methods for Chemical Analysis of Water and Wastewater, EPA 600/4-79-020); U.S. Environmental Protection Agency; Environmental Monitoring and Support Laboratory; ORD Publication Offices of Center for Environmental Research Information; Cincinnati, OH, 1984; EPA-600/4-84-017.

TABLE 2-1

DETERMINATIVE METHODS FOR ORGANIC ANALYTES

Analytes are listed in alphabetical order and alternative analyte names are in parenthesis. The applicable method listing does not include immunoassay or screening methods.

Analyte	Applicable Method
Abate (Temephos)	8085
Acenaphthene	8100, 8270, 8275, 8310, 8410
Acenaphthylene	8100, 8270, 8275, 8310, 8410
Acetaldehyde	8315
Acetone	8015, 8260, 8261, 8315
Acetonitrile	8015, 8033, 8260, 8261
Acetophenone	8261, 8270
2-Acetylaminofluorene	8270
1-Acetyl-2-thiourea	8270
Acifluorfen	8085, 8151
Acrolein (Propenal)	8015, 8260, 8261, 8315, 8316
Acrylamide	8032, 8316
Acrylonitrile	8015, 8031, 8260, 8261, 8316
Alachlor	8081, 8085
Aldicarb (Temik)	8318, 8321
Aldicarb sulfone	8318, 8321
Aldicarb sulfoxide	8321
Aldrin	8081, 8085, 8270
Allyl alcohol	8015, 8260
Allyl chloride	8021, 8260, 8261
Ametryn	8085
2-Aminoanthraquinone	8270
Aminoazobenzene	8270
4-Aminobiphenyl	8270
Aminocarb	8321
2-Amino-4,6-dinitrotoluene (2-Am-DNT)	8095, 8330
4-Amino-2,6-dinitrotoluene (4-Am-DNT)	8095, 8330
3-Amino-9-ethylcarbazole	8270
t-Amyl alcohol (TAA)	8015
t-Amyl ethyl ether (TAEE, 4,4-Dimethyl-3-oxahexane)	8015, 8260, 8261
t-Amyl methyl ether (TAME)	8015, 8260, 8261
Anilazine	8270
Aniline	8131, 8261, 8270
o-Anisidine	8270
Anthracene	8100, 8270, 8275, 8310, 8410
Aramite	8270
Aroclor-1016 (PCB-1016)	8082, 8270
Aroclor-1221 (PCB-1221)	8082, 8270
Aroclor-1232 (PCB-1232)	8082, 8270
Aroclor-1242 (PCB-1242)	8082, 8270
Aroclor-1248 (PCB-1248)	8082, 8270
Aroclor-1254 (PCB-1254)	8082, 8270

Aroclor-1260 (PCB-1260)	8082, 8270
Aspon	8141
Asulam	8321
Atraton	8085
Atrazine	8041, 8085, 8141
Azinphos-ethyl (Ethyl guthion)	8085, 8141
Azinphos-methyl (Guthion)	8085, 8141, 8270
Barban	8270, 8321
Baygon (Propoxur)	8318, 8321
Bendiocarb	8141, 8318, 8321
Benefin	8091
Benfluralin	8085
Benomyl	8321
Bentazon	8151
Benzal chloride	8121
Benzaldehyde	8315
Benz(a)anthracene	8100, 8270, 8275, 8310, 8410
Benzene	8015, 8021, 8260, 8261
Benzenethiol (Thiophenol)	8270
Benzidine	8270, 8325
Benzo(b)fluoranthene	8100, 8270, 8275, 8310
Benzo(j)fluoranthene	8100
Benzo(k)fluoranthene	8100, 8270, 8275, 8310
Benzoic acid	8270, 8410
Benzo(g,h,i)perylene	8100, 8270, 8275, 8310
Benzo(a)pyrene	8100, 8270, 8275, 8310, 8410
p-Benzoquinone	8270
Benzotrichloride	8121
Benzoylprop ethyl	8325
Benzyl alcohol	8270
Benzyl chloride	8021, 8121, 8260
α-BHC (α-Hexachlorocyclohexane)	8081, 8085, 8121, 8270
β-BHC (β-Hexachlorocyclohexane)	8081, 8085, 8121, 8270
δ-BHC (δ-Hexachlorocyclohexane)	8081, 8085, 8121, 8270
γ-BHC (Lindane, γ-Hexachlorocyclohexane)	8081, 8085, 8121, 8270
Bis(2-n-butoxyethyl)phthalate	8061
Bis(2-chloroethoxy)methane	8111, 8270, 8410
Bis(2-chloroethyl)ether	8111, 8270, 8410, 8430
Bis(2-chloroethyl)sulfide	8260
Bis(2-chloro-1-methylethyl)ether	8021, 8111, 8270, 8410
Bis(2-ethoxyethyl)phthalate	8061
Bis(2-ethylhexyl)phthalate	8061, 8270, 8410
Bis(2-methoxyethyl)phthalate	8061
Bis(4-methyl-2-pentyl)phthalate	8061
Bolstar (Sulprofos)	8085, 8141
Bromacil	8085, 8321
Brominal (Bromoxynil)	8085, 8270
Bromoacetone	8021, 8260
4-Bromoaniline	8131
Bromobenzene	8021, 8260
Bromochloromethane	8021, 8260, 8261

2-Bromo-6-chloro-4-nitroaniline	8131
Bromodichloromethane	8021, 8260, 8261
2-Bromo-4,6-dinitroaniline	8131
Bromoform	8021, 8260, 8261
Bromomethane	8021, 8260, 8261
4-Bromophenyl phenyl ether	8111, 8270, 8275, 8410
Bromoxynil (Brominal)	8085, 8270
Butachlor	8085
Butanal	8315
n-Butanol (1-Butanol, *n*-Butyl alcohol)	8260
2-Butanone (Methyl ethyl ketone, MEK)	8015, 8260, 8261
Butifos (DEF)	8085
Butralin	8091
t-Butyl alcohol	8015, 8260
Butyl benzyl phthalate	8061, 8270, 8410
Butylate	8085, 8141, 8321
n-Butylbenzene	8021, 8260, 8261
sec-Butylbenzene	8021, 8260, 8261
tert-Butylbenzene	8021, 8260, 8261
2-*sec*-Butyl-4,6-dinitrophenol (DNBP, Dinoseb)	8041, 8085, 8151, 8270, 8321
Captafol	8081, 8085, 8270
Captan	8085, 8270
Carbaryl (Sevin)	8270, 8318, 8321, 8325
Carbendazim	8321
Carbofuran (Furaden)	8270, 8318, 8321
Carbofuran phenol	8321
Carbon disulfide	8260, 8261
Carbon tetrachloride	8021, 8260, 8261, 8535
Carbophenothion	8081, 8085, 8141, 8270
Carbosulfan	8321
Carboxin	8085
Casoron (Dichlobenil)	8085
Chloral hydrate	8260
Chloramben	8151
Chlordane (NOS)	8081, 8270
cis-Chlordane	8081
trans-Chlordane	8085, 8081
Chlorfenvinphos	8141, 8270
Chloroacetonitrile	8260
2-Chloroaniline	8131
3-Chloroaniline	8131
4-Chloroaniline	8131, 8270, 8410
Chlorobenzene	8021, 8260, 8261
Chlorobenzilate	8081, 8270
2-Chlorobiphenyl	8082, 8275
2-Chloro-1,3-butadiene (Chloroprene)	8021, 8260
1-Chlorobutane	8260
Chlorodibromomethane (Dibromochloromethane)	8021, 8260, 8261
2-Chloro-4,6-dinitroaniline	8131
1-Chloro-2,4-dinitrobenzene	8091
1-Chloro-3,4-dinitrobenzene	8091

Chloroethane	8021, 8260, 8261
2-Chloroethanol	8021, 8260, 8430
2-(2-Chloroethoxy) ethanol	8430
2-Chloroethyl vinyl ether	8021, 8260
Chloroform	8021, 8260, 8261
1-Chlorohexane	8260
Chloromethane	8021, 8260, 8261
5-Chloro-2-methylaniline	8270
Chloromethyl methyl ether	8021
2-Chloro-5-methylphenol	8041
4-Chloro-2-methylphenol	8041
4-Chloro-3-methylphenol	8041, 8270, 8410
3-(Chloromethyl) pyridine hydrochloride	8270
1-Chloronaphthalene	8270, 8275
2-Chloronaphthalene	8121, 8270, 8410
Chloroneb	8081
2-Chloro-4-nitroaniline	8131
4-Chloro-2-nitroaniline	8131
1-Chloro-2-nitrobenzene	8091
1-Chloro-4-nitrobenzene	8091
2-Chloro-6-nitrotoluene	8091
4-Chloro-2-nitrotoluene	8091
4-Chloro-3-nitrotoluene	8091
2-Chlorophenol	8041, 8270, 8410
3-Chlorophenol	8041
4-Chlorophenol	8410
2-Chlorophenyl 4-nitrophenyl ether	8111
3-Chlorophenyl 4-nitrophenyl ether	8111
4-Chlorophenyl 4-nitrophenyl ether	8111
4-Chlorophenyl phenyl ether	8111, 8270, 8410
o-Chlorophenyl thiourea	8325
4-Chloro-1,2-phenylenediamine	8270
4-Chloro-1,3-phenylenediamine	8270
Chloroprene (2-Chloro-1,3-butadiene)	8021, 8260
Chloropropham	8085, 8321
Chloropropylate	8081
Chlorothalonil	8081
2-Chlorotoluene	8021, 8260, 8261
4-Chlorotoluene	8021, 8260, 8261
Chloroxuron	8321
Chlorpyrifos	8085, 8141
Chlorpyrifos methyl	8141
Chlorthalonil (Daconil)	8085
Chrysene	8100, 8270, 8275, 8310, 8410
Coumaphos	8085, 8141, 8270
p-Cresidine	8270
o-Cresol (2-Methylphenol)	8041, 8270, 8410
m-Cresol (3-Methylphenol)	8041, 8270
p-Cresol (4-Methylphenol)	8041, 8270, 8410
Crotonaldehyde	8015, 8260, 8315
Crotoxyphos	8141, 8270

5,5-Diphenylhydantoin	8270
1,2-Diphenylhydrazine	8270
Diphenyltin dichloride	8323
Di-*n*-propyl phthalate	8410
Disperse Blue 3	8321
Disperse Blue 14	8321
Disperse Brown 1	8321
Disperse Orange 3	8321
Disperse Orange 30	8321
Disperse Red 1	8321
Disperse Red 5	8321
Disperse Red 13	8321
Disperse Red 60	8321
Disperse Yellow 5	8321
Disulfoton	8085, 8141, 8270, 8321
Diuron	8085, 8321, 8325
1,3-DNB (1,3-Dinitrobenzene)	8091, 8095, 8270, 8330
DNBP (2-*sec*-Butyl-4,6-dinitrophenol, Dinoseb)	8041, 8085, 8151, 8270, 8321
2,4-DNT (2,4-Dinitrotoluene)	8091, 8095, 8270, 8330, 8410
2,6-DNT (2,6-Dinitrotoluene)	8091, 8270, 8330, 8410
EDB (1,2-Dibromoethane, Ethylene dibromide)	8011, 8021, 8260
Endosulfan I	8081, 8085, 8270
Endosulfan II	8081, 8085, 8270
Endosulfan sulfate	8081, 8085, 8270
Endrin	8081, 8085, 8270
Endrin aldehyde	8081, 8085, 8270
Endrin ketone	8081, 8085, 8270
Epichlorohydrin	8021, 8260
EPN	8141, 8085, 8270
Eptam (EPTC)	8085, 8141, 8321
EPTC (Eptam)	8085, 8141, 8321
ETBE (Ethyl *tert*-butyl ether)	8015, 8261
Ethalfluralin (Sonalan)	8085
Ethanol	8015, 8260, 8261
Ethion	8085, 8141, 8270
Ethoprop	8085, 8141
Ethyl acetate	8015, 8260, 8261
Ethyl benzene	8015, 8021, 8260, 8261
Ethyl *t*-butyl ether (ETBE)	8015, 8260, 8261
Ethyl carbamate	8270
Ethyl cyanide (Propionitrile)	8015, 8260, 8261
Ethyl guthion (Azinphos-ethyl)	8085, 8141
Ethyl methacrylate	8260, 8261
Ethyl methanesulfonate	8270
Ethylene dibromide (EDB, 1,2-Dibromoethane)	8011, 8021, 8260
Ethylene glycol	8430
Ethylene oxide	8015, 8260
Etridiazole	8081
Famphur	8141, 8270, 8321
Fenamiphos	8085
Fenarimol	8085

Fenitrothion	8085, 8141
Fensulfothion	8085, 8141, 8270, 8321
Fenthion	8085, 8141, 8270
Fenuron	8321
Fluchloralin	8270
Fluometuron	8321
Fluoranthene	8100, 8270, 8275, 8310, 8410
Fluorene	8100, 8270, 8275, 8310, 8410
Fluridone	8085
Fonophos	8085, 8141
Formaldehyde	8315
Formetanate hydrochloride	8318, 8321
Furaden (Carbofuran)	8270, 8318, 8321
Gardona (Tetrachlovinphos, Stirophos)	80858141, 8270
Garlon (Triclopyr)	8085
Gasoline range organics (GRO)	8015
Guthion (Azinphos-methyl)	8085, 8141, 8270
Halowax-1000	8081
Halowax-1001	8081
Halowax-1013	8081
Halowax-1014	8081
Halowax-1051	8081
Halowax-1099	8081
Heptachlor	8081, 8085, 8270
Heptachlor epoxide	8081, 8085, 8270
2,2',3,3',4,4',5-Heptachlorobiphenyl	8082, 8275
2,2',3,4,4',5,5'-Heptachlorobiphenyl	8082, 8275
2,2',3,4,4',5',6-Heptachlorobiphenyl	8082
2,2',3,4',5,5',6-Heptachlorobiphenyl	8082, 8275
Heptanal	8315
Hexachlorobenzene	8081, 8085, 8121, 8270, 8275, 8410
2,2',3,3,4,4'-Hexachlorobiphenyl	8275
2,2',3,4,4',5'-Hexachlorobiphenyl	8082, 8275
2,2',3,4,5,5'-Hexachlorobiphenyl	8082
2,2',3,5,5',6-Hexachlorobiphenyl	8082
2,2',4,4',5,5'-Hexachlorobiphenyl	8082
2-exo,3-endo,6-exo,8,9,10-Hexachlorobornane (Hx-Sed)	8276
Hexachlorobutadiene (1,3-Hexachlorobutadiene)	8021, 8121, 8260, 8261, 8270, 8410
α-Hexachlorocyclohexane (α-BHC)	8081, 8085, 8121, 8270
β-Hexachlorocyclohexane (β-BHC)	8081, 8085, 8121, 8270
δ-Hexachlorocyclohexane (δ-BHC)	8081, 8085, 8121, 8270
γ-Hexachlorocyclohexane (γ-BHC, Lindane)	8081, 8085, 8121, 8270
Hexachlorocyclopentadiene	8081, 8085, 8121, 8270, 8410
Hexachloroethane	8121, 8260, 8270, 8410
Hexachlorophene	8270
Hexachloropropene	8141, 8270
Hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX)	8095, 8330, 8510
Hexamethyl phosphoramide (HMPA)	, 8270
Hexanal	8315
2-Hexanone	8260, 8261
Hexazinone	8085

Mestranol	8270
Mesurol (Methiocarb)	8141, 8318, 8321
Methacrylonitrile	8260, 8261
Metalaxyl	8085
Methanol	8015, 8260
Methapyrilene	8270
Methiocarb (Mesurol)	8141, 8318, 8321
Methomyl (Lannate)	8318, 8321
Methoxychlor	8081, 8085, 8270
Methyl acrylate	8260
Methyl-*t*-butyl ether (MTBE)	8015, 8260, 8261
Methyl chlorpyrifos	8085
Methyl ethyl ketone (MEK, 2-Butanone)	8015, 8260, 8261
Methyl iodide (Iodomethane)	8260, 8261
Methyl isobutyl ketone (MIBK, 4-Methyl-2-pentanone)	8260, 8261
Methyl methacrylate	8260, 8261
Methyl methanesulfonate	8270
Methyl paraoxon	8085
Methyl parathion (Parathion, methyl)	8085, 8270, 8141, 8321
3-Methylcholanthrene	8100, 8270
Methylcyclohexane	8270
2-Methyl-4,6-dinitrophenol	8041
Methylene chloride (Dichloromethane, DCM)	8021, 8260, 8261
4,4'-Methylenebis (2-chloroaniline)	8270
4,4'-Methylenebis (*N,N*-dimethylaniline)	8270
1-Methylnaphthalene	8261
2-Methylnaphthalene	8261, 8270, 8410
4-Methyl-2-pentanone (MIBK, Methyl isobutyl ketone)	8260, 8261
2-Methylphenol (*o*-Cresol)	8041, 8270, 8410
3-Methylphenol (*m*-Cresol)	8041, 8270
4-Methylphenol (*p*-Cresol)	8041, 8270, 8410
2-Methyl-1-propanol (Isobutyl alcohol)	8260, 8261
2-Methyl-2-propanol (*t*-Butyl alcohol)	8015, 8260
2-Methylpyridine (2-Picoline)	8015, 8260, 82618270
Methyl-2,4,6-trinitrophenyl-nitramine (Tetryl)	8330
Metolachlor	8085
Metolcarb	8318, 8321
Metribuzin	8085
Mevinphos	8085, 8141, 8270
Mexacarbate	8270, 8318, 8321
MGK-264	8085
MIBK (Methyl isobutyl ketone, 4-Methyl-2-pentanone)	8260, 8261
Mirex	8081, 8085, 8270
Molinate	8085, 8141, 8321
Monobutyltin trichloride	8323
Monocrotophos	8141, 8270, 8321
Monophenyltin trichloride	8323
Monuron	8321, 8325
MTBE (Methyl-*t*-butyl ether)	8015, 8260, 8261
Naled	8141, 8270, 8321
Naphthalene	8021, 8100, 8260, 8261, 8270, 8275, 8310, 8410

Stirophos (Tetrachlorvinphos, Gardona)	8085, 8141, 8270
Strobane	8081
Strychnine	8270
Styrene	8021, 8260, 8261
Sulfallate	8270
Sulfotepp	8085, 8141
Sulprofos (Bolstar)	8085, 8141
2,4,5-T	8151, 8321
2,4,5-T (acid)	8085
TAA (t-Amyl alcohol)	8015
TAEE (t-Amyl ethyl ether, 4,4-Dimethyl-3-oxahexane)	8015, 8261
TAME (t-Amyl methyl ether)	8015, 8261
2,4,5-TB	8085
2,3,7,8-TCDD	8280, 8290
TCDD, total	8280, 8290
2,3,7,8-TCDF	8280, 8290
TCDF, total	8280, 8290
Tebuthiuron	8085, 8321
Temephos (Abate)	8085
Temik (Aldicarb)	8318, 8321
TEPP (Tetraethyl pyrophosphate)	8141, 8270
Terbacil	8085
Terbufos	8141, 8270
Terbutryn (Igran)	8085
1,2,3,4-Tetrachlorobenzene	8121
1,2,3,5-Tetrachlorobenzene	8121
1,2,4,5-Tetrachlorobenzene	8121, 8270
2,2',3,5'-Tetrachlorobiphenyl	8082, 8275
2,2',4,5'-Tetrachlorobiphenyl	8275
2,2',5,5'-Tetrachlorobiphenyl	8082, 8275
2,3',4,4'-Tetrachlorobiphenyl	8082, 8275
1,1,1,2-Tetrachloroethane	8021, 8260
1,1,2,2-Tetrachloroethane	8021, 8260, 8261
Tetrachloroethene (Perchloroethylene, Tetrachloroethylene)	8021, 8260, 8261
2,3,4,5-Tetrachloronitrobenzene	8091
2,3,5,6-Tetrachloronitrobenzene	8091
2,3,4,5-Tetrachlorophenol	8041, 8085
2,3,4,6-Tetrachlorophenol	8041, 8085, 8270
2,3,5,6-Tetrachlorophenol	8041
Tetrachlorvinphos (Stirophos, Gardona)	8085, 8141, 8270
Tetraethyl dithiopyrophosphate	8270
Tetraethyl pyrophosphate (TEPP)	8141, 8270
Tetrahydrofuran (THF)	8261
Tetrazene	8331
Tetryl (Methyl-2,4,6-trinitrophenylnitramine)	8330
THF (Tetrahydrofuran)	8261
Thiodicarb	8318, 8321
Thiofanox	8321
Thionazin (Zinophos)	8141, 8270
Thiophanate-methyl	8321
Thiophenol (Benzenethiol)	8270

TABLE 2-2

METHOD 8011 (MICROEXTRACTION AND GAS CHROMATOGRAPHY)

1,2-Dibromo-3-chloropropane (DBCP)
1,2-Dibromoethane (EDB)

TABLE 2-3

METHOD 8015 (GC/FID) - NONHALOGENATED VOLATILES

Acetone	Ethylene oxide
Acetonitrile	Gasoline range organics (GRO)
Acrolein	Isopropyl alcohol
Acrylonitrile	Methanol
Allyl alcohol	Methyl ethyl ketone (MEK, 2-Butanone)
t-Amyl alcohol (TAA)	*N*-Nitroso-di-*n*-butylamine
t-Amyl ethyl ether (TAEE)	Paraldehyde
t-Amyl methyl ether (TAME)	2-Pentanone
Benzene	2-Picoline
t-Butyl alcohol	1-Propanol (*n*-Propyl alcohol)
Crotonaldehyde	Propionitrile
Diesel range organics (DRO)	Pyridine
Diethyl ether	Toluene
Diisopropyl ether (DIPE)	*o*-Toluidine
Ethanol	*m*-Xylene
Ethyl acetate	*o*-Xylene
Ethyl benzene	*p*-Xylene
Ethyl *tert*-butyl ether (ETBE)	Triethylamine

TABLE 2-4

METHOD 8021 (GC, PHOTOIONIZATION AND ELECTROLYTIC CONDUCTIVITY DETECTORS) - AROMATIC AND HALOGENATED VOLATILES

Allyl chloride
Benzene
Benzyl chloride
Bis(2-chloro-1-methylethyl) ether
Bromoacetone
Bromobenzene
Bromochloromethane
Bromodichloromethane
Bromoform
Bromomethane
n-Butylbenzene
sec-Butylbenzene
tert-Butylbenzene
Carbon tetrachloride
Chlorobenzene
Chlorodibromomethane
Chloroethane
2-Chloroethanol
2-Chloroethyl vinyl ether
Chloroform
Chloromethane
Chloromethyl methyl ether
Chloroprene
2-Chlorotoluene
4-Chlorotoluene
1,2-Dibromo-3-chloropropane
1,2-Dibromoethane
Dibromomethane
1,2-Dichlorobenzene
1,3-Dichlorobenzene
1,4-Dichlorobenzene
Dichlorodifluoromethane
1,1-Dichloroethane
1,2-Dichloroethane
1,1-Dichloroethene
cis-1,2-Dichloroethene
trans-1,2-Dichloroethene
1,2-Dichloropropane
1,3-Dichloropropane
2,2-Dichloropropane
1,3-Dichloro-2-propanol
1,1-Dichloropropene
cis-1,3-Dichloropropene
trans-1,3-Dichloropropene
Epichlorhydrin
Ethylbenzene
Hexachlorobutadiene
Isopropylbenzene
p-Isopropyltoluene
Methylene chloride
Naphthalene
n-Propylbenzene
Styrene
1,1,1,2-Tetrachloroethane
1,1,2,2-Tetrachloroethane
Tetrachloroethene
Toluene
1,2,3-Trichlorobenzene
1,2,4-Trichlorobenzene
1,1,1-Trichloroethane
1,1,2-Trichloroethane
Trichloroethene
Trichlorofluoromethane
1,2,3-Trichloropropane
1,2,4-Trimethylbenzene
1,3,5-Trimethylbenzene
Vinyl chloride
o-Xylene
m-Xylene
p-Xylene

TABLE 2-5

METHODS 8031 AND 8033 (GC WITH NITROGEN-PHOSPHORUS DETECTION) AND METHOD 8032 (GC WITH ELECTRON CAPTURE DETECTION)

Method 8031: Acrylonitrile

Method 8032: Acrylamide

Method 8033: Acetonitrile

TABLE 2-6

METHOD 8041 (GC) - PHENOLS

2-Chloro-5-methylphenol	2,5-Dinitrophenol
4-Chloro-2-methylphenol	Dinoseb (2-*sec*-butyl-4,6-dinitro phenol)
4-Chloro-3-methylphenol	2-Methyl-4,6-dinitrophenol
2-Chlorophenol	2-Methylphenol (*o*-Cresol)
3-Chlorophenol	3-Methylphenol (*m*-Cresol)
4-Chlorophenol	4-Methylphenol (*p*-Cresol)
2-Cyclohexyl-4,6-dinitrophenol	2-Nitrophenol
2,3-Dichlorophenol	3-Nitrophenol
2,4-Dichlorophenol	4-Nitrophenol
2,5-Dichlorophenol	Pentachlorophenol
2,6-Dichlorophenol	Phenol
3,4-Dichlorophenol	2,3,4,5-Tetrachlorophenol
3,5-Dichlorophenol	2,3,4,6-Tetrachlorophenol
2,3-Dimethylphenol	2,3,5,6-Tetrachlorophenol
2,4-Dimethylphenol	2,3,4-Trichlorophenol
2,5-Dimethylphenol	2,3,5-Trichlorophenol
2,6-Dimethylphenol	2,3,6-Trichlorophenol
3,4-Dimethylphenol	2,4,5-Trichlorophenol
2,4-Dinitrophenol	2,4,6-Trichlorophenol

TABLE 2-7

METHOD 8061 (GC/ECD) - PHTHALATE ESTERS

Bis(2-*n*-butoxyethyl) phthalate	Diethyl phthalate
Bis(2-ethoxyethyl) phthalate	Dihexyl phthalate
Bis(2-ethylhexyl) phthalate	Diisobutyl phthalate
Bis(2-methoxyethyl) phthalate	Di-*n*-butyl phthalate
Bis(4-methyl-2-pentyl) phthalate	Dimethyl phthalate
Butyl benzyl phthalate	Di-*n*-octyl phthalate
Diamyl phthalate	Dinonyl phthalate
Dicyclohexyl phthalate	Hexyl 2-ethylhexyl phthalate

TABLE 2-8

METHOD 8070 (GC) - NITROSAMINES

N-Nitrosodimethylamine
N-Nitrosodiphenylamine
N-Nitrosodi-*n*-propylamine

TABLE 2-9

METHOD 8081 (GC) - ORGANOCHLORINE PESTICIDES

- Alachlor
- Aldrin
- α-BHC
- β-BHC
- δ-BHC
- γ-BHC (Lindane)
- Captafol
- Carbophenothion
- Chlordane (NOS)
- *cis*-Chlordane
- *trans*-Chlordane
- Chlorobenzilate
- Chloroneb
- Chloropropylate
- Chlorothalonil
- Dacthal (DCPA)
- DBCP
- 4,4'-DDD
- 4,4'-DDE
- 4,4'-DDT
- Diallate
- Dichlone
- Dichloran
- Dicofol
- Dieldrin
- Endosulfan I
- Endosulfan II
- Endosulfan sulfate
- Endrin
- Endrin aldehyde
- Endrin ketone
- Etridiazole
- Halowax-1000
- Halowax-1001
- Halowax-1013
- Halowax-1014
- Halowax-1051
- Halowax-1099
- Heptachlor
- Heptachlor epoxide
- Hexachlorobenzene
- Hexachlorocyclopentadiene
- Isodrin
- Methoxychlor
- Mirex
- Nitrofen
- *trans*-Nonachlor
- Pentachloronitrobenzene (PCNB)
- Permethrin (*cis* + *trans*)
- Perthane
- Propachlor
- Strobane
- Toxaphene
- Trifluralin

TABLE 2-10

METHOD 8082 (GC) - POLYCHLORINATED BIPHENYLS

Aroclor 1016
Aroclor 1221
Aroclor 1232
Aroclor 1242
Aroclor 1248
Aroclor 1254
Aroclor 1260
2-Chlorobiphenyl
2,3-Dichlorobiphenyl
,2',3,3',4,4',5-Heptachlorobiphenyl
2,2',3,4,4',5,5'-Heptachlorobiphenyl
2,2',3,4,4',5',6-Heptachlorobiphenyl
2,2',3,4',5,5',6-Heptachlorobiphenyl
2,2',3,4,5,5'-Hexachlorobiphenyl
2,2',3,5,5',6-Hexachlorobiphenyl
2,2',4,4',5,5'-Hexachlorobiphenyl
2,2',3,3',4,4',5,5',6-Nonachlorobiphenyl
2,2',3,4,5'-Pentachlorobiphenyl
2,2',4,5,5'-Pentachlorobiphenyl
2,3,3',4',6-Pentachlorobiphenyl
2,2',3,5'-Tetrachlorobiphenyl
2,2',5,5'-Tetrachlorobiphenyl
2,3',4,4'-Tetrachlorobiphenyl
2,2',5-Trichlorobiphenyl
2,4',5-Trichlorobiphenyl

TABLE 2-11

METHOD 8085 (GC/AED) – PESTICIDES

Abate (Temephos)
Acifluorfen
Alachlor
Aldrin
Ametryn
Atraton
Atrazine
Azinphos ethyl (Ethyl guthion)
Azinphos methyl (Guthion)
Benfluralin
α-BHC
β-BHC
δ-BHC
γ-BHC (Lindane)
Bromacil
Bromoxynil (Brominal)
Butachlor
Butylate
Captafol
Captan
Carbophenothion
Carboxin
trans-Chlordane
Chlorpropham
Chlorpyrifos
Chlorthalonil (Daconil)
Cyanazine
Cycloate
Coumaphos
2,4-D acid
2,4-DB acid
DCPA (Dacthal)
2,4'-DDD
4,4'-DDD
2,4'-DDE
4,4'-DDE
2,4'-DDT
4,4'-DDT
DEF (Butifos)
Demeton-O
Demeton-S
Diallate
Diazinon
Dicamba
Dichlobenil (Casoron)
3,5-Dichlorobenzoic acid
Dichlorprop
Dichlorvos (DDVP)
Diclofol (Kelthane)
Diclofop-methyl
Dieldrin
Dimethoate
Dinoseb
Dioxathion
Diphenamid
Disulfoton (Disyston)
Diuron
Endosulfan I
Endosulfan II
Endosulfan sulfate
Endrin
Endrin aldehyde
Endrin ketone
EPN
Eptam (EPTC)
Ethalfluralin (Sonalan)
Ethion
Ethoprop
Fenamiphos
Fenarimol
Fenitrothion
Fensulfothion
Fenthion
Fluridone
Fonofos
Gardona (Tetrachlovinphos)
Heptachlor
Heptachlor epoxide
Hexachlorobenzene
Hexachlorocyclopentadiene
Hexazinone

TABLE 2-11 (continued)

Imidan (Phosmet)
Ioxynil
Malathion
MCPA acid
MCPP acid
Merphos
Metalaxyl
Methoxychlor
Methyl chlorpyrifos
Methyl paraoxon
Methyl parathion
Metolachlor
Metribuzin
Mevinphos
MGK-264
Mirex
Molinate
Napropamide
4-Nitrophenol
Norflurazon
Oxyfluorfen
Parathion
Pebulate
Pendimethalin
Pentachlorophenol (PCP)
Phorate
Phosphamidon
Picloram
Profluralin
Prometon (Pramitol 5p)
Prometryn
Pronamide (Kerb)
Propachlor (Ramrod)
Propargite (S-181)
Propazine
Propetamidophos
Ronnel
Simazine
Sulfotepp
Sulprofos (Bolstar)
Silvex
2,4,5-T acid
2,4,5-TB
Tebuthiuron
Terbacil
Terbutryn (Igran)
2,3,4,5-Tetrachlorophenol
2,3,4,6-Tetrachlorophenol
Triademefon
Triallate
2,4,5-Trichlorophenol
2,4,6-Trichlorophenol
Triclopyr (Garlon)
Trifluralin (Treflan)
Vernolate

TABLE 2-12

METHOD 8091 (GC) - NITROAROMATICS AND CYCLIC KETONES

Benefin
Butralin
1-Chloro-2,4-dinitrobenzene
1-Chloro-3,4-dinitrobenzene
1-Chloro-2-nitrobenzene
1-Chloro-4-nitrobenzene
2-Chloro-6-nitrotoluene
4-Chloro-2-nitrotoluene
4-Chloro-3-nitrotoluene
2,3-Dichloronitrobenzene
2,4-Dichloronitrobenzene
2,5-Dichloronitrobenzene
3,4-Dichloronitrobenzene
3,5-Dichloronitrobenzene
Dinitramine
1,2-Dinitrobenzene
1,3-Dinitrobenzene
1,4-Dinitrobenzene
2,4-Dinitrotoluene
2,6-Dinitrotoluene
Isopropalin
1,2-Naphthoquinone
1,4-Naphthoquinone
Nitrobenzene
2-Nitrotoluene
3-Nitrotoluene
4-Nitrotoluene
Penoxalin [Pendimethalin]
Pentachloronitrobenzene
Profluralin
2,3,4,5-Tetrachloronitrobenzene
2,3,5,6-Tetrachloronitrobenzene
1,2,3-Trichloro-4-nitrobenzene
1,2,4-Trichloro-5-nitrobenzene
2,4,6-Trichloronitrobenzene
Trifluralin

TABLE 2-13

METHOD 8095 (GC) - EXPLOSIVES

2-Amino-4,6-dinitrotoluene
4-Amino-2,6-dinitrotoluene
3,5-Dinitroaniline
1,3-Dinitrobenzene
2,4-Dinitrotoluene
2,6-Dinitrotoluene
Hexahydro-1,3,5-trinitro-1,3,5-triazine
Nitrobenzene
Nitroglycerine
2-Nitrotoluene
3-Nitrotoluene
4-Nitrotoluene
Octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine
Pentaerythritoltetranitrate
1,3,5-Trinitrobenzene
2,4,6-Trinitrophenylmethylnitramine
2,4,6-Trinitrotoluene

TABLE 2-14

METHOD 8100 - POLYNUCLEAR AROMATIC HYDROCARBONS

Acenaphthene
Acenaphthylene
Anthracene
Benz(*a*)anthracene
Benzo(*b*)fluoranthene
Benzo(*j*)fluoranthene
Benzo(*k*)fluoranthene
Benzo(*g,h,i*)perylene
Benzo(*a*)pyrene
Chrysene
Dibenz(*a,h*)acridine
Dibenz(*a,j*)acridine
Dibenz(*a,h*)anthracene
7H-Dibenzo(*c,g*)carbazole
Dibenzo(*a,e*)pyrene
Dibenzo(*a,h*)pyrene
Dibenzo(*a,i*)pyrene
Fluoranthene
Fluorene
Indeno(1,2,3-*cd*)pyrene
3-Methylcholanthrene
Naphthalene
Phenanthrene
Pyrene

TABLE 2-15

METHOD 8111 (GC) - HALOETHERS

Bis(2-chloroethoxy)methane
Bis(2-chloroethyl) ether
Bis(2-chloro-1-methylethyl) ether
4-Bromophenyl phenyl ether
4-Chlorophenyl phenyl ether
2-Chlorophenyl 4-nitrophenyl ether
3-Chlorophenyl 4-nitrophenyl ether
4-Chlorophenyl 4-nitrophenyl ether
2,4-Dibromophenyl 4-nitrophenyl ether
2,4-Dichlorophenyl 3-methyl-4-nitrophenyl ether
2,3-Dichlorophenyl 4-nitrophenyl ether
2,4-Dichlorophenyl 4-nitrophenyl ether
2,5-Dichlorophenyl 4-nitrophenyl ether
2,6-Dichlorophenyl 4-nitrophenyl ether
3,4-Dichlorophenyl 4-nitrophenyl ether
3,5-Dichlorophenyl 4-nitrophenyl ether
4-Nitrophenyl phenyl ether
2,3,4-Trichlorophenyl 4-nitrophenyl ether
2,3,5-Trichlorophenyl 4-nitrophenyl ether
2,3,6-Trichlorophenyl 4-nitrophenyl ether
2,4,5-Trichlorophenyl 4-nitrophenyl ether
2,4,6-Trichlorophenyl 4-nitrophenyl ether
3,4,5-Trichlorophenyl 4-nitrophenyl ether

TABLE 2-16

METHOD 8121 (GC) - CHLORINATED HYDROCARBONS

Benzal chloride
Benzotrichloride
Benzyl chloride
2-Chloronaphthalene
1,2-Dichlorobenzene
1,3-Dichlorobenzene
1,4-Dichlorobenzene
Hexachlorobenzene
Hexachlorobutadiene
α-Hexachlorocyclohexane (α-BHC)
β-Hexachlorocyclohexane (β-BHC)
δ-Hexachlorocyclohexane (δ-BHC)
γ-Hexachlorocyclohexane (γ-BHC)
Hexachlorocyclopentadiene
Hexachloroethane
Pentachlorobenzene
1,2,3,4-Tetrachlorobenzene
1,2,3,5-Tetrachlorobenzene
1,2,4,5-Tetrachlorobenzene
1,2,3-Trichlorobenzene
1,2,4-Trichlorobenzene
1,3,5-Trichlorobenzene

TABLE 2-17

METHOD 8131 (GC) - ANILINE AND SELECTED DERIVATIVES

Aniline
4-Bromoaniline
2-Bromo-6-chloro-4-nitroanilne
2-Bromo-4,6-dintroaniline
2-Chloroaniline
3-Chloroaniline
4-Chloroaniline
2-Chloro-4,6-dinitroaniline
2-Chloro-4-nitroaniline
4-Chloro-2-nitroaniline
2,6-Dibromo-4-nitroaniline
3,4-Dichloroaniline
2,6-Dichloro-4-nitroaniline
2,4-Dinitroaniline
2-Nitroaniline
3-Nitroaniline
4-Nitroaniline
2,4,5-Trichloroaniline
2,4,6-Trichloroaniline

TABLE 2-18

METHOD 8141 (GC) - ORGANOPHOSPHORUS COMPOUNDS

- Aspon
- Atrazine
- Azinphos-ethyl
- Azinphos-methyl
- Bendiocarb
- Bolstar (Sulprofos)
- Butylate
- Carbophenothion
- Chlorfenvinphos
- Chlorpyrifos
- Chlorpyrifos methyl
- Coumaphos
- Crotoxyphos
- Demeton-O, and -S
- Diazinon
- Dichlorofenthion
- Dichlorvos (DDVP)
- Dicrotophos
- Dimethoate
- Dioxathion
- Disulfoton
- EPN
- EPTC
- Ethion
- Ethoprop
- Famphur
- Fenitrothion
- Fensulfothion
- Fenthion
- Fonophos
- Hexamethyl phosphoramide (HMPA)
- Leptophos
- Malathion
- Merphos
- Methiocarb
- Mevinphos
- Molinate
- Monocrotophos
- Naled
- Parathion, ethyl
- Parathion, methyl
- Pebulate
- *o*-Phenylenediamine
- Phorate
- Phosmet
- Phosphamidon
- Propham
- Prosulfocarb
- Ronnel
- Simazine
- Stirophos (Tetrachlorvinphos, Gardona)
- Sulfotepp
- Terbufos
- Tetraethyl pyrophosphate (TEPP)
- Thionazin (Zinophos)
- Tokuthion (Prothiofos)
- Triallate
- Trichlorfon
- Trichloronate
- Tri-*o*-cresyl phosphate (TOCP)

TABLE 2-19

METHOD 8151 (GC USING METHYLATION OR PENTAFLUOROBENZYLATION DERIVATIZATION) - CHLORINATED HERBICIDES

- Acifluorfen
- Bentazon
- Chloramben
- 2,4-D
- Dalapon
- 2,4-DB
- DCPA diacid
- Dicamba
- 3,5-Dichlorobenzoic acid
- Dichloroprop
- Dinoseb
- 5-Hydroxydicamba
- MCPA
- MCPP
- 4-Nitrophenol
- Pentachlorophenol
- Picloram
- 2,4,5-T
- 2,4,5-TP (Silvex)

TABLE 2-20

METHOD 8260 (GC/MS) - VOLATILE ORGANIC COMPOUNDS

Acetone
Acetonitrile
Acrolein (Propenal)
Acrylonitrile
Allyl alcohol
Allyl chloride
t-Amyl ethyl ether (TAEE)
t-Amyl methyl ether (TAME)
Benzene
Benzyl chloride
Bis(2-chloroethyl)sulfide
Bromoacetone
Bromobenzene
Bromochloromethane
Bromodichloromethane
Bromoform
Bromomethane
n-Butanol
2-Butanone (MEK)
t-Butyl alcohol
n-Butylbenzene
sec-Butylbenzene
tert-Butylbenzene
Carbon disulfide
Carbon tetrachloride
Chloral hydrate
Chloroacetonitrile
Chlorobenzene
1-Chlorobutane
Chlorodibromomethane
Chloroethane
2-Chloroethanol
2-Chloroethyl vinyl ether
Chloroform
1-Chlorohexane
Chloromethane
Chloroprene
2-Chlorotoluene
4-Chlorotoluene
Crotonaldehyde
Cyclohexane
1,2-Dibromo-3-chloropropane
1,2-Dibromoethane
Dibromomethane
1,2-Dichlorobenzene
1,3-Dichlorobenzene
1,4-Dichlorobenzene
cis-1,4-Dichloro-2-butene
trans-1,4-Dichloro-2-butene
Dichlorodifluoromethane
1,1-Dichloroethane
1,2-Dichloroethane
1,1-Dichloroethene
cis-1,2-Dichloroethene
trans-1,2-Dichloroethene
1,2-Dichloropropane
1,3-Dichloropropane
2,2-Dichloropropane
1,3-Dichloro-2-propanol
1,1-Dichloropropene
cis-1,3-Dichloropropene
trans-1,3-Dichloropropene
1,2,3,4-Diepoxybutane
Diethyl ether
Diisopropyl ether (DIPE)
1,4-Dioxane
Epichlorohydrin
Ethanol
Ethyl acetate
Ethyl t-butyl ether (ETBE)
Ethyl methacrylate
Ethylbenzene
Ethylene oxide
Hexachlorobutadiene
Hexachloroethane
2-Hexanone
Iodomethane
Isobutyl alcohol
Isopropylbenzene
p-Isopropyltoluene
Malononitrile
Methacrylonitrile
Methanol
Methyl acrylate
Methyl-t-butyl ether (MTBE)
Methyl methacrylate
Methylcyclohexane
Methylene chloride
4-Methyl-2-pentanone (MIBK)
Naphthalene
Nitrobenzene
2-Nitropropane
N-Nitroso-di-n-butylamine
Paraldehyde
Pentachloroethane
Pentafluorobenzene

TABLE 2-20 (continued)

2-Pentanone
2-Picoline
1-Propanol
2-Propanol
Propargyl alcohol
ß-Propiolactone
Propionitrile (Ethyl cyanide)
n-Propylamine
n-Propylbenzene
Pyridine
Styrene
1,1,1,2-Tetrachloroethane
1,1,2,2-Tetrachloroethane
Tetrachloroethene
Toluene
o-Toluidine
1,2,3-Trichlorobenzene
1,2,4-Trichlorobenzene
1,1,1-Trichloroethane
1,1,2-Trichloroethane
Trichloroethene
Trichlorofluoromethane
1,2,3-Trichloropropane
1,2,4-Trimethylbenzene
1,3,5-Trimethylbenzene
Vinyl acetate
Vinyl chloride
o-Xylene
m-Xylene
p-Xylene

TABLE 2-21

METHOD 8261 (VD/GC/MS) - VOLATILE ORGANIC COMPOUNDS

Acetone
Acetonitrile
Acetophenone
Acrolein
Acrylonitrile
Allyl Chloride
t-Amyl ethyl ether (TAEE) (4,4-Dimethyl-3-oxahexane)
t-Amyl methyl ether (TAME)
Aniline
Benzene
Bromochloromethane
Bromodichloromethane
Bromoform
Bromomethane
2-Butanone
n-Butylbenzene
sec-Butylbenzene
tert-Butylbenzene
Carbon disulfide
Carbon tetrachloride
Chlorobenzene
Chlorodibromomethane
Chloroethane
Chloroform
Chloromethane
2-Chlorotoluene
4-Chlorotoluene
1,2-Dibromo-3-chloropropane
Dibromomethane
1,2-Dichlorobenzene
1,3-Dichlorobenzene
1,4-Dichlorobenzene
cis-1,4-Dichloro-2-butene
trans-1,4-Dichloro-2-butene
Dichlorodifluoromethane
1,1-Dichloroethane
1,2-Dichloroethane
1,1-Dichloroethene
cis-1,2-Dichloroethene
trans-1,2-Dichloroethene
1,2-Dichloropropane
1,3-Dichloropropane
2,2-Dichloropropane
1,1-Dichloropropene
cis-1,3-Dichloropropene
trans-1,3-Dichloropropene
Diethyl ether
Diisopropyl ether (DIPE)
1,4-Dioxane
Ethanol
Ethyl acetate
Ethyl *t*-butyl ether (ETBE)
Ethyl methacrylate
Ethylbenzene
Hexachlorobutadiene
2-Hexanone
Iodomethane
Isobutyl alcohol
Isopropylbenzene
p-Isopropyltoluene
Methacrylonitrile
Methyl *t*-butyl ether (MTBE)
Methyl methacrylate
Methylene chloride
1-Methylnaphthalene
2-Methylnaphthalene
4-Methyl-2-pentanone
Naphthalene
N-Nitrosodibutylamine
N-Nitrosodiethylamine
N-Nitrosodimethylamine
N-Nitrosodi-*n*-propylamine
N-Nitrosomethylethylamine
Pentachloroethane
2-Picoline
Propionitrile
n-Propylbenzene
Pyridine
Styrene
1,1,2,2-Tetrachloroethane
Tetrachloroethene
Tetrahydrofuran
Toluene
o-Toluidine
1,2,3-Trichlorobenzene
1,2,4-Trichlorobenzene
1,1,1-Trichloroethane
1,1,2-Trichloroethane
Trichloroethene
Trichlorofluoromethane

TABLE 2-21 (continued)

- 1,2,3-Trichloropropane
- 1,2,4-Trimethylbenzene
- 1,3,5-Trimethylbenzene
- Vinyl chloride
- *o*-Xylene
- *m*-Xylene
- *p*-Xylene

TABLE 2-22

METHOD 8270 (GC/MS) - SEMIVOLATILE ORGANIC COMPOUNDS

- Acenaphthene
- Acenaphthylene
- Acetophenone
- 2-Acetylaminofluorene
- 1-Acetyl-2-thiourea
- Aldrin
- 2-Aminoanthraquinone
- Aminoazobenzene
- 4-Aminobiphenyl
- 3-Amino-9-ethylcarbazole
- Anilazine
- Aniline
- *o*-Anisidine
- Anthracene
- Aramite
- Aroclor-1016
- Aroclor-1221
- Aroclor-1232
- Aroclor-1242
- Aroclor-1248
- Aroclor-1254
- Aroclor-1260
- Azinphos-methyl
- Barban
- Benz(a)anthracene
- Benzidine
- Benzo(b)fluoranthene
- Benzo(k)fluoranthene
- Benzoic acid
- Benzo(g,h,i)perylene
- Benzo(a)pyrene
- *p*-Benzoquinone
- Benzyl alcohol
- α-BHC
- β-BHC
- δ-BHC
- γ-BHC (Lindane)
- Bis(2-chloroethoxy)methane
- Bis(2-chloroethyl)ether
- Bis(2-chloro-1-methylethyl)ether
- Bis(2-ethylhexyl)phthalate
- 4-Bromophenyl phenyl ether

Table 2-22 (continued)

Bromoxynil

Butyl benzyl phthalate

Captafol

Captan

Carbaryl

Carbofuran

Carbophenothion

Chlordane (NOS)

Chlorfenvinphos

4-Chloroaniline

Chlorobenzilate

5-Chloro-2-methylaniline

4-Chloro-3-methylphenol

3-(Chloromethyl)pyridine hydrochloride

1-Chloronaphthalene

2-Chloronaphthalene

2-Chlorophenol

4-Chloro-1,2-phenylenediamine

4-Chloro-1,3-phenylenediamine

4-Chlorophenyl phenyl ether

Chrysene

Coumaphos

p-Cresidine

Crotoxyphos

2-Cyclohexyl-4,6-dinitrophenol

4,4'-DDD

4,4'-DDE

4,4'-DDT

Demeton-O

Demeton-S

Diallate (*cis* or *trans*)

2,4-Diaminotoluene

Dibenz(*a,j*)acridine

Dibenz(*a,h*)anthracene

Dibenzofuran

Dibenzo(*a,e*)pyrene

1,2-Dibromo-3-chloropropane

Di-*n*-butyl phthalate

Dichlone

1,2-Dichlorobenzene

1,3-Dichlorobenzene

1,4-Dichlorobenzene

3,3'-Dichlorobenzidine

2,4-Dichlorophenol

2,6-Dichlorophenol

Dichlorovos

Dicrotophos

Dieldrin

Diethyl phthalate

Diethyl sulfate

Diethylstilbestrol

Dimethoate

3,3'-Dimethoxybenzidine

Dimethyl phthalate

Dimethylaminoazobenzene

7,12-Dimethylbenz(*a*)anthracene

3,3'-Dimethylbenzidine

α,α-Dimethylphenethylamine

Table 2-22 (continued)

2,4-Dimethylphenol
1,2-Dinitrobenzene
1,3-Dinitrobenzene
1,4-Dinitrobenzene
4,6-Dinitro-2-methylphenol
2,4-Dinitrophenol
2,4-Dinitrotoluene
2,6-Dinitrotoluene
Dinocap
Dinoseb
Di-*n*-octyl phthalate
Diphenylamine
5,5-Diphenylhydantoin
1,2-Diphenylhydrazine
Disulfoton
Endosulfan I
Endosulfan II
Endosulfan sulfate
Endrin
Endrin aldehyde
Endrin ketone
EPN
Ethion
Ethyl carbamate
Ethyl methanesulfonate
Famphur
Fensulfothion
Fenthion
Fluchloralin
Fluoranthene
Fluorene
Heptachlor
Heptachlor epoxide
Hexachlorobenzene
Hexachlorobutadiene
Hexachlorocyclopentadiene
Hexachloroethane
Hexachlorophene
Hexachloropropene
Hexamethylphosphoramide
Hydroquinone
Indeno(1,2,3-cd)pyrene
Isodrin
Isophorone
Isosafrole
Kepone
Leptophos
Malathion
Maleic anhydride
Mestranol
Methapyrilene
Methoxychlor
Methyl methanesulfonate
Methyl parathion
3-Methylcholanthrene
4,4'-Methylenebis(2-chloroaniline)

Table 2-22 (continued)

4,4'-Methylenebis(N,N-dimethylaniline)
2-Methylnaphthalene
2-Methylphenol
3-Methylphenol
4-Methylphenol
Mevinphos
Mexacarbate
Mirex
Monocrotophos
Naled
Naphthalene
1,4-Naphthoquinone
1-Naphthylamine
2-Naphthylamine
Nicotine
5-Nitroacenaphthene
2-Nitroaniline
3-Nitroaniline
4-Nitroaniline
5-Nitro-o-anisidine
Nitrobenzene
4-Nitrobiphenyl
Nitrofen
2-Nitrophenol
4-Nitrophenol
Nitroquinoline-1-oxide
N-Nitrosodi-n-butylamine
N-Nitrosodiethylamine
N-Nitrosodimethylamine
N-Nitrosodiphenylamine
N-Nitrosodi-n-propylamine
N-Nitrosomethylethylamine
N-Nitrosomorpholine
N-Nitrosopiperidine
N-Nitrosopyrrolidine
5-Nitro-o-toluidine
Octamethyl pyrophosphoramide
4,4'-Oxydianiline
Parathion
Pentachlorobenzene
Pentachloronitrobenzene
Pentachlorophenol
Phenacetin
Phenanthrene
Phenobarbital
Phenol
1,4-Phenylenediamine
Phorate
Phosalone
Phosmet
Phosphamidion
Phthalic anhydride
2-Picoline (2-methylpyridine)
Piperonyl sulfoxide
Pronamide
Propylthiouracil

Table 2-22 (continued)

Pyrene
Resorcinol
Safrole
Strychnine
Sulfallate
Terbufos
1,2,4,5-Tetrachlorobenzene
2,3,4,6-Tetrachlorophenol
Tetrachlorvinphos
Tetraethyl dithiopyrophosphate
Tetraethyl pyrophosphate
Thionazine
Thiophenol (Benzenethiol)
Toluene diisocyanate
o-Toluidine
Toxaphene
1,2,4-Trichlorobenzene
2,4,5-Trichlorophenol
2,4,6-Trichlorophenol
O,O,O-Triethylphosphorothioate
Trifluralin
Trimethyl phosphate
2,4,5-Trimethylaniline
1,3,5-Trinitrobenzene
Tris(2,3-dibromopropyl)phosphate
Tri-p-tolyl phosphate

TABLE 2-23

METHOD 8275 (TE/GC/MS) - SEMIVOLATILE ORGANIC COMPOUNDS

Acenaphthene
Acenaphthylene
Anthracene
Benz(*a*)anthracene
Benzo(*k*)fluoranthene
Benzo(*b*)fluoranthene
Benzo(*g,h,i*)perylene
Benzo(*a*)pyrene
4-Bromophenyl phenyl ether
2-Chlorobiphenyl
1-Chloronaphthalene
Chrysene
2,2',3,3'4,4',5,5',6,6'- Decachlorobiphenyl
Dibenz(*a,h*)anthracene
Dibenzofuran
Dibenzothiophene
3,3'-Dichlorobiphenyl
Fluoranthene
Fluorene
2,2',3,3',4,4',5- Heptachlorobiphenyl
2,2',3,4,4',5,5'- Heptachlorobiphenyl
2,2',3,4',5,5',6- Heptachlorobiphenyl
Hexachlorobenzene
2,2',3,3',4,4'- Hexachlorobiphenyl
2,2',3,4,4',5'- Hexachlorobiphenyl
Indeno(1,2,3-*cd*)pyrene
Naphthalene
2,2',3,3'4,4',5,5',6- Nonachlorobiphenyl
2,2',3,3',4,4',5,5'- Octachlorobiphenyl
2,2',4,5,5'-Pentachlorobiphenyl
2,3',4,4',5-Pentachlorobiphenyl
Phenanthrene
Pyrene
2,2'3,5'-Tetrachlorobiphenyl
2,2'4,5'-Tetrachlorobiphenyl
2,2',5,5'-Tetrachlorobiphenyl
2,3',4,4'-Tetrachlorobiphenyl
1,2,4-Trichlorobenzene
2,2',5-Trichlorobiphenyl
2,3',5-Trichlorobiphenyl
2,4',5-Trichlorobiphenyl

TABLE 2-23A

METHOD 8276 (GC-NICI/MS) - TOXAPHENE AND TOXAPHENE CONGENERS

2-endo,3-exo,5-endo,6-exo,8,9,10-Heptachlorobornane (Hp-Sed)
2-exo,3-endo,6-exo,8,9,10-Hexachlorobornane (Hx-Sed)
2,2,5,5,8,9,9,10,10-Nonachlorobornane (P62)
2-endo,3-exo,5-endo,6-exo,8,8,9,10,10-Nonachlorobornane (P50)
2-endo,3-exo,5-endo,6-exo,8,8,10,10-Octachlorobornane (P26)
2-endo,3-exo,5-endo,6-exo,8,9,10,10-Octachlorobornane (P40)
2-exo,3-endo,5-exo,8,9,9,10,10-Octachlorobornane (P41)
2-exo,5,5,8,9,9,10,10-Octachlorobornane (P44)
Toxaphene

TABLE 2-24

METHODS 8280 (HRGC/LRMS) AND 8290 (HRGC/HRMS) - POLYCHLORINATED DIBENZO-*p*-DIOXINS (PCDDs) AND POLYCHLORINATED DIBENZOFURANS (PCDFs)

1,2,3,4,6,7,8-HpCDD	2,3,4,6,7,8-HxCDF
HpCDD, total	HxCDF, total
1,2,3,4,6,7,8-HpCDF	OCDD
1,2,3,4,7,8,9-HpCDF	OCDF TCDF, total
HpCDF, total	1,2,3,7,8-PeCDD
1,2,3,4,7,8-HxCDD	PeCDD, total
1,2,3,6,7,8-HxCDD	1,2,3,7,8-PeCDF
1,2,3,7,8,9-HxCDD	2,3,4,7,8-PeCDF
HxCDD, total	PeCDF, total
1,2,3,4,7,8-HxCDF	2,3,7,8-TCDD
1,2,3,6,7,8-HxCDF	TCDD, total
1,2,3,7,8,9-HxCDF	2,3,7,8-TCDF

TABLE 2-25

METHOD 8310 (HPLC) - POLYNUCLEAR AROMATIC HYDROCARBONS

Acenaphthene	Chrysene
Acenaphthylene	Dibenzo(*a,h*)anthracene
Anthracene	Fluoranthene
Benz(*a*)anthracene	Fluorene
Benzo(*b*)fluoranthene	Indeno(1,2,3-*cd*)pyrene
Benzo(*k*)fluoranthene	Naphthalene
Benzo(*g,h,i*)perylene	Phenanthrene
Benzo(*a*)pyrene	Pyrene

TABLE 2-26

METHOD 8315 - CARBONYL COMPOUNDS

Acetaldehyde	Decanal	Octanal
Acetone	2,5-Dimethylbenzaldehyde	Pentanal (Valeraldehyde)
Acrolein	Formaldehyde	Propanal (Propionaldehyde)
Benzaldehyde	Heptanal	*m*-Tolualdehyde
Butanal (Butyraldehyde)	Hexanal (Hexaldehyde)	*o*-Tolualdehyde
Crotonaldehyde	Isovaleraldehyde	*p*-Tolualdehyde
Cyclohexanone	Nonanal	

TABLE 2-27

METHOD 8316 (HPLC)

Acrolein
Acrylamide
Acrylonitrile

TABLE 2-28

METHOD 8318 (HPLC) - *N*-METHYLCARBAMATES

Aldicarb (Temik)	Dioxacarb	Mexacarbate
Aldicarb sulfone	Formetanate hydrochloride	Oxamyl
Bendiocarb	3-Hydroxycarbofuran	Promecarb
Carbaryl (Sevin)	Methiocarb (Mesurol)	Propoxur (Baygon)
Carbofuran (Furadan)	Methomyl (Lannate)	Thiodicarb
m-Cumenyl methylcarbamate	Metolcarb	

TABLE 2-29

METHOD 8321 (HPLC/TS/MS) - NONVOLATILE ORGANIC COMPOUNDS

Azo Dyes

Disperse Brown 1
Disperse Orange 3
Disperse Orange 30
Disperse Red 1
Disperse Red 5
Disperse Red 13
Disperse Yellow 5
Solvent Red 3
Solvent Red 23

Anthraquinone Dyes

Disperse Blue 3
Disperse Blue 14
Disperse Red 60

Organophosphorus Compounds

Asulam
Dichlorvos (DDVP)
Dimethoate
Disulfoton
Famphur
Fensulfothion
Merphos
Methomyl
Monocrotophos
Naled
Parathion methyl
Phorate
Thiofanox
Trichlorfon
Tris(2,3-dibromopropyl) phosphate (Tris-BP)

Chlorinated Phenoxyacid Compounds

2,4-D
2,4-D, butoxyethanol ester
2,4-D, ethylhexyl ester
Dalapon
2,4-DB
Dicamba
Dichlorprop
Dinoseb
MCPA
MCPP
Silvex (2,4,5-TP)
2,4,5-T
2,4,5-T, butyl ester
2,4,5-T, butoxyethanol ester

Table 2-29 (continued)

Carbamates

Aldicarb
Aldicarb sulfone
Aldicarb sulfoxide
Aminocarb
Barban
Bendiocarb
Benomyl
Bromacil
Butylate
Carbaryl
Carbendazim
Carbofuran
Carbofuran phenol
Carbosulfan
Chloropropham
Chloroxuron
m-Cumenyl methyl carbamate
Diuron
EPTC
Fenuron
Fluometuron
Formetanate hydrochloride
3-Hydroxycarbofuran
Linuron
Methiocarb
Methomyl
Metolcarb
Mexacarbate
Molinate
Monuron
Neburon
Oxamyl
Pebulate
o-Phenylenediamine
Physostigmine
Physostigmine salicylate
Promecarb
Propham
Propoxur
Prosulfocarb
Siduron
Tebuthiuron
Thiodicarb
Thiophanate-methyl
Triallate

TABLE 2-29A

METHOD 8323 (MS) - ORGANOTINS BY MICRO-LIQUID CHROMATOGRAPHY-ELECTROSPRAY ION TRAP MASS SPECTROMETRY

Dibutyltin dichloride
Diphenyltin dichloride
Monobutyltin trichloride
Monophenyltin trichloride
Tributyltin chloride
Triphenyltin chloride

TABLE 2-30

METHOD 8325 (HPLC/PB/MS) - NONVOLATILE ORGANIC COMPOUNDS

Benzidine
Benzoylprop ethyl
Carbaryl
o-Chlorophenyl thiourea
3,3'-Dichlorobenzidine
3,3'-Dimethoxybenzidine
3,3'-Dimethylbenzidine
Diuron
Linuron (Lorox)
Monuron
Rotenone
Siduron

TABLE 2-31

METHOD 8330 (HPLC) - NITROAROMATICS AND NITRAMINES

2-Amino-4,6-dinitrotoluene (2-Am-DNT)
4-Amino-2,6-dinitrotoluene (4-Am-DNT)
3,5-Dinitroanaline (3,5-DNA)
1,3-Dinitrobenzene (1,3-DNB)
2,4-Dinitrotoluene (2,4-DNT)
2,6-Dinitrotoluene (2,6-DNT)
Hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX)
Methyl-2,4,6-trinitrophenyl-nitramine (Tetryl)
Nitrobenzene (NB)
2-Nitrotoluene (2-NT)
3-Nitrotoluene (3-NT)
4-Nitrotoluene (4-NT)
Nitroglycerin
Octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine (HMX)
Pentaerythritol tetranitrate (PETN)
1,3,5-Trinitrobenzene (1,3,5-TNB)
2,4,6-Trinitrotoluene (2,4,6-TNT)

TABLE 2-32

METHOD 8331 (HPLC)

Tetrazene

TABLE 2-33

METHOD 8332 (HPLC)

Nitroglycerine

TABLE 2-34

METHOD 8410 - SEMIVOLATILE ORGANIC COMPOUNDS

Acenaphthene
Acenaphthylene
Anthracene
Benzo(*a*)anthracene
Benzo(*a*)pyrene
Benzoic acid
Bis(2-chloroethoxy)methane
Bis(2-chloroethyl)ether
Bis(2-chloro-1-methylethyl)ether
Bis(2-ethylhexyl) phthalate
4-Bromophenyl phenyl ether
Butyl benzyl phthalate
4-Chloroaniline
4-Chloro-3-methylphenol
2-Chloronaphthalene
2-Chlorophenol
4-Chlorophenol
4-Chlorophenyl phenyl ether
Chrysene
Dibenzofuran
Di-*n*-butyl phthalate
1,2-Dichlorobenzene
1,3-Dichlorobenzene
1,4-Dichlorobenzene
2,4-Dichlorophenol
Diethyl phthalate
Dimethyl phthalate
4,6-Dinitro-2-methylphenol
2,4-Dinitrophenol
2,4-Dinitrotoluene
2,6-Dinitrotoluene
Di-*n*-octyl phthalate
Di-*n*-propyl phthalate
Fluoranthene
Fluorene
Hexachlorobenzene
1,3-Hexachlorobutadiene
Hexachlorocyclopentadiene
Hexachloroethane
Isophorone
2-Methylnaphthalene
2-Methylphenol

Table 2-34 (continued)

4-Methylphenol	*N*-Nitrosodiphenylamine
Naphthalene	*N*-Nitroso-di-*n*-propylamine
2-Nitroaniline	Pentachlorophenol
3-Nitroaniline	Phenanthrene
4-Nitroaniline	Phenol
	Pyrene
2-Nitrophenol	1,2,4-Trichlorobenzene
4-Nitrophenol	2,4,5-Trichlorophenol
N-Nitrosodimethylamine	2,4,6-Trichlorophenol

TABLE 2-35

METHOD 8430 (GC/FT-IR) - BIS(2-CHLOROETHYL) ETHER AND ITS HYDROLYSIS PRODUCTS

Bis(2-chloroethyl) ether

2-Chloroethanol

2-(2-Chloroethoxy) ethanol

Diethylene glycol

Ethylene glycol

TABLE 2-35A

METHOD 8440 - TOTAL RECOVERABLE PETROLEUM HYDROCARBONS BY INFRARED SPECTROPHOTOMETRY

This method does not give a specific compound list but is applicable to total recoverable petroleum hydrocarbons.

TABLE 2-36

METHOD 8510 (COLORIMETRIC SCREENING) - RDX AND HMX

Hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX)
Octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine (HMX)

TABLE 2-36A

METHOD 8520 (CONTINUOUS MEASUREMENT OF FORMALDEHYDE IN AMBIENT AIR)

Formaldehyde

TABLE 2-37

METHOD 8535 (COLORIMETRIC SCREENING) - VOLATILE ORGANIC HALIDES

Carbon tetrachloride
Perchloroethylene (Tetrachloroethene)
Trichloroethylene
Trihalomethanes

TABLE 2-38

METHOD 8540 (UV-INDUCED COLORIMETRY) - PENTACHLOROPHENOL

Pentachlorophenol

TABLE 2-39

DETERMINATIVE METHODS FOR INORGANIC ANALYTES

Analyte	Applicable Methods
Aluminum	6010, 6020, 7000, 7010
Antimony	6010, 6020, 6200, 6800, 7000, 7062
Arsenic	6010, 6020, 6200, 7010, 7061, 7062, 7063
Barium	6010, 6020, 6200, 6800, 7000, 7010
Beryllium	6010, 6020, 7000, 7010
Boron	6010, 6800
Bromide	6500, 9056, 9211
Cadmium	6010, 6020, 6200, 6800, 7000, 7010
Calcium	6010, 6020, 6200, 6800, 7000
Chloride	6500, 9056, 9057, 9212, 9250, 9251, 9253
Chromium	6010, 6020, 6200, 6800, 7000, 7010
Chromium, hexavalent	6800, 7195, 7196, 7197, 7198, 7199
Cobalt	6010, 6020, 6200, 7000, 7010
Copper	6010, 6020, 6200, 6800, 7000, 7010
Cyanide	9010, 9012, 9013, 9014, 9015, 9016, 9213
Fluoride	6500, 9056, 9214
Iron	6010, 6020, 6200, 6800, 7000, 7010
Lead	6010, 6020, 6200, 6800, 7000, 7010
Lithium	6010, 7000
Magnesium	6010, 6020, 6800, 7000
Manganese	6010, 6020, 6200, 7000, 7010
Mercury	6010, 6020, 6200, 6800, 7470, 7471, 7472, 7473, 7474
Molybdenum	6010, 6200, 6800, 7000, 7010
Nickel	6010, 6020, 6200, 6800, 7000, 7010
Nitrate	6500, 9056, 9210
Nitrite	6500, 9056, 9216
Osmium	7000
Perchlorate	6850, 6860
Phosphate	6500, 9056
Phosphorus	6010
Phosphorus, white	7580
Potassium	6010, 6020, 6200, 6800, 7000
Rubidium	6200
Selenium	6010, 6020, 6200, 6800, 7010, 7741, 7742
Silica	6010
Silver	6010, 6020, 6200, 6800, 7000, 7010
Sodium	6010, 6020, 7000
Strontium	6010, 6200, 6800, 7000
Sulfate	6500, 9035, 9036, 9038, 9056
Sulfide	9030, 9031, 9215
Thallium	6010, 6020, 6200, 6800, 7000, 7010
Thorium	6200
Tin	6010, 6200, 7000
Titanium	6010, 6200

TABLE 2-39 (cont)

Vanadium	6010, 6020, 6200, 6800, 7000, 7010
Zinc	6010, 6020, 6200, 6800, 7000, 7010
Zirconium	6200

TABLE 2-40A

RECOMMENDED SAMPLE CONTAINERS, PRESERVATION TECHNIQUES, AND HOLDING TIMES FOR ORGANIC CHEMICALS[a]

(Note: Footnotes are located on the last page of the table.)

VOLATILE ORGANICS

Sample Matrix	Container	Preservative[1]	Holding Time[1]
Concentrated waste samples	Method 5035: See the method. Method 5021: See the method. Methods 5031 and 5032: See the methods. Use PTFE-lined lids for all procedures.	Cool to 0 - 6 °C.	14 days
Aqueous samples with no residual chlorine present	Methods 5030, 5031, and 5032: 3 x 40-mL vials with PTFE-lined septum caps	Cool to 0 - 6 °C and adjust pH to less than 2 with H_2SO_4, HCl, or solid $NaHSO_4$	14 days
		If carbonaceous materials are present, or if MTBE and other fuel oxygenate ethers are present and a high temperature sample preparative method is to be used, do not acid preserve the samples.	*7 days*
		If the reactive compound 2-chloroethyl vinyl ether[b] is an analyte of interest, collect a second set of samples without acid preservatives and analyze immediately.	*7 days*

TABLE 2-40A (continued)

RECOMMENDED SAMPLE CONTAINERS, PRESERVATION TECHNIQUES, AND HOLDING TIMES FOR ORGANIC CHEMICALS[a]

VOLATILE ORGANICS (continued)

Sample Matrix	Container	Preservative[1]	Holding Time[1]
Aqueous samples WITH residual chlorine present	Methods 5030, 5031, and 5032: 3 x 40-mL vials with PTFE-lined septum caps	Collect sample in a 125-mL container which has been pre-preserved with 4 drops of 10% sodium thiosulfate solution. Gently swirl to mix sample and transfer to a 40-mL VOA vial. Cool to 0 - 6 °C and adjust pH to less than 2 with H_2SO_4, HCl, or solid $NaHSO_4$.	14 days
		If carbonaceous materials are present, or if MTBE and other fuel oxygenate ethers are present and a high temperature sample preparative method is to be used, do not acid preserve the samples.	*7 days*
		If the reactive compound 2-chloroethyl vinyl ether[b] is an analyte of interest, collect a second set of samples without acid preservatives and analyze immediately.	*7 days*
Acrolein and acrylonitrile in aqueous samples	Methods 5030, 5031, and 5032: 3 x 40-mL vials with PTFE-lined septum caps	Adjust to pH 4-5. Cool to 0 - 6 °C. *These compounds are highly reactive and should be analyzed as soon as possible.*	7 days
Solid samples (e.g., soils, sediments, sludges, ash)	Method 5035: See the method. Method 5021: See the method. Methods 5031 and 5032: See the methods.	See the individual methods.	14 days
		If vinyl chloride, styrene, or 2-chloroethyl vinyl ether are analytes of interest, collect a second set of samples without acid preservatives and analyze as soon as possible.	7 days

TABLE 2-40A (continued)

RECOMMENDED SAMPLE CONTAINERS, PRESERVATION TECHNIQUES, AND HOLDING TIMES FOR ORGANIC CHEMICALS[a]

SEMIVOLATILE ORGANICS/ORGANOCHLORINE PESTICIDES AND HERBICIDES

Sample Matrix	Container	Preservative[1]	Holding Time[1]
Concentrated waste samples	125-mL wide-mouth glass with PTFE-lined lid	None	Samples extracted within 14 days and extracts analyzed within 40 days following extraction.
Aqueous samples with no residual chlorine present	4 x 1-L amber glass container with PTFE-lined lid, or other size, as appropriate, to allow use of entire sample for analysis.	Cool to 0 - 6 °C.	Samples extracted within 7 days and extracts analyzed within 40 days following extraction.
Aqueous samples WITH residual chlorine present	4 x 1-L amber glass container with PTFE-lined lid, or other size, as appropriate, to allow use of entire sample for analysis.	Add 3 mL 10% sodium thiosulfate solution per gallon (or 0.008%). Addition of sodium thiosulfate solution to sample container may be performed in the laboratory prior to field use. Cool to 0 - 6 °C.	Samples extracted within 7 days and extracts analyzed within 40 days following extraction.
Solid samples (e.g., soils, sediments, sludges, ash)	250-mL wide-mouth glass container with PTFE-lined lid	Cool to 0 - 6 °C.	Samples extracted within 14 days and extracts analyzed within 40 days following extraction.

TABLE 2-40A (continued)

RECOMMENDED SAMPLE CONTAINERS, PRESERVATION TECHNIQUES, AND HOLDING TIMES FOR ORGANIC CHEMICALS[a]

POLYCHLORINATED BIPHENYLS, POLYCHLORINATED DIBENZO-*p*-DIOXINS, AND POLYCHLORINATED DIBENZOFURANS

Sample Matrix	Container	Preservative[1]	Holding Time[2]
Concentrated waste samples	125-mL wide-mouth glass with PTFE-lined lid	None	None
Aqueous samples with no residual chlorine present	4 x 1-L amber glass container with PTFE-lined lid, or other size, as appropriate, to allow use of entire sample for analysis.	Cool to 0 - 6 °C.	None
Aqueous samples WITH residual chlorine present	4 x 1-L amber glass container with PTFE-lined lid, or other size, as appropriate, to allow use of entire sample for analysis.	Add 3 mL 10% sodium thiosulfate solution per gallon (or 0.008%). Addition of sodium thiosulfate solution to sample container may be performed in the laboratory prior to field use. Cool to 0 - 6 °C	None
Solid samples (e.g., soils, sediments, sludges, ash)	250-mL wide-mouth glass container with PTFE-lined lid.	Cool to 0 - 6 °C.	None

[a] The information presented in this table does not represent EPA requirements, but rather is intended solely as guidance. Selection of containers, preservation techniques, and applicable holding times should be based on the stated project-specific DQOs.

[1] The exact sample, extract, and standard storage temperature should be based on project-specific requirements and/or manufacturer's recommendations for commercially available standards. Furthermore, alternative storage temperatures may be appropriate based on demonstrated analyte stability in a given matrix, provided the stated DQOs for a project-specific application are still attainable.

[2] A longer holding time may be appropriate if it can be demonstrated that the reported analyte concentrations are not adversely affected from preservation, storage, and analyses performed outside the recommended holding times.

TABLE 2-40B

RECOMMENDED CONTAINERS, PRESERVATION TECHNIQUES, AND HOLDING TIMES FOR INORGANIC AND OTHER ANALYTES IN AQUEOUS MATRICES
(SEE CHAPTER THREE FOR MORE DETAILED GUIDANCE, INCLUDING REGARDING SOLID MATRICES)

(Footnotes are located on the next page.)

Name	Container[1]	Preservation[2]	Holding Time[3]
Inorganic Tests:			
Chloride	P, G	None required	28 days
Cyanide, total and amenable to chlorination	P, G	Cool to 0 - 6 °C; if oxidizing agents present add 5 mL 0.1N $NaAsO_2$ per L or 0.06 g of ascorbic acid per L; adjust pH>12 with 50% NaOH. See Method 9010 for other interferences.	14 days
Hydrogen ion (pH)	P, G	None required	As soon as possible
Nitrate	P, G	Cool to 0 - 6 °C.	48 hours
Sulfate	P, G	Cool to 0 - 6 °C.	28 days
Sulfide	P, G	Cool to 0 - 6 °C , add zinc acetate, NaOH to pH >9	7 days
Metals:			
Chromium VI	P, G	Cool to 0 - 6 °C.	24 hours
Mercury	P, G	HNO_3 to pH<2	28 days
Mercury (soil/sediment)	P, G	Cool to 0 - 6 °C.	28 days
Mercury Species in soil/sediment	P, G	Cool to 0 - 6 °C.	5 days
All Other Metals	P, G	HNO_3 to pH<2	6 months
Hexane Extractable Material (HEM; Oil and grease)	G	Cool to 0 - 6 °C,HCl or H_2SO_4 to pH<2	28 days
Organic carbon, total (TOC)	P, G	Cool to 0 - 6°C, store in dark; HCl or H_2SO_4 to pH<2	28 days
Radiological Tests:			

Name	Container[1]	Preservation[2]	Holding Time[3]
Alpha, beta and radium	P, G	HNO_3 to pH<2	6 months

[a] The information presented in this table does not represent EPA requirements, but rather is intended solely as guidance. Selection of containers, preservation techniques and applicable holding times should be based on the stated project-specific DQOs. See Chapter Three, Chapter Four, or the individual methods for more information.

[1] Polyethylene (P) or glass (G)

[2] The exact sample, extract, and standard storage temperature should be based on project-specific requirements and/or manufacturer's recommendations for commercially available standards. Furthermore, alternative storage temperatures may be appropriate based on demonstrated analyte stability in a given matrix, provided the stated DQOs for a project-specific application are still attainable.

[3] A longer holding time may be appropriate if it can be demonstrated that the reported analyte concentrations are not adversely affected by preservation, storage, and analyses performed outside the recommended holding times.

TABLE 2-41
PREPARATION METHODS FOR ORGANIC ANALYTES
(Note: Footnotes are located on the last page of the table.)

	Matrix			
Analyte Type	Aqueous[1]	Solids	Sludges and Emulsions[1,2]	Organic Liquids, Tars, Oils
Acid Extractable	35103520 (pH ≤ 2)	3540 3541 3542[13] 3545 3546 3550	3520 (pH ≤ 2)	3650 3580[3]
Acrolein[12], Acrylonitrile[12], and Acetonitrile	5031 5032[12]	5031 5032[12]	5031 5032[12]	3585
Acrylamide	8032[4]			
Aniline and Selected Derivatives	3510 3520 (pH >11) 5031[11]	3540 3541 3545 3550	3520 (pH >11)	3580[3]
Aromatic Volatiles	5021 5030 5032	5021 5032 5035	5030 5032	3585
Base/Neutral Extractable	3510 3511 3520 (pH >11)	3540 3541 3542[13] 3545 3546 3550	3520 (pH >11)	3650 3580[3]
Carbamates	8318[5] 8321	8318[5] 8321	8318[5]	8318[5]
Chlorinated Herbicides	3535 (pH < 1) 8151[6] (pH ≤ 2) 8321	3545 3546 8151[6] 8321	8151[6] (pH ≤ 2)	3580[3]
Chlorinated Hydrocarbons	3510 3520 (pH as received)	3540 3541 3550	3520 (pH as received)	3580[3]
Dyes	3510 3520	3540 3541 3545 3550		

TABLE 2-41 (continued)
PREPARATION METHODS FOR ORGANIC ANALYTES

	Matrix			
Analyte Type	Aqueous[1]	Solids	Sludges and Emulsions[1,2]	Organic Liquids, Tars, Oils
Explosives	3535 8330[7] 8331[8]	8330[7] 8331[8]		
Formaldehyde	8315[9]	8315[9]		
Haloethers			3510 3520	3540 3541 3545 3550
Halogenated Volatiles	5021 5030 5032	5021 5032 5035	5030	5021 (methanol extr) 5035 / 5030 (methanol extr) 5032 3585
Nitroaromatics and Cyclic Ketones	3510 3520 (pH 5-9) 3535	3540 3541 3545 3550	3520 (pH 5-9)	3580[3]
Nitrosamines	3510 3520	3540 3541 3545 3550		
Non-halogenated Volatiles	5021 5030 5031 5032	5021 5031 5032 5035	5021 5031 5032	5021 (methanol extr) 5035 / 5030 (methanol extr) 5032 3585
Organochlorine Pesticides	3510 3520 3535 (pH 5-9)	3540 3541 3545 3546 3550 3562	3520 (pH 5-9)	3580[3]
Organophosphorus Pesticides	3510 3520 (pH 5-8) 3535	3540 3541 3545 3546	3520 (pH 5-8)	3580[3]

TABLE 2-41 (continued)
PREPARATION METHODS FOR ORGANIC ANALYTES

	Matrix			
	Aqueous[1]	Solids	Sludges and Emulsions[1,2]	Organic Liquids, Tars, Oils 3650 3580[3]
Phenols	3510 3520 (pH ≤ 2) 3535	3540 3541 3545 3546 3550 3562	3520 (pH ≤ 2)	3650 3580[3]
Phthalate Esters	3510 3520 3535 (pH 5-7)	3540 3541 3545 3546 3550	3520 (pH 5- 7)	3580[3]
Polychlorinated Biphenyls	3510 3520 3535 (pH 5-9)	3540 3541 3545 3546 3562	3520 (pH 5-9)	3580[3]
PCDDs and PCDFs	8280[10] 8290[10]	3545 3546 8280[10] 8290[10]	8280[10] 8290[10]	8280[10] 8290[10]
Polynuclear Aromatic Hydrocarbons	3510 3511 3520 (pH as received)	3540 3541 3545 3546 3550 3561	3520 (pH as received)	3580[3]
Volatile Organics	5021 5030 5031 5032	5021 5031 5032 5035	5021 5030 5031 5032	5021 (methanol extr) 5035 / 5030 (methanol extr) 5032 3585
Wipes (Chemical Agents only)		3572		

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[1] The pH at which extraction should be performed is shown in parentheses.

[2] If attempts to break an emulsion are unsuccessful, these methods may be used.

[3] Method 3580 is only appropriate if the sample is soluble in the specified solvent.

[4] Method 8032 contains the extraction, cleanup, and determinative procedures for this analyte.

[5] Method 8318 contains the extraction, cleanup, and determinative procedures for these analytes.

[6] Method 8151 contains the extraction, cleanup, and determinative procedures for these analytes.

[7] Method 8330 contains the extraction, cleanup, and determinative procedures for these analytes.

[8] Method 8331 is for Tetrazene only, and contains the extraction, cleanup, and determinative procedures for this analyte.

[9] Method 8315 contains the extraction, cleanup, and determinative procedures for this analyte.

[10] Methods 8280 and 8290 contain the extraction, cleanup, and determinative procedures for these analytes.

[11] Method 5031 may be used when only aniline is to be determined.

[12] Method 5032 may be used for acrolein and acrylonitrile.

[13] Method 3542 is used for extraction of semivolatiles from stack samples collected using Method 0010.

TABLE 2-42

CLEANUP METHODS FOR ORGANIC ANALYTE EXTRACTS

Analyte Type	Method
Acid Extractable	3650, 3640
Base/Neutral Extractable	3650, 3640
Carbamates	8318[1]
Chlorinated Herbicides	8151[2]
Chlorinated Hydrocarbons	3620, 3640
Haloethers	3620, 3640
Nitroaromatics & Cyclic Ketones	3620, 3640
Nitrosamines	3610, 3620, 3640
Organochlorine Pesticides	3620, 3630, 3640 3660
Organophosphorus Pesticides	3620
Phenols	3630, 3640, 3650 8041[3]
Phthalate Esters	3610, 3611, 3620 3640
Polychlorinated Biphenyls	3620, 3630, 3640 3660, 3665
Polychlorinated Dibenzo-*p*-Dioxins and Polychlorinated Dibenzofurans	8280[4] 8290[4]
Polynuclear Aromatic Hydrocarbons	3610, 3611 3630, 3640, 3650

[1] Method 8318 contains the extraction, cleanup, and determinative procedures for these analytes.
[2] Method 8151 contains the extraction, cleanup, and determinative procedures for these analytes.
[3] Method 8041 includes a derivatization technique followed by GC/ECD analysis, if interferences are encountered using GC/FID.
[4] Methods 8280 and 8290 contain the extraction, cleanup, and determinative procedures for these analytes.

TABLE 2-43

DETERMINATIVE METHODS ORGANIC ANALYTES

Analyte Type	GC/MS Method	Specific GC Method[6]	HPLC Method
Acid Extractable	8270	8410[6]	
Acrolein, Acrylonitrile, Acetonitrile	8260, 8261	8015, 8031, 8033[1]	8315[2], 8316
Acrylamide	8260	8032	8316
Aniline and Selected Derivatives	8270	8131	
Aromatic Volatiles	8260, 8261	8021	
Base/Neutral Extractable	8270	8410[6]	8325[4]
Carbamates			8318, 8321
Chlorinated Herbicides	8270[3]	8151	8321
Chlorinated Hydrocarbons	8270	8121	
Diesel Range Organics (DRO)		8015, 8440[7]	
Dyes			8321
Explosives		8095	8330, 8331, 8332
Formaldehyde			8315
Gasoline Range Organics (GRO)		8015	
Haloethers	8270	8111, 8430	
Halogenated Volatiles	8260, 8261	8011, 8021	
Nitroaromatics and Cyclic Ketones	8270	8091	8330[5]
Nitrosoamines	8270	8070	
Non-halogenated Volatiles	8260	8015	8315
Organochlorine Pesticides	8270[3], 8276	8081, 8085[6]	
Organophosphorus Pesticides	8270[3]	8141, 8085[6]	8321
Phenols	8270	8041, 8410[6]	
Phthalate Esters	8270	8061, 8410[6]	
Polychlorinated Biphenyls	8270[3]	8082	
PCDDs and PCDFs	8280, 8290		
Polynuclear Aromatic Hydrocarbons	8270	8100, 8410[6]	8310
Volatile Organics	8260, 8261	8011, 8015, 8021, 8031, 8032, 8033	8315, 8316

[1] Of these analytes, Method 8033 is for acetonitrile only.
[2] Of these analytes, Method 8315 is for acrolein only.
[3] This method is an alternative confirmation method, not the method of choice.
[4] Benzidines and related compounds.
[5] Nitroaromatics (see "Explosives").
[6] Includes GC/ES methods, e.g., Methods 8085 and 8410.
[7] FT-IR determinative method only. Does not use GC.

TABLE 2-44

PREPARATION METHODS FOR INORGANIC ANALYSES [1]

Matrix	Method
Surface water	3005, 3010, 3015, 3020
Groundwater	3005, 3010, 3015, 3020
Extracts	3010, 3015, 3020
Aqueous samples containing suspended solids	3010, 3015, 3020
Oils	3031, 3040, 3051, 3052[2]
Oil sludges	3031, 3052[2]
Tars	3031, 3052[2]
Waxes	3031, 3040, 3052[2]
Paints	3031, 3052[2]
Paint sludges	3031, 3052[2]
Petroleum products	3031, 3040, 3052[2]
Sediments	3050, 3051, 3052[2], 3060[3], 3200[4]
Sludges	3050, 3051, 3052[2], 3060[3]
Soil samples	3050, 3051, 3052[2], 3060[3], 3200[4]
Ashes	3052[2]
Biological tissues	3052[2]

[1] It is the responsibility of the analyst to refer to each analytical method to determine applicability of the chosen method to a specific waste type and target analyte.

[2] For total decomposition analysis ONLY.

[3] For the analysis of samples for hexavalent chromium ONLY.

[4] For the analysis of samples for mercury or mercury species ONLY.

TABLE 2-45

USE OF LEACHING, EXTRACTION AND DIGESTION METHODS FOR INORGANIC ANALYSIS (In order of increasing strength)

Method	Method Name	Reagents & Conditions	Use
1310	Extraction Procedure (EP) Toxicity Test Method and Structural Integrity Test	Dilute acetic acid	Simulate leaching that would result from codisposal of a solid waste and municipal waste in a sanitary landfill[1]
1311	Toxicity Characteristic Leaching Procedure	Extraction Fluid # 1 -- Dilute glacial acetic acid and NaOH, pH 4.93 ± 0.05 Extraction Fluid # 2 -- Dilute glacial acetic acid, pH 2.88 ± 0.05	Simulate leaching that would result from codisposal of a solid waste and municipal waste in a sanitary landfill[1]
1312	Synthetic Precipitation Leaching Procedure	Dilute H_2SO_4 and HNO_3 (synthetic acid rain)	Simulate acid rain leaching of a waste
1313	Liquid-Solid Partitioning as a Function of Extract pH Batch Extraction Procedure	Dilute HNO_3, KOH	Industrial wastes, soils, sludges, combustion residues, sediments, stabilized materials, construction materials, and mining wastes
1316	Liquid-Solid Partitioning as a Function of Liquid-to-Solid Ratio in Solid Materials Using a Parallel Batch Procedure	None	Industrial wastes, soils, sludges, combustion residues, sediments, stabilized materials, construction materials, and mining wastes
1320	Multiple Extraction Procedure	Dilute H_2SO_4 and HNO_3 (synthetic acid rain)	Simulate long-term acid rain leaching of a waste
3005	Acid Digestion of Waters for Total Recoverable or Dissolved Metals Analysis by FLAA or ICP Spectroscopy	HNO_3, heat	Surface water and groundwater
3010	Acid Digestion of Aqueous Samples and Extracts for Total Metals for Analysis by FLAA or ICP Spectroscopy	HNO_3, HCl, heat	Aqueous samples and extracts
3015	Microwave Assisted Acid Digestion of Aqueous Samples and Extracts	HNO_3 or alternatively HNO_3 and HCl, (pressure, heat)	Aqueous samples and extracts

TABLE 2-45 (continued)

USE OF LEACHING, EXTRACTION AND DIGESTION METHODS FOR INORGANIC ANALYSIS (In order of increasing strength)

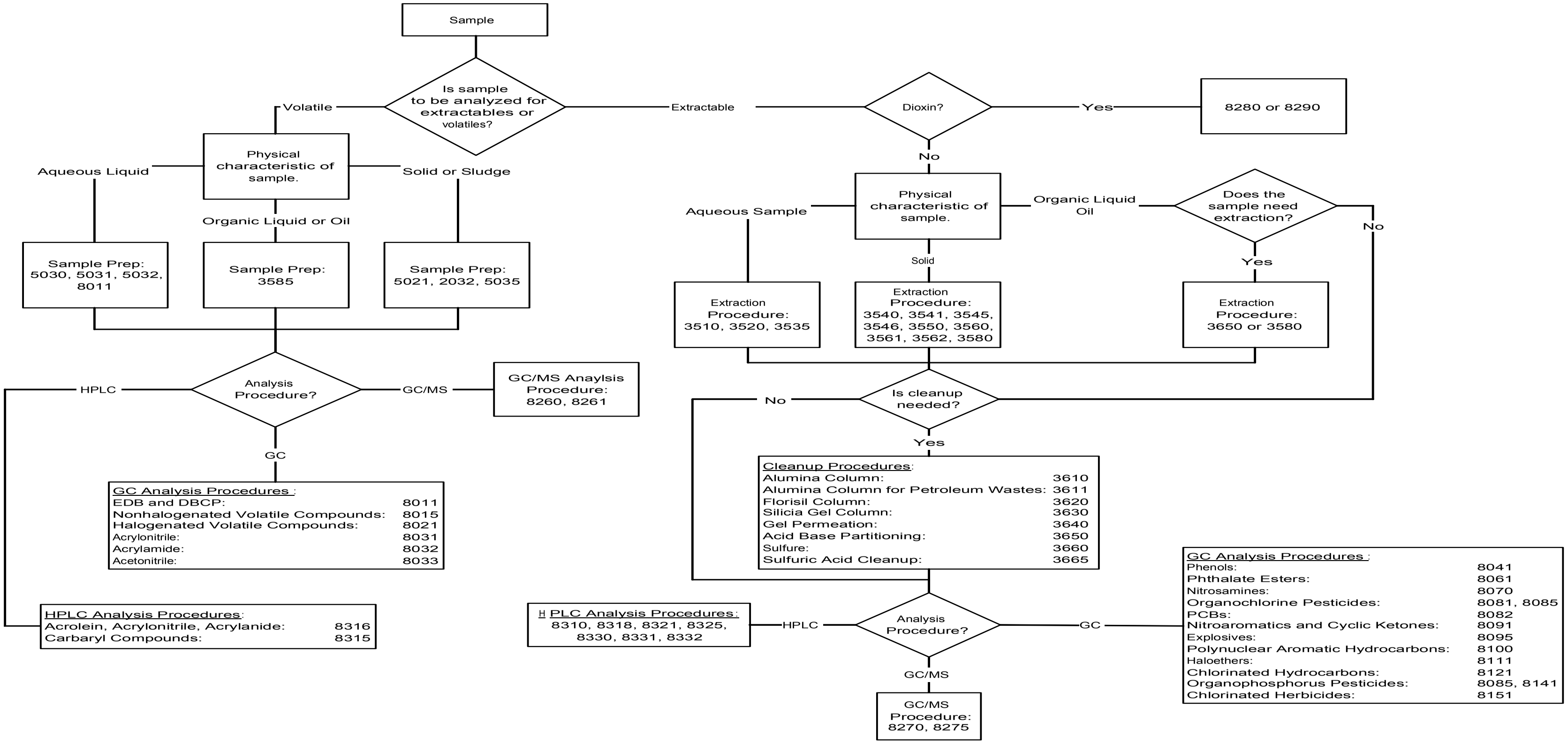
Method	Method Name	Reagents & Conditions	Use
3020	Acid Digestion of Aqueous Samples and Extracts for Total Metals for Analysis by GFAA Spectroscopy	HNO_3, heat	Aqueous samples and extracts for GFAA work only
3031	Acid Digestion of Oils for Metals Analysis by Atomic Absorption or ICP Spectrometry	Potassium permanganate, H_2SO_4, HNO_3, HCl, heat	Oils, oily sludges, tars, waxes, paint, paint sludge, and other viscous petroleum products
3040	Dissolution Procedure for Oils, Greases, or Waxes	Solvent (e.g., xylene, kerosene, or MIBK)	Dissolution of oils, oily wastes, greases and waxes
3050	Acid Digestion of Sediments, Sludges, and Soils	HNO_3 and H_2O_2, heat (for GFAA or ICPMS) HNO_3, H_2O_2, and HCl, heat (for ICP-AES or FLAA)	Sediments, soils, and sludges
3051	A Microwave Assisted Acid Digestion of Sediments Sludges, Soils, and Oils	HNO_3, or alternatively HNO_3 and HCl, microwave assisted (pressure, heat)	Sludges, sediments, soils and oils
3052	Microwave Assisted Acid Digestion of Siliceous and Organically Based Matrices	HNO_3, HF, HCl (optional) H_2O_2 (optional), heat, pressure	Siliceous, organic and other complex matrices for total sample decomposition
3060A	Alkaline Digestion for Hexavalent Chromium	Na_2CO_3/NaOH, heat	Soils, sludges, sediments and some industrial wastes for the analysis of hexavalent chromium only.

[1] As described in the respective background documents developed in support of the rulemakings, which added required use of these methods to the Toxicity Characteristic regulation (Method 1311 replaced Method 1310 for Toxicity Characteristic determinations on March 29, 1990, 55 FR 11862).

TABLE 2-46
SCREENING METHODS FOR ORGANIC ANALYTES

	Matrix			
Analyte Type	Aqueous	Solids	Sludges and Emulsions	Organic Liquids, Tars, Oils
Chlordane		4041		
2,4-Dichlorophenoxyacetic acid	4015	4015		
Hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX)		4051 8510		
Octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine (HMX)		8510		
Pentachlorophenol	4010	4010 8540	4010	
Petroleum Hydrocarbons		4030		
Poly-Chlorinated Biphenyls (PCBs)	4425 (coplanar)	4020 4425 (coplanar)		4020 (non-aqueous)
Polychlorinated Dibenzodioxins	4425	4425		
Polychlorinated Dibenzofurans	4425	4425		
Polynuclear Aromatic Hydrocarbons (PAHs)	4425	4035 4425		
Toxaphene		4040		
Triazine Pesticides	4670 (quantitative)			
1,1,1,-Trichloro-2,2-bis(chlorophenyl)ethane (DDT) and breakdown products		4042		
Trinitrotoluene (TNT)		4050 8515		

FIGURE 2-1
ORGANIC ANALYSIS OPTIONS FOR SOLID AND LIQUID MATRICES



For illustrative purposes only.

See the disclaimer and Sec. 2.1 for information on the flexibility inherent in SW-846 methods.

NOTE: Not all clean-up methods are applicable to all listed methods. Consult the individual methods for further information on what clean-up methods are applicable and appropriate.

FIGURE 2-2
SCHEMATIC OF SEQUENCE TO DETERMINE
IF A WASTE IS HAZARDOUS BY CHARACTERISTIC

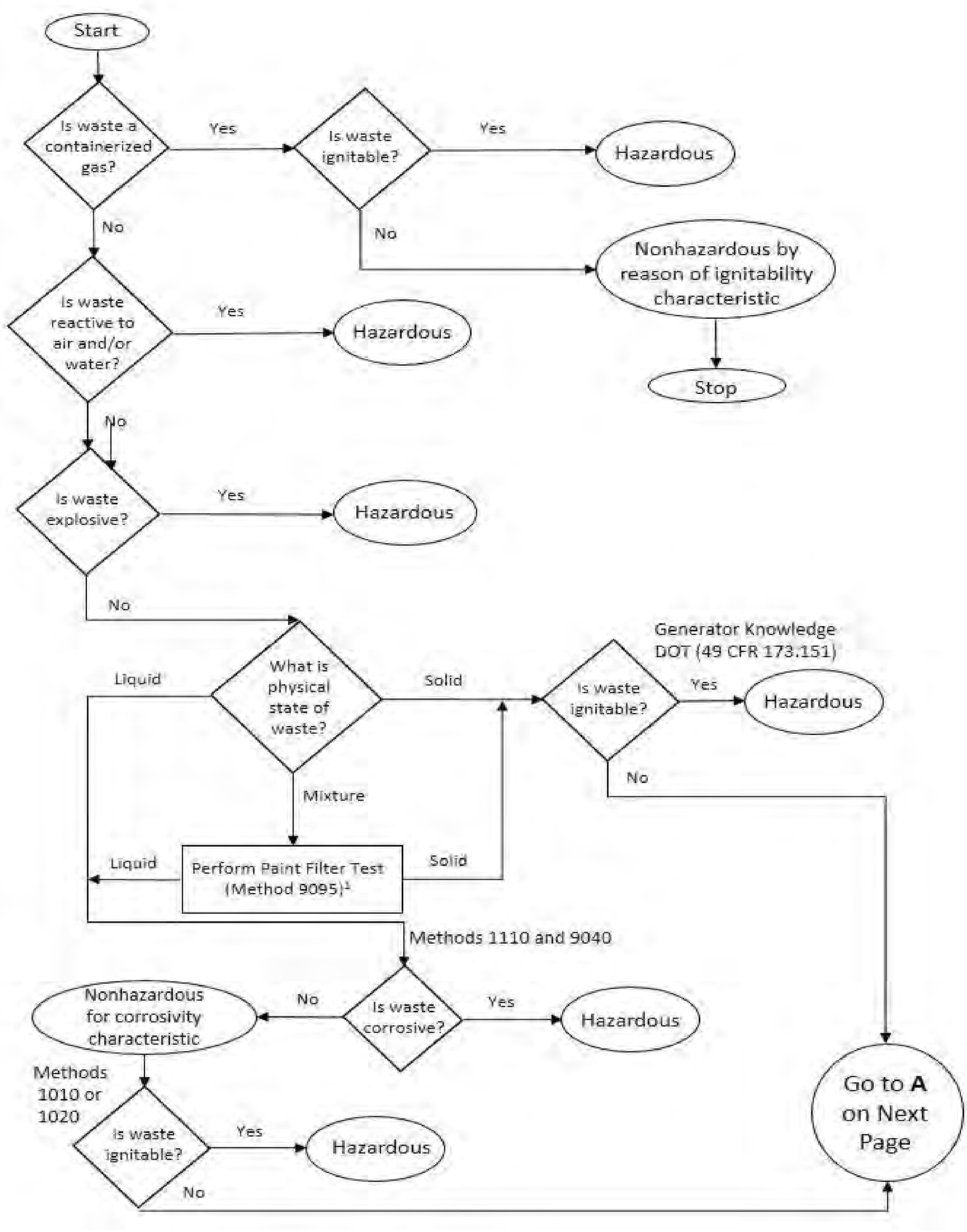
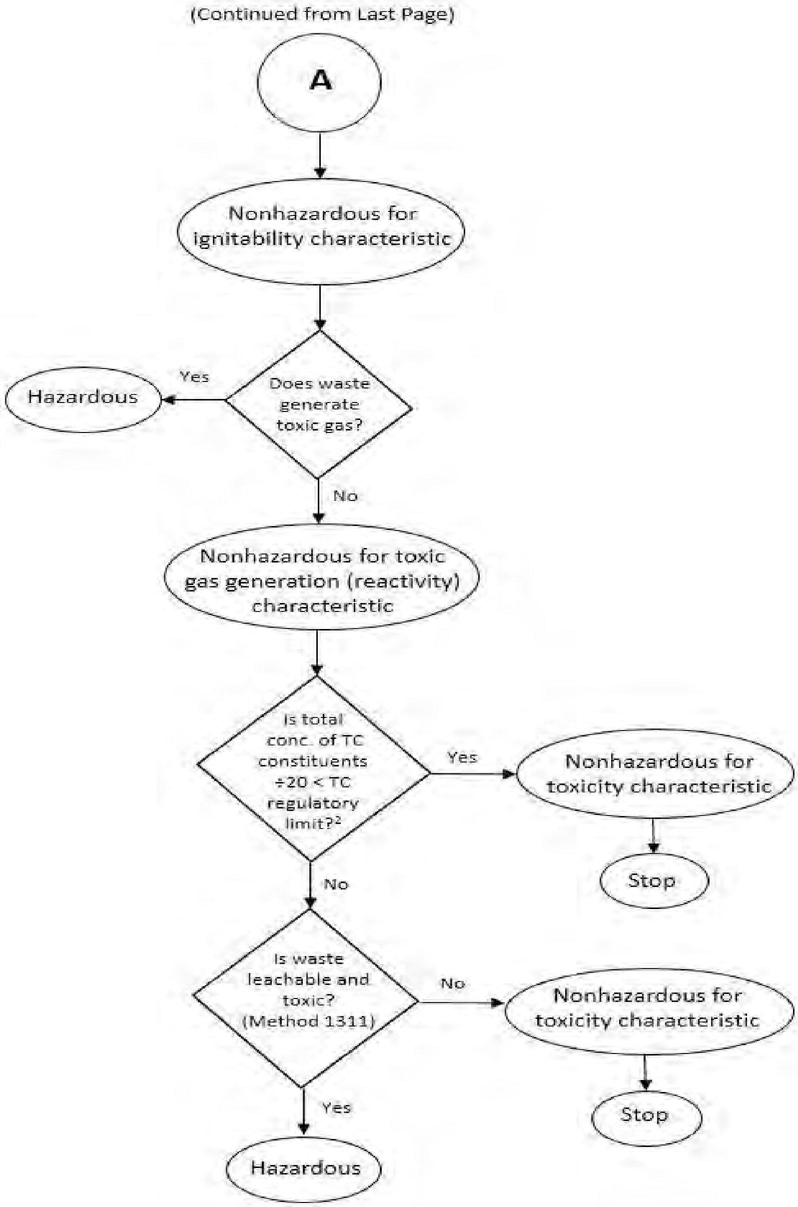


FIGURE 2-2 (continued)



1. Users can find information regarding the corrosivity characteristic for samples in a gel matrix at:http://yosemite.epa.gov/osw/rcra.nsf/0/7D573EA3E0F1576D8525670F006BEA5F/$file/11719.pdf.
2. Biphasic or multiphasic waste can present a unique challenge. More information can be found on this topic in the Federal Register (Dec 21, 1995 FR (page 66389). This can be found online at: http://nepis.epa.gov/Exe/ZyNET.exe/10001E3Y.txt?ZyActionD=ZyDocument&Client=EPA&Index=1995%20Thru%201999&Docs=&Query=&Time=&EndTime=&SearchMethod=1&TocRestrict=n&Toc=&TocEntry=&QField=&QFieldYear=&QFieldMonth=&QFieldDay=&UseQField=&IntQFieldOp=0&ExtQFieldOp=0&XmlQuery=&File=D%3A\ZYFILES\INDEX%20DATA\95THRU99\TXT\00000000\10001E3Y.txt&User=ANONYMOUS&Password=anonymous&SortMethod=h|-&MaximumDocuments=1&FuzzyDegree=0&ImageQuality=r75g8/r75g8/x150y150g16/i425&Display=p|f&DefSeekPage=x&SearchBack=ZyActionL&Back=ZyActionS&BackDesc=Results%20page&MaximumPages=1&ZyEntry=48

FIGURE 2-3A
RECOMMENDED SW-846 METHODS FOR ANALYSIS OF EP LEACHATES

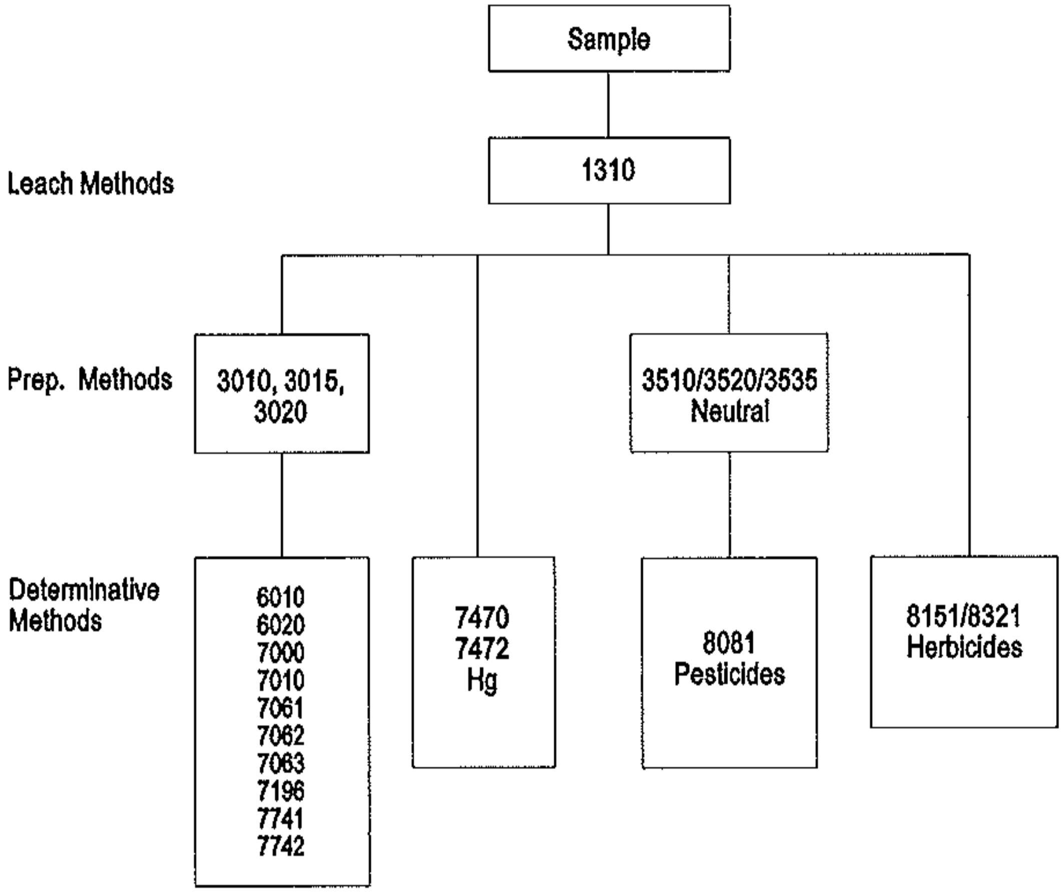


FIGURE 2-3B

RECOMMENDED SW-846 METHODS FOR ANALYSIS OF TCLP LEACHATES

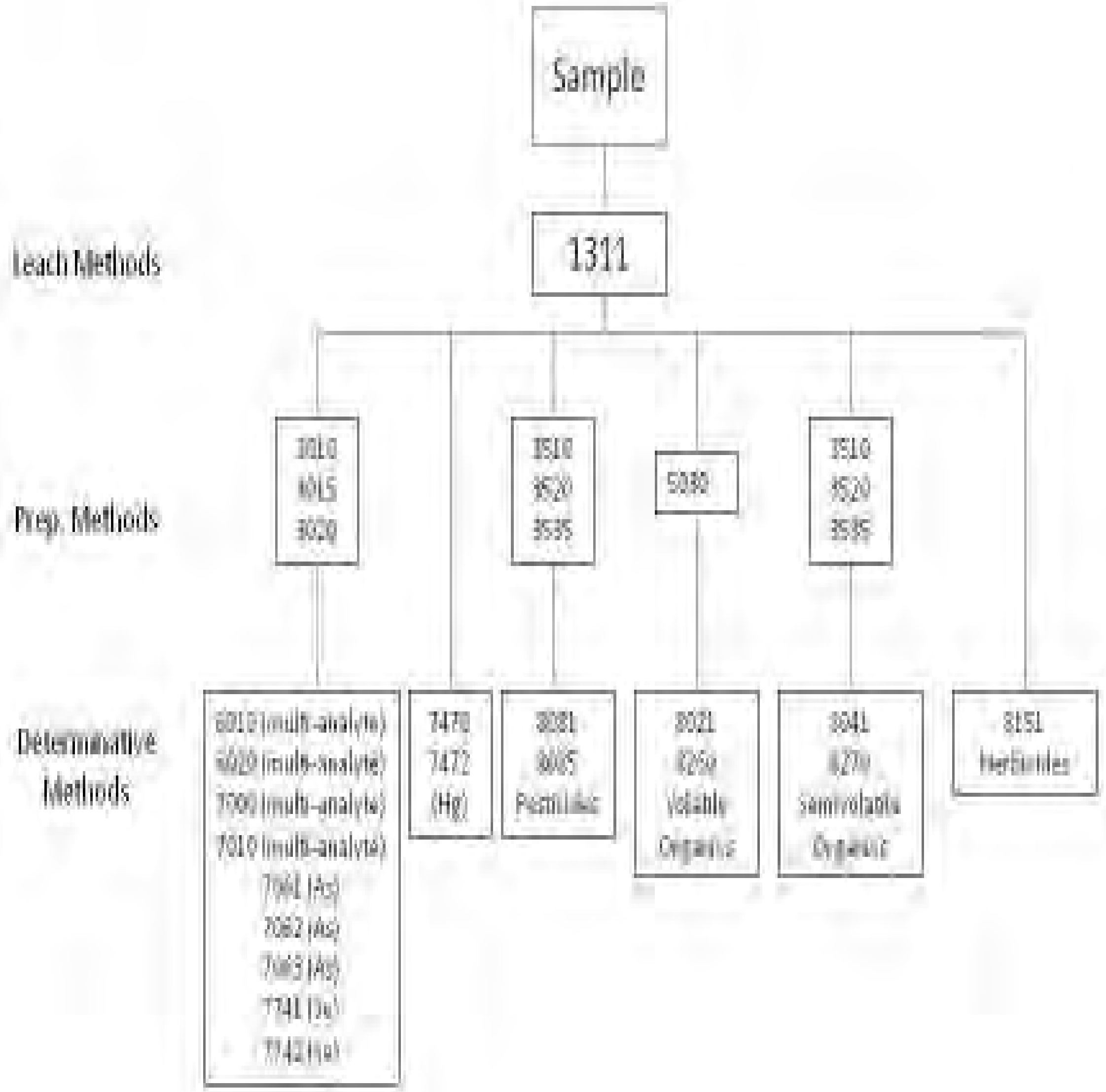
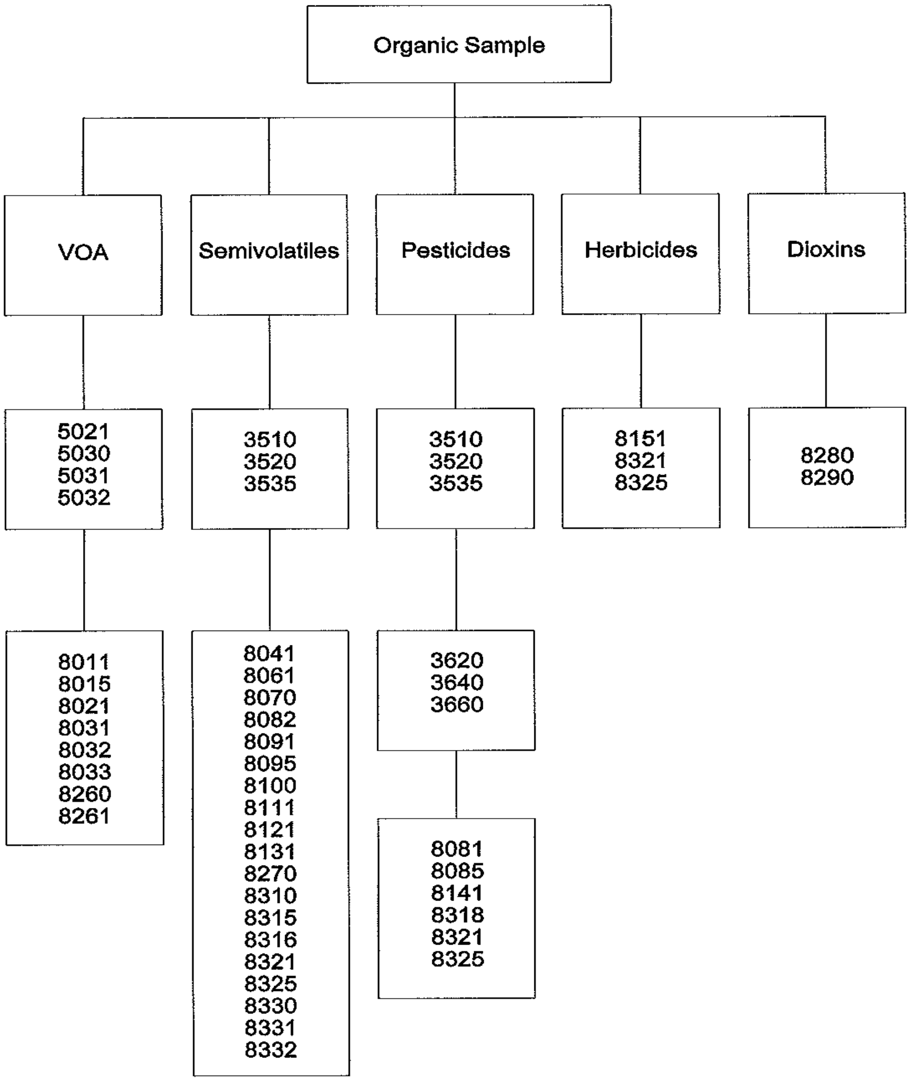
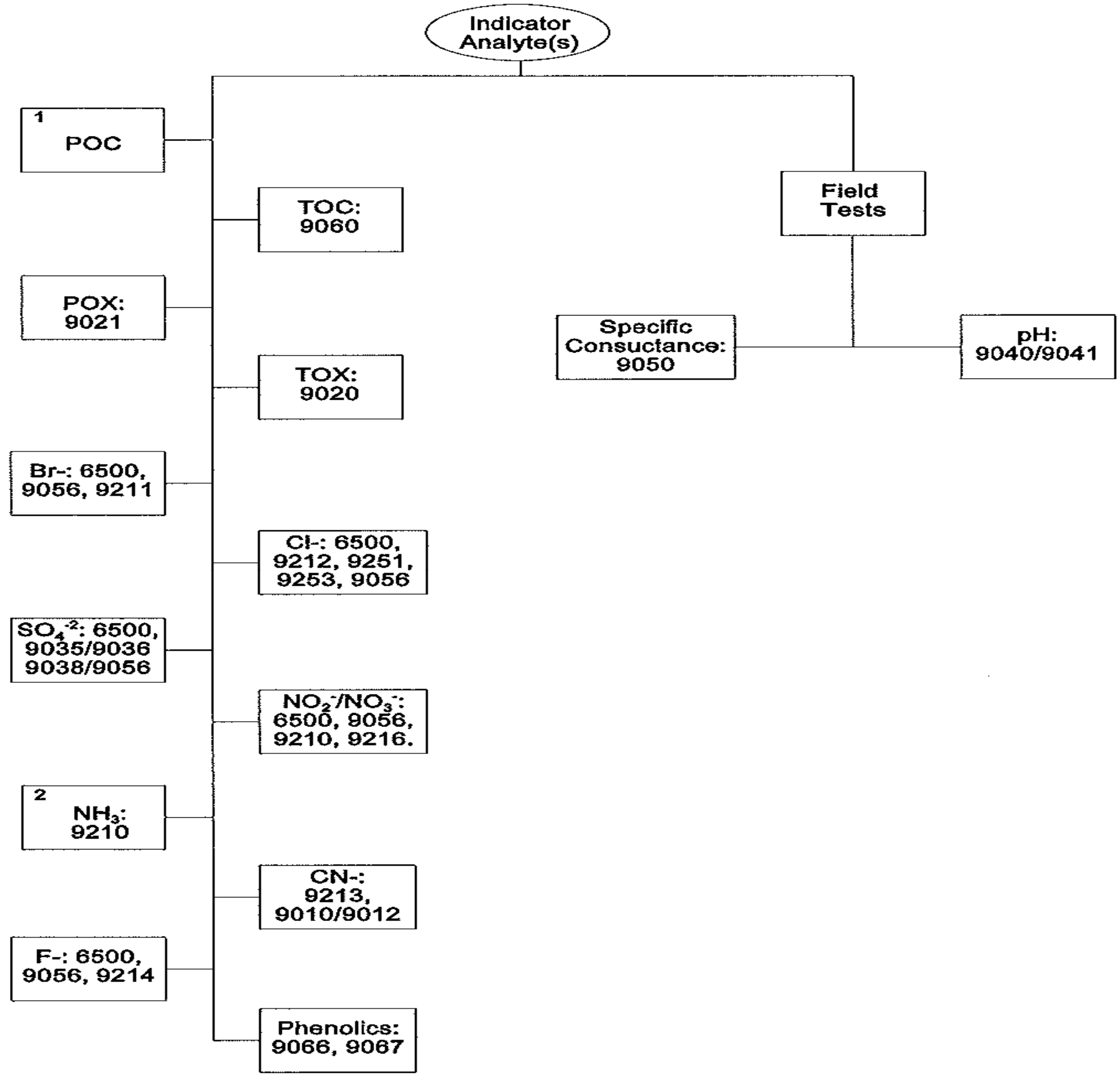


FIGURE 2-4A
GROUNDWATER ANALYSIS - ORGANIC ANALYTES



For illustrative purposes only.
See the disclaimer and Sec. 2.1 for information on the flexibility inherent in SW-846 methods.

FIGURE 2-4B
GROUNDWATER ANALYSIS - INDICATOR ANALYTES

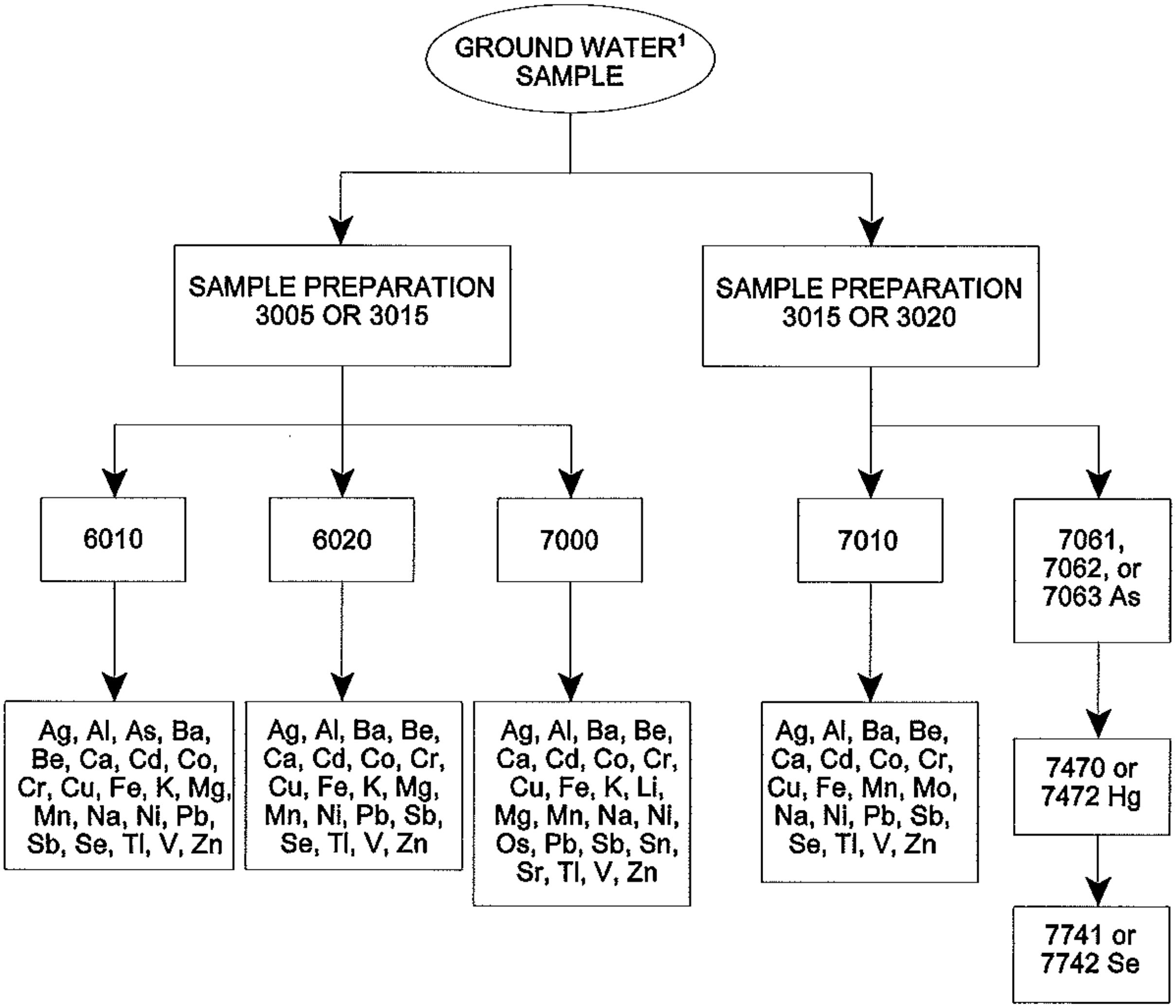


1- Barcelona 1984, (See Reference 1)
2- Riggin, 1984, (See Reference 2)

For illustrative purposes only. See the disclaimer and Sec. 2.1 regarding the flexibility inherent in SW-846 methods.

FIGURE 2-4C

GROUNDWATER ANALYSIS - INORGANIC ANALYTES



For illustrative purposes only. See the disclaimer and Sec. 2.1 regarding the flexibility inherent in SW-846 methods.

Appendix A: Summary of Updates/Changes in Chapter 2

1. Improved overall method formatting for consistency with new SW-846 methods style guidance. The entire document was reformatted in Microsoft Word.docx format from the original .WPD and .PDF files.
2. The revision number was changed to five and the published date to July 2014.
3. A Table of Contents was compiled and added to make finding information easier.
4. Minor editorial and grammatical changes (e.g., removing extra spaces between words, adding commas, etc.) were made throughout Sections 1.0 to 2.7. The disclaimer statement in Section 1.0 was numbered to keep the format consistent, as it started at Section 2.0 originally.
5. Graphics in the Figures Section were modified from Corel Drawing Objects V.10 to .jpg graphical images where needed to remove artifacts from the conversion process. The text titles of each figure was centered and formatted.
6. This appendix was added to document non-significant changes made during the editorial process.
7. Bis(2-chloroisopropyl) ether was corrected to Bis(2-chloro-1-methylethyl) ether in Tables 2-1, 2-4, 2-15, 2-22, and 2-34.
8. Revised Table 2-40A to reflect current sample preservation guidance for styrene and vinyl chloride in aqueous samples (i.e., deletion of previously recommended practice of collecting a second set of samples without acid preservatives and analyze immediately, if styrene and vinyl chloride are analytes of interest).
9. Revised Table 2-41.
10. Revised Table 2-45 to include Methods 1313 and 1316.
11. Added Table 2-46.
12. Added Figure(s) for new leaching procedure(s).
13. Revised Table 2-40B to include Mercury Speciation hold times in addition to totals.
14. All other tables were updated with the target compound list in the current published methods.

DOCUMENT

6

METHOD 1315[1]

MASS TRANSFER RATES OF CONSTITUENTS IN MONOLITHIC OR COMPACTED GRANULAR MATERIALS USING A SEMI-DYNAMIC TANK LEACHING PROCEDURE

SW-846 is not intended to be an analytical training manual. Therefore, method procedures are written based on the assumption that they will be performed by analysts who are formally trained in at least the basic principles of chemical analysis and in the use of the subject technology.

In addition, SW-846 methods, with the exception of required methods used for the analysis of method-defined parameters, are intended to be guidance methods that contain general information on how to perform an analytical procedure or technique, which a laboratory can use as a basic starting point for generating its own detailed standard operating procedure (SOP), either for its own general use or for a specific project application. Performance data included in this method are for guidance purposes only and must not be used as absolute quality control (QC) acceptance criteria for purposes of laboratory QC or accreditation.

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[1] This method has been derived from the MT001 and MT002 procedures (Ref. 12). The method is analogous to the monolithic mass transfer methods NEN 7345 (Ref. 9) developed under Dutch regulation and CEN/TS 15863 (Ref. 13) developed for the Comité Européen de Normalisation (CEN).

1.0 SCOPE AND APPLICATION

1.1 This method is designed to provide the mass transfer rates (release rates) of inorganic analytes contained in a monolithic or compacted granular material, under diffusion-controlled release conditions, as a function of leaching time. Observed diffusivity and tortuosity may be estimated through analysis of the resulting leaching test data.

1.2 This method is suitable to a wide range of solid materials which may be in monolithic form (e.g., cements, solidified wastes) or may be compacted granular materials (e.g., soils, sediments and stacked granular wastes) which behave as a monolith, in that the predominant water flow is around the material and release is controlled by diffusion to the boundary. The method is not required by federal regulations to determine whether waste passes or fails the toxicity characteristic as defined at 40 CFR 261.24.

1.3 This leaching characterization method provides intrinsic material parameters for release of inorganic species under mass transfer controlled leaching conditions. This test method is intended as a means for obtaining a series of eluents which may be used to estimate the diffusivity of constituents and physical retention parameters of the solid material under specified laboratory conditions.

1.4 This method is not applicable to characterize the release of organic analytes with the exception of general dissolved organic carbon.

1.5 This method is a characterization method and does not provide a solution considered to be representative of eluate under field conditions. This method is similar in structure and use to predecessor methods such as MT001.1 (see Ref. 12), NEN 7345 (see Ref. 9), ANSI/ANS 16.1 (see Ref. 15), and ASTM C1308 (see Ref. 11). However, this method differs from previous methods in that: 1) leaching intervals are modified to improve QC; 2) sample preparation accounts for mass transfer from compacted granular samples; and, 3) mass transfer may be interpreted by more complex release models that account for physical retention of the porous medium and chemical retention at the pore wall through geochemical speciation modeling.

1.6 The geometry of monolithic samples may be rectangular (e.g., bricks or tiles), cubes, wafers or cylinders. Samples may also have a variety of faces exposed to eluent, forming anything from 1-dimensional (1-D) through 3-dimensional (3-D) mass transfer cases. In all cases, a minimum sample size of 5 cm in the direction of mass transfer must be employed and the liquid-surface-area ratio (L/A) must be maintained at 9 ± 1 mL/cm^2.

Monolithic samples should be suspended or held in the leaching fluid such that at least 98% of the entire sample surface area is exposed to eluent and the bulk of the eluent (e.g., a minimum of 2 cm between any exposed surface and the vessel wall) is in contact with the exposed sample surface. Figure 1 provides examples of appropriate sample holders and leaching configurations for 3-D and 1-D cases.

1.7 Compacted granular materials are granular solids, screened to pass through a 2-mm sieve, compacted following a modified Proctor compaction effort (see Ref. 10). The sample geometry must be open-faced cylinders due to limitations of mechanical packing. However, the diameter and height of the sample holder may be altered to correspond appropriately with the diameter and volume of the leaching vessel. In all cases, the sample size of at least 5 cm in the direction of mass transfer must be employed and the L/A must be maintained at 9 ± 1 mL/cm^2.

The sample should be positioned at the bottom of the leaching vessel with a minimum of 5 cm of distance between the solid-liquid interface and the top of the vessel. The distance between the non-leaching faces (i.e., outside of the mold surfaces) and the leaching vessel wall should be minimized to < 0.5 cm, such that the majority of the eluent volume is on top of the sample. Figure 2 shows an example of a holder and leaching configuration for a compacted granular sample.

1.8 The solvent system used in this characterization method is reagent water. Other systems (e.g., groundwater, seawater, and simulated liquids) may be used to infer material performance under specific environmental conditions. However, interaction between the eluent and the solid matrix may result in precipitation and pore blocking, which may interfere with characterization or complicate data interpretation.

1.9 Prior to employing this method, analysts are advised to consult the base method for each type of procedure that may be employed in the overall analysis (e.g., Methods 9040, 9045 and 9050, and the determinative methods for the target analytes) for additional information on QC procedures, development of QC acceptance criteria, calculations, and general guidance. Analysts also should consult the disclaimer statement at the front of the manual and the information in Chapter Two for: 1) guidance on the intended flexibility in the choice of methods, apparatus, materials, reagents, and supplies; and, 2) the responsibilities of the analyst for demonstrating that the techniques employed are appropriate for the analytes of interest, in the matrix of interest, and at the levels of concern.

In addition, analysts and data users are advised that, except where explicitly specified in a regulation, the use of SW-846 methods is *not* mandatory in response to federal testing requirements. The information contained in this method is provided by the Environmental Protection Agency (EPA or the Agency) as guidance to be used by the analyst and the regulated community in making judgments necessary to generate results that meet the data quality objectives for the intended application.

1.10 This method is restricted to use by, or under supervision of, properly experienced and trained personnel. Each analyst must demonstrate the ability to generate acceptable results with this method.

2.0 SUMMARY OF METHOD

This method comprises leaching of continuously water-saturated monolithic or compacted granular material in an eluent-filled tank with periodic renewal of the leaching solution. The vessel and sample dimensions are chosen such that the sample is fully immersed in the leaching solution. Monolithic samples may be cylinders or parallelepipeds, while granular materials are compacted into cylindrical molds at optimum moisture content using modified Proctor compaction methods (see Ref. 10). In either case, the exposure of a regular geometric area to the eluent is recommended. Samples are contacted with reagent water at a specified L/A. The leaching solution is exchanged with fresh reagent water at nine pre-determined intervals (see NOTE below). The sample is freely drained and the mass is recorded to monitor the amount of eluent absorbed into the solid matrix at the end of each leaching interval. The eluate pH and specific conductance is measured for each time interval and analytical samples are collected and preserved accordingly based on the determinative methods to be performed. Eluate concentrations are plotted as a function of time, as a mean interval flux, and as a cumulative release as a function of time. These data are used to estimate mass transfer parameters (i.e., observed diffusivity) for each constituent of potential concern (COPC). A flowchart for performing this method is shown in Figure 3.

NOTE: The leaching schedule may be extended for additional exchanges with individual intervals of 14 days to provide more information about longer-term release.

3.0 DEFINITIONS

3.1 Constituent of potential concern (COPC) – A chemical species of interest, which may or may not be regulated, but may be characteristic of release-controlling properties of the sample geochemistry.

3.2 Release – The dissolution or partitioning of a COPC from the solid phase to the aqueous phase during laboratory testing (or under field conditions). In this method, mass release is expressed in units of mg COPC/kg dry solid material.

3.3 Liquid-to-surface area ratio (L/A) – The ratio representing the total liquid volume used in the leaching interval to the external geometric surface area of the solid material. L/A is typically expressed in units of mL of eluent/cm^2 of exposed surface area.

3.4 Observed mass diffusivity – The apparent, macroscopic rate of release due to mass transfer from a solid into a liquid as measured using a leaching test under conditions where mass transfer controls release. The observed diffusivity accounts for all physical and chemical retention factors influencing mass transfer and is typically expressed in units of cm^2/s.

3.5 Effective mass diffusivity – The intrinsic rate of mass transfer in a porous medium accounting for physical retention. The effective mass diffusivity is typically expressed in units of cm^2/s.

3.6 Physical retention factor – A mass transfer rate term that describes the retardation of diffusion due to intrinsic physical properties of a porous medium (e.g., effective porosity, tortuosity).

3.7 Chemical retention factor – A mass transfer rate term that describes the chemical processes (e.g., dissolution/precipitation, adsorption/desorption, complexation) occurring at the pore water interface with the solid mineral phases within the porous structure of the solid material.

3.8 Eluent – The solution used to contact the solid material in a leaching test. The eluent is usually free of COPCs but may contain other species used to control the test conditions of the extraction.

3.9 Eluate – The solution collected as an extract from a leaching test that contains the eluent plus constituents leached from the solid phase.

3.10 Refer to Chapter One and Chapter Three, and the manufacturer's instructions for definitions that may be relevant to this procedure.

4.0 INTERFERENCES

4.1 Solvents, reagents, glassware, and other sample processing hardware may yield artifacts and/or interferences to sample analysis. All of these materials must be demonstrated to be free from interferences under the conditions of the analysis by analyzing method blanks. Specific selection of reagents and purification of solvents by distillation in all-glass systems may be necessary. Refer to each method to be used for specific guidance on QC procedures and to Chapters Three and Four for general guidance on glassware cleaning. Also refer to Methods 9040, 9045, and 9050 and the determinative methods to be used for information regarding potential interferences.

4.2 The reaction of atmospheric gases can influence the measured concentrations of constituents in eluates. For example, reaction of carbon dioxide with eluents from highly alkaline or strongly reducing materials will result in neutralization of eluate pH and precipitation of carbonates. Leaching vessels, especially those used when testing highly alkaline materials, should be designed to be airtight in order to minimize the reaction of samples with atmospheric gases.

4.3 Use of certain solvent systems may lead to precipitation at the material surface boundary, which may reduce mass transport rates. For example, exposure of cement-based materials to seawater leads to sealing of the porous block (see Ref. 8).

5.0 SAFETY

5.1 This method does not address all safety issues associated with its use. The laboratory is responsible for maintaining a safe work environment and a current awareness file of Occupational Safety and Health Administration (OSHA) regulations regarding the safe handling of the chemicals specified in this method. A reference file of safety data sheets (SDSs) should be available to all personnel involved in these analyses.

5.2 During preparation and processing of extracts and/or eluents/eluates, some waste materials may generate heat or evolve potentially harmful gases when contacted with acids and bases. Adequate prior knowledge of the material being tested should be used to establish appropriate personal protection and workspace ventilation.

6.0 EQUIPMENT AND SUPPLIES

The mention of trade names or commercial products in this manual is for illustrative purposes only, and does not constitute an EPA endorsement or exclusive recommendation for use. The products and instrument settings cited in SW-846 methods represent those products and settings used during the method development or subsequently evaluated by the Agency. Glassware, reagents, supplies, equipment, and settings other than those listed in this manual may be employed provided that method performance appropriate for the intended application has been demonstrated and documented.

This section does not list common laboratory glassware (e.g., beakers and flasks) that might be used.

6.1 Sample holder

6.1.1 Monolithic samples

6.1.1.1 A mesh or structured holder constructed of an inert material such as high density polyethylene (HDPE) or other material resistant to high and low pH is recommended.

6.1.1.2 The holder should be designed such that at least 98% of the external surface area of the sample may be exposed to eluent.

6.1.1.3 The holder should be designed to match the geometry of the mass transfer such that the bulk of the eluent may be in contact with the sample and the exposed surfaces of the sample centered within the leaching fluid.

NOTE: In the case of 1-D mass transfer from the axial face of a cylindrical sample, the outer diameter (OD) of the holder should be matched as closely as possible to the inner diameter (ID) of the leaching vessel so that the majority of the eluent is above the sample (e.g., in contact with the exposed material surface), while allowing for easy placement and removal of the holder in the leaching vessel (see Figure 1).

6.1.2 Compacted granular samples

6.1.2.1 A cylindrical mold constructed of an inert material such as HDPE or other material resistant to high and low pH is recommended.

6.1.2.2 The holder should be capable of withstanding the compaction force required to prepare the sample (see Sec. 11.3) without breaking or distorting.

NOTE: The outer diameter of the holder for a compacted granular sample should be matched as closely as possible to the inner diameter of the leaching vessel so that the majority of the eluent is above the sample (e.g., in contact with the exposed material surface) while allowing for easy placement and removal of the holder in the leaching vessel.

6.2 Leaching vessel

6.2.1 A straight-sided container constructed of a material resistant to high and low pH is recommended. Jars or buckets composed of HDPE, polycarbonate (PC), polypropylene (PP), or polyvinyl chloride (PVC) are recommended when evaluating the mobility of inorganic species.

6.2.2 The leaching vessel should have an airtight seal that can sustain long periods of standing without gas exchange with the atmosphere.

6.2.3 The container must be of sufficient volume to accommodate both the solid sample and an eluent volume based on an L/A of 9 ± 1 mL /cm^2 sample surface area. Ideally, the vessel should be sized such that the headspace is minimized within the tolerance of the L/A.

6.3 Leaching setup

Example photos of three possible leaching equipment arrangements for monolithic and compacted granular samples are shown in Figures 1 and 2, respectively. The equipment used in the each of these cases is described below.

6.3.1 Figure 1a shows a monolithic sample 3-D configuration with the following accessories:

- Sample holder – PP sink washers, 43-mm OD, 37-mm ID, 6-mm high, with four holes drilled at the quadrants to accept 2-mm OD nylon string knotted at the top
- Sample stand – PVC pipe, 47-mm OD, 51-mm high, cut to have four legs approximately 8-mm wide and 30-mm high
- Leaching Vessel – PP bucket, 140-mm ID at top, 120-mm ID at bottom, 200-mm high (Berry Plastics #T51386CP3, VWR Scientific, or equivalent)

6.3.2 Figure 1b shows a monolithic sample 1-D configuration with the following accessories:

- Sample holder – Polyethylene (PE) mold, 54-mm OD, 100-mm high (MA Industries, Peach Tree City, GA, or equivalent), with the test sample cured in mold and cut to 51-mm high
- Leaching vessel – 250-mL PC jar, 60-mm ID, 100-mm high (Nalgene #2116-0250, Fisher Scientific, or equivalent)

6.3.3 Figure 2 shows a compacted granular sample 1-D Configuration with the following accessories:

- Sample holder – PE mold, 100-mm OD, 200-mm high, (MA Industries, Peach Tree City, GA, or equivalent) cut to 63-mm high with three tabs drilled for 0.7-mm fishing line knotted at the top
- Leaching vessel – 1000-mL PC jar, 110-mm ID at top, 130-mm high (Nalgene #2116-1000, Fisher Scientific, or equivalent)
- Glass beads, borosilicate – 2-mm diameter

6.4 Filtration apparatus – Pressure or vacuum filtration apparatus composed of appropriate materials to maximize the collection of extracts and minimize the loss of COPCs (Nalgene #300-4000 or equivalent)

6.5 Filtration membranes – Composed of hydrophilic polypropylene or equivalent material with an effective pore size of 0.45 µm (e.g., Andwin Scientific GH Polypro 28143-288 or equivalent)

6.6 pH meter – Laboratory model with the capability for temperature compensation (e.g., Accumet 20, Fisher Scientific or equivalent) and a minimum resolution of 0.1 pH units

6.7 pH combination electrode – Composed of chemically resistant materials

6.8 Conductivity meter – Laboratory model (e.g., Accumet 20, Fisher Scientific or equivalent), with a minimum resolution of 5% of the measured value

6.9 Conductivity electrodes – Composed of chemically resistant materials

6.10 Proctor compactor (for compacted granular samples only) – Equipped with a slide hammer capable of dropping a 4.5-kg weight over a 0.46-m interval (see Ref. 10 for further details)

7.0 REAGENTS AND STANDARDS

7.1 Reagent-grade chemicals, at a minimum, should be used in all tests. Unless otherwise indicated, all reagents should conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society (ACS), where such specifications are available. Other grades may be used, provided the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination. Inorganic reagents and extracts should be stored in plastic to prevent interaction of constituents from glass containers.

7.2 Reagent water – Reagent water must be interference-free. All references to water in this method refer to reagent water unless otherwise specified.

7.3 Other reagents may be used in place of reagent water on a case-specific basis.

8.0 SAMPLE COLLECTION, PRESERVATION, AND STORAGE

8.1 See Chapter Three, "Inorganic Analytes," and Chapter 4, "Organic Analytes," for sample collection and preservation instructions.

8.2 Both plastic and glass containers are suitable for the collection of samples. All sample containers must be prewashed with a metal-free detergent and triple-rinsed with nitric acid and reagent water, depending on the history of the container. For further information, see Chapter Three.

9.0 QUALITY CONTROL

9.1 Refer to Chapter One for guidance on quality assurance (QA) and quality control (QC) protocols. When inconsistencies exist between QC guidelines, method-specific QC criteria take precedence over both technique-specific criteria and Chapter One criteria, and technique-specific QC criteria take precedence over Chapter One criteria. Any effort involving the collection of analytical data should include development of a structured and systematic planning document, such as a quality assurance project plan (QAPP) or a sampling and analysis plan (SAP), which translates project objectives and specifications into directions for those who will implement the project and assess the results.

Each laboratory should maintain a formal QA program. The laboratory should also maintain records to document the quality of the data generated. Development of in-house QC limits for each method is encouraged. Use of instrument-specific QC limits is encouraged, provided such limits will generate data appropriate for use in the intended application. All data sheets and QC data should be maintained for reference or inspection.

9.2 In order to demonstrate the purity of reagents and sample contact surfaces, method blanks should be tested for each leaching interval. Refer to Chapter One for specific QC procedures.

9.3 The analysis of extracts should follow appropriate QC procedures, as specified in the determinative methods for the COPCs. Refer to Chapter One for specific QC procedures.

9.4 Initial demonstration of proficiency (IDP)

Leachate methods are not amenable to typical IDPs when reference materials with known values are not available. However, prior to using this method an analyst should have documented proficiency in the skills required for successful implementation of the method. For example, skill should be demonstrated in the use of an analytical balance, the determination of pH using Methods 9040 and 9045 and the determination of conductance using Method 9050.

10.0 CALIBRATION AND STANDARDIZATION

10.1 The balance should be calibrated and certified, at a minimum, annually or in accordance with laboratory policy.

10.2 Prior to measurement of eluate pH, the pH meter should be calibrated using a minimum of two standards that bracket the range of pH measurements. Refer to Methods 9040 and 9045 for additional guidance.

10.3 Prior to measurement of eluate conductivity, the meter should be calibrated using at least one standard at a value greater than the range of conductivity measurements. Refer to Method 9050 for additional guidance.

11.0 PROCEDURE

A flowchart of this method is presented in Figure 3. Microsoft Excel® data templates are available to aid in collecting and archiving of laboratory and analytical data.[2]

11.1 Preparatory Procedures – Determination of solids and moisture content

The moisture and solids content of the sample material are used to relate leaching results to dry-material masses. When preparing compacted granular samples for testing, the moisture content or solid content is used to determine the optimum moisture content following the modified Proctor test. This method calculates moisture content on the basis of the "wet" or "as-tested" sample.

WARNING: The drying oven should be contained in a hood or otherwise properly ventilated. Significant laboratory contamination or inhalation hazards may result when drying heavily contaminated samples. Consult the laboratory safety officer for proper handling procedures prior to drying samples that may contain volatile, hazardous, flammable, or explosive materials.

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[2] These Excel® templates form the basis for uploading method data into the data management program, LeachXS Lite™. Both the data templates and LeachXS Lite™ are available at http://vanderbilt.edu/leaching.

11.1.1 Place 5 - 10 g of solid sample material into a tared dish or crucible. Dry the sample to a constant mass at 105 ± 2 °C. Check for constant mass by returning the dish to the drying oven for 24 hours, cooling to room temperature in a desiccator and re-weighing. The two mass readings should agree within the larger of 0.2% or 0.02 g.

NOTE: The oven-dried sample is not used for the extraction and should be properly disposed of once the dry mass is determined.

11.1.2 Calculate and report the solids content as follows:

$$SC = \frac{M_{dry}}{M_{test}}$$

Where: SC = solids content of "as-tested" material (g-dry/g)
M_{dry} = mass of dry material specified in the method (g-dry)
M_{test} = mass of "as-tested" solid equivalent to the dry-material mass (g)

11.1.3 Calculate and report the moisture content (wet basis) as follows:

$$MC_{wet} = \frac{M_{test} - M_{dry}}{M_{test}}$$

Where: MC_{wet} = moisture content on a wet basis (g_{H_2O}/g)
M_{dry} = mass of dry material specified in the method (g-dry)
M_{test} = mass of "as-tested" solid equivalent to the dry-material mass (g)

11.2 Preparation of monolithic samples

11.2.1 If the material to be tested is granular, disregard this section and proceed to Sec. 11.3.

11.2.2 A representative sample of monolithic material should be obtained by molding material components in place (e.g., cementitious media) or by coring or cutting a sample from a larger existing specimen.

11.2.3 The geometry of monolithic samples may be rectangular (e.g., bricks or tiles), cubes, wafers, or cylinders. Samples may also have a variety of faces exposed to eluent forming 1-, 2-, or 3-D mass transfer cases. Examples of monolithic sample leaching setups are shown in Figure 1.

11.2.4 A minimum sample size of 5 cm in the direction of mass transfer must be employed and the L/A must be maintained at 9 ± 1 mL/cm^2.

NOTE: Since the sample holder and leaching vessel must correspond to the specifications in Sec. 6.1, it is often easier to modify the sample size and geometry rather than the holder and vessel dimensions.

11.2.5 Proceed to Sec. 11.4.

11.3 Preparation of compacted granular samples

Compacted granular materials, in most cases, must be open-faced cylinders due to the limitations of mechanical packing. However, the diameter and height of the sample holder may be altered to work appropriately with the diameter and volume of the leaching vessel. In all cases, a minimum sample size of 5 cm in the direction of mass transfer must be employed and the L/A must be maintained at 9 ± 1 mL/cm^2.

Granular samples are compacted into the sample holder using a variation on the modified Proctor compaction (see Ref. 10) to include the use of 6-cm high-test molds. Shorter or taller molds (or packing depths) may be used as long as the compaction effort of 56,000 $\text{ft-lb}_f/\text{ft}^3$ is achievable. The number of packing layers should be maintained at the five layers specified in Ref. 10. However, the number of blows per layer in a 4-in diameter mold may be changed according to the follow formula:

$$\frac{56{,}000\,\text{ft - lb}_f}{\text{ft}^3}\Bigg|\frac{\text{blow}}{1.5\,\text{ft}\times 10\,\text{lb}_f}\Bigg|\frac{\pi\left(0.\overline{3}\big/2\ \text{ft}\right)^2\times h\,\text{ft}}{5\,\text{layer}}=\frac{65.2\times h\,\text{blow}}{\text{layer}}$$

Where: *h* is the measured height of the sample mold (ft).

Thus, for the mold height of 4.584 in (0.382 ft) specified in the ASTM procedure, 25 blows per each of 5 layers are required. When a 6-cm (0.196 ft) mold height is used (as suggested in this method), 13 blows per each of 5 layers are required to obtain the same compaction effort.

The granular sample should be compacted at a moisture content corresponding to 90% of the modified Proctor optimum packing density in order to provide a uniform approach to obtaining a sample density that approximates field conditions. Optimum moisture content refers to the amount of moisture or fractional mass of water (g_{H_2O}/g material) in the granular sample that is present at the optimum packing density (g-dry material/cm^3). Optimum packing density is defined in Ref. 10. The optimum moisture content of the test material is determined from a pre-test that measures the packing density of granular materials compacted at different levels of moisture content.

11.3.1 Pre-test to determine optimum moisture content

The pre-test is conducted as a series of five batch-wise packing trials with consecutive increases in moisture content until the maximum packing density has been surpassed. The optimum moisture content is determined as the maximum of a third-order polynomial fit through the graph of dry-packing density as a function of moisture content (wet basis).

11.3.1.1 Place 1500 g of "as received" material into a pail or bowl and mix well by hand to homogenize. As an alternative to hand mixing, a mechanical paddle mixer may be used.

<u>NOTE</u>: The pre-test may be conducted from a bulk supply of solid material (e.g., 10 kg total for five batches) as long as the starting mass for each trial is recorded and incremental water additions are used.

11.3.1.2 Mix a known amount of tap water with the bulk material in the pail or bowl until homogenized based on visual inspection. For the first point in the pre-test, no water needs to be added.

NOTE: The amount of water added should be enough to increase the moisture content in approximately 3 - 5% increments. Smaller additions may be needed in order to provide finer resolution of the packing density as a function of the moisture content curve.

11.3.1.3 Calculate the new moisture content (wet basis) for the trial as follows:

$$MC^{i}_{(wet)} = \frac{M_{test} \times MC_{wet} + W_{added}}{M_{test} + W_{added}}$$

Where: $MC^{i}_{(wet)}$ = moisture content on a wet basis of the pre-test trial (g_{H_2O}/g)
M_{test} = mass of "as-tested" solid equivalent to the dry-material mass (g)
$MC_{(wet)}$ = moisture content on a wet basis of the "as-tested" material (g_{H_2O}/g)
W_{added} = mass of water added to the "as-tested" material (g_{H_2O}/g)

11.3.1.4 Compact approximately 1000 g of material into a tared 10-cm diameter mold into three consecutive layers of material. The compacted mass should have a level, flat surface as a top face.

11.3.1.5 Measure and record the height, diameter, and mass of the resulting compacted material.

11.3.1.6 Calculate and record the packing density (dry basis) as follows:

$$\rho_{pack} = \frac{m \times SC}{\pi \times h}\left(\frac{2}{d}\right)^2$$

Where: ρ_{pack} = packing density (dry basis) (g-dry/cm^3)
m = mass of the compacted sample (g)
SC = solids content of "as-tested" granular material (g-dry/g)
d = measured diameter of the compacted sample (cm)
h = measured height of the compacted sample (cm)

11.3.1.7 Repeat Sec. 11.3.1.1 - 11.3.1.6 for four subsequent trials until the value of the calculated packing density decreases.

11.3.1.8 Plot the packing density as a function of moisture content. Figure 4 shows an example of a packing density curve.

11.3.1.9 Determine the optimum moisture content at the maximum of the packing density curve. This value may be read directly from the graph or determined by the maximum of a third-order polynomial fit through the five pre-test data points (see the Microsoft Excel® spreadsheet template available at http://www.vanderbilt.edu/leaching/downloads/test-methods/).

11.3.2 Compacted granular test sample preparation

11.3.2.1 Using the optimum moisture content determined in Sec. 11.3.1.9, calculate the amount of "as-received" material that is required to pack the sample holder to within 3 mm of the rim of the holder.

$$M_{test} = \frac{\rho_{opt} \times \pi \times (h - 0.3)}{SC} \left(\frac{d}{2} \right)^2$$

Where: M_{test} = mass of "as tested" solid equivalent to the dry-material mass (g)
ρ_{opt} = optimal packing density (dry basis) (g-dry/cm^3) – determined in Sec. 11.3.1.9
h = measured height of the sample mold (cm)
SC = solids content of "as-tested" granular material (g-dry/g)
d = measured diameter of the sample mold (cm)

11.3.2.2 Adjust the moisture content of the "as-received" material to the optimum moisture content using reagent water and mix until homogenized.

11.3.2.3 Pack the sample material into the sample holder using the modified Proctor compaction as described in Ref. 10.

11.3.2.4 Place a monolayer of borosilicate glass beads (Sec. 6.3.3) on the exposed sample surface to minimize scouring and mass loss during testing.

11.3.2.5 Begin the leach test procedure promptly or cover the sample with plastic wrap to minimize moisture loss to the atmosphere.

11.4 Leaching procedure

This protocol is a semi-dynamic, tank-leaching procedure (see schematic in Figure 5) where the sample is exposed to eluate for a series of leaching intervals interspersed with eluent exchanges. The chemical composition of each eluate is determined and mass transfer from the bulk solid is determined as a function of cumulative leaching time. The schedule of leaching intervals for this method is shown in Table 1.

11.4.1 Pre-test measurements – For the surface area calculation, measure and record the dimensions of the test specimen. This should include the diameter and height for a cylinder; length, width, and depth for a parallelepiped; or diameter of exposed surface for a compacted granular sample.

11.4.2 Measure and record the mass of the specimen. This value should be monitored for each eluent exchange.

11.4.3 If a holder is used, place the specimen in the monolith holder.

11.4.4 Measure and record the mass of the specimen and holder, if applicable.

11.4.5 The recommended temperature for conducting this method is room temperature (20 ± 2 °C). When conducted at temperature readings or variations other than those recommended, record the ambient temperature at each eluent renewal.

11.5 Eluent exchange

11.5.1 Fill a clean leaching vessel with the required volume of reagent water based on an L/A of 9 ± 1 mL/cm^2. Record the amount of eluent used.

11.5.2 Carefully place the specimen or the specimen and holder in the leaching vessel (Figure 6a) so that the sample is centered in the eluent (see Figure 6b). Submersion should be gentle enough so that the physical integrity of the monolith is maintained and scouring of the solid is minimized.

11.5.3 Cover the leaching vessel with the airtight lid and place in a safe location until the end of the leaching interval. Table 1 shows the schedule of leaching intervals and cumulative release times for this method.

NOTE: Eluates of alkaline materials may be susceptible to neutralization through reaction with carbon dioxide. Precautions (e.g., ensuring airtight vessels or purging headspace) should be taken to minimize the effect of carbonation on eluates that may sit stationary for more than one week.

11.5.4 Prior to the end of the leaching interval, repeat Sec. 11.5.1 in order to prepare a vessel for the next leaching interval.

11.5.5 At the end of the leaching interval (see Table 1), carefully remove the specimen or the specimen and holder from the vessel (Figure 6c). Drain the liquid from the surface of the specimen into the eluate for approximately 20 sec.

11.5.6 Measure and record the mass of the specimen or the mass of the specimen and holder (Figure 6d).

NOTE: The change in sample mass between intervals is an indication of the potential absorption of eluent by the matrix (mass gain) or erosion of the matrix (mass loss). In the case where a holder is used, moisture may condense on the holder during the leaching interval and sample absorption may not be evident.

NOTE: Mass gain may also be indicative of carbonate precipitation if the vessel is not tightly sealed and carbon dioxide is absorbed from the atmosphere.

11.5.7 Place the specimen or the specimen and holder into the clean leaching vessel filled with new eluent as prepared in Sec. 11.5.4.

11.5.8 Cover the new leaching vessel with the airtight lid and place in a safe location until the end of the leaching interval.

11.6 Eluate processing

11.6.1 Measure and record the pH, specific conductivity, and oxidation reduction potential (ORP) of the eluate of the decanted eluate from the previous leaching interval (see Methods 9040, 9045, and 9050).

NOTE: Measurement of pH, conductivity, and ORP should be taken within 15 minutes of eluent exchange (Sec. 11.5) to avoid neutralization of the solution due to exposure to carbon dioxide, especially when alkaline materials are tested.

NOTE: The measurement of ORP is optional, but strongly recommended, especially when testing materials where oxidation is likely to change the chemistry of COPCs.

11.6.2 Filter the remaining eluate through a 0.45-µm membrane (Sec. 6.5).

11.6.3 Immediately preserve and store the volume(s) of eluate required for chemical analysis. Preserve all analytical samples in a manner that is consistent with the determinative chemical analyses to be performed.

11.6.4 Collect all subsequent eluate by repeating the eluent exchange and eluate processing procedures in Secs. 11.5 and 11.6.

12.0 DATA ANALYSIS AND CALCULATIONS

12.1 Data reporting

12.1.1 Figure 7 shows an example of a data sheet which may be used to report the concentration results of this method. At a minimum, the basic test report should include the following:

a) Name of the laboratory
b) Laboratory technical contact information
c) Date and time at the start of the test
d) Name or code of the solid material
e) Material description (including monolithic or compacted granular)
f) Moisture content of material used (g_{H_2O}/g)
g) Dimensions (cm) and geometry of sample used
h) Mass of solid material used (g)
i) Mass of sample and holder at start of test (g)
j) Eluate type (e.g., reagent water)
k) Eluate-specific information (see Sec. 12.1.2 below)

12.1.2 The minimum set of data that should be reported for each eluate includes:

a) Eluate sample ID
b) Target eluent exchange date and time
c) Actual eluent exchange date and time
d) Volume of eluent used (mL)
e) Mass of sample and holder (g)
f) Measured eluate pH

g) Measured eluate conductivity (mS/cm)
h) Measured ORP (mV) (optional)
i) Concentration of all COPCs
j) Analytical QC qualifiers as appropriate

12.2 Data presentation

12.2.1 Interval concentrations

12.2.1.1 At the conclusion of the schedule of leaching intervals (see Table 1), the concentration of COPCs in each eluate may be plotted as a function of cumulative leaching time. An example of this is shown in Figure 8 for mass transport from a monolithic field sample of fixated scrubber sludge and lime.

12.2.1.2 If data is available from Method 1313, interval concentrations and Method 1313 data may be plotted on the same graph as a function of eluate pH. This QC step is conducted in order to determine whether the concentration of COPCs approached equilibrium in any leaching interval (i.e., the driving force for mass transport from the matrix may not be constant, which is a common assumption of dynamic-tank leach testing). Figure 9 shows this type of graph for the release from a field sample of fixated scrubber sludge and lime.

12.2.2 Interval mass release

At the conclusion of the schedule of leaching intervals (see Table 1), the interval mass released can be calculated for each leaching interval as follows:

$$M_{t_i} = \frac{C_i \times V_i}{A}$$

Where: M_{t_i} = mass released during the current leaching interval, i (mg/m^2)
C_i = constituent concentration in the eluate for interval i (mg/L)
V_i = eluate volume in interval i (L)
A = specimen external geometric surface area exposed to the eluent (m^2)

12.2.3 Mean interval flux

The flux of a COPC in an interval may be plotted as a function of the generalized mean of the square root of cumulative leaching time ($\sqrt{t}$). An example of a flux graph is show in Figure 10 for the release from a field sample of fixated scrubber sludge with lime. This graph may be used to interpret the mechanism of release (see Ref. 5 for further details).

12.2.3.1 The flux across the exposed surface of the sample can be calculated by dividing the interval mass release by the interval duration as follows:

$$F_i = \frac{M_i}{t_i - t_{i-1}}$$

Where: F_i = flux for interval, i ($mg/m^2 \cdot s$)
M_i = mass released during the current leaching interval, i (mg/m^2)
t_i = cumulative time at the end of the current leaching interval, i (s)
t_{i-1} = cumulative time at the end of the previous leaching interval, i-1 (s)

12.2.3.2 The time used to plot each interval mass is the generalized mean of the square root of the cumulative leaching time using the cumulative time at the end of the i^{th} interval, t_i, and the cumulative time at the end of the previous interval, t_{i-1}.

$$\overline{t_i} = \left(\frac{\sqrt{t_i} + \sqrt{t_{i-1}}}{2} \right)^2$$

Where: $\overline{t_i}$ = generalized mean leaching time for the current interval, i (s)

t_i = cumulative time at the end of the current leaching interval, i (s)
t_{i-1} = cumulative time at the end of the previous leaching interval, i-1 (s)

NOTE: If the concentrations of a COPC in the eluates approach that shown in Method 1313 for liquid-solid equilibrium, the flux curve will show the pattern in Figure 10 with intervals of the same duration having the same flux value. When the eluate concentration approaches saturation, the driving force for mass transfer approaches zero, interval flux is limited, and intervals with like durations will display similar flux limitations.

12.2.4 Cumulative release

12.2.4.1 The interval release calculated in 12.2.2 can be summed to provide the cumulative mass release as a function of leaching time. Figure 11 shows the cumulative release curves for a field sample of fixated scrubber sludge with lime.

12.2.4.2 Interpretation of the cumulative release of constituents is illustrated using the analytical solution for simple radial diffusion from a cylinder into an infinite bath presented by Crank (see Ref. 8).

$$M_t = 2\rho C_o \left(\frac{D^{obs}\ t}{\pi} \right)^{1/2}$$

Where: M_t = cumulative mass released during leaching interval i (mg/m^2)
ρ = density of the "as-tested" sample (kg/m^3)
C_o = concentration of available COPC in the solid matrix (mg/kg)
D^{obs} = observed diffusivity (m^2/s)
t = leaching time (s)

When transformed to a log-log scale, the analytical solution presented by Crank becomes linear with the square root of time.

$$\log\left[M_t\right] = \log\left[2\rho C_o\left(\frac{D^{obs}}{\pi}\right)^{1/2}\right] + \frac{1}{2}t$$

Thus, under the assumptions of the analytical solution presented by Crank, the mass release should be proportional to the square root of time. A line showing the square root of time is plotted in Figure 11 along with the data. Since flux is the derivative of release, a similar treatment of flux as a function of leaching time using the simple diffusion model would be proportional to the negative square root of time as shown in Figure 10.

Models other than the simple diffusion model presented by Crank may also be used to interpret mass release. For example, the Shrinking Unreacted Core Model (see Ref. 2) and the Coupled Dissolution-Diffusion Model (see Ref. 7) incorporate chemical release parameters (e.g., as derived from Method 1313 data) into the model to better estimate release mechanisms and predictions (see Ref. 5 for further details).

12.2.5 Observed diffusivity

An observed diffusivity for each COPC can be determined using the logarithm of the cumulative release plotted versus the logarithm of time. In the case of a diffusion-controlled mechanism, this plot is expected to be a straight line with a slope of 0.5. An observed diffusivity can then be determined for each leaching interval where the slope is 0.50 ± 0.15 (see Ref. 1 and Ref. 14) by the following:

$$D_i^{obs} = \pi\left[\frac{M_{t_i}}{2\rho C_o\left(\sqrt{t_i} - \sqrt{t_{i-1}}\right)}\right]^2$$

Where: D_i^{obs} = observed diffusivity of a COPC for leaching interval i (m^2/s)

M_{t_i} = mass released during leaching interval i (mg/m^2)

t_i = cumulative contact time at the end of the current leaching interval, i (s)
t_{i-1} = cumulative contact time at the end of the previous leaching interval, i−1 (s)
ρ = sample density (dry basis) (kg-dry/m^3)
C_0 = initial leachable content (i.e., available release potential) (mg/kg)

The mean observed diffusivity for each COPC is then determined by taking the average of the interval observed diffusivities. It should be reported with the computed uncertainty (i.e., standard deviation).

NOTE: Since the analysis presented above assumes a diffusion process, only those interval mass transfer coefficients corresponding to leaching intervals with slopes of 0.50 ± 0.15 are included in the overall average mass-transfer coefficient.

12.3 Data representation by constituent

A concise representation of all relevant data for a single constituent may be presented as shown in Figure 12 for arsenic from a field core of fixated scrubber sludge with lime (FSSL) material. The data shows eluate pH generation as a function of leaching time (Figure 12a), comparison between eluate concentrations and Method 1313 data as a function of eluate pH (Figure 12b), constituent flux as a function of generalized mean cumulative leaching time (Figure 12c), and constituent release as a function of cumulative leaching time (Figure 12d).

12.4 Interpolation/extrapolation to target time values

The collected time dependence data may be interpolated or extrapolated to the nearest target cumulative time (Σt) value for purposes of comparing different data sets (e.g., test replicates of the same or different materials). The most transparent and straightforward method is linear interpolation/extrapolation of data after $\log_{10}$ transformation.

12.4.1 Log_{10} transformation

Collected concentration values are transformed by taking the $\log_{10}$ of the measured concentration at each test position, i:

$$C_i = \log_{10}(c_i)$$

Where: C_i = $\log_{10}$-transformed concentration at test position i ($\log_{10}$[mg/L])
c_i = the concentration measured at test position i (mg/L)

12.4.2 Linear interpolation/extrapolation

Given a set of coordinate data sorted by increasing order according to Σt value (e.g., $\Sigma t_1 < \Sigma t_2 < \cdots < \Sigma t_n$), an interpolated/extrapolated $\log_{10}$-transformed concentration at a known Σt target is calculated as:

$$C_T = a_T + b_T \sum t_T$$

Where: C_T = the concentration at target Σt value, Σt_T ($\log_{10}$[s])
a_T and b_T are coefficients of the linear interpolation/extrapolation equation
Σt_T = a target cumulative time value

Depending on the values of observed Σt values relative to target Σt values, the calculations of the coefficients a_T and b_T in the equation may differ according to the following algorithm:

- If $\Sigma t_T < \Sigma t_1$, then $b_T = (C_2 - C_1) / (\Sigma t_2 - \Sigma t_1)$ and $a_T = C_2 - b_T \cdot \Sigma t_2$ (extrapolation from the two points with closest Σt values)
- If $\Sigma t_T \geq \Sigma t_n$, then $b_T = (C_n - C_{n-1}) / (\Sigma t_n - \Sigma t_{n-1})$ and $a_T = C_n - b_T \cdot \Sigma t_n$ (extrapolation from the two points with closest Σt values)
- If $\Sigma t_{j-1} \leq \Sigma t_T < \Sigma t_j$, then $b_T = (C_j - C_{j-1}) / (\Sigma t_j - \Sigma t_{j-1})$ and $a_T = y_j - b_T \cdot \Sigma t_j$ (interpolation from the two closest points surrounding Σt_T)

NOTE: Interpolation or extrapolation of data should only be conducted within a distance of ±20% of the target Σt value. Since the allowable L/S tolerance about a target L/S value is variable (see Table 1), interpolation/extrapolation should not create data at a target Σt value where collected data is missing.

13.0 METHOD PERFORMANCE

13.1 Performance data and related information are provided in SW-846 methods only as examples and guidance. The data do not represent required performance criteria for users of the methods. Instead, performance criteria should be developed on a project-specific basis, and the laboratory should establish in-house QC performance criteria for the application of this method. Performance data must not be used as absolute QC acceptance criteria for laboratory QC or accreditation.

13.2 Interlaboratory validation of this method was conducted using a solidified waste analog (material code SWA) and a contaminated smelter site soil (material code CFS). Repeatability and reproducibility was determined for mean interval flux excluding the first wash-off interval (see Table 2) and for cumulative mass released after 63 days of leaching (see Table 3). More details on the interlaboratory validation may be found in Ref. 4.

13.3 Ref. 5 and Ref. 12 may provide additional guidance and insight on the use, performance, and application of this method.

14.0 POLLUTION PREVENTION

14.1 Pollution prevention encompasses any technique that reduces or eliminates the quantity and/or toxicity of waste at the point of generation. Numerous opportunities for pollution prevention exist in laboratory operations. The EPA has established a preferred hierarchy of environmental management techniques that places pollution prevention as the management option of first choice. Whenever feasible, laboratory personnel should use pollution prevention techniques to address their waste generation. When wastes cannot be feasibly reduced at the source, the Agency recommends recycling as the next best option.

14.2 For information about pollution prevention that may be applicable to laboratories and research institutions consult *Less is Better: Laboratory Chemical Management for Waste Reduction*, a free publication available from the ACS, Committee on Chemical Safety, https://www.acs.org/content/dam/acsorg/about/governance/committees/chemicalsafety/publications/less-is-better.pdf.

15.0 WASTE MANAGEMENT

The EPA requires that laboratory waste management practices be conducted consistent with all applicable rules and regulations. Laboratories are urged to protect air, water, and land by minimizing and controlling all releases from hoods and bench operations, complying with the letter and spirit of any sewer discharge permits and regulations, and by complying with all solid and hazardous waste regulations, particularly the hazardous waste identification rules and land disposal restrictions. For further information on waste management, consult *The Waste Management Manual for Laboratory Personnel* available at: http://www.labsafetyinstitute.org/FreeDocs/WasteMgmt.pdf.

16.0 REFERENCES

1. International Ash Working Group (IAWG), *Municipal Solid Waste Incinerator Residues*, Amsterdam, the Netherlands, 1997.

2. Crank, *Mathematics of Diffusion*, Oxford University Press,, London, 1986.

3. A.C. Garrabrants, and D.S. Kosson, "Leaching Processes and Evaluation Tests for Inorganic Constituents Release from Cement-Based Matrices," in *Solidification/Stabilization of Hazardous, Radioactive and Mixed Wastes*, R. Spence, and C. Shi (eds), CRC Press, 2005.

4. A.C. Garrabrants, D.S. Kosson, R. DeLapp, P. Kariher, P.F.A.B. Seignette, H.A. van der Sloot, L. Stefanski, and M. Baldwin, "Interlaboratory Validation of the Leaching Environmental Assessment (LEAF) Method 1314 and Method 1315," EPA 600/R-12/624, *U.S. Environmental Protection Agency*, Washington, DC, 2012.

5. A.C. Garrabrants, D.S. Kosson, H.A. van der Sloot, F. Sanchez, and O. Hjelmar, "Background Information for the Leaching Environmental Assessment Framework (LEAF) Test Methods," EPA/600/R-10-170, *U.S. Environmental Protection Agency*, Washington, DC, 2010.

6. J. de Groot, and H. A. van der Sloot, "Determination of Leaching Characteristics of Waste Materials Leading to Environmental Product Certification," in *Solidification and Stabilization of Hazardous, Radioactive, and Mixed Wastes*, 2nd Volume, ASTM STP 1123, T. M. Gilliam, and C. C. Wiles (eds), American Society for Testing and Materials, Philadelphia, PA, 1992.

7. Hinsenveld, and P.L. Bishop, "Use of the shrinking core/exposure model to describe the leachability from cement stabilized wastes," in *Stabilization and Solidification of Hazardous, Radioactive, and Mixed Wastes,*, 3rd Volume, ASTM STP 1240, T. M. Gilliam, and C. C. Wiles (eds), American Society for Testing and Materials,, Philadelphia, PA, 1996.

8. D.E. Hockley, and H.A. van der Sloot, "Long-term Processes in a Stabilized Coal Waste Block Exposed to Seawater," *Environmental Science and Technology*, 25(8) 1408-1414, 1991.

9. NEN 7345, "Leaching Characteristics of Solid Earth and Stony Materials - Leaching Tests - Determination of the Leaching of Inorganic Constituents from Molded and Monolithic Materials with the Diffusion Test," *Dutch Standardization Institute*, Delft, The Netherlands, 1995.

10. ASTM D1557-07, "Standard Method for Laboratory Compaction Characteristics of Soil Using Modified Effort (56,000 ft-lbf/ft3 (2,700 kN-m/m3))," *ASTM International*, West Conshohocken, PA,

11. ASTM D1308-95, "Standard Method for Accelerated Leach Test for Diffusive Releases from Solidified Waste and a Computer Program to Model Diffusive, Fractional Leaching from Cylindrical Waste Forms," *ASTM International*, West Conshohocken, PA, 2001.

12. D.S. Kosson, H.A. van der Sloot, F. Sanchez, and A.C. Garrabrants, "An Integrated Framework for Evaluating Leaching in Waste Management and Utilization of Secondary Materials," *Environmental Engineering Science*, 19(3) 159-204, 2002.

13. CEN/TS 15863, "Characterization of waste – Leaching Behaviour Tests – Dynamic Monolithic Leaching Test with Periodic Leachant Renewal," *Comité Européen de Normalisation*, Brussels, Belgium, 2009.

14. Sanchez, "Étude de la lixiviation de milieux poreux contenant des espèces solubles: Application au cas des déchets solidifiés par liants hydrauliques," doctoral thesis, Institut National des Sciences Appliquées de Lyon, Lyon, France, 1996.

15. ANSI/ANS 16.1, "American National Standard Measurement of the Leachability of Solidified Low-Level Radioactive Wastes by a Short-term Test Procedure," *American Nuclear Society*, La Grange Park, IL, 1986.

17.0 TABLES, DIAGRAMS, FLOWCHARTS, AND VALIDATION DATA

The following pages contain the tables and figures referenced by this method.

TABLE 1

SCHEDULE OF ELUATE RENEWALS

Interval Label	Interval Duration (h)	Interval Duration (d)	Cumulative Leaching Time (d)
T01	2.0 ± 0.25	–	0.08
T02	23.0 ± 0.5	–	1.0
T03	23.0 ± 0.5	–	2.0
T04	–	5.0 ± 0.1	7.0
T05	–	7.0 ± 0.1	14.0
T06	–	14.0 ± 0.1	28.0
T07	–	14.0 ± 0.1	42.0
T08	–	7.0 ± 0.1	49.0
T09	–	14.0 ± 0.1	63.0

NOTE: This schedule may be extended for additional 14-day contact intervals to provide more information regarding longer-term release.

TABLE 2

METHOD PRECISON FOR MEAN INTERVAL FLUX (2nd – 9th Intervals)

Analyte	Symbol	Reapeatability – SWA %RSD_r	Repeatability – CFS %RSD_r	Reproducibility – SWA %RSD_R	Reproducibility – CFS %RSD_R
Aluminum	Al	7.3	13.3	25.3	25.3
Antimony	Sb	9.2	14.8	21.8	23.8
Arsenic	As	19.9	-	31.1	-
Barium	Ba	13.2	7.5	44.8	18.3
Boron	B	10.8	7.2	27.3	27.1
Cadmium	Cd	-	7.6	-	23.2
Calcium	Ca	8.1	6.6	28.7	26.0
Chromium	Cr	10.2	-	23.8	-
Lead	Pb	-	4.3	-	19.8
Potassium	K	12.4	10.8	28.8	40.1
Selenium	Se	10.9	13.3	30.8	32.4
Vanadium	V	8.5	11.3	22.3	30.6

Material	Reapeatability – SWA %RSD_r	Repeatability – CFS %RSD_r	Repeatability – Overall	Reproducibility – SWA %RSD_R	Reproducibility – CFS %RSD_R	Reproducibility – Overall
Mean	11%	10%	11%	29%	27%	28%

NOTE: First interval is removed from mean interval flux because of variances associated with wash-off of surface contaminants that do not pertain to the method precision.

Data taken from Ref. 4.

TABLE 3

METHOD PRECISON FOR CUMULATIVE RELEASE AFTER 63 DAYS

Analyte	Symbol	Repeatability – SWA %RSD$_r$	Repeatability – CFS %RSD$_r$	Reproducibility – SWA %RSD$_R$	Reproducibility – CFS %RSD$_R$
Aluminum	Al	5.4	5.3	23.6	22.9
Antimony	Sb	6.9	5.9	19.7	14.4
Arsenic	As	15.9	-	31.0	-
Barium	Ba	7.5	3.9	35.6	16.5
Boron	B	8.4	3.7	22.6	25.7
Cadmium	Cd	-	4.8	-	18.4
Calcium	Ca	4.6	3.2	23.9	24.6
Chromium	Cr	7.7	-	17.7	-
Lead	Pb	-	1.6	-	12.0
Potassium	K	10.8	6.3	24.8	44.4
Selenium	Se	8.7	3.6	26.7	20.5
Vanadium	V	5.7	4.2	21.1	22.8

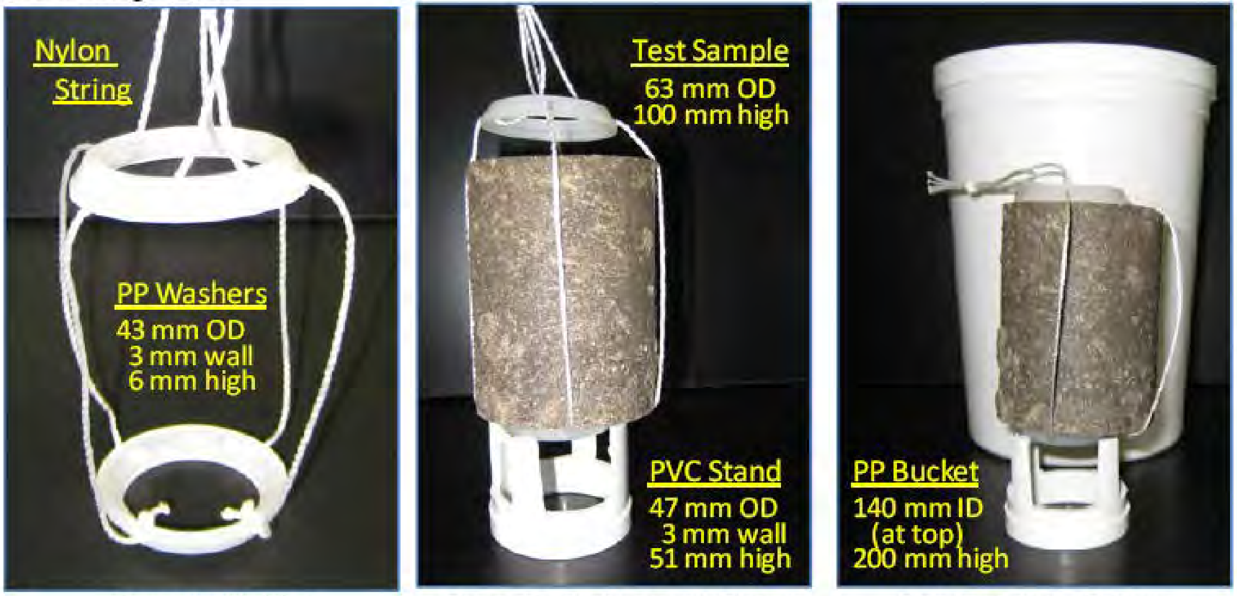
Material	Repeatability – SWA %RSD$_r$	Repeatability – CFS %RSD$_r$	Repeatability – Overall	Reproducibility – SWA %RSD$_R$	Reproducibility – CFS %RSD$_R$	Reproducibility – Overall
Mean	8%	4%	6%	25%	22%	23%

Data taken from Ref. 4.

FIGURE 1

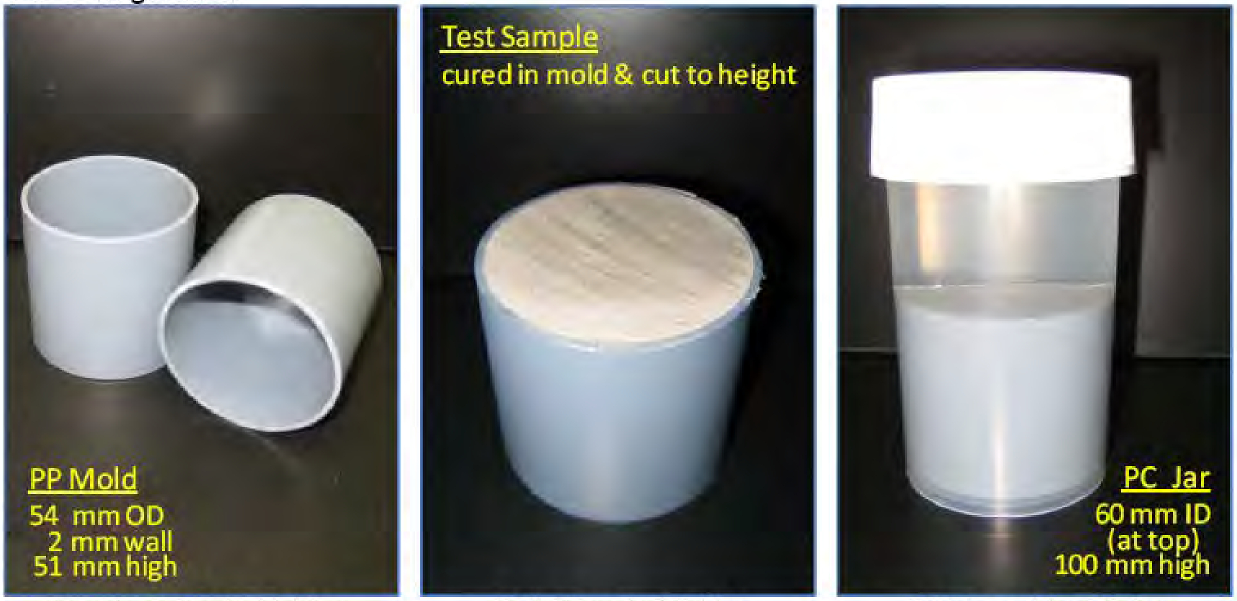
EXAMPLES OF MONOLITHIC SAMPLE HOLDERS

3-D Configuration



Sample Holder | Sample, Holder and Stand | 3-D Leaching Setup

1-D Configuration



Empty Sample Holder | Full Sample Holder | 1-D Leaching Setup

FIGURE 2

EXAMPLE COMPACTED GRANULAR SAMPLE HOLDER AND SETUP

Empty Sample Holder

Compacted Sample

1-D Leaching Setup

FIGURE 3

METHOD FLOWCHART

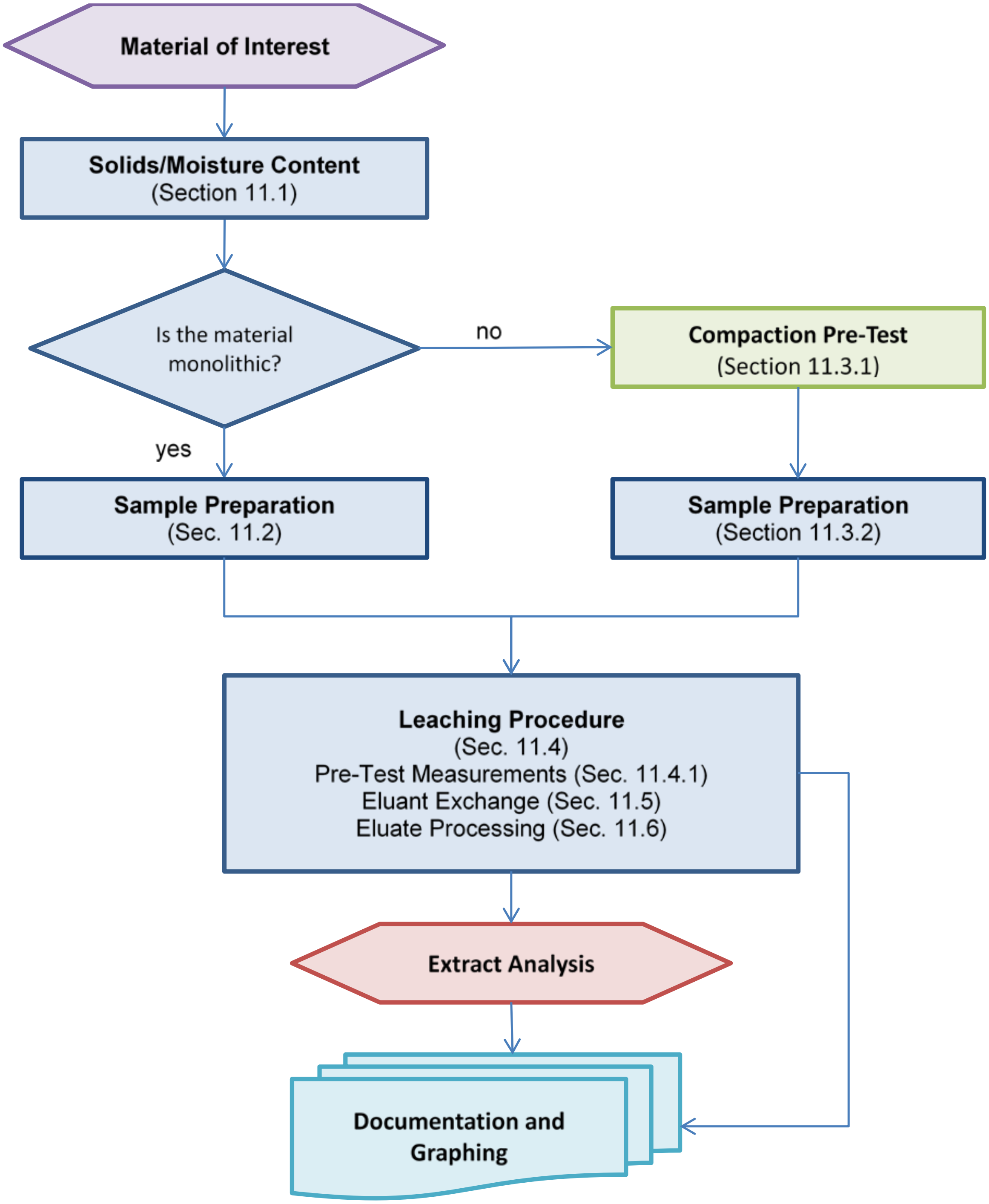


FIGURE 4

EXAMPLE CURVE OF PACKING DENSITY AS A FUNCTION OF MOISTURE CONTENT

$$y = 55.975x^3 – 65.036x^2 + 1.8352$$

$$r^2 = 0.983$$

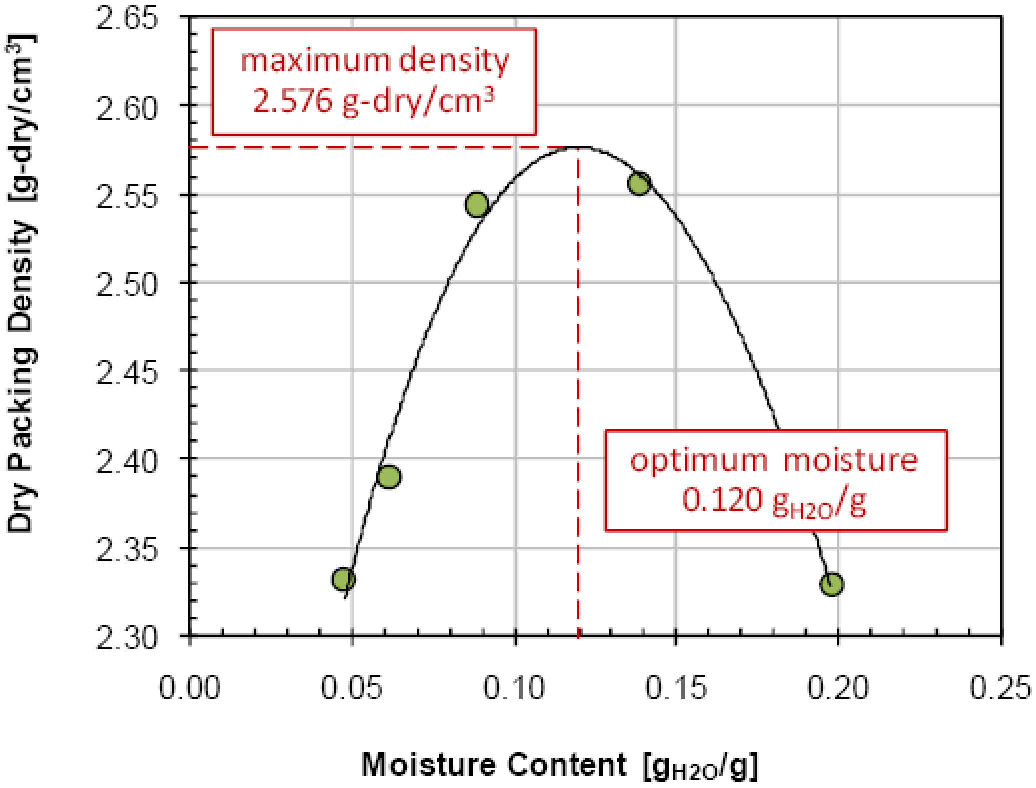


FIGURE 5

SCHEMATIC OF SEMI-DYNAMIC MASS TRANSFER TEST PROCESS

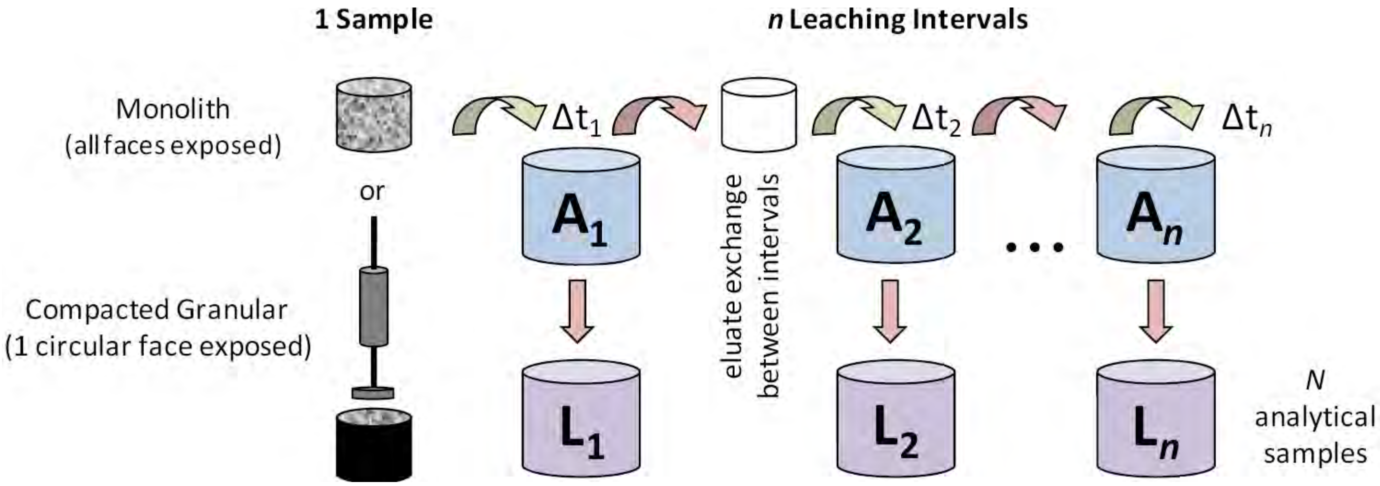
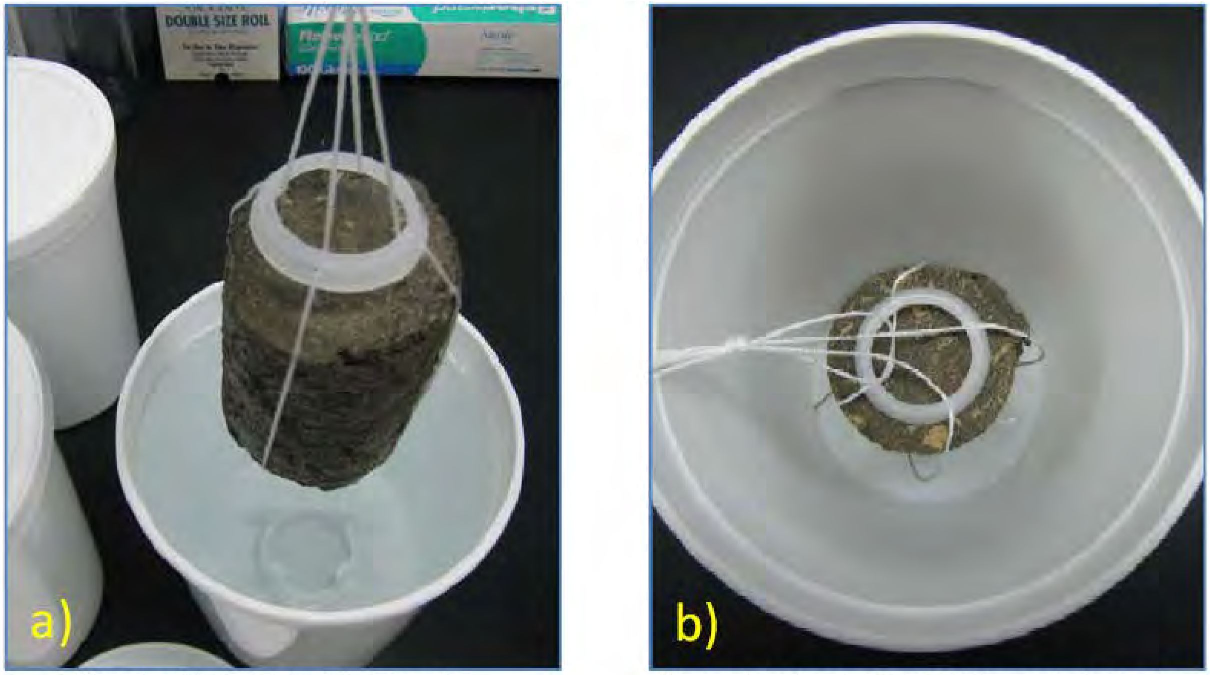


Figure obtained and modified from Ref. 1.

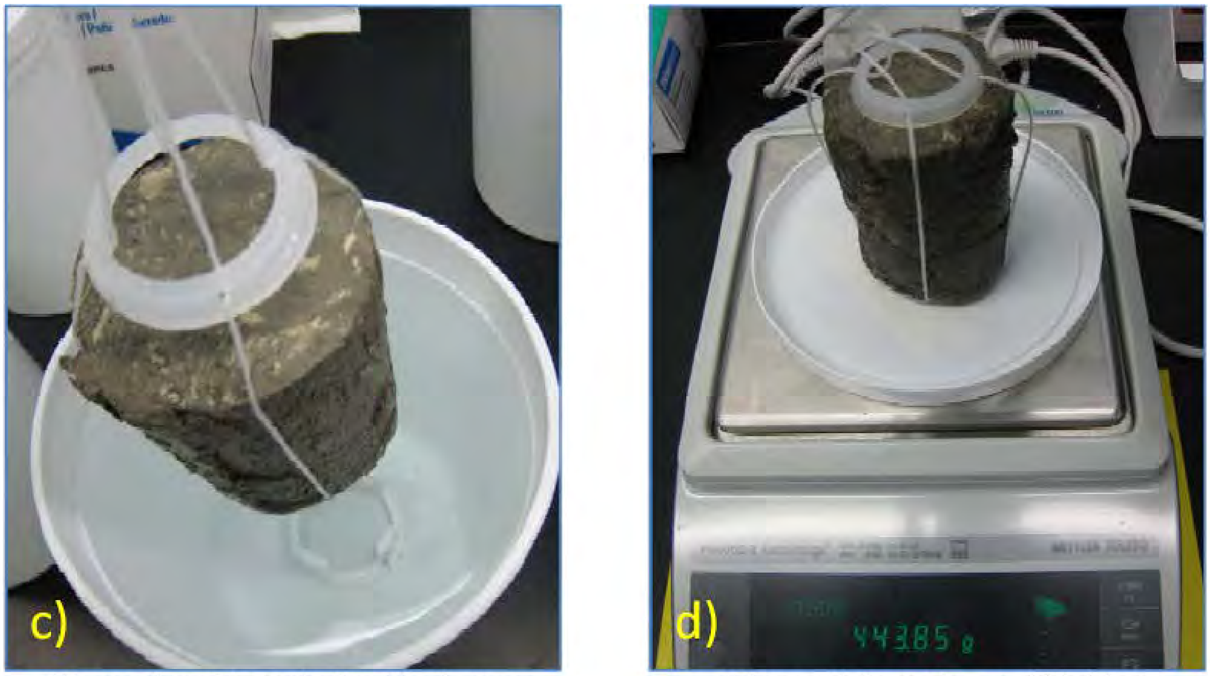
FIGURE 6

EXAMPLE LEACHING PROCEDURE STEPS



Start of Leaching Interval

Sample Centered in Eluant (top view)

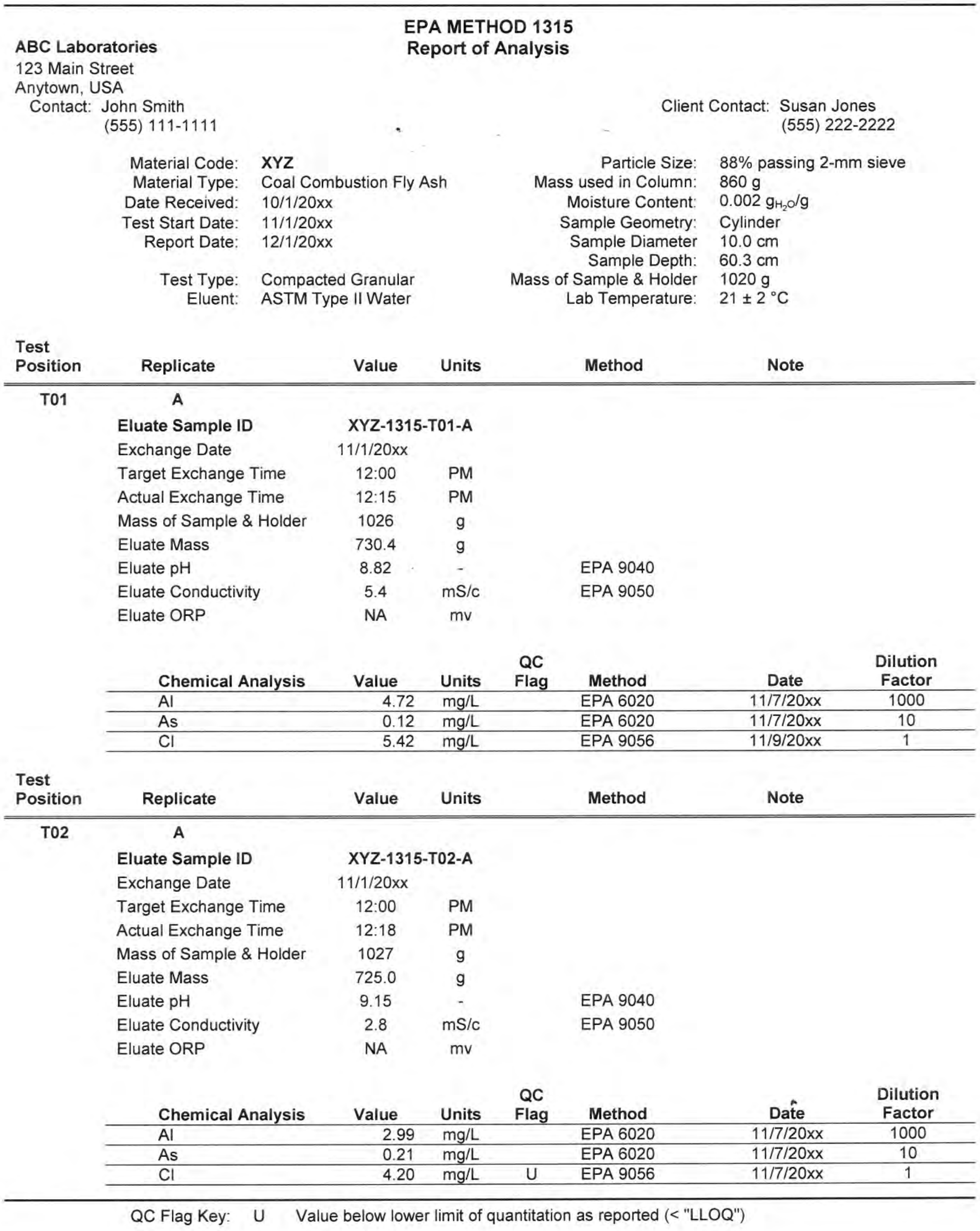


Removing Sample for Exchange

Mass of Sample and Holder

FIGURE 7

EXAMPLE DATA REPORTING FORMAT



EPA METHOD 1315
Report of Analysis

ABC Laboratories
123 Main Street
Anytown, USA
Contact: John Smith
(555) 111-1111

Client Contact: Susan Jones
(555) 222-2222

Material Code:	**XYZ**	Particle Size:	88% passing 2-mm sieve
Material Type:	Coal Combustion Fly Ash	Mass used in Column:	860 g
Date Received:	10/1/20xx	Moisture Content:	$0.002\ g_{H_2O}/g$
Test Start Date:	11/1/20xx	Sample Geometry:	Cylinder
Report Date:	12/1/20xx	Sample Diameter	10.0 cm
		Sample Depth:	60.3 cm
Test Type:	Compacted Granular	Mass of Sample & Holder	1020 g
Eluent:	ASTM Type II Water	Lab Temperature:	21 ± 2 °C

Test Position	Replicate	Value	Units	Method	Note
T01	**A**				
	Eluate Sample ID	**XYZ-1315-T01-A**			
	Exchange Date	11/1/20xx			
	Target Exchange Time	12:00	PM		
	Actual Exchange Time	12:15	PM		
	Mass of Sample & Holder	1026	g		
	Eluate Mass	730.4	g		
	Eluate pH	8.82	-	EPA 9040	
	Eluate Conductivity	5.4	mS/c	EPA 9050	
	Eluate ORP	NA	mv		

Chemical Analysis	Value	Units	QC Flag	Method	Date	Dilution Factor
Al	4.72	mg/L		EPA 6020	11/7/20xx	1000
As	0.12	mg/L		EPA 6020	11/7/20xx	10
Cl	5.42	mg/L		EPA 9056	11/9/20xx	1

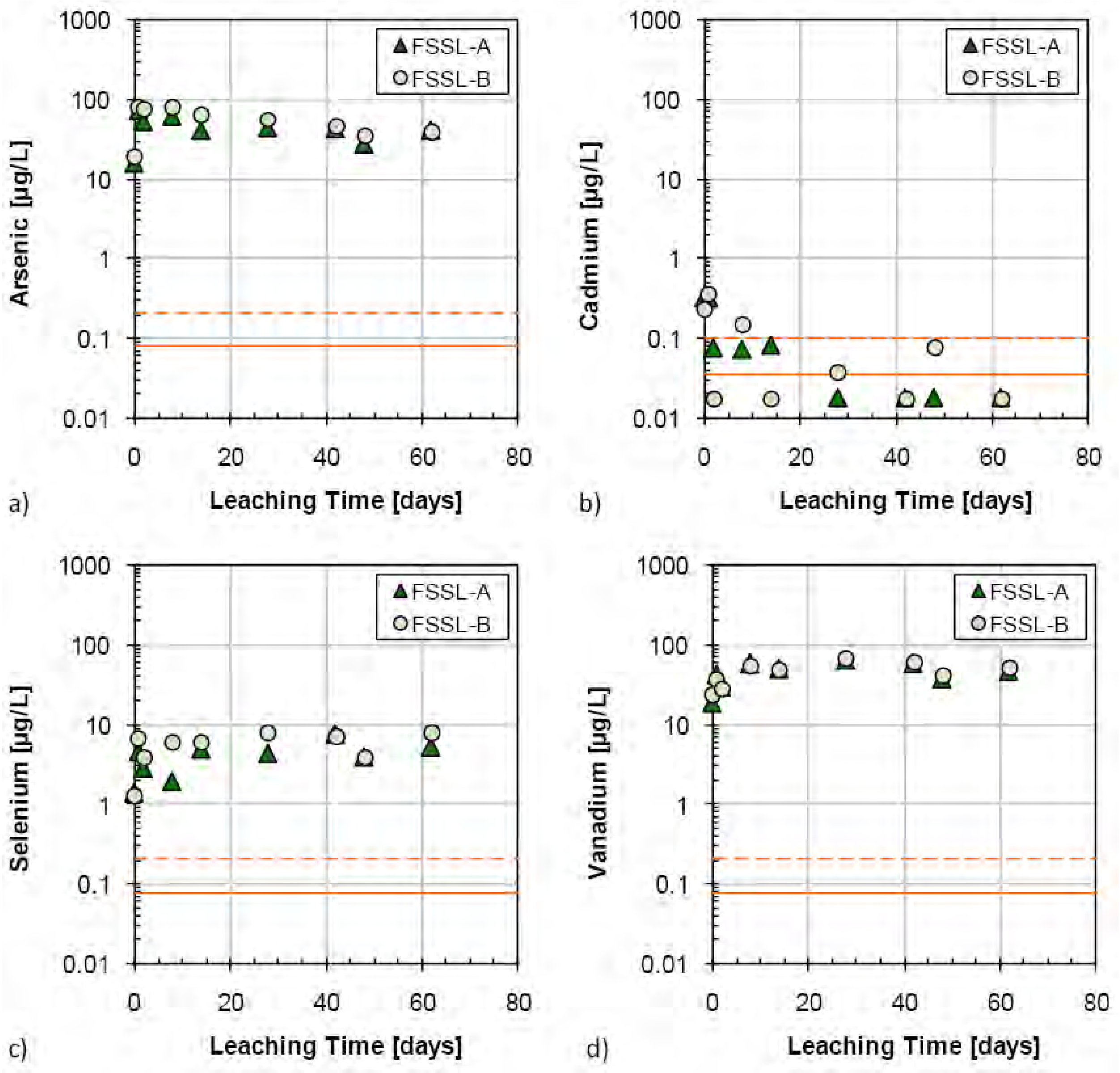
Test Position	Replicate	Value	Units	Method	Note
T02	**A**				
	Eluate Sample ID	**XYZ-1315-T02-A**			
	Exchange Date	11/1/20xx			
	Target Exchange Time	12:00	PM		
	Actual Exchange Time	12:18	PM		
	Mass of Sample & Holder	1027	g		
	Eluate Mass	725.0	g		
	Eluate pH	9.15	-	EPA 9040	
	Eluate Conductivity	2.8	mS/c	EPA 9050	
	Eluate ORP	NA	mv		

Chemical Analysis	Value	Units	QC Flag	Method	Date	Dilution Factor
Al	2.99	mg/L		EPA 6020	11/7/20xx	1000
As	0.21	mg/L		EPA 6020	11/7/20xx	10
Cl	4.20	mg/L	U	EPA 9056	11/7/20xx	1

QC Flag Key: U Value below lower limit of quantitation as reported (< "LLOQ")

FIGURE 8

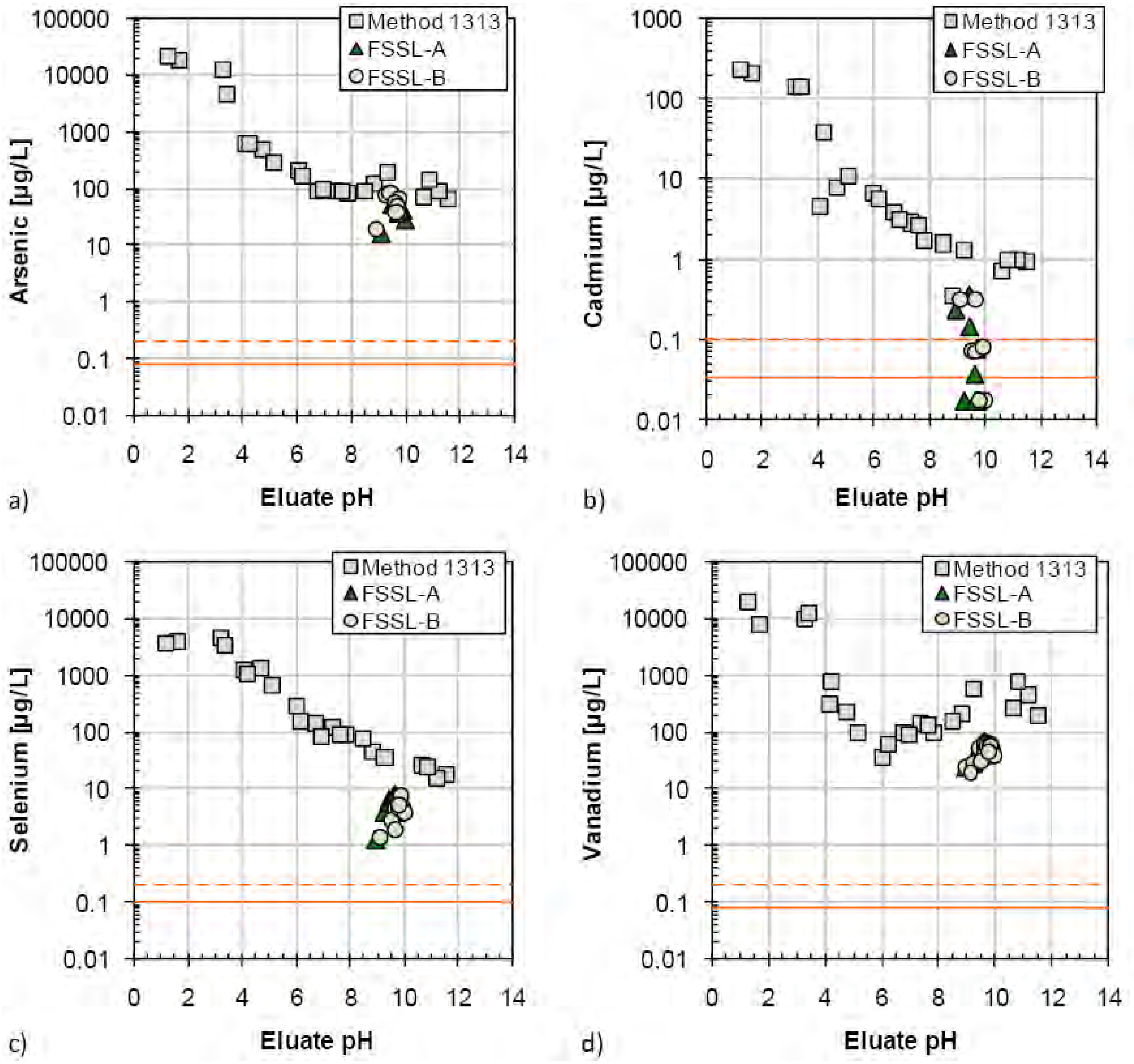
EXAMPLE INTERVAL CONCENTRATION GRAPHS



NOTE: Orange lines represent cumulative release if all eluate extracts were at the quantitation limit (dashed) and detection limit (solid). Chemical analyses below the detection limit are shown at ½ the detection limit value.

FIGURE 9

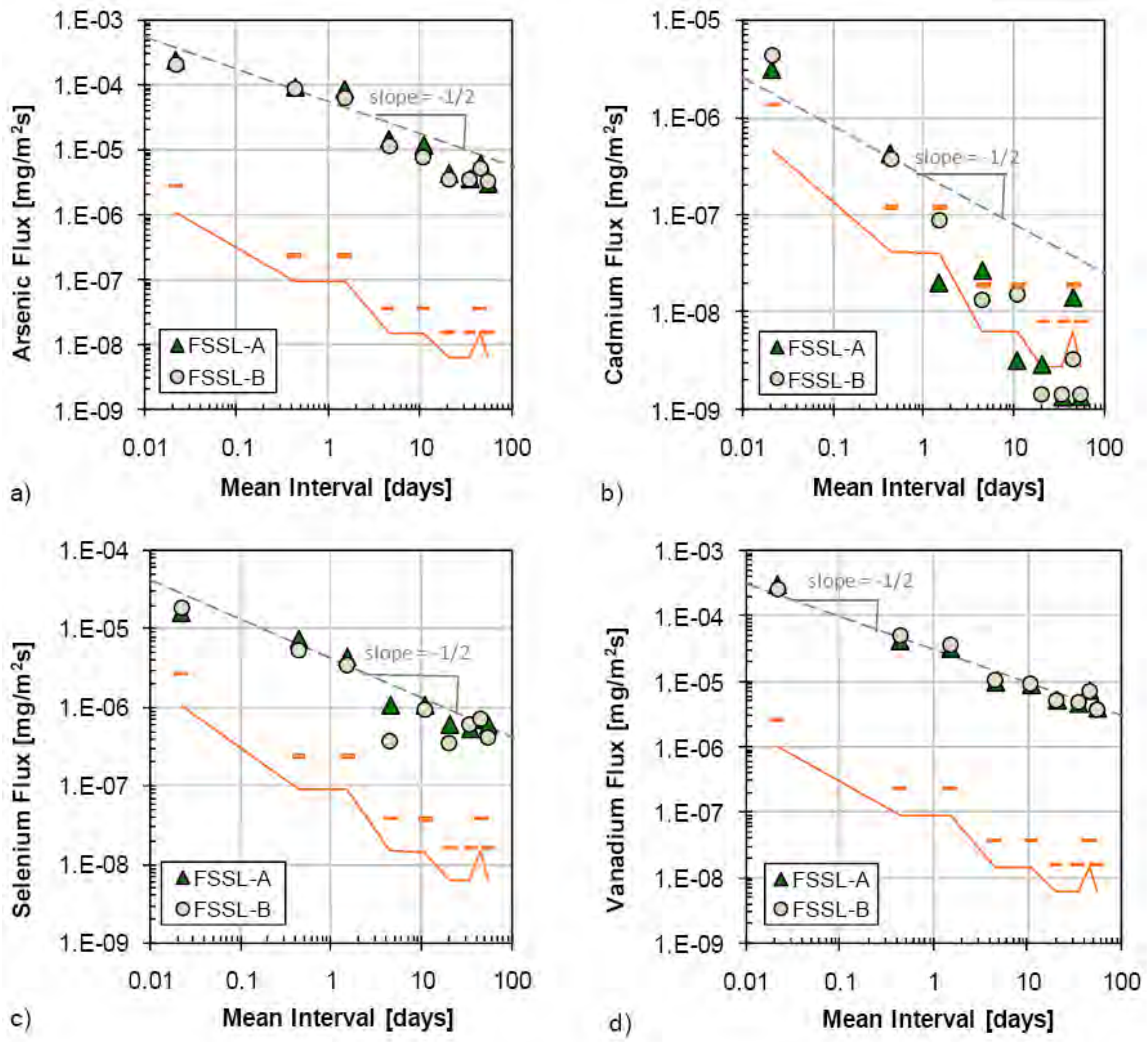
EXAMPLE OF SATURATION CHECK BETWEEN INTERVAL CONCENTRATIONS AND METHOD 1313 DATA



<u>NOTE</u>: Orange lines represent cumulative release if all eluate extracts were at the quantitation limit (dashed) and detection limit (solid). Chemical analyses below the detection limit are shown at ½ the detection limit value.

FIGURE 10

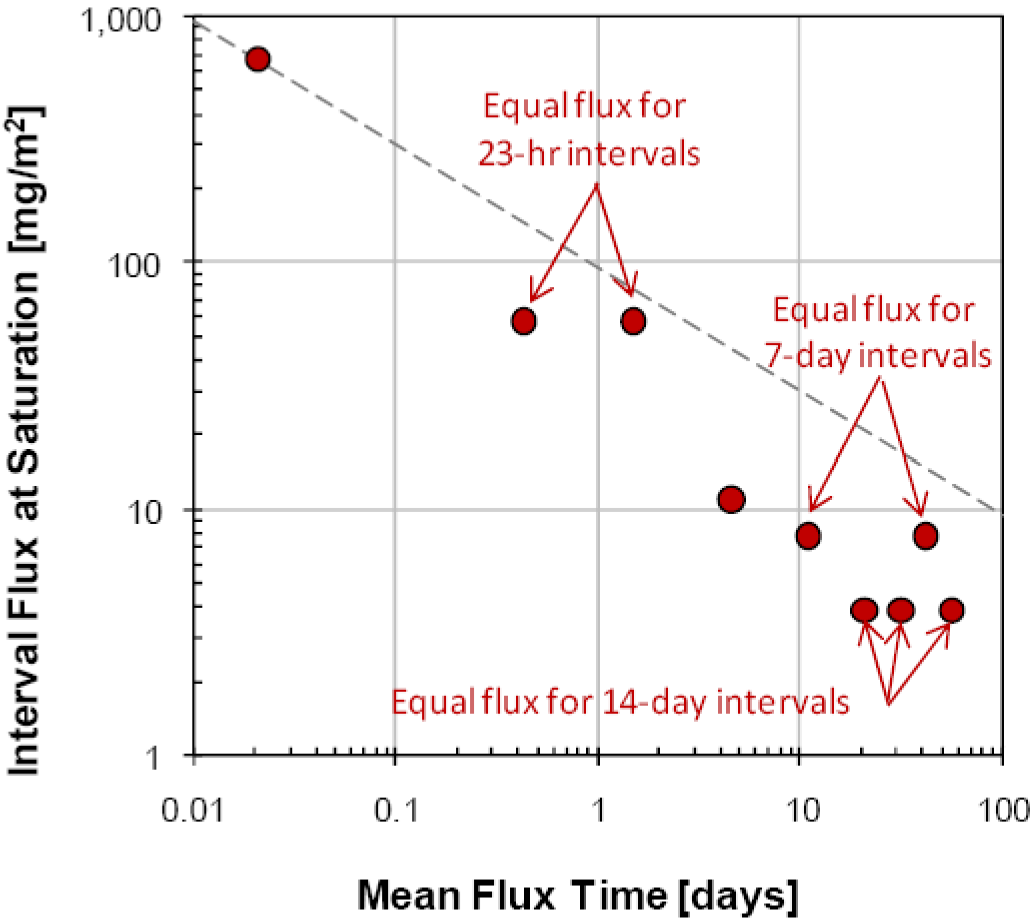
EXAMPLE INTERVAL FLUX GRAPHS



<u>NOTE</u>: Orange data represent cumulative release if all eluate extracts were at the quantitation limit (dashes) and detection limit (solid line).

FIGURE 11

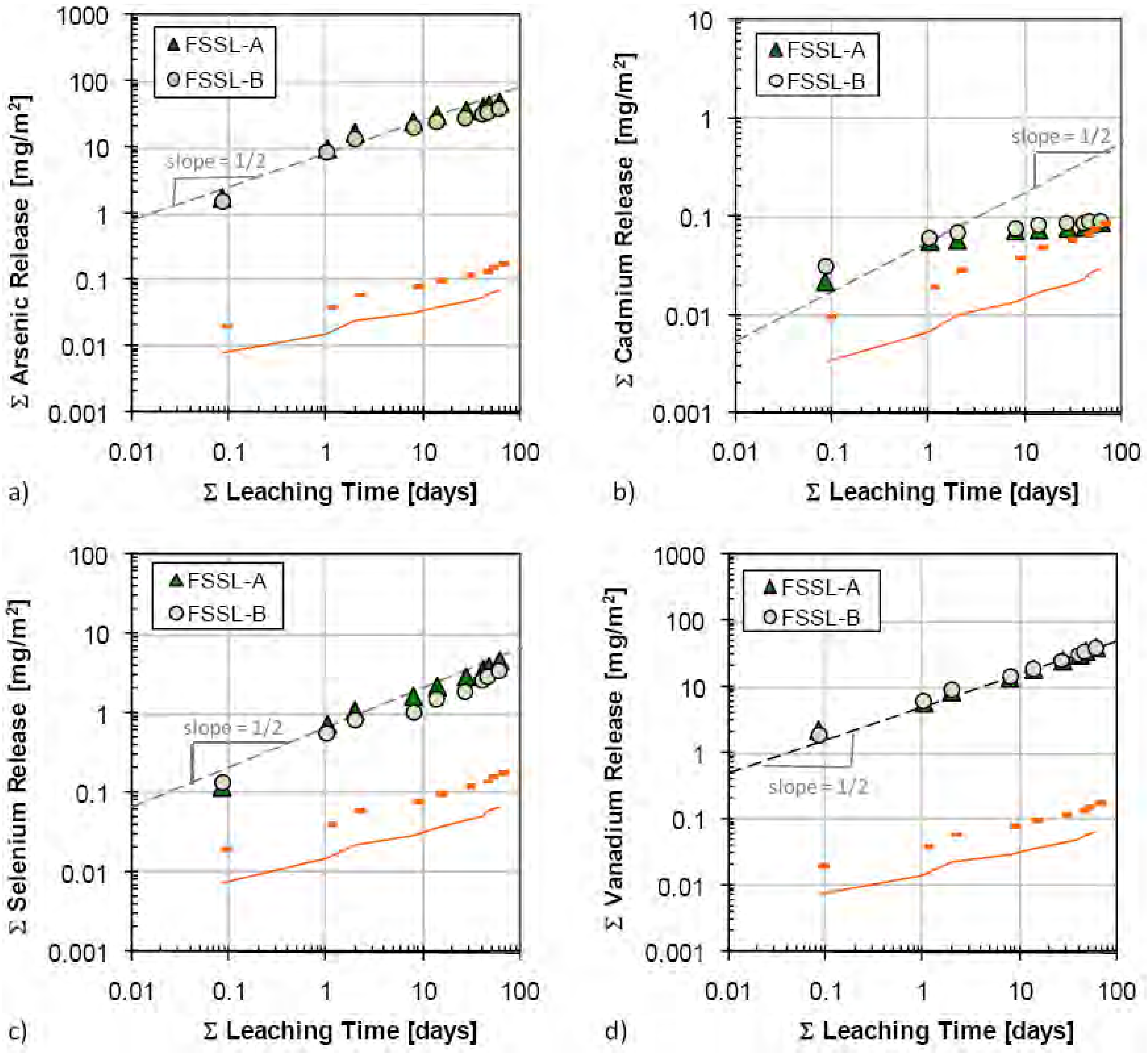
INTERVAL FLUX AT ELUATE SATURATION



NOTE: This figure assumes that the concentration in the eluate approaches saturation during the leaching interval (i.e., the driving force for diffusion approaches zero). When the leaching solution is saturated, the resulting mass release and interval flux is constant for intervals of the same duration.

FIGURE 12

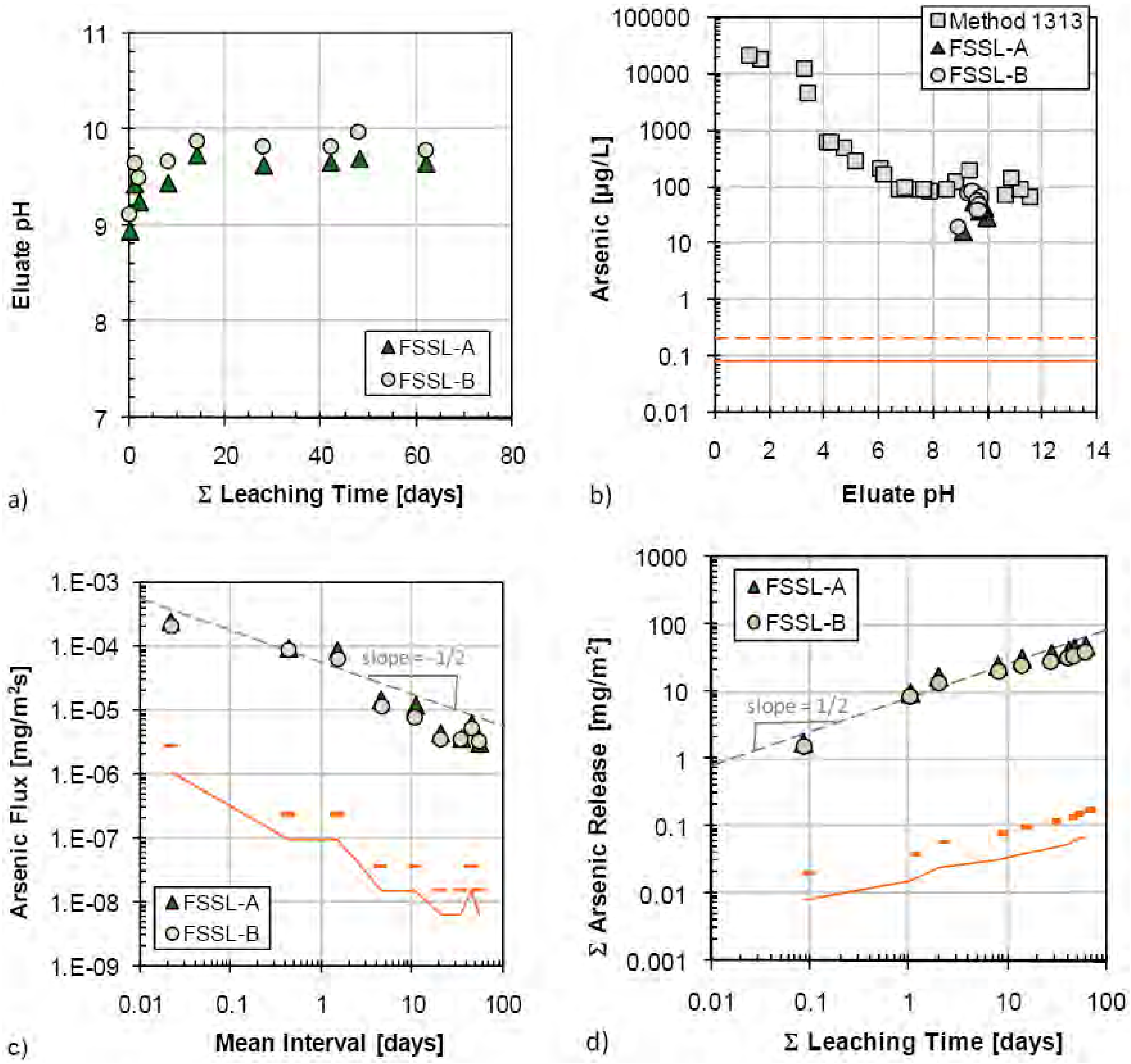
EXAMPLE CUMULATIVE RELEASE GRAPHS



NOTE: Orange data represent cumulative release if all eluate extracts were at the quantitation limit (dashes) and detection limit (solid line).

FIGURE 13

DATA REPRESENTATION BY CONSTITUENT (QUAD FORMAT)



NOTE: Orange data represent cumulative release if all eluate extracts were at the quantitation limit (dashes) and detection limit (solid line).

DOCUMENT

7

METHOD 1316[1]

LIQUID-SOLID PARTITIONING AS A FUNCTION OF LIQUID-TO-SOLID RATIO IN SOLID MATERIALS USING A PARALLEL BATCH PROCEDURE

SW-846 is not intended to be an analytical training manual. Therefore, method procedures are written based on the assumption that they will be performed by analysts who are formally trained in at least the basic principles of chemical analysis and in the use of the subject technology.

In addition, SW-846 methods, with the exception of required methods used for the analysis of method-defined parameters, are intended to be guidance methods that contain general information on how to perform an analytical procedure or technique, which a laboratory can use as a basic starting point for generating its own detailed standard operating procedure (SOP), either for its own general use or for a specific project application. Performance data included in this method are for guidance purposes only and must not be used as absolute quality control (QC) acceptance criteria for purposes of laboratory QC or accreditation.

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[1] This method has been derived from the SR003 procedure (Ref. 4) using Environmental Protection Agency-reviewed and accepted methodologies (see Ref. 3, Ref. 6, and Ref. 7). The method is analogous to batch L/S-dependence method EN12457 (Ref. 5) developed for the Comité Européen de Normalisation (CEN).

1.0 SCOPE AND APPLICATION

1.1 This method is designed to provide the liquid-solid partitioning (LSP) of inorganic constituents (e.g., metals, radionuclides) and non-volatile organic constituents (e.g., polycyclic aromatic hydrocarbons (PAHs)), dissolved organic carbon) at the natural pH of the solid material as a function of liquid-to-solid ratio (L/S) under conditions that approach liquid-solid chemical equilibrium. Table 1 shows the range of target L/S values tested under this method.

1.2 The eluate concentrations at a low L/S provide insight into pore solution composition either in a granular bed (e.g., soil column) or in the pore space of low-permeability material (e.g., solidified monolithic or compacted granular fill). In addition, analysis of eluates for dissolved organic carbon and of the solid phase for total organic carbon allow for evaluation of the impact of organic carbon release and the influence of dissolved organic carbon on the LSP of inorganic constituents.

1.3 This method is intended to be used as part of environmental leaching assessment for the evaluation of disposal, beneficial use, treatment effectiveness and site remediation. The method is not required by federal regulations to determine whether waste passes or fails the toxicity characteristic as defined at 40 CFR 261.24.

1.4 This method is suitable for assessing the leaching potential of a wide range of solid materials. Examples of solid materials include: industrial wastes, soils, sludges, combustion residues, sediments, stabilized materials, construction materials, and mining wastes.

1.5 This method is a leaching characterization method used to provide intrinsic material parameters that control leaching of inorganic species under equilibrium conditions. This test method is intended as a means for obtaining an extract (i.e., the eluate) of a solid material which may be used to estimate the solubility and release of inorganic constituents under the laboratory conditions described in this method. Extract concentrations may be used in conjunction with information regarding environmental management scenarios to estimate anticipated leaching concentrations, and release rate and extent for individual material constituents in the management scenarios evaluated. Extract concentrations may also be used along with geochemical speciation modeling to infer the mineral phases that control the LSP in the pore structure of the solid material.

1.6 This method is not applicable to characterize the release of volatile organic analytes (e.g., benzene, toluene and xylenes).

1.7 This method provides solutions that are considered to be indicative of leachate under field conditions only where the field leaching pH and L/S ranges are encompassed by the laboratory extract final conditions and the LSP is controlled by aqueous-phase saturation of the constituent of interest. When LSP is controlled by the amount of the constituent present in the solid that may dissolve (i.e., for highly soluble species), the mass released (mg/kg), rather than the concentration, is indicative of field conditions.

1.8 The solvent used in this method is reagent water.

1.9 Analysts are advised to take reasonable measures to ensure that the sample is homogenized to the extent practical prior to employment of this method. Particle size reduction may provide additional assurance of sample homogenization. Table 2 designates a minimum dry equivalent mass of sample to be added to each extraction vessel and the associated extraction contact time as a function maximum particle diameter. If the heterogeneity of the sample is suspected as the cause of unacceptable levels of precision in replicate test results or is considered significant based on professional judgment, the sample mass used in the test procedure may be increased to a greater minimum dry equivalent mass than shown in Table 1 with the amount of extractant increased proportionately to maintain the designated L/S.

1.10 In the preparation of solid materials for use in this method, particle size reduction of samples with large grain size is used to enhance the approach towards liquid-solid equilibrium under the designated contact time interval of the extract process. The extract contact time for samples reduced to a finer maximum particle size will be shorter.

1.11 Prior to employing this method, analysts are advised to consult the base method for each type of procedure that may be employed in the overall analysis (e.g., Methods 9040, 9045, and 9050) for additional information on QC procedures, development of QC acceptance criteria, calculations, and general guidance. Analysts also should consult the disclaimer statement at the front of the manual and the information in Chapter Two for: 1) guidance on the intended flexibility in the choice of methods, apparatus, materials, reagents, and supplies, and 2) the responsibilities of the analyst for demonstrating that the techniques employed are appropriate for the analytes of interest, in the matrix of interest, and at the levels of concern.

In addition, analysts and data users are advised that, except where explicitly specified in a regulation, the use of SW-846 methods is not mandatory in response to federal testing requirements. The information contained in this method is provided by the Environmental Protection Agency (EPA or the Agency) as guidance to be used by the analyst and the regulated community in making judgments necessary to generate results that meet the data quality objectives (DQOs) for the intended application.

1.12 This method is restricted to use by, or under supervision of, properly experienced and trained personnel. Each analyst must demonstrate the ability to generate acceptable results with this method.

2.0 SUMMARY OF METHOD

This method consists of five parallel extractions of a particle size-reduced solid material in reagent water over a range of L/S values from 0.5 to 10 mL eluent/g dry material (see Table 1). In addition to the five test extractions, a method blank without solid sample is carried through the procedure in order to verify that analyte interferences are not introduced as a consequence of reagent impurities or equipment contamination. If multiple materials or replicate tests are carried out in parallel, only one set of method blanks is necessary. In total, six bottles (i.e., five test positions and one method blank) are tumbled in an end-over-end fashion for a specified contact time based on the maximum particle size of the solid (see Table 2). At the end of the contact interval, the liquid and solid phases are roughly separated via settling or centrifugation. Extract pH and specific conductance measurements are then taken on an aliquot of the liquid phase. The bulk of the eluate is clarified by pressure or vacuum filtration in preparation for constituent analysis. Analytical aliquots of the extracts are collected and preserved accordingly based on the determinative methods to be performed. The eluate constituent concentrations are plotted as a function of L/S and compared to QC and assessment limits.

3.0 DEFINITIONS

3.1 Constituent of potential concern (COPC) – A chemical species of interest, which may or may not be regulated, but may be characteristic of release-controlling properties of the sample geochemistry.

3.2 Release – The dissolution or partitioning of a COPC from the solid phase to the aqueous phase during laboratory testing (or under field conditions). In this method, mass release is expressed in units of mg COPC/kg dry solid material.

3.3 Liquid-solid partitioning (LSP) – The distribution of COPCs between the solid and liquid phases at the conclusion of the extraction.

3.4 Liquid-to-solid ratio (L/S) – The fraction of the total liquid volume (including the moisture contained in the "as used" solid sample) to the dry mass equivalent of the solid material. L/S is typically expressed in volume units of liquid per dry mass of solid material (mL/g-dry).

3.5 "As-tested" sample – The solid sample at the conditions (e.g., moisture content and particle-size distribution) present at the time of the start of the test procedure. The "as-tested" conditions will differ from the "as-received" sample conditions if particle-size reduction and drying were necessarily performed.

3.6 Dry-mass equivalent – The mass of "as-tested" (i.e., "wet") sample that equates to the mass of dry solids plus associated moisture, based on the moisture content of the "as-tested" material. The dry-mass equivalent is typically expressed in mass units of the "as-tested" sample (g).

3.7 Eluent – The solution used to contact the solid material in a leaching test. The eluent is usually free of COPCs but may contain other species used to control the test conditions of the extraction.

3.8 Eluate – The solution collected as an extract from a leaching test that contains the eluent plus constituents leached from the solid phase.[2]

3.9 Refer to Chapter One, Chapter Three, and the manufacturers' instructions for definitions that may be relevant to this procedure.

4.0 INTERFERENCES

Solvents, reagents, glassware, and other sample processing hardware may yield artifacts and/or interferences to sample analysis. All of these materials must be demonstrated to be free from interferences under the conditions of the analysis by analyzing method blanks. Specific selection of reagents may be necessary. Refer to each method to be used for specific guidance on QC procedures

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[2] The definition of "eluate" is used in this method to differentiate the output solution of a leaching test from the "leachate" solution collected from, or measured in, the field. The distinction between terms is made to minimize confusion when comparing laboratory results to field data (Ref. 5).

and to Chapters Three and Four for general guidance on glassware cleaning. Also refer to Methods 9040, 9045, and 9050 for a discussion of interferences.

5.0 SAFETY

This method does not address all safety issues associated with its use. The laboratory is responsible for maintaining a safe work environment and a current awareness file of Occupational Safety and Health Administration (OSHA) regulations regarding the safe handling of the chemicals specified in this method. A reference file of material safety data sheets (MSDSs) should be available to all personnel involved in these analyses.

6.0 EQUIPMENT AND SUPPLIES

The mention of trade names or commercial products in this manual is for illustrative purposes only, and does not constitute an EPA endorsement or exclusive recommendation for use. The products and instrument settings cited in SW-846 methods represent those products and settings used during the method development or subsequently evaluated by the Agency. Glassware, reagents, supplies, equipment, and settings other than those listed in this manual may be employed provided that method performance appropriate for the intended application has been demonstrated and documented.

This section does not list all common laboratory glassware (e.g., beakers and flasks) that might be used.

6.1 Extraction vessels

6.1.1 Six wide-mouth bottles (i.e., five for test positions plus one for a method blank) constructed of inert material, resistant to high and low pH conditions and interaction with the constituents of interest, as described in the following sections.

6.1.1.1 For the evaluation of inorganic COPCs, bottles made of high density polyethylene (HDPE) (e.g., Nalgene #3140-0250 or equivalent), polypropylene (PP), or polyvinyl chloride (PVC) are recommended.

6.1.1.2 For the evaluation of non-volatile organic and mixed organic/inorganic COPCs, bottles made of glass or Type-316 stainless steel are recommended. Polytetrafluoroethene (PTFE) is not recommended for non-volatile organics, due to the sorption of species with high hydrophobicity (e.g., PAHs). Borosilicate glass is recommended over other types of glass, especially when inorganic analytes are of concern.

6.1.2. The extraction vessels must be of sufficient volume to accommodate both the solid sample and an extractant volume based on the schedule of L/S values shown in Table 1. For example, a 500-mL bottle is recommended when 100 g dry equivalent mass is contacted with 200 mL of eluent (see T03 in Table 1).

6.1.3 The vessels must have a leak-proof seal that can sustain end-over-end tumbling for the duration of the designated contact time.

6.1.4 If centrifugation is anticipated to be beneficial for initial phase separation, the extraction vessels should be capable of withstanding centrifugation at 4000 ± 100 rpm for a minimum of 10 ± 2 min. Alternately, samples may be extracted in bottles that do not meet this centrifugation specification (e.g., Nalgene I-Chem #311-0250 or equivalent) and the solid-liquid slurries transferred into appropriate centrifugation vessels for phase separation as needed.

6.2 Balance – Capable of 0.01 g resolution for masses less than 500 g

6.3 Rotary tumbler – Capable of rotating the extraction vessels end-over-end at a constant speed of 28 ± 2 rpm (e.g., Environmental Express, Charleston, SC or equivalent)

NOTE: The holding capacity of tumblers may vary and modifications (e.g., packing or bottle-holding inserts) may be necessary to accommodate the extraction vessels.

6.4 Filtration apparatus – Pressure or vacuum filtration apparatus composed of appropriate materials to maximize collection of extracts and minimize loss of COPCs (e.g., Nalgene #300-4000 or equivalent) (see Sec. 6.1)

6.5 Filtration membranes – Composed of polypropylene or equivalent material with an effective pore size of 0.45 µm (e.g., Gelman Sciences GH Polypro #66548 from Fisher Scientific or equivalent)

6.6 pH meter – Laboratory model capable of temperature compensation (e.g., Accumet 20, Fisher Scientific or equivalent) with a minimum resolution of 0.1 pH units

6.7 pH combination electrode – Composed of chemically resistant materials

6.8 Conductivity meter – Laboratory model (e.g., Accumet 20, Fisher Scientific or equivalent), with a minimum resolution of 5% of the measured value

6.9 Conductivity electrodes – Composed of chemically resistant materials

6.10 Adjustable-volume pipettor – Oxford Benchmate series or equivalent.

The necessary delivery range will depend on the buffering capacity of the solid material and acid/base strength used in the test.

6.11 Disposable pipettor tips

6.12 Centrifuge (recommended) – Capable of centrifuging the extraction vessels at a rate of 4000 ± 100 rpm for 10 ± 2 min

7.0 REAGENTS AND STANDARDS

7.1 Reagent-grade chemicals, at a minimum, should be used in all tests. Unless otherwise indicated, all reagents should conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society (ACS), where such specifications are available. Other grades may be used, provided the reagents are of sufficiently high purity to permit use without lessening the accuracy of the determination. Inorganic reagents and extracts should be stored in plastic to prevent interaction of constituents from glass containers. Organic reagents should be stored in glass to prevent leaching of contaminants from plastic containers.

7.2 Reagent water must be interference free. All references to water in this method refer to reagent water unless otherwise specified.

7.3 Consult Methods 9040 and 9050 for additional information regarding the preparation of reagents required for pH and specific conductance measurements.

8.0 SAMPLE COLLECTION, PRESERVATION, AND STORAGE

8.1 See Chapter Three, "Inorganic Analytes," and Chapter Four, "Organic Analytes," for sample collection and preservation information.

8.2 All solid samples should be collected using an appropriate sampling plan.

8.3 All containers should be composed of materials that minimize interaction with solution COPCs. For further information, see Chapters Three and Four.

8.4 Preservatives should not be added to samples before extraction.

8.5 Samples can be refrigerated, unless refrigeration results in an irreversible physical change to the sample.

8.6 Analytical extracts or leachates should be preserved according to the guidance given in the individual determinative methods for the COPCs.

8.7 Extract holding times should be consistent with the holding times specified in the individual determinative methods for the COPCs.

9.0 QUALITY CONTROL

9.1 Refer to Chapter One for guidance on quality assurance (QA) and quality control (QC) protocols. When inconsistencies exist between QC guidelines, method-specific QC criteria take precedence over both technique-specific criteria and Chapter One criteria, and technique-specific QC criteria take precedence over Chapter One criteria. Any effort involving the collection of analytical data should include development of a structured and systematic planning document, such as a quality assurance project plan (QAPP) or a sampling and analysis plan (SAP), which translates project objectives and specifications into directions for those who will implement the project and assess the results.

Each laboratory should maintain a formal QA program. The laboratory should also maintain records to document the quality of the data generated. Development of in-house QC limits for each method is encouraged. Use of instrument-specific QC limits is encouraged, provided such limits will generate data appropriate for use in the intended application. All data sheets and QC data should be maintained for reference or inspection.

9.2 In order to demonstrate the purity of reagents and sample contact surfaces, a method blank (e.g., a bottle without solid material but with eluent carried through the extraction, filtration and analytical sample preparation process) should be tested.

9.3 The analysis of extracts should follow appropriate QC procedures, as specified in the determinative methods for the COPCs. Refer to Chapter One for specific QC procedures.

9.4 Solid materials should be tested within one month of receipt unless the project requires that the "as-received" samples are tested sooner (e.g., the material is part of a time-dependent study or the material may change during storage due to oxidation or carbonation).

9.5 Initial demonstration of proficiency (IDP)

Leachate methods are not amenable to typical IDPs when reference materials with known values are not available. However, prior to using this method an analyst should have documented proficiency in the skills required for successful implementation of the method. For example, skill should be demonstrated in the use of an analytical balance, the determination of pH using methods 9040 and 9045 and the determination of conductance using method 9050.

10.0 CALIBRATION AND STANDARDIZATION

10.1 The balance should be calibrated and certified, at a minimum, annually or in accordance with laboratory policy.

10.2 Prior to measurement of eluate pH, the pH meter should be calibrated using a minimum of two standards that bracket the range of pH measurements. Refer to Methods 9040 and 9045 for additional guidance.

10.3 Prior to measurement of eluate conductivity, the meter should be calibrated using at least one standard at a value greater than the range of conductivity measurements. Refer to Method 9050 for additional guidance.

11.0 PROCEDURE

A flowchart of the method is presented in Figure 1. Microsoft Excel® data templates are available to aid in collecting and archiving of laboratory and analytical data.[3]

11.1 Particle size reduction (if required)

11.1.1 In this method, particle size reduction is used to prepare large-grained samples for extraction so that the approach toward liquid-solid equilibrium is enhanced and mass transport through large particles is minimized. A longer extract contact time is required for larger maximum particle size designations. This method designates three maximum particle sizes and associated contact times (see Table 2). The selection of an appropriate maximum

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[3] These Excel® templates form the basis for uploading method data into the data management program, LeachXS Lite™. Both the data templates and LeachXS Lite™ are available at http://vanderbilt.edu/leaching.

particle size from this table should be based on professional judgment regarding the practical effort required to size reduce the solid material.

11.1.2 Particle size reduction of "as received" sample may be achieved through crushing, milling, or grinding with equipment made from chemically inert materials. During the reduction process, care should be taken to minimize loss of sample and potentially volatile constituents in the sample.

11.1.3 If the moisture content of the "as-received" material is greater than 15% (wet basis), air drying or desiccation may be necessary. Oven drying is not recommended for preparation of test samples due to the potential for mineral alteration. In all cases, the moisture content of the "as received" material should be recorded.

NOTE: If the solid material is susceptible to interaction with the atmosphere (e.g., carbonation, oxidation), drying should be conducted in an inert environment.

11.1.4 When the material seems to be of a relatively uniform particle size, calculate the percentage less than the sieve size as follows:

$$\%\ \text{Passing} = \frac{M_{sieved}}{M_{total}} \times 100\%$$

Where: M_{sieved} = mass of sample passing the sieve (g)
M_{total} = mass of total sample (g) (e.g., M_{sieved} + mass not passing sieve)

11.1.5 The fraction retained by the sieve should be recycled for further particle size reduction until at least 85% of the initial mass has been reduced below the designated maximum particle size. Calculate and record the final percentage passing the sieve and the designated maximum particle size. For the uncrushable fraction of the "as received" material, record the fraction mass and nature (e.g., rock, metal or glass shards, etc).

11.1.6 Store the size-reduced material in an airtight container in order to prevent contamination via gas exchange with the atmosphere. Store the container in a cool, dark and dry place prior to use.

11.2 Determination of solids and moisture content

11.2.1 In order to provide the dry mass equivalent of the "as-tested" material, the solids content of the subject material should be determined. Often, the moisture content of the solid sample is recorded. In this method, the moisture content is determined and recorded on the basis of the "wet" or "as-tested" sample.

WARNING: The drying oven should be contained in a hood or otherwise properly ventilated. Significant laboratory contamination or inhalation hazards may result when drying heavily contaminated samples. Consult the laboratory safety officer for proper handling procedures prior to drying samples that may contain volatile, hazardous, flammable or explosive materials.

11.2.2 Place a 5 to 10-g sample of solid material into a tared dish or crucible. Dry the sample to a constant mass at 105 ± 2 °C. Check for constant mass by returning the dish to the drying oven for 24 hours, cooling to room temperature in a desiccator and re-weighing. The two mass readings should agree within the larger of 0.2% or 0.02 g.

NOTE: The oven-dried sample is not used for the extraction and should be properly disposed of once the dry mass is determined.

11.2.3 Calculate and report the solids content as follows:

$$SC = \frac{M_{dry}}{M_{test}}$$

Where: SC = solids content of "as-tested" material (g-dry/g)
M_{dry} = mass of dry material specified in the method (g-dry)
M_{test} = mass of "as-tested" solid equivalent to the dry-material mass (g)

11.2.4 Calculate and report the moisture content (wet basis) as follows:

$$MC_{wet} = \frac{M_{test} - M_{dry}}{M_{test}}$$

Where: $MC_{(wet)}$ = moisture content on a wet basis (g_{H_2O}/g)
M_{dry} = mass of dry material specified in the method (g-dry)
M_{test} = mass of "as-tested" solid equivalent to the dry-material mass (g)

11.3 Extraction setup schedule (Microsoft Excel® spreadsheet template available at http://www.vanderbilt.edu/leaching/downloads/test-methods/).

An Excel® template accompanies this method and may be used to set up the extraction schedule. If using the provided template, disregard Sec. 11.3 and proceed to the extraction procedure Sec. 11.4.

11.3.1 Using the schedule shown in Table 1 as a guide, set up five test extractions and one method blank. The mass of solids in an extraction may be scaled to minimize headspace in each extraction vessel. However, the volume of eluent should always be based on the target L/S in Column B of Table 1.

11.3.2 Calculate and record the amount of "as-tested" material equivalent to the dry mass in Column D of Table 1 as follows:

$$M_{test} = \frac{M_{dry}}{SC}$$

Where: M_{test} = mass of "as-tested" solid equivalent to the dry-material mass (g)
M_{dry} = mass of dry material specified in the method (g-dry)
SC = solids content of "as-tested" material (g-dry/g)

11.3.3 Calculate and record the volume of moisture contained in the "as-tested" sample in Column E of Table 1 as follows:

$$V_{W,sample} = \frac{M_{test} \times (1 - SC)}{\rho_w}$$

Where: $V_{W,sample}$ = volume of water in the “as tested” sample (mL)
M_{test} = mass of "as-tested" solid equivalent to the dry-material mass (g)
SC = solids content of the "as tested" sample (g-dry/g)
ρ_w = density of water (1.0 g/mL at room temperature)

11.3.4 Calculate and record the volume of reagent water required to bring each extraction to the target L/S in Column F of Table 1 as follows:

$$V_{RW} = M_{dry} \times LS - V_{W,sample}$$

Where: V_{RW} = volume of reagent water required to complete L/S (mL)
M_{dry} = mass of dry material specified in the method (g-dry)
LS = liquid-to-dry-solid ratio (10 mL/g)
$V_{W,sample}$ = volume of water in "as tested" sample (mL)

The size of the extraction bottle should be sufficient to contain the combined volume of solid material and eluent, ideally with a minimum amount of headspace.

11.4 Extraction procedure

11.4.1 Label five bottles with test position numbers and an additional bottle as a method blank according to Column A in Table 1.

11.4.2 Place the dry-mass equivalent (± 0.1 g) of "as-tested" sample as shown in Column D in Table 1 into each of the five test position extraction vessels.

NOTE: Do not put solid material in the method blank extraction vessel.

11.4.3 Add the appropriate volume (± 0.5 mL) of reagent water to both the test position and method blank extraction vessels as specified in Column F of Table 1.

11.4.4 Tighten the leak-proof lid on each bottle and tumble all extractions (i.e., test positions and method blanks) in an end-over-end fashion at a speed of 28 ± 2 rpm at room temperature (20 ± 2 °C). The contact time for this method will vary depending on the maximum particle size as shown in Table 2.

NOTE: The length of the contact time is designed to enhance the approach toward liquid-solid equilibrium. Longer contact times are required for larger particles to compensate for the effects of intra-particle diffusion. See Table 2 for required contact times based on the maximum particle size.

11.4.5 Remove the extraction vessels from the rotary tumbler and clarify the extracts by allowing the bottles to stand for 15 ± 5 min. Alternately, centrifuge the extraction vessels at 4000 ± 100 rpm for 10 ± 2 min.

NOTE: If clarification is significantly incomplete after settling or centrifugation, eluate measurements for pH, conductivity, and oxidization-reduction potential (ORP) may be taken on filtered samples. In this case, perform the filtration in Sec. 11.4.8 prior to eluate measurement in Sec. 11.4.6 and note the deviation from the written procedure.

CAUTION: Following separation from the solid phase, eluate samples lack the buffering provided by the solid phase and therefore may be susceptible to pH change resulting from interaction with air.

11.4.6 For each extraction vessel, decant a minimum volume (approximately 5 mL) of clear, unpreserved supernatant into a clean container.

11.4.7 Measure and record the pH, specific conductivity, and ORP of the extracts (see Methods 9040, 9045, and 9050).

NOTE: Measurement of pH, conductivity, and ORP should be taken within 15 minutes of eluate processing (Sec. 11.4.8) to avoid neutralization of the solution due to exposure to carbon dioxide, especially when alkaline materials are tested.

NOTE: The measurement of ORP is optional, but strongly recommended, especially when testing materials where oxidation is likely to change the LSP of COPCs.

11.4.8 Separate the solid from the remaining liquid in each extraction vessel by pressure or vacuum filtration through a clean 0.45-µm pore size membrane (Sec. 6.5). The filtration apparatus may be exchanged for a clean apparatus as often as necessary until all liquid has been filtered.

11.4.9 Immediately, preserve and store the volume(s) of eluate required for chemical analysis. Preserve all analytical samples in a manner that is consistent with the determinative chemical analyses to be performed.

12.0 DATA ANALYSIS AND CALCULATIONS (EXCEL® TEMPLATE PROVIDED)

12.1 Data reporting

12.1.1 Figure 2 shows an example of a data sheet that may be used to report the concentration results of this method. This example is included in the Excel® template. At a minimum, the basic test report should include:

a) Name of the laboratory
b) Laboratory technical contact information
c) Date and time at the start of the test
d) Name or code of the solid material
e) Particle size (85 wt% less than designated particle size)
f) Ambient temperature during extraction (°C)
g) Extraction contact time (h)
h) Eluate-specific information (see Sec. 12.1.2 below)

12.1.2 The minimum set of data that should be reported for each eluate includes:

a) Eluate sample ID
b) Target L/S (mL/g-dry)
c) Mass of "as tested" solid material used (g)
d) Moisture content of material used (g_{H_2O}/g)
e) Volume of eluent used (mL)
f) Measured final eluate pH
g) Measured eluate conductivity (mS/cm)
h) Measured ORP (mV) (optional)
i) Concentrations of all COPCs
j) Analytical QC qualifiers as appropriate

12.2 Data interpretation and presentation (optional)

12.2.1 LSP curve

12.2.1.1 A constituent LSP curve can be generated for each COPC after chemical analysis of all extracts by plotting the constituent concentration in the liquid phase as a function of L/S used for each extraction. The curve indicates the equilibrium concentration of the COPC as a function of L/S at the natural pH.

12.2.1.2 The lower limit of quantitation (LLOQ) for the analytical technique for each COPC may be shown as a horizontal line. COPC concentrations below this line indicate negligible or non-quantitative concentrations.

NOTE: The LLOQ is highly matrix-dependent and should be determined as part of a QA/QC plan.

12.2.1.3 Figure 3 provides example LSP curves as a function of L/S for a coal combustion fly ash and a coal combustion flue gas desulfurization filter cake.

13.0 METHOD PERFORMANCE

13.1 Performance data and related information are provided in SW-846 methods only as examples and guidance. The data do not represent required performance criteria for users of the methods. Instead, performance criteria should be developed on a project-specific basis, and the laboratory should establish in-house QC performance criteria for the application of this method. Performance data must not be used as absolute QC acceptance criteria for purposes of laboratory QC or accreditation.

13.2 Interlaboratory validation of this method was conducted using a coal combustion fly ash (material code EaFA), a contaminated smelter site soil (material code CFS) and a solidified waste analog (material code SWA). The median values and inner quartile ranges (IQRs) for repeatability and reproducibility were determined for eluate concentration results across all study materials and pH target values (see Table 3). More details on the interlaboratory validation may be found in Ref. 2.

13.3 Ref. 1 and Ref. 4 may provide additional guidance and insight on the use, performance and application of this method.

14.0 POLLUTION PREVENTION

14.1 Pollution prevention encompasses any technique that reduces or eliminates the quantity and/or toxicity of waste at the point of generation. Numerous opportunities for pollution prevention exist in laboratory operations. The EPA has established a preferred hierarchy of environmental management techniques that places pollution prevention as the management option of first choice. Whenever feasible, laboratory personnel should use pollution prevention techniques to address their waste generation. When wastes cannot be feasibly reduced at the source, the Agency recommends recycling as the next best option.

14.2 For information about pollution prevention that may be applicable to laboratories and research institutions consult *Less is Better: Laboratory Chemical Management for Waste Reduction,* a free publication available from the ACS, Committee on Chemical Safety, http://portal.acs.org/portal/fileFetch/C/WPCP_012290/pdf/WPCP_012290.pdf.

15.0 WASTE MANAGEMENT

The EPA requires that laboratory waste management practices be conducted consistent with all applicable rules and regulations. Laboratories are urged to protect the air, water, and land by minimizing and controlling all releases from hoods and bench operations, complying with the letter and spirit of any sewer discharge permits and regulations, and by complying with all solid and hazardous waste regulations, particularly the hazardous waste identification rules and land disposal restrictions. For further information on waste management, consult *The Waste Management Manual for Laboratory Personnel* available from ACS at the web address listed in Sec. 14.2.

16.0 REFERENCES

1. A.C. Garrabrants, D.S. Kosson, H.A. van der Sloot, F. Sanchez, and O. Hjelmar, "Background Information for the Leaching Environmental Assessment Framework (LEAF) Test Methods," EPA/600/R-10-170, *U.S. Environmental Protection Agency*, Washington, DC, 2010.

2. A.C. Garrabrants, D.S. Kosson, L. Stefanski, R. DeLapp, P.F.A.B. Seignette, H.A. van der Sloot, P. Kariher, and M. Baldwin, "Interlaboratory Validation of the Leaching Environmental Assessment (LEAF) Method 1313 and Method 1316," EPA 600/R-12/623, *Environmental Protection Agency*, Washington DC, 2012.

3. D.S. Kosson, F. Sanchez, P. Kariher, L.H. Turner, R. DeLapp, and P. Seignette, "Characterization of Coal Combustion Residues from Electric Utilities – Leaching and Characterization Data," EPA-600/R-09/151, *U.S. Environmental Protection Agency*, Washington DC, 2009.

4. D.S. Kosson, H.A. van der Sloot, F. Sanchez, and A.C. Garrabrants, "An Integrated Framework for Evaluating Leaching in Waste Management and Utilization of Secondary Materials," *Environmental Engineering Science*, 19(3) 159-204, 2002.

5. EN12457, "Characterization of Waste – Leaching – Compliance Test for Leaching of Granular Waste Materials and Sludges," *Comité Européen de Normalisation*, Brussels, Belgium, 2001.

6. F. Sanchez, R. Keeney, D.S. Kosson, and R. DeLapp, "Characterization of Mercury-Enriched Coal Combustion Residues from Electric Utilities Using Enhanced Sorbents for Mercury Control," EPA-600/R-06/008, *U.S. Environmental Protection Agency*, Washington DC, 2006.

7. F. Sanchez, D.S. Kosson, R. Keeney, R. DeLapp, L. Turner, and P. Kariher, "Characterization of Coal Combustion Residues from Electric Utilities Using Wet Scrubbers for Multi-Pollutant Control," EPA-600/R-08/077, *U.S. Environmental Protection Agency*, Washington DC, 2008.

17.0 TABLES, DIAGRAMS, FLOWCHARTS, AND VALIDATION DATA

The following pages contain the tables and figures referenced by this method.

TABLE 1

EXAMPLE SCHEDULE FOR EXTRACTION SETUP

A	B	C	D	E	F	G
Test Position	Target LS	Minimum Dry Mass (g-dry)	Mass of "As-Tested" Sample (g)	Moisture in "As-Tested" Sample (mL)	Volume of Reagent Water (mL)	Recommended Bottle Size (mL)
T01	10.0	20	22.2	2.2	198	250
T02	5.0	40	44.4	4.4	196	250
T03	2.0	100	111.1	11.1	189	500
T04	1.0	200	222.2	22.2	178	500
T05	0.5	400	444.4	44.4	156	1000
B03	QC	–	–	–	200	250
Total	–	–	844.4	–	1120	–

NOTE: 1) This schedule assumes a target liquid volume of 200 mL.
2) This schedule is based on "as tested" solids content of 0.90 g-dry/g.
3) Test position marked B01 is a method blank of reagent water.

Table data modified from Ref. 4.

TABLE 2

EXTRACTION PARAMETERS AS FUNCTION OF MAXIMUM PARTICLE SIZE

Particle Size (85% less than) (mm)	US Sieve Size	Minimum Dry Mass (g-dry)	Contact Time (h)	Recommended Vessel size (mL)
0.3	50	20 ± 0.05	24 ± 2	250
2.0	10	40 ± 0.1	48 ± 2	500
5.0	4	80 ± 0.1	72 ± 2	1000

TABLE 3

MEDIAN METHOD PRECISION ACROSS STUDY MATERIALS

Analyte	Symbol	Repeatability - Median %RSD$_r$	Repeatability - IQR %RSD$_r$	Reproducibility - Median %RSD$_R$	Reproducibility - IQR % RSD$_R$
Antimony	Sb	12%	8-13%	21%	17-27%
Arsenic	As	15%	12-28%	31%	23-34%
Barium	Ba	7%	5-9%	16%	13-30%
Boron	B	7%	5-10%	13%	9-34%
Calcium	Ca	6%	3-7%	8%	7-19%
Molybdenum	Mo	7%	6-9%	18%	11-31%
Selenium	Se	8%	4-9%	20%	13-24%
Vanadium	V	6%	4-12%	16%	13-26%
Median of Medians	–	7%	3-28%	17%	7-34%

Data taken from Ref. 2.

FIGURE 1

METHOD FLOWCHART

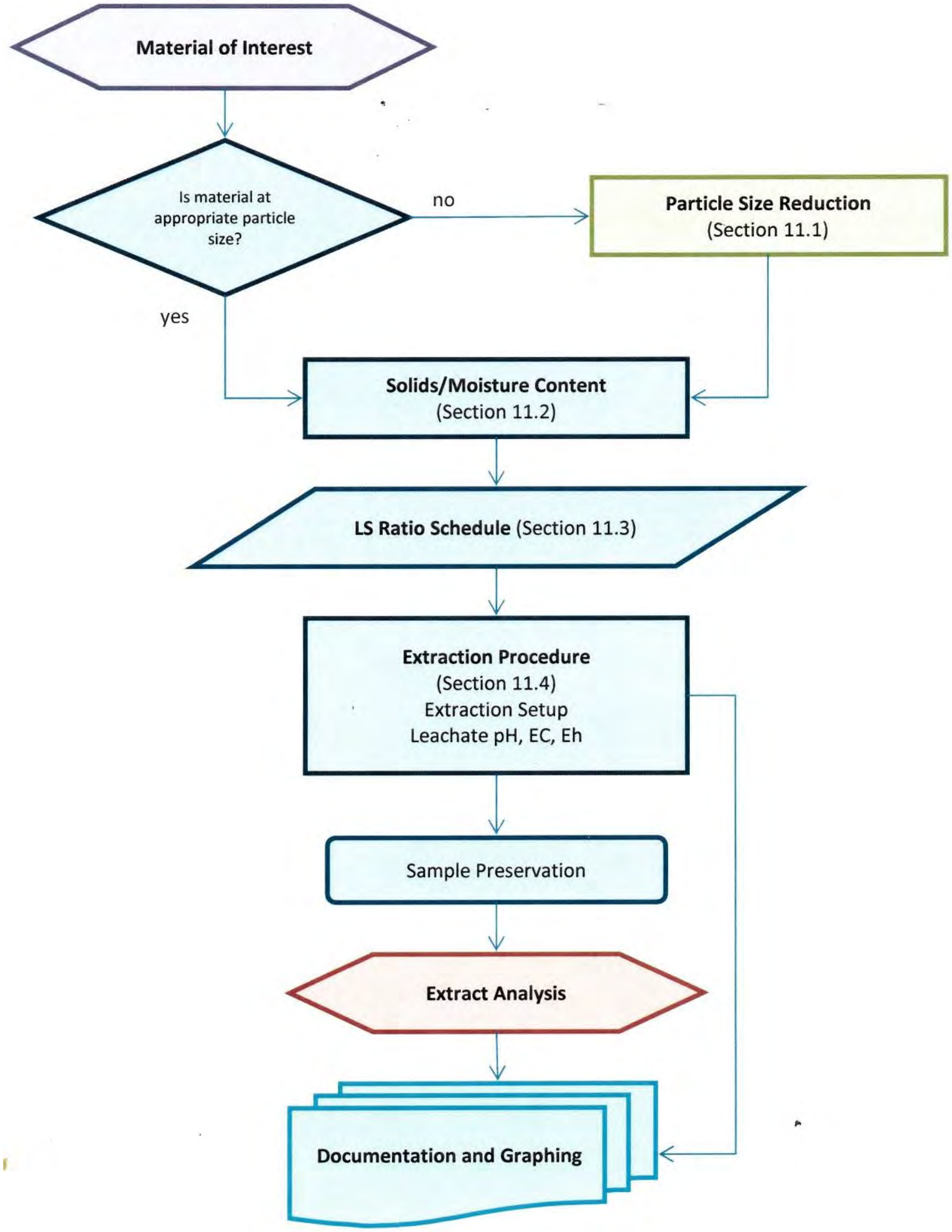
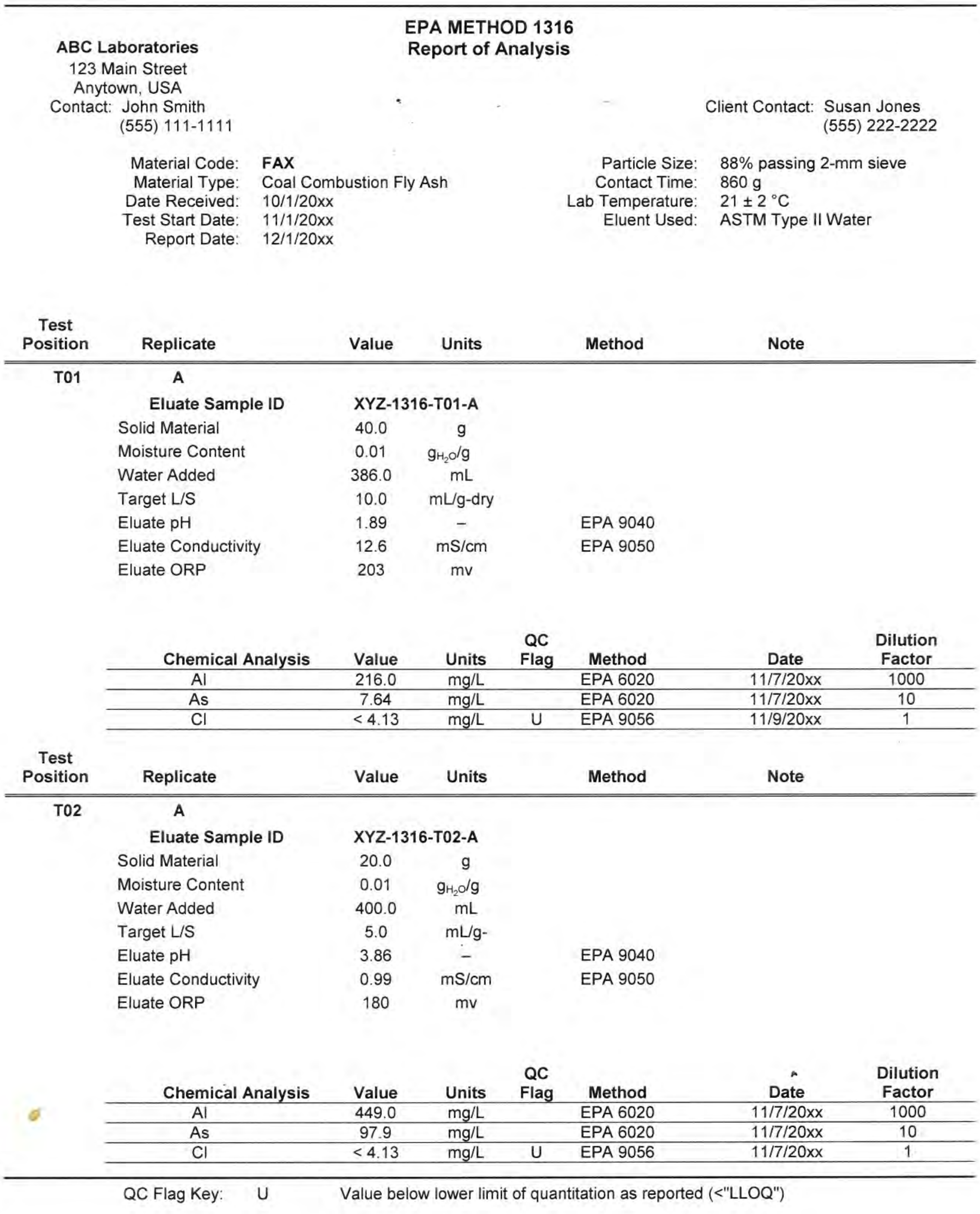


FIGURE 2

EXAMPLE DATA REPORTING FORMAT



EPA METHOD 1316
Report of Analysis

ABC Laboratories
123 Main Street
Anytown, USA
Contact: John Smith
(555) 111-1111

Client Contact: Susan Jones
(555) 222-2222

Material Code: **FAX**
Material Type: Coal Combustion Fly Ash
Date Received: 10/1/20xx
Test Start Date: 11/1/20xx
Report Date: 12/1/20xx

Particle Size: 88% passing 2-mm sieve
Contact Time: 860 g
Lab Temperature: 21 ± 2 °C
Eluent Used: ASTM Type II Water

Test Position	Replicate	Value	Units	Method	Note
T01	**A**				
	Eluate Sample ID	**XYZ-1316-T01-A**			
	Solid Material	40.0	g		
	Moisture Content	0.01	g_{H_2O}/g		
	Water Added	386.0	mL		
	Target L/S	10.0	mL/g-dry		
	Eluate pH	1.89	–	EPA 9040	
	Eluate Conductivity	12.6	mS/cm	EPA 9050	
	Eluate ORP	203	mv		

Chemical Analysis	Value	Units	QC Flag	Method	Date	Dilution Factor
Al	216.0	mg/L		EPA 6020	11/7/20xx	1000
As	7.64	mg/L		EPA 6020	11/7/20xx	10
Cl	< 4.13	mg/L	U	EPA 9056	11/9/20xx	1

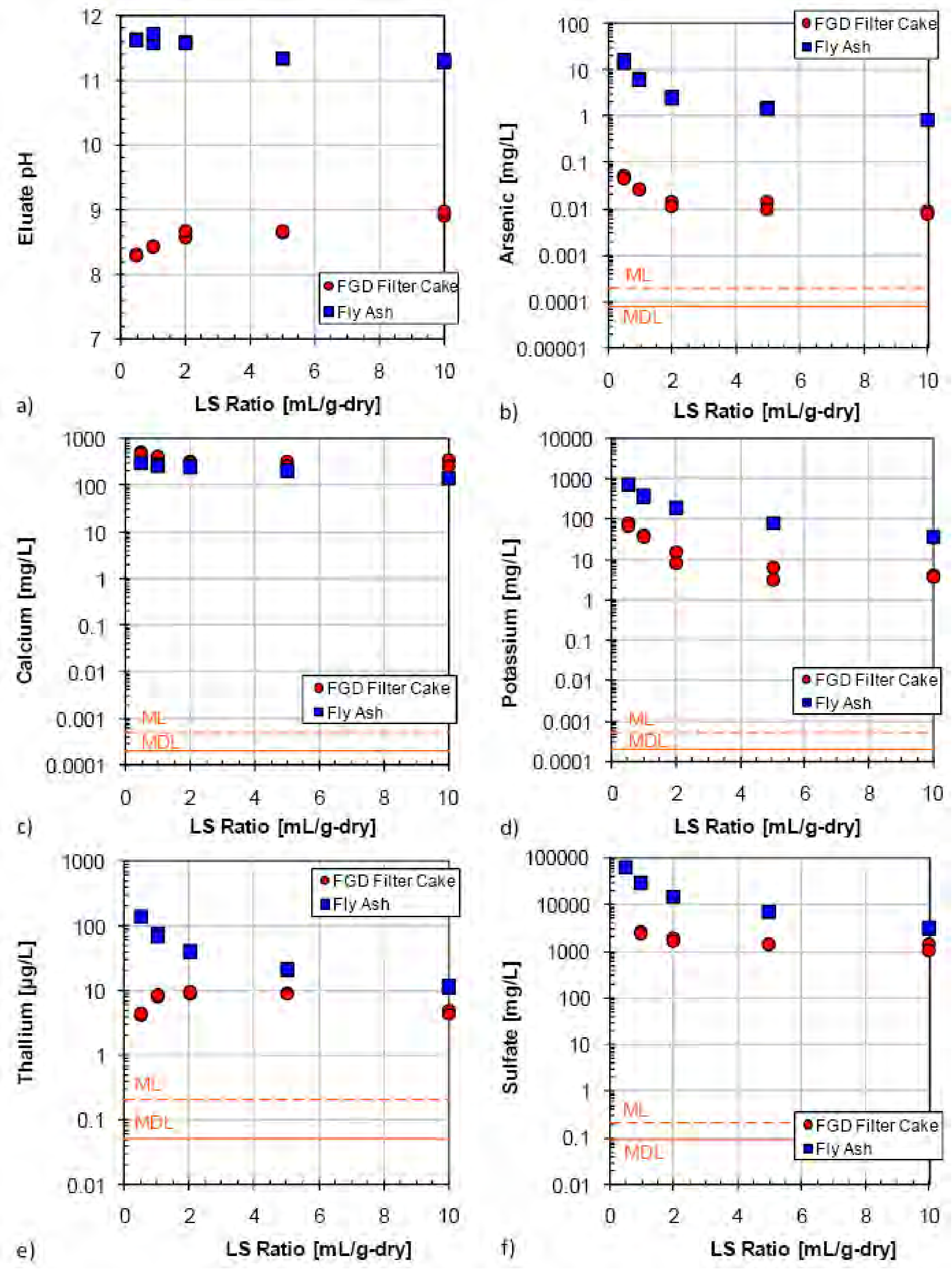
Test Position	Replicate	Value	Units	Method	Note
T02	**A**				
	Eluate Sample ID	**XYZ-1316-T02-A**			
	Solid Material	20.0	g		
	Moisture Content	0.01	g_{H_2O}/g		
	Water Added	400.0	mL		
	Target L/S	5.0	mL/g-		
	Eluate pH	3.86	–	EPA 9040	
	Eluate Conductivity	0.99	mS/cm	EPA 9050	
	Eluate ORP	180	mv		

Chemical Analysis	Value	Units	QC Flag	Method	Date	Dilution Factor
Al	449.0	mg/L		EPA 6020	11/7/20xx	1000
As	97.9	mg/L		EPA 6020	11/7/20xx	10
Cl	< 4.13	mg/L	U	EPA 9056	11/7/20xx	1

QC Flag Key: U Value below lower limit of quantitation as reported (<"LLOQ")

FIGURE 3

EXAMPLE CONCENTRATON RESULTS FROM A COAL COMBUSTION FLY ASH AND FLUE-GAS DESULFURIZATION FILTER CAKE



DOCUMENT

8

U.S. ENVIRONMENTAL PROTECTION AGENCY REGION I

LOW STRESS (low flow) PURGING AND SAMPLING PROCEDURE FOR THE COLLECTION OF GROUNDWATER SAMPLES FROM MONITORING WELLS

Quality Assurance Unit
U.S. Environmental Protection Agency – Region 1
11 Technology Drive
North Chelmsford, MA 01863

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Prepared by: ROBERT REINHART Digitally signed by ROBERT REINHART Date: 2017.09.19 16:15:38 -04'00' ____________
(Robert Reinhart, Quality Assurance Unit) Date

Approved by: JOHN SMALDONE Digitally signed by JOHN SMALDONE Date: 2017.09.20 15:11:00 -04'00' ____________
(John Smaldone, Quality Assurance Unit) Date

Revision Page

Date	**Rev #**	**Summary of changes**	**Sections**
7/30/96	1	Finalized	
01/19/10	2	Updated	All sections
3/23/17	3	Updated	All sections
9/20/17	4	Updated	Section 7.0

Table of Contents

1.0 USE OF TERMS

Equipment blank: The equipment blank shall include the pump and the pump's tubing. If tubing is dedicated to the well, the equipment blank needs only to include the pump in subsequent sampling rounds. If the pump and tubing are dedicated to the well, the equipment blank is collected prior to its placement in the well. If the pump and tubing will be used to sample multiple wells, the equipment blank is normally collected after sampling from contaminated wells and not after background wells.

Field duplicates: Field duplicates are collected to determine precision of the sampling procedure. For this procedure, collect duplicate for each analyte group in consecutive order (VOC original, VOC duplicate, SVOC original, SVOC duplicate, etc.).

Indicator field parameters: This SOP uses field measurements of turbidity, dissolved oxygen, specific conductance, temperature, pH, and oxidation/reduction potential (ORP) as indicators of when purging operations are sufficient and sample collection may begin.

Matrix Spike/Matrix Spike Duplicates: Used by the laboratory in its quality assurance program. Consult the laboratory for the sample volume to be collected.

Potentiometric Surface: The level to which water rises in a tightly cased well constructed in a confined aquifer. In an unconfined aquifer, the potentiometric surface is the water table.

QAPP: Quality Assurance Project Plan

SAP: Sampling and Analysis Plan

SOP: Standard operating procedure

Stabilization: A condition that is achieved when all indicator field parameter measurements are sufficiently stable (as described in the “Monitoring Indicator Field Parameters” section) to allow sample collection to begin.

Temperature blank: A temperature blank is added to each sample cooler. The blank is measured upon receipt at the laboratory to assess whether the samples were properly cooled during transit.

Trip blank (VOCs): Trip blank is a sample of analyte-free water taken to the sampling site and returned to the laboratory. The trip blanks (one pair) are added to each sample cooler that contains VOC samples.

2.0 SCOPE & APPLICATION

The goal of this groundwater sampling procedure is to collect water samples that reflect the total mobile organic and inorganic loads (dissolved and colloidal sized fractions) transported through the subsurface under ambient flow conditions, with minimal physical and chemical alterations from sampling operations. This standard operating procedure (SOP) for collecting groundwater samples will help ensure that the project's data quality objectives (DQOs) are met under certain low-flow conditions.

The SOP emphasizes the need to minimize hydraulic stress at the well-aquifer interface by maintaining low water-level drawdowns, and by using low pumping rates during purging and sampling operations. Indicator field parameters (e.g., dissolved oxygen, pH, etc.) are monitored during purging in order to determine when sample collection may begin. Samples properly collected using this SOP are suitable for analysis of groundwater contaminants (volatile and semi-volatile organic analytes, dissolved gases, pesticides, PCBs, metals and other inorganics), or naturally occurring analytes. This SOP is based on Puls, and Barcelona (1996).

This procedure is designed for monitoring wells with an inside diameter (1.5-inches or greater) that can accommodate a positive lift pump with a screen length or open interval ten feet or less and with a water level above the top of the screen or open interval (Hereafter, the "screen or open interval" will be referred to only as "screen interval"). This SOP is not applicable to other well-sampling conditions.

While the use of dedicated sampling equipment is not mandatory, dedicated pumps and tubing can reduce sampling costs significantly by streamlining sampling activities and thereby reducing the overall field costs.

The goal of this procedure is to emphasize the need for consistency in deploying and operating equipment while purging and sampling monitoring wells during each sampling event. This will help to minimize sampling variability.

This procedure describes a general framework for groundwater sampling. Other site specific information (hydrogeological context, conceptual site model (CSM), DQOs, etc.) coupled with systematic planning must be added to the procedure in order to develop an appropriate site specific SAP/QAPP. In addition, the site specific SAP/QAPP must identify the specific equipment that will be used to collect the groundwater samples.

This procedure does not address the collection of water or free product samples from wells containing free phase LNAPLs and/or DNAPLs (light or dense non-aqueous phase liquids). For this type of situation, the reader may wish to check: Cohen, and Mercer (1993) or other pertinent documents.

This SOP is to be used when collecting groundwater samples from monitoring wells at all Superfund, Federal Facility and RCRA sites in Region 1 under the conditions described herein. Request for modification of this SOP, in order to better address specific situations at individual wells, must include adequate technical justification for proposed changes. All changes and modifications must be approved and included in a revised SAP/QAPP before implementation in field.

3.0 BACKGROUND FOR IMPLEMENTATION

It is expected that the monitoring well screen has been properly located (both laterally and vertically) to intercept existing contaminant plume(s) or along flow paths of potential contaminant migration. Problems with inappropriate monitoring well placement or faulty/improper well installation cannot be overcome by even the best water sampling procedures. This SOP presumes that the analytes of interest are moving (or will potentially move) primarily through the more permeable zones intercepted by the screen interval.

Proper well construction, development, and operation and maintenance cannot be overemphasized. The use of installation techniques that are appropriate to the hydrogeologic setting of the site often prevent "problem well" situations from occurring. During well development, or redevelopment, tests should be conducted to determine the hydraulic characteristics of the monitoring well. The data can then be used to set the purging/sampling rate, and provide a baseline for evaluating changes in well performance and the potential need for well rehabilitation. Note: if this installation data or well history (construction and sampling) is not available or discoverable, for all wells to be sampled, efforts to build a sampling history should commence with the next sampling event.

The pump intake should be located within the screen interval and at a depth that will remain under water at all times. It is recommended that the intake depth and pumping rate remain the same for all sampling events. The mid-point or the lowest historical midpoint of the saturated screen length is often used as the location of the pump intake. For new wells, or for wells without pump intake depth information, the site’s SAP/QAPP must provide clear reasons and instructions on how the pump intake depth(s) will be selected, and reason(s) for the depth(s) selected. If the depths to top and bottom of the well screen are not known, the SAP/QAPP will need to describe how the sampling depth will be determined and how the data can be used.

Stabilization of indicator field parameters is used to indicate that conditions are suitable for sampling to begin. Achievement of turbidity levels of less than 5 NTU, and stable drawdowns of less than 0.3 feet, while desirable, are not mandatory. Sample collection may still take place provided the indicator field parameter criteria in this procedure are met. If after 2 hours of purging indicator field parameters have not stabilized, one of three optional courses of action may be taken: a) continue purging until stabilization is achieved, b) discontinue purging, do not collect any samples, and record in log book that stabilization could not be achieved (documentation must describe attempts to achieve stabilization), c) discontinue purging, collect samples and provide full explanation of attempts to achieve stabilization (note: there is a risk that the analytical data obtained, especially metals and strongly hydrophobic organic analytes, may reflect a sampling bias and therefore, the data may not meet the data quality objectives of the sampling event).

It is recommended that low-flow sampling be conducted when the air temperature is above 32°F (0°C). If the procedure is used below 32°F, special precautions will need to be taken to prevent the groundwater from freezing in the equipment. Because sampling during freezing temperatures may adversely impact the data quality objectives, the need for water sample collection during months when these conditions are likely to occur should be evaluated during site planning and special sampling measures may need to be developed. Ice formation in the flow-through-cell will cause the monitoring probes to act erratically. A transparent flow-through-cell needs to be used to observe if ice is forming in the cell. If ice starts to form on the other pieces of the sampling equipment, additional problems may occur.

4.0 HEALTH & SAFETY

When working on-site, comply with all applicable OSHA requirements and the site’s health/safety procedures. All proper personal protection clothing and equipment are to be worn. Some samples may contain biological and chemical hazards. These samples should be handled with suitable protection to skin, eyes, etc.

5.0 CAUTIONS

The following cautions need to be considered when planning to collect groundwater samples when the below conditions occur.

If the groundwater degasses during purging of the monitoring well, dissolved gases and VOCs will be lost. When this happens, the groundwater data for dissolved gases (e.g., methane, ethene, ethane, dissolved oxygen, etc.) and VOCs will need to be qualified. Some conditions that can promote degassing are the use of a vacuum pump (e.g., peristaltic pumps), changes in aperture along the sampling tubing, and squeezing/pinching the pump’s tubing which results in a pressure change.

When collecting the samples for dissolved gases and VOCs analyses, avoid aerating the groundwater in the pump’s tubing. This can cause loss of the dissolved gases and VOCs in the groundwater. Having the pump's tubing completely filled prior to sampling will avoid this problem when using a centrifugal pump or peristaltic pump.

Direct sun light and hot ambient air temperatures may cause the groundwater in the tubing and flow-through-cell to heat up. This may cause the groundwater to degas which will result in loss of VOCs and dissolved gases. When sampling under these conditions, the sampler will need to shade the equipment from the sunlight (e.g., umbrella, tent, etc.). If possible, sampling on hot days, or during the hottest time of the day, should be avoided. The tubing exiting the monitoring well should be kept as short as possible to avoid the sun light or ambient air from heating up the groundwater.

Thermal currents in the monitoring well may cause vertical mixing of water in the well bore. When the air temperature is colder than the groundwater temperature, it can cool the top of the water column. Colder water which is denser than warm water sinks to the bottom of the well and the warmer water at the bottom of the well rises, setting up a convection cell. "During low-flow sampling, the pumped water may be a mixture of convecting water from within the well casing and aquifer water moving inward through the screen. This mixing of water during low-flow sampling can substantially increase equilibration times, can cause false stabilization of indicator parameters, can give false indication of redox state, and can provide biological data that are not representative of the aquifer conditions" (Vroblesky 2007).

Failure to calibrate or perform proper maintenance on the sampling equipment and measurement instruments (e.g., dissolved oxygen meter, etc.) can result in faulty data being collected.

Interferences may result from using contaminated equipment, cleaning materials, sample containers, or uncontrolled ambient/surrounding air conditions (e.g., truck/vehicle exhaust nearby).

Cross contamination problems can be eliminated or minimized through the use of dedicated sampling equipment and/or proper planning to avoid ambient air interferences. Note that the use of dedicated sampling equipment can also significantly reduce the time needed to complete each sampling event, will promote consistency in the sampling, and may reduce sampling bias by having the pump's intake at a constant depth.

Clean and decontaminate all sampling equipment prior to use. All sampling equipment needs to be routinely checked to be free from contaminants and equipment blanks collected to ensure that the equipment is free of contaminants. Check the previous equipment blank data for the site (if they exist) to determine if the previous cleaning procedure removed the contaminants. If contaminants were detected and they are a concern, then a more vigorous cleaning procedure will be needed.

6.0 PERSONNEL QUALIFICATIONS

All field samplers working at sites containing hazardous waste must meet the requirements of the OSHA regulations. OSHA regulations may require the sampler to take the 40 hour OSHA health and safety training course and a refresher course prior to engaging in any field activities, depending upon the site and field conditions.

The field samplers must be trained prior to the use of the sampling equipment, field instruments, and procedures. Training is to be conducted by an experienced sampler before initiating any sampling procedure.

The entire sampling team needs to read, and be familiar with, the site Health and Safety Plan, all relevant SOPs, and SAP/QAPP (and the most recent amendments) before going onsite for the sampling event. It is recommended that the field sampling leader attest to the understanding of these site documents and that it is recorded.

7.0 EQUIPMENT AND SUPPLIES

A. Informational materials for sampling event

A copy of the current Health and Safety Plan, SAP/QAPP, monitoring well construction data, location map(s), field data from last sampling event, manuals for sampling, and the monitoring instruments’ operation, maintenance, and calibration manuals should be brought to the site.

B. Well keys.

C. Extraction device

Adjustable rate, submersible pumps (e.g., centrifugal, bladder, etc.) which are constructed of stainless steel or polytetrafluoroethylene (PTFE, i.e. Teflon®) are preferred. PTFE, however, should not be used when sampling for per- and polyfluoroalkyl substances (PFAS) as it is likely to contain these substances.

Note: If extraction devices constructed of other materials are to be used, adequate information must be provided to show that the substituted materials do not leach contaminants nor cause interferences to the analytical procedures to be used. Acceptance of these materials must be obtained before the sampling event.

If bladder pumps are selected for the collection of VOCs and dissolved gases, the pump setting should be set so that one pulse will deliver a water volume that is sufficient to fill a 40 mL VOC vial. This is not mandatory, but is considered a “best practice”. For the proper operation, the bladder pump will need a minimum amount of water above the pump; consult the manufacturer for the recommended submergence. The pump’s recommended submergence value should be determined during the planning stage, since it may influence well construction and placement of dedicated pumps where water-level fluctuations are significant.

Adjustable rate, peristaltic pumps (suction) are to be used with caution when collecting samples for VOCs and dissolved gases (e.g., methane, carbon dioxide, etc.) analyses. Additional information on the use of peristaltic pumps can be found in Appendix A. If peristaltic pumps are used, the inside diameter of the rotor head tubing needs to match the inside diameter of the tubing installed in the monitoring well.

Inertial pumping devices (motor driven or manual) are not recommended. These devices frequently cause greater disturbance during purging and sampling, and are less easily controlled than submersible pumps (potentially increasing turbidity and sampling variability, etc.). This can lead to sampling results that are adversely affected by purging and sampling operations, and a higher degree of data variability.

D. Tubing

PTFE (Teflon®) or PTFE-lined polyethylene tubing are preferred when sampling is to include VOCs, SVOCs, pesticides, PCBs and inorganics. As discussed in the previous section, PTFE tubing should not be used when sampling for PFAS. In this case, a suitable alternative such as high-density polyethylene tubing should be used.

PVC, polypropylene or polyethylene tubing may be used when collecting samples for metal and other inorganics analyses.

Note: If tubing constructed of other materials is to be used, adequate information must be provided to show that the substituted materials do not leach contaminants nor cause interferences to the analytical procedures to be used. Acceptance of these materials must be obtained before the sampling event.

The use of 1/4 inch or 3/8 inch (inside diameter) tubing is recommended. This will help ensure that the tubing remains liquid filled when operating at very low pumping rates when using centrifugal and peristaltic pumps.

Silastic tubing should be used for the section around the rotor head of a peristaltic pump. It should be less than a foot in length. The inside diameter of the tubing used at the pump rotor head must be the same as the inside diameter of tubing placed in the well. A tubing connector is used to connect the pump rotor head tubing to the well tubing. Alternatively, the two pieces of tubing can be connected to each other by placing the one end of the tubing inside the end of the other tubing. The tubing must not be reused.

E. The water level measuring device

Electronic ”tape”, pressure transducer, water level sounder/level indicator, etc. should be capable of measuring to 0.01 foot accuracy. Recording pressure transducers, mounted above the pump, are especially helpful in tracking water levels during pumping operations, but their use must include check measurements with a water level “tape” at the start and end of each sampling event.

F. Flow measurement supplies

Graduated cylinder (size according to flow rate) and stopwatch usually will suffice.

Large graduated bucket used to record total water purged from the well.

G. Interface probe

To be used to check on the presence of free phase liquids (LNAPL, or DNAPL) before purging begins (as needed).

H. Power source (generator, nitrogen tank, battery, etc.)

When a gasoline generator is used, locate it downwind and at least 30 feet from the well so that the exhaust fumes do not contaminate samples.

I. Indicator field parameter monitoring instruments

Use of a multi-parameter instrument capable of measuring pH, oxidation/reduction potential (ORP), dissolved oxygen (DO), specific conductance, temperature, and coupled with a flow-through-cell is required when measuring all indicator field parameters, except turbidity. Turbidity is collected using a separate instrument. Record equipment/instrument identification (manufacturer, and model number).

Transparent, small volume flow-through-cells (e.g., 250 mLs or less) are preferred. This allows observation of air bubbles and sediment buildup in the cell, which can interfere with the operation of the monitoring instrument probes, to be easily detected. A small volume cell facilitates rapid turnover of water in the cell between measurements of the indicator field parameters.

It is recommended to use a flow-through-cell and monitoring probes from the same manufacturer and model to avoid incompatibility between the probes and flow-through-cell.

Turbidity samples are collected before the flow-through-cell. A “T” connector coupled with a valve is connected between the pump’s tubing and flow-through-cell. When a turbidity measurement is required, the valve is opened to allow the groundwater to flow into a container. The valve is closed and the container sample is then placed in the turbidimeter.

Standards are necessary to perform field calibration of instruments. A minimum of two standards are needed to bracket the instrument measurement range for all parameters except ORP which use a Zobell solution as a standard. For dissolved oxygen, a wet sponge used for the 100% saturation and a zero dissolved oxygen solution are used for the calibration.

Barometer (used in the calibration of the Dissolved Oxygen probe) and the conversion formula to convert the barometric pressure into the units of measure used by the Dissolved Oxygen meter are needed.

J. Decontamination supplies

Includes (for example) non-phosphate detergent, distilled/deionized water, isopropyl alcohol, etc.

K. Record keeping supplies

Logbook(s), well purging forms, chain-of-custody forms, field instrument calibration forms, etc.

L. Sample bottles

M. Sample preservation supplies (as required by the analytical methods)

N. Sample tags or labels

O. PID or FID instrument

If appropriate, to detect VOCs for health and safety purposes, and provide qualitative field evaluations.

P. Miscellaneous Equipment

Equipment to keep the sampling apparatus shaded in the summer (e.g., umbrella) and from freezing in the winter. If the pump's tubing is allowed to heat up in the warm weather, the cold groundwater may degas as it is warmed in the tubing.

8.0 EQUIPMENT/INSTRUMENT CALIBRATION

Prior to the sampling event, perform maintenance checks on the equipment and instruments according to the manufacturer's manual and/or applicable SOP. This will ensure that the equipment/instruments are working properly before they are used in the field.

Prior to sampling, the monitoring instruments must be calibrated and the calibration documented. The instruments are calibrated using U.S Environmental Protection Agency Region 1 *Calibration of Field Instruments (temperature, pH, dissolved oxygen, conductivity/specific conductance, oxidation/reduction [ORP], and turbidity),* March 23, 2017, or latest version or from one of the methods listed in 40CFR136, 40CFR141 and SW-846.

The instruments shall be calibrated at the beginning of each day. If the field measurement falls outside the calibration range, the instrument must be re-calibrated so that all measurements fall within the calibration range. At the end of each day, a calibration check is performed to verify that instruments remained in calibration throughout the day. This check is performed while the instrument is in measurement mode, not calibration mode. If the field instruments are being used to monitor the natural attenuation parameters, then a calibration check at mid-day is highly recommended to ensure that the instruments did not drift out of calibration. Note: during the day if the instrument reads zero or a negative number for dissolved oxygen, pH, specific conductance, or turbidity (negative value only), this indicates that the instrument drifted out of calibration or the instrument is malfunctioning. If this situation occurs the data from this instrument will need to be qualified or rejected.

9.0 PRELIMINARY SITE ACTIVITIES (as applicable)

Check the well for security (damage, evidence of tampering, missing lock, etc.) and record pertinent observations (include photograph as warranted).

If needed, lay out a sheet of clean polyethylene for monitoring and sampling equipment, unless equipment is elevated above the ground (e.g., on a table, etc.).

Remove well cap and if appropriate measure VOCs at the rim of the well with a PID or FID instrument and record reading in field logbook or on the well purge form.

If the well casing does not have an established reference point (usually a V-cut or indelible mark in the well casing), make one. Describe its location and record the date of the mark in the logbook (consider a photographic record as well). All water level measurements must be recorded relative to this reference point (and the altitude of this point should be determined using techniques that are appropriate to site's DQOs.

If water-table or potentiometric surface map(s) are to be constructed for the sampling event, perform synoptic water level measurement round (in the shortest possible time) before any purging and sampling activities begin. If possible, measure water level depth (to 0.01 ft.) and total well depth (to 0.1 ft.) the day before sampling begins, in order to allow for re-settlement of any particulates in the water column. This is especially important for those wells that have not been recently sampled because sediment buildup in the well may require the well to be redeveloped. If measurement of total well depth is not made the day before, it should be measured after sampling of the well is complete. All measurements must be taken from the established referenced point. Care should be taken to minimize water column disturbance.

Check newly constructed wells for the presence of LNAPLs or DNAPLs before the initial sampling round. If none are encountered, subsequent check measurements with an interface probe may not be necessary unless analytical data or field analysis signal a worsening situation. This SOP cannot be used in the presence of LNAPLs or DNAPLs. If NAPLs are present, the project team must decide upon an alternate sampling method. All project modifications must be approved and documented prior to implementation.

If available check intake depth and drawdown information from previous sampling event(s) for each well. Duplicate, to the extent practicable, the intake depth and extraction rate (use final pump dial setting information) from previous event(s). If changes are made in the intake depth or extraction rate(s) used during previous sampling event(s), for either portable or dedicated extraction devices, record new values, and explain reasons for the changes in the field logbook.

10.0 PURGING AND SAMPLING PROCEDURE

Purging and sampling wells in order of increasing chemical concentrations (known or anticipated) are preferred.

The use of dedicated pumps is recommended to minimize artificial mobilization and entrainment of particulates each time the well is sampled. Note that the use of dedicated sampling equipment can also significantly reduce the time needed to complete each sampling event, will promote consistency in the sampling, and may reduce sampling bias by having the pump's intake at a constant depth.

A. Initial Water Level

Measure the water level in the well before installing the pump if a non-dedicated pump is being used. The initial water level is recorded on the purge form or in the field logbook.

B. Install Pump

Lower pump, safety cable, tubing and electrical lines slowly (to minimize disturbance) into the well to the appropriate depth (may not be the mid-point of the screen/open interval). The Sampling and Analysis Plan/Quality Assurance Project Plan should specify the sampling depth (used previously), or provide criteria for selection of intake depth for each new well. If possible keep the pump intake at least two feet above the bottom of the well, to minimize mobilization of particulates present in the bottom of the well.

Pump tubing lengths, above the top of well casing should be kept as short as possible to minimize heating the groundwater in the tubing by exposure to sun light and ambient air temperatures. Heating may cause the groundwater to degas, which is unacceptable for the collection of samples for VOC and dissolved gases analyses.

C. Measure Water Level

Before starting pump, measure water level. Install recording pressure transducer, if used to track drawdowns, to initialize starting condition.

D. Purge Well

From the time the pump starts purging and until the time the samples are collected, the purged water is discharged into a graduated bucket to determine the total volume of groundwater purged. This information is recorded on the purge form or in the field logbook.

Start the pump at low speed and slowly increase the speed until discharge occurs. Check water level. Check equipment for water leaks and if present fix or replace the affected equipment. Try to match pumping rate used during previous sampling event(s). Otherwise, adjust pump speed until there is little or no water level drawdown. If the minimal drawdown that can be achieved exceeds 0.3 feet, but remains stable, continue purging.

Monitor and record the water level and pumping rate every five minutes (or as appropriate) during purging. Record any pumping rate adjustments (both time and flow rate). Pumping rates should, as needed, be reduced to the minimum capabilities of the pump to ensure stabilization of the water level. Adjustments are best made in the first fifteen minutes of pumping in order to help minimize purging time. During pump start-up, drawdown may exceed the 0.3 feet target and then "recover" somewhat as pump flow adjustments are made. Purge volume calculations should utilize stabilized drawdown value, not the initial drawdown. If the initial water level is above the top of the screen do not allow the water level to fall into the well screen. The final purge volume must be greater than the stabilized drawdown volume plus the pump’s tubing volume. If the drawdown has exceeded 0.3 feet and stabilizes, calculate the volume of water between the initial water level and the stabilized water level. Add the volume of the water which occupies the pump’s tubing to this calculation. This combined volume of water needs to be purged from the well after the water level has stabilized before samples are collected.

Avoid the use of constriction devices on the tubing to decrease the flow rate because the constrictor will cause a pressure difference in the water column. This will cause the groundwater to degas and result in a loss of VOCs and dissolved gasses in the groundwater samples.

Note: the flow rate used to achieve a stable pumping level should remain constant while monitoring the indicator parameters for stabilization and while collecting the samples.

Wells with low recharge rates may require the use of special pumps capable of attaining very low pumping rates (e.g., bladder, peristaltic), and/or the use of dedicated equipment. For new monitoring wells, or wells where the following situation has not occurred before, if the recovery rate to the well is less than 50 mL/min., or the well is being essentially dewatered during purging, the well should be sampled as soon as the water level has recovered sufficiently to collect the volume needed for all anticipated samples. The project manager or field team leader will need to make the decision when samples should be collected, how the sample is to be collected, and the reasons recorded on the purge form or in the field logbook. A water level measurement needs to be performed and recorded before samples are collected. If the project manager decides to collect the samples using the pump, it is best during this recovery period that the pump intake tubing not be removed, since this will aggravate any turbidity problems. Samples in this specific situation may be collected without stabilization of indicator field parameters. Note that field conditions and efforts to overcome problematic situations must be recorded in order to support field decisions to deviate from normal procedures described in this SOP. If this type of problematic situation persists in a well, then water sample collection should be changed to a passive or no-purge method, if consistent with the site's DQOs, or have a new well installed.

E. Monitor Indicator Field Parameters

After the water level has stabilized, connect the "T" connector with a valve and the flow-through-cell to monitor the indicator field parameters. If excessive turbidity is anticipated or encountered with the pump startup, the well may be purged for a while without connecting up the flow-through-cell, in order to minimize particulate buildup in the cell (This is a judgment call made by the sampler). Water level drawdown measurements should be made as usual. If possible, the pump may be installed the day before purging to allow particulates that were disturbed during pump insertion to settle.

During well purging, monitor indicator field parameters (turbidity, temperature, specific conductance, pH, ORP, DO) at a frequency of five minute intervals or greater. The pump's flow rate must be able to "turn over" at least one flow-through-cell volume between measurements (for a 250 mL flow-through-cell with a flow rate of 50 mLs/min., the monitoring frequency would be every five minutes; for a 500 mL flow-through-cell it would be every ten minutes). If the cell volume cannot be replaced in the five minute interval, then the time between measurements must be increased accordingly. Note: during the early phase of purging, emphasis should be put on minimizing and stabilizing pumping stress, and recording those adjustments followed by stabilization of indicator parameters. Purging is considered complete and sampling may begin when all the above indicator field parameters have stabilized. Stabilization is considered to be achieved when three consecutive readings are within the following limits:

Turbidity (10% for values greater than 5 NTU; if three Turbidity values are less than 5 NTU, consider the values as stabilized),
Dissolved Oxygen (10% for values greater than 0.5 mg/L, if three Dissolved Oxygen values are less than 0.5 mg/L, consider the values as stabilized),
Specific Conductance (3%),
Temperature (3%),
pH (± 0.1 unit),
Oxidation/Reduction Potential (±10 millivolts).

All measurements, except turbidity, must be obtained using a flow-through-cell. Samples for turbidity measurements are obtained before water enters the flow-through-cell. Transparent flow-through-cells are preferred, because they allow field personnel to watch for particulate build-up within the cell. This build-up may affect indicator field parameter values measured within the cell. If the cell needs to be cleaned during purging operations, continue pumping and disconnect cell for cleaning, then reconnect after cleaning and continue monitoring activities. Record start and stop times and give a brief description of cleaning activities.

The flow-through-cell must be designed in a way that prevents gas bubble entrapment in the cell. Placing the flow-through-cell at a 45 degree angle with the port facing upward can help remove bubbles from the flow-through-cell (see Appendix B Low-Flow Setup Diagram). Throughout the measurement process, the flow-through-cell must remain free of any gas bubbles. Otherwise, the monitoring probes may act erratically. When the pump is turned off or cycling on/off (when using a bladder pump), water in the cell must not drain out. Monitoring probes must remain submerged in water at all times.

F. Collect Water Samples

When samples are collected for laboratory analyses, the pump's tubing is disconnected from the "T" connector with a valve and the flow-through-cell. The samples are collected directly from the pump's tubing. Samples must not be collected from the flow-through-cell or from the "T" connector with a valve.

VOC samples are normally collected first and directly into pre-preserved sample containers. However, this may not be the case for all sampling locations; the SAP/QAPP should list the order in which the samples are to be collected based on the project's objective(s). Fill all sample containers by allowing the pump discharge to flow gently down the inside of the container with minimal turbulence.

If the pump's flow rate is too high to collect the VOC/dissolved gases samples, collect the other samples first. Lower the pump's flow rate to a reasonable rate and collect the VOC/dissolved gases samples and record the new flow rate.

During purging and sampling, the centrifugal/peristaltic pump tubing must remain filled with water to avoid aeration of the groundwater. It is recommended that 1/4 inch or 3/8 inch (inside diameter) tubing be used to help ensure that the sample tubing remains water filled. If the pump tubing is not completely filled to the sampling point, use the following procedure to collect samples: collect non-VOC/dissolved gases samples first, then increase flow rate slightly until the water completely fills the tubing, collect the VOC/dissolved gases samples, and record new drawdown depth and flow rate.

For bladder pumps that will be used to collect VOC or dissolved gas samples, it is recommended that the pump be set to deliver long pulses of water so that one pulse will fill a 40 mL VOC vial.

Use pre-preserved sample containers or add preservative, as required by analytical methods, to the samples immediately after they are collected. Check the analytical methods (e.g. EPA SW-846, 40 CFR 136, water supply, etc.) for additional information on preservation.

If determination of filtered metal concentrations is a sampling objective, collect filtered water samples using the same low flow procedures. The use of an in-line filter (transparent housing preferred) is required, and the filter size (0.45 μm is commonly used) should be based on the sampling objective. Pre-rinse the filter with groundwater prior to sample collection. Make sure the filter is free of air bubbles before samples are collected. Preserve the filtered water sample immediately. Note: filtered water samples are not an acceptable substitute for unfiltered samples when the monitoring objective is to obtain chemical concentrations of total mobile contaminants in groundwater for human health or ecological risk calculations.

Label each sample as collected. Samples requiring cooling will be placed into a cooler with ice or refrigerant for delivery to the laboratory. Metal samples after acidification to a pH less than 2 do not need to be cooled.

G. Post Sampling Activities

If a recording pressure transducer is used to track drawdown, re-measure water level with tape.

After collection of samples, the pump tubing may be dedicated to the well for re-sampling (by hanging the tubing inside the well), decontaminated, or properly discarded.

Before securing the well, measure and record the well depth (to 0.1 ft.), if not measured the day before purging began. Note: measurement of total well depth annually is usually sufficient after the initial low stress sampling event. However, a greater frequency may be needed if the well has a “silting” problem or if confirmation of well identity is needed.

Secure the well.

11.0 DECONTAMINATION

Decontaminate sampling equipment prior to use in the first well, and then following sampling of each subsequent well. Pumps should not be removed between purging and sampling operations. The pump, tubing, support cable and electrical wires which were in contact with the well should be decontaminated by one of the procedures listed below.

The use of dedicated pumps and tubing will reduce the amount of time spent on decontamination of the equipment. If dedicated pumps and tubing are used, only the initial sampling event will require decontamination of the pump and tubing.

Note if the previous equipment blank data showed that contaminant(s) were present after using the below procedure or the one described in the SAP/QAPP, a more vigorous procedure may be needed.

Procedure 1

Decontaminating solutions can be pumped from either buckets or short PVC casing sections through the pump and tubing. The pump may be disassembled and flushed with the decontaminating solutions. It is recommended that detergent and alcohol be used sparingly in the decontamination process and water flushing steps be extended to ensure that any sediment trapped in the pump is removed. The pump exterior and electrical wires must be rinsed with the decontaminating solutions, as well. The procedure is as follows:

Flush the equipment/pump with potable water.

Flush with non-phosphate detergent solution. If the solution is recycled, the solution must be changed periodically.

Flush with potable or distilled/deionized water to remove all of the detergent solution. If the water is recycled, the water must be changed periodically.

Optional - flush with isopropyl alcohol (pesticide grade; must be free of ketones {e.g., acetone}) or with methanol. This step may be required if the well is highly contaminated or if the equipment blank data from the previous sampling event show that the level of contaminants is significant.

Flush with distilled/deionized water. This step must remove all traces of alcohol (if used) from the equipment. The final water rinse must not be recycled.

Procedure 2

Steam clean the outside of the submersible pump.

Pump hot potable water from the steam cleaner through the inside of the pump. This can be accomplished by placing the pump inside a three or four inch diameter PVC pipe with end cap. Hot water from the steam cleaner jet will be directed inside the PVC pipe and the pump exterior will be cleaned. The hot water from the steam cleaner will then be pumped from the PVC pipe through the pump and collected into another container. Note: additives or solutions should not be added to the steam cleaner.

Pump non-phosphate detergent solution through the inside of the pump. If the solution is recycled, the solution must be changed periodically.

Pump potable water through the inside of the pump to remove all of the detergent solution. If the solution is recycled, the solution must be changed periodically.

Pump distilled/deionized water through the pump. The final water rinse must not be recycled.

12.0 FIELD QUALITY CONTROL

Quality control samples are required to verify that the sample collection and handling process has not compromised the quality of the groundwater samples. All field quality control samples must be prepared the same as regular investigation samples with regard to sample volume, containers, and preservation. Quality control samples include field duplicates, equipment blanks, matrix spike/matrix spike duplicates, trip blanks (VOCs), and temperature blanks.

13.0 FIELD LOGBOOK

A field log shall be kept to document all groundwater field monitoring activities (see Appendix C, example table), and record the following for each well:

Site name, municipality, state.

Well identifier, latitude-longitude or state grid coordinates.

Measuring point description (e.g., north side of PVC pipe).

Well depth, and measurement technique.

Well screen length.

Pump depth.

Static water level depth, date, time and measurement technique.

Presence and thickness of immiscible liquid (NAPL) layers and detection method.

Pumping rate, drawdown, indicator parameters values, calculated or measured total volume pumped, and clock time of each set of measurements.

Type of tubing used and its length.

Type of pump used.

Clock time of start and end of purging and sampling activity.

Types of sample bottles used and sample identification numbers.

Preservatives used.

Parameters requested for analyses.

Field observations during sampling event.

Name of sample collector(s).

Weather conditions, including approximate ambient air temperature.

QA/QC data for field instruments.

Any problems encountered should be highlighted.

Description of all sampling/monitoring equipment used, including trade names, model number, instrument identification number, diameters, material composition, etc.

14.0 DATA REPORT

Data reports are to include laboratory analytical results, QA/QC information, field indicator parameters measured during purging, field instrument calibration information, and whatever other field logbook information is needed to allow for a full evaluation of data usability.

Note: the use of trade, product, or firm names in this sampling procedure is for descriptive purposes only and does not constitute endorsement by the U.S. EPA.

15.0 REFERENCES

Cohen, R.M. and J.W. Mercer, 1993, *DNAPL Site Evaluation*; C.K. Smoley (CRC Press), Boca Raton, Florida.

Robert W. Puls and Michael J. Barcelona, *Low-Flow (Minimal Drawdown) Ground-Water Sampling Procedures*, April 1996 (EPA/540/S-95/504).

U.S. Environmental Protection Agency, 1992, *RCRA Ground-Water Monitoring: Draft Technical Guidance*; Washington, DC (EPA/530-R-93-001).

U.S. Environmental Protection Agency, 1987, *A Compendium of Superfund Field Operations Methods*; Washington, DC (EPA/540/P-87/001).

U.S Environmental Protection Agency, Region 1, *Calibration of Field Instruments (temperature, pH, dissolved oxygen, conductivity/specific conductance, oxidation/reduction [ORP], and turbidity),* March 23, 2017 or latest version.

U.S Environmental Protection Agency, EPA SW-846.

U.S Environmental Protection Agency, 40 CFR 136.

U.S Environmental Protection Agency, 40 CFR 141.

Vroblesky, Don A., Clifton C. Casey, and Mark A. Lowery, Summer 2007, Influence of Dissolved Oxygen Convection on Well Sampling, *Ground Water Monitoring & Remediation* 27, no. 3: 49-58.

APPENDIX A

PERISTALTIC PUMPS

Before selecting a peristaltic pump to collect groundwater samples for VOCs and/or dissolved gases, (e.g., methane, carbon dioxide, etc.) consideration should be given to the following:

- The decision of whether or not to use a peristaltic pump is dependent on the intended use of the data.
- If the additional sampling error that may be introduced by this device is NOT of concern for the VOC/dissolved gases data's intended use, then this device may be acceptable.
- If minor differences in the groundwater concentrations could affect the decision, such as to continue or terminate groundwater cleanup or whether the cleanup goals have been reached, then this device should NOT be used for VOC/dissolved gases sampling. In these cases, centrifugal or bladder pumps are a better choice for more accurate results.

EPA and USGS have documented their concerns with the use of the peristaltic pumps to collect water sample in the below documents.

- "Suction Pumps are not recommended because they may cause degassing, pH modification, and loss of volatile compounds" *A Compendium of Superfund Field Operations Methods*, EPA/540/P-87/001, December 1987.
- "The agency does not recommend the use of peristaltic pumps to sample ground water particularly for volatile organic analytes" *RCRA Ground-Water Monitoring Draft Technical Guidance*, EPA Office of Solid Waste, November 1992.
- "The peristaltic pump is limited to shallow applications and can cause degassing resulting in alteration of pH, alkalinity, and volatiles loss", *Low-flow (Minimal drawdown) Ground-Water Sampling Procedures*, by Robert Puls & Michael Barcelona, April 1996, EPA/540/S-95/504.
- "Suction-lift pumps, such as peristaltic pumps, can operate at a very low pumping rate; however, using negative pressure to lift the sample can result in the loss of volatile analytes", USGS Book 9 Techniques of Water-Resources Investigation, Chapter A4. (Version 2.0, 9/2006).

APPENDIX B

SUMMARY OF SAMPLING INSTRUCTIONS

These instructions are for using an adjustable rate, submersible pump or a peristaltic pump with the pump's intake placed at the midpoint of a 10 foot or less well screen or an open interval. The water level in the monitoring well is above the top of the well screen or open interval, the ambient temperature is above 32°F, and the equipment is not dedicated. Field instruments are already calibrated. The equipment is setup according to the diagram at the end of these instructions.

1. Review well installation information. Record well depth, length of screen or open interval, and depth to top of the well screen. Determine the pump's intake depth (e.g., mid-point of screen/open interval).

2. On the day of sampling, check security of the well casing, perform any safety checks needed for the site, lay out a sheet of polyethylene around the well (if necessary), and setup the equipment. If necessary a canopy or an equivalent item can be setup to shade the pump's tubing and flow-through-cell from the sun light to prevent the sun light from heating the groundwater.

3. Check well casing for a reference mark. If missing, make a reference mark. Measure the water level (initial) to 0.01 ft. and record this information.

4. Install the pump's intake to the appropriate depth (e.g., midpoint) of the well screen or open interval. Do not turn-on the pump at this time.

5. Measure water level and record this information.

6. Turn-on the pump and discharge the groundwater into a graduated waste bucket. Slowly increase the flow rate until the water level starts to drop. Reduce the flow rate slightly so the water level stabilizes. Record the pump's settings. Calculate the flow rate using a graduated container and a stop watch. Record the flow rate. Do not let the water level drop below the top of the well screen.

If the groundwater is highly turbid or discolored, continue to discharge the water into the bucket until the water clears (visual observation); this usually takes a few minutes. The turbid or discolored water is usually from the well-being disturbed during the pump installation. If the water does not clear, then you need to make a choice whether to continue purging the well (hoping that it will clear after a reasonable time) or continue to the next step. Note, it is sometimes helpful to install the pump the day before the sampling event so that the disturbed materials in the well can settle out.

If the water level drops to the top of the well screen during the purging of the well, stop purging the well, and do the following:

> Wait for the well to recharge to a sufficient volume so samples can be collected. This may take a while (pump may be removed from well, if turbidity is not a problem). The project manager will need to make the decision when samples should be collected and the reasons recorded in the site's log book. A water level measurement needs to be performed and recorded before samples are collected. When samples are being collected, the water level must not drop below the top of the screen or open interval. Collect the samples from the pump's tubing. Always collect the VOCs and dissolved gases samples first. Normally, the samples requiring a small volume are collected before the large volume samples are collected just in case there is not sufficient water in the well to fill all the sample containers. All samples must be collected, preserved, and stored according to the analytical method. Remove the pump from the well and decontaminate the sampling equipment.

If the water level has dropped 0.3 feet or less from the initial water level (water level measure before the pump was installed); proceed to Step 7. If the water level has dropped more than 0.3 feet, calculate the volume of water between the initial water level and the stabilized water level. Add the volume of the water which occupies the pump's tubing to this calculation. This combined volume of water needs to be purged from the well after the water level has stabilized before samples are be collected.

7. Attach the pump's tubing to the "T" connector with a valve (or a three-way stop cock). The pump's tubing from the well casing to the "T" connector must be as short as possible to prevent the groundwater in the tubing from heating up from the sun light or from the ambient air. Attach a short piece of tubing to the other end of the end of the "T" connector to serve as a sampling port for the turbidity samples. Attach the remaining end of the "T" connector to a short piece of tubing and connect the tubing to the flow-through-cell bottom port. To the top port, attach a small piece of tubing to direct the water into a calibrated waste bucket. Fill the cell with the groundwater and remove all gas bubbles from the cell. Position the flow-through-cell in such a way that if gas bubbles enter the cell they can easily exit the cell. If the ports are on the same side of the cell and the cell is cylindrical shape, the cell can be placed at a 45-degree angle with the ports facing upwards; this position should keep any gas bubbles entering the cell away from the monitoring probes and allow the gas bubbles to exit the cell easily (see Low-Flow Setup Diagram). Note:

make sure there are no gas bubbles caught in the probes' protective guard; you may need to shake the cell to remove these bubbles.

8. Turn-on the monitoring probes and turbidity meter.

9. Record the temperature, pH, dissolved oxygen, specific conductance, and oxidation/reduction potential measurements. Open the valve on the "T" connector to collect a sample for the turbidity measurement, close the valve, do the measurement, and record this measurement. Calculate the pump's flow rate from the water exiting the flow-through-cell using a graduated container and a stop watch, and record the measurement. Measure and record the water level. Check flow-through-cell for gas bubbles and sediment; if present, remove them.

10. Repeat Step 9 every 5 minutes or as appropriate until monitoring parameters stabilized. Note: at least one flow-through-cell volume must be exchanged between readings. If not, the time interval between readings will need to be increased. Stabilization is achieved when three consecutive measurements are within the following limits:

Turbidity (10% for values greater than 5 NTUs; if three Turbidity values are less than 5 NTUs, consider the values as stabilized),
Dissolved Oxygen (10% for values greater than 0.5 mg/L, if three Dissolved Oxygen values are less than 0.5 mg/L, consider the values as stabilized),
Specific Conductance (3%),
Temperature (3%),
pH (± 0.1 unit),
Oxidation/Reduction Potential (±10 millivolts).

If these stabilization requirements do not stabilize in a reasonable time, the probes may have been coated from the materials in the groundwater, from a buildup of sediment in the flow-through-cell, or a gas bubble is lodged in the probe. The cell and the probes will need to be cleaned. Turn-off the probes (not the pump), disconnect the cell from the "T" connector and continue to purge the well. Disassemble the cell, remove the sediment, and clean the probes according to the manufacturer's instructions. Reassemble the cell and connect the cell to the "T" connector. Remove all gas bubbles from the cell, turn-on the probes, and continue the measurements. Record the time the cell was cleaned.

11. When it is time to collect the groundwater samples, turn-off the monitoring probes, and disconnect the pump's tubing from the "T" connector. If you are using a centrifugal or peristaltic pump check the pump's tubing to determine if the tubing is completely filled with water (no air space).

All samples must be collected and preserved according to the analytical method. VOCs and dissolved gases samples are normally collected first and directly into pre-preserved sample containers. However, this may not be the case for all sampling locations; the SAP/QAPP should list the order in which the samples are to be collected based on the project's objective(s). Fill all sample containers by allowing the pump discharge to flow gently down the inside of the container with minimal turbulence.

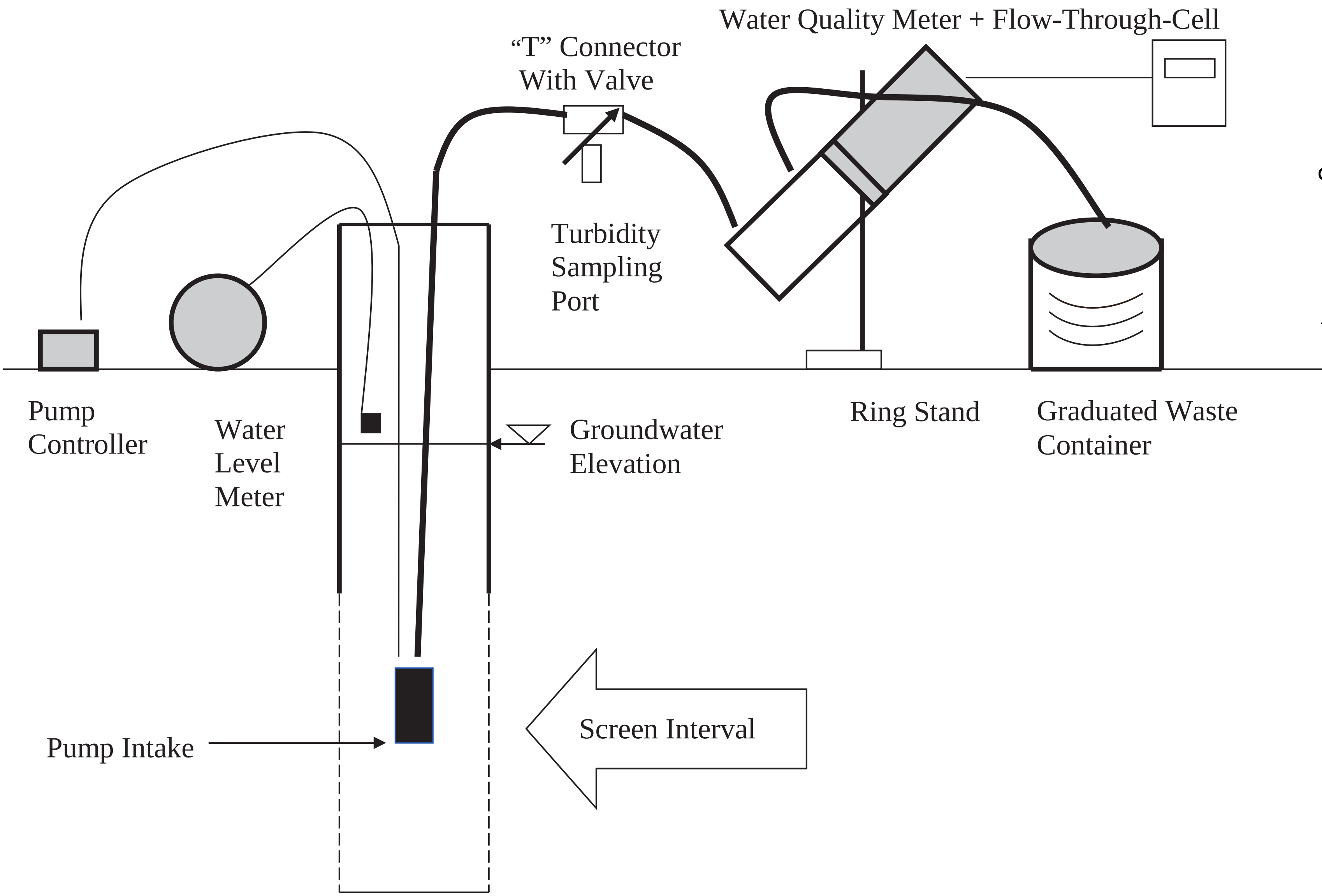
If the pump's tubing is not completely filled with water and the samples are being collected for VOCs and/or dissolved gases analyses using a centrifugal or peristaltic pump, do the following:

> All samples must be collected and preserved according to the analytical method. The VOCs and the dissolved gases (e.g., methane, ethane, ethene, and carbon dioxide) samples are collected last. When it becomes time to collect these samples increase the pump's flow rate until the tubing is completely filled. Collect the samples and record the new flow rate.

12. Store the samples according to the analytical method.

13. Record the total purged volume (graduated waste bucket). Remove the pump from the well and decontaminate the sampling equipment.

Low-Flow Setup Diagram



APPENDIX C

EXAMPLE (Minimum Requirements)

WELL PURGING-FIELD WATER QUALITY MEASUREMENTS FORM

Location (Site/Facility Name)________________________________
Well Number_________________ Date________________________
Field Personnel____
Sampling Organization____
Identify MP____

Depth to ________/_________ of screen
(below MP) top bottom
Pump Intake at (ft. below MP)_________
Purging Device; (pump type)__________
Total Volume Purged ________________

Clock Time 24 HR	Water Depth below MP ft	Pump Dial[1]	Purge Rate ml/min	Cum. Volume Purged liters	Temp. "C	Spec. Cond.[2] µS/cm	pH	ORP[3] mv	DO mg/L	Tur-bidity NTU	Comments
Stabilization Criteria					3%	3%	±0.1	±10 mv	10%	10%	

1. Pump dial setting (for example: hertz, cycles/min, etc).
2. µSiemens per cm(same as µmhos/cm)at 25°C.
3. Oxidation reduction potential (ORP)

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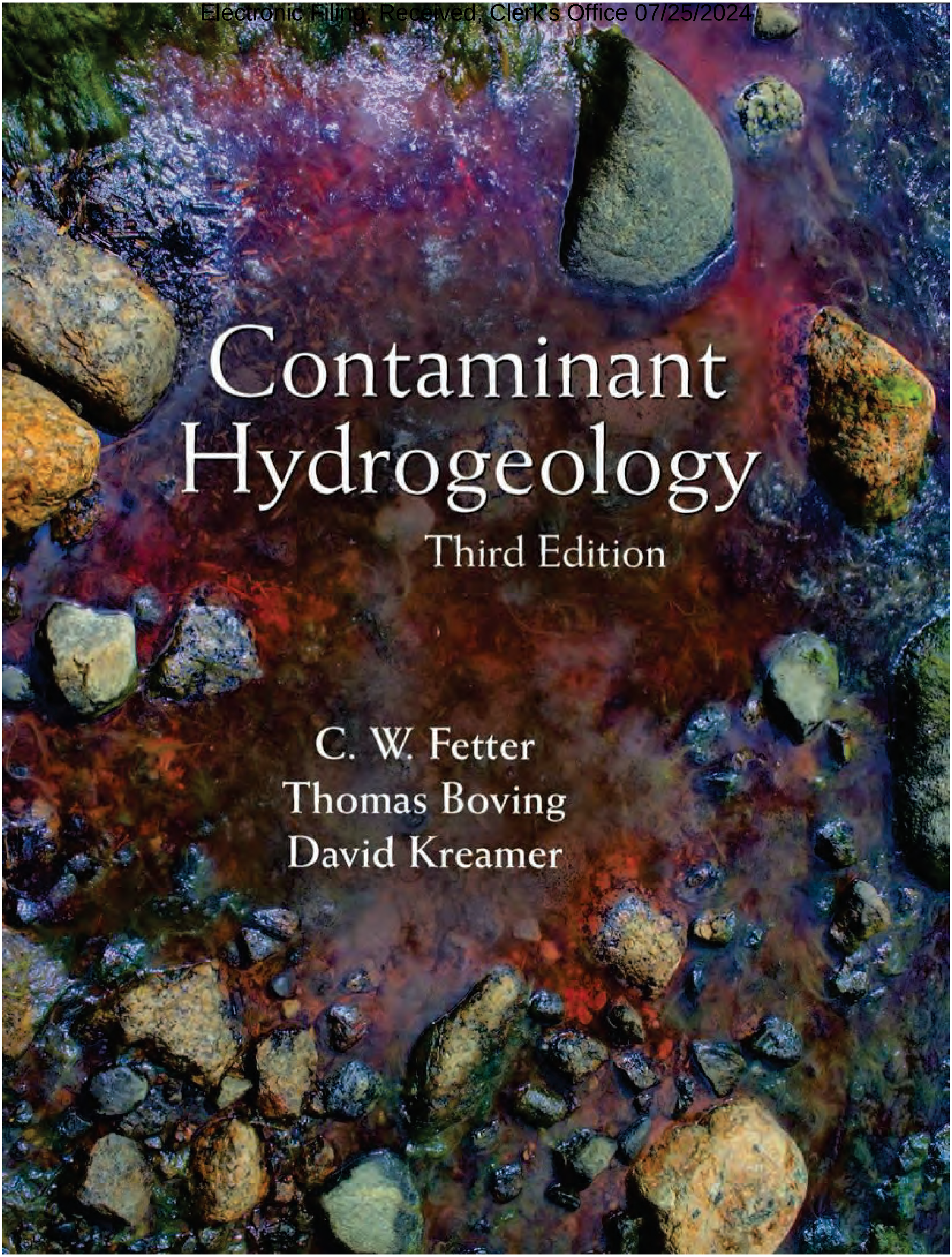

Contaminant Hydrogeology

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TABLE 1.3 *Cont'd*

Contaminant	Examples of uses
Other hydrocarbons	
Alkyl sulfonates	Detergents
Cyclohexane	Organic synthesis, solvent, oil extraction
1,3,5,7-Cyclooctatetraene	Organic research
Dicyclopentadiene (DCPD)	Intermediate for insecticides, paints and varnishes, flame retardants
2,3-Dimethylhexane	NA
Fuel oil	Fuel, heating
Gasoline	Fuel
Jet fuels	Fuel
Kerosene	Fuel, heating solvent, insecticides
Lignin	Newsprint, ceramic binder, dyestuffs, drilling fuel additive, plastics
Methylene blue activated substances (MBAS)	Dyestuffs, analytical chemistry
Propane	Fuel, solvent, refrigerants, propellants, organic synthesis
Tannin	Chemical manufacturing, tanning, textiles, electroplating, inks, pharmaceuticals, photography, paper
4,6,8-Trimethyl-1-nonene	NA
Undecane	Petroleum research, organic synthesis
Metals and cations	
Aluminum	Alloys, foundry, paints, protective coatings, electrical industry, packaging, building and construction, machinery and equipment
Antimony	Hardening alloys, solders, sheet and pipe, pyrotechnics
Arsenic	Alloys, dyestuffs, medicine, solders, electronic devices, insecticides, rodenticides, herbicide, preservative
Barium	Alloys, lubricant
Beryllium	Structural material in space technology, inertial guidance systems, additive to rocket fuels, moderator and reflector of neutrons in nuclear reactors
Cadmium	Alloys, coatings, batteries, electrical equipment, fire-protection systems, paints, fungicides, photography
Calcium	Alloys, fertilizers, reducing agent
Chromium	Alloys, protective coatings, paints, nuclear and high-temperature research

(Cont'd)

TABLE 1.3 *Cont'd*

Contaminant	Examples of uses
Cobalt	Alloys, ceramics, drugs, paints, glass, printing, catalyst, electroplating, lamp filaments
Copper	Alloys, paints, electrical wiring, machinery, construction materials, electroplating, piping, insecticides
Iron	Alloys, machinery, magnets
Lead	Alloys, batteries, gasoline additive, sheet and pipe, paints, radiation shielding
Lithium	Alloys, pharmaceuticals, coolant, batteries, solders, propellants
Magnesium	Alloys, batteries, pyrotechnics, precision instruments, optical mirrors
Manganese	Alloys, purifying agent
Mercury	Alloys, electrical apparatus, instruments, fungicides, bactericides, mildew proofing, paper, pharmaceuticals
Molybdenum	Alloys, pigments, lubricant
Nickel	Alloys, ceramics, batteries, electroplating, catalyst
Palladium	Alloys, catalyst, jewelry, protective coatings, electrical equipment
Potassium	Alloys, catalyst
Selenium	Alloys, electronics, ceramics, catalyst
Silver	Alloys, photography, chemical manufacturing, mirrors, electronic equipment, jewelry, equipment, catalyst, pharmaceuticals
Sodium	Chemical manufacturing, catalyst, coolant, nonglare lighting for highways, laboratory reagent
Thallium	Alloys, glass, pesticides, photoelectric applications
Titanium	Alloys, structural materials, abrasives, coatings
Vanadium	Alloys, catalysts, target material for x-rays
Zinc	Alloys, electroplating, electronics, automotive parts, fungicides, roofing, cable wrappings, nutrition
Nonmetals and anions	
Ammonia	Fertilizers, chemical manufacturing, refrigerants, synthetic fibers, fuels, dyestuffs
Boron	Alloys, fibers and filaments, semiconductors, propellants
Chlorides	Chemical manufacturing, water purification, shrink-proofing, flame retardants, food processing

(Cont'd)

TABLE 1.3 *Cont'd*

Contaminant	Examples of uses
Cyanides	Polymer production (heavy duty tires), coatings, metallurgy, pesticides
Fluorides	Toothpastes and other dentrifices, additive to drinking water, aluminum smelting
Nitrates	Fertilizers, food preservatives
Nitrites	Fertilizers, food preservatives
Phosphates	Detergents, fertilizers, food additives
Sulfates	Fertilizers, pesticides
Sulfites	Pulp production and processing, food preservatives
Microorganisms	
Bacteria (coliform)	
Giardia	
Viruses	
Radionuclides	
Cesium 137	Gamma radiation source for certain foods
Chromium 51	Diagnosis of blood volume, blood cell life, cardiac output, etc.
Cobalt 60	Radiation therapy, irradiation, radiographic testing, research
Iodine 131	Medical diagnosis, therapy, leak detection, tracers (e.g., to study efficiency of mixing pulp fibers, chemical reactions, and thermal stability of additives to food products), measuring film thicknesses
Iron 59	Medicine, tracer
Lead 210	NA
Phosphorus 32	Tracer, medical treatment, industrial measurements (e.g., tire-tread wear and thickness of films and ink)
Plutonium 238,243	Energy source, weaponry
Radium 226	Medical treatment, radiography
Radium 228	Naturally occurring
Radon 222	Medicine, leak detection, radiography, flow rate measurement
Ruthenium 106	Catalyst
Scandium 46	Tracer studies, leak detection, semiconductors
Strontium 90	Medicine, industrial applications (e.g., measuring thicknesses, density control)

(Cont'd)

TABLE 1.3 *Cont"d*

Contaminant	Examples of uses
Thorium 232	Naturally occurring
Tritium	Tracer, luminous instrument dials
Uranium 238	Nuclear reactors, mining operations
Zinc 65	Industrial tracers (e.g., to study wear in alloys, galvanizing, body metabolism, function of oil additives in lubricating oils)
Zirconium 95	NA

[a]NA: No information in Standard sources.

Source: Office of Technology Assessment 1984, with additions.

It should be noted that many compounds can have multiple names, making identification of compounds difficult for the environmental practitioner. In one example from Table 1.3, the compound butoxymethylbenzene can also be known by at least 26 other names or numerical distinctions (Chemspider 2015). Nomenclature can be further confused, as there are other names given for the same compound by different suppliers and vendors. Using the same example of butoxymethylbenzene above, a selective list of vendors in 2015 and their designations for the compound would include at least 14 different additional names or numerical distinctions (Zincdocking 2015). This multiple nomenclature for the same compound can be even more confused with the manufacture and use of mixtures of potential groundwater pollutants, some containing unspecified impurities. There are many types of industrial chemical mixtures in use or being developed, with multiple names and descriptions, including tens of thousands of pesticide products. Also, in recent years there has been increased concern over "emerging" organic contaminants, which were previously not yet industrially developed, not yet discovered in the environment often due to analytical limitations, or alternatively, not yet recognized as potential pollutants. These compounds include pharmaceuticals, personal care products, industrial chemicals, and hormones. Table 1.4 lists some of these compounds and their uses.

The occurrence of the substances found on Tables 1.3 and 1.4 can be detected only if a groundwater sample has been collected and analyzed. In low concentrations most of these substances are colorless, tasteless, and odorless. Specific analytical techniques must be employed to detect the presence and concentration of each substance Some methods can be employed to analyze a sample for all of the compounds of a particular class. For example, certain organic compounds fall into a class called volatile organic compounds. There are analytical methods that could target all compounds of this class. Likewise, there are methods available to analyze for many of the metals in a single sample. However, other compounds require a specific test. With so many potential contaminants, it is possible that a sample could be collected and tested and a specific contaminant still not be found because no analysis was done for that compound or element.

compounds are potential groundwater contaminants that can leach from soil used for land applications of wastes and wastewater.

1.5.2 Category II: Sources Designed to Store, Treat and/or Dispose of Substances

Landfills Landfills are, by definition, designed to minimize adverse effects of waste disposal (Miller, 1980). However, many were poorly designed and are leaking liquids, generically termed leachate, which are contaminating groundwater. Landfills can contain nonhazardous municipal waste, nonhazardous industrial waste, or hazardous waste as defined by the Resource Conservation and Recovery Act. Peterson (1983) reported that there were 12,991 landfills in the United States in the 1980s, including 2,395 open dumps. According to the EPA, by 2009 landfills were much larger, but there were only 1,908 solid waste municipal landfills reported. This does not include landfills for construction and demolition wastes, nonhazardous industrial waste landfills, or hazardous waste landfills. There are an unknown number of abandoned landfills.

Materials placed in landfills include such things as municipal garbage and trash, demolition debris, sludge from wastewater-treatment plants, incinerator ash, foundry sand and other foundry wastes, and toxic and hazardous materials. Although no longer permitted in the United States, liquid hazardous waste was disposed in landfills in the past. The U.S. Environmental Protection Agency (2015) estimated that in 2012 over 250 million tons of municipal waste was generated, which is over a three-fold increase in the last half century. The World Bank (2012) has estimated worldwide municipal waste generation at 1.3 billion tons per year with estimates of expected increase to 2.2 billion tons annually in 2025, and over 11 billion by 2100. Total solid waste generation (beyond just municipal waste) is considerably larger at an estimated 11.2 billion tons in 2011 (United Nations Environmental Programme). Interactive waste atlases have also been developed to summarize worldwide waste data (e.g., http://www.atlas.d-waste.com/).

Leachate is formed from the liquids found in the waste as well as by leaching of the solid waste by rainwater. Table 1.9 contains information on the chemical composition of leachate from municipal landfills. To minimize the amount of leachate generated, modern landfills are built in sections, with a low-permeability cover placed over the waste as soon as possible to limit the infiltration of rainwater. Modern landfills also have low-permeability liner systems and collection pipes to remove the leachate that forms so that it can be taken to a wastewater-treatment plant. A modern landfill that is properly sited with respect to the local geology and that has a properly designed and constructed liner, leachate collection system, and low-permeability cover has limited potential to contaminate groundwater. However, many landfills do not have liners and leachate collection systems. In the past, landfills tended to be placed in any convenient hole or low spot, such as a sand pit, quarry, or marsh. Groundwater contamination from such landfills is highly probable.

Municipal landfills are usually located near urban areas. The trend is toward large landfills that can handle many thousands of tons of waste per year. Hazardous-waste landfills are now regulated under the Resource Conservation and Recovery Act. There is frequently strong local opposition to the siting of either a municipal or a hazardous waste landfill. This is referred to as the NIMBY syndrome: Not In My Back Yard!

Homeowners may pour waste liquids into ditches or the sanitary sewer; combustibles may be burned in the backyard. These are undesirable practices that can easily result in environmental pollution, including groundwater contamination.

Surface impoundments Pits, ponds, and lagoons are used by industries, farmers, and municipalities for the storage and/or treatment of both liquid nonhazardous and hazardous waste and the discharge of nonhazardous waste. Prior to the passage of the Resource Conservation and Recovery Act, liquid hazardous wastes were also discharged into pits. These pits may be unlined or lined with natural material, such as clay, or artificial materials, such as plastic sheets, rubber membranes, or asphalt.

Impoundments are used to treat wastewater by such processes as settling of solids, biological oxidation, chemical coagulation and precipitation, and pH adjustment. They may also be used to store wastewater prior to treatment. Water from surface impoundments may be discharged to a receiving water course such as a stream or a lake. Unless a discharging impoundment is lined, it will also lose water by seepage into the subsurface. Nondischarging impoundments release water either by evaporation or seepage into the ground or a combination of both. Evaporation ponds are effective only in arid regions, where potential evapotranspiration far exceeds precipitation. Even evaporation ponds that were originally lined may leak and result in groundwater contamination if the liner deteriorates from contact with the pond's contents.

Impoundments are used for wastewater treatment by municipalities and industries such as paper manufacturing, petroleum refining, metals industry, mining, and chemical manufacturing. They are also used for treatment of agricultural waste, such as farm animal waste from feedlots. Power plants use surface impoundments as cooling ponds. Mining operations use surface ponds for the separation of tailings, which is waste rock from the processing of ore that occurs in a slurry mixture of liquid and solid.

Although it is now prohibited, until the 1970s lagoons were used for the disposal of untreated wastewater from manufacturing, ore processing, and other industrial uses into the groundwater. Brine pits were used for many years in the oil patch for the disposal of brines pumped up with the oil. Miller (1980) lists 57 cases of groundwater contamination caused by the leakage of wastewater from surface impoundments. In most of the reported cases water-supply wells had been affected; at the time when use of such impoundments was allowed, groundwater monitoring was not required; usually the only way that leakage was detected was by contamination of a supply well.

In one case in Illinois, up to 500,000 gals per day of mineralized wastewater, containing high total dissolved solids (TDS), which included chloride, sulfate, and calcium, from an ore-processing plant were discharged into waste-disposal ponds excavated in a glacial drift aquifer for a period of about 40 years. Concentrations of chloride, sulfate, TDS, and hardness were elevated in an underlying bedrock aquifer as much as a mile away from the site (U.S. Nuclear Regulatory Commission 1983).

Wastewater from the manufacturing of nerve gas and pesticides at the Rocky Mountain Arsenal at Denver was discharged into unlined evaporation ponds from 1942 until 1956. In 1956 a new pond lined with asphalt was constructed; ultimately that liner failed and the lined pond also leaked. Contamination of nearby farm wells was first detected in 1951 and was especially severe in the drought year of 1954, when irrigated crops died. Groundwater contamination extended at least 8 miles from the ponds and was indicated by high chloride content. Ultimately the groundwater under and near the Rocky Mountain Arsenal was found to contain dozens of synthetic organic chemicals, including two that are especially mobile in the subsurface: diisopropylmethylphosphonate (DIMP), a by-product of the manufacture of nerve gas, and dicyclopentadiene (DCPD) a chemical used in the manufacture of pesticides (Konikow and Thompson 1984; Spanggord, Chou, and Mabey 1979). By 2010, after 23 years of active remediation the cleanup of contaminated soil and groundwater at the Rocky Mountain Arsenal, the cost has been $2.1 billion dollars as parcels of the land are taken off the National Priorities list and tracts of land are converted to a National Wildlife Refuge.

There is very little information available on the number of surface impoundments worldwide, nor much up-to-date information from individual countries. Several decades ago the EPA performed a survey of the surface impoundments located in the United States (U.S. EPA 1983). They reported a total of 180,973 impoundments, including 37,185 municipal; 19,437 agricultural; 27,912 industrial; 25,038 mining; 65,688 brine pits for oil and gas; and 5,913 miscellaneous. A later U.S. EPA (2001) survey conducted in the 1990s estimated about 18,000 industrial impoundments. Energy related industrial surface impoundments are of particular concern, as these can hold many sorts of materials including coal combustion residues, water associated with *in situ* uranium leaching, and/or brines associated with deep oil and gas development. The large number of impoundments provides a significant threat to groundwater resources (OTA 1984).

Mine wastes Mining can produce spoils, or unneeded soil, sediment, and rock moved during the mining process, and tailings, or solid waste left over after the processing of ore. These wastes may be piled on the land surface, used to fill low areas, used to restore the land to pre-mining contours, or placed in engineered landfills with leachatecollection systems. Mine wastes can generate leachate as rainwater passes through them. If sulfate or sulfide minerals are present, sulfuric acid can be generated, and the resulting drainage water can be acidic. This is likely to occur with coal-mining wastes, copper and gold ores, and ores from massive sulfide mineralization. Mine-waste leachate may also contain heavy metals and, in the case of uranium and thorium mines, radionuclides. Neutralization of the mine wastes can prevent the formation of acidic leachate and prevent the mobilization of many, but not all, metallic ions and radionuclides. The mine-waste disposal issue is a large one. In the United States, mining is estimated to produce waste material annually with a weight of nearly nine times that of refuse generated by all cities and towns (U.S. EPA 2003). The mining of many metals traditionally requires huge quantities of rock to be removed, for example, the production of a single ton of copper ore typically generates well over 100 times the tonnage of waste rock and about 200 times the tonnage of mined overburden, depending on the local geology. Leachate produced by unneutralized or uncontained mine wastes is a threat to surface and groundwater.

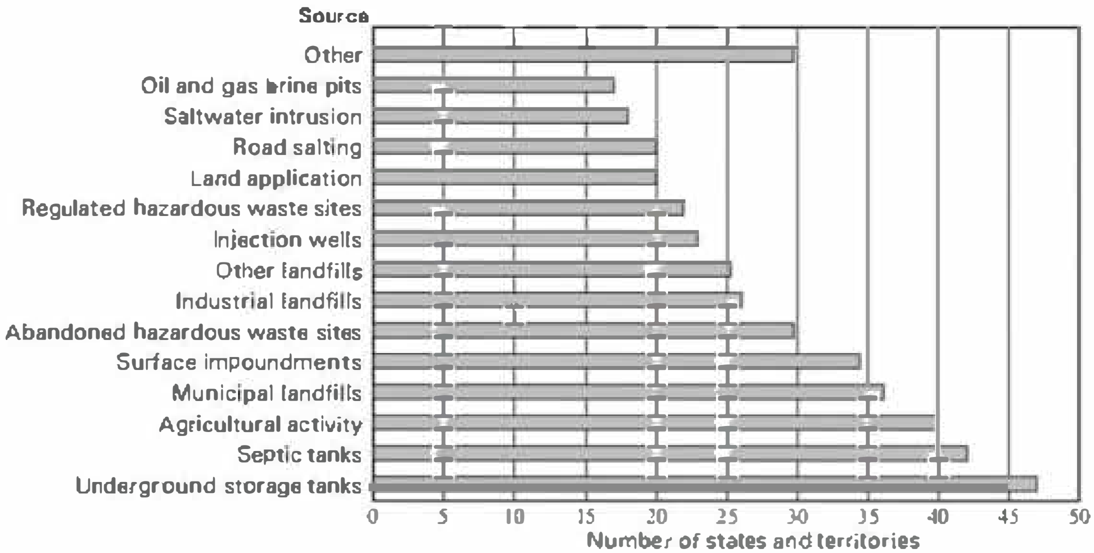
In some cases, *in situ* leach mining is used instead of physical removal of ore-containing rock. In these instances, a chemical mobilizing agent called a lixiviant is pumped down a well where it flows into an ore-bearing formation. After ore is dissolved, the pregnant solution circulating underground is removed using extraction wells. Problems can arise with *in situ* leach mining as the geologic structures associated with many ore

1.6 Relative Ranking of Groundwater-Contamination Sources and Substances

Every site of groundwater contamination is unique in its geology, contaminant mixtures, surrounding human-made structures, and pollutant sources. Therefore the risks associated with different localities and their contaminants can vary greatly, and the approaches for site characterization and remediation are typically tailored to each individual site. Although there are many potential sources of groundwater contamination, some pose much more of a threat to groundwater than others. Section 305(b) of the Federal Clean Water Act requires individual States in the U.S. to submit reports to the Environmental Protection Agency on the sources of groundwater contamination in the state and the type of contaminants observed. The data submitted were used to compile *National Water Quality Inventory—1988 Report to Congress* (U.S. EPA 1990).

The states indicated all the groundwater-contamination sources that they considered to be major threats to groundwater in their state. Figure 1.3 shows that more than half the states and territories listed underground storage tanks, septic tanks, agricultural activities, municipal landfills, and abandoned hazardous-waste sites as major threats to groundwater. Other frequently listed sources include industrial landfills, other landfills, injection wells, regulated hazardous-waste sites, land application, road salt, saltwater intrusion, and brine pits from oil and gas wells.

FIGURE 1.3 Frequency of various contamination sources considered by states and territories of the United States to be major threats to groundwater quality.



Source: UNICEF 2012.

Additionally, every two years the Agency for Toxic Substance and Disease Registry (ATSDR) and the Environmental Protection Agency in the United States prepare a list of hazardous substances most commonly found at facilities on the National Priorities List (NPL), also called the "Superfund" program. The list is a prioritization of harmful substances based on a combination of their frequency of occurrence, their toxicity, and compounds that was denser than water and had limited solubility in water. Large volumes of tar were generated and due to routine leaks and spills, leaking tar storage tanks and deliberate disposal, tar was released into the environment. When some of the plants were decommissioned tanks containing tar were just buried in place. Today many of the former manufactured gas plant sites still have soil and groundwater contamination associated with the tar (Luthy et al. 1994).

1.8 Review of Mathematics and the Flow Equation

1.8.1 Derivatives

Soil-moisture movement, groundwater flow, and solute transport may be described by means of partial differential equations. Thus, a brief review is in order.

If a bicyclist is traveling down a highway, we can measure the time that it takes the rider, who has a flying start, to go from a starting point ($S(t_1)$, or the location at the starting time, (t_1), to a point somewhere down the highway ($S(t_2)$, or the location at elapsed time t_2). If we wish to know the average speed of the rider over this distance, we divide the distance from point $S(t_1)$ to point $S(t_2)$ by the elapsed time, $t_2 - t_1$.

$$\frac{\Delta S}{\Delta t} = \frac{S(t_2) - S(t_1)}{t_2 - t_1} \tag{1.1}$$

The rider will be going more slowly uphill and faster downhill. The average speed will thus include a lot of variation. If we were to measure the rider's speed over a shorter part of the course, there would be less variation in speed. As the length of time over which the distance traveled is measured becomes shorter and shorter, the variation in speed decreases. If the time becomes infinitesimally small—for example, the time that it takes the rider to travel a few microns—we obtain an instantaneous speed. This is known as the first derivative of distance with respect to time and is defined by

$$\frac{dS(t_1)}{dt} = \lim_{t \to t_1} \frac{S(t) - S(t_1)}{t - t_1} \tag{1.2}$$

where t is any arbitrary time. Figure 1.4 shows a graph of distance traveled by our bicyclist as a function of time. The slope of the line from time t_1 to time t_2 is the average speed over that part of the highway and is expressed as $\Delta S/\Delta t$. *The instantaneous speed at time* t_1 is the slope of the tangent to the curve at that point, which is expressed as dS/dt.

Note that the slope of distance versus time on Figure 1.4 keeps changing. This reflects the changes in speed that occur as the rider goes up and down hills. As the rider goes over the crest of a hill, he or she will perhaps be going rather slowly. As the rider goes downhill, the velocity will increase. We can compare the crest-of-the-hill velocity with the bottom-of the-hill velocity and see that it has increased. This is a measure of the acceleration that occurs as gravity and the leg muscles of the bicyclist combine to increase speed. Figure 1.5 shows the speed of the rider as he or she goes over a hill. At $t = 0$ the rider is coming over the crest of the hill and the speed is 10 mi/hr. At $t = 30$ sec, when the rider is near the bottom of the hill, the speed is 26 mi/hr. The average rate of change in speed is (26 mi/hr–10 mi/hr)/

FIGURE 1.4 Graph of distance traveled versus time graphically showing speed, which is the first derivative of distance with respect to time.

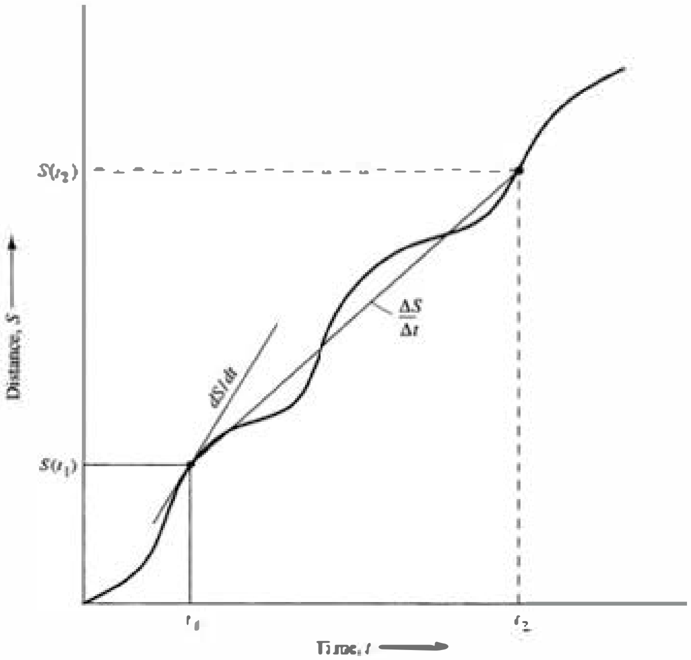
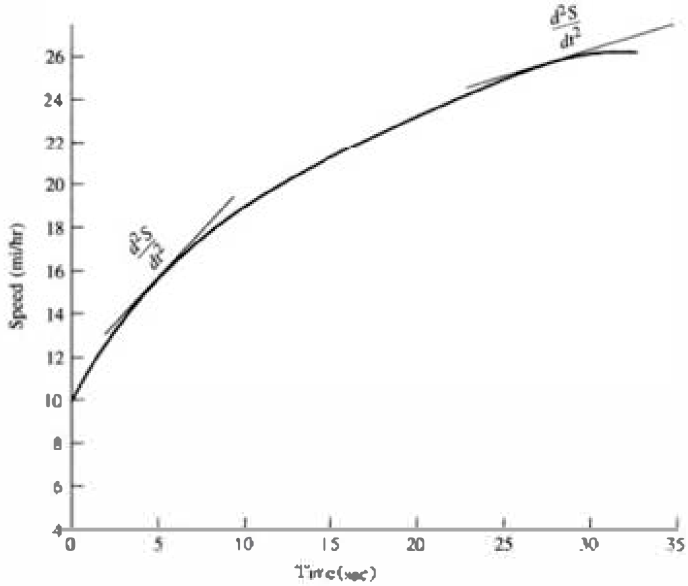


FIGURE 1.5 Graph of speed versus time graphically showing acceleration, which is the second derivative of distance with respect to time.



30 sec, or 0.53 mi/hr/sec. The rate of change is faster near the top of the hill where the slope is steeper and there is less wind resistance, since the rider is moving more slowly. From 0 to 5 sec the speed changes from 10 to 15 mi/hr, or 1.0 mi/hr/sec. Acceleration

is the rate of change of speed with time, which is a second derivative. It is the slope of a tangent to the curve at a given time. It can be expressed as

$$\frac{d\left(\frac{dS}{dt}\right)}{dt} \quad \text{or} \quad \frac{d^2S}{dt^2}$$

The tangent at 5 sec. can be seen to be steeper than the tangent at 30 sec. where the rate of change is less.

In hydrogeology we have many parameters that are a function of more than one independent variable. For example, hydraulic head is a function of the three space variables: $h = h(x, y, z)$. We frequently differentiate bead with respect to one of the space variables while holding the other two variables constant. Such derivatives of a parameter with respect to a single variable are called partial derivatives. The second derivative of hydraulic head with respect to the space variables is

$$\frac{\partial^2 h}{\partial x^2} + \frac{\partial^2 h}{\partial y^2} + \frac{\partial^2 h}{\partial z^2}$$

1.8.2 Darcy's Law

The first experimental study of water movement through a porous medium was performed by Henry Darcy (Darcy 1856). He found that the one-dimensional flow of water through a pipe filled with sand was proportional to the cross-sectional area and the head loss along the pipe and inversely proportional to the flow length. Darcy's law can be expressed as

$$Q = -KA\frac{dh}{dl} \tag{1.3}$$

where

Q = volumetric discharge
K = proportionality constant known as hydraulic conductivity
A = cross-sectional area
dh/dl = gradient of hydraulic head

This equation can also be expressed in terms of specific discharge, or Darcy flux, q, which is the volumetric flow rate, Q, divided by the cross-sectional area, A.

$$q = -K\frac{dh}{dl} \tag{1.4}$$

Darcy's law was obtained for one-dimensional flow. However, as was previously stated, head is a function of all three dimensions: $h = h(x, y, z)$.

The hydraulic conductivity is the measure of the ability of the fractured or porous media to transmit water. It can have different values, depending upon the actual direction that the water is flowing through the porous media. In such a case the medium is said to be **anisotropic**. The value of the hydraulic conductivity can be measured in three principle directions, K_x, K_y, and K_z. If the hydraulic conductivity is the same in all directions, then $K_x = K_y = K_z = K$ and the medium is said to be **isotropic**.

1.8.3 Scalar, Vector, and Tensor Properties of Hydraulic Head and Hydraulic Conductivity

We first need to define some terms relating to tensors. A zero-order tensor, also called a scalar, is a quantity characterized only by its size or magnitude. Examples in hydrogeology include hydraulic head, chemical concentration, and temperature. A firstorder tensor, or vector, is a quantity that has both a magnitude and a direction. Vectors require three components, each having a magnitude and direction. Velocity, specific discharge, mass flux, and heat flux are examples. A second-order tensor—or, simply, tensor—acts like the product of two vectors, requiring nine components to account for all possible products of the three components of each vector. Examples in hydrogeology are intrinsic permeability, hydraulic conductivity, thermal conductivity, and hydrodynamic dispersion.

The hydraulic head is a scalar. However, the gradient of the head is a vector as it has both a magnitude and a direction. The gradient of h is designated as grad h:

$$\text{grad } h = i\frac{\partial h}{\partial x} + j\frac{\partial h}{\partial y} + k\frac{\partial h}{\partial z} \tag{1.5}$$

where **i**, **j**, and **k** are unit vectors in the x, y, and z directions. An equivalent notation is the use of the vector differential operator, del, which has the symbol ∇. This operator is equivalent to

$$i\frac{\partial}{\partial x} + j\frac{\partial}{\partial y} + k\frac{\partial}{\partial z} \tag{1.6}$$

Another vector is the specific discharge, **q**. It has three components, q_x, q_y, and q_z, when measured along the Cartesian coordinate axes. Associated with any vector is a positive scalar with a value equal to the magnitude of the vector. If q is the magnitude of the vector **q**, this can be expressed as

$$q = |q| \tag{1.7}$$

A second-order tensor, such as **K**, hydraulic conductivity, can be described by nine components. In matrix form they are expressed as:

$$K = \begin{bmatrix} K_{xx} K_{xy} K_{xz} \\ K_{yx} K_{yy} K_{yz} \\ K_{zx} K_{zy} K_{zz} \end{bmatrix} \tag{1.8}$$

If the tensor is symmetric, $K_{ij} = K_{ji}$; then inspection of (1.8) shows that there are only six independent components of **K**.

If the coordinate system is oriented along the principal axes, the tensor becomes

$$K = \begin{bmatrix} K_{xx} & 0 & 0 \\ 0 & K_{yy} & 0 \\ 0 & 0 & K_{zz} \end{bmatrix} \tag{1.9}$$

For the special case of an isotropic media—that is, the value of **K** does not depend upon the direction in which it is measured—the tensor becomes

$$K = \begin{bmatrix} K & 0 & 0 \\ 0 & K & 0 \\ 0 & 0 & K \end{bmatrix} \tag{1.10}$$

The three components of the specific discharge vector, q, are

$$q_x = -K_{xx}\frac{\partial h}{\partial x} - K_{xy}\frac{\partial h}{\partial y} - K_{xz}\frac{\partial h}{\partial z}$$

$$q_y = -K_{yx}\frac{\partial h}{\partial x} - K_{yy}\frac{\partial h}{\partial y} - K_{yz}\frac{\partial h}{\partial z} \tag{1.11}$$

$$q_z = -K_{zx}\frac{\partial h}{\partial x} - K_{zy}\frac{\partial h}{\partial y} - K_{zz}\frac{\partial h}{\partial z}$$

For the special case where we orient the axes of the *x*, *y*, and *z* coordinate system with the three principal directions of anisotropy, **K** is the matrix shown in (1.9) and the three components of the specific discharge vector are

$$q_x = -K_{xx}\frac{\partial h}{\partial x}$$

$$q_y = -K_{yy}\frac{\partial h}{\partial y} \tag{1.12}$$

$$q_z = -K_{zz}\frac{\partial h}{\partial z}$$

For an isotropic material, **K** is represented by the matrix in (1.10) and

$$q = -K\frac{\partial h}{\partial x} - K\frac{\partial h}{\partial y} - K\frac{\partial h}{\partial z} \tag{1.13}$$

or

$$q = -K \text{ grad } h \tag{1.14}$$

If we multiply two vectors together and the result is a scalar, then the product is called a **dot product, or inner product**. For example, the del operator dotted into a vector yields a scalar, called the divergence. Based on grad h, we can find a velocity vector v such that the magnitude and direction vary throughout the porous media. If we apply the del operator to v, we obtain the following:

$$\nabla \cdot v = \operatorname{div} v = \frac{\partial v_x}{\partial x} + \frac{\partial v_y}{\partial y} + \frac{\partial v_z}{\partial z} \tag{1.15}$$

If we apply the del operator to grad h, the result is the second derivative of head:

$$\nabla \cdot \text{grad } h = \frac{\partial^2 h}{\partial x^2} + \frac{\partial^2 h}{\partial y^2} + \frac{\partial^2 h}{\partial z^2} \tag{1.16}$$

1.8.4 Derivation of the Flow Equation in a Deforming Medium

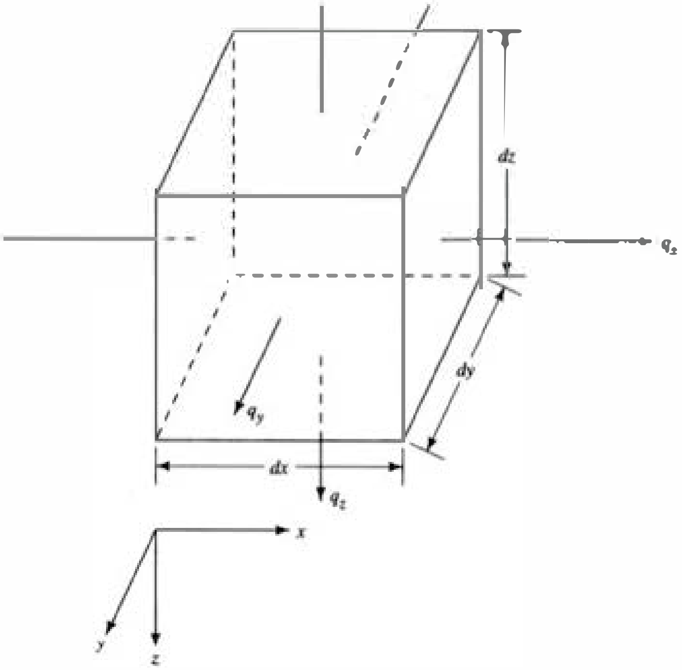
The law of mass conservation states that there can be no net change in the mass of fluid in a small representative elementary volume (REV) of a porous medium. In other words, the mass entering the REV less the mass leaving the REV is equal to the change in mass storage with time.

The representative elementary volume is shown on Figure 1.6. The three sides have length dx, dy, and dz, respectively. The area of the two faces normal to the x axis is $dy\,dz$, the area of the faces normal to the y axis is $dx\,dz$, and the area of the faces normal to the z axis is $dx\,dy$.

The component of mass flux into the REV parallel to the x axis is the fluid density times the flux rate:

$$\text{Mass influx along } x \text{ axis} = p_w q_x \, dy \, dz \tag{1.17}$$

FIGURE 1.6 Representative elementary volume for fluid flow.



where

p_w = fluid density (M/L^3)
q_x = specific discharge or volume of flow per cross-sectional area (L/T)
$dy\,dz$ = cross-sectional area (L^2)

The units of mass inflow are mass per unit time (M/T).*

The mass outflow rate will be different than the inflow rate and can be given as:

$$\text{Mass outflow rate parallel to } x \text{ axis} = \left[p_w q_x + \frac{\partial(p_w q_x)dx}{\partial x} \right] dy\,dz \qquad (1.18)$$

The net mass accumulation within the control volume due to the flow component parallel to the x axis is the mass inflow minus the mass outflow, or

$$\frac{-\partial(p_w q_x)dx\,dy\,dz}{\partial x}$$

Similar terms exist for the net mass accumulation due to flow components parallel to the y and z axes:

$$\frac{-\partial(p_w q_y)dy\,dx\,dz}{\partial y}$$

$$\frac{-\partial(p_w q_z)dz\,dx\,dy}{\partial z}$$

These three terms can be summed to find the total net mass accumulation within the control volume

$$-\left[\left(\frac{\partial}{\partial x}(p_w q_x) + \frac{\partial}{\partial y}(p_w q_y) + \frac{\partial}{\partial z}(p_w q_z\right)\right] dx\,dy\,dz \qquad (1.19)$$

The mass of water in the REV, M, is the density of water, p_w, times the porosity, n, times the volume, $dx\,dy\,dz$. The change in mass with respect to time is

$$\frac{\partial M}{\partial t} = \frac{\partial}{\partial t}(p_w n\,dx\,dy\,dz) \qquad (1.20)$$

From the law of conservation of mass, Equation 1.19 must equal Equation 1.20.

$$-\left[\frac{\partial}{\partial x}(p_w q_x) + \frac{\partial}{\partial y}(p_w q_y) + \frac{\partial}{\partial z}(p_w q_z)\right] dx\,dy\,dz = \frac{\partial}{\partial t}(p_w n)\,dx\,dy\,dz \qquad (1.21)$$

---

* The units of a variable can be expressed in terms of their fundamental dimensions. These are length, L, mass, M, and time, T. The fundamental dimensions for density are mass per unit volume. Volume is length cubed, so the shorthand expression for the fundamental dimensions of density is M/L^3. Specific discharge has the dimensions of velocity, so the fundamental dimensions are L/T, and area has fundamental dimensions of L^2.

We can assume that although density of the fluid may change with time, at any given time it will be the same everywhere in the REV. Under this assumption Equation 1.21 can be simplified to

$$-\left[\frac{\partial q_x}{\partial x}+\frac{\partial q_y}{\partial y}+\frac{\partial q_z}{\partial z}\right]=\frac{1}{p_w}\frac{\partial}{\partial t}(p_w n) \qquad \textbf{(1.22)}$$

We may substitute Darcy's law for the specific discharge components given on the left side. If the xyz coordinate system is aligned with the principal axes of anisotropy, then Equation 1.12 may be used, and the left side of Equation 1.22 becomes

$$\frac{\partial}{\partial x}\left(K_{xx}\frac{\partial h}{\partial x}\right)+\frac{\partial}{\partial y}\left(K_{yy}\frac{\partial h}{\partial y}\right)+\frac{\partial}{\partial z}\left(K_{zz}\frac{\partial h}{\partial z}\right) \qquad \textbf{(1.23)}$$

The change in mass within the REV is due to changes in the porosity and the density of water as the head changes with time. Thus the change in the volume of water in storage is proportional to the change in head with time. The right side of Equation 1.22 can be expressed as a proportionality constant, Ss, the specific storage, times the change in head with time.

$$\frac{1}{p_w}\frac{\partial}{\partial t}(p_w n)=S_s\frac{\partial h}{\partial t} \qquad \textbf{(1.24)}$$

Combining Equations 1.22, 1.23, and 1.24 we obtain the main equation for transient flow in an anisotropic medium when the coordinate system is oriented along the principal axes of anisotropy:

$$\frac{\partial}{\partial x}\left(K_{xx}\frac{\partial h}{\partial x}\right)+\frac{\partial}{\partial y}\left(K_{yy}\frac{\partial h}{\partial y}\right)+\frac{\partial}{\partial z}\left(K_{zz}\frac{\partial h}{\partial z}\right)=S_s\frac{\partial h}{\partial t} \qquad \textbf{(1.25)}$$

1.8.5 Mathematical Notation

In del and tensor notation Equation 1.25 becomes

$$\nabla\cdot K\cdot\nabla h=S_s\frac{\partial h}{\partial t} \qquad \textbf{(1.26)}$$

Another form of expression is called Einstein's summation notation. For example, Darcy's law in the familiar, one-dimensional form is

$$q=-K\frac{dh}{dl} \qquad \textbf{(1.27)}$$

It is implied in the preceding equation that the specific discharge is parallel to the direction of dh/dl and that the medium is isotropic. In a more general form, specific discharge, q, is a vector with components q_1, q_2, and q_3. Grad h is a vector that we will call **h**. This vector also has components h_1, h_2, and h_3. Hydraulic conductivity, **K**, is a tensor with nine components. To describe Darcy's law in the most general form, we need three equations.

$$q_1 = K_{11}h_1 + K_{12}h_2 + K_{13}h_3 \tag{1.28a}$$

$$q_2 = K_{21}h_1 + K_{22}h_2 + K_{23}h_3 \tag{1.28b}$$

$$q_3 = K_{31}h_1 + K_{32}h_2 + K_{33}h_3 \tag{1.28c}$$

The inner product can be expressed in index notation as

$$q_i = \sum_j K_{ij} h_i \quad (i, j = 1,2,3) \tag{1.29}$$

In Einstein's summation notation, the Σ is dropped with the understanding that the summation is over the repeated indices:

$$q_i = K_{ij} h_j \quad (i, j = 1,2,3) \tag{1.30}$$

In vector notation this can be expressed as either

$$q = K \cdot \mathrm{grad}\, h \tag{1.31}$$

$$q = K \cdot h \tag{1.32}$$

In del notation this is

$$q = K \cdot \nabla h \tag{1.33}$$

In general, we will use the standard form of differential equations rather than any of the shorthand notation. However, the literature cited in this text often uses the compact forms and the reader should be aware of them.

References

Agency for Toxic Substances and Disease Registry (ATSDR). 2015) Priority List of Hazardous Substances. Available from https://www.atsdr.cdc.gov/spl/#modalIdString_myTable2015

Alavanja, M. C. R. 2009. Pesticides use and exposure extensive worldwide. *Reviews on Environmental Health* 24:303–309.

American Cancer Society. 2015. Cancer Facts & Figures 2014. Accessed August 21, 2015 from http://water.epa.gov/drink/contaminants/index.cfm#List

American Water Resources Association. 1975. Status of water borne diseases in the U.S. and Canada. *Journal of American Water Works Association* 67:95–98.

Ames, B. N., L. S. Gold, and W. C. Willett. 1995. The causes and prevention of cancer. *Proceedings of the National Academy of Science* 92:5258-5265.

2

Mass Transport in Saturated Media

2.1 Introduction

In this chapter we will consider the transport of solutes dissolved in groundwater. This is known as **mass** or **solute transport**. The methods presented in this chapter are based on partial differential equations for dispersion that have been developed for homogeneous media (Ogata and Banks 1961; Ogata 1970; Bear 1972; Bear and Verruijt 1987). These equations are similar in form to the familiar partial differential equations for fluid flow. Since those pioneering developments, much work has been done on the theories of mass transport in response to the great interest in problems of groundwater contamination (e.g., Bedient et al. 1994; Zhang and Bennett 1997; Grathwohl 1998; Domenico and Schwartz 1998; Yoram 2003; Yeh et al. 2015; Essaid et al. 2015). One of the outcomes has been the development of what is essentially a new branch of subsurface hydrology, where the flow of fluid and solutes is treated by statistical models; these models can account for the role of varying hydraulic conductivity and other spatially variable hydraulic parameters that accompany aquifer heterogeneity.

Many of the contaminant transport and fate concepts discussed in this chapter were developed based on tracer tests conducted in the field and at the laboratory scale. While a discussion of how tracer tests should be conducted and how the data can be interpreted is beyond the scope of this book, there are ample references and textbooks devoted to this topic (e.g., Davis et al. 1980; U.S. EPA 1985; Payne et al. 2008; Leibundgut et al. 2009; Suthersan et al. 2014).

2.2 Transport by Concentration Gradients

A solute in water will move from an area of greater concentration toward an area where it is less concentrated. This process is known as **molecular diffusion**, or **diffusion**. Diffusion will occur as long as a concentration gradient exists, even if the fluid is not moving. The mass of fluid diffusing is proportional to the concentration gradient, which can be expressed as **Fick's first law**; in one dimension, Fick's first law is

$$F = -D_d\left(dC / dx\right) \tag{2.1}$$

where

F = mass flux of solute (M/L^2T) per unit area per unit time
D_d = diffusion coefficient (L^2/T)

TABLE 2.1 Diffusion coefficients in water.

Cations		
H^+	9.31×10^{-9} m²/sec	1.00×10^{-7} ft²/sec
Na^+	1.33×10^{-9} m²/sec	1.43×10^{-8} ft²/sec
K^+	1.96×10^{-9} m²/sec	2.11×10^{-8} ft²/sec
Rb^+	2.06×10^{-9} m²/sec	2.22×10^{-8} ft²/sec
Cs^+	2.07×10^{-9} m²/sec	2.23×10^{-8} ft²/sec
Mg^{2+}	7.05×10^{-10} m²/sec	7.59×10^{-9} ft²/sec
Ca^{2+}	7.93×10^{-10} m²/sec	8.54×10^{-9} ft²/sec
Sr^{2+}	7.94×10^{-10} m²/sec	8.55×10^{-9} ft²/sec
Ba^{2+}	8.48×10^{-10} m²/sec	9.13×10^{-9} ft²/sec
Ra^{2+}	8.89×10^{-10} m²/sec	9.57×10^{-9} ft²/sec
Mn^{2+}	6.88×10^{-10} m²/sec	7.41×10^{-9} ft²/sec
Fe^{2+}	7.19×10^{-10} m²/sec	7.74×10^{-9} ft²/sec
Cr^{3+}	5.94×10^{-10} m²/sec	6.39×10^{-9} ft²/sec
Fe^{3+}	6.07×10^{-10} m²/sec	6.53×10^{-9} ft²/sec
Anions		
OH^-	5.27×10^{-9} m²/sec	5.67×10^{-8} ft²/sec
F^-	1.46×10^{-9} m²/sec	1.57×10^{-8} ft²/sec
Cl^-	2.03×10^{-9} m²/sec	2.19×10^{-8} ft²/sec
Br^-	2.01×10^{-9} m²/sec	2.16×10^{-8} ft²/sec
HS^-	1.73×10^{-9} m²/sec	1.86×10^{-8} ft²/sec
HCO_3^-	1.18×10^{-9} m²/sec	1.27×10^{-8} ft²/sec
SO_4^{2-}	1.07×10^{-9} m²/sec	1.15×10^{-8} ft²/sec
CO_3^{2-}	9.55×10^{-10} m²/sec	1.03×10^{-8} ft²/sec
Organic Compounds		
Tetrachloroethene (PCE)*	7.5×10^{-10} m²/sec	8.07×10^{-9} ft²/sec
Trichloroethene (TCE)*	8.3×10^{-10} m²/sec	8.93×10^{-9} ft²/sec
1,1,1,-Trichloroethane (TCA)*	8.0×10^{-10} m²/sec	8.61×10^{-9} ft²/sec
Benzene**	9.0×10^{-10} m²/sec	9.69×10^{-9} ft²/sec
Toluene**	8.0×10^{-10} m²/sec	8.61×10^{-9} ft²/sec
Ethylbenzene**	7.2×10^{-10} m²/sec	7.75×10^{-9} ft²/sec
1,4-Dioxane***	1.6×10^{-9} m²/sec	1.72×10^{-8} ft²/sec

Source: Y.-H. Li and S. Gregory, 1974. Diffusion of ions in sea water and in deep-sea sediments. Geochemica et Cosmochemica Acta, Vol. 38. © 1974, with the kind permission of Elsevier Science. *Cohen and Mercer, 1993; **U.S. EPA, 2015; ***Mohr 2010. Diffusion coefficients of ions at 25°C; organic compounds are in pure water at 20°C.

C = solute concentration (M/L^3)

dC/dx = concentration gradient ($M/L^3/L$)

The negative sign indicates that the movement is from areas of greater concentration to those of lesser concentration. Values of D_d for ions and select organic compounds in water at 25°C can be found in Table 2-1. They do not vary much with concentration, but they are somewhat temperature-dependent, being about 50% less at 5°C (Robinson and Stokes 2002). The values of D_d are only applicable when studying diffusion in aqueous systems. For systems where the concentrations are changing with time, Fick's second law applies. In one dimension this is

$$\partial C / \partial t = D_d \, \partial^2 C / \partial x^2 \tag{2.2}$$

where $\partial C / \partial t$ = change in concentration with time ($M/L^3/T$).

In porous media, diffusion cannot proceed as fast as it can in water because the ions must follow longer pathways as they travel around mineral grains. To account for this, an effective diffusion coefficient, D^*, must be used.

$$D^* = \omega D_d \tag{2.3}$$

where ω is a coefficient that is related to the tortuosity (Bear 1972). **Tortuosity** is a measure of the effect of the shape of the flowpath followed by water molecules in a porous media. If L is the straight-line distance between the ends of a tortuous flowpath of length L_e, the tortuosity, T, can be defined as $T = L_e/L$. Tortuosity in a porous media is always greater than 1, because the flowpaths that water molecules take must diverge around solid particles. Flowpaths across a representative sample of a well-sorted sediment would tend to be shorter than those across a poorly sorted sediment in which the smaller grains were filling the voids between the larger grains. Thus the well-sorted sediment would tend to have a lower value for tortuosity than the poorly sorted sediment. (Tortuosity has also been defined as $(L/L_e)^2$ (Carman 1997; Bear 1972). With this definition, tortuosity always has a value less than 1. This definition will not be used in this text.)

The value of ω, which is always less than 1, can be found from diffusion experiments in which a solute is allowed to diffuse across a volume of a porous medium. Perkins and Johnson (1963) found that ω was equal to 0.7 for sand column studies using a uniform sand. For laboratory studies using limestone and sandstone cores, Boving and Grathwohl (2001) found that ω ranges from 0.35 to 0.098 and that ω is related to the porosity, n, of these rocks by:

$$\omega = n^{-1.2}$$

Diffusion will cause a solute to spread away from the place where it is introduced into a porous medium, even in the absence of groundwater advective flow. Figure 2.1 shows the distribution of a solute introduced at concentration C_0, at time t_0, over an interval $(x - a)$ to $(x + a.)$ At succeeding times t_1 and t_2, the solute has spread out, resulting in a lower concentration over the interval $(x - a)$ to $(x + a)$ but increasing concentrations outside of this interval.

The solute concentration follows a normal, or Gaussian, distribution and can be described by two statistical properties, the mean, C and variance, σ_c^2, which are defined in Section 2.12.2.

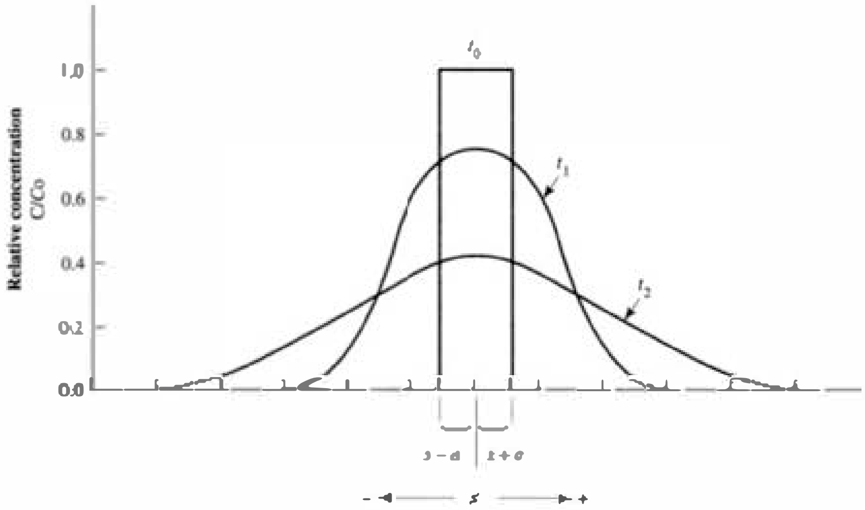
The effective diffusion coefficient, D^*, can be defined as (De Josselin and De Jong 1958)

$$D^* = \frac{\sigma_c^2}{2t} \tag{2.4}$$

This is an alternative definition of effective diffusion coefficient to the one given in Equation 2.3.

The process of diffusion is complicated by the fact that the ions must maintain electrical neutrality as they diffuse. If we have a solution of NaCl, the Na^+ cannot diffuse faster than the Cl^- unless there is some other negative ion in the region into which the Na^+ is diffusing. If the solute is adsorbed onto the mineral surfaces of the porous medium, the net rate of diffusion will be obviously less than for a nonadsorbed species.

Figure 2.1 Spreading of a solute slug with time due to diffusion. A slug of solute was injected into the aquifer at time t_0 with a resulting initial concentration of C_0.



Diffusion can occur when the concentration of a chemical species is greater in one stratum than in an adjacent stratum. For example, solid waste containing a high concentration of chloride ion may be placed directly on the clay liner of a landfill. The concentration of chloride in the leachate contained in the solid waste is so much greater than the concentration of chloride in the pore water of the clay liner that the latter may be considered to be zero as a simplifying assumption in determining a conservative estimate of the maximum diffusion rate. If the solid waste and the clay are both saturated, the chloride ion will diffuse from the solid waste, where its concentration is greater, into the clay liner, even if there is no fluid flow. The concentration of chloride in the solid waste, C_0, will be assumed to be a constant with time, as it can be replaced by dissolution of additional chloride. The concentration of chloride in the clay liner, $C_i(x, t)$, at some distance x from the solid waste interface and sometime t after the waste was placed, can be determined from Equation 2.5 (Crank 1956). This is a solution to Equation 2.2 for the appropriate boundary and initial conditions.

$$C_i(x,t) = C_0 \operatorname{erfc} \frac{x}{2\left(D^* t\right)^{0.5}} \tag{2.5}$$

where

C_i = the concentration at distance x from the source at time t since diffusion began

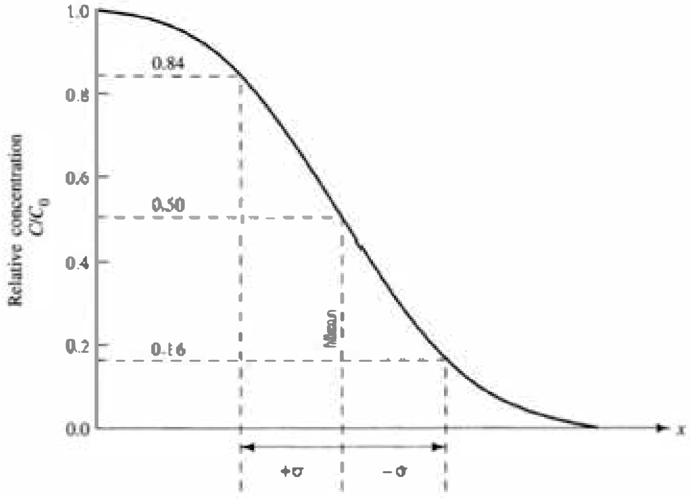
C_0 = the original concentration, which remains a constant

erfc = the complementary error function (Appendix A)

The complementary error function, erfc, is a mathematical function that is related to the normal, or Gaussian, distribution. This means that the solution described by Equation 2.5 is normally distributed, as is expected for a diffusional process. Figure 2.2

shows the profile of relative concentration for a solute diffusing from a region where the concentration is C_0 to a region where it was initially zero. Because the profile is normally distributed, 84% of the values will be less than the value that is one standard deviation more than the mean and 16% of the values will be less than the value that is one standard deviation less than the mean. The standard deviation is the square root of the variance.

Figure 2.2 The profile of a diffusing front as predicted by the complementary error function.



The complementary error function is tabulated in Appendix A or it can be calculated in the spreadsheet program Excel using the syntax: ERFC(x). It is related to the error function, erf, by

$$\text{erfc}(B) = 1 - \text{erf}(B)$$

The value of erfc(B) is 0 for all positive values of B greater than 3.0 and 1.0 for a B of 0. For some applications it may be necessary to find erfc of a negative number. Appendix A does not give values for erfc(B) for negative values of B. These must be computed from the relationship

$$\text{erfc}(-B) = 1 + \text{erf } B$$

The error function, erf(B) is defined as:

$$\text{erf}(B) = \frac{2}{\sqrt{\pi}} \int_0^B e^{-t^2}\, dt$$

The above equation cannot be solved analytically. However, it is tabulated in Appendix A. It can also be approximated by the analytical expression:

$$\text{erf}(B) = \sqrt{1 - \exp\left(\frac{-4B^2}{\pi}\right)}$$

Thus values of erfc(B) range from 0 to +2, since the maximum value of erf(B) is 1.0 for 3.0 and all greater numbers.

EXAMPLE PROBLEM

Assume a D of 1×10^{-9} m²/sec and an ω of 0.5, to give a D^* of 5×10^{-10} m²/sec. Find the value of the concentration ratio, C_i/C_0, at a distance of 5m after 100 yr of diffusion.

1. Convert 100 yr to seconds:

$$100\,\text{yr} \times 365\,\text{da/yr} \times 1440\,\text{min/da} \times 60\,\text{sec/min} = 3.15 \times 10^9\,\text{sec}$$

2. Insert values into Equation 2.5:

$$\frac{C_i}{C_0} = \text{erfc}\,\frac{5}{2(5 \times 10^{-10}\,\text{m}^2/\text{sec} \times 3.15 \times 10^9\,\text{sec})^{0.5}}$$

3. Solve:

$$\frac{C_i}{C_0} = \text{erfc}\left(\frac{5}{2.51}\right) = \text{erfc}\,1.99 = 0.005$$

In 100 yr, diffusion over a 5-m distance would yield a concentration that is 0.5% of the original.

From the preceding example problem it is obvious that diffusion is not a particularly rapid means of transporting dissolved solutes. Diffusion is the predominant mechanism of transport only in low-permeability hydrogeologic regimes. However, it is possible for solutes to move through a porous or a fractured medium by diffusion even if the groundwater is not flowing.

2.3 Transport by Advection

Dissolved solids are carried along with the flowing groundwater. This process is called **advective transport, or advection.** The amount of solute that is being transported is a function of its concentration in the groundwater and the quantity of the groundwater flowing. For one-dimensional flow normal to a unit cross-sectional area of the porous media, the quantity of water flowing is equal to the *average linear velocity* times *the effective porosity.* **Average linear velocity**, v_x, is the rate at which the flux of water across the unit cross-sectional area of pore space occurs. It is not the average rate at which the water molecules are moving along individual flowpaths, which is greater than the average linear velocity due to tortuosity. The **effective porosity**, n_e, is the porosity through which flow can occur. Noninterconnected and dead-end pores are not included in the effective porosity, so that $n_e < n$.

$$v_x = \frac{K}{n_e}\frac{dh}{dl} \qquad \textbf{(2.6)}$$

where

v_x = average linear velocity (L/T)
K = hydraulic conductivity (L/T)

n_e = effective porosity
dh/dl = hydraulic gradient (L/L)

Note that the abbreviation n is used in the context of flow and transport under saturated conditions. When discussing unsaturated flow, θ is preferred because it refers to the water content of the porous matrix, as defined in Chapter 4. When the matrix is fully saturated n equals θ. The one-dimensional mass flux, F_x due to advection is equal to the quantity of water flowing times the concentration of dissolved solids and is given by Equation 2.7:

$$F_x = v_x n_e C \tag{2.7}$$

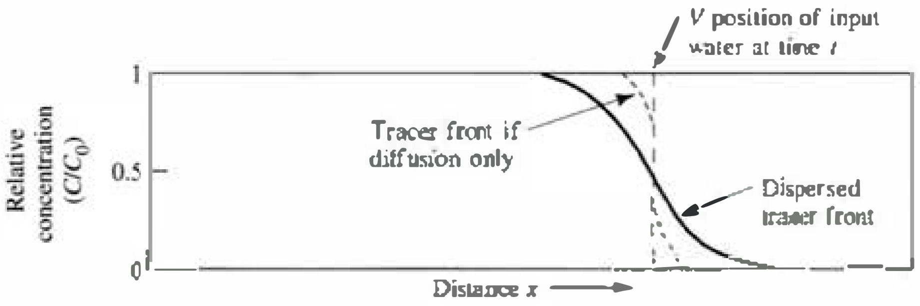
The one-dimensional advective transport equation is

$$\frac{\partial C}{\partial t} = -v_x \frac{\partial C}{\partial x} \tag{2.8}$$

(The derivation of this equation is given in Section 2.6.)

Solution of the advective transport equation yields a sharp concentration front. On the advancing side of the front, the concentration is equal to that of the invading groundwater, whereas on the other side of the front it is unchanged from the background value. This is known as plug flow, with all the pore fluid being replaced by the invading solute front. The sharp interface that results from plug flow is shown in Figure 2.3. The vertical dashed line at V represents an advancing solute front due to advection alone.

Figure 2.3 Advective transport and the influence of longitudinal dispersion and diffusion on the transport of a solute in one-dimensional flow.



Source: C.W. Fetter. 1994. *Applied Hydrogeology*, 3rd ed. Upper Saddle River, New Jersey: Prentice-Hall, Inc.

Due to the heterogeneity of geologic materials, advective transport in different strata can result in solute fronts spreading at different rates in each stratum. If one obtains a sample of water for purposes of monitoring the spread of a dissolved contaminant from a borehole that penetrates several strata, the water sample will be a composite of the water from each stratum. Due to the fact that advection will transport solutes at different rates in each stratum, the composite sample may be a mixture of water containing the transported solute coming from one stratum and uncontaminated groundwater coming from a different stratum where the average linear velocity is lower. The concentration of the contaminant in the composite sample would thus be less than in the source.

EXAMPLE PROBLEM

Dissolved nitrate in a concentration of 18.0 mg/L is being advected with flowing groundwater at a velocity of 0.331 m/day in an aquifer with a porosity of 0.225. Groundwater from the aquifer discharges into a stream. What is the mass flux of nitrate into the stream if the aquifer is 1.80 m thick and 123 m wide where it discharges into the stream?

From Equation 2.7 the one dimensional mass flux is

$$F_x = v_x n_e C$$

Given: $v_x = 0.331$ m/da

$n_e = 0.225$

$C = 18.0$ mg/L

For consistent units the concentration should be in gm/m³.

$$C = 18.0 \text{ mg/L} \times 1/1000 \text{ gm/mg} \times 1000 \text{ L/m}^3$$

$$C = 18.0 \text{ gm/m}^3$$

The one dimensional mass flux is:

$$F_x = 0.331 \text{ m/da} \times 0.225 \times 18.0 \text{ gm/m}^3$$

$$F_x = 1.34 \text{ gm/da-m}^2$$

The flux into the stream is the one dimensional mass flux times the cross sectional area where the aquifer discharges into the stream.

Total flux $= 1.34 \text{ gm/da-m}^2 \times 123 \text{ m} \times 1.80 \text{ m}$

Total flux $= 297$ gm/da

2.4 Mechanical Dispersion

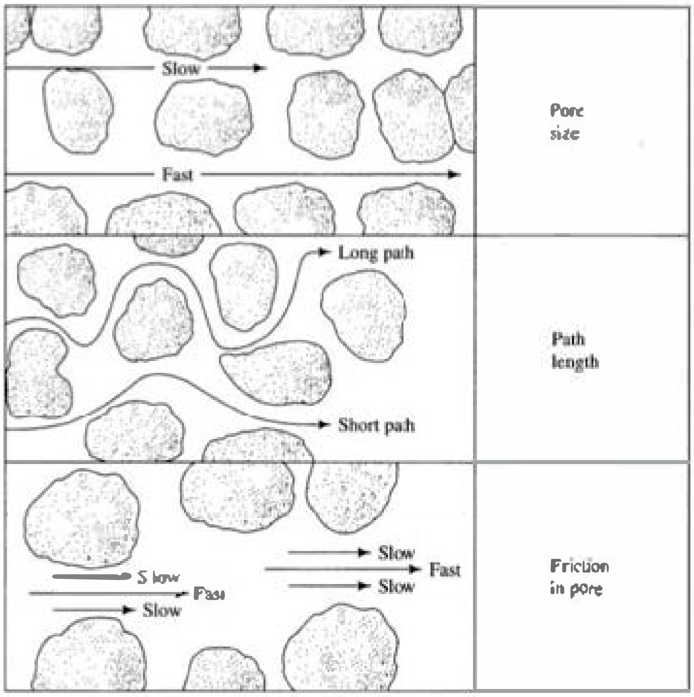
Groundwater is moving at rates that are both greater and less than the average linear velocity. At the macroscopic scale—that is, over a domain including a sufficient volume that the effects of individual pores are averaged (Bear 1972)—there are three basic causes of this phenomenon: (1) As fluid moves through the pores, it will move faster in the center of the pores than along the edges. (2) Some of the fluid particles will travel along longer flow paths in the porous media than other particles to go the same linear distance. (3) Some pores are larger than others, which allows the fluid flowing through these pores to move faster. These factors are illustrated in Figure 2.4.

If all groundwater containing a solute were to travel at exactly the same rate, it would displace water that does not contain the solute and create an abrupt interface between the two waters. However, because the invading solute-containing water is not all traveling at the same velocity, mixing occurs along the flowpath. This mixing is called **mechanical dispersion**, and it results in a dilution of the solute at the advancing edge of flow. The mixing that occurs along the direction of the flowpath is called **longitudinal dispersion**.

An advancing solute front will also tend to spread in directions normal to the direction of flow because at the pore scale the flowpaths can diverge, as shown in Figure 2.5. The result of this is mixing in directions normal to the flow path called **transverse dispersion**.

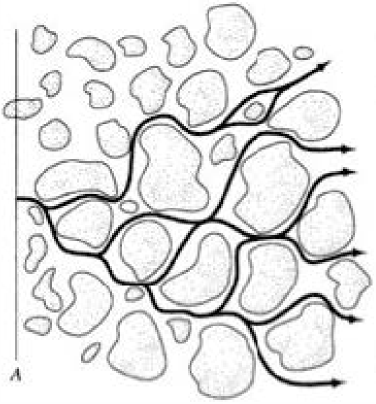
If we assume that mechanical dispersion can be described by Fick's law for diffusion (Equations 2.1 and 2.2) and that the amount of mechanical dispersion is a function of the average linear velocity, then we can introduce a coefficient of mechanical dispersion. This is equal to a property of the medium called *dynamic dispersivity*, or

FIGURE 2.4 Factors causing longitudinal dispersion at the scale of individual pores.



Source: C. W. Fetter. 1994. *Applied Hydrogeology, 3d ed.* Upper Saddle River, New Jersey: Prentice-Hall, Inc.

FIGURE 2.5 Flowpaths in a porous medium that cause lateral (transverse) hydrodynamic dispersion.



Source: C. W. Fetter. 1994. *Applied Hydrogeology, Third Edition.* Upper Saddle River, New Jersey: Prentice-Hall, Inc.

simply *dispersivity*, α, times the average linear velocity. If i is the principle direction of flow, the following definitions apply:

$$\text{Coefficient of longitudinal mechanical dispersion} = \alpha_i v_i \tag{2.9}$$

where

v_i = the average linear velocity in the i direction (L/T)
α_i = the dynamic dispersivity in the i direction (L)

and

$$\text{Coefficient of transverse mechanical dispersion} = \alpha_j v_i \tag{2.10}$$

where

v_i = the average linear velocity in the i direction (L/T)
α_j = the dynamic dispersivity in the j direction (L)

2.5 Hydrodynamic Dispersion

The process of molecular diffusion cannot be separated from mechanical dispersion in flowing groundwater. The two are combined to define a parameter called the **hydrodynamic dispersion coefficient**, D. It is represented by the following formulas:

$$D_L = \alpha_L v_i + D^* \tag{2.11a}$$

$$D_T = \alpha_T v_i + D^* \tag{2.11b}$$

where

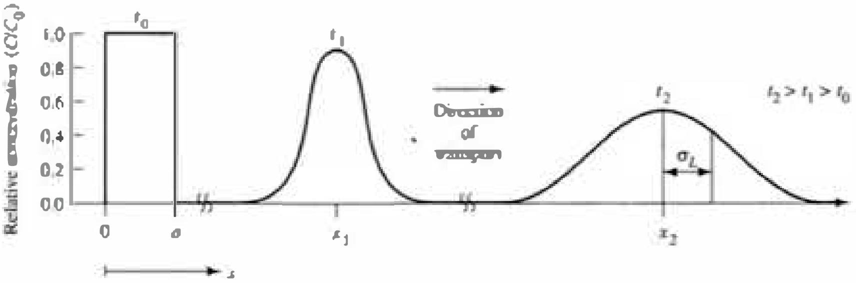
D_L = hydrodynamic dispersion coefficient parallel to the principal direction of flow (longitudinal)
D_T = hydrodynamic dispersion coefficient perpendicular to the principal direction of flow (transverse)
α_L = longitudinal dynamic dispersivity
α_T = transverse dynamic dispersivity

Figure 2.3 shows the effect of diffusion and mechanical dispersion on the relative concentration (C'/C_0) of a solute acting as a tracer that has been injected into a porous medium under one-dimensional flow conditions. The vertical line at V represents the advective transport without dispersion. Effects of diffusion and mechanical dispersion are shown.

The process of hydrodynamic dispersion can be illustrated by Figure 2.6. A mass of solute is instantaneously introduced into the aquifer at time t_0 over the interval $x = 0 + a$. The resulting initial concentration is C_0. The advecting groundwater carries the mass of solute with it. In the process the solute slug spreads out, so that the maximum concentration decreases with time, as shown for times t_1 and t_2. The diffusional model of hydrodynamic dispersion predicts that the concentration curves will have a Gaussian distribution that is described by the mean and the variance. With this distribution the coefficients of longitudinal and transverse hydrodynamic dispersion can be defined as

$$D_L = \frac{\sigma_L^{\,2}}{2t} \tag{2.12a}$$

FIGURE 2.6 Transport and spreading of a solute slug with time due to advection and dispersion. A slug of solute was injected at $x = 0 + a$ at time t_0 with a resulting concentration of C_0. The groundwater flow is to the right.



$$D_T = \frac{\sigma_T{}^2}{2t} \tag{2.12b}$$

where

t = time

σ_T^2 = variance of the transverse spreading of the plume

σ_L^2 = variance of the longitudinal spreading of the plume

■ 2.6 Derivation of the Advection-Dispersion Equation for Solute Transport

This derivation of the advection-dispersion equation is based on work by Freeze and Cherry (1979), Bear (1972), and Ogata (1970). Working assumptions are that the porous medium is homogeneous, isotropic, and saturated with fluid and that flow conditions are such that Darcy's law is valid.

The derivation is based on the conservation of mass of solute flux into and out of a small representative elementary volume (REV) of the porous media. The REV is the smallest volume that is representative for the entirety of whole medium. A measurement made at the REV scale will yield a value typically of the whole (Hill 1963). The REV concept serves as a cornerstone in the continuum modeling of transport phenomena in porous media (Bachmat and Bear 1987). The flow is at a macroscopic scale, which means that it accounts for the differences in flow from pore to pore. A representative elementary volume is illustrated in Figure 1.6.

The average linear velocity, v, has components v_x, v_y, and v_z. The concentration of solute, C, is mass per unit volume of solution. Mass of solute per unit volume of aquifer is the product of the effective porosity, n_e, and C. Porosity is considered to be a constant because the aquifer is homogeneous.

The solute will be transported by advection and hydrodynamic dispersion. In the i direction the solute transport is given by

$$\text{Advective transport} = v_i n_e C\,dA \tag{2.13}$$

$$\text{Dispersive transport} = n_e D_i \frac{\partial C}{\partial i}\,dA \tag{2.14}$$

where dA is the cross-sectional area of the element and the i direction is normal to that cross-sectional face.

The total mass of solute per unit cross-sectional area transported in the i direction per unit time, F_i, is the sum of the advective and the dispersive transport and is given by

$$F_i = v_i n_e C - n_e D_i \frac{\partial C}{\partial i} \tag{2.15}$$

The negative sign indicates that the dispersive flux is from areas of greater to areas of lesser concentration.

The total amount of solute entering the representative elementary volume is

$$F_x\,dz\,dy + F_y\,dz\,dx + F_z\,dx\,dy$$

The total amount of solute leaving the representative elementary volume is

$$\left(F_x + \frac{\partial F_x}{\partial x}dx\right)dz\;dy + \left(F_y + \frac{\partial F_y}{\partial y}dy\right)dz\;dx + \left(F_z + \frac{\partial F_z}{\partial z}dz\right)dx\;dy$$

The difference between the mass of the solute entering the representative elementary volume and the amount leaving it is

$$-\left(\frac{\partial F_x}{\partial x} + \frac{\partial F_y}{\partial y} + \frac{\partial F_z}{\partial z}\right)dx\;dy\;dz$$

The rate of mass change in the representative elementary volume is

$$n_e \frac{\partial C}{\partial t} dx\;dy\;dz$$

By the law of mass conservation, the rate of mass change in the representative elementary volume must be equal to the difference in the mass of the solute entering and the mass leaving.

$$\frac{\partial F_x}{\partial x} + \frac{\partial F_y}{\partial y} + \frac{\partial F_z}{\partial z} = -n_e \frac{\partial C}{\partial t} \tag{2.16}$$

Equation 2.15 can be used to find the values of F_x, F_y, and F_z. These are substituted in Equation 2.16, which becomes, after cancellation of n_e from both sides,

$$\left[\frac{\partial}{\partial x}\left(D_x \frac{\partial C}{\partial x}\right) + \frac{\partial}{\partial y}\left(D_y \frac{\partial C}{\partial y}\right) + \frac{\partial}{\partial z}\left(D_z \frac{\partial C}{\partial z}\right)\right]$$
$$-\left[\frac{\partial}{\partial x}(v_x C) + \frac{\partial}{\partial y}(v_y C) + \frac{\partial}{\partial z}(v_z C)\right] = \frac{\partial C}{\partial t} \tag{2.17}$$

Equation 2.17 is the three-dimensional equation of mass transport for a *conservative* solute—that is, one that does not interact with the porous media or undergo biological or radioactive decay.

In a homogeneous medium, D_x, D_y, and D_z do not vary in space. However, because the coefficient of hydrodynamic dispersion is a function of the flow direction, even in an isotropic, homogeneous medium, $D_x \neq D_y \neq D_z$. For those domains where the average linear velocity, v_x, is uniform in space; Equation 2.17 for one-dimensional flow in a homogeneous, isotropic porous media is

$$D_L \frac{\partial^2 C}{\partial x^2} - v_x \frac{\partial C}{\partial x} = \frac{\partial C}{\partial t} \tag{2.18}$$

In a homogeneous medium with a uniform velocity field, Equation 2.17 for two-dimensional flow with the direction of flow parallel to the x axis is

$$D_L \frac{\partial^2 C}{\partial x^2} + D_T \frac{\partial^2 C}{\partial y^2} - v_x \frac{\partial C}{\partial x} = \frac{\partial C}{\partial t} \tag{2.19}$$

where

D_L = the longitudinal hydrodynamic dispersion (L^2/T)
D_T = the transverse hydrodynamic dispersion (L^2/T)

Equation 2.17 for radial flow from a well can be written in polar coordinates (Ogata 1970) as

$$\frac{\partial}{\partial r}\left(D \frac{\partial C}{\partial r}\right) + \frac{D}{r}\frac{\partial C}{\partial r} - u \frac{\partial C}{\partial r} = \frac{\partial C}{\partial t} \tag{2.20}$$

where

r = radial distance to the well
u = average pore velocity of injection, which is found from

$$u = \frac{Q}{2\pi n_e R r^2}$$

where

Q = the rate of injection into the well
n_e = effective porosity
R = length of well screen or open bore hole

2.7 Diffusion versus Dispersion

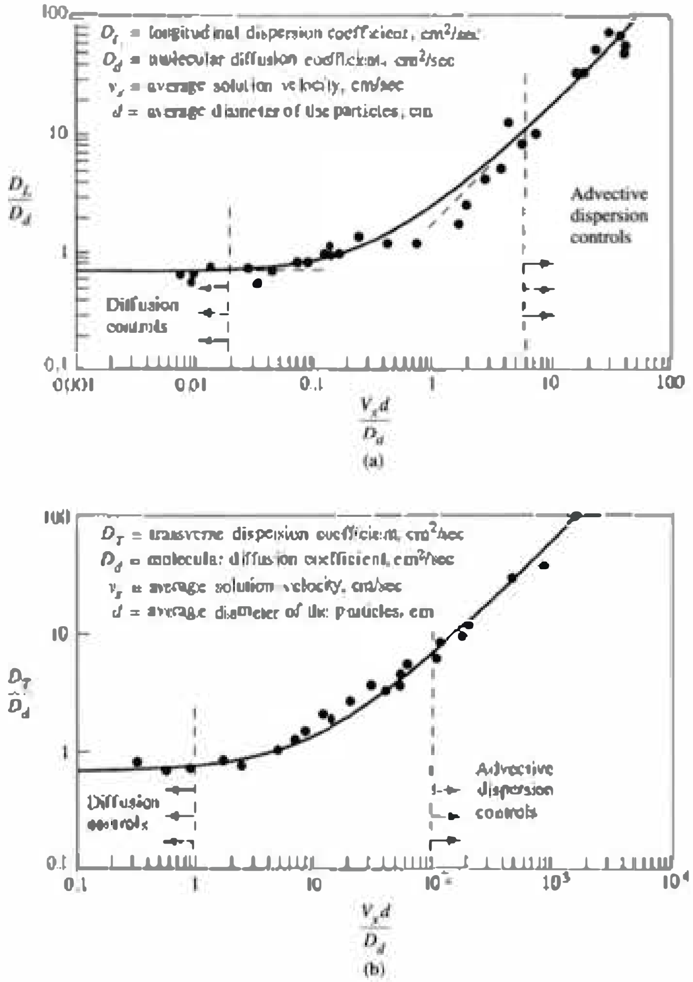
In the previous section the mass transport equation was derived on the basis of hydrodynamic dispersion, which is the sum of mechanical dispersion and diffusion. It would have been possible to separate the hydrodynamic dispersion term into the two components and have separate terms in the equation for them. However, as a practical matter, under most conditions of groundwater flow, diffusion is insignificant and is neglected.

It is possible to evaluate the relative contribution of mechanical dispersion and diffusion to solute transport. A **Peclet number**, P_e, is a dimensionless number that can relate the effectiveness of mass transport by advection to the effectiveness of mass transport by either dispersion or diffusion. Peclet numbers have the general form of $v_x d/D_d$ or $v_x L/D_L$, where v_x is the advective velocity, d and L are characteristic flow lengths, D_d is the coefficient of molecular diffusion, and D_L is the longitudinal hydrodynamic dispersion coefficient. The column Peclet number, which defines the ratio of transport by advection to the rate of transport by molecular diffusion in column studies, is a dimensionless parameter defined as $v_x d/D_d$, where d is the average grain diameter and D_d is the coefficient of molecular diffusion. A plot of the ratio of D_L/D_d versus the Peclet number is given in Figure 2.7a. Shown on this figure are the results of a number of experimental measurements using sand columns and tracers as well as some experimental curves from several investigators (Perkins and Johnson 1963). Delgado (2007) presents empirical correlations for the prediction of the dispersion coefficients (D_T and D_L) based Peclet number and Schmidt number (S_c). The dimensionless Schmidt number relates the viscous diffusion rate to the molecular diffusion rate. S_c is defined as:

$$S_c = \frac{\mu}{\rho D}$$

where μ and ρ are the dynamic viscosity (M/LT) and density of the fluid, respectively. D is the diffusion coefficient.

FIGURE 2.7 Graph of dimensionless dispersion coefficients versus Peclet number, $P_e = v_x d/D_d$. (a) D_L/D_e versus P_e and (b) D_T/D_e versus P_e.



Source: T.K. Perkins and O.C. Johnson. 1963. *Society of Petroleum Engineers Journal* 3:70–84. Society of Petroleum Engineers.

At zero flow velocity D_l is equal to D^*, since $D_l = a_l v_x + D^*$. In this manner the value of ω, the tortuosity factor, can be experimentally determined as $D^* = \omega D_d$. At very low velocities, the ratio of D_L/D_d is a constant with a value of about 0.7, which is the experimentally determined value of ω for uniform sand. This shows up on the left side of Figure 2.7(a) as a horizontal line. In this zone diffusion is the predominant force, and dispersion can be neglected. Between a Peclet number of about 0.4 to 6 there is a transition zone, where the effects of diffusion and longitudinal mechanical dispersion are more or less equal.

Figure 2.7(b) shows the plot of D_T/D_d as a function of Peclet number. Although the curve has the same shape as in (a), it occurs at Peclet numbers roughly 100 times greater. This means that diffusion has more control over transverse dispersion at higher Peclet numbers than it does for longitudinal dispersion. Higher Peclet numbers occur with higher velocities and/or longer flow paths. At higher Peclet numbers mechanical dispersion is the predominant cause of mixing of the contaminant plume (Perkins and Johnson 1963; Bear 1972; Bear and Verruijt 1987) and the effects of diffusion can be ignored. Under these conditions D_l can be replaced with $a_l v_l$ in the advection-dispersion equations.

2.8 Moment Analysis

Contaminant hydrogeologists, like other scientists, have to work with a lot of data, such as periodic measurements of pollutant concentrations in monitoring wells or hydraulic values that determine the flow and transport of these pollutants. If writing a report or publishing data in peer reviewed manuscripts, one is expected to back up the significance of the data with a proper statistical analysis. A review of statistical concepts and methods is not the focus of this book, but excellent introductions into groundwater statistics are provided by Helsel and Hirsch (2002) or Interstate Technology and Regulatory Council (2013).

One statistical method, however, that is quite useful for the analysis of contaminant fate and transport data, especially results from laboratory or field-scale tracer tests, warrants a more detailed discussion. The method is known as moment analysis. This method can be an important tool for calculating mass recoveries in tracer experiments, travel velocities of a plume, and the description of the shape of the plume in terms of dispersivity, skewness, and kurtosis. Both temporal and spatial data can be used for this analysis. The relationship between the spatial and temporal moments and the properties of an evolving solute plume are based on work by Aris (1956) and subsequent modifications by Goltz and Roberts (1987), who developed moment concepts for the analysis of three-dimensional solute transport data. The spatial moment technique was utilized by Marle et al. (1967), Ghüven et al. (1984) and Valocchi (1989) to study solute transport in steady horizontal flow in a perfectly stratified aquifer. Valocchi (1990) provides an overview of the usefulness of temporal moment analysis for studying reactive solute transport in aggregated porous media.

The method of moment was employed for the analysis of many natural gradient field tracer tests. For instance, the spatial moments of the bromide tracer distribution were used to calculate the tracer mass, velocity, and dispersivity during the large-scale tracer test at the Canadian Air Force Base (CFB) in Borden, Ontario (Freyberg 1986; Farrell and Woodbury 1994) or the transport of nonreactive and reactive tracers in a sand and gravel aquifer on Cape Cod, Massachusetts (Leblanc et al. 1991; Garabedian et al. 1991) or at the Twin Lake aquifer test site within the property of the Chalk River

Nuclear Laboratories, where in 1982 and 1983 a pulse of groundwater labeled with ^{131}Iodine was injected (Moltyaner and Killey 1988; Moltyaner and Wills 1991).

The analysis of moments ordinarily is accomplished by numerically solving one or more triple integrals of tracer concentration in the three-dimensional space of the test domain (Freyberg 1986; Glotz and Roberts 1987; Valochhi 1989; Garabedian et al. 1991). The absolute moments (M) in three dimensions are defined as follows:

$$M_{jkn} = \iiint_{-\infty}^{\infty} C x^j y^k z^n \, dx \, dy \, dz$$

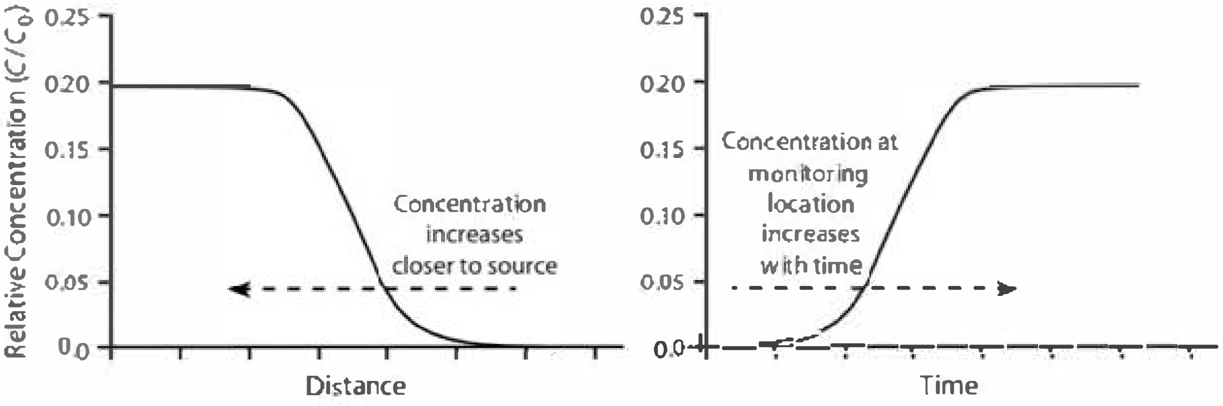
where C is the solute concentration at the spatial coordinates x, y, and z. For one-dimensional data sets, the moment analysis can be simplified to the temporal and spatial forms summarized in Table 2.2.

Temporal moments can be interpreted with the help of breakthrough curves (BTC) (Figure 2.8). A BTC is a graph of concentration versus time. This format of depiction is appropriate when the position of the observer is fixed (Eulerian approach). A BTC

TABLE 2.2 One-dimensional moments.

Moment	Temporal Moments	Spatial Moments
Zeroth Absolute Moment	$M_t^0 = \int_0^\infty C\,dt$	$M_s^0 = \int_0^\infty C\,dx$
First Normalized Moment	$M_t^1 = \dfrac{\int_0^\infty Ct\,dt}{\int_0^\infty C\,dt} = \dfrac{\int_0^\infty Ct\,dt}{M_t^0}$	$M_s^1 = \dfrac{\int_0^\infty Cx\,dx}{\int_0^\infty C\,dx} = \dfrac{\int_0^\infty Cx\,dx}{M_x^0}$
Adjusted First Temporal Moment	$M_{adj}^1 = \dfrac{\int_0^x Ct\,dt}{M_t^0} - \dfrac{1}{2}T_0$	Not defined
Second Central Moment	$M_t^2 = \dfrac{\int_0^\infty \left(t - M_t^1\right)^2 C\,dt}{M_t^0}$	$M_s^2 = \dfrac{\int_0^\infty \left(x - M_s^1\right)^2 C\,dx}{M_s^0}$
Third Central Moment	$M_t^3 = \dfrac{\int_0^\infty \left(t - M_t^1\right)^3 C\,dt}{M_t^0}$	$M_s^3 = \dfrac{\int_0^\infty \left(x - M_s^1\right)^3 C\,dx}{M_s^0}$
Fourth Central Moment	$M_t^4 = \dfrac{\int_0^\infty \left(t - M_t^1\right)^4 C\,dt}{M_t^0}$	$M_s^4 = \dfrac{\int_0^\infty \left(x - M_s^1\right)^4 C\,dx}{M_s^0}$

FIGURE 2.8 Representation of concentration data resulting from a continuous contaminant release scenario: (a) concentration versus distance and (b) concentration versus time. The concentration-time graph is called a breakthrough curve (BTC).



is typically used to report solute concentrations in column effluent during of tracer experiment or at the location of a specific monitoring well. In contrast, a graph of concentration versus distance is not a BTC. It represents a snapshot of concentration data collected more or less simultaneously at various locations within the test domain (Lagrangian approach). Such a graph is useful, for example, for reporting the tracer concentration in groundwater samples collected along the principal axis of a contaminant plume.

It is convenient to normalize the higher order temporal and spatial moments by scaling them to the zeroth temporal moment (M_t^0) or zeroth spatial moment (M_s^0), respectively. Higher moments are centralized by subtracting the first normalized temporal or spatial moment ($M_{t,s}^1$) from the elapsed time (t) or distance (x), respectively, since the start of the measurements.

The significance of M_t^0 is that it integrates the area under the concentration versus distance curve (Figure 2.8) and thus presents the mass of solute and a measure for calculating the solute mass recovery and mass balance. The M_t^0 aides in determining the amount of mass passing by a sampling point (i.e., monitoring well). A constant value of M_s^0 at different distances from the origin indicates that no mass loss occurred and therefore suggests a recalcitrance of a compound to sorption of degradation processes. The M_s^1 calculates the mean, i.e., the location of the center of mass of a plume and thus aides in calculating the plume travel velocity. M_t^1 describes the travel time of a dissolved compound (Figure 2.9). While not defined for spatial coordinate data, the adjusted first temporal moment, M_{adj}^1, is:

$$M_{adj}^1 = \frac{\int_0^{\infty} C\ t\ dt}{M^0} - \frac{1}{2} T_0$$

where T_0 is the pulse length, i.e., the duration of the tracer slug injection. M_{adj}^1 permits the calculation of the tracer front travel time (Figure 2.11) and therefore M_{adj}^1 can be used to calculate the retardation factor from the inflection point of the BTC, i.e., where $C/C_{max} = 0.5$. The parameter C_{max} is the maximum concentration measured during the tracer test (Figure 2.9).

FIGURE 2.9 Ideal breakthrough curve (BTC). The arrival time is the time for the center of mass to arrive at the monitoring location. The travel time is the breakthrough time of the tracer front.

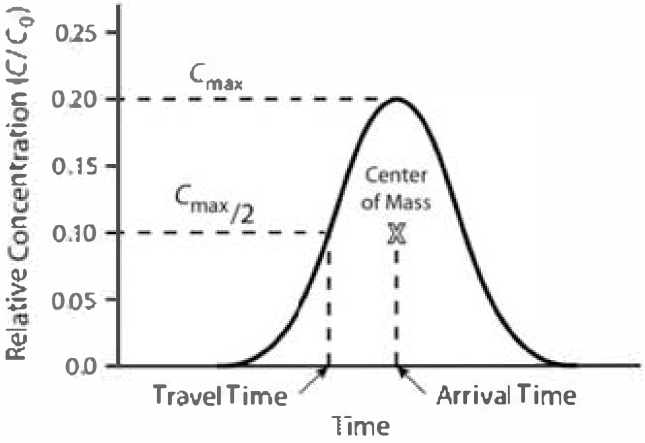
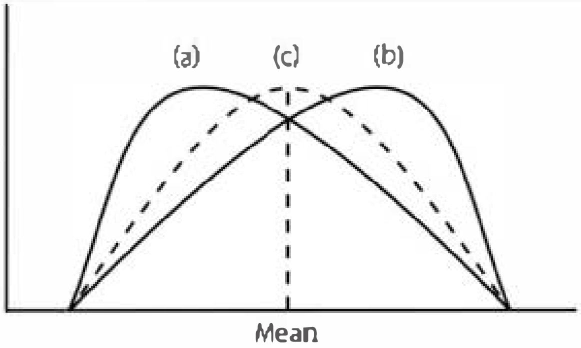


FIGURE 2.10 Skewness: (a) positive, (b) negative and (c) not skewed around the mean ($M^3 = 0$).



The second temporal moment (M_t^2) is the variance (σ^2) and provides a measure for the spread of a plume about the location of the center of mass. The analysis of the second spatial moment (M_s^2) can be used to determine the longitudinal dispersion coefficient, D_L, in either temporal or spatial coordinates:

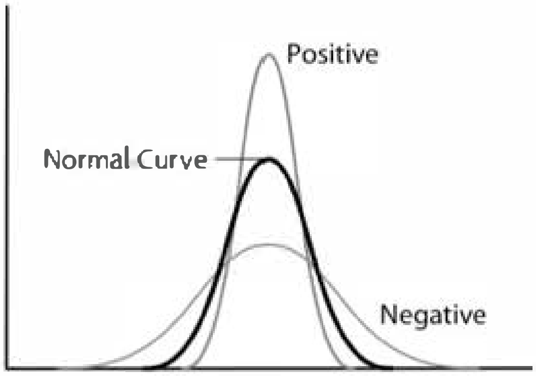
$$D_L = \frac{\sigma_L^2}{2t}$$

$$D_L = \frac{\sigma_L^2 v}{2x}$$

where σ_L^2 is the variance, t is time since the start of the tracer test and v is the linear flow velocity (constant).

The skewness of a curve is described by the third moment (M^3). A positive value indicates that the graph is skewed to the right, whereas a negative value means skewness to the left (Figure 2.10). A value of approximately zero suggests that the data is normally distributed. The fourth moment (M^4) is a measure of kurtosis (Figure 2.11). For a conservative tracer, both M^3 and M^4 should be approximately zero. Deviations

FIGURE 2.11 Negative and positive kurtosis. The M^4 is zero for when the tracer concentration data is normally distributed.



from that value indicate non-ideal transport conditions. Other applications of moment analysis are discussed in Suthersan et al. 2017.

EXAMPLE

A tracer test was conducted and concentration measurements have been collected downgradient from the injection location and at three different times ($t_1 = 30$ *d*, $t_2 = 60$ *d*, and $t_3 = 90$ *d*). Figure 2.12 shows the concentration versus distance data in terms of dimensionless concentration (C/C_0) at three observations points.

In this example, the tracer is nonreactive because the area under the curves (M^0) remains the same for all three data sets. Had the value of M^0 decreased however, it

FIGURE 2.12 The spatial position of the tracer concentrations profiles at times t_1, t_2, and t_3.

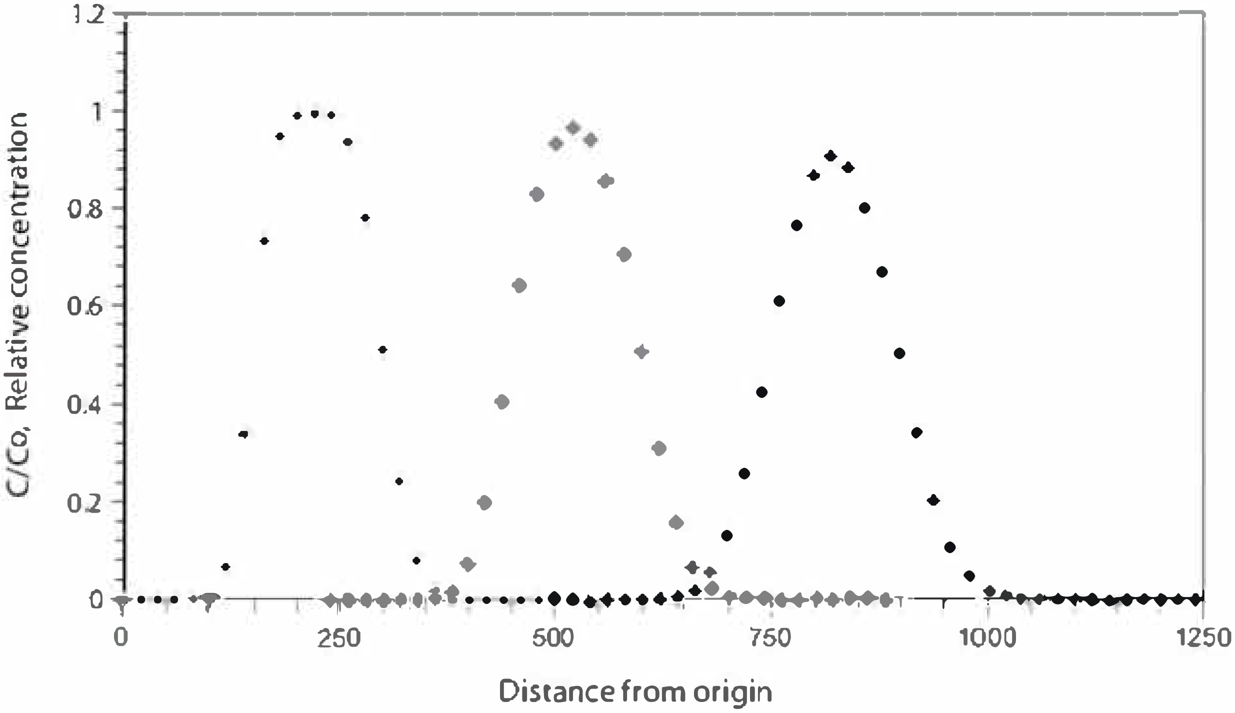
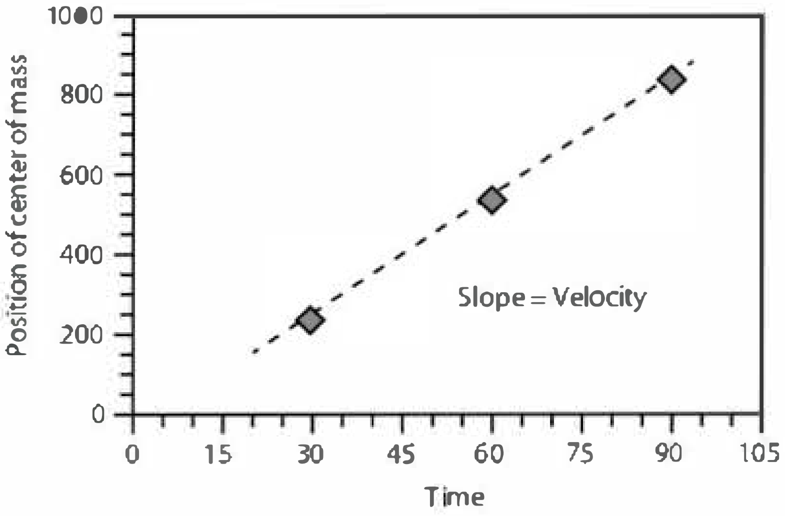


FIGURE 2.13 The velocity of a migrating plume can be estimated from the location of the center of mass (First spatial moment).



would have indicated that a fraction of the tracer was lost during the experiment. In that case, a plot of M^0 versus distance would reveal if the rate of loss is linear or nonlinear.

The velocity of a migrating plume was estimated from the location of the center of mass (M^1) at different times (Figure 2.12). In this example, the velocity remained constant throughout the experiment, which is expected for a nonreactive tracer. If the flow velocity is identical to the groundwater flow velocity, the tracer can be considered "conservative," i.e., its flow is not retarded. By comparing the M^1 of a conservative tracer with that of other tracers that might have been co-injected at the start of the tracer test, one can calculate the relative travel times or relative travel distances and thus the retardation factors for each tracer.

When plotting M^2 for each of the three data sets against the time of measurement, the slope of the regression line is equal to $2D_L$. The M^3 and M^4 values indicate that the three data sets are not skewed and that they do not show kurtosis; once again indicating that the tracer was nonreactive.

2.9 Analytical Solutions of the Advection-Dispersion Equation

2.9.1 Methods of Solution

The advection-dispersion equations can be solved by either numerical or analytical methods. Analytical methods involve the solution of the partial differential equations using calculus based on the initial and boundary value conditions. They are limited to simple geometry and in general require that the aquifer be homogeneous. A number of analytical solutions are presented in this chapter. They are useful in that they can be solved with spreadsheet, like EXCEL, or even a pencil and paper, if one is so inclined.

Numerical methods involve the solution of the partial differential equation by numerical methods of analysis. They are more powerful than analytical solutions in the sense that aquifers of any geometry can be analyzed and aquifer heterogeneities can be accommodated. However, there can be other problems with numerical models, such as numerical errors, which can cause solutions to show excess spreading of solute fronts or plumes that are not related to the dispersion of the tracer that is the subject of the modeling. Bear and Verruijt (1987) present a good introduction to the use of numerical models to solve mass transport equations. These solutions are normally found by methods of computer modeling, a topic beyond the scope of this text. Instead, the reader is referred to Bear and Cheng (2010), who offer an overview about the methodology and procedures for constructing conceptual and mathematical models for groundwater flow and the fate and transport of contaminants in both saturated and unsaturated zones. Also, Kuzmin (2010) provides a guide to numerical methods for solving transport equations with particular focus on finite element models.

2.9.2 Boundary and Initial Conditions

In order to obtain a unique solution to a differential equation it is necessary to specify the initial and the boundary conditions that apply. The initial conditions describe the values of the variable under consideration, in this case concentration, at some initial time equal to 0. The **boundary conditions** specify the interaction between the area under investigation and its external environment.

There are three types of boundary conditions for mass transport. The boundary condition of the first type is a **fixed concentration.** The boundary condition of the second type is a **fixed gradient.** A **variable flux** boundary constitutes the boundary condition of the third type.

Boundary and initial conditions are shown in a shorthand form. For one-dimensional flow we need to specify the conditions relative to the location, x, and the time, t. By convention this is shown in the form

$$C(x,t)=C(t)$$

where $C(t)$ is some known function.

For example, we can write

$$C(0,t)=C_0, \quad t\geq 0$$
$$C(x,0)=0, \quad x\geq 0$$
$$C(\infty,t)=0, \quad t\geq 0$$

The first statement says that for all time t equal to or greater than zero, at $x=0$ the concentration is maintained at C_0. This is a fixed-concentration boundary condition located at $x=0$ (first-type boundary). The second statement is an initial condition that says at time $t=0$, the concentration is zero everywhere within the flow domain, that is, where x is greater than or equal zero. As soon as flow starts, solute at a concentration of C_0 will cross the $x=0$ boundary.

The third condition shows that the flow system is infinitely long and that no matter how large time gets, the concentration will still be zero at the end of the system (first-type boundary condition at $x=\infty$).

We could also have specified an initial condition that within the domain the initial solute concentration was C_i. This would be written as

$$C(x,0) = C_i, \quad x \geq 0$$

Other examples of concentration (first-type) boundary conditions are exponential decay of the source term and pulse loading at a constant concentration for a period of time followed by another period of time with a different constant concentration.

Exponential decay for the source term can be expressed as

$$C(0,t) = C_0 e^{-it}$$

where i = a decay constant.

Pulse loading where the concentration is C_0 for times from 0 to t_0 and then is 0 for all time more than t_0 is expressed as

$$C(0,t) = C_0 \qquad 0 < t \leq t_0$$

$$C(0,t) = 0 \qquad t > t_0$$

Fixed-gradient boundaries are expressed as

$$\left.\frac{dC}{dx}\right|_{x=0} = f(t) \quad \text{or} \quad \left.\frac{dC}{dx}\right|_{x=\infty} = f(t)$$

where $f(t)$ is some known function. A common fixed-gradient condition is $dC/dx = 0$, or a no-gradient boundary.

The variable-flux boundary, a third type, is given as

$$-D\frac{\partial C}{\partial x} + v_x C = v_x C(t)$$

where $C(t)$ is a known concentration function. A common variable-flux boundary is a constant flux with a constant input concentration, expressed as

$$\left.\left(-D\frac{dC}{dx} + vC\right)\right|_{x=0} = C_0$$

2.9.3 One-Dimensional Step Change in Concentration (First-Type Boundary)

Sand column experiments have been used to evaluate both the coefficients of diffusion and dispersion at the laboratory scale. A tube is filled with sand and then saturated with water. Water is made to flow through the tube at a steady rate, creating, in effect, a permeameter. A solution containing a tracer is then introduced into the sand column in place of the water. The initial concentration of the solute in the column is zero, and the concentration of the tracer solution is C_0. The tracer in the water exiting the tube is analyzed, and the ratio of C, the tracer concentration at time t, over C_0, the injected tracer concentration, is plotted as a function of time. This is called a **fixedstep function.**

The boundary and initial conditions are given by

$$\begin{array}{lll} C(x,0)=0 & x \geq 0 & \text{Initial condition} \\ \left.\begin{array}{ll} C(0,t)=C_0 & t \geq 0 \\ C(\infty,t)=0 & t \geq 0 \end{array}\right\} & & \text{Boundary conditions} \end{array}$$

The solution to Equation 2.18 for these conditions is (Ogata and Banks 1961)

$$C=\frac{C_0}{2}\left[\operatorname{erfc}\left(\frac{L-v_x t}{2\sqrt{D_L t}}\right)+\exp\left(\frac{v_x L}{D_L}\right)\operatorname{erfc}\left(\frac{L+v_x t}{2\sqrt{D_L t}}\right)\right] \tag{2.21}$$

This equation may be expressed in dimensionless form as

$$C_R\left(t_R,P_e\right)=0.5\left\{\operatorname{erfc}\left[\left(\frac{P_e}{4t_R}\right)^{1/2}\times(1-t_R)\right]+\exp(P_e)\operatorname{erfc}\left[\left(\frac{P_e}{4t_R}\right)^{1/2}(1+t_R)\right]\right\} \tag{2.22}$$

where

t_R = $v_x t/L$
C_R = C/C_0
P_e = Peclet number when flow distance, L, is chosen as the reference length ($P_e = v_x L/D_L$)
erfc = complementary error function

Equation 2.21 can be solved in Microsoft Excel after installing the *Plume1D*() add-in (Renshaw 2015a).

2.9.4 One-Dimensional Continuous Injection into a Flow Field (Second-Type Boundary)

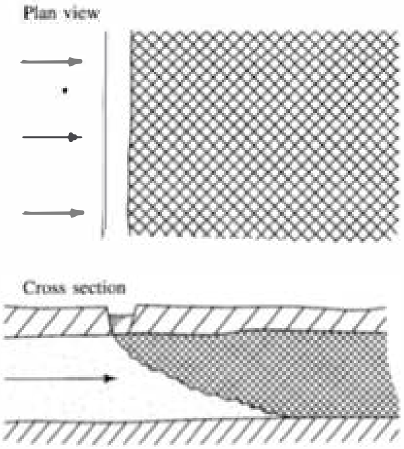
In nature there are not many situations where there would be a sudden change in the quality of the water entering an aquifer. A much more likely condition is that there would be leakage of contaminated water into the groundwater flowing in an aquifer. For the one-dimensional case, this might be a canal that is discharging contaminated water into an aquifer as a line source (Figure 2.14).

The rare of injection is considered to be constant, with the injected mass of the solute proportional to the duration of the injection. The initial concentration of the solute in the aquifer is zero, and the concentration of the solute being injected is C_0. The solute is free to disperse both up-gradient and down-gradient.

The boundary and initial conditions are

$$\begin{array}{lll} C(x,0)=0 & -\infty < x < +\infty & \text{Initial condition} \\ \left.\begin{array}{ll} \int_{-\infty}^{+\infty} n_e C(x,t)\,dx = C_0 n_e v_x t & t>0 \\ C(\infty,t)=0 & t \geq 0 \end{array}\right] & & \text{Boundary conditions} \end{array}$$

FIGURE 2.14 Leakage from a canal as a line source for injection of a contaminant into an aquifer.



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The second boundary condition states that the injected mass of contaminant over the domain from $-\infty$ to $+\infty$ is proportional to the length of time of the injection.

The solution to this flow problem (Sauty 1980) is

$$C = \frac{C_0}{2}\left[\operatorname{erfc}\left(\frac{L - v_x t}{2\sqrt{D_L t}}\right) - \exp\left(\frac{v_x L}{D_L}\right)\operatorname{erfc}\left(\frac{L + v_x t}{2\sqrt{D_L t}}\right)\right] \tag{2.23}$$

In dimensionless form this is

$$C_R(t_R, P_e) = 0.5\left\{\operatorname{erfc}\left[\left(\frac{P_e}{4t_R}\right)^{1/2}(1 - t_R)\right] - \exp(P_e)\operatorname{erfc}\left[\left(\frac{P_e}{4t_R}\right)^{1/2}(1 + t_R)\right]\right\} \tag{2.24}$$

It can be seen that Equations 2.21 and 2.23 are very similar, the only difference being that the second term is subtracted rather than added in 2.23.

Sauty (1980) gives an approximation for the one-dimensional dispersion equation as

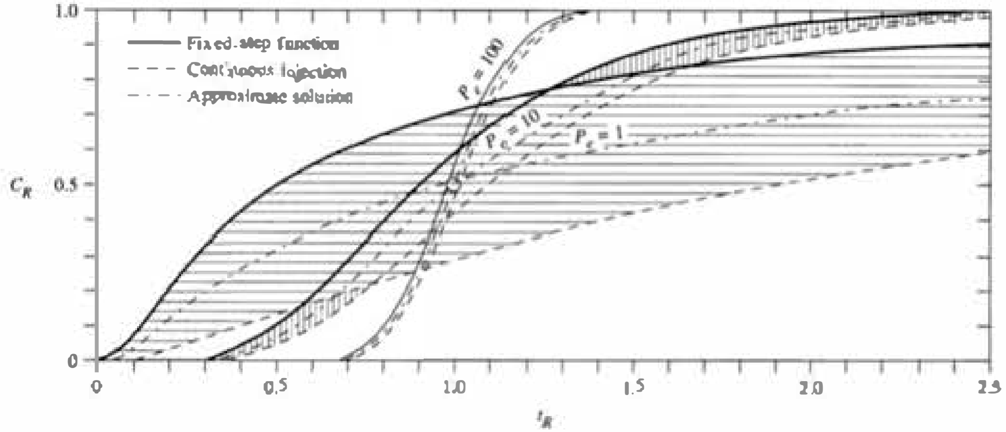
$$C = \frac{C_0}{2}\left[\operatorname{erfc}\left(\frac{L - v_x t}{2\sqrt{D_L t}}\right)\right] \tag{2.25}$$

In dimensionless form this is

$$C_R(t_R, P_e) = 0.5\operatorname{erfc}\left[\left(\frac{P_e}{4t_R}\right)^{1/2}(1 - t_R)\right] \tag{2.26}$$

This approximation comes about because for large Peclet numbers, the second term of Equations 2.21 and 2.23 is much smaller than first term and can be neglected. Figure 2.15 demonstrates under what conditions this approximation is valid. In Figure 2.15 the dimensionless concentration, C_R, is plotted as a function of dimensionless time, t_R, for continuous tracer injection using the fixed-step function, Equation 2.22, the continuous-injection function, Equation 2.24, and the approximate solution, Equation 2.26. Curves are plotted for three Peclet numbers, 1, 10, and 100 (Section 2.7). The Peclet number defines the rate of transport by advection to the rate of transport by hydrodynamic dispersion. For Peclet number 1, the fixedstep function and the continuous-injection function give quite different results, whereas for Peclet number 100 they are almost identical. The approximate solution lies midway between the other two. This figure suggests that for Peclet numbers less than about 10, the exact solutions need to be considered, whereas for Peclet numbers greater than 10, the approximate solution is probably acceptable, especially as the Peclet number approaches 100. This Peclet number increases with flow-path length as advective transport becomes more dominant over dispersive transport. Thus for mass transport near the inlet boundary, it is important to use the correct equation, but as one goes away from the inlet boundary, it is less important that the correct form of the equation is employed.

FIGURE 2.15 Dimensionless-type curves for the continuous injection of a tracer into a one-dimensional flow field.



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EXAMPLE PROBLEM

Pickles are made in large wooden vats. At the Happy Gherkin Pickle Factory one of the vats has been leaking brine directly into the water table. The concentration of chloride in the brine is 1575 mgL^{-1}. The flow in the aquifer that receives the brine is essentially one-dimensional and has the following characteristics.

Hydraulic conductivity = 2.93×10^{-4} ms^{-1}

Hydraulic gradient = 0.00678

Effective porosity = 0.259

The estimated effective diffusion coefficient for chloride is 2×10^{-9} m^{2}s^{-1}.

Calculate the concentration of chloride above any background value at a distance 125 m from the leaking vat 0.50 years after the leak began.

We will apply equation 2.25 to this problem. Note that this is an approximate solution as the second term of equation 2.23 has been dropped.

$$C = \frac{C_0}{2}\left[\operatorname{erfc}\left(\frac{L - v_x t}{2\sqrt{D_L t}}\right)\right]$$

1. Calculate v_x

$$v_x = \frac{K}{n_e}\frac{dh}{dl}$$

$$v_x = \frac{2.93 \times 10^{-4} ms^{-1}}{0.259} \times 0.00678$$

$$v_x = 7.67 \times 10^{-6} ms^{-1}$$

2. Find the value of the coefficient of longitudinal hydrodynamic dispersion, D_L. This can be found from equation 2.11a.

$$D_L = \alpha_L v_x + D^*$$

   a. The first step is to find the value of α_L. This can be estimated from equation 2.48, which will be introduced in a later section.

$$\alpha_L = 0.83(\log L)^{2.414}$$

$$\alpha_L = 083(\log 125)^{2.414} \ m$$

$$\alpha_L = 4.96 \text{ m}$$

   b. The next step is to calculate D_L.

$$D_L = 4.96\text{m} \times 7.67 \times 10^{-6} \text{ms}^{-1} + 2 \times 10^{-9} \text{m}^2\text{s}^{-1}$$

$$D_L = 3.80 \times 10^{-5} \text{m}^2\text{s}^{-1} + 2 \times 10^{-9} \text{m}^{2-1}$$

   The second term reflecting the effective diffusion coefficient can be neglected as it is so much smaller than the first term.

3. In order to have consistent units, the time must be expressed in seconds.

   0.5 y × 365 d/y × 1440 min/d × 60 s/min = 1.578×10^7 s.

4. The values of the variables are then substituted into Equation 2.25.

$$C_0 = 1575 \text{ mgL}^{-1}$$

$$v_x = 7.67 \times 10^{-6} \text{ms}^{-1}$$

$$L = 125\text{m}$$

$$D_L = 3.80 \times 10^{-5} \text{m}^2\text{s}^{-1}$$

$$t = 1.578 \times 10^7 \text{s}$$

$$C = \frac{1575\,\mathrm{mgL^{-1}}}{2}\,\mathrm{erfc}\left(\frac{125\,\mathrm{m} - (7.67 \times 10^{-6}\,\mathrm{ms^{-1}} \times 1.578 \times 10^{7}\,\mathrm{s})}{2\sqrt{3.80 \times 10^{-5}\,\mathrm{m^2 s^{-1}} \times 1.578 \times 10^{7}\,\mathrm{s}}}\right)$$

$$C = 787.5\,\mathrm{erfc}\left(\frac{125\,\mathrm{m} - 121.0\,\mathrm{m}}{2\sqrt{5.99 \times 10^{2}\,\mathrm{m^2}}}\right)\mathrm{mgL^{-1}}$$

$$C = 787.5\,\mathrm{erfc}\left(\frac{4.0\,\mathrm{m}}{2 \times 24.49\,\mathrm{m}}\right)\mathrm{mgL^{-1}}$$

$$C = 787.5\,\mathrm{erfc}(0.0816)\ \mathrm{mg/L}$$

$$C = 787.5 \times 0.908\,\mathrm{mgL^{-1}} = 715\,\mathrm{mgL^{-1}}$$

2.9.5 Third-Type Boundary Condition

A solution for Equation 2.18 for the following boundary condition was given by van Genuchten (1981).

$$C(x,0) = 0 \qquad \text{Initial condition}$$

$$\left(-D\frac{\partial C}{\partial x} + v_x C\right)\bigg|_{x=0} = v_x C_0 \qquad \text{Boundary conditions}$$

$$\frac{\partial C}{\partial x}\bigg|_{x\to\infty} = (\text{finite})$$

The third condition specifies that as x approaches infinity, the concentration gradient will still be finite. Under these conditions the solution to Equation 2.18 is:

$$C = \frac{C_0}{2}\left[\mathrm{erfc}\left[\frac{L - v_x t}{2\sqrt{D_L t}}\right] + \left(\frac{v_x{}^2 t}{\pi D_L}\right)^{1/2} \exp\left[-\frac{(L - v_x t)^2}{4 D_L t}\right]\right. \tag{2.27}$$

$$\left. -\frac{1}{2}\left(1 + \frac{v_x L}{D_L} + \frac{v_x{}^2 t}{D_L}\right)\exp\left(\frac{v_x L}{D_L}\right)\mathrm{erfc}\left[\frac{L - v_x t}{2\sqrt{D_L t}}\right]\right]$$

This equation also reduces to the approximate solution, Equation 2.25, as the flow length increases.

2.9.6 One-Dimensional Slug Injection into a Flow Field

If a slug of contamination is instantaneously injected into a uniform, one-dimensional flow field, it will pass through the aquifer as a pulse with a peak concentration, C_{max}, at some time after injection, t_{max}. The solution to Equation 2.18 under these conditions (Sauty 1980) is in dimensionless form:

$$C_R = (t_R, P_e) = \frac{E}{(t_R)^{1/2}} \exp\left(-\frac{P_e}{4t_R}(1 - t_R)^2\right) \tag{2.28}$$

with

$$E = \left(t_{R\max}\right)^{1/2} \cdot \exp\left(\frac{P_e}{4t_{R\max}}\left(1 - t_{R\max}\right)^2\right) \tag{2.29}$$

where

$t_{R\max}$ = $(1 + P_e^{-2})^{1/2} - P_e^{-1}$ (dimensionless time at which peak concentration occurs)

C_R = $C/C_{\max}$

In Figure 2.16, C_R ($C/C_{\max}$) for a slug injected into a uniform one-dimensional flow field is plotted against dimensionless time, t_R, for several Peclet numbers. It can be seen that the time for the peak concentration ($C_{\max}$) to occur increases with the Peclet number, up to a limit of $t_R = 1$. Breakthrough becomes more symmetric with increasing P_e.

2.9.7 Continuous Injection into a Uniform Two-Dimensional Flow Field

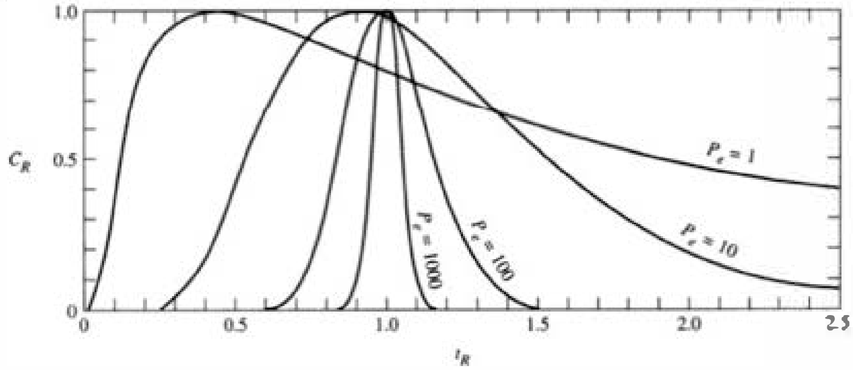
If a tracer is continuously injected into a uniform flow field from a single point that fully penetrates the aquifer, a two-dimensional plume will form that looks similar to Figure 2.16. It will spread along the axis of flow due to longitudinal dispersion and normal to the axis of flow due to transverse dispersion. This is the type of contamination that would spread from the use of an injection well, which would be a point source.

Flow is governed by Equation 2.19, the mass transport equation in two dimensions. The well is located at the origin ($x = 0$, $y = 0$), and there is a uniform flow velocity at a rate v_x parallel to the x axis. There is a continuous injection at the origin, of a solute with a concentration C_0 at a rate Q over the aquifer thickness, b.

The solution of Equation 2.19 can be found from a Green function (Bear 1972; Fried 1975) for the injection of a unit amount of a contaminant as:

$$C(x,y,t) = \frac{1}{4\pi t\left(D_L D_T\right)^{0.5}} \exp\left[-\frac{\left(x - v_x t\right)^2}{4D_L t} - \frac{y^2}{4D_T t}\right]$$

FIGURE 2.16 Dimensionless-type curve for the injection of a slug of a tracer into a one-dimensional flow field.



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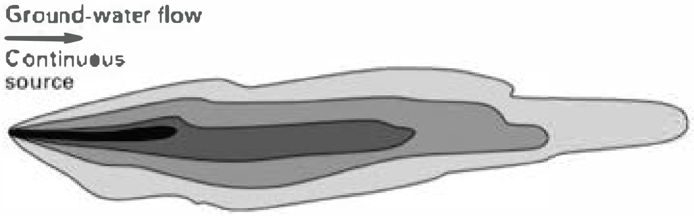
Since the Green function is for a unit injection, and we have an injection rate that can be defined as $C_0(Q/b)$, the solution to the above is:

$$C(x,y,t) = \frac{C_0(Q/b)dt}{4\pi t(D_L D_T)^{0.5}} \exp\left[-\frac{(x - v_x t)^2}{4D_L t} - \frac{y^2}{4D_T t} \right]$$

If the injection rate, Q/b, is continuous then the solution at time t is:

FIGURE 2.17 Plume resulting from the continuous injection of a tracer into a two-dimensional flow field. (Source: C. W. Fetter. 1994. *Applied Hydrogeology, Third Edition*. Upper Saddle River, New Jersey: Prentice-Hall, Inc.)



$$C(x,y,t) = \frac{C_0(Q/b)}{4\pi(D_L D_T)^{0.5}} \int_{\theta=0}^{\theta=t} \exp\left[-\frac{(x - v_x\theta)^2}{4D_L\theta} - \frac{y^2}{4D_T\theta} \right] \frac{d\theta}{\theta} \tag{2.30}$$

Steady-state conditions are obtained when time approaches infinity. Therefore equation 2.30 is integrated from 0 to ∞. The result is:

$$C(x,y) = \frac{C_0(Q/b)}{2\pi(D_L D_T)^{1/2}} \exp\left(\frac{v_x x}{2D_L}\right) K_0\left[\left(\frac{v_x^2}{4D_L}\left(\frac{x^2}{D_L} + \frac{y^2}{D_T}\right)\right)^{1/2}\right] \tag{2.30a}$$

where

K_0 = the modified Bessell function of the second kind and zero order (values are tabulated in Appendix B)
Q = the rate that the contaminant is injected
b = the thickness of the aquifer over which the contaminant is injected

Equation 2.30a can be solved in EXCEL after installing the Plume2DSS() add-in (Renshaw 2015b).

EXAMPLE PROBLEM

A waste liquid containing fluoride at a concentration of 133 mg/L was pumped into a shallow disposal pit located above a thin, 1.75 m thick,(two-dimensional) aquifer at a rate of 3.66 m³/day for many years. The average linear velocity of the groundwater was 0.187 m/day. Assume that the transverse dispersion is 10% of the longitudinal dispersion. If the disposal pit is assumed to be at a location of $x_0 = 0$ and $y_0 = 0$, what would the concentration of fluoride be in a monitoring well located at $x = 123$ m and $y = 16$ m? Assume that the fluoride is non-reactive and non-adsorbed by the aquifer

1. First the value of α_L must be calculated using equation 2.48.

   $\alpha = 0.83(\log(L))^{2.414}$

   L is equal to $x - x_0$ or 123 m.

   $\alpha_L = 0.83(\log(123))^{2.414}$

   $\alpha_L = 4.919$ m

2. Next the value of D_L and D_T must be found.

   $D_L = v_x \alpha_L$

   $D_L = 0.187 \text{ m/da} \times 4.919 \text{ m} = 0.920 \text{ m}^2\text{/da}$

   $D_T = 0.10 D_L$

   $D_T = 0.092 \text{ m}^2 / \text{da}$

   The variables are then inserted into equation 2.30a.

   $C_0 = 133$ mg/L

   $Q = 3.66 \text{ m}^3\text{/da}$

   $b = 1.75$m

$$C = \frac{C_0(Q/b)}{2\pi(D_L D_T)^{1/2}} \exp\left(\frac{v_x x}{2D_L}\right) K_0\left[\left(\frac{v_x{}^2}{4D_L}\left(\frac{x^2}{D_L} - \frac{y^2}{D_T}\right)\right)^{1/2}\right]$$

$$C = \frac{133\text{mg/L} \times (3.66\text{m}^3/\text{da}/1.75\text{m})}{2 \times \pi \times (0.92\text{m}^2/\text{da} \times 0.092\text{m}^2/\text{da})^{1/2}} \times \exp\left(\frac{0.187\text{m/da} \times 123\text{m}}{2 \times 0.92\text{m}^2/\text{da}}\right)$$

$$K_0\left[\left(\frac{0.187^2\text{m}^2/\text{da}^2}{4 \times 0.92\text{m}^2/\text{da}}\left(\frac{123^2\text{m}^2}{0.92\text{m}^2/\text{da}} + \frac{16^2\text{m}^2}{0.092\text{m}^2/\text{da}}\right)\right)^{1/2}\right]$$

$$C = \frac{278.0\text{mg/L}}{1.828} \exp\left(\frac{23.0}{1.84}\right) K_0\left[\left[0.0095 \times (16445 + 2783)\right]^{1/2}\right]$$

$$C = 152.1 \exp(12.5) K_0(13.52) \text{mg/L}$$

$$C = 152.1 \times 268337 \times 4.544 \times 10^{-7} \text{mg/L}$$

Note: Although K_0, a modified Bessell function of the zero order and second kind, can be obtained from Appendix B for a limited range of values, the table did not contain K_0 of 13.52. The value listed above, 4.54×10^{-7} was generated by a EXCEL function BESSELK(x,n).

According to Equation 2.30, as the value of D_L approaches zero, the concentration will approach infinity. As this is a physical impossibility, if the value of D_L is very small, then the one-dimensional equation, 2.23, should be used with a large value for time.

Equation 2.30 can also be solved for a specific value of time, so that the spread of a two-dimensional plume with time can be determined. In order to solve for time, Equation 2.30 can be written thusly:

$$C(x,y,t)=\frac{C_0(Q/b)}{4\pi(D_L D_T)^{1/2}}\exp\left(\frac{v_x x}{2D_L}\right)\int_{\theta=0}^{\theta=t}\exp\left[-\frac{\theta}{4D_L}-\left(\frac{x^2}{4D_L}+\frac{y^2}{4D_T}\right)\frac{1}{\theta}\right]\frac{d\theta}{\theta}$$

If we set $t_D = v_x^2/4\,D_L$, then the above becomes:

$$C(x,y,t)=\frac{C_0(Q/b)}{4\pi(D_L D_T)^{1/2}}\exp\left(\frac{v_x x}{2D_L}\right)\int_{t_D=0}^{t_D=\infty}\exp\left[-t_D-\frac{B^2}{4t_D}\right]\frac{dt_D}{t_D}$$

with

$$B^2=\frac{{v_x}^2x^2}{4{D_L}^2}+\frac{{v_x}^2y^2}{4D_L D_T}$$

The integral in the above equation was solved by Hantush (1956). This solution is

$$C(x,y,t)=\frac{C_0(Q/b)}{4\pi(D_L D_T)^{1/2}}\exp\left(\frac{v_x x}{2D_L}\right)\left[W(0,B)-W(t_D,B)\right] \qquad \textbf{(2.31)}$$

with t_D and B as defined above.

It should be noted that in effect t_D is a dimensionless form of time. The values of $W[t_D, B]$ can be found in Hantush (1956) and a limited series is tabulated in Appendix C. It can also be determined in EXCEL after installing the Leaky() add-in (Renshaw 2015c). In well hydraulics this is known as the leaky well function, $W[u, r/b]$.

EXAMPLE PROBLEM

An underground tank which formerly held benzene but now holds water is leaking at a rate of 1.93m³/year. However, the water still contains some benzene at a concentration of 12,950 µg/L. The groundwater which flows beneath the leaking tank goes directly north. A drinking water supply well is located at a spot that can be located by going 123.5m due north of the leaking tank and then 7.2m due east. Assume that the average linear velocity of the groundwater is 0.235 m/day and the longitudinal dispersivity is 12m and the lateral dispersivity is 1.2m and the aquifer thickness is 1.00m. What would the benzene concentration be after 2.00 years?

This is an example of a continuous leakage into a two dimensional flow field; equation 2-31.

1. The values of D_L and D_T must be calculated from equations 2-11a and 2-11b. We will ignore the effective diffusion coefficient as it is so much smaller than dispersivity.

$$D_L=\alpha_L v_X=12\text{ m}\times 0.235\text{ m/day}=2.82\text{ m}^2\text{/day}$$

$$D_T=\alpha_T v_X=1.2\text{ m}\times 0.235\text{ m/day}=0.282\text{ m}^2\text{/day}$$

2. The value of B must be calculated.

$$B=\left[\frac{(v_x x)^2}{4D_L{}^2}+\frac{(v_x y)^2}{4D_L D_T}\right]^{\frac{1}{2}}$$

$$B=\left[\frac{(0.235\text{m/da}\times 123.5\text{m})^2}{4\times(2.8\text{m}^2/\text{da})^2}+\frac{(0.235/\text{da}\times 7.2\text{m})^2}{4\times 2.8\text{m}^2/\text{da}\times 0.28\text{m}^2/\text{da}}\right]^{\frac{1}{2}}$$

$$B=\left[\frac{842\text{m}^4/\text{da}^2}{31.4\text{m}^4/\text{da}^2}+\frac{2.86\text{m}^4/\text{da}^2}{3.14\text{m}^4/\text{da}^2}\right]^{\frac{1}{2}}$$

$$B=\sqrt{26.8+0.91}$$

$$B=5.26$$

3. The next step is to find t_D. Convert time in years to time in days by multiplying by 365 days per year.

$$t_D=\frac{v_x{}^2 t}{4D_L}$$

$$t_D=\frac{(0.235\text{m/da})^2\times 730\text{da}}{4\times 2.82\text{m}^2/\text{da}}$$

$$t_D=3.57$$

4. One must now find W[0, B] and W[t_D, B] from Appendix C.

$W[0, B] = W[0, 5.26] = 0.0098$

$W[t_D, B] = W[3.57, 5.26] = 0.0019$

5. The values are then substituted into Equation 2.31. The rate of leakage, Q, is converted into cubic meters per day by dividing by 365. The aquifer thickness is 1.00m.

$Q = 1.93\ \text{m}^3/\text{year}/365\ \text{da/year} = 0.0053\ \text{m}^3/\text{da}$

$$C(x,y,t)=\frac{C_0 Q/b}{4\pi(D_L D_T)^{1/2}}\exp\left(\frac{v_x x}{2D_L}\right)[W(0,B)-W(t_D,B)]$$

$$C(x,y,t)=\frac{12{,}950\,\mu\text{g/L}\times 0.0053\text{m}^3/\text{da}/1\text{m}}{4\pi(2.82\text{m}^2/\text{da}\times 0.28\text{m}^2/\text{da})^{1/2}}\exp\left(\frac{0.236\text{m/da}\times 123.5\text{m}}{2\times 2.82\text{m}^2/\text{da}}\right)[0.0098-0.0019]$$

$$C(x,y,t)=0.0061\exp(5.16)[0.0079]\,\mu\text{g/L}$$

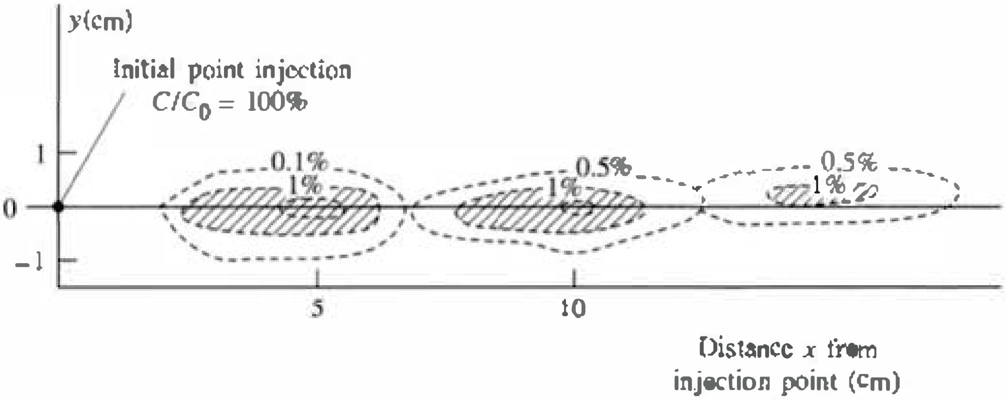
$$C(x,y,t)=0.0061\times 174\times 0.0079\,\mu\text{g/L}$$

$$C(x,y,t)=0.0084\,\mu\text{g/L}$$

2.9.8 Slug Injection into a Uniform Two-Dimensional Flow Field

If a slug of contamination is injected over the full thickness of a two-dimensional uniform flow field in a short period of time, it will move in the direction of flow and spread with time. This result is illustrated by Figure 2.18 and represents the pattern of contamination at three increments that result from a one-time spill. Figure 2.18 is based on the results of a laboratory experiment conducted by Bear (1961). Figure 2.19 shows the spread of a plume of chloride that was injected into an aquifer as a part of a large-scale field test (Mackay et al. 1986). The plume that resulted from the field test is more complex than the laboratory plume due to the heterogeneities encountered in the real world and the fact the plume may not be following the diffusional model of dispersion.

FIGURE 2.18 Injection of a slug of a tracer into a two-dimensional flow field shown at three time increments.



Experimental results from J. Bear. 1961. *Journal of Geophysical Research* 66:2455–2467. Copyright by the American Geophysical Union. Reproduced with permission.

De Josselin and De Jong (1958) derived a solution to this problem on the basis of a statistical treatment of lateral and transverse dispersivities. Bear (1961) later verified it experimentally. If a tracer with concentration C_0 is injected into a two-dimensional flow field over an area A at a point (x_0, y_0), the concentration at a point (x, y), at time t after the injection is

$$C(x,y,t) = \frac{C_0 A}{4\pi t (D_L D_T)^{1/2}} \exp\left[-\frac{((x-x_0)-v_x t)^2}{4D_L t} - \frac{(y-y_0)^2}{4D_T t}\right] \tag{2.32}$$

EXAMPLE PROBLEM

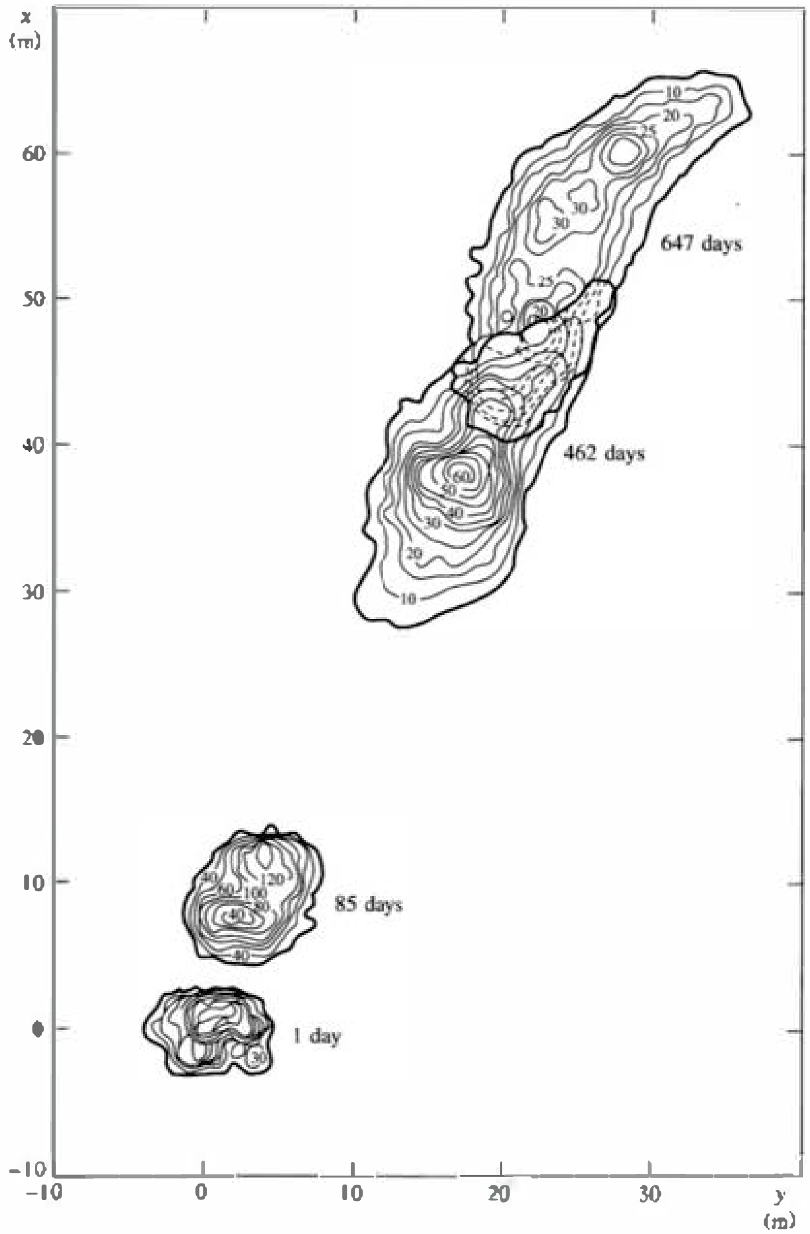
A tank truck, which is carrying water containing 1275 mg/L of dissolved benzene overturns and spills a volume of water sufficient to saturate a thin aquifer over an area of 5 m². The aquifer contains groundwater flowing with an average linear velocity of 0.45 m/day. Assume that the values of D_L and of D_T are 2.1 m²/day and 0.21 m²/day respectively.

There is a nearby private well at a seasonal cottage. If the center of the spill is at location $x_0 = 0$ and $y_0 = 0$, then the location of the well is $x = 72$ m and $y = 5.5$ m. The owners of the private well are away for the season and will not return for another 200 days.

If there is no degradation or retardation of the benzene as it moves through the aquifer, what will the concentration of benzene be in the private well when the owner returns.

The correct equation to use is 2.32 for a slug injection of contamination into a two dimensional aquifer.

FIGURE 2.19 Vertically averaged chloride concentration at 1 day, 85 days, 462 days, and 647 days after the injection of a slug into a shallow aquifer.



Source: D.M.Mackay et al. 1986. *Water Resources Research* 22:2017–2029. Copyright by the American Geophysical Union. Reproduced with permission.

$$C = \frac{C_0 A}{4\pi t\sqrt{D_L D_T}} \exp\left[-\frac{((x - x_0) - v_x t)^2}{4D_L t} - \frac{(y - y_0)^2}{4D_T t}\right]$$

$$C = \frac{1275\text{mgL}^{-1} \times 5\text{m}^2}{4 \times \pi \times 200\text{da} \times \sqrt{2.1\text{m}^2\text{da}^{-1} \times 0.21\text{m}^2\text{da}^{-1}}} \times$$

$$\exp\left[-\frac{((72\text{m} - 0) - (0.45\text{mda}^{-1} \times 200\text{da}))^2}{4 \times 2.1\text{md}^{-1} \times 200\text{da}} - \frac{(5.5\text{m})^2}{4 \times 0.21\text{m}^2\text{da}^{-1} \times 200\text{da}}\right]$$

$$C = \frac{6375\text{mgL}^{-1} \times \text{m}^2}{4 \times \pi \times 200\text{da} \times 0.664\text{m}^2\text{da}^{-1}} \exp\left[-\frac{(72-90)^2\text{m}^2}{1680\text{m}^2} - \frac{30.25\text{m}^2}{168\text{m}^2}\right]$$

$$C = 3.82\text{mgL}^{-1}\exp[-0.192 - 0.180]$$

$$C = 3.82\exp(-0.372) = 3.82 \times 0.6892 = 2.63\text{mgL}^{-1}$$

The maximum concentration of a contaminant from a slug injection is found in the center of the plume, or the *center of mass.* If the flow is in the direction of the x axis, and the spill was at location $x_0 = 0$ and $y_0 = 0$, the center of mass of a conservative substance at any time t since the spill will be at a location where $x = v_x t$ and $y = 0$. If we substitute these values into equation 2-32, we obtain:

$$C_{max} = \frac{C_0 A}{4t\pi\sqrt{D_T D_L}} \exp\left[-\frac{((v_x t - 0) - v_x t))^2}{4D_L t} - \frac{(0-0)^2}{4D_T t}\right]$$

$$C_{max} = \frac{C_0 A}{4t\pi\sqrt{D_T D_L}} \exp(0)$$

$$C_{max} = \frac{C_0 A}{4t\pi\sqrt{D_T D_L}} \tag{2.32a}$$

The distribution of contamination in the plume will follow a normal or Gaussian distribution. From equations 2-12a and 2-12b the standard deviation of the distribution is given by:

$$\sigma_x = \sqrt{2D_L t} \qquad \sigma_y = \sqrt{2D_T t}$$

By definition, 99.7% of the mass of contamination will be contained within an area represented by three standard deviations away from the center of mass of the plume. Thus the plume can be defined by the location of the center of mass, $3\sigma_x$ and $3\sigma_y$.

EXAMPLE PROBLEM

A truck carrying dilute brine with 2130 mg/L chloride from the cleanup of a pond containing waste from a producing oil well overturns and spills the dilute brine over an area of 455 square feet. The underlying thin aquifer has an average linear groundwater velocity of 1.23 ft/day. Where would the center of mass of the plume be in

133 days, what would the maximum concentration be and how far beyond and to the side of the center of mass would the plume spread?

1. The plume would be advected by the flowing groundwater so that the center of mass would be at $x = v_x t$.

   $$x = 1.23 \text{ ft/da} \times 133 \text{ da} = 164 \text{ feet.}$$

2. The maximum concentration at the center of mass can be found from equation 2.32a.

   $$C_{max} = \frac{C_0 A}{4t\pi\sqrt{D_T D_L}}$$

   a. We need to find the values of D_L and D_T. This can be done using equations 2.11a and 2.11b; but, first we need to use equation 2.82 to estimate α_L

   $$\alpha_L = 0.83(\log(L))^{2.414}$$
   $$= 5.66 \text{ ft}$$
   $$D_L = \alpha_L v_x$$
   $$= 5.66 \text{ ft} \times 1.23 \text{ ftda}^{-1}$$
   $$= 6.96 \text{ ft}^2\text{da}^{-1}$$

   We can assume D_T to be 10% of D_L

   $$D_T = 0.696 \text{ ft}^2\text{da}^{-1}$$

   The appropriate variables are substituted into equation 2.32.

   $$C_{max} = \frac{2130 mgL^{-1} \times 455 ft^2}{4 \times \pi \times 133 da\sqrt{6.96\ ft^2 da^{-1} \times 0.696\ ft^2 da^{-1}}}$$

   $$C_{max} = 263 mgL^{-1}$$

3. The size of the plume can be determined from the standard deviations.

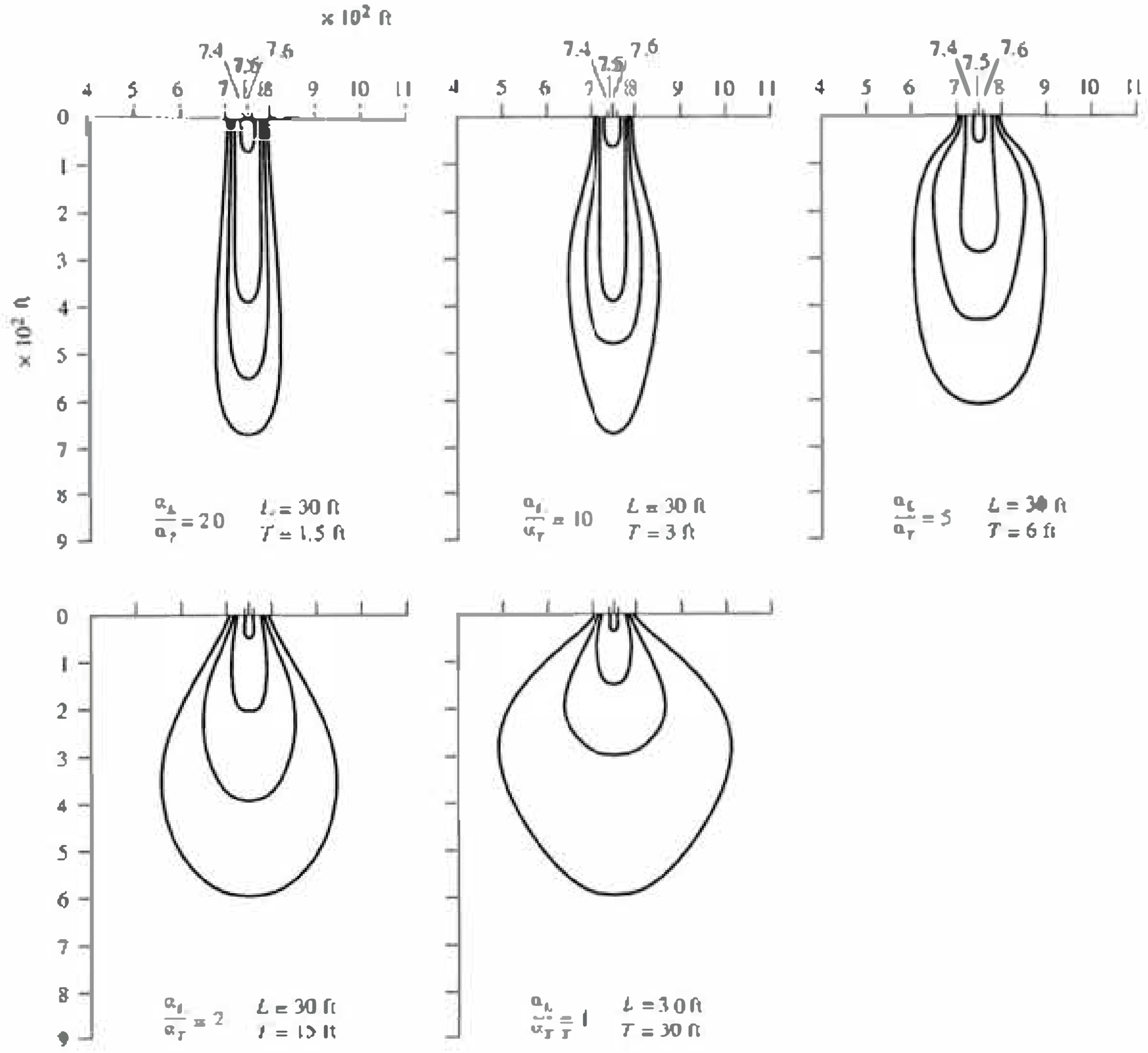
   $$\sigma_x = \sqrt{2D_L t} \qquad \sigma_y = \sqrt{2D_T t}$$
   $$\sigma_x = \sqrt{2 \times 6.96 ft^2 da^{-1} \times 133 da} \qquad \sigma_y = \sqrt{2 \times 6.96\ ft^2 da^{-1} \times 133\ da}$$
   $$\sigma_x = 43.0 \text{ ft} \qquad \sigma_y = 13.6 \text{ ft}$$

The leading edge of the plume is $3\sigma_x$ feet ahead of the center of mass or 129 feet and the plume had spread out $3\sigma_y$ feet on either side of the center of the mass or 40.8 feet.

2.10 Effects of Transverse Dispersion

The ratio of longitudinal to transverse dispersivity (α_L/α_T) in an aquifer is an important control over the shape of a contaminant plume in two-dimensional mass transport. The lower the ratio, the broader the shape of the resulting plume will be. Figure 2.20 shows various two-dimensional shapes of a contaminant plume, where the only factor varied was the ratio of longitudinal to transverse dispersivity. This illustrates the fact that it is important to have some knowledge of the transverse dispersivity in addition to the longitudinal dispersivity. There is a paucity of data in the literature on the relationships of longitudinal to transverse dispersivities. From the few field studies available, α_L/α_T is in the range of 6 to 20 (Anderson 1979; Klotz et al. 1980). In addition, dispersivity ratios based on field studies are based on fitting the diffusional model of dispersion to cases where it might not be applicable.

FIGURE 2.20 The effect of changing dispersivity ratio on the spread of a contaminant plume from a continuous source.



Source: Robert L. Stollar

chloride was 48 mgL^{-1} and after 4000 seconds, t_2, it was 252 mgL^{-1}. What is the dispersivity of the sand in the soil column?

The number of pore volumes at a given time can be calculated from Equation 2.33:

$$PV = v_x t / L$$

For the first measurement at t_1:

$$PV = 1.35 \times 10^{-2}\ \mathrm{cm\,s^{-1}}\ 500\ \mathrm{s}/40\ \mathrm{cm} = 0.17\ \text{pore volumes}$$

For the second measurement at t_2:

$$PV = 1.35 \times 10^{-2}\ \mathrm{cm\,s^{-1}} \times 4000\ \mathrm{s}/40\ \mathrm{cm} = 1.35\ \text{pore volumes}$$

At t_1, C/C_0 is 48/300, which equals 0.16. With a pore volume of 0.17

$$(PV - 1)/PV^{1/2} = (0.17 - 1)/(0.17)^{1/2} = -2.01$$

At t_2, C/C_0 is 252/300, which equals 0.84. With a pore volume of 1.32

$$(PV - 1)/PV^{1/2} = (1.32 - 1)/(1.32)^{1/2} = 0.28$$

Since C/C_0 at t_1 is conveniently equal to 0.16, then $(PV - 1)/PV^{1/2}$ for t_1 turns out to be $J_{0.16}$. Likewise C/C_0 at t_2 is 0.84 so that $(PV - 1)/PV^{1/2}$ for t_2 is $J_{0.84}$.

The value of D_L can be found from Equation 2.35:

$$D_L = \left(\frac{v_x L}{8}\right)(J_{0.84} - J_{0.16})^{1/2}$$

$$D_L = (1/8) \times (1.35 \times 10^{-2}\ \mathrm{cm\,s^{-1}} \times 40\ \mathrm{cm}) \times (0.28 - - 2.01)^{1/2}$$

$$= 6.75 \times 10^{-2} \times 1.51\ \mathrm{cm^2\,s^{-1}}$$

$$= 0.102\ \mathrm{cm^2\,s^{-1}}$$

2.11.2 Quantifying Dispersivity in the Field

A value for dispersivity can be determined in the field by two means. If there is a contaminated aquifer, the plume of known contamination can be mapped and the advection-dispersion equation solved with dispersivity as the unknown. Pinder (1973) used this approach in a groundwater modeling study of a plume of dissolved chromium in a sand and gravel aquifer on Long Island, New York He started with initial guesses of α_L and α_T and then varied them during successive model runs until the computer model yielded a reasonable reproduction of the observed contaminant plume. One of the difficulties of this approach is that the concentration and volume of the contaminant source are often not known.

A much more common approach is the use of a tracer that is injected into the ground via a well. There are a variety of variations to this approach. Natural gradient tests involve the injection of a tracer into an aquifer, followed by the measurement of the plume that developed under the prevailing water table gradient (e.g., Sudicky and Cherry 1979;

Gillham et al. 1984; Mackay et al. 1986; LeBlanc et al. 1991; Garabedian et al. 1991; Olsen and Tenbus 2004). The plume is measured by means of small amounts of water withdrawn from down-gradient observation wells and multilevel piezometers. Many of these field tests showed that thin plumes with less than expected transverse dispersivity often occur in field situations. This underlines a growing acceptance of the need for high resolution, vertically discrete, multilevel aquifer monitoring. Multilevel monitoring will be discussed in Chapter 8. One and two-well tests have also been used in which a tracer is pumped into the ground and then groundwater containing the tracer is pumped back out of the ground (e.g., Fried 1975; Grove and Beetem 1971; Sauty 1978; Pickens et al 1981; Pickens and Grisak, 1981). These so-called forced hydraulic gradient tests have the advantage that they can be completed in much shorter time relative to natural gradient tests. However, these tests require treatment if the pumped groundwater is contaminated. Also, the results of forced hydraulic gradient tests do not truly reflect the natural groundwater flow conditions. Ptak et al. (2004) reviewed the advantages and disadvantages of natural or forced hydraulic gradient tests for both nonreactive and reactive tracer compounds can be used.

2.11.3 Single-Well Tracer Test

A single-well tracer test involves the injection of water containing a conservative tracer into an aquifer via an injection well and then the subsequent pumping of that well to recover the injected fluid. The fluid velocities of the water being pumped and injected are much greater than the natural groundwater gradients.

Equation 2.20 can be written (Hoopes and Harleman 1967) as

$$\frac{\partial C}{\partial t} + u\frac{\partial C}{\partial r} = \alpha_L u \frac{\partial^2 C}{\partial r^2} + \frac{D^*}{r}\frac{\partial}{\partial r}\left(r\frac{\partial C}{\partial r}\right) \tag{2.37}$$

Gelhar and Collins (1971) derived a solution to Equation 2.37 for the withdrawal phase of an injection-withdrawal well test in which the diffusion term is neglected because it is very much smaller than the dispersion term. The relative concentration of the water being withdrawn from the injection well is

$$\frac{C}{C_0} = \frac{1}{2}\operatorname{erfc}\left(\frac{(U_p - U_i) - 1}{\{\frac{16}{3}(\alpha_L / R_f)[2-(1-U_p/U_i)]^{1/2}[1-(U_p/U_i)]\}^{1/2}}\right) \tag{2.38}$$

where

U_p = cumulative volume of water withdrawn during various times
U_i = total volume of water injected during the injection phase
R_f = average frontal position of the injected water at the end of the injection period, which is defined by

$$R_f = \left(\frac{Qt}{\pi b n}\right)^{1/2} \tag{2.39}$$

where

Q = rate of injection
t = total time of injection

b = aquifer thickness
n = porosity

EXAMPLE PROBLEM

Pickens and Grisak (1981) performed a single-well injection-withdrawal tracer test into a confined sand aquifer about 8.2 m thick with an average hydraulic conductivity of 1.4×10^{-2} cm/sec and a porosity of 0.38. The sediment tested in the column study described in the dispersivity example problem above came from this aquifer.

The injection well was 5.7 cm in diameter and the full thickness of the aquifer was screened. Clear water was injected at a constant rate for 24 hr prior to the start of the test to establish steady-state conditions. The tracer used during the tests was ^{131}I, a radioactive iodine isotope, which was added to the injected water. All measurements were corrected for the radioactive decay that occurred during the test.

Two tests were performed on the well. The first test, SWI, had an injection rate of 0.886 L/sec and injection continued for 1.25 da. A total volume of 95.6 m^3 of water was injected, and the injection front reached an average radial distance away from the well of 3.13 m. Water was then pumped for 2.0 da at the same rate, so that a total of 153 m^3 of water was withdrawn. The second test, SW2, was longer. Water with the tracer was added at a rate of 0.719 L/sec for 3.93 da. A total of 244 m^3 of water was added, and the average position of the injection front reached to 4.99 m from the well. During the withdrawal phase a total of 886 m^3 of water was pumped over a period of 16.9 da at an average rate of 0.606 L/sec.

The results of the test are shown in Figure 2.22. Relative concentration, C/C_0, is plotted against U_p / U_i. The dots represent field values and the solid lines are curves, which were computed using Equation 2.38. Various curves were computed for different values of α_L, and the curves with the best fit to the field data were plotted on the graphs. In Figure 2.22(a) the calculated curve was based on a longitudinal dispersivity of 3.0 cm, whereas for curve 2.22(b) the best-fit curve was based on a longitudinal dispersivity of 9.0 cm. This test illustrates the scale-dependent nature of dispersion. The second test, in which a larger volume of water was injected, tested a larger volume of the aquifer than the first test and yielded a higher dispersivity value.

■ 2.12 Scale Effect of Dispersion

The two example problems derived from Pickens and Grisak (1981) illustrate what has been called the scale effect of dispersion (Fried 1975). At the laboratory scale the mean value of α_L was determined to be 0.035 cm (0.014 in) when the flow length was 30 cm (12 in). With the single-well injection-withdrawal test, α_L was 3 cm (1.2 in) when the solute front traveled 3.1 m (10.2 ft) and 9 cm (3.5 in) when the solute front traveled 5.0 m (16.4 ft). In a two-well recirculating withdrawal-injection tracer test with wells located 8 m (26.2 ft) apart α_L was determined to be 50 cm (19.6 in). All these values were obtained from the same site. The greater the flow length, the larger the value of longitudinal dispersivity needed to fit the data to the advection-dispersion equation.

spread. In this region the variance of the plume will grow proportionally to the time or mean travel distance, as it does at the laboratory column scale. The advective-dispersion model is based on the assumption that dispersion follows Fick's law. Some authors contend that dispersion follows Fick's law only at the laboratory scale, where it is caused by local mechanical dispersion, and for very long flow paths, where the effects of advection through heterogeneous materials and local transverse dispersion create macroscale dispersion that follows Fick's law (e.g., Gelhar 1986; Dagan 1988). The contention that macroscale dispersion becomes Fickian (i.e., follows Fick's law) at long travel times and distances is somewhat controversial, especially if the flow is through geological formations that are heterogeneous at different scales (Anderson 1990).

2.13 Stochastic Models of Solute Transport

2.13.1 Introduction

The normal manner of determining a field-scale dispersion coefficient is to look for a natural tracer or inject a tracer into an aquifer and observe the resulting development of a plume. A solute-transport model is then constructed and the computed solute distribution is fitted to the observed field data by adjusting the dispersion coefficients. Dispersion coefficients obtained in this manner are fitted curve parameters and do not represent an intrinsic property of the aquifer. This is especially true when the aquifer is assumed to be homogeneous and is described by a single value for hydraulic conductivity and porosity. It is apparent that flow and transport modeling based on a single value for porosity and hydraulic conductivity is a gross simplification of the complexity of nature. For analytical solutions, we are constrained to use of a single value for average linear velocity, and for numerical models we often use a single value because that is all we have.

A **deterministic model** is one where a partial differential equation is solved, either numerically or analytically, for a given set of input values, aquifer parameters, and boundary conditions. The resulting output variable has a specific value at a given place in the aquifer. It is assumed that the distribution of aquifer parameters is known. The equations given earlier in this chapter are examples of deterministic models.

A **stochastic model** is a model in which there is a statistical uncertainty in the value of the output variables, such as solute distribution. The probabilistic nature of this outcome is due to the fact that there is uncertainty in the value and distribution of the underlying aquifer parameters, such as the distribution and value of hydraulic conductivity and porosity (Freeze 1975; Dagan 1988).

A widespread misconception about stochastic and deterministic models is that the latter use physical laws, while the stochastic models are largely empirical and based entirely on statistical data-analysis. In reality, any physically-based model becomes a stochastic model once its inputs, parameters, or outputs are treated as random (Bierkens and van Geer; 2014).

The idea behind stochastic modeling is very attractive. It is obvious that it takes a great effort to determine hydraulic conductivity and porosity at more than a few locations in an aquifer system. If we could determine the distribution of aquifer properties with a high degree of detail, then a numerical solution of a deterministic model would yield results with a high degree of reliability. However, with limited knowledge of aquifer parameters, a deterministic model makes only a prediction of the value of an output variable at a given point and time in the aquifer. The stochastic model is based on a probabilistic distribution of aquifer parameters. At the outset it is recognized in the stochastic model that the result will be only some range of possible outcomes. The stochastic model thus recognizes the probabilistic nature of the answer, whereas the deterministic model suggests that there is only one "correct" answer. Of course, the experienced hydrogeologist recognizes the uncertainty even in the deterministic answer. There have been literally hundreds of papers written on various aspects of stochastic modeling of groundwater flow and solute transport. Textbooks like Zhang (2001), Rubin (2003), and Dagan and Neuman (2005) provide insights into analyzing and modeling subsurface heterogeneity using stochastics concepts and models for managing water resources, preserving subsurface water quality, storing energy and wastes, besides other applications.

2.13.2 Stochastic Descriptions of Heterogeneity

Stochastic hydrology is about combining deterministic model outcomes with a probability distribution of the errors, or alternatively, considering the hydrological variable as random and determining its probability distribution and some "best prediction" (Bierkens and van Geer 2014). The greatest uncertainty in the input parameters of a model is the value of hydraulic conductivity, because it varies over such a wide range for geologic materials. If we make a measurement of hydraulic conductivity at a given location, the only uncertainty in its value at that location is due to errors in measuring its value. However, at all locations where hydraulic conductivity is not measured, additional uncertainty exists. If we make a number of measurements of the value of hydraulic conductivity, we can estimate this uncertainty using certain statistical techniques.

Let us define Y as the log of the hydraulic conductivity, K, and assume that the log value Y is normally distributed. We will assume a one-dimensional series of Y values $\{Y_1, Y_2, Y_3, Y_4, \ldots Y_n\}$ (Freeze et al. 1990). Therefore,

$$Y_i = \log K_i \tag{2.40}$$

The population that consists of all of the values of Y has a mean value, μ_y, and a standard deviation, σ_Y. The only way to obtain precise values of μ_y and σ_y would be to sample the aquifer everywhere, clearly an impossible task, but we can find estimates of their values based on the locations where we have actually measured K. If we have a series of Y values $\{Y_1, Y_2, Y_3, \ldots Y_n\}$, as in Figure 2.27(a), based on measured value of K, then our estimate of the population mean is obtained from the mean value of the sampled values, Y, which can be found from

$$\bar{Y} = \frac{1}{n}\sum_{i=1}^{n} Y_i \tag{2.41}$$

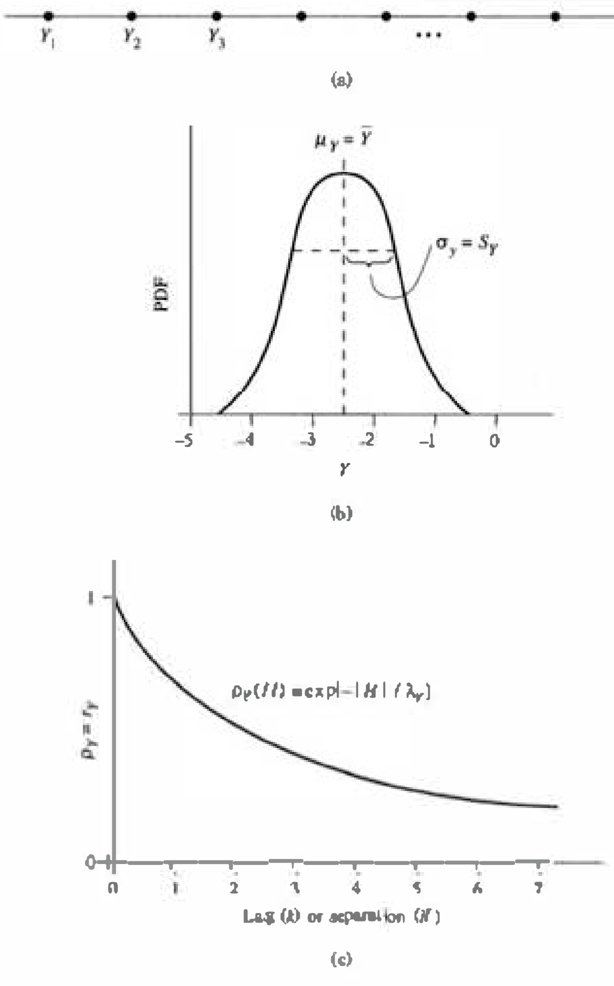
The estimate of the variance of the population is also obtained by the variance of the sampled values, S_y^2, which is found from the following equation:

$$S_Y{}^2 = \frac{1}{n}\sum_{i=1}^{n}(Y_i - \bar{Y})(Y_i - \bar{Y}) \tag{2.42}$$

For a normally distributed population, the probabilistic value is called a probability density function (PDF) and is described by the mean and the variance. The variance is a measure of the degree of heterogeneity of the aquifer. The greater the value, the more heterogeneous the aquifer. The PDF can be represented as a bell-shaped curve with the peak equal to the mean, as in Figure 2.27(b), and the spread of the bell can be defined by either the variance or the standard deviation, S_y which is the square root of the variance.

If we have measured the value of Y_i at a number of locations and wish to estimate the value Y_j at some other location j that is not close to any of the measured values, how can we estimate the value of Y_j? One approach is to say that the most likely estimate of Y_j is the mean of the measured values of Y_i, and the uncertainty in this value is normally distributed with a standard deviation equal to the standard deviation of the measured values, S_y. In doing so we have accepted the ergodic hypothesis. This means that there is a 16% chance that the value of Y_j is greater than $\overline{Y} - S_Y$, a 50% chance that it is greater than Y, and an 84% chance that it is greater than $\overline{Y} - S_Y$. In broad terms ergodicity describes a dynamic system which has the same behavior averaged over time as averaged over space.

FIGURE 2.27(a) One-dimensional sequence of log hydraulic conductivity values, Y; (b) probability distribution function for Y; (c) autocorrelation function for Y.



Source: R.A. Freeze et al. 1990. *Ground Water* 28:738-766. Used with permission. Copyright Ground Water Publishing Co.

Hydraulic conductivity values measured at locations close to each other are likely to be somewhat similar. The farther apart the measurements, the less likely that the values will be similar. This is due to the fact that as distances become greater, the chance that there will be a change in geologic formation increases. The function that describes this is the **autocorrelation function**, ρ_Y. The value of the autocorrelation function decreases with the distance between two measurements. An estimate of the autocorrelation function, r_y, can be obtained from the measured sample values by the following equation:

$$r_Y(k) = \frac{1}{S_Y{}^2}\frac{1}{n}\sum_{i=1}^{n}(Y_i - \bar{Y})(Y_{i-k} - \bar{Y}) \tag{2.43}$$

with k, the lag, being a whole number representing a position in the sequence away from the i position. Figure 2.27(c) shows an autocorrelation function plotted against the lag. If the lag is zero, then Equation 2.43 reduces to $r_Y = S_Y{}^2 / S_Y{}^2 = 1$. This means that a Y value is perfectly correlated with itself.

The autocorrelation factor can be expressed in terms of either lag, ρ_{Yk} or distance, $\rho_Y(H)$. When a measurement of Y_i is made at position X_i and a measurement of Y_{i-k} is made at position X_{i-k}, the absolute value of $X_i - X_{i-k}$ is called the **separation**, H.

If the autocorrelation function has an exponential form, then it can be expressed as

$$\rho_Y(H) = \exp[-|H| / \lambda_Y] \tag{2.44}$$

where λ_Y, the **correlation length**, is representative of the length over which Y is correlated. It is the distance over which $\rho_Y(H)$ decays to a value of e^{-1}. The **integral scale**, ε_Y, is the area under the curve.

$$\varepsilon_Y = \int_0^\infty \rho_Y(H)\,dH \tag{2.45}$$

Integration of Equation 2.45 will show that $\varepsilon_Y = \lambda_Y$, so that the correlation structure can be described by either the correlation length or the integral scale.

The **autocovariance**, τ_{Yk} or $\tau_Y(H)$, is equal to the autocorrelation times the variance.

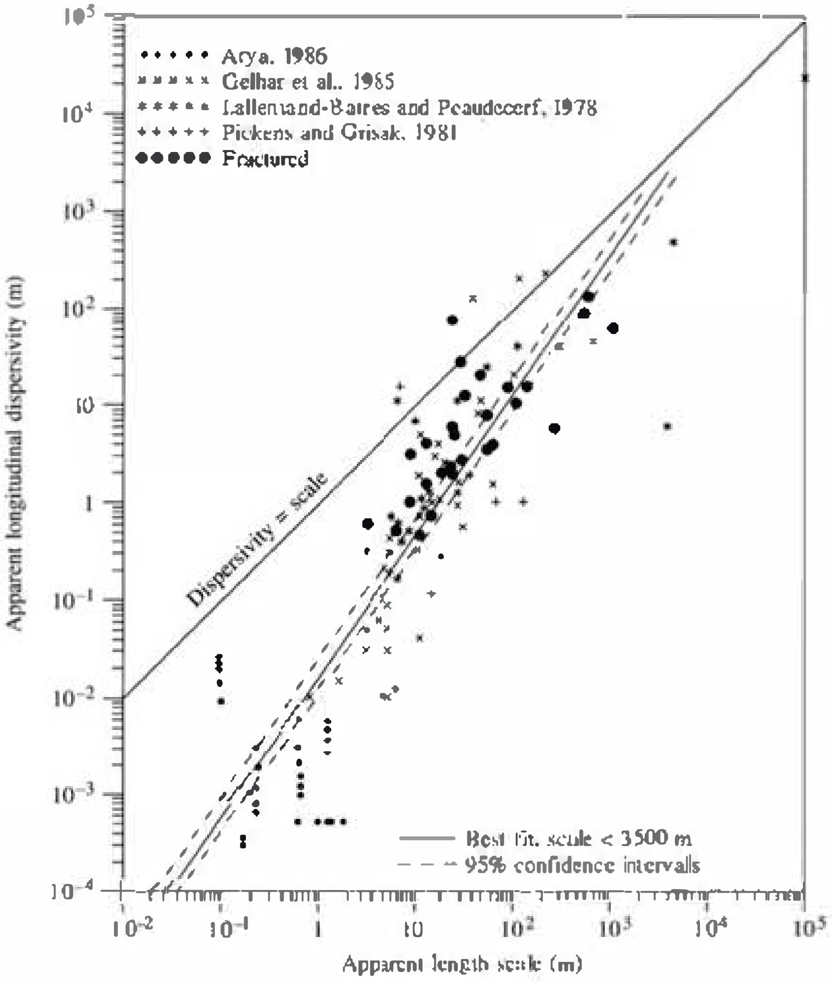
$$\tau_Y(H) = \sigma_Y{}^2 \rho_Y(H) \tag{2.46}$$

We can describe the distribution of heterogeneity of Y by the use of three stochastic functions, μ_Y, σ_Y (or σ_Y^2), and λ_Y. If a stochastic process is said to be stationary, the values of μ_Y, σ_Y (or σ_Y^2), and λ_Y do not vary in space in the region being studied. If the hydraulic conductivity of an aquifer can be described as a stationary stochastic process, the aquifer is uniformly heterogeneous.

2.13.3 Stochastic Approach to Solute Transport

If we accept the idea that we don't know the value of the hydraulic conductivity and the porosity everywhere, then we must accept the idea that it is not possible to predict the actual concentration of a solute that has undergone transport through an aquifer. The best estimate of the concentration is the **ensemble mean concentration**, ‹C›, or the mean of all the means of an ensemble of all possible random but equivalent populations, and the associated variance. The movement of a solute body may be described by

FIGURE 2.28 Apparent longitudinal dispersivity from field and laboratory studies as a function of the scale of the study. Results from the calibration of numerical models are not included.



Source: S. Neuman. 1990. *Water Resources Research* 26:1749-1758. Copyright by the American Geophysical Union. Used with permission.

the motion of the center of mass of the body and the second-order spatial moment, or the moment of inertia (Dagan 1988). Hence, from the variance of the log transformed hydraulic conductivity distribution and the correlation length, a simple stochastic model allows predicting an asymptotic macrodispersivity value. However, it is important to note that the process of advective transport dominates macrodispersion. This means that whether one uses a deterministic model or a stochastic model, the large picture of solute transport will emerge, since both account primarily for advective transport, with the dispersion factor tending to smear the leading edge of the plume.

2.14 Regression Analysis of Relationship between Apparent Longitudinal Dispersivity and Field Scale

Neuman (1990) plotted the apparent longitudinal dispersivity as measured in field and lab studies, α_{m}, as a function of the travel distance, L_s, or apparent length scale

(Figure 2.28). Dispersivities that are measured in the field were considered apparent dispersivities because they were obtained by calculations that depend upon the theory that the observer was using. Also, Neuman (1990) excluded for theoretical reasons all data with an apparent length scale greater than 3500 m (approximately 11,500 ft). Regression analysis showed that although the data are widely scattered, a best-fit line with narrow 95% confidence bands could be obtained. The equation for the line is

$$\alpha_{app} = 0.0175 L_s^{1.46} \tag{2.47}$$

This line of best fit has a regression coefficient, r^2, of 0.74, which means that it accounts for 74% of the variation about the mean. The other 26% may be due to experimental and interpretive errors or may represent deviation of the real system from that described by Equation 2.47. The 95% confidence intervals about the coefficient of 0.0175 are 0.0113and 0.0272 and the 95% confidence intervals about the exponent of 1.46 are 1.30 and 1.61.

Equation 2.47 obtained by Neuman (1990) was based on data that he considered to be highly reliable. In doing so he discarded data that were less reliable, such as that obtained by the calibration of numerical models. Neuman recognized that as the flow path grew longer, the same equation relating apparent longitudinal dispersivity to field scale could not be used, so that he used two linear equations, one for flow distances less than 100m (328 ft) and one for flow distances greater than 100m (328 ft) (Equation 2.47). However, a discontinuity occurs in his method at 100m (328 ft); i.e., the two equations give different answers. Neuman and Di Federico (2003) demonstrated experimentally and theoretically that the scaling behavior of hydrogeologic variables is impacted strongly by their scale of spatial resolution.

Xu and Eckstein (1995) have overcome these problems by assigning different degrees of reliability to data: low, medium and high. They were then able to obtain a nonlinear relationship based on a regression analysis using all available data. The resulting equation had a correlation coefficient of 0.72, which is similar to that obtained by Neuman (1990) using only highly reliable data. Neuman (1990) also did not consider any data with a flow field longer than 3500m (~11,500 ft) because he did not consider it to be reliable, while Xu and Eckstein (1995) included these data.

The equation of Xu and Eckstein is:

$$\alpha_{m,L} = 0.83(\log L_s)^{2.414} \tag{2.48}$$

If one examines Figure 2.24, which includes data of low reliability, it appears that as the field scale increases, the rate of change of dispersion decreases. Being nonlinear as plotted on log-log paper, Equation 2.48 also has a decreasing rate of change of dispersion with increasing field scale. At a field scale of greater than a few thousand meters there is very little change in apparent dispersion with distance.

By analyzing jointly dispersivity values derived from models having variable scales of spatial resolution, Schulze-Makuch (2005) proposed a power law relationship that empirically best described the dispersivity data in regard to scale of measurement:

$$\alpha_L = cL^m$$

where c is a parameter characteristic for a geological medium, m is a scaling exponent, and L is the flow distance. The scaling exponent for consolidated and unconsolidated geological media varied between 0.40 and 0.92, and 0.44 and 0.94, respectively. For example, an unconsolidated sandy aquifer: c = 0.20 and m = 0.44. For a distance of 100 m (328 ft), the longitudinal dispersivity value is αL = 1.6 m. Similar equations exist for other types of aquifers. No upper bound on the relationships was apparent for a flow distance up to ~10,000 m (~6 miles) for all media except for granites where this relation currently can only be extended to a flow distance of 100 m (328 ft). However, the relationship proposed by Schulze-Makuch (2005) was criticized by Neuman (2006) for neglecting the spatial resolution scales of the models from which the dispersion data had been derived. A theoretical interpretation of the scaling behavior has been summarized in a nonmathematical way in the review paper of Neuman and Di Federico (2003).

2.15 Deterministic Models of Solute Transport

Although workers in stochastic theory have asserted that the theoretical basis for the deterministic advective-dispersive solute transport equation is suspect except for long times and large distances (Anderson 1984), it has been used with a great deal of success in many field and model applications. Today, mathematical transport and fate modeling of contaminants in groundwater and soils has become an important tool for the interpretation of contaminated sites, the development of remedial strategies, and the human health risk assessment process.

Over the past decades, many papers and textbooks have been written about deterministic models for contaminant transport modeling (e.g., Anderson and Woessner 1991; Zheng and Bennet 2002). In general, a deterministic mathematical model simulates groundwater flow and/or solute fare and transport indirectly by means of a set of governing equations, such as Darcy's law and law of mass conservation, thought to represent the physical processes that occur in the system (Anderson and Woessner 1991). The first step in the modeling process is to develop a conceptual model that is simpler than reality. Simplification can be achieved, for example, by combining strata with similar hydrogeologic properties into a single layer or aquifer. The next step requires translating the conceptual model into a mathematical model, which can then be solved in a computer simulation. A numerical mathematical model solves the underlying governing partial differential equations (PDEs) within a set of suitable boundary conditions, and if the transport problem is of transient nature, initial conditions. This step usually requires that additional simplifying assumptions have to be made to reduce the complexity of the mathematical model. For example, a coarser grid can be defined in parts of the flow domain where less accuracy is required, or fixed value boundaries (e.g., no-flux or constant head boundaries) can be defined, or the length of the simulation time steps can be manipulated to reduce the number of computations. These adjustments make the model amenable to either exact or numerical solution, but the modeler must weigh the risk of oversimplifying the flow domain against the problem of no longer reproducing the system adequately. A parsimonious model therefore is a model that accomplishes a desired level of explanation or prediction with the fewest predictor variables possible.

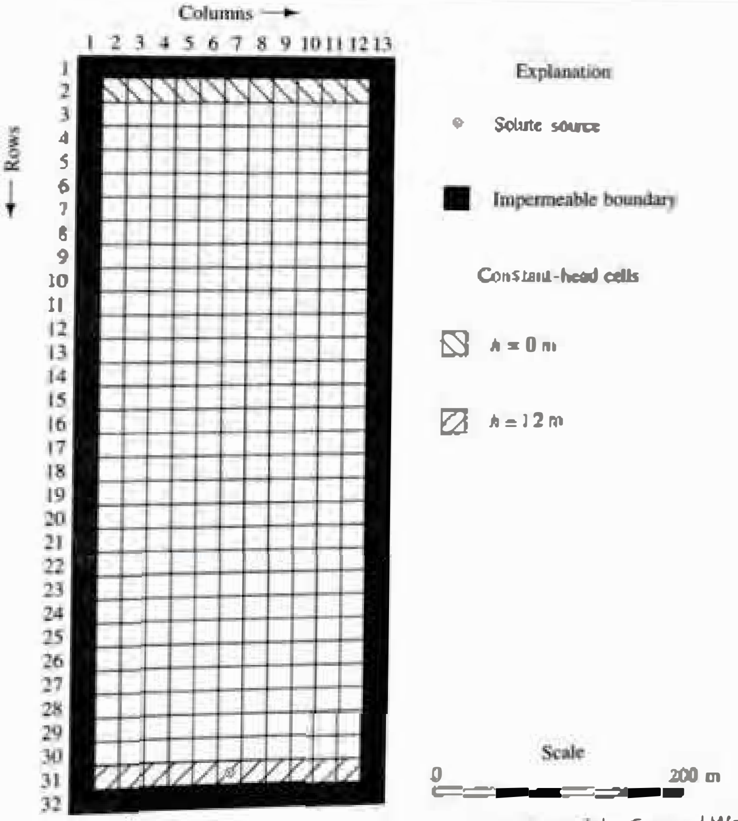
The flow and transport equations underlying the model are solved at discrete points within the flow domain. The two classical choices for the numerical solution of PDEs are the finite difference method (FDM) and the finite element method (FEM).

Other methods exists, such as the finite volume method (FVM) or the analytic element method (AEM), but models build around these numerical solution schemes are currently not used widely. A detailed discussion of numerical methods is beyond the scope of this textbook and the reader is referred to Peiro and Sherwin (2005).

The current standard FDM program is MODFLOW, which was developed by the U.S. Geological Survey (USGS) for three-dimensional flow modeling (McDonald and Harbaugh 1988). Over the years, many modules have been added to the MODFLOW program, including modules to simulate coupled groundwater/surface-water systems, solute transport, variable-density flow (including saltwater), aquifer-system compaction and land subsidence, parameter estimation, and groundwater management (USGS 2014). MODFLOW can be used in conjunction with MT3DMS, which is a 3D multi-species transport model (Zheng et al. 2010). MT3DMS solves the advection-dispersion-reaction equation based on the methods of characteristics, MOC (Konikow et al. 1994). The FDM model domain is subdivided or discretized into a grid of rectangular blocks or cells within which the physical properties of the domain are assumed to be homogeneous. The block structure of the FDM models often make them difficult to adopt to more complex modeling domains. Under those circumstances, FEM models provide greater flexibility in design because the modeling domain is discretized by triangular elements. Common FDM programs include SUTRA, a variable-density, variably-saturated flow, solute or energy transport model by the U.S. Geological Survey (2015a) or FEFLOW, a commercial modelling environment for subsurface flow, solute and heat transport processes. Another versatile commercial FVM model is HYDRUS 2D/3D, which also offers unsaturated flow modeling capabilities (Simunek et al. 1999; Simunek et al. 2006) and modeling of agricultural pollutants especially those from nonpoint source pollution stemming from plant and animal production (Simunek et al. 2013). There are many more noteworthy models available and many are in public domain. The U.S. Geological Survey maintains a website from which public domain software packages for the simulation of groundwater flow and transport can be downloaded (USGS 2015b).

A model study by Davis (1986) demonstrates that deterministic models can be developed that incorporate heterogeneities. He modeled two aquifers with identical boundary conditions (Figure 2.29). One was uniform (Figure 2.30(a)) and one had variable transmissivity in the form of more permeable channels (Figure 2.30b). The deterministic model, based on the two-dimensional solute-transport equation, was used with small values of α_L and a α_T, 0.0003 m (0.01 in), and 0.00009 m (0.003 in), respectively. The resulting solute plume in the uniform media is very long and narrow. See Figure 2.31(b). If larger values of α_L and α_T are used—3 m (10 ft) and 1 m (3 ft), respectively—then a much broader plume results. See Figure 2.31(a). However, if the heterogeneous aquifer is used with the small values of dispersivity, the resulting plume, shown in Figure 2.31(c) has a size very similar to that created in the uniform media by using large values of dispersivity. This demonstrates that if deterministic models include the aquifer heterogeneities, then it may be possible to use dispersivity values that are more on the order of lab-scale values. Davis (1986) used the advective-dispersion equation in a model with varying transmissivities and with a value of α_L of only 0.01 m (0.4 in) was able to reproduce a solute plume that extended over a flow length of about 500 m (1,640 ft). He found that a fine mesh for the finitedifference model grid was necessary for accurate results. Figure 2.32 compares the results of his model results with the field data.

FIGURE 2.29 Finite-difference grid and boundary conditions for a deterministic model of solute transport.



Source: A. D. Davis. 1986. *Ground Water* 24:609–615. Used with permission. Copyright Ground Water Publishing Co.

FIGURE 2.30 Model areas for finite difference solute transport model with (a) uniform transmissivity and (b) with heterogeneous transmissivity.

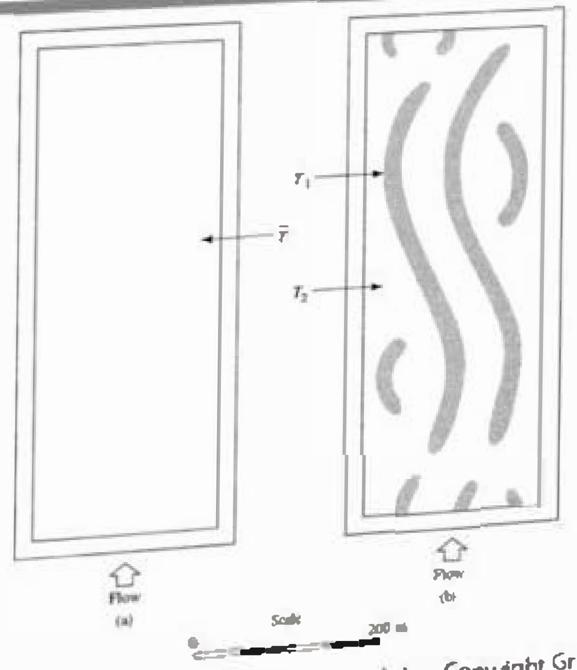


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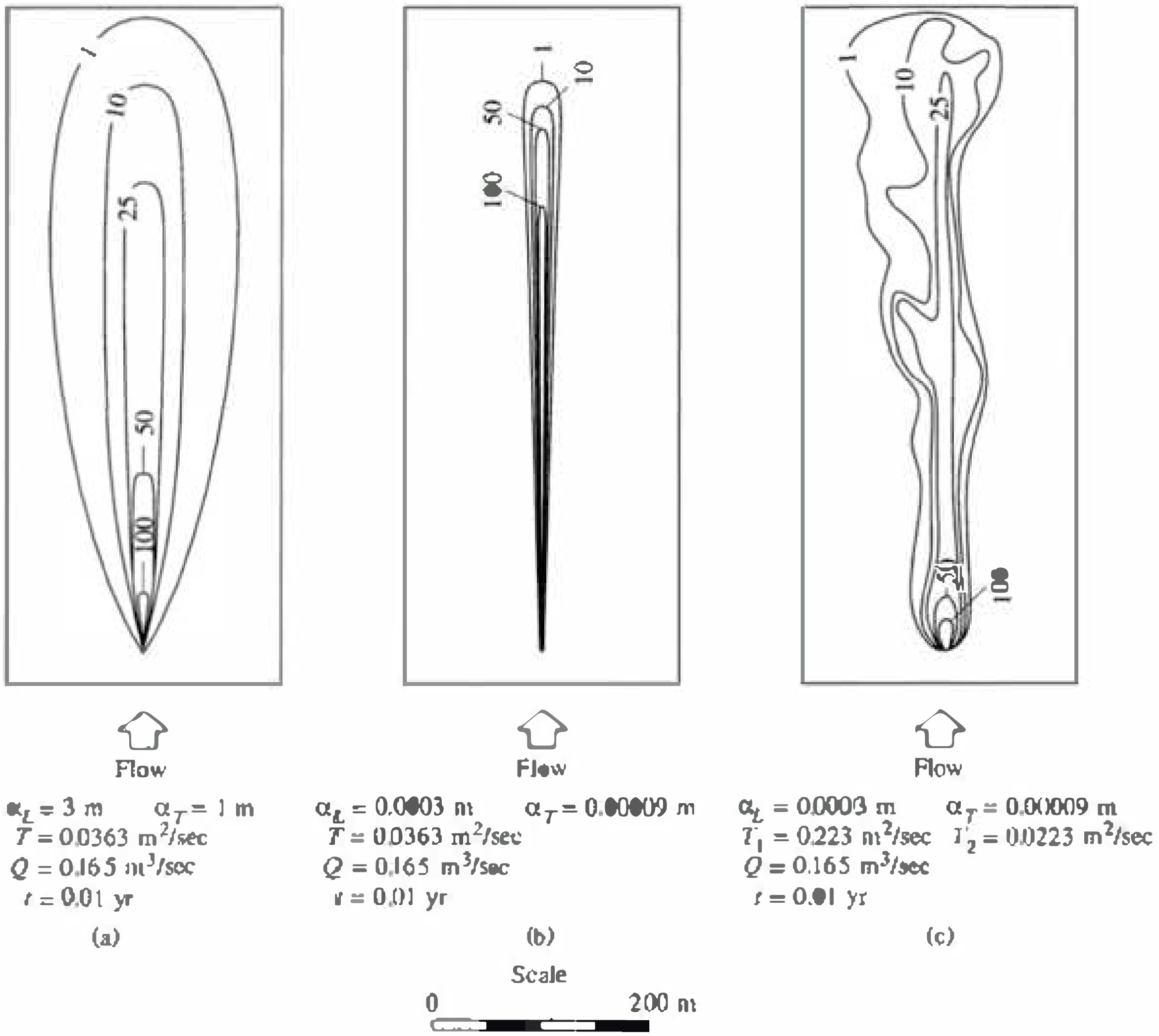
FIGURE 2.31 Model results for finite-difference solute-transport model. (a) Uniform media with large dispersivity values, (b) uniform media with small dispersivity values, and (c) heterogeneous media with small dispersivity values.



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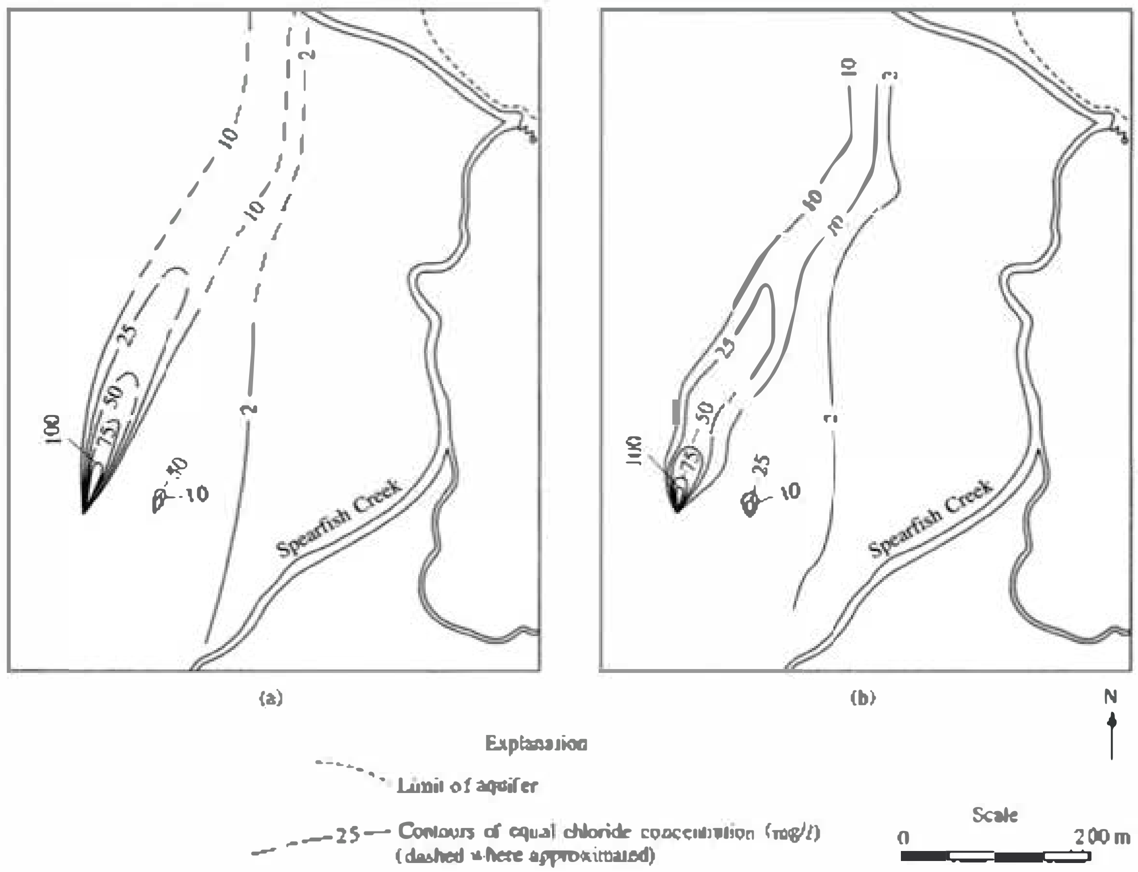
Case Study: Borden Landfill Plume

Probably the best known subsurface contaminant transport field test site is located on the Canadian Forces Base in Borden, Ontario (Sudicky and Illman 2011). An abandoned landfill in a shallow sand aquifer at Borden has been extensively studied (Cherry 1983; Macfarlane et al. 1983) and Frind and Hokkanen (1987) made a very interesting study of the plume based on a deterministic model.

The landfill was active from 1940 to 1976 and covers about 5.4 ha to a depth of 5 to 10 m (16 to 32 ft). Figure 2.33 shows the location of water table wells and multilevel sampling devices. The multilevel sampling devices are concentrated along the long axis of the plume of groundwater contamination. The vertical location of the sampling points along cross section A-A′ are shown in Figure 2.34. The aquifer is about 20 m (65 ft) thick beneath the landfill and thins to about 9.5 m (31 ft) in the direction of groundwater flow. The aquifer consists of laminated fine to medium sand. An average hydraulic conductivity of 1.16 × 10⁻² cm/sec horizontally and 5.8×10^{-4} cm/sec vertically was used in the model with a porosity of 0.38. In 1979 a very extensive study of the water quality of the plume was conducted. Figure 2.35 shows the plume of chloride contamination along cross section A-A'. In 1979 the plume extended about 750 m (2,460 ft) from the landfill and had sunk to the bottom of the aquifer and then moved laterally with the flowing groundwater. The sinking of the plume is believed to be caused by recharge concentrated in a sand pit to the north of the landfill, which is in the direction of flow.

FIGURE 2.32 Comparison of (a) field observations at solute plume in an aquifer and (b) solute plume as computed by finite-difference solute-transport model for a heterogeneous aquifer.



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The finite-difference grid system for the crosssectional model is shown in Figure 2.36. Equipotential lines for observed conditions were essentially vertical (Figure 2.37). The model was calibrated against the water-table contours for steady-state conditions.

Sensitivity analyses were performed to determine the impact of varying α_L and α_T. Field tests had indicated that the value of α_L at the site is on the order of 5 to 10 m (16 to 32 ft) (Sudicky et al. 1983). Figure 2.38 shows the sensitivity of the plume to the value of α_T. The value of α_L was kept at 10 m (32 ft) and α_T was varied from 0.005 m (0.02 in) to 1.0 m (3 ft). It can be seen that the shape of the plume is very sensitive to the value of α_T. With a high value of α_T, the plume spread through the entire vertical thickness of the aquifer, whereas with a low value it tended to sink toward the bottom. Figure 2.39 illustrates the fact that the plume was not very sensitive to changes in the value of α_L over the range tested. The value of α_T was kept constant at 0.01 m (0.4 in), whereas α_L varied from 2.5 to 20 m (8 to 65 ft). This figure is slightly misleading in that there is a 10:1 vertical exaggeration, so that the vertical spreading is more obvious than the horizontal. Also, the value of α_T was varied by a factor of 200, whereas α_L was varied only by a factor of 8.

FIGURE 2.33 Location of landfill at Canadian Forces Base, Borden, Ontario, showing location of cross section and monitoring network.

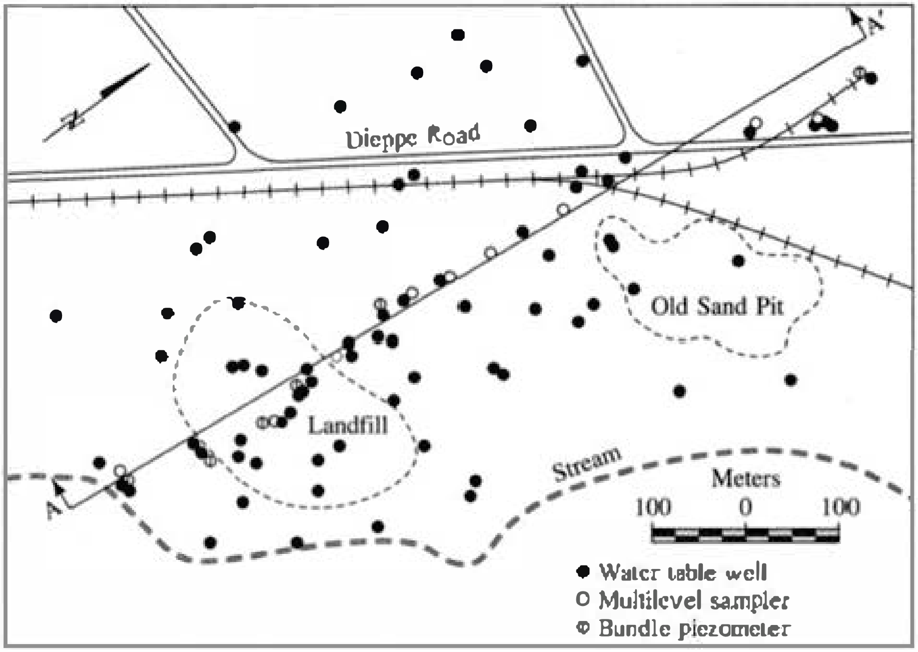

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FIGURE 2.34 Cross section of aquifer at the Border landfill showing the location of multilevel monitoring devices.

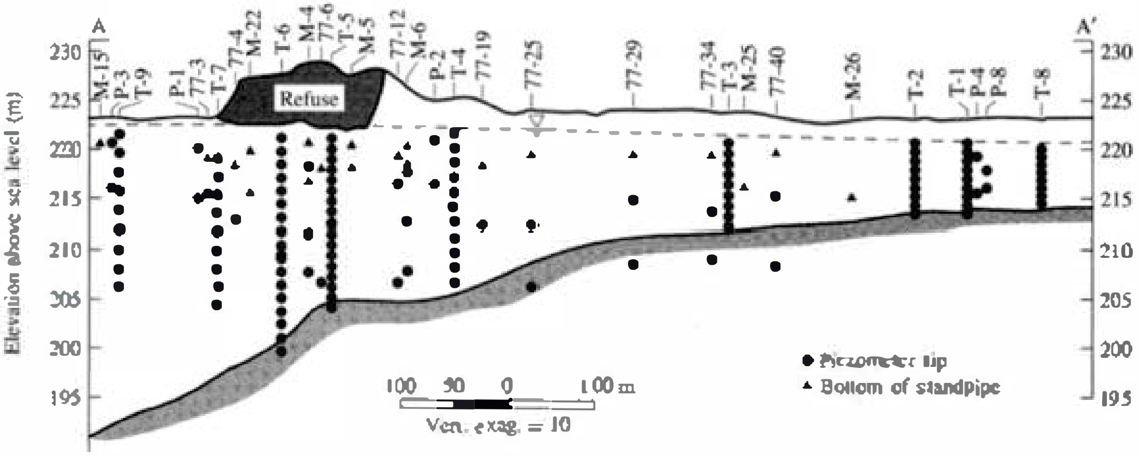

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FIGURE 2.35 Chloride plume along the Borden landfill across section in 1979. Values are in milligrams per liter.

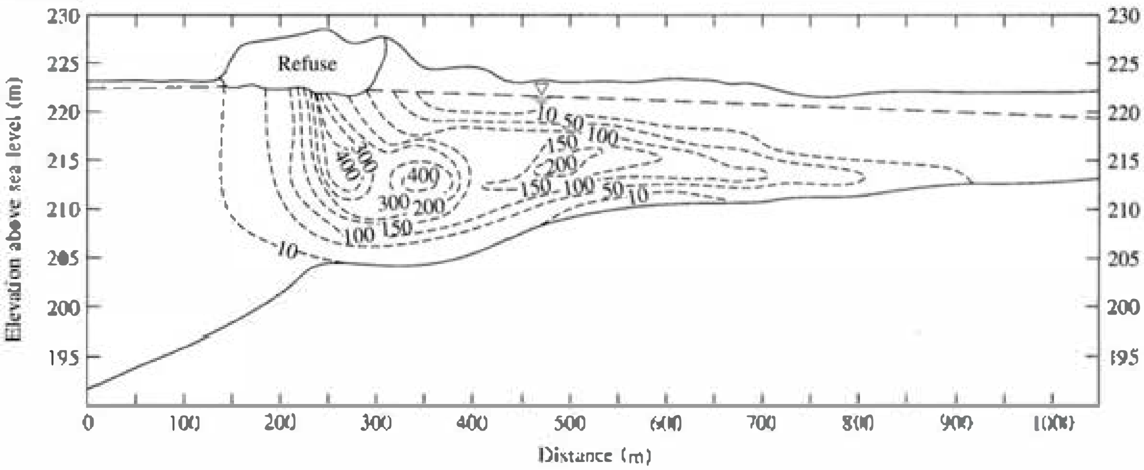

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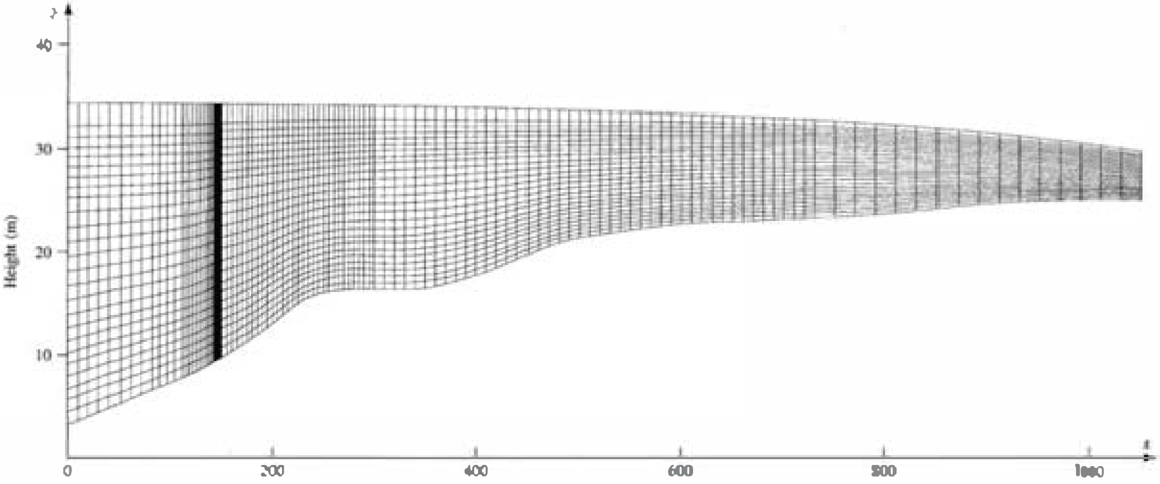
FIGURE 2.36 Finite-difference grid for Borden landfill solute transport model.



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Additional sensitivity analyses were conducted with respect to the water table boundary conditions and the concentration, size, and growth pattern of the source. The authors found that in order to reproduce the observed distribution, a source history that included multiple periods of high concentration was needed. Figure 2.40(a) shows the shape of the observed plume, Figure 2.40(b) illustrates the shape of a plume generated by a source with a history in which the concentration gradually increased (smooth source concentration), and Figure 2.40(c) contains the computed plume with the best match to the observed plume. It was generated by a run of the model in which the source concentration had two different periods of peak concentration. Although the solution was not unique—that is, several different combinations of model inputs might yield the same output—the shape of the plume could be reproduced with good accuracy. This was especially true at the leading edge of the plume, which is the most important part from the standpoint of predicting the movement of the plume into uncontaminated areas of the aquifer.

FIGURE 2.37 Equipotential lines from the calibration of the Borden landfill solute-transport model; values in meters above datum.

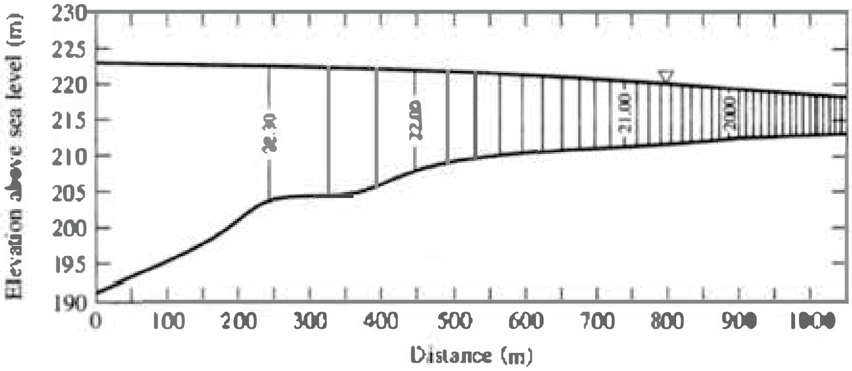

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FIGURE 2.38 Sensitivity analysis of the Borden landfill solute-transport model with respect to transverse dispersivity.

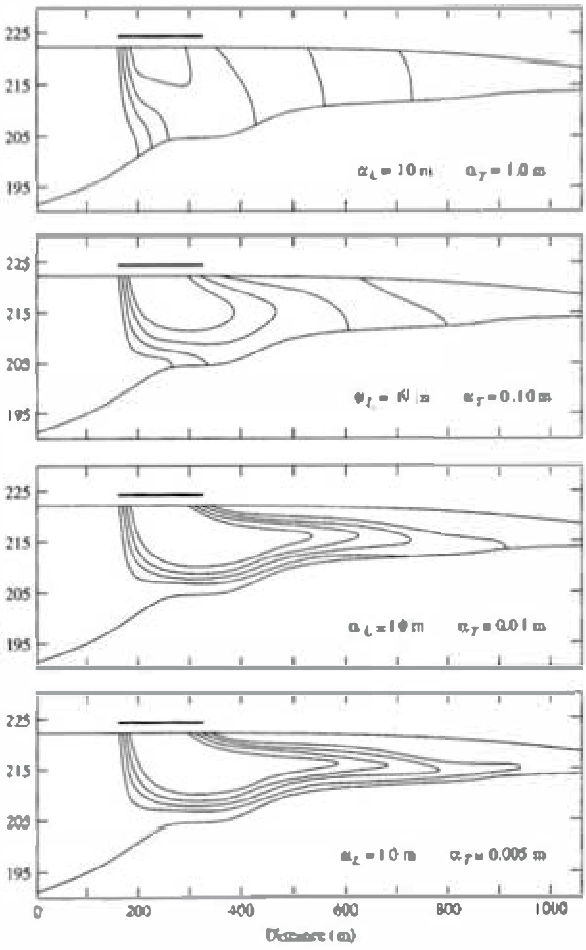

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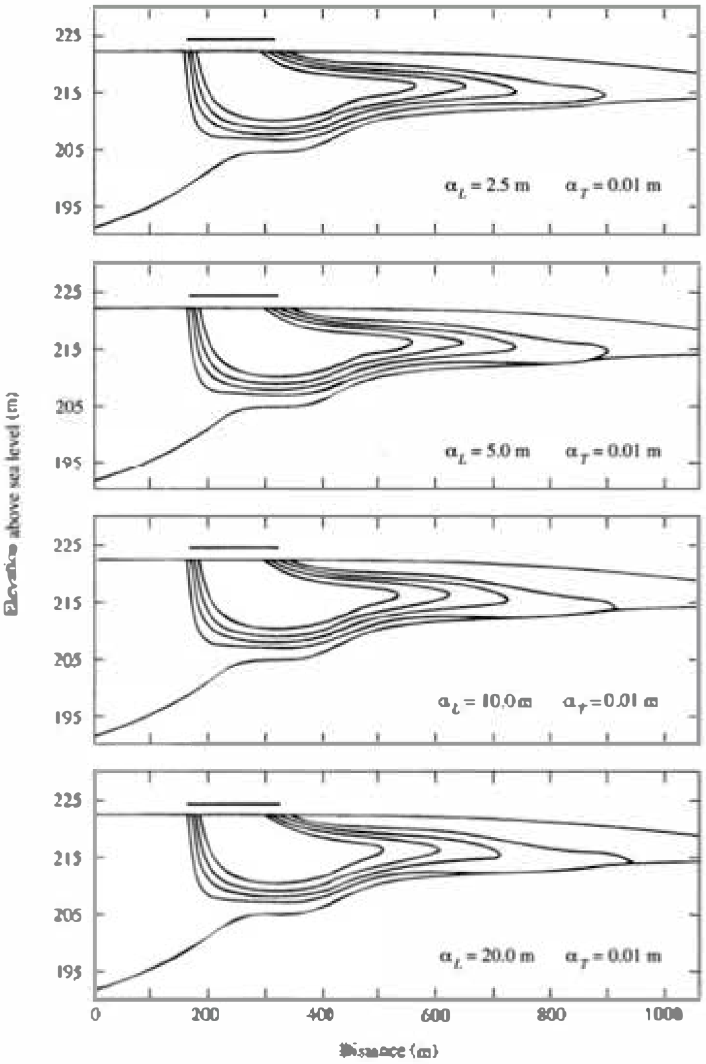
FIGURE 2.39 Sensitivity analysis of the Borden landfill solute-transport model with respect to longitudinal dispersivity.



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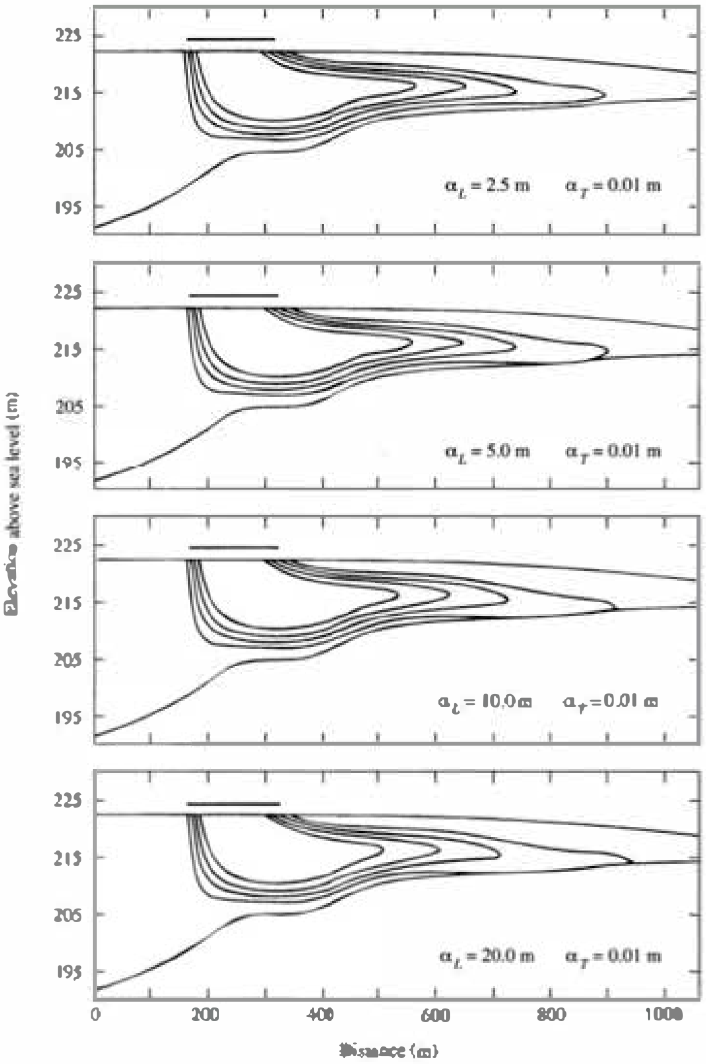
2.16 Transport in Fractured Media

Solute transport in fractured rock media is as important a process as transport in porous media. Understanding fluid flow and mass transport in fractured rocks is essential for assessing the groundwater resources of hard-rock aquifers and predicting the movement of hazardous chemicals if contamination occurs. Transport in fractured media is also important when assessing the suitability of underground sites for hazardous waste disposal, such as the heavily investigated former candidate site for a nuclear waste repository at Yucca Mountain in Nevada. However, less research has been done on this topic than on transport in porous media. One reason may is that existing theory of fluid flow through porous media is of limited usefulness when applied to fractured

FIGURE 2.39 Sensitivity analysis of the Borden landfill solute-transport model with respect to longitudinal dispersivity.



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2.16 Transport in Fractured Media

Solute transport in fractured rock media is as important a process as transport in porous media. Understanding fluid flow and mass transport in fractured rocks is essential for assessing the groundwater resources of hard-rock aquifers and predicting the movement of hazardous chemicals if contamination occurs. Transport in fractured media is also important when assessing the suitability of underground sites for hazardous waste disposal, such as the heavily investigated former candidate site for a nuclear waste repository at Yucca Mountain in Nevada. However, less research has been done on this topic than on transport in porous media. One reason may is that existing theory of fluid flow through porous media is of limited usefulness when applied to fractured rocks (USGS 2015c). The rock in which fractures exist is porous. Hence, fluid moves in the fractures as well as in the rock matrix. Solutes in the fractures can diffuse into the fluid contained in the rock matrix and vice versa (Neretnieks 1980; National Research Council 2015). The fractures themselves are not smooth channels but contain dead-end passages that hold nonmoving water into which solutes can diffuse (Raven et al. 1988).

Berkowitz et al. (1988) suggested that solute transport in fractured media can be considered at a number of different scales. A very-near-field scale would be a single fracture near the source. A near-field scale would include a few fractures near the source. At a larger scale, the far field, the fracture network and the porous media matrix would have separate, discernible impacts on flow. At a very-far-field scale, which exists at considerable distance from the source, the entire flow domain can be considered as an equivalent porous medium in which the repeating fractures became large pores.

A number of different approaches to solute transport in fractured media have been attempted. These include analysis of transport in a single fracture in which effects of the transport in the fractures as well as interactions with a porous matrix are considered (e.g., Grisak and Pickens 1980; 1981; Tang et al. 1981; Rasmuson and Neretnieks 1981; Rasmussen 1984; Sudicky and Frind 1984). Sudicky and Frind (1982) and Barker (1982) examined transport in a media that consists of equally spaced fractures in a porous media. Endo and others (1984) made a deterministic study of flow in an irregular network of fractures contained in an impermeable host rock, whereas Schwartz et al. (1983) and Smith and Schwartz (1984) approached the same problem using a stochastic model. Berkowitz et al. (1988) and Schwartz and Smith (1988) examined the conditions under which the porous media matrix and the fractures can be considered to be a continuum that is representative of an equivalent porous media. Raven et al. (1988) made a field study of flow through a single fracture to test a model that incorporates the effects of nonflowing water in the fractures. Tsang et al. (1988) and Moreno et al. (1988) examine fracture flow on the basis of the assumption that most of the flow is concentrated in a few channels.

Dietrich et al. (2005) proposed a multi-continuum model in which separate, coupled hydraulic components in a heterogeneous aquifer are modeled. It is assumed that each component is distributed continuously in space and satisfies the condition of a porous medium (Bear and Bachmat 1990). For fracture matrix systems, this could be two fracture continua, such as a micro- and macro-fracture system, and a matrix continuum with appropriate equivalent parameters. The matrix and fractures are locally idealized as continua and the fractures are implemented discretely at their actual locations within the domain. It is obvious that the amount of data required to set up a discrete model of the actual domain is very large and to some extent not measureable. Consequently, the discrete model concept is preferentially used for relatively small domains and it is a suitable tool for principle studies of flow and transport processes (Dietrich et al. 2005).

One of the first considerations in dealing with fracture flow is deciding how to treat flow in a single fracture. Some authors (e.g., Tang et al. 1981; Schwartz and Smith 1988) assume that the fluid in a fracture is all moving at a constant velocity. Conversely, Endo et al. (1984) treated flow in a fracture to be two-dimensional, with a parabolic velocity profile across the width of the fracture, as shown in Figure 2.41. Transport within a single fracture is due to advection, which occurs at different rates, depending upon the position between the parallel walls of the fracture, and molecular diffusion, both normal and parallel to the flow direction.

FIGURE 2.40 Comparison of (a) the observed chloride plume at the Borden landfill with (b) the chloride plume simulated by the solute transport model with a smooth source concentration and (c) the chloride plume simulated by the solute transport model with a doubly peaked source concentration.

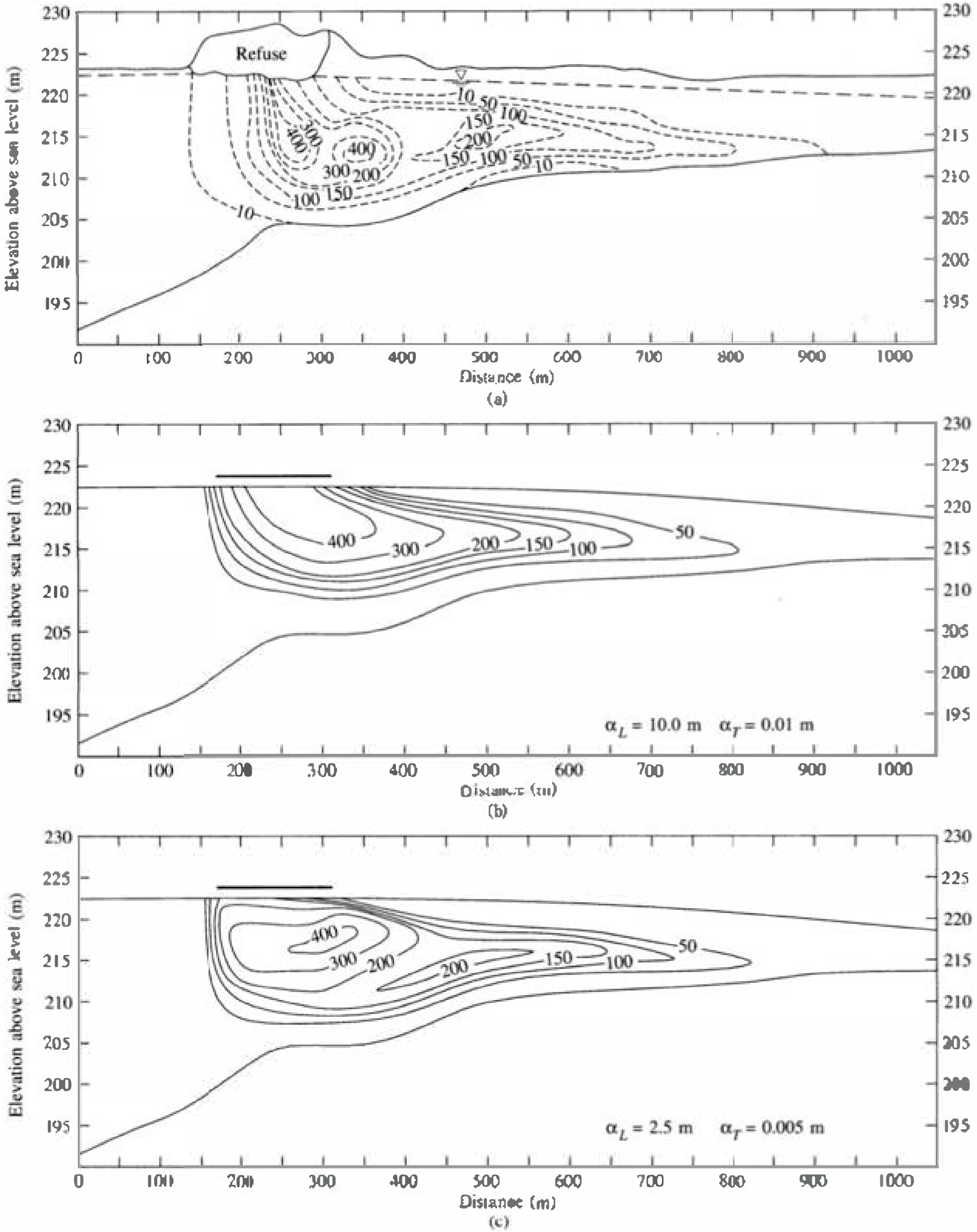

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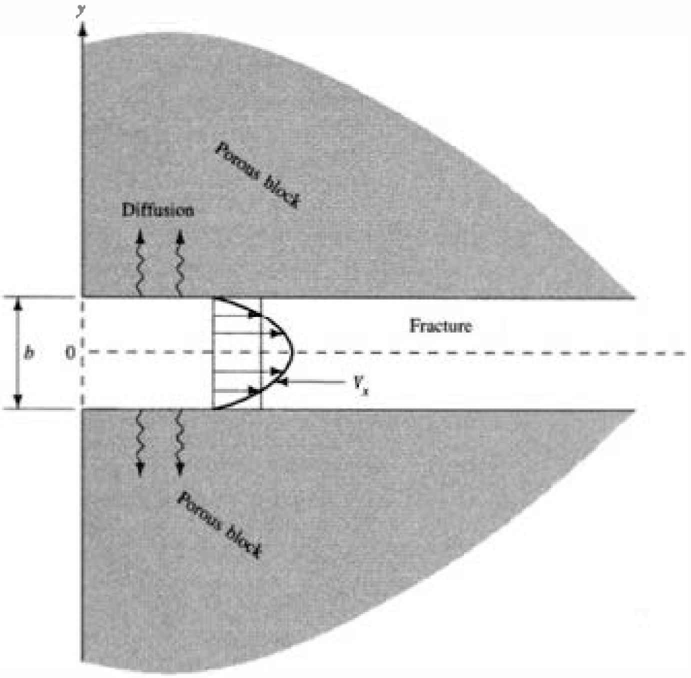
FIGURE 2.41 Horizontal distribution of flow in a vertical fracture and diffusion into the porous media matrix.



Hull et al. (1987) examined the conditions whereby diffusion within the fracture needs to be considered. In a fracture with parallel sides, the solute transport within the fracture is described by

$$\frac{\partial C}{\partial t} = D^*\left(\frac{\partial^2 C}{\partial x^2}+\frac{\partial^2 C}{\partial y^2}\right) - 6V\left[(\tau)-(\tau)^2\right]\frac{\partial C}{\partial x} \tag{2.49}$$

where

V = average fluid velocity in a fracture

τ = fractional transverse position in a fracture

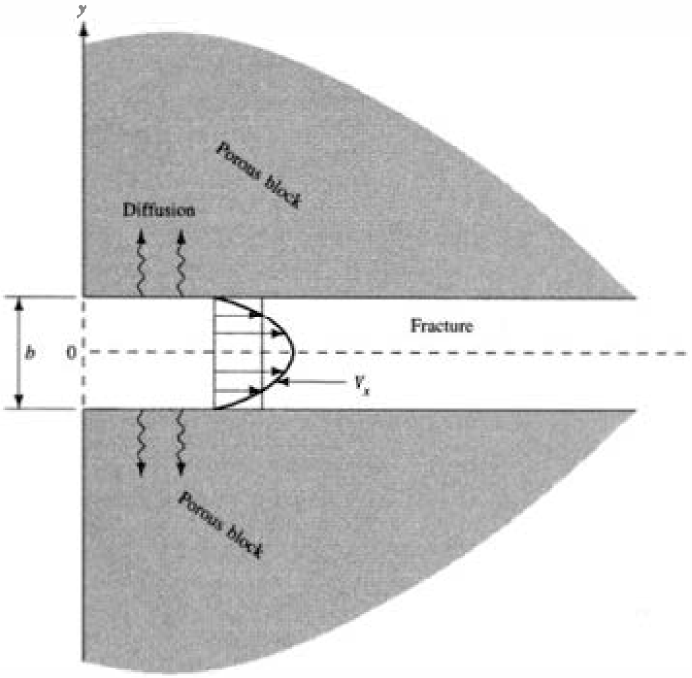
At high flow rates, advection will dominate and the concentration will follow the velocity profile of Figure 2.41. At low velocities, diffusion will be important, since the concentration gradient at the solute front will be high and the distance will be short. Under these conditions, diffusion will homogenize the solute across the width of the fracture.

If L is the length of the fracture between cross fractures and β is the aperture of the fracture, the fracture residence time is L/V. This can be compared with $(\beta/2)^3/D$ to determine if diffusion needs to be considered (Crank 1956). If diffusion induces a change in the tracer concentration of less than 2% over a distance of 10% of the width of the fracture, the diffusion can be considered negligible, and the residence time in the fracture will be

$$\frac{L}{V} < 0.003\frac{(\beta/2)^2}{D} \tag{2.50}$$

If diffusion affects the tracer concentration to the extent that the tracer front is at 98% of the equilibrium value at all points across the fracture, the diffusion has homogenized the front, and the residence time in the fracture will be

FIGURE 2.41 Horizontal distribution of flow in a vertical fracture and diffusion into the porous media matrix.



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$$\frac{\partial C}{\partial t} = D^* \left(\frac{\partial^2 C}{\partial x^2} + \frac{\partial^2 C}{\partial y^2} \right) - 6V\left[(\tau) - (\tau)^2 \right] \frac{\partial C}{\partial x} \tag{2.49}$$

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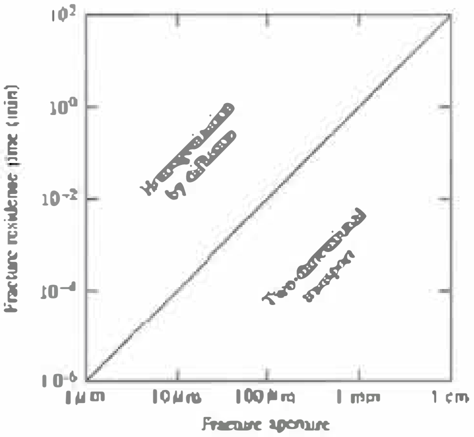
If diffusion affects the tracer concentration to the extent that the tracer front is at 98% of the equilibrium value at all points across the fracture, the diffusion has homogenized the front, and the residence time in the fracture will be

FIGURE 2.42 Fracture residence time necessary for homogenization of the tracer across the fracture width by molecular diffusion.



Source: Modified from L. C. Hull, J. D. Miller, and T. M. Clemo, 1987. *Water Resources Research* 23:1505–1513. Copyright by the American Geophysical Union. Reproduced with permission.

$$\frac{L}{V} < 0.05\frac{(\beta/2)^2}{D} \tag{2.51}$$

Figure 2.42 indicates the circumstances under which fracture flow can be considered to be one- or two-dimensional. Fracture residence time (L/V) is plotted against fracture aperture on this figure, which is based on a diffusion coefficient of 1.7×10^{-9} m²/sec (1.93×10^{-8} ft²/sec). The figure shows the conditions under which diffusion will homogenize the flow so that the transport within the fracture can be treated as one-dimensional (uniform conditions across the aperture). However, diffusion will still spread the tracer in advance of the advecting water. For even large fractures of 1mm aperture, this will occur with a residence time of 1min or more. This suggests that for most flow situations, one does not need to consider the velocity distribution across the fracture.

When the flow in a fracture is homogeneous, the mass transport can then be described by the one-dimensional advection-dispersion equation with the longitudinal dispersion coefficient equal to (Hull et al. 1987)

$$D_L = \frac{(V\beta)^2}{210D} \tag{2.52}$$

One approach to solute transport modeling is to determine the flux of water through the fractures and then use a numerical technique known as a random walk model to simulate diffusion of the solute (Hull et al. 1987). This ignores any diffusion into the porous media matrix. According to Witherspoon et al. (1980), flow through a fracture can be described by Darcy's law using an equivalent hydraulic conductivity for a fracture, K_f, given by

$$K_f = \frac{\rho g}{12\mu}\beta^2 \tag{2.53}$$

The quantity of flow, Q, can be found from the cubic law

$$Q = \frac{\rho g}{12\mu} Ia\beta^3 \tag{2.54}$$

where

g = acceleration of gravity
I = hydraulic gradient along the fracture
a = width of the fracture-that is, the third dimension after length and aperture
μ = viscosity of fluid

If the velocity in the channel needs to be described in two dimensions, this can be done with three equations: one for the maximum velocity in the center of the fracture, one for the flow velocity profile across the aperture, and one for the vertical velocity profile in the fracture.

The maximum velocity can be found from (Hull et al. 1987):

$$V_x\,(\max)=\left[1.5+1.1664\left(\frac{a}{\beta}\right)^{-1.0557}\right]V \qquad \textbf{(2.55)}$$

The velocity profile across the aperture is given by.

$$V_x(y)=4\left(\tau-\tau^2\right) \qquad \textbf{(2.56)}$$

where τ = fractional transverse position in a fracture, y/β.

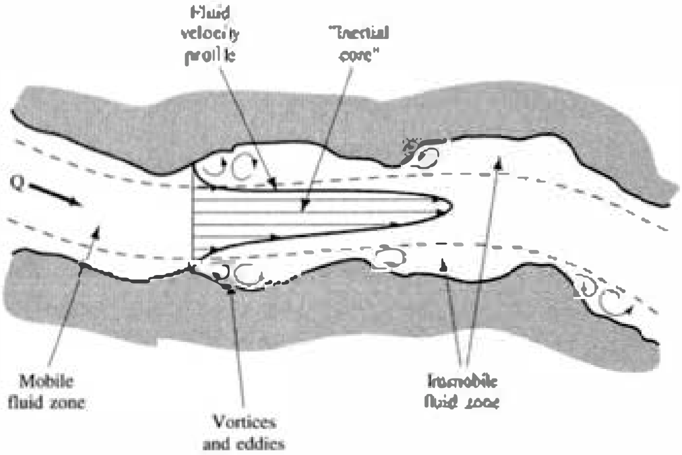
The vertical velocity profile is given by

$$V_x(\zeta)=15.56\zeta-97.72\zeta^2+308\zeta^3-513\zeta^4+431\zeta^5-143.7\zeta^6 \qquad \textbf{(2.57)}$$

where ζ = fractional vertical position in a fracture, z/a.

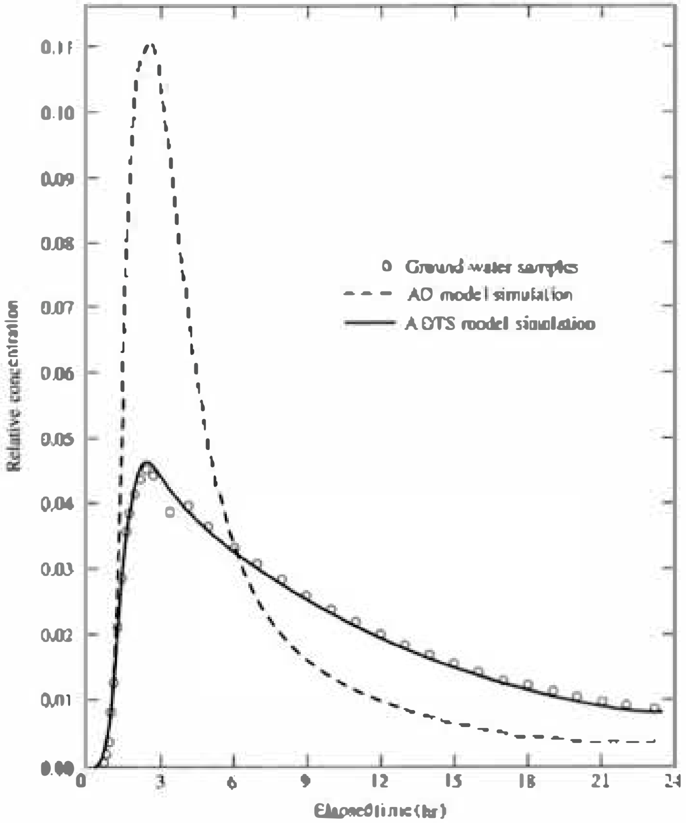
Raven et al. (1988) pointed out that the fractures through which flow occurs are not smooth, parallel plates but have irregular walls that promote the formation of zones along the edge of the fracture where the water is immobile (Figure 2.43). The fluid moves through the mobile zone, but the solutes can diffuse into the immobile fluid zones. The solute would be stored in the immobile fluid during the early part of solute transport and would be released from storage if the solute concentration in the mobile fluid would decrease—for example, as might happen during the latter part of a slug injection test. They derived an advection-dispersion equation for mass transport in the fracture with “transient solute storage in the immobile fluid zone (advection-dispersion transient storage model or ADTS). A field test was performed on the flow through a single fracture that had been isolated by packers in the borehole. Water was injected into one borehole and withdrawn from another. The water contained a tracer for the first few hours of the test, and then water without the tracer was again injected. Figure 2.44 contains circles representing the field data, in terms of relative concentration, plotted versus elapsed time. Also shown on this figure are the results of a conventional advection-dispersion (AD) model and an advection-dispersion transient storage (ADTS) model. Both models matched the observed data for the first few hours of the test. However, the ADTS model was far superior in matching the field data over the entire course of the test. The effect of transient storage was to reduce the peak concentration and to increase the concentrations above what would be produced by advection-dispersion alone during the later periods of the test.

FIGURE 2.43 Zones of mobile and immobile water in a fracture.



Source: K. G. Raven, K. S. Novakowski, and P. A. Lapcevic. 1988. *Water Resources Research* 24:2019–2032. Copyright by the American Geophysical Union. Reproduced with permission.

FIGURE 2.44 Comparison of field data from a tracer test in fractured rock with results of model simulation using an advection-diffusion (AD) model and an advection-diffusion transient storage (ADTS) model.



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2.17 Summary

Solutes dissolved in groundwater are transported in two ways. Diffusion will cause solutes to move in the direction of the concentration gradient—that is, from areas of higher to lower concentration. This transport can occur even if the groundwater is not flowing and may be the major factor in mass transport in geologic materials of very low permeability.

Solutes are also transported by the process of advection. This occurs as the flowing groundwater carries the dissolved solutes with it. At the scale of a few pore diameters, groundwater will move parallel to the flow path at different rates due to differences in pore size. This causes the solute plume to spread along the direction of the flow path, a process called longitudinal dispersion. The solute plume will also spread laterally as flow paths diverge around mineral grains, a process known as transverse dispersion. At the laboratory column scale, the movement of a contaminant through a uniform porous media can be described by the advection-dispersion equation, which accounts for advection, diffusion, and porescale dispersion.

In field-scale studies it has been found that the coefficient of longitudinal dispersion obtained from the advection-dispersion equation increases with the length of the flow path. This is due to the heterogeneous nature of aquifer materials. As the length of the flow path increases, the range of permeability values that affect the rate of groundwater flow also increases. This causes the resulting solute plume to spread out more and more. This can be called macrodispersion. An apparent diffusion coefficient can be statistically correlated with the length of the flow path by the expression $\alpha_m = 0.83(\log L_s)^{2.414}$.

Stochastic methods of analysis have also been developed to analyze solute transport at the field scale. Stochastic methods are based on the variation in the hydraulic conductivity values because it is that variation that causes the solute plume to spread. The groundwater velocity depends upon the porosity as well as the hydraulic conductivity, but the hydraulic conductivity varies over a much greater range than porosity.

At the field scale the spreading due to hydraulic conductivity variation is much greater than that due to pore-scale dispersion. Both stochastic and advection-dispersion models demonstrate that the primary movement of the solute plume is due to advection. The stochastic model yields the movement of the center of mass of the solute plume from the average rate of movement of the groundwater. The variance of the solute concentration about the mean position, or the second spatial moment, is also obtained from stochastic models.

Chapter Notation

A	Cross-sectional area
a	Width of a fracture
b	Aquifer thickness
B	$[(v_x x)^2/(2D_L)^2 + (v_x y)^2/(4D_L D_y)]^{1/2}$
C	Solute concentration
C_i	Concentration at some point x and time t
C_0	Initial concentration, i.e. concentration at time 0
C_R	Dimensionless solute concentration (C/C_0)
$\langle C \rangle$	Ensemble mean concentration
c_0	Constant related to anisotropy
d	Characteristic flow length for Peclet number, P
dh/dl	Hydraulic gradient
D^*	Effective diffusion coefficient
D	Diffusion coefficient
D_d	Molecular diffusion coefficient
D_i	Coefficient of hydrodynamic dispersion in the i direction

D_L	Coefficient of longitudinal hydrodynamic dispersion
D_T	Coefficient of transverse hydrodynamic dispersion
E	Euler number ([illegible]-577...)
E_1	Exponential integral
f	Fractal dimension
F	Mass flux of solute per unit area per unit time
g	Acceleration of gravity
G	Topological dimension
h	Hydraulic head
H	Separation of autocorrelation function
[illegible]	Decay constant
I	Hydraulic gradient along a fracture
J	Constant length
k	Lag in autocorrelation function
K	Hydraulic conductivity
K_f	Equivalent hydraulic conductivity of a fracture
K_G	Geometric mean of hydraulic conductivity
K_0	Modified Bessel function of second kind and zero order
L	Straight-line distance between ends of a flowpath
L_e	Length of a tortuous flowpath
L_f	Length of a fractal flowpath
L_s	Straight-line length between ends of a fractal flowpath
M	Total mass of solute
N	Number of units
n	Porosity
n_e	Effective porosity
P_e	Peclet number ($v_x L / D_L$)
PV	Pore volume
Q	Rate at which a tracer is being injected into an aquifer
r	Radial distance to a well
R	Length of well screen or open borehole
R_f	Average frontal position of water injected into a well
r_Y	Autocorrelation of sampled values of Y
S_Y	Standard deviation of sampled values of Y
S_Y^2	Variance of sampled values of Y
t	Time
t'	Dimensionless time (tU/ϵ_h)
t_D	Dimensionless rime $\left(\frac{V_x^2 t}{D_L}\right)$
t_R	Dimensionless time ($v_x t/L$)
T	Tortuosity
T_f	Fractal tortuosity
u	Average velocity of injection of water into a well
u	Fluctuation in the velocity vector
u_{ij}	Covariance
U	⟨V⟩ ensemble mean of velocity vectors
U_i	Total volume of water injected into a well
U_p	Cumulative volume of water withdrawn from a well
v_f	Velocity along a fractal flowpath
v_x	Average linear velocity in the x direction
V	Average fluid velocity in a fracture
$\mathbf{V}$	Velocity vector
$\langle \mathbf{V} \rangle$	Ensemble mean of the velocity vectors
$W[t, B]$	Hantush leaky well function
x	Coordinate vector
x_f	Length of fractal flowpath
(x_0, y_0)	Origin of an xy field
x_c	Straight-line distance
$\mathbf{X}'$	Residual of the displacement of a particle
$\langle \mathbf{X} \rangle$	Ensemble mean of the center of mass
$X_{jl}(t)$	Second spatial moment of the solute mass at time t and location j, l
$\mathbf{X}_t$	Total particle displacement
$\bar{Y}$	Mean of sample values of Y
Y_i	$\log K_i$
Z_o	Constant related to a semivariogram
α	Dynamic dispersivity
α_L	Longitudinal dynamic dispersivity
α_T	Transverse dynamic dispersivity
α_m	Apparent dispersivity
β	Aperture of a fracture
ϵ_h	Correlation length for horizontal hydraulic conductivity

ϵ_v	Correlation length for vertical hydraulic conductivity
η	Fractal unit of measurement
η_c	Fractal cutoff limit
γ_Y	Semivariogram of Y
λ_Y	Correlation length of autocorrelation
μ	Viscosity of a fluid
μ_Y	Mean of population of Y
ν	Hurst coefficient for fractal dimensions
ω	Coefficient related to tortuosity
Ω	Anisotropy ratio (ϵ_v/ϵ_h)
ρ	Density of a fluid
ρ_Y	Autocorrelation of the population of Y
σ_Y	Standard deviation of population of Y
σ_Y^2	Variance of population of Y
τ	Fractional transverse position in a fracture
τ_Y	Autocovariance
θ	Angle in polar coordinate system
ξ	Fourier transform wave vector number
ζ	Fractional vertical position in a fracture

References

Anderson, M. P. 1979. Using models to simulate the movement of contaminants through groundwater flow systems. *Critical Reviews in Environmental Controls* 9:97–156.

Anderson, M. P. 1984. "Movement of contaminants in groundwater: Groundwater transport—advection and dispersion." In *Groundwater Contamination*, 37-45. Washington, DC: National Academy Press.

Anderson, M. P. 1990. Aquifer heterogeneity—a geological perspective. *Proceedings, Fifth Canadian/American Conference on Hydrogeology.* National Water Well Association, pp. 3-22.

Anderson, M. P., and W. W. Woessner. 1991. *Applied Groundwater Modeling: Simulation of Flow and Advective Transport.* San Diego, CA: Academic Press.

Aris, R. 1956. On the dispersion of a solute in a fluid flowing through a tube. *Proceedings of The Royal Society of London* 235:67–77.

Ayra, A. 1986. Dispersion and reservoir heterogeneity. Ph.D. Dissertation. University of Texas, Austin.

Bachmat, Y., and J. Bear. 1987. On the concept and size of a representative elementary volume (REV). *Advances in Transport Phenomena in Porous Media* 128:3–20.

Bakr, A. A. 1976. Effect of spatial variations of hydraulic conductivity on groundwater flow. Ph.D. Dissertation. New Mexico Institute of Mining and Technology, Socorro.

Barker, J. A. 1982. Laplace transform solutions for solute transport in fissured aquifers. *Advances in Water Resources* 5:98–104.

Bear, J. 1961. Some experiments on dispersion. *Journal of Geophysical Research* 66:2455–2467.

Bear, J. 1972. *Dynamics of fluids in porous media.* New York: American Elsevier Publishing Company, 764 pp.

Bear, J., and A. Verruijt. 1987. *Modeling Groundwater Flow and Pollution.* Dordrecht, Netherlands: D. Reidel Publishing Company, 414 pp.

Bear, J., and A. H.-D. Cheng. 1990. "Modeling Groundwater Flow and Contaminant Transport." In *Theory and Applications of Transport in Porous Media. Volume 23.* Reprint 2010. Springer, 396 pp.

Bedient, P. B., H. S. Rifai, and C. J. Newell. 1994. *Ground Water Contamination: Transport and Remediation.* Englewood Cliffs, NJ: Prentice Hall.

Berkowitz, B., J. Bear, and C. Braester. 1988. Continuum models for contaminant transport in fractured porous formations. *Water Resources Research* 24:1225-1236.

Bierkens, M., and F. van Geer. 2014. Stochastic Hydrology. Lecture notes. Accessed October 3, 2015 at http://www.earthsurfacehydrology.nl/wp-content/uploads/2012/01/Syllabus_StochasticHydrology.pdf

Brigham, W. E. 1974. Mixing equations in short laboratory columns. *Society of Petroleum Engineers Journal* 14:91–99.

Boving, T. B., and P. Grathwohl. 2001. Tracer diffusion coefficients in sedimentary rocks: Correlation to porosity and hydraulic conductivity. *Journal of Contaminant Hydrology* 53:85–100.

Carman, P. C. 1997. Fluid flow through a granular bed. *Chemical Engineering Research and Design* 75: S32–S48.

6

Inorganic Chemicals in Groundwater

6.1 Introduction

Groundwater is a solvent that is in contact with various earth materials. As a result, groundwater naturally contains dissolved cations and anions as well as some nonionic inorganic material, such as silica (SiO_2). Naturally occurring groundwater can contain dissolved solids that range in concentration from less than 100 mg/L to more than 500,000 mg/L (Hem 1985). The major ion constituents of natural water include calcium, magnesium, sodium, potassium, chloride, sulfate, and bicarbonate/carbonate. Dissolved gasses can include nitrogen, carbon dioxide, methane, oxygen, and hydrogen sulfide. There are a number of ions that can be naturally present in small amounts that can affect the water quality. In addition, inorganic ions that impact upon water quality can be released to the subsurface via human activity. For example, at least 18 inorganic elements can be used in pesticides (chromium, chlorine, fluorine, tin, arsenic, selenium, barium, cadmium, sulfur, phosphorus, mercury, zinc, lead, copper, thallium, bismuth, boron, and antimony), and many metals can be joined with carbon to form organometalic pesticides (Clarkson 2001).

We have already seen in Chapter 3 that ions can be removed from solution by ion exchange and sorption. In this chapter we will examine other chemical processes that act to remove inorganic ions from solution. We will also examine the chemical properties of a number of inorganic materials frequently found in groundwater. The geochemical zonation that can occur near landfills that have received municipal waste will be used to illustrate some basic principles.

6.2 Units of Measurement and Concentration

Chemical analyses are usually reported on the basis of weight of solute per volume of solvent. Common units are **milligrams per liter** (mg/L) and **micrograms per liter** (μg/L). Equivalent weight units are frequently used when the chemical behavior of a solute is being considered. The equivalent weight of an ion is the formula weight divided by the electrical charge. If the concentration of the ion in milligrams per liter is divided by the formula weight, the resulting concentration is expressed in terms of **milliequivalents per liter**. One **mole** of a substance is its formula weight in grams. A 1-**molal** solution has 1 mole of solute in 1000 g of solvent. A 1-**molar** (1-*M*) solution has 1 mole of solute in a liter of solution.

If a solution is dilute and there is no need to make density corrections, the molality can be determined from the concentration by the following equation:

$$\text{Molality} = \frac{\text{milligrams per liter} \times 10^{-3}}{\text{formula weight in grams}} \qquad (6.1)$$

6.3 Chemical Equilibrium and the Law of Mass Action

The law of mass action states that the rate of a chemical reaction will be proportional to the active masses of the participating substances (Hem 1985). If there are two substances, A and B, reacting to form two other substances, C and D, and if the process is reversible, then the reaction can be written as

$$a\mathrm{A} + b\mathrm{B} \rightleftharpoons c\mathrm{C} + d\mathrm{D} \qquad (6.2)$$

The rate of the forward reaction, R_1, is

$$R_1 = k'_1[\mathrm{A}]^a[\mathrm{B}]^b \qquad (6.3)$$

whereas the rate of the reverse reaction, R_2, is

$$R_2 = k'_2[\mathrm{C}]^c[\mathrm{D}]^d \qquad (6.4)$$

where:

[A] = active concentration of substance A
k'_1 = proportionality constant for the forward reaction
k'_2 = proportionality constant for the reverse

If the reaction progresses to a point where the forward reaction rate is equal to the reverse reaction rate, then

$$k'_1[A]a[B]b \rightleftharpoons k'_2[C]c[D]d \qquad (6.5)$$

Equation 6.5 can be rearranged to yield the following expression:

$$\frac{[C]^c[D]^d}{[A]^a[B]^b} = \frac{k'_1}{k'_2} = K_{eq} \qquad (6.6)$$

where K_{eq} is the equilibrium constant.

If two or more ions react to form a solid precipitate and the reaction is reversible, then it can be represented as

$$a\mathrm{A} + b\mathrm{B} \rightleftharpoons c\mathrm{AB} \qquad (6.7)$$

The equilibrium relationship of this reaction is:

$$K_{sp} = \frac{[\mathrm{A}]^a[\mathrm{B}]^b}{[\mathrm{AB}]^c} \qquad (6.8)$$

where K_{sp} is called a solubility **product**. The activity of the solid together with the water is defined as unity. Solubility products can be used to compute the concentration of a solute in equilibrium with a solid phase, either via dissolution of the solid into an undersaturated solution or following precipitation of the solid from a saturated solution.

If one is dealing with a very dilute aqueous solution, then molal concentrations can be used to determine chemical equilibrium. However, for the general case, one must use **chemical activities** to employ the law of mass action.

The chemical activity of ion X, $[X]$, is equal to the molal concentration of X, m_x, times a factor known as an **activity coefficient**, γ_x:

$$[X] = m_x \gamma_x \tag{6.9}$$

The activity coefficient varies with the total amount of cations and anions in solution. The concentration and charge of the various ions in a solution determine its **ionic strength**. Ionic strength can be computed from the following formula:

$$I = \frac{1}{2}\sum m_i z_i^2 \tag{6.10}$$

where

I = ionic strength
m_i = molality of the ith ion
z_i = charge of the ith ion

Once the ionic strength is determined, the activity coefficient can be calculated using the Debye-Hückel equation:

$$-\log \gamma_i = \frac{A z_i^2 \sqrt{I}}{1 + a_i B \sqrt{I}} \tag{6.11}$$

where

γ_i = the activity coefficient for ionic species i
z_i = the charge on ionic species i
I = ionic strength of the solution
A = constant equal to 0.5085 at 25°C
B = constant equal to 0.3281 at 25°C
a_i = the effective diameter of the ion from Table 6.1

The Debye-Hückel equation can be used with solutions that have an ionic strength of 0.1 or less (approximately 5000 mg/L). Figure 6.1 is a graph showing the relationship of activity coefficient to ionic strength for specific ions; it was calculated using the Debye-Hückel equation. Specific curves are for ions with the same effective diameter and charge as listed in Table 6.1. Not all the ions to which a curve applies are listed on the figure. For example, the curve labeled Ca^{2+} and Fe^{2+} can also be used for Cu^{2+}, Zn^{2+}, Sn^{2+}, Mn^{2+}, Ni^{2+}, and Co^{2+}, because all these ions have the same effective diameter and charge.

Chemical equilibrium is a useful concept in studies of contaminant hydrogeology. Ionic contaminants discharged into groundwater may react with naturally occurring of a solute in equilibrium with a solid phase, either via dissolution of the solid into an undersaturated solution or following precipitation of the solid from a saturated solution.

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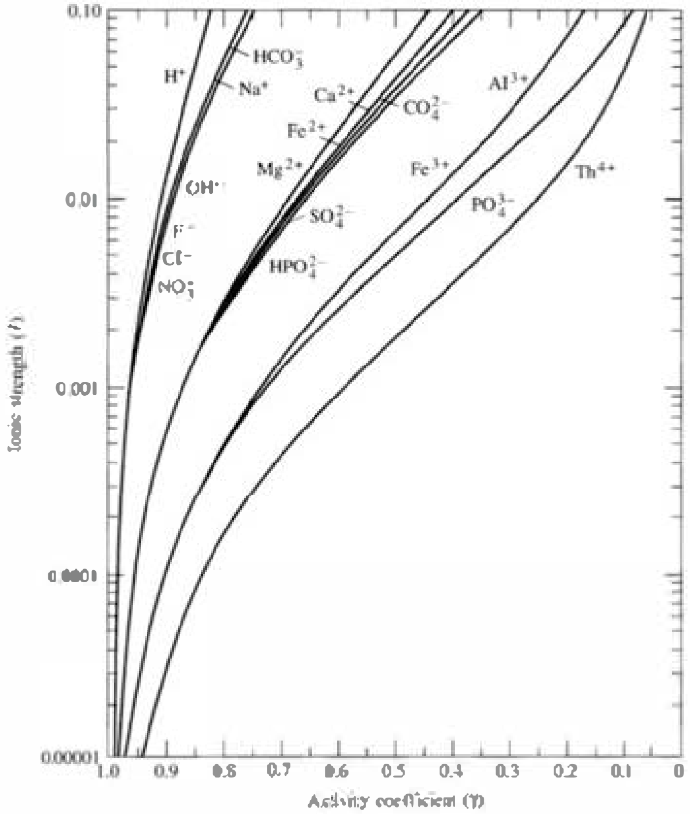
Chemical equilibrium is a useful concept in studies of contaminant hydrogeology. Ionic contaminants discharged into groundwater may react with naturally occurring

TABLE 6.1 Values of the parameter a_i in the Debye-Hückel equation.

a_i	Ion
11	Th^{4+}, Sn^{4+}
9	Al^{3+}, Fe^{3-}, Cr^{3+}, H^+
8	Mg^{2+}, Be^{2+}
6	Co^{2+}, Cu^{2+}, Zn^{2+}, Sn^{2-}, Mn^{2+}, Fe^{2+}, Ni^{2+}, Co^{2+}, Li^+
5	$Fe(CN)_6^{4-}$, Sr^{2+}, Ba^{2+}, Cd^{2+}, Hg^{2+}, S^{2-}, Pb^{2+}, CO_3^{2-}, SO_3^{2-}, MoO_4^{2-}
4	PO_4^{3-}, $Fe(CN)_6^{3-}$, Hg_2^{2-}, SO_4^{2-}, SeO_4^{2-}, CiO_4^{3-}, HPO_4^{2-}, No^-, HCO_3^-, $H_2PO_4^-$
3	OH^-, F^-, CNS^-, CNO^-, HS^-, ClO_4^-, K^+, Cl^-, Br^-, I^-, CN^-, NO_2^-, NO_3^-, Rb^-, Cs^+, NH_4^+, Ag^+

Source: J. Kielland, 1937. Individual activity coefficients of ions in aqueous solutions *American Chemical Society Journal* 59:1676-1678. Published by the American Chemical Society. Used with permission.

FIGURE 6.1 Relationship of activity coefficients of dissolved ions as a function of the ionic strength of a solution at 25°C.



Source: J. D. Hem, 1985. *Study and interpretation of the chemical characteristics of natural waters.* Water Supply Paper 2254, U.S. Geological Survey.

ions in the groundwater to form a precipitate or they may mobilize ions sorbed on solid surfaces. They may also undergo oxidation or reduction. Both these processes are reversible and can be described by chemical equilibrium. Many geochemical processes in groundwater are not readily reversible, such as weathering of silicate minerals. These reactions must be treated using kinetics. However, as this type of reaction is not of significant interest in contaminant hydrogeology, we do not typically consider kinetic models.

Table 6.2 contains the solubility products for a large number of minerals, including many that can be formed from trace metals that can be ground-water contaminants.

6.4 Oxidation-Reduction Reactions

In some chemical reactions the participating elements change their valence state through the gain or loss of electron(s). If an electron is gained, there is a loss of positive valence called a reduction. A loss of negative valence is called an oxidation. Together, these are referred to as oxidation-reduction, or redox, reactions. In environmental systems they may be controlled by microorganisms that do not participate in the reaction but act as catalysts. The microbes occur as a biofilm on the surfaces of the aquifer materials. They obtain energy by oxidation of organic compounds or hydrogen or reduced inorganic forms of iron, nitrogen, and sulfur. Electron acceptors are necessary for these biologically mediated redox reactions to occur. Under aerobic conditions oxygen is the electron acceptor, whereas under anaerobic conditions nitrate, sulfate, and carbon dioxide are the electron acceptors (McCarty et al. 1984).

An example of a reduction is

$$Fe^{2+} + 2e^- \rightleftharpoons Fe^0 \qquad (6.12)$$

In this example, ferrous iron is reduced to metallic iron by the addition of two electrons. This is a half-reaction, since the electrons must be supplied either by an electrical current or by a simultaneous reaction in which another element is oxidized and releases the requisite number of electrons. The standard electrical potential of a half-reaction is the voltage represented by the flow of electrons when the reaction is at equilibrium. Under standard conditions (25°C and 1 atm pressure) the standard potential is represented by the symbol E^0. The potential is in volts, with a negative value representing reducing conditions and a positive value representing oxidizing conditions (Hem 1985). By convention, the standard potential for the reduction of H^+ to hydrogen gas is 0:

$$2H^+ + 2e^- \rightleftharpoons H_2 \quad \text{(gas)} \qquad (6.13)$$

An example of oxidation occurs where ferrous iron loses an electron to form ferric iron:

$$Fe^{2+} \rightleftharpoons Fe^{3+} + e^- \qquad (6.14)$$

Oxidation-reduction reactions involve elements that can occur in more than one valence state. In Equations 6.12 and 6.14, iron occurred in the metallic (0) as well as the +2 and +3 states. Metals can usually occur in the metallic state with a zero valence and at least one other valence state. Some elements that are environmentally important can occur in several different valence states. Table 6.3 lists several elements that occur in different valence states and examples of compounds and ions formed from those elements.

In order for oxidation or reduction to occur in a chemical reaction, one element must be reduced while a second element is being oxidized. For example, the complete equation for the oxidation of ferrous iron to ferric iron is

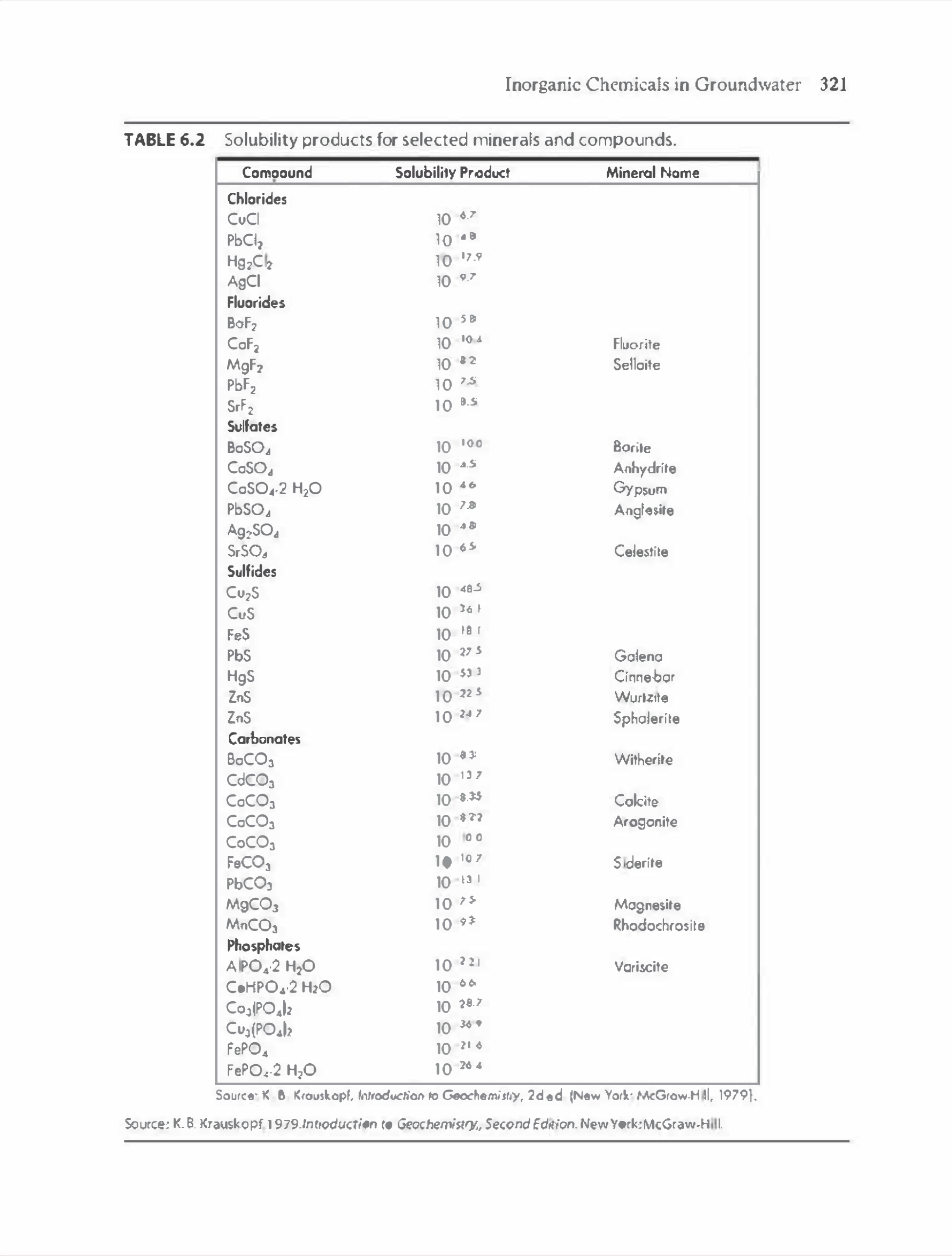


TABLE 6.2 Solubility products for selected minerals and compounds.

Compound	Solubility Product	Mineral Name
Chlorides		
$CuCl$	$10^{-6.7}$	
$PbCl_2$	$10^{-4.8}$	
Hg_2Cl_2	$10^{-17.9}$	
$AgCl$	$10^{-9.7}$	
Fluorides		
BaF_2	$10^{-5.8}$	
CaF_2	$10^{-10.4}$	Fluorite
MgF_2	$10^{-8.2}$	Sellaite
PbF_2	$10^{-7.5}$	
SrF_2	$10^{-8.5}$	
Sulfates		
$BaSO_4$	$10^{-10.0}$	Barite
$CaSO_4$	$10^{-4.5}$	Anhydrite
$CaSO_4 \cdot 2\ H_2O$	$10^{-4.6}$	Gypsum
$PbSO_4$	$10^{-7.8}$	Anglesite
Ag_2SO_4	$10^{-4.8}$	
$SrSO_4$	$10^{-6.5}$	Celestite
Sulfides		
Cu_2S	$10^{-48.5}$	
CuS	$10^{-36.1}$	
FeS	$10^{-18.1}$	
PbS	$10^{-27.5}$	Galena
HgS	$10^{-53.3}$	Cinnabar
ZnS	$10^{-22.5}$	Wurtzite
ZnS	$10^{-24.7}$	Sphalerite
Carbonates		
$BaCO_3$	$10^{-8.3}$	Witherite
$CdCO_3$	$10^{-13.7}$	
$CaCO_3$	$10^{-8.35}$	Calcite
$CaCO_3$	$10^{-8.22}$	Aragonite
$CoCO_3$	$10^{-10.0}$	
$FeCO_3$	$10^{-10.7}$	Siderite
$PbCO_3$	$10^{-13.1}$	
$MgCO_3$	$10^{-7.5}$	Magnesite
$MnCO_3$	$10^{-9.3}$	Rhodochrosite
Phosphates		
$AlPO_4 \cdot 2\ H_2O$	$10^{-22.1}$	Variscite
$CaHPO_4 \cdot 2\ H_2O$	$10^{-6.6}$	
$Ca_3(PO_4)_2$	$10^{-28.7}$	
$Cu_3(PO_4)_2$	$10^{-36.9}$	
$FePO_4$	$10^{-21.6}$	
$FePO_4 \cdot 2\ H_2O$	$10^{-26.4}$	

Source: K. B. Krauskopf, *Introduction to Geochemistry*, 2d ed. (New York: McGraw-Hill, 1979).

Source: K. B. Krauskopf. 1979. *Introduction to Geochemistry*, Second Edition. New York: McGraw-Hill.

TABLE 6.3 Selected elements that can exist in more than one oxidation state.

Element	Valence State	Examples
Carbon	+4	HCO_3^-, CO_3^{2-}
	0	C
	−4	CH_4
Chromium	+6	CrO_4^{2-}, $Cr_2O_7^{2-}$
	+3	Cr^{3+}, $Cr(OH)_3$
Copper	+1	CuCl
	+2	CuS
Mercury	+1	Hg_2Cl_2
	+2	HgS
Iron	+2	Fe^{2+}, FeS
	+3	Fe^{3+}, $Fe(OH)_3$
Nitrogen	+5	NO_3^-
	+3	NO_2^-
	0	N
	−3	NH_4^+, NH_3
Oxygen	0	O
	−1	H_2O_2
	−2	H_2O, O^{2-}
Sulfur	−2	H_2S, S^{2-}, PbS
	+2	$S_2O_3^{2-}$
	+5	$S_2O_6^{2-}$
	+6	SO_4^{2-}

$$4\,Fe^{2+} + O_2 + 4\,H^+ \rightleftharpoons 2\,H_2O + 4\,Fe^{3+} \quad (6.15)$$

This complete reaction is composed of two half-reactions:

$$4\,Fe^{2+} \rightleftharpoons 4\,Fe^{3+} + 4\,e^- \quad (6.16)$$

$$O_2 + 4\,H^+ + 4\,e^- \rightleftharpoons 2\,H_2O \quad (6.17)$$

An aqueous solution has an oxidation potential indicated by the symbol Eh. This can be calculated from the Nernst equation:

$$\mathrm{Eh} = E^0 - \frac{RT}{nF}\ln\frac{[\text{products}]}{[\text{reactants}]} \quad (6.18)$$

where:

Eh = oxidation potential of the aqueous solution in volts
E° = standard potential of redox reaction in volts
R = gas constant, 0.00199 Kcal/(mole·K)
T = temperature in Kelvins
F = Faraday constant, 23.06 Kcal/V
n = number of electrons in half-reaction
[ ] = activity of products and reactants

The standard potential for a reaction can be determined from the relationship

$$E^0 = \frac{-\Delta G_R^0}{nF} \tag{6.19}$$

where ΔG_R^0 in volts is the free energy, or Gibbs free energy, of the reaction.

The free energy of a reaction is the sum of the free energies of the products minus the sum of the free energies of the reactants. For the reaction

$$a\mathrm{A} + b\mathrm{B} \rightleftharpoons c\mathrm{C} + d\mathrm{D}$$

the free energy can be found from:

$$\Delta G_R^0 = c\Delta G_c^0 + d\Delta G_d^0 - a\Delta G_a^0 - b\Delta G_b^0 \tag{6.20}$$

Values of free energy for many elements, ions, and compounds are found in standard reference works. Table 6.4 contains values for a number of species.

The equilibrium constant for a reaction is related to the free energy of the reaction by

$$\Delta G_R^0 = -RT \ln K_{eq} \tag{6.21}$$

At standard temperature and pressure and with ΔG_R^0 in kilocalories, Equation 6.21 can be rewritten as

$$\log K_{eq} = \frac{-\Delta G_R^0}{1.364} \tag{6.22}$$

The oxidation potential of an aqueous solution can be measured using a redox or ORP electrode. If the value is positive, the solution is oxidizing, and if it is negative, the solution is reducing. Oxidation potential is measured in volts relative to the hydrogen electrode, which is at zero. Commercially available Eh meters are available that can be attached to a groundwater sampling pump. The groundwater sample is pumped under positive pressure into the flowthrough cell where the electrode is located. The water sample is never subjected to a vacuum, which could cause degassing. Moreover, it is not exposed to the atmosphere, where it can come into contact with atmospheric oxygen. This has simplified the accurate and precise measurement of Eh in groundwater Eh is directly proportional to pE, which is defined as the logarithm of the electron concentration in a solution, and is an analogous measure of the **oxidation/reduction potential**, ORP.

6.5 Relationship between pH and Eh

6.5.1 pH

Water undergoes a dissociation into two ionic species:

$$\mathrm{H_2O} \rightleftharpoons \mathrm{H^+} + \mathrm{OH^-} \tag{6.23}$$

The equilibrium constant for this reaction is

$$K_{eq} = \frac{[\mathrm{H^+}][\mathrm{OH^-}]}{[\mathrm{H_2O}]} \tag{6.24}$$

TABLE 6.4 Standard Gibbs free energy of formation for selected species.

Species	ΔG° kcal/mole	Species	ΔG° kcal/mole	Species	ΔG° kcal/mole
Arsenic		**Manganese**		$UO_2(c)$ (uraninite)	-246.61^{a}
$As_2O_5(c)$	-187.0^{a}	$MnO_2(c)$ (pyrolusite)	-111.18^{b}	$UO_2^{+}(aq)$	-229.69^{a}
$As_4O_6(c)$	-275.46^{a}	Mn_2O_3 (bixbyite)	-210.6^{b}	$UO_2^{2+}(aq)$	-227.68^{a}
$As_2S_3(c)$	-40.3^{a}	Mn_3O_4 (hausmannite)	-306.7^{b}	$(UO_2)_2(OH)_2^{2+}(aq)$	-560.99^{a}
$FeAsO_4(c)$	-185.13^{a}	$Mn(OH)_2$ (c) amorphous	-147.0^{b}	$(UO_2)_3(OH)_5^{+}(aq)$	-945.16^{a}
$H_3AsO_4(aq)$	-183.1^{a}	$MnCO_3(c)$ (rhodochrosite)	-195.2^{b}	$(UO_2)_3(OH)_7^{-}$	-1037.5^{a}
$H_2AsO_4^{-}(aq)$	-180.04^{a}	$Mn^{2+}(aq)$	-54.5^{b}	$UO_2CO_3^{0}(c)$	-367.07^{a}
$HAsO_4^{2-}(aq)$	170.82^{a}	$MnOH^{+}(aq)$	-96.8^{b}	$UO_2(CO_3)_2^{2-}(aq)$	-503.2^{a}
$AsO_4^{3-}(aq)$	-155.0^{a}	**Molybdenum**		$UO_2(CO_3)_3^{4-}(aq)$	-635.69^{a}
$HAsO_2(aq)$	-96.25^{a}	$MoO_3(c)$	-159.66^{b}	**Miscellaneous species**	
$AsO_2^{-}(aq)$	-83.66^{a}	$MoO_2(c)$	-127.40^{b}	$ZnFe_2O_4(c)$	-254.2^{a}
Chromium		$FeMoO_4(c)$	-233^{b}	$CuFeO_2(c)$	-114.7^{b}
$Cr_2O_3(c)$	-252.9^{f}	$MoO_4^{2-}(aq)$	-199.9^{b}	$CuFe_2O_4(c)$	-205.26^{b}
$HCrO_4^{-}$	-182.8^{f}	**Silver**		$NiFe_2O_4(c)$	-232.6^{b}
$Cr_2O_7^{2-}(aq)$	-311.0^{f}	$Ag_2O(c)$	-2.68^{b}	$H_2O(l)$	-56.687^{a}
$CrO_4^{2-}(aq)$	-173.96^{i}	$AgCl(c)$	-26.24^{b}	$OH^{-}(aq)$	-37.594^{a}
Copper		$Ag_2S(c)$	-9.72^{b}	$O_2(aq)$	-3.9^{a}
$CuO(c)$	-31.0^{b}	$Ag_2CO_3(c)$	-104.4^{b}	$HSO_4^{-}(aq)$	-180.69^{a}
$CuSO_4 \cdot 3Cu(OH)_2(c)$ (brochantite)	-434.5^{b}	$Ag^{+}(aq)$	18.43^{b}	$SO_4^{2-}(aq)$	-177.97^{a}
$Cu_2O(c)$	-34.9^{b}	$AgOH(aq)$	-22.0^{b}	$H_2S(aq)$	-6.66^{a}
$Cu_2S(c)$	-20.6^{b}	$Ag(OH)_2^{-}(aq)$	-62.2^{b}	$HS^{-}(aq)$	2.88^{a}
$Cu^{2+}(aq)$	15.67^{b}	$AgCl(aq)$	-17.4^{b}	$S^{2-}(aq)$	20.5^{a}
$CuSO_4(aq)$	-165.45^{b}	$AgCl_2^{-}(aq)$	-51.5^{b}	$CO_2(g)$	-94.254^{a}
$HCuO_2^{-}(aq)$	-61.8^{b}	**Vanadium**		$CO_2(aq)$	-92.26^{a}
$CuO_2^{2-}(aq)$	-43.9^{b}	$H_4VO_4^{+}$	-253.67^{b}	$H_2CO_3(aq)$	-148.94^{a}
$Cu^{+}(aq)$	11.95^{b}	$H_3VO_4^{0}$	-249.2^{i}	$HCO_3^{-}(aq)$	-140.26^{a}
Iron		$H_2VO_4^{-}$	-244^{i}	$CO_3^{2-}(aq)$	-126.17^{a}
$Fe(OH)_3(c)$ ppt	-166.0^{h}	$HVO_4^{2-}(aq)$	-233.0^{i}	$Cl^{-}(aq)$	-31.37^{a}
$Fe(OH)_2(c)$ ppt	-116.3^{f}	$VO_4^{3-}(aq)$	-214.9^{i}	$CH_4(g)$	-12.13^{a}
$FeCO_3(c)$ (siderite)	-159.35^{b}	$VO^{2+}(aq)$	-106.7^{i}	$CH_4(aq)$	-8.22^{a}
$FeS_2(c)$ (pyrite)	-39.9^{b}	$V(OH)_3^{0}(aq)$	-212.9^{i}	$H^{+}(aq)$	0.00
Fe_2O_3 (hematite)	-177.4^{b}	$VOH^{2+}(aq)$	-111.41^{h}	$Cl(aq)$	-31.38^{a}
$Fe^{3+}(aq)$	-1.1^{b}	$V(OH)_2^{+}$	-163.2^{i}	$PO_4^{3-}(aq)$	-243.5^{a}
$FeOH^{2+}(aq)$	-54.83^{b}	$VOOH^{+}$	-155.65^{i}	$HPO_4^{2-}(aq)$	-260.34^{a}
$Fe(OH)_2^{+}(aq)$	-106.7^{i}	V^{3+}	-57.8^{b}	$H_2PO_4^{-}(aq)$	-270.14^{k}
$Fe^{2+}(aq)$	-18.85^{b}	**Uranium**		$H_3PO_4^{0}(c)$	-273.10^{a}
$FeOH^{+}(aq)$	-62.58^{i}	$U^{4+}(aq)$	-126.44^{a}	$Na^{+}(aq)$	-62.59^{c}
$Fe(OH)_3^{-}(aq)$	-147.0^{b}	$UOH^{3+}(aq)$	-182.24^{a}	$K^{+}(aq)$	-67.51^{a}
$Fe(OH)_4^{-}(aq)$	-198.4^{i}	$U(OH)_4^{0}(c)$	-347.18^{a}	$NH_4^{+}(aq)$	-18.99^{c}
$FeO(c)$	-60.03^{g}			$Pb^{2+}(aq)$	-5.83^{a}
$Fe_2S(c)$ (pyrite)	-38.3^{g}			$O_2(g)$	0.00
$FeS(c)$	-24.22^{g}				

c = solid

aq = aqueous solutions

g = gas

[a] Wageman, D.D., W.H. Evans, V.B. Parker, I. Halow, S.M. Baily, and R.H. Schumm. 1968. *Selected values of chemical thermodynamic properties*. National Bureau of Standards Technical Note 270-3; 264 pp.

[b] Wageman, D.D., W.H. Evans, V.B. Parker, I. Halow, S.M. Baily, and R.H. Schumm. 1969. *Selected values of chemical thermodynamic properties*. National Bureau of Standards Technical Note 270-4; 141 pp.

(Cont'd)

TABLE 6.4 *Cont't*

[c] CODATA Task Group on Key Values for Thermodynamics. 1976. Recommended key values for thermodynamics 1975. *Journal of Chemical Thermodynamics* 8:603–5.

[d] CODATA Task Group on Key Values for Themodynamics. 1977. Recommended key values for thermodynamics 1976. *Journal of Chemical Thermodynamics* 9:705-6.

[e] Giridhar J., and Donald Langmuir. 1991. Determination of E° for the UO_2^{2+}/U^{4+} couple from measurement of the equilibrium: $UO_2^{2+} + Cu(s) + 4H^+ = U^{4+} + Cu^{2+} + 2H_2O$ at 25°C and some geochemical implications. *Radiochemica Acta* 54: 133-38.

[f] *Handbook of Chemistry and Physics*. Selected Values of Chemical Thermodynamic Properties. Boca Raton, Fla.: CRC Press.

[g] Robie, R. A., B. S. Hemingway, and J. R. Fisher. 1978. *Thermodynamic properties of minerals and related substances* at 298.15 K *and* 1 bar (10⁵ *pascals) pressure and higher temperatures*. U. S. Geological Survey Bulletin 1452; 456 pp.

[h] Feitknecht, Walter, and P. W. Schindler. 1963. Solubility constants of metal oxides, metal hydroxides and metal salts in aqueous solution. *Pure and applied Chemistry* 6:130–57.

[i] Baes, C. F., Jr., and R. E. Messmer. 1976. *The Hydrolysis of Cations*. New York: Wiley, 489 pp.

[j] Wageman, D. D., W. H. Evans, V. B. Parker, I. Halow, S. M. Baily, and R. H. Schumm. 1968. *Selected values of chemical thermodynamic properties*. National Bureau of Standards Technical Note 270-5.

[k] Langmuir, Donald. 1977. Uranium solution mineral equilibria at low temperatures. *Geochimica et Cosmochimica Acta* 42:547–69.

The value of this equilibrium constant depends upon the temperature, but at 25°C it is 1×10^{-14}. Water that is neutral has the same number of H^+ and OH^- ions. If there are more H^+ ions, water is acidic, and if there are more OH^- ions, it is basic.

The pH of an aqueous solution is a measure of the number of hydrogen ions or protons present. The definition of pH is the negative logarithm of the hydrogenion activity. It ranges from 0 (most acidic) to 14 (most basic), and at 25°C a pH of 7 means that the solution is neutral. Because $[H_2O]$ is unity, from Equation 6.24 we have the relationship $[H^+][OH^-] = K_{eq} = 10^{-14}$. The pH of a solution is measured with a pH meter and an electrode. It should be measured in the field, preferably in a flowthrough cell so that dissolved gas isn't exchanged with the atmosphere prior to the measurement. The pH of a solution is especially sensitive to the amount of dissolved CO_2.

6.5.2 Relationship of Eh and pH

We thus have two ways to characterize a solution. The pH describes the number of protons present and the Eh is related to the number of electrons. Eh and pH can be related through the Nernst equation for a reaction that contains water and H^+ ions. Such a reaction can be written (Robertson 1975)

$$bB + mH^+ + ne^- \rightleftharpoons aA + wH_2O \qquad \textbf{(6.25)}$$

where

A = reactant
B = product
n = number of electrons released
a = moles of reactant
w = moles of water
b = moles of product
m = moles of hydrogen ions

The Nernst equation for Reaction 6.25 is

$$\mathrm{Eh} = E^{\circ} - \frac{RT}{nF}\ln\frac{[\mathrm{A}]^{a}[\mathrm{H_2O}]^{w}}{[\mathrm{B}]^{b}[\mathrm{H}^{+}]^{m}} \tag{6.26}$$

The activity of water is unity. For a particular reaction, E° is given and R, T, and F are constants. The significant variables are the Eh and the activities of the reactant, the product, and the hydrogen-ion activity, which can be expressed as a pH. Equation 6.26 can be rearranged and expressed in base 10 logs as either

$$\mathrm{Eh} = E^{\circ} - 2.303\frac{RT}{nF}\log\frac{[\mathrm{A}]^{a}}{[\mathrm{B}]^{b}[\mathrm{H}^{+}]^{m}} \tag{6.27}$$

or

$$\mathrm{Eh} = E^{\circ} - 2.303\frac{RT}{nF}\log\frac{[\mathrm{A}]^{a}}{[\mathrm{B}]^{b}} + 2.303\frac{RTm}{nF}\log[\mathrm{H}^{+}] \tag{6.28}$$

At 25°C and 1 atm of pressure, Equation 6.28 can be expressed as

$$\mathrm{Eh} = E^{\circ} - \frac{0.0592}{n}\log\frac{[\mathrm{A}]^{a}}{[\mathrm{B}]^{b}} - 0.0592\frac{m}{n}\mathrm{pH} \tag{6.29}$$

6.5.3 Eh-pH Diagrams

The Eh-pH relationship is particularly useful when applied in the form of an Eh-pH diagram, with Eh the ordinate and pH the abscissa. If a solution has several ions present that can react to form different products or occur in different valence states, the stable product or valence state at a given concentration of reactants will be a function of the pH and Eh of the solution.

Figure 6.2 is a basic Eh-pH diagram. The range of pH is 0 to 14. For Eh, it is convenient to specify a range of about +1.4 to −1.0 V. In certain regions of the Eh-pH field, water will be oxidized to O_2, and in other regions water will be reduced to H_2. We will calculate these regions as an example problem.

EXAMPLE PROBLEM

Calculate the stability field for water at standard conditions.

The oxidation of water is given by

$$O_2(g) + 4H^{+} + 4e^{-} \rightleftharpoons 2H_2O(l)$$

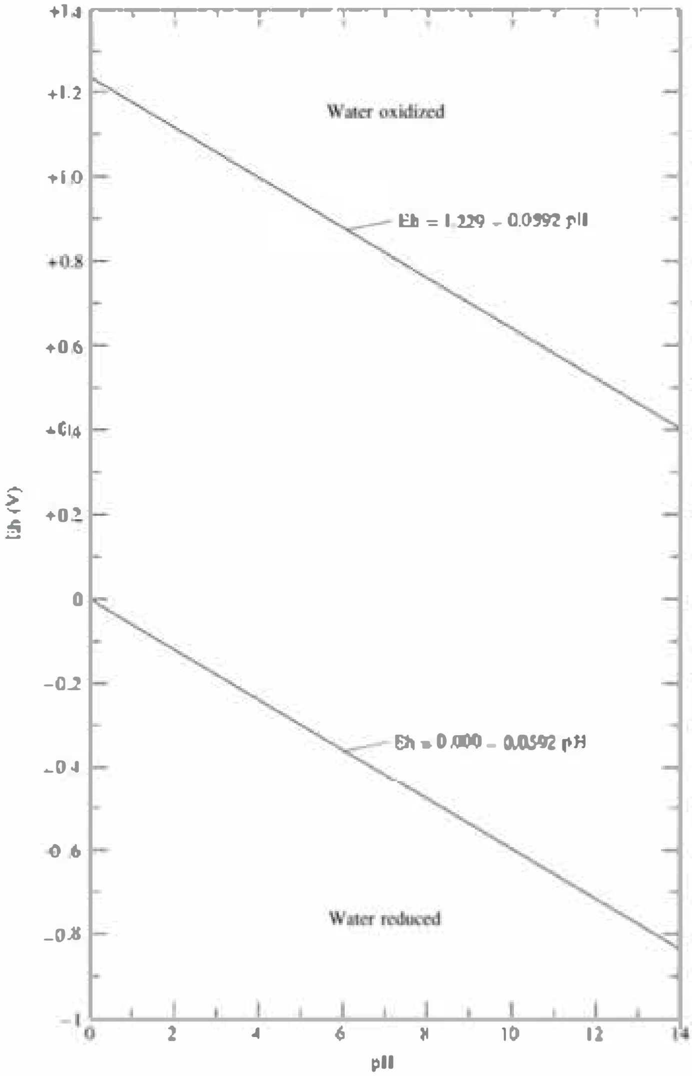
From Table 6.4,

$$\Delta G^{0}_{H_2O(l)} = -56.69\ \mathrm{kcal}$$

$$\Delta G^{0}_{O_2(g)} = 0$$

$$\Delta G^{0}_{H^{+}} = 0$$

FIGURE 6.2 Eh-pH diagram showing the stability field for water.



From Equation 6.20,

$$\Delta G_R^0 = 2\Delta G^0_{H_2O(l)} - \Delta G^0_{O_2(g)} - 4\Delta G^0_{H^+}$$

$$\Delta G_R^0 = 2(-56.69) - 0 - 4(0) = -113.38\ kcal$$

The value of ΔG_R^0 in kilocalories is converted to a standard potential by use of Equation 6.19:

$$E^0 = \frac{-\Delta G_R^0}{nF} = \frac{-(-113.38)}{4 \cdot 23.06} = 1.229\ \text{V}$$

The Nernst equation (Equation 6.24) can be expressed as:

$$\text{Eh} = E^0 - \frac{RT}{nF} 2.303 \log \frac{[H_2O]}{[O_2][H^+]^4}$$

The activity of dissolved gaseous oxygen is expressed as a partial pressure, P_{o2}. At standard conditions it has a value of 1atm. The activity of water is unity. The Nernst equation thus reduces to

$$Eh = 1.229 - \frac{0.00199 \cdot 298}{4 \cdot 23.06} 2.303 \log \left[H^+\right]^{-4}$$

This expression can be reduced to

$$Eh_{(Volts)} = 1.229 - 0.0592pH$$

This equation defines the upper boundary of stability for water, above which oxidation would break apart the water molecule.

The reduction of hydrogen ions to form gaseous hydrogen is

$$2H^+ + 2e^- \rightleftharpoons H_{2(gas)}$$

From Table 6.4,

$$\Delta G^0_{H^+} = 0$$

$$\Delta G^0_{H_2(gas)} = 0$$

The value of ΔG^0_R for the formation of hydrogen gas is obviously zero. Therefore, the value of E^0 is also zero.

From the Nernst equation,

$$Eh = E^0 - \frac{0.00199 \cdot 298}{2 \cdot 23.06} 2.303 \log \frac{p_{H_2}}{\left[H^+\right]^2}$$

The value of P_{H2} is 1 atm and the calculated value of E^0 is 0, hence the preceding expression can be reduced to

$$Eh_{(volts)} = 0.000 - 0.0592pH$$

This equation forms the lower boundary of the stability field for water. These boundaries are plotted in Figure 6.2.

6.5.4 Calculating Eh-pH Stability Fields

The stability fields within the Eh-pH diagram for various forms of an element can be computed using chemical thermodynamics. Basic sources of thermodynamic data include Bagman et al. (1968; 1969; 1971) and Robie et al. (1978).

Boundaries for an element between dissolved species that have different valence states are computed using the Nernst equation (Equation 6.27, 6.28, or 6.29). If both ions are at the same valence state, then the equation for chemical equilibrium is used. If one is calculating the boundary between a solid species and a dissolved form, the chemical activity of the solid species is 1. For some of the boundaries of solid species, it will be necessary to assume an activity for the dissolved species.

EXAMPLE PROBLEM

Calculate an Eh-pH diagram for iron in which the solid species are $Fe(OH)_3$ and FeO and the activity of dissolved iron is 56 µg/L(10^{-6} M).

Soluble forms of the ferrous ion and the ferric ion include $Fe2^+$, $Fe3^+$, $FeOH2^+$, and $Fe(OH)_2^+$. Transformations between these ions are determined by redox equations:

$$FeOH^{2+} + H^+ + e^- \rightleftharpoons Fe^{2+} + H_2O \tag{6.30}$$

$$Fe(OH)_2^+ + H^+ + e^- \rightleftharpoons Fe^{2+} + 2H_2O \tag{6.31}$$

$$Fe^{3+} + e^- \rightleftharpoons Fe^{2+} \tag{6.32}$$

The free energy and the standard potential for these reactions can be determined from Equations 6.20 and 6.19, respectively.

From Table 6.4 free energies are as follows.

$FeOH^{2+} = -54.83$ kcal/mol

$Fe(OH)_2^+ = -106.7$ kcal/mol

$Fe^{2+} = -18.85$ kcal/mol

$Fe^{3+} = -1.1$ kcal/mol

$H_2O = -56.69$ kcal/mol

$FeO = -60.03$ kcal/mol

$Fe(OH)_3 = -166$ kcal/mol

$Fe(OH)_4^- = -198.4$ kcal/mol

$H^+ = 0$

For Reaction 6.30 ($FeOH^{2+} + H^+ + e^- \rightleftharpoons Fe2^+ + H_2O$):

$$\Delta G_R^0 = \left[\Delta G_{H_2O}^0 + \Delta G_{Fe^{2+}}^0\right] - \left[\Delta G_{FeOH^{2+}} + \Delta G_{H^+}^0\right]$$

$$\Delta G_R^0 = -56.69 + (-18.85) - (-54.83) - 0$$

$$\Delta G_R^0 = -20.71 \text{kcal/mol}$$

$$E^0 = \frac{-\Delta G^0{}_R}{nF} = \frac{-(-20.71)}{1 \cdot 23.06} V$$

$$E^0 = +0.898 V$$

For Reaction 6.31 ($Fe(OH)_2^+ + 2H^+ + e^- \rightleftharpoons Fe^{2+} + 2H_2O$):

$$\Delta G_R^0 = 2\Delta G_{H_2O}^0 + \Delta G_{Fe^{2+}}^0 - \Delta G_{Fe(OH)_2{}^+}^0 - 2\Delta G_{H^+}^0$$

$$\Delta G_R^0 = 2(-56.69) + (-18.85) - (-106.7) - 2(0)$$

$$\Delta G_R^0 = -25.53 \text{kcal/mol}$$

$$E^0 \frac{-\Delta G_R^0}{nF} = \frac{-(-25.53)}{1 \cdot 23.06} V$$

$$E^0 = +1.107 V$$

For Reaction 6.32 ($Fe^{3+} + e^- \rightleftharpoons Fe^{2+}$):

$$\Delta G_R^0 = \Delta G_{Fe^{2+}}^0 - \Delta G_{Fe^{3+}}^0$$
$$\Delta G_R^0 = -18.85 - (-1.1)$$
$$\Delta G_R^0 = -17.75$$
$$E^0 = \frac{-\Delta G_R^0}{nF} = \frac{-(-17.75)}{1 \cdot 23.06} V$$
$$E^0 = +0.770 V$$

The boundaries between the stability fields are determined from the Nernst equation. At the boundary between two fields, the activities of the iron species on the left of the reaction is equal to the activity of the iron species on the right of the equation—i.e., the two species are at equilibrium.

For Reaction 6.30 ($FeOH^{2+} + H^+ + e^- \rightleftharpoons Fe^{2+} + H_2O$):

$$Eh = E^0 - \frac{0.0592}{n} \log \frac{[Fe^{2+}]}{[FeOH^{2+}]} - 0.0592 \frac{m}{n} pH$$

Since $[FeOH^{2+}] = [Fe^{2+}]$, m (the number of hydrogen ions) = 1, n(the number of electrons)= 1, $E^0 = +0.898$ V, and log 1 = 0:

$$Eh_{(volts)} = 0.898 - 0.0592\,pH \tag{6.33}$$

For Reaction 6.31 ($Fe(OH)_2^+ + 2H^+ + e^- \rightleftharpoons Fe^{2+} + 2H_2O$):

$$Eh = E^0 - \frac{0.0592}{n} \log \frac{[Fe^{2+}]}{[Fe(OH)_2^+]} - 0.0592 \frac{m}{n} pH$$

Since $[Fe(OH)_2^+] = [Fe^{2+}]$, $m = 2$, $n = 1$, and $E^0 = +1.107$ V:

$$Eh_{(volts)} = 1.107 - 0.1184\,pH \tag{6.34}$$

For Reaction 6.32 ($Fe^{3+} + e^- \rightleftharpoons Fe^{2+}$):

$$Eh = E^0 - \frac{0.0592}{n} \log \frac{[Fe^{2+}]}{[Fe^{3+}]} - 0.0592 \frac{m}{n} pH$$

This reaction is independent of pH because neither $[H^+]$ nor $[OH^-]$ appears in the reaction. Hence the value of m is 0. Because as $[Fe^{3+}] = [Fe^{2+}]$ and log 1= 0, Eh is a constant equal to E^0, which is 0.770 V:

$$Eh = 0.770\,V \tag{6.35}$$

The boundary between two dissolved species that are at the same valence state can be determined from chemical equilibrium.

For iron there are two boundaries between dissolved ions of ferric iron. These boundaries are represented by these reactions:

$$\mathrm{Fe^{3+} + H_2O \rightleftharpoons FeOH^{2+} + H^+} \tag{6.36}$$

$$\mathrm{FeOH^{2+} + H_2O \rightleftharpoons Fe(OH)_2^{\ +} + H^+} \tag{6.37}$$

For Reaction 6.36 $\left(\mathrm{Fe^{3+} + H_2O \rightleftharpoons FeOH^{2+} + H^+}\right)$, the equilibrium constant can be obtained from the free energy of the reaction. The first step is to find the free energy of the reaction using Equation 6.20.

$$\Delta G_R^0 = \Delta G^0_{\mathrm{FeOH^{2+}}} + \Delta G^0_{\mathrm{H+}} - \Delta G^0_{\mathrm{Fe^{3+}}} - \Delta G^0_{\mathrm{H_2O}}$$

$$\Delta G_R^0 = -54.83 + 0 - (-1.1) - (-56.69)$$

$$\Delta G_R^0 = +2.96 \text{ kcal/mol}$$

The next step is to determine the equilibrium constant using Equation 6.22.

$$\log k_{eq} = -\frac{\Delta G_R^0}{1.364} = -\frac{2.96}{1.364} = -2.17$$

$$K_{eq} = 10^{-2.17}$$

From Equation 6.6,

$$K_{eq} = \frac{\left[\mathrm{FeOH^{2+}}\right]\left[\mathrm{H^+}\right]}{\left[\mathrm{Fe^{3+}}\right]\left[\mathrm{H_2O}\right]} = 10^{-2.17}$$

Since $[\mathrm{H_2O}] = 1$ and at the boundary $[\mathrm{FeOH^{2+}}] = [\mathrm{Fe^{3+}}]$,

$$[\mathrm{H^+}] = 10^{-2.17} \tag{6.38}$$

This means that a vertical line at a pH of 2.17 separates these two stability fields.

For Reaction 6.37 $\left(\mathrm{FeOH^{2+} + H_2O \rightleftharpoons Fe(OH)_2^{\ +} + H^+}\right)$, find the free energy of the reaction:

$$\Delta G_R^0 = \Delta G^0_{\mathrm{Fe(OH)_2^+}} + \Delta G^0_{\mathrm{H+}} - \Delta G^0_{\mathrm{FeOH^{2+}}} - \Delta G^0_{\mathrm{H_2O}}$$

$$\Delta G_R^0 = -106.7 + 0 - (-54.83) - (-56.69)$$

$$\Delta G_R^0 = +4.82 \text{ kcal/mol}$$

Next find the value of K_{eq}:

$$\log K_{eq} = \frac{-\Delta G_R^0}{1.364} = \frac{-4.82}{1.364} = -3.53$$

$$K_{eq} = 10^{-3.53}$$

Finally, from Equation 6.6,

$$K_{eq} = \frac{\left[\mathrm{Fe(OH)}^{2+}\right]\left[\mathrm{H}^+\right]}{\left[\mathrm{FeOH}^{2+}\right]\left[\mathrm{H_2O}\right]} = 10^{-3.53}$$

Since [H_2O] = land {Fe(OH)$^{2+}$] = [FeOH^{2+}],

$$[\mathrm{H}^-] = 10^{-3.53} \tag{6.39}$$

Lines that delineate the stability field for solids can be obtained by similar reasoning. Remember that the activity of a solid in equilibrium with dissolved species is 1. The location of the boundaries of solid species is a function of the amount of dissolved iron present.

In this situation there are two stable iron precipitates, Fe(OH)3 and FeO. The reactions at the boundaries include

$$\mathrm{Fe(OH)_3 + H^+ \rightleftharpoons Fe(OH)_2{}^+ + H_2O} \tag{6.40}$$

$$\mathrm{Fe(OH)_3 + 3H^+ + e^- \rightleftharpoons Fe^{2+} + 3H_2O} \tag{6.41}$$

$$\mathrm{Fe(OH)_4{}^- + H^+ \rightleftharpoons Fe(OH)_3 + H_2O} \tag{6.42}$$

$$\mathrm{Fe(OH)_3 + e^- \rightleftharpoons FeO + H_2O + OH^-} \tag{6.43}$$

$$\mathrm{Fe(OH)_4{}^- + 2H^+ + e^- \rightleftharpoons FeO + 3H_2O} \tag{6.44}$$

$$\mathrm{FeO + 2H^+ \rightleftharpoons Fe^{2+} + H_2O} \tag{6.45}$$

Reaction 6.40 $\mathrm{Fe(OH)_3 + H^+ \rightleftharpoons Fe(OH)_2{}^+ + H_2O}$ is solved using an equilibrium approach:

$$\Delta G_R^0 = \Delta G^0_{\mathrm{Fe(OH)_2{}^+}} + \Delta G^0_{\mathrm{H_2O}} - \Delta G^0_{\mathrm{Fe(OH)_3}} - \Delta G^0_{\mathrm{H^+}}$$

$$\Delta G_R^0 = -106.7 + (-56.69) - (-166) - 0 = 2.61$$

$$\log K_{eq} = -\frac{\Delta G_R^0}{1.364} = -\frac{2.61}{1.364} = -1.91$$

$$K_{eq} = 10^{-1.91}$$

$$K_{eq} = \frac{\left[\mathrm{Fe(OH)_2{}^+}\right]\left[\mathrm{H_2O}\right]}{\left[\mathrm{Fe(OH)_3}\right]\left[\mathrm{H^+}\right]} = 10^{-1.91}$$

Since [Fe(OH)3] = land [H2O] = I,

$$\left[H^+\right] = \frac{\left[Fe(OH)_2{}^+\right]}{10^{-1.91}}$$

Reaction 6.41 $Fe(OH)_3 + 3H^+ + e^- \rightleftharpoons Fe^{2+} + 3H_2O$ is solved using the Nernst equation:

$$\Delta G_R^0 = \Delta G_{Fe^{2+}}^0 + 3\Delta G_{H_2O}^0 - \Delta G_{Fe(OH)_3}^0 - 3\Delta G_{H^+}^0$$

$$\Delta G_R^0 = -18.85 + 3(-56.69) - (-166) - 0$$

$$\Delta G_R^0 = -22.95 \text{ kcal/mol}$$

$$E^0 = \frac{-\Delta G_R^0}{nF} = \frac{(-22.95)}{1 \cdot 23.06} = +0.994V$$

$$Eh = E^0 - \frac{0.0592}{n}\log\frac{\left[Fe^{2+}\right]}{\left[Fe(OH)_3\right]} - 0.0592\frac{m}{n}pH$$

Since there are three hydrogen ions ($m = 3$) and one electron ($n = 1$) and $[Fe(OH)_3]$ = I, then

$$Eh_{(Volts)} = 0.994 - 0.0592 \log\left[Fe^{2+}\right] - 0.178pH \qquad \textbf{(6.47)}$$

Reaction 6.42 $\left(Fe(OH)_4{}^- + H^+ \rightleftharpoons Fe(OH)_3 + H_2O\right)$ is solved by using an equilibrium approach:

$$\Delta G^0{}_R = \Delta G^0{}_{Fe(OH)_3} + \Delta G^0{}_{H_2O} - \Delta G^0{}_{Fe(OH)_4^-} - \Delta G^0{}_{H^+}$$

$$\Delta G^0{}_R = -166 - 56.69 - (-198.4) - 0$$

$$\Delta G^0{}_R = -24.29$$

$$\log K_{eq} = \frac{\Delta G^0{}_R}{1.364} = \frac{24.29}{1.364} = 17.8$$

$$K_{eq} = 10^{17.8}$$

$$K_{eq} = \frac{\left[Fe(OH)_3\right]\left[H_2O\right]}{\left[Fe(OH)_4{}^-\right]\left[H^+\right]} = 10^{17.8}$$

Since $[Fe(OH)_3] = 1$ and $[H_2O] = 1$,

$$\left[H^+\right] = \frac{10^{-17.8}}{\left[Fe(OH)_4{}^-\right]} \qquad \textbf{(6.48)}$$

Equation 6.43 $\left(\mathrm{Fe(OH)_3} + e^- \rightleftharpoons \mathrm{FeO} + \mathrm{H_2O} + \mathrm{OH}^-\right)$ is solved using the Nernst equation:

$$\Delta G^0{}_R = \Delta G^0{}_{\mathrm{FeO}} + \Delta G^0{}_{\mathrm{H_2O}} + \Delta G^0{}_{OH^-} - \Delta G^0{}_{\mathrm{Fe(OH)_3}}$$

$$\Delta G^0{}_R = -60.03 + (-56.69) + (-37.59) - (-166)$$

$$\Delta G^0{}_R = +11.69$$

$$\mathrm{E}^0 = \frac{-\Delta G^0{}_R}{nF} = \frac{-11.69}{1 \cdot 23.06} = -0.507\,\mathrm{V}$$

$$\mathrm{Eh} = E^0 - \frac{0.0592}{n} \log \frac{[\mathrm{FeO}][\mathrm{H_2O}][\mathrm{OH^-}]}{[\mathrm{Fe(OH)_3}]}$$

Since $[\mathrm{Fe(OH)_3}] = 1$, $[\mathrm{FeO}] = 1$, $[\mathrm{H_2O}] = 1$, and $n = 1$,

$$\mathrm{Eh} = -0.507 - 0.0592 \log[\mathrm{OH^-}]$$

Because the diagram uses pH as a variable, $[\mathrm{OH^-}]$ must be expressed in terms of pH. By definition, $[\mathrm{OH^-}] = 10^{-14}/[\mathrm{H^+}]$; therefore, $\log[\mathrm{OH^-}] = \log 10^{-14} - \log[\mathrm{H^+}]$, so that

$$\mathrm{Eh} = -0.5.7 - 0.0592(\mathrm{pH} - 14)$$

$$\mathrm{Eh}_{(\mathrm{volts})} = 0.322 - 0.0592\ \mathrm{pH} \tag{6.49}$$

Reaction 6.44 $\left(\mathrm{Fe(OH)_4}^- + 2\mathrm{H^+} + e^- \rightleftharpoons \mathrm{FeO} + 3\mathrm{H_2O}\right)$ is solved using the Nernst equation:

$$\Delta G^0{}_R = \Delta G^0{}_{\mathrm{FeO}} + 3\Delta G^0{}_{\mathrm{H_2O}} - \Delta G^0{}_{\mathrm{Fe(OH)_4^-}} - 2\Delta G^0{}_{H+}$$

$$\Delta G^0{}_R = -60.03 + 3(-56.69) - (-198.4) - 0$$

$$\Delta G^0{}_R = -31.7\ \mathrm{kcal/mol}$$

$$E^0 = \frac{-\Delta G^0{}_R}{nF} = \frac{-(-31.7)}{1 \cdot 23.06} = +1.375$$

$$\mathrm{Eh} = E^0 - \frac{0.0592}{n} \log \frac{[\mathrm{FeO}][\mathrm{H_2O}]^3}{[\mathrm{Fe(OH)_4}^-][\mathrm{H^+}]^2}$$

Since $[\mathrm{FeO}]$ and $[\mathrm{H_2O}]$ are 1and $n = 1$,

$$\mathrm{Eh} = +1.375 - 0.0592 \log \frac{1}{[\mathrm{Fe(OH)_4}^-][\mathrm{H^+}]^2}$$

This can be expressed in terms of pH as

$$\mathrm{Eh} = 1.375 + 0.0592 \log\left[\mathrm{Fe(OH)_4}^- + 2(0.0592) \log\left[\mathrm{H^+}\right]\right.$$

$$\mathrm{Eh}_{(\mathrm{volts})} = 1.375 + 0.0592 \log\left[\mathrm{Fe(OH)_4}^-\right] - 0.118\mathrm{pH} \qquad \textbf{(6.50)}$$

Reaction 6.45 ($FeO + 2H^+ \rightleftharpoons Fe^{2+} + H_2O$) is solved as an equilibrium reaction:

$$\Delta G^0{}_R = \Delta G^0{}_{\mathrm{Fe^{2+}}} + \Delta G^0{}_{\mathrm{H_2O}} - \Delta G^0{}_{\mathrm{FeO}} - 2\Delta G^0{}_{H^+}$$

$$\Delta G^0{}_R = -18.85 + (-56.69) - (-60.03) - 2(0)$$

$$\Delta G^0{}_R = -15.51 \text{ kcal/mol}$$

$$\log k_{eq} = \frac{-\Delta G^0{}_R}{1.364} = 11.36$$

$$k_{eq} = 10^{11.36}$$

$$k_{eq} = \frac{[\mathrm{Fe^{2+}}][\mathrm{H_2O}]}{[\mathrm{FeO}][\mathrm{H^+}]^2}$$

Since $[H_2O]$ and $[FeO] = 1$,

$$[\mathrm{H^+}]^2 = \frac{[\mathrm{Fe^{2+}}]}{10^{11.36}}$$

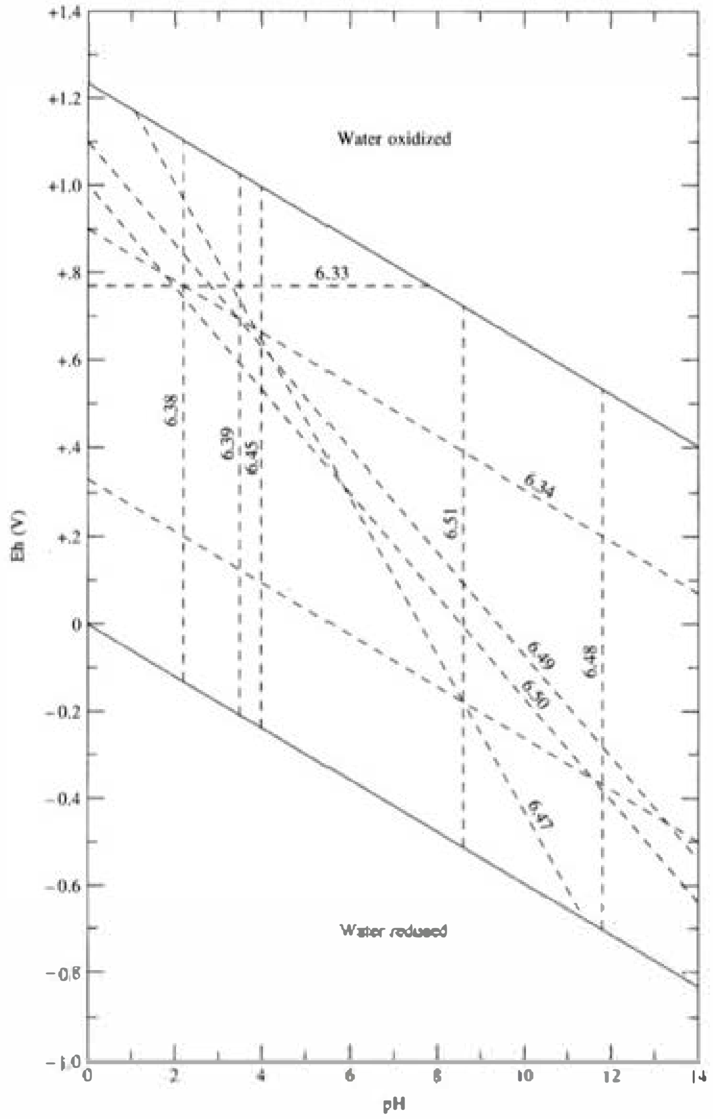
$$[\mathrm{H^+}] = \sqrt{\frac{[\mathrm{Fe^{2+}}]}{10^{11.36}}} \qquad \textbf{(6.51)}$$

Several of the equations, including Equations 6.46, 6.47, 6.48, 6.50, and 6.51, depend upon the activity of the dissolved iron.

The following equations, which are independent of dissolved iron activity, have been derived.

Boundary	**Equation Number**	**Equation**
$FeOH^{2+} - Fe^{2+}$	6.31	$\mathrm{Eh}_{(\mathrm{volts})} = 0.898 - 0.0592\mathrm{pH}$
$Fe(OH)_2{}^+ - Fe^{2+}$	6.32	$\mathrm{Eh}_{(\mathrm{volts})} = 1.107 - 0.118\mathrm{pH}$
$Fe^{3+} - Fe^{2+}$	6.33	$\mathrm{Eh}_{(\mathrm{volts})} = 0.770$
$Fe^{3+} - FeOH^{2+}$	6.38	$\mathrm{pH} = 2.17$
$Fe(OH)^{2+} - Fe(OH)_2{}^+$	6.39	$\mathrm{pH} = 3.53$
$Fe(OH)_3 - FeO$	6.49	$\mathrm{Eh}_{(\mathrm{volts})} = 0.322 - 0.0592\mathrm{pH}$

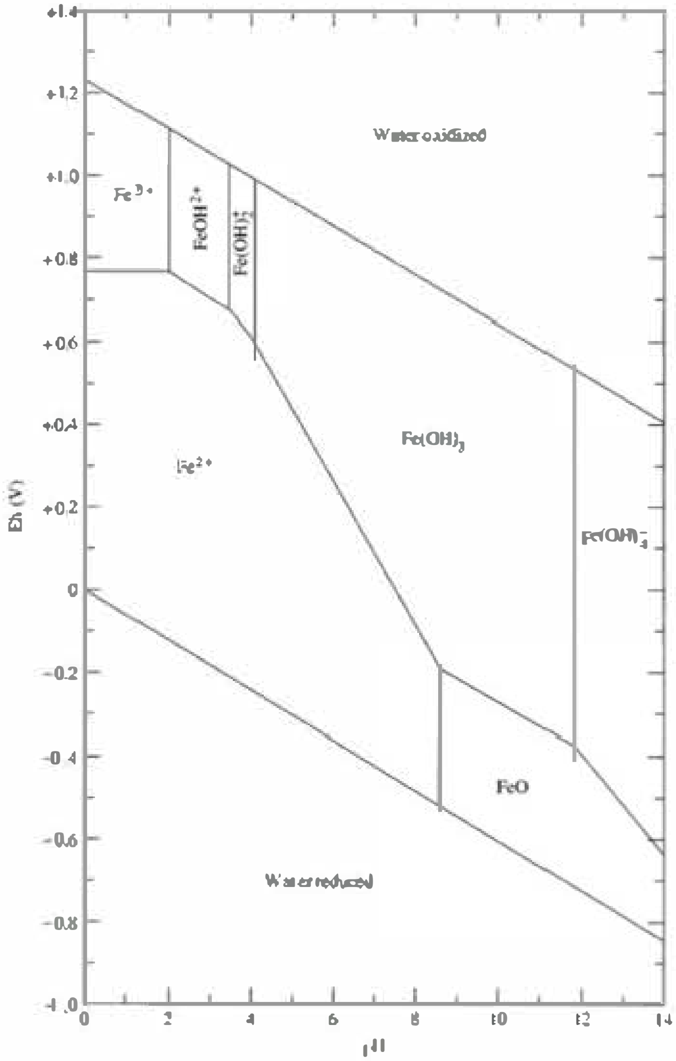
FIGURE 6.3 Equations for an Eh-pH diagram for dissolved iron with dissolved iron activity of 10^{-6} Mol under standard conditions. (Numbers adjacent to dotted lines refer to equations discussed in the text.)



The iron Eh-pH diagram of Figure 6.4 is for a system that contains only dissolved iron. If other elements are present, such as sulfur, then additional iron compounds are possible. Figure 6.5 shows an Eh-pH diagram for a system with an iron activity of 56 µg/L (10^{-6} mol), sulfur of 96 mg/L as SO_4^{2-}, and carbon dioxide of 61 mg/L as HCO_3^-. Solids in the shaded area are thermodynamically stable. Under the conditions specified in this diagram, iron carbonate ($FeCO_3$) saturation was not reached and none is recorded as a solid phase.

The area of the region in which iron is precipitated rather than dissolved is a function of the concentration of dissolved iron. The more dissolved iron that is present, the greater the size of the stability field for the precipitates. This is illustrated in Figure 6.6. In this diagram the sulfur is 96 mg/L as SO_4^{2-} and the carbonate is 61 mg/L as HCO_3^-. Dissolved iron ranges from 5.6 µg/L to 56 mg/L.

FIGURE 6.4 Final Eh-pH diagram for a dissolved iron system with dissolved iron at 10^{-6} moles under standard conditions.



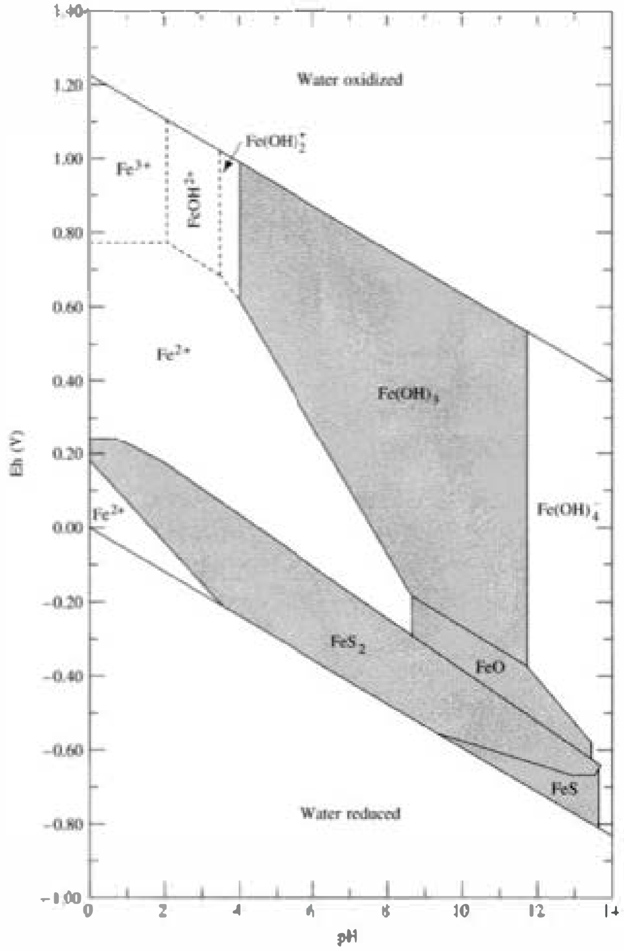
Eh-pH diagrams have been used in the ground-water literature to explain such phenomena as the solubility of ferric oxyhydroxides (Whittemore and Langmuir 1975), hexavalent chromium (Robertson 1975), manganese (Hem 1985), iron, copper, silver, chromium, manganese, vanadium, molybdenum, and arsenic (Hem 1977), uranium (Langmuir 1978), thorium (Langmuir and Herman 1980), and arsenic (Matisoff et al. 1982).

6.6 Metal Complexes and Facilitated Particle Transport

6.6.1 Hydration of Cations

Although we consider that metallic ions exist in solution as an isolated ion, such as Cu^{2+}, in fact that is not the case. The Cu^{2+} ion is surrounded by polar water atoms that are chemically bound to the ion. Metallic ions, in general, have six water molecules

FIGURE 6.5 Eh-pH diagram showing fields of stability for dissolved iron under standard conditions. Activity of dissolved iron is 10^{-6} mol (56 μg/L), of sulfur species is 96 mg/L as SO_4^{2-}, and of carbon dioxide species is 61 mg/L as HCO_3^-.



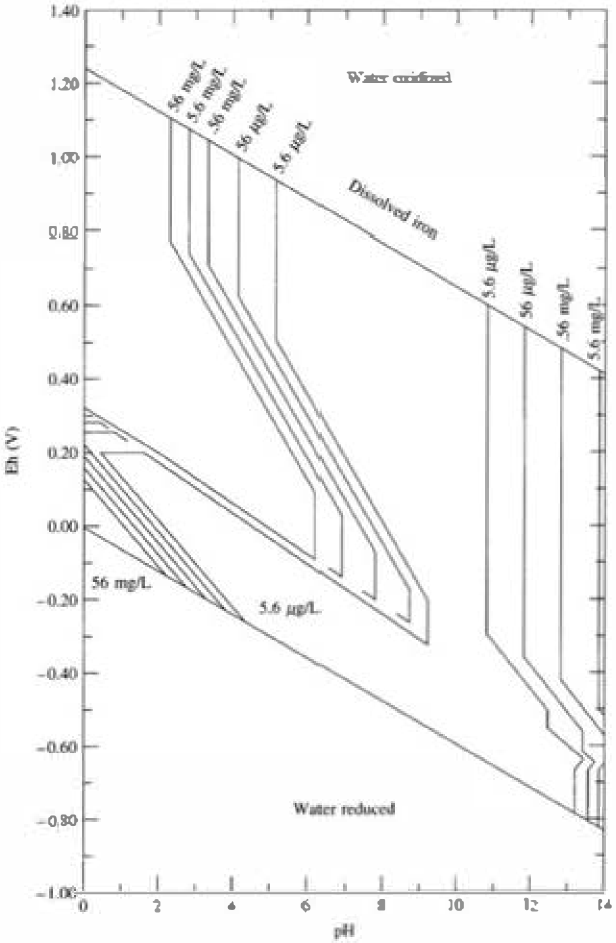
Source: J. D. Hem. 1985. *Study and interpretation of the chemical characteristics of natural waters*. Water Supply Paper 2254. U.S. Geological Survey.

surrounding them. The hydrated cupric ion is $Cu(H_2O)_6^{2+}$. Even outside the shell of chemically bound water molecules, there is a region where the polar water molecules are ordered by the electrostatic charge of the metallic ion. Anions in close association with a metal cation are called ligands; together they form a coordination compound. Water is considered to be a ligand that is bound to the metal ion. If other ligands bind to the metal, they must replace some of the water molecules acting as ligands. The stability of a complex relative to cation or ligand exchange can be described by equilibrium constants for the reaction.

6.6.2 Complexation

The following inorganic anions act as simple ligands in natural waters: OH^-, CO_3^{2-}, SO_4^{2-}, Cl^-, Br^-, F^-, NO_3^-, SiO_3^{2-}, S^{2-}, $S_2O_3^-$, PO_4^{3-}, $P_2O_7^{4-}$, $P_3O_{10}^{5-}$, and CN^-. Ammonia (NH_3) is a polar molecule that can also act as a ligand. Ligands can bond either covalently or electrostatically with a metal to form a complex ion or compound. We have already

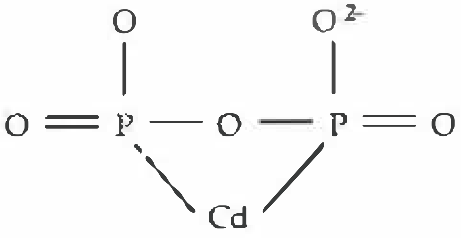
FIGURE 6.6 Equilibrium activity of dissolved iron as a function of Eh and pH under standard conditions, sulfur activity of 96 mg/L as SO_4^{2-} and activity of carbon dioxide of 61 mg/L as HCO_3^-.



Source: J. D. Hem. 1985. *Study and interpretation of the chemical characteristics of natural waters.* Water Supply Paper 2254, U.S. Geological Survey.

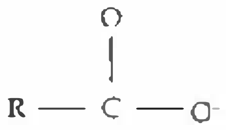
looked at the complex forms of the ferric ion and the hydroxyl ion. They form a series of complex ions: $FeOH^{2+}$, $Fe(OH)_2^+$, $Fe(OH)_3$ and $Fe(OH)_4^-$. Complex formation is involved with chemical equilibrium of ionic compounds and oxidation-reduction reactions.

In the case of monovalent ions, there is only one site where the ligand bonds to the metal ion and the ligand is called monodentate (literally, "one tooth"). If the ligand has more than one site that can bond (polydentate), then it forms what is known as a chelating **agent**. For example, the pyrophosphate ion, $P_2O_7^{4-}$, can bond to a metal ion, such as cadmium, at two locations:



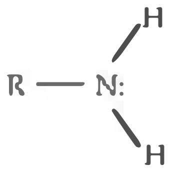
6.6.3 Organic Complexing Agents

Both natural waters and wastewaters contain a number of organic compounds that can act as chelating agents. In general, these organic compounds have a functional group that contains oxygen, nitrogen, phosphorous, or sulfur. If R symbolizes one or more carbon atoms with the appropriate number of hydrogens, then organic complexes can include functional groups such as

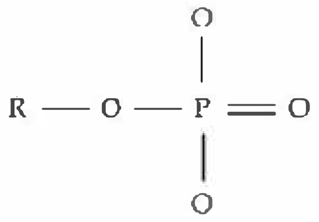


Carboxylate

Alcohol



Amine



Phosphate

There are a number of organic complexing agents that occur in nature. They are associated with humic substances that form from the decomposition of vegetation. These are complex organic molecules with molecular weights ranging upward into the tens of thousands. If a humic substance is extracted with a strong base and then acidified, there are three products. The nonextractable organic material is called humin. Substances called fulvic acids remain in the acidic solution, and other substances called humic acids precipitate from the acidified extract. These represent classes of compounds that contain many different individual organic molecules. Humic and fulvic acids contain many functional groups that can chelate to metals. Metals may be kept in solution by chelation with soluble fulvic acids or they may bind to the insoluble humic substances by cation exchange (Manahan 1984).

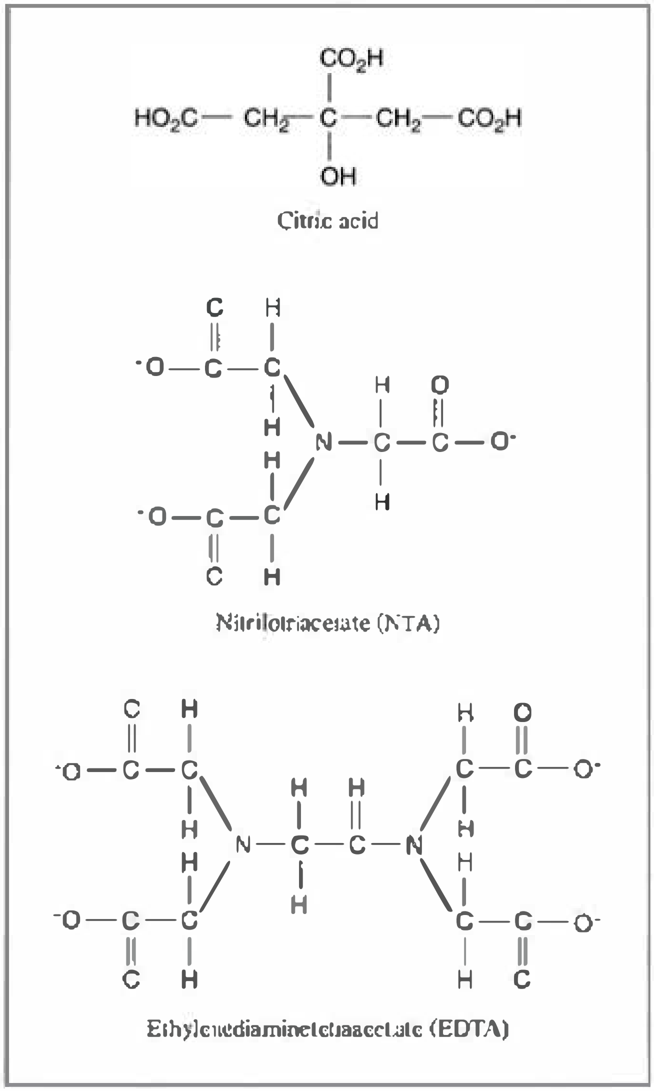
Synthetic organic complexing agents are used in a number of industrial processes. They can be used as cleaning compounds, as constituents of detergent, in metal plating baths, and in water conditioning. These compounds include sodium tripolyphosphate, sodium ethylenediaminetetraacetate (EDTA), citric acid, and sodium nitrilotriacetate (NTA). The structures of some of these compounds are given in Figure 6.7. Synthetic chelating agents may keep metals in solution under conditions where the unchelated metal would precipitate or undergo cation exchange.

EDTA in wastewater can vastly increase the mobility of associated metals in the subsurface. Monitoring wells near radioactive waste disposal trenches at the Oak Ridge (Tennessee) National Laboratory contained significant levels of sodium EDTA, which was used as a cleaning agent. The same wells also contained radioactive ^{60}Co, a metal that is normally not expected to migrate very far due to cation exchange. The ^{60}Co had been chelated by the EDTA and hence had greatly increased mobility in the subsurface (Means et al. 1978).

6.6.4 Facilitated Particle Transport

Many metals and other inorganic compounds have a great sorptive capacity and an affinity for particles suspended in water. Normally in subsurface environments this limits contaminant mobility in that most mobile particles and colloids are filtered out of flowing groundwater in porous media. However, particles suspended in groundwater

FIGURE 6.7 Structure of chelating agents including (a) citric acid, (b) nitrilotriacetate (NTA), and (c) ethylenediaminetetraacetate (EDTA).



can be mobilized in flow through fractured rock or karst rocks where groundwater moves through larger conduits and suspended particles are not filtered by the geologic medium. Contaminants sorbing on these particles, including many metals, essentially can "hitch a ride" on moving grains and colloids and this can increase the effective speed of contaminant movement through aquifers by orders of magnitude. This enhanced mobility is called **facilitated particle transport**.

Facilitated particle transport can pose problems in modeling contaminant movement and dispersion because of accelerated movement, and also impact the representativeness of groundwater sampling protocols. Many standard techniques for measuring metal concentrations in groundwater require samples to be filtered and acidified in the field. In conditions where groundwater contains contaminants sorbed on suspended particles and colloids, some practitioners collect both filtered and unfiltered samples for comparative chemical analysis.

6.7 Chemistry of Nonmetallic Inorganic Contaminants

6.7.1 Fluoride

Fluoride occurs in water as the F^- ion. In natural waters the amount of fluoride present is generally less than 1.0 mg/L, although concentrations as great as 67 mg/L have been reported (Hem 1985). Fluoride is present in minerals such as fluorite (CaF_2) and apatite ($Ca_5(Cl,F,OH)(PO_4)_3$). Weathering of these minerals may release fluoride. It may be released as a contaminant from industrial processes utilizing hydrofluoric acid. Cryolite (Na_3AlF_6) is used as a flux in the electrolytic production of aluminum. The manufacture of phosphate fertilizer from phosphate-rich rock may also release fluoride. Effluent from a Florida fertilizer plant had fluoride ranging from 2810 to 5150 mg/L (Cross and Ross 1970).

Fluoride can form complexes in water with a number of cations, including aluminum, beryllium, and ferric iron (Hem 1985). Dissolved fluoride can react with calcium to form fluorite. The solubility product for fluorite is $10^{-10.4}$. Precipitation of fluorite can act as a control on the amount of dissolved fluoride in solution if dissolved calcium is present. Table 6.5 shows the equilibrium amount of dissolved fluoride calculated for various activities of calcium. Actual activities of fluoride are likely to be somewhat higher due to the effect of the ionic strength of the solution as well as the effect of any complexes that might form with the fluoride ion.

Fluoride can dissolve into groundwater from anthropogenic sources, but also from volcanic activity and other natural geologic sources through subsurface rock-water interaction. Magmatic fluorine is often in the form of hydrogen fluoride (HF) which is one of the most soluble gases in magmas, exsolving from molten rock only partially, and leaving large amounts of fluoride in cooled volcanic and plutonic rocks. High subsurface temperatures and acidic conditions enhance the dissolution of fluoride from these rocks into groundwater. Portions of the earth's large magmatic provinces, such as the Deccan flood basalts of India, the Siberian traps of central Asia, and the East African Rift Valley are endemic for fluorosis from consumption of high fluoride concentration in groundwater, as are smaller more isolated locales at the base of volcanoes (Brindha and Elango 2011; D'Alessandro 2006).

Corbett and Manner (1984) have reported on the distribution of fluoride in water from both unconsolidated and bedrock aquifers of northeastern Ohio. They found that 239 out of 255 wells had fluoride concentrations less than 1mg/L. However, 14 of

TABLE 6.5 Equilibrium fluoride concentrations as a function of calcium activity.

Calcium		Fluoride	
Activity (mol)	Concentration (mg/L)	Activity (mol)	Concentration (mg/L)
2×10^{-2}	800	4.48×10^{-5}	0.85
10^{-2}	400	6.31×10^{-5}	1.20
5×10^{-3}	200	8.92×10^{-5}	1.70
10^{-3}	40	2.00×10^{-4}	3.79
5×10^{-4}	20	2.82×10^{-4}	5.36
10^{-4}	4	6.31×10^{-4}	11.99

the wells had fluoride ranging from 1 to 5.9 mg/L. All these high-fluoride wells were associated with a specific bedrock formation. Such information is useful from a public health standpoint because there is a 2.0-mg/L drinking-water criteria for fluoride. Some fluoride is needed to build strong teeth in growing children; however, fluoride in excess of 2.0 mg/L will cause teeth to discolor. Chronic ingestion of high fluoride in drinking water can also produce a serious condition known as skeletal fluorosis, which can damage bones and joints.

6.7.2 Chlorine and Bromine

The halides chlorine and bromine have similar chemistry, although chlorine is far more abundant in nature than bromine. Even though the elements can exist in a number of oxidation states, the chloride and bromide ions (Cl^-, Br^-) are the only ones of significance in natural waters. These halides are widely distributed in rocks and soil, and can be naturally leached into groundwaters. The chloride ion occurs in natural waters in fairly low concentrations, usually less than 100 mg/L, unless the water is brackish or saline. Chloride is used by humans in many applications and can be added to the subsurface via industrial discharges, sewage, animal wastes, and road salting. Chlorine gas is used as a disinfectant for purification of water and is a strong oxidizing agent when dissolved in water. Commercial fertilizers can contain chloride as KCl. Chlorine and bromine are components of halogenated organic compounds used for industrial solvents and pesticides. These compounds have been released to the environment both intentionally through the use of pesticides and accidentally through spills and leaks. Recent increases in shale hydrocarbon development have produced large quantities of post-fracking brine waters (which flow back upwards to the surface after well development), as has brine production from dewatering associated with coal bed methane extraction (also called coal seam gas). These large quantities of brine have increasingly been disposed of through underground injection. Fracking flowback water with Cl^- concentrations as high as 151,000 mg/L have been reported (Haluszczak et al. 2013).

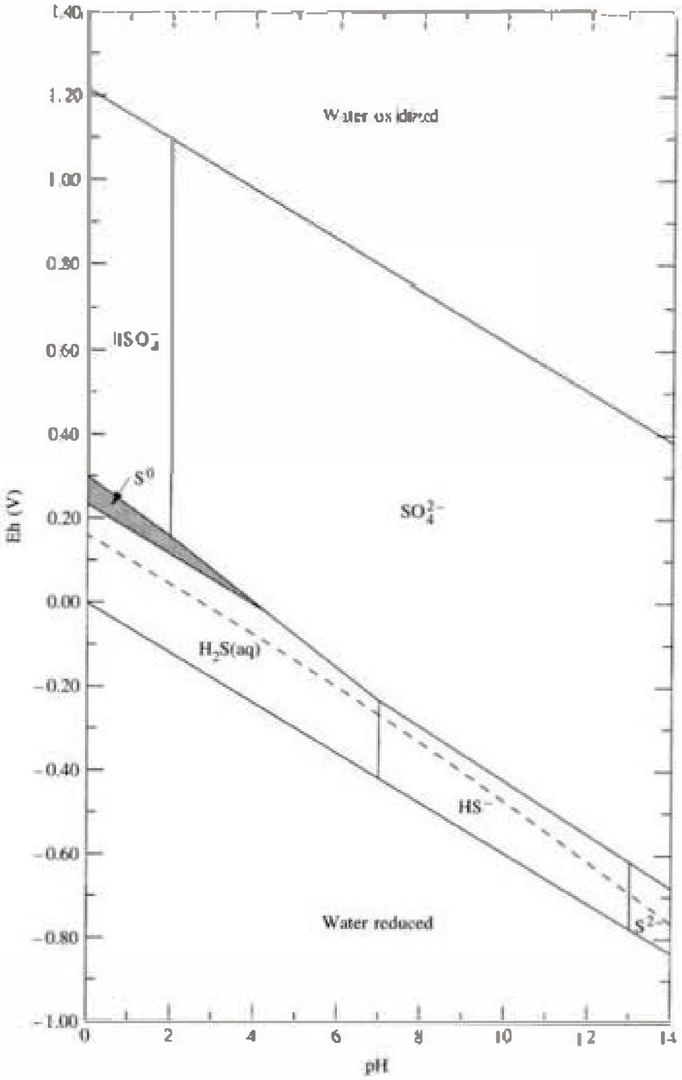
Chloride and bromide ions are not reactive. They don't participate in redox reactions, aren't sorbed onto mineral or organic surfaces, and don't form insoluble precipitates. Chloride is sometimes used as a tracer in groundwater studies because it is conservative. Distinctive ratios of Cl^- and Br^- and other elements in groundwater have been valuable in reconstruction groundwater's movement and origin, including determining mixing ratios of different source waters. These ions are highly mobile in the subsurface and are often eventually transported to closed basins or oceans. Additionally, concentrations of chlorine isotopes in groundwater have effectively been used for groundwater dating techniques, including bomb-pulse chlorine-36 put into atmosphere with nuclear weapons testing and falling with rainfall, infiltrating and percolating into groundwater (Challan 2016). These forensic groundwater analytical techniques aid in the tracking of groundwater pollution (see Chapter 8).

6.7.3 Sulfur

Sulfur is naturally released to the environment by the weathering of minerals containing the element. Rock containing pyrite can be oxidized to release sulfur, with microorganisms acting as a catalyst and mediating the oxidation. This is the source of the acidic water that drains from many areas that have been mined. Sulfuric acid is widely used in industrial processes. Sulfur can be released to the environment by the processing of sulfide ores and by the burning of fossil fuels, all of which contain sulfur to some degree. Sulfur is also a component of many fertilizers and can leach into groundwater systems from agricultural sources.

Sulfur can exist in valence states ranging from S^{-2} to S^{+6}. Figure 6.8 is an Eh-pH diagram showing the stability of the two oxidized forms of sulfur, $HSO4^-$ and SO_4^{2-}, and the three reduced forms, S^{2-}, HS^-, and H_2S (aqueous). The field of stability for elemental sulfur is also shown. The total sulfur activity used in computing the diagram is 10^{-3} mol/L or 96 mg/L as SO_4^{2-}. If a greater total sulfur activity were used, the stability field for elemental sulfur would be larger. Although this is a very useful diagram

FIGURE 6.8 Eh-pH diagram for sulfur species at standard conditions with total dissolved sulfur activity of 96 mg/L.



Source: J. D. Hem. 1985. *Study and interpretation of the chemical characteristics of natural waters*. Water Supply Paper 2254, U.S. Geological Survey.

for understanding the equilibrium conditions for dissolved sulfur, the redox reactions can be slow if microbes are not mediating the reactions. Hence, it may take a long time for the system to reach equilibrium.

Gypsum (calcium sulfate) is quite soluble in water ($K_{eq} = 10^{-4.6}$) and, except for waters with extremely high sulfate, would not be a sink for sulfate. Strontium sulfate is sparingly soluble ($K_{eq} = 10^{-6.5}$), whereas barium sulfate is nearly insoluble ($K_{eq} = 10^{-10.0}$). However, strontium and barium are not found in much abundance in natural waters. Sulfate could act as a sink for strontium and barium. Sulfur isotopes can be used to distinguish pollutant sources in some cases.

6.7.4 Nitrogen

Nitrogen is another element that can occur in both oxidized and reduced forms as well as the elemental state. The common forms of inorganic nitrogen include nitrate, NO_3^-, nitrite, NO_2^-, nitrogen gas, N_2, ammonium, NH_4^+, and cyanide, CN^-. Nitrogen is also a major constituent of organic matter in the form of amino acids. The majority (78%) of the Earth's atmosphere is nitrogen gas. Atmospheric nitrogen can be "fixed", or converted to nitrate, by cyanobacteria in lakes and the ocean and by bacteria living on the roots of plants such as legumes and lichens. Atmospheric nitrogen can also be converted to oxidized and reduced forms via fertilizer production and by heating it to high temperatures in internal combustion engines, power plants, lightning discharges and forest fires. Rainwater contains dissolved nitrate and ammonia. Nitrogen is released to the subsurface from sewage, animal wastes, and fertilizers.

In soil and groundwater, oxidation and reduction of nitrogen species is accomplished by microorganisms. Under oxidizing conditions ammonia is converted to nitrite, which is converted to nitrate. Nitrite is a very reactive ion and is almost immediately converted to nitrate, so that little nitrite is normally found in the environment. Under reducing conditions nitrate is converted primarily to nitrogen gas, a process known as **denitrification**. Organic matter will decay to ammonia under reducing conditions. Septic tank effluent, for example, normally has high ammonia and very little nitrate. If the receiving groundwater is reducing, the nitrogen will stay in the ammonia form. If it is oxidizing, bacteria will convert the ammonia to nitrate (Feth 1966). Nitrate is chemically conservative, can be mobile in the subsurface environment, and understandably, high nitrate concentrations in drinking water are most often associated with privately owned wells. Since the 1940s, health concerns and regulatory standards for nitrogen in groundwater center on infant methemoglobinemia (commonly called the "blue baby" disease). The high gastric pH of infants and their great fluid intake relative to body weight contribute to their internal bacterial reduction of ingested nitrate to nitrite, and the generated nitrite inhibits the function of blood hemoglobin in the transfer of oxygen.

Nitrate contamination of groundwater has been documented in a number of areas (e.g., Hill 1982; Flipse et al. 1984; and Silver and Fielden 1980). Hill studied the distribution of nitrate in groundwater from a shallow unconsolidated sand aquifer. It was found that the groundwater beneath areas of forest or permanent pasture has less than 1.0 mg/L of nitrate as nitrogen. The groundwater beneath heavily fertilized potato fields typically contained in excess of 10 mg/L nitrate as nitrogen. Gray and Morgan-Jones (1980) found that the nitrate content of groundwater in a study area increased over the past 40 years and that the use of fertilizers in this catchment area also increased over the same time period.

Nitrogen occurs as two isotopes, ^{14}N and ^{15}N. Of the two, ^{14}N is by far the most abundant in the atmosphere. The relative abundance of ^{15}N—that is, the $^{15}N/^{14}N$ ratio—in nitrate may be used to distinguish nitrate that comes from animal and human waste from nitrate that comes from mineral fertilizers (Flipse et al. 1984).

The $^{15}N/^{14}N$ ratio is usually expressed as a $\delta^{15}N$ value, which is defined as

$$\delta^{15}\mathrm{N}(\permil) = \frac{\left(^{15}\mathrm{N}/^{14}\mathrm{N}\right)\mathrm{sample} - \left(^{15}\mathrm{N}/^{14}\mathrm{N}\right)\mathrm{standard}}{\left(^{15}\mathrm{N}/^{14}\mathrm{N}\right)\mathrm{standard}} \times 1000$$

where ‰ stands for parts per thousand.

If the $\delta^{15}N$ is positive, then the nitrate of the sample has been enriched in ^{15}N with respect to the standard. For nitrogen, the standard is the atmospheric composition. Nitrate from animal and human waste typically has a $\delta^{15}N$ in excess of +10‰.

Flipse and Bonner (1985) found that mineral fertilizers used on Long Island had $\delta^{15}N$ values that averaged 0.2‰ at one site and –5.9‰ at another. However, the $\delta^{15}N$ of the groundwater beneath the sites that had been fertilized was about +6‰. This increase in $\delta^{15}N$ from the mineral fertilizer was attributed to fractionation that occurred during infiltration of the nitrogen. However, the resulting $\delta^{15}N$ was still clearly lower than that expected from animal and human waste.

6.7.5 Arsenic

Arsenic can occur in valence states of +5, +3, +1, 0 and –3. However, the important states of dissolved arsenic in water are the arsenate $H_nAsO_4^{3-n}$, with a valence state of +5, and the arsenite $H_nAsO_3^{2-n}$, with a valence state of +3. An Eh-pH diagram for arsenic that shows the fields of stability for the arsenates and arsenites is given in Figure 6.9. Dissolved arsenic species can be absorbed by ferric hydroxides. Arsenic (+5) is more strongly sorbed than arsenic (+3). Ferric hydroxides are stable over a wide Eh-pH range, so this fact limits the mobility of arsenic. However, conditions that reduce Fe^{3+} to Fe^{2+} and As^{5+} to As^{3+} increase the mobility of arsenic in the environment, because the precipitated ferric hydroxides become soluble ferrous hydroxides (Matisoff et al. 1982). In an oxidizing environment with a pH above 4.09, we will find colloidal ferric iron hydroxides, which will sorb arsenic and would thus expect to have little arsenic in solution. Under strongly reducing conditions, if both iron and hydrogen sulfide are present, arsenic sulfide coprecipitates with iron sulfide. Mildly reducing conditions that lack hydrogen sulfide present conditions under which one would expect to find the most mobile arsenic, as iron would be in the soluble ferrous state and arsenic would be in the arsenite form (Hounslow 1980).

Arsenic has been released to the environment through the burning of coal and the smelting of ores. In the past it was used in the formulation of insecticides and embalming corpses. Starting at the time of the Civil War in the United States (1860–1865), arsenic was an ingredient in a popular embalming fluid. As much as 3 lb of arsenic could have been used per corpse. The use of arsenic in embalming fluids was banned by the federal government in 1910 because its use interfered with the investigation of suspected arsenic poisonings. However, graveyards from the Civil War and the late nineteenth century may be a source of arsenic contamination (Konefes 1990). It has some modern industrial uses. Groundwater has been found to have high (up to 96 μg/L) concentrations from natural sources in northeastern Ohio (Matisoff et al. 1982). Elevated arsenic (up to 5 mg/L) in groundwater in Nova Scotia, Canada, was reportedly due to the weathering of piles of mining waste that contained arsenopyrite (Grantham and Jones 1977). In the western United States high (>50 μg/L) concentrations of arsenic are common in groundwater. These are associated with areas of sedimentary rocks derived from volcanic areas, geothermal systems and gold and uranium mining districts. Irrigation in some areas has liberated arsenic to the extent that concentrations of up to 1 mg/L are found in shallow groundwater beneath irrigated fields (Welch, Lico, and Hughes 1988).

Naturally occurring arsenic in groundwater can also be a huge problem. In what one writer called "one of the largest mass poisonings in history," thousands of tube wells were drilled in shallow aquifers contaminated with naturally-occurring arsenic in Bangladesh and India in the 1980s and 1990s before the problem was recognized (Brahic 2004). As a result, arsenic has posed risk to an estimated 57 million people in Bangladesh (Hossain 2006), and 100,000 are estimated to have been affected by high concentrations in shallow well water in the region (Brahic 2004). Annually, another 270,000 have been estimated to have had cancer related deaths, as long-term exposure to arsenic has been related to cancer of the kidneys, lungs, bladder and skin (Brahic 2004). The problem was unrecognized for many years, in part because a study by the British Geological Survey (BGS) and Britain's National Environment Research Council (NERC) did not adequately test for arsenic in reconnaissance groundwater quality surveys which subsequently served as the basis for drawing up national water policies and the drilling of thousands of wells.

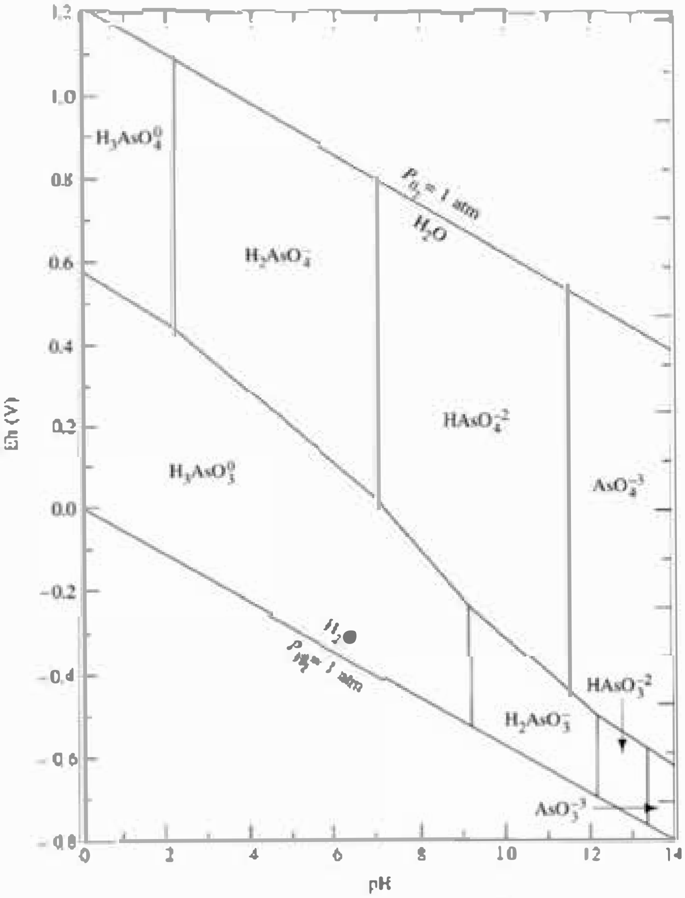
6.7.6 Selenium

Selenium occurs in oxidizing solutions as selenite, SeO_3^{2-}, with a +4 valence and as selenate, SeO_4^{2-}, with a +6 valence. It can be reduced to the insoluble elemental form, Se^0. It may also form a precipitate ferroselenite, $FeSe_2$, under reducing conditions. Selenite may be sorbed onto amorphous ferric hydroxides. Selenium has a number of industrial uses, such as the manufacture of pigments, stainless steel, and rubber compounds. It is contained in phosphate fertilizers. Selenium has been known to concentrate in irrigation return water draining from land that has soil high in selenium, and can be present in waste liquids from metal smelting. It is naturally present in coal, particularly bituminous coal, and can be concentrated approximately 1,250 times in the burning process at coal-fired power plants (coal versus precipitator ash), and can be present in elevated concentrations in waste scrubber water, ash ponds or other liquid wastes which could leach and percolate into the subsurface.

In small concentrations selenium is an essential nutrient, but in large amounts it is harmful to humans, fish, and wildlife (Coefield 2009). High selenium in groundwater-dependent ecosystems can wipe out entire species and cause massive wildlife and fish kills. High selenium has been problematic at many sites and from activities worldwide, including (Lemly 2002):

1. Nickel and silver mining in Torun, Poland.
2. Municipal landfill leachates in Stockholm, Sweden; Minnesota, U.S.A.; and in London, U.K.
3. Irrigation runoff in Chihuahua, Mexico; Utah, U.S.A.; and in Kesterson National Wildlife Refuge, California, U.S.A.
4. Coal combustion waste in Texas, Pennsylvania, Kentucky, North Carolina, U.S.A. and Alberta Canada.
5. Phosphate mining waste in Idaho, U.S.A.
6. Gold mining waste in Buenos Aires, Argentina; Quito, Ecuador; and Yukon, Canada.
7. Metal smelting waste in Ontario, Canada.
8. Oil-refinery waste in Louisiana, U.S.A.

FIGURE 6.9 Eh-pH diagram for arsenic species under standard conditions.



Source: A. H. Welch, M. S. Lico, and J. L. Hughes 1988. Arsenic in ground water of the western United States. *Groundwater* 26:333–347. Used with permission.

6.7.7 Phosphorus

Phosphorus can occur in a number of valence states, but in natural water it is really significant only in the +5 state. Dissolved phosphorus in water occurs as phosphoric acid (H_3PO_4) and its dissociation products, the orthophosphate ions: $H_2PO_4^-$, HPO_4^{2-} and PO_4^{3-}. The proportion of each present in an aqueous solution is a function of pH. Dissolved phosphorus is readily sorbed onto soil and has a very low mobility in groundwater. in alkaline soils it can react with calcium carbonate to form a mineral precipitate, hydroxyapatite.

$$3HPO_4^{2-} + 5CaCO_3 + 2H_2O \rightarrow Ca_5(PO_4)_3(OH) + 5HCO_3^- + OH^-$$

Phosphate is released to the environment from mineral fertilizers, animal wastes, sewage, and detergents.

6.8 Chemistry of Metals

Metals are cations, and most have fairly limited mobility in soil and groundwater because of cation exchange or sorption on the surface of mineral grains. They can also form precipitates of varying solubility under specific Eh-pH conditions. Geologically, metal ores are typically in the form of sulfides, oxides, silicates, or "native" metals. Metals are mobile in groundwater if the Eh-pH range is such that soluble ions exist and the soil has a low cation-exchange capacity (Dowdy and Volk 1983). They can also be mobile if they are chelated or if they are attached to a mobile colloid. Conditions that promote mobility include an acidic, sandy soil with low organic and clay content. Discharge of a metal in an acidic solution would keep the metal soluble and promote mobility.

6.8.1 Beryllium

Beryllium occurs only in the +2 valence state. In natural waters we can have Be^{2+}, $Be(OH)^+$, $Be(OH)_2$ and $Be(OH)_3^-$. Beryllium oxide and hydroxide have low solubilities and can act as a control on beryllium concentration. At equilibrium with $Be(OH)_2$, the dissolved form would have an activity of about 100 µg/L at a pH of 6 (Hem 1985). Nonetheless, beryllium can find its way into groundwater from industrial wastewater discharges or from natural weathering and dissolution of rocks, particularly igneous rock containing granites and pegmatites. Beryllium is used for making metal alloys for the aerospace industry, nuclear reactors, and is used in electrical equipment and microwave ovens.

6.8.2 Strontium

Strontium also occurs in the +2 valence state and has a chemistry similar to that of calcium. The solubility product for strontium sulfate, $SrSO_4$, is $10^{-6.4}$. This suggests that there might be an equilibrium control on strontium concentration if sulfate is present in the water. Strontium carbonate, $SrCO_3$, has a solubility product of 10^{-10}. In general, strontium is present in groundwaters in concentrations of less than 1 mg/L.

However, in tracing groundwater pathways and subsurface movement of potential contaminants, the isotopic ratio of $^{87}Sr/^{86}Sr$ can be a "powerful tool in distinguishing among solute sources," as the ratio can reflect mineral interaction with groundwater, differences in initial water quality, recharge waters of varying evaporative concentrations or pCO_2 concentration, and differences in relative mobilities of different groundwaters (USGS 2015).

6.8.3 Barium

This alkaline earth element also has a valence of +2. Its distribution is controlled by the solubility of barite, $BaSO_4$. Barite has a solubility product of 10^{-10}. If the activity of sulfate is 96 mg/L (10^{-3} *M*), then the activity of barium is 10^{-7} *M*, or 0.014 mg/L. Barium is also found as witherite ($BaCO_3$), and other compounds, but is not found in the environment as a free element because of its high reactivity. Barium sulfate can be an additive to oil-well drilling fluid, medical waste, and because in its ionic form barium is soluble and toxic, it is a component of some rodenticides.

6.8.4 Vanadium

This transition metal has oxidation states of + 3, +4, and +5. In aqueous solutions it forms 10 different oxides and hydroxides. Dissolved iron can react with vanadium to form an insoluble ferrous vanadate, which can act as a control on vanadium in natural water (Hem 1977).

$$FeOH^+ + 2H_2VO_4^- + H^+ \rightleftharpoons Fe(VO_3)_2 + 3H_2O$$

6.8.5 Chromium

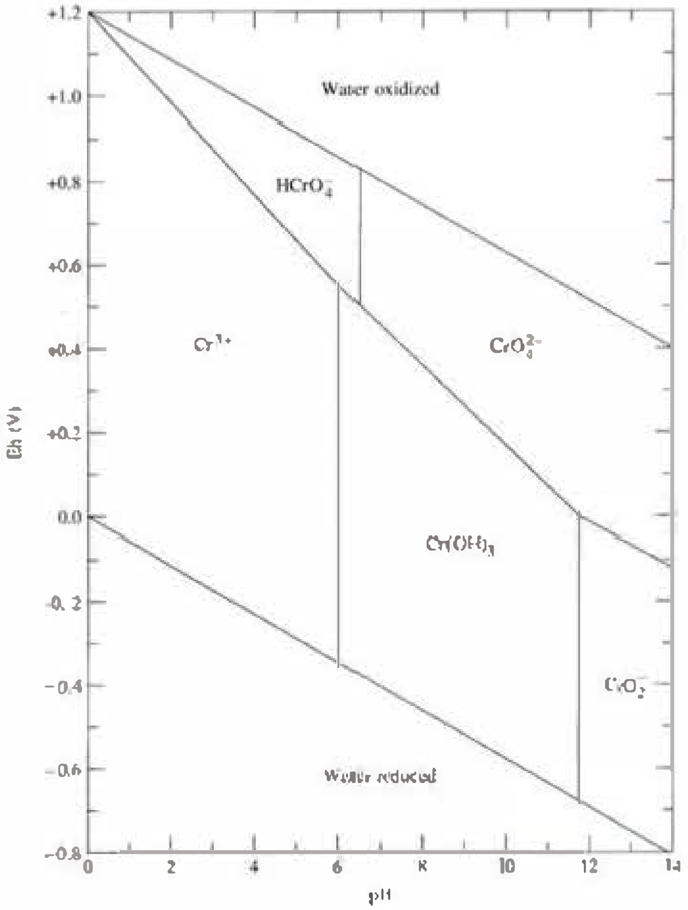
Chromium in natural waters occurs in a +3 and a +6 valence state Stable ionic forms in aqueous systems include Cr^{3+}, $CrOH^{2+}$, $Cr(OH)_2^+$, $Cr_2O_7^{2+}$ and CrO_4^{2-}. Chromous hydroxide, $Cr(OH)_3$ is a possible precipitate under reducing conditions. Figure 6.10 is an Eh-pH diagram for the stability field for chromous hydroxide. Under some conditions chromate might react with ferrous iron to produce a chromous hydroxide precipitate (Robertson 1975).

$$CrO_4^{2-} + 3Fe^{2+} + 8H_2O \rightleftharpoons 3Fe(OH)_3 + Cr(OH)_3 + 4H^+$$

In general the hexavalent chromium in groundwater is soluble and mobile and trivalent chromium will be insoluble and immobile. Industrial discharges of hexavalent chromium are common from metal-plating industries. This material may be quite mobile in groundwater. A hexavalent chromium spill on Long Island, New York, U.S.A., traveled more than 900 m (≈3000 ft) from a waste-discharge pond to a stream (Perlmutter, Lieber, and Frauenthal 1963). Hexavalent chromium from a natural source has been found in groundwater in Paradise Valley, Arizona, U.S.A. (Robertson 1975), and the Blacksmith Institute reports that groundwater containing 6.2 mg/L Cr (VI) was found in Kanpur, India (the Indian government limit is 0.05 mg/L) from tannery operations, potentially affecting 30,000 people. Popular attention was focused on groundwater pollution from hexavalent chromium in Hinkley, California, U.S.A., after it was dramatized in the 2000 film *Erin Brockovich*.

Chromium in groundwater is much more mobile in the aqueous Cr^{6+} phase than as Cr^{3+}. In a study of a three dimensional chromium plume in a glaciofluvial aquifer in Connecticut, Nikolaos et al. (1994) tested the sorbed chromium in the soil and the dissolved chromium in the groundwater. The mean soil concentration was 0.675 g/kg while 25 mg/L was dissolved in the groundwater. A mass balance calculation reveled that more than 99% of the mass of chromium was immobilized in the soil. This has important implications for groundwater remediation. The mobile chromium in the groundwater could be removed by pump and treat methods. However, if the geochemical equilibrium is upset and chromium is desorbed from the soil, then it would be very difficult to ever remove all of the chromium by pump and treat. As a part of a remedial investigation at a chromium spill site, one must determine how strongly the chromium is bound to the soil. Methods of extracting the dissolved portion without upsetting the equilibrium that binds the majority of the chromium to the soil must be developed.

FIGURE 6.10 Eh-pH diagram for chromium under standard conditions.



Source: Modified from F. N. Robertson. 1975. Hexavalent chromium in the ground water in Paradise Valley, Arizona. *Groundwater* 13:516–527. Used with permission.

Case History

Henderson (1994) investigated a chromium spill in the Trinity Sand aquifer near Odessa, Texas. He found that the mobile Cr^{6+} was being reduced to Cr^{3+} by ferrous iron (Fe^{2+}) and organic carbon. The trivalent chromium is then sorbed onto the soil surfaces which are coated with solid iron oxyhydroxides. The soil contained up to 5 g/kg and 95 to 99 percent was in the trivalent state. Prior to the initiation of the study, the chromium plating operation had ceased operations, so that the source of hexavalent chromium ended. Over the course of the study, the plume of groundwater contaminated with Cr^{6+} stopped growing, and even began to shrink (Figure 6.11). The cause of this degradation is the reduction of the Cr^{6+} to Cr^{3+} which forms chromium hydroxide ($CrOH_3$) and its subsequent sorption onto the soil.

The calculated half life of the chromium was 2.5 years. The reduction in dissolved hexavalent chromium mass in the aquifer is illustrated in Figure 6.12. The shaded area represents observed conditions at four different sampling events. The curved line is a first order reduction with the 2.5 year half life.

With the transformation of dissolved to solid chromium as a function of time, the groundwater in the aquifer is undergoing natural remediation. Computer modeling of the plume resulted in a diminution of the dissolved Cr^{6+} below a 100 μg/L drinking water standard by no later than the year 2006 (Figure 6.13). Operation and maintenance at the site were still ongoing in 2017.

6.8.6 Cobalt

Cobalt occurs with valence states of +2 and +3. In the Eh and pH range of natural waters, only the +2 valence state is stable. It is thought that cobalt can coprecipitate or be absorbed by manganese and iron oxides. Cobalt carbonate has a solubility product of 10^{-10}. At a pH of 8.0 with 100 mg/L of carbonate, the equilibrium solubility of cobalt is 6 μg/L (Hem, 1985). The solubility product of cobalt sulfide is very low, $10^{-21.3}$. Virtually no cobalt would be in solution in a reducing environment. Radioactive cobalt is a waste product of certain defense activities (Means, Crerar, and Duguid 1978). Cobalt occurs in nature as smaltite ($CoAs_2$), and cobaltite (CoAsS). In the United States, stable cobalt has been identified at 426 of the 1,636 current or former National Priorities List (NPL) sites, whereas radioactive cobalt has been found at 13 sites (ATSDR 2015).

6.8.7 Nickel

This metal occurs in aqueous solutions in the +2 valence state. Nickel ores include a variety of minerals, consisting of nickel, antimony, sulfur, and arsenic: NiSb, $NiAs_2$, NiAsS, and NiSbS. Nickel carbonate is more soluble than cobalt carbonate ($K_{sp} = 10^{-6.9}$), whereas the sulfide has a similar solubility ($K_{sp} = 10^{-19.4}$). Nickel is widely used in industry.

6.8.8 Molybdenum

Molybdenum occurs as the ore mineral molybdenite, MoS_2. The most common oxidation states are +4 and +6. Under oxidizing conditions the Mo^{6+} state dominates. Below pH 1.8 one finds H_2MoO_4 (aqueous). Between pH 1.8 and pH 5.3, $HMoO_4^-$ occurs, whereas above pH 5.3 the molybdate ion, MoO_4^{2-}, is stable. If ferrous iron is present, ferrous molybdate ($FeMoO_4$) presents a possible solubility control, since this has a solubility product of $10^{-10.45}$ at a pH range of 5.3 to 8.5 (Hem 1977). Molybdenum may also sorb onto amorphous ferric hydroxide (Kaback and Runnels 1980). The solubility product of calcium molybdate, $CaMoO_4$, is $10^{-8.7}$ (Hem 1985). Molybdenum is used as an alloy in steel and as an additive to lubricants. Waste sources include mining and smelting of ore.

6.8.9 Copper

Copper occurs in either a +I or a +2 valence state. Dissolved copper species in water include Cu^{2+}, $HCuO_2^-$, CuO_2^{2-}, and $Cu+$. Cupric copper and ferrous iron can undergo an oxidation-reduction:

$$2Cu^{2+} + 2Fe^{2+} + 7H_2O \rightleftharpoons Cu_2O + 2Fe(OH)_3 + 8H^+$$

Both cupric and cuprous sulfide have very low solubility products. Copper concentrations can be very high in acid mine drainage from metal mines, up to several hundred milligrams per liter. Copper can be leached from copper water-supply pipes and fixtures, especially by waters that have a pH of less than 7 (Hem 1985).

6.8.10 Silver

Silver, a rare element, is widely used in industry. It occurs in the +I valence state. Silver chloride, AgCl, has a solubility product of $10^{-9.7}$, which limits the solubility of silver in waters with chloride ion. Silver can also be naturally reduced to the metallic state by ferrous iron:

$$Ag^+ + Fe^{2+} + 3H_2O \rightleftharpoons Fe(OH)_3 + Ag + 3H^+$$

Silver sulfide has a low solubility. Thus, in water with chloride, iron, and sulfur present, stable solid forms of silver occur over the entire Eh-pH field (Hem 1977). As a result, there is very little soluble silver in natural waters.

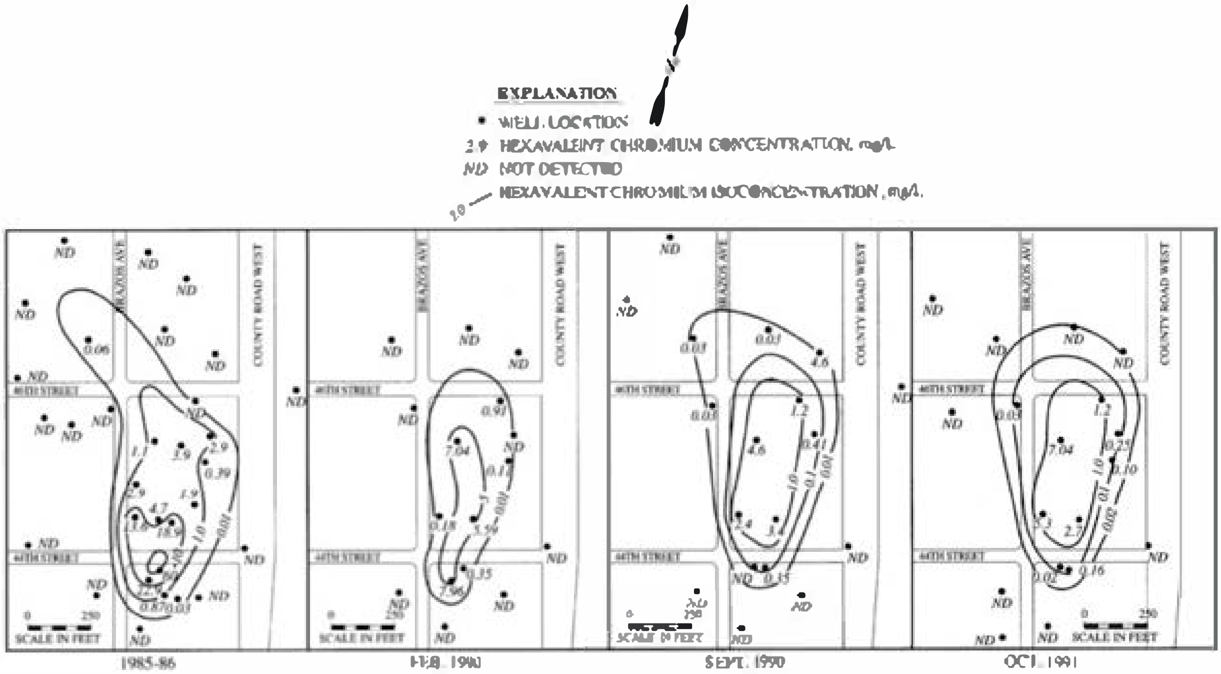
6.8.11 Zinc

Zinc is a fairly common metal and is extensively used in metallurgy and as a pigment, zinc oxide, which is often worn on the noses of lifeguards and other people in the sun. It occurs in the +2 valence state. Zinc carbonate has a rather low equilibrium constant, 10^{-10}, which would limit the solubility at pH ranges where the carbonate ion predominates. In a pH range of 8 to 11 and with 610 mg/L of HCO_3^-, there should be less than 100 µg/L of dissolved zinc (Hem 1985).

6.8.12 Cadmium

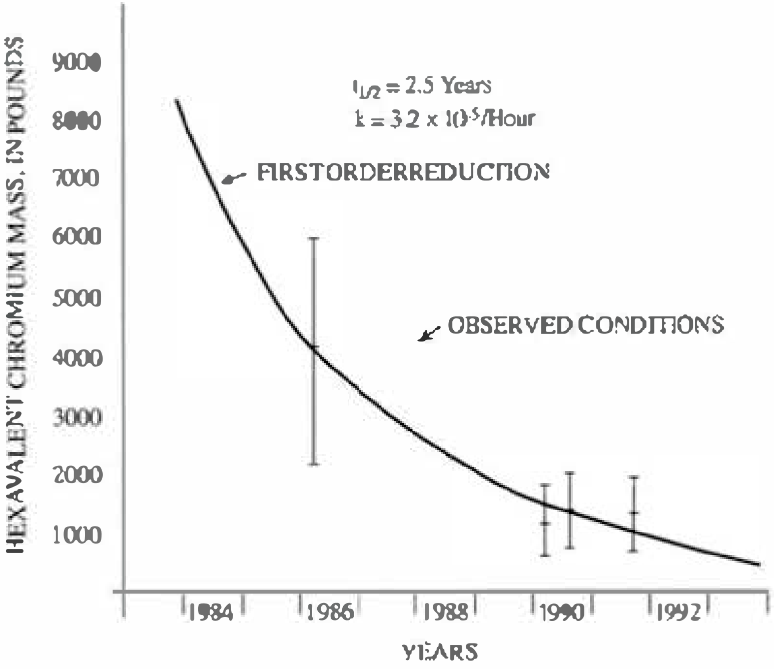
Cadmium has a very low maximum contaminant level (MCL) in drinking water, 4 µg/L, due to its toxicity. It exists in aqueous solution in the +2 valence state. Cadmium carbonate has a very low solubility product, $10^{-13.7}$. Although this could serve as a control on solubility under some conditions, cadmium can be mobile in the environment. On Long Island, New York, a metal-plating waste containing cadmium and chromium traveled about 3000 ft in a shallow aquifer (Perlmutter, Lieber, and Frauenthal 1963). Cadmium has been implicated in an outbreak of a disease in Japan resulting in a softening of the bones of the victims that resulted in extreme bone pain.

FIGURE 6.11 Shrinkage of the maximum extent of an observed plume of Cr^{6+} with time.



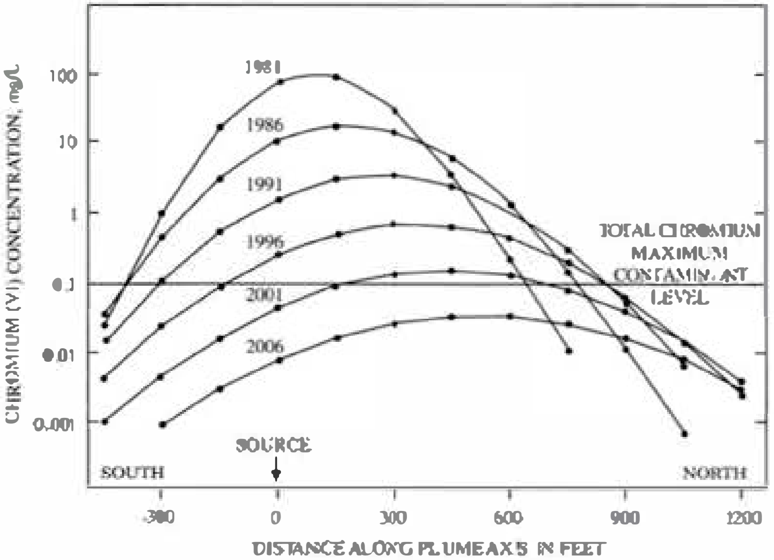
Source: T.Henderson. 1994. Geochemical reduction of hexavalent chromium in the Trinity Sand aquifer. *Groundwater* 32:477-486. Used with permission.

FIGURE 6.12 Reduction of the dissolved mass of Cr^{6+} with time.



Source: T.Henderson. 1994. Geochemical reduction of hexavalent chromium in the Trinity Sand aquifer. *Groundwater* 32:477–486. Used with permission.

FIGURE 6.13 Result of fate and transport modeling of concentration of Cr^{6+} along the axis of the plume.



Source: T. Henderson. 1994. Geochemical reduction of hexavalent chromium in the Trinity Sand aquifer. *Groundwater* 32:477–486. Used with permission.

The cadmium was traced to rice and soybeans grown in soil contaminated by airborne cadmium that came from a nearby lead-and zinc-smelting operation (Emmerson 1970).

6.8.13 Mercury

Mercury has the lowest MCL for any inorganic chemical, 2 μg/L. It is considered to be very toxic. It has been known to concentrate in the food chain, especially in fish. Several outbreaks of mercury poisoning have been confirmed in Japan. Local discharges of mercury from industrial processes into surface-water bodies resulted in high mercury levels in fish. Inhabitants of fishing villages ate fish up to three times a day. Mortality of those affected was about 40%, and the poisoning was passed to unborn babies by apparently healthy mothers (Waldbott 1973). Mercury occurs as a metal and in the valence states +1 and +2. Most of the inorganic mercury compounds have a low solubility. The solubility product of Hg_2Cl_2 is $10^{-17.9}$, and for HgS it is about 10^{-50}. Under most natural conditions there is little soluble inorganic mercury. However, methanegenerating bacteria can convert metallic mercury to organic forms such as methyl mercury, $HgCH_3^+$. The monomethyl mercury ion is soluble in water. Bacteria can also produce dimethyl mercury, $Hg(CH_3)_2$, which is volatile. Other organic forms of mercury, such as ethylmercuric chloride (C_2H_5HgCl), are manufactured and used as fungicides.

6.8.14 Lead

Lead occurs in aqueous solution as Pb^{2+} and in various hydroxides. Various lead compounds have solubility products that indicate that under the right Eh-pH conditions, lead solubility would be limited in natural waters: $PbCl_2$, $K_{sp} = 10^{-4.8}$; PbF_2, $K_{sp} = 10^{-7.5}$; $PbSO_4$, $K_{sp} = 10^{-7.8}$; $PbCO_3$, $K_{sp} = 10^{-13.1}$ and PbS, $K_{sp} = 10^{-27.5}$. Lead and the other metals are cations that can be expected to undergo cation and exchange with clays. Hence, the mobility of lead in groundwater is limited. Lead is present in nature as a trace element. In two different studies soils in uncontaminated areas were reported to contain 17 μg of lead per gram of soil (μg Pb/g) (Nriagu 1972) and 29 μg Pb/g (Ure and Berrow 1972). However, there are a number of anthropogenic sources of lead, including mining and smelting, paint, use of sewage sludge as a soil conditioner, lead arsenate pesticides, and leaded gasoline. Urban areas especially have much higher levels of lead in the soil due primarily to paint flaking from buildings and burning of leaded gasoline (Davis 1990). A study of lead in soils near highways in the Minneapolis St. Paul, USA, area revealed concentrations ranging from 128 to 700 μg Pb/g (Singer and Hanson 1969). A study in California, U.S.A. found that lead in soil decreased with distance from a freeway which ran through a rural area, with 118 μg Pb/g found 15 meters from the expressway and 85 μg Pb/g as much as 362 meters away (Page et al. 1971). Lead additives were used as anti-knock compounds in gasoline, but are now restricted or banned in many parts of the world.

Elevated lead is also found in soil around lead smelters. Davies (1990) estimates that in the immediate area of a well established lead smelter (1 to 3 km away), lead in soil is likely to be on the order of 1500 μg Pb/g. In a study conducted in southeastern Missouri, USA, the investigators were able to distinguish lead from automobile exhaust from lead from smelter activities on the basis of the ratio of stable lead isotopes, $^{206}Pb/^{204}Pb$ (Rabinowitz and Wetherill 1972). In that study they found lead in soil near smelters averaging 2600 μg Pb/g and near highways averaging 270 μg Pb/g.

In general urban soils have higher lead content than rural soils. In a major study of metals in urban soils in Great Britain a total of 4,126 lawns were tested, with a geometric mean lead content of 266 μg Pb/g and a range of thirteen to 14,100 μg Pb/g (Culbard et al. 1988). In London a total of 578 samples had a geometric mean lead content of 654 μg Pb/g.

Soluble lead is absorbed by soils, and its mobility is limited. The two most important factors in determining the amount of lead that will be sorbed by soil are the pH and the cation exchange capacity (CEC) of the soil (Zimdahl and Skogerbe 1977). This relationship can be described by an equation, with the amount of lead sorbed per gram of soil represented by N^*:

$$N^*_{(mol/gm)} = 2.81 \times 10^{-6} CEC_{(meq/100g)} + 1.07 \times 10^{-5} pH - 4.93 \times 10^{-5}$$

The above equation shows that with a pH greater than 4.61 the amount of lead sorbed by the soil increases and that below a pH of 4.61, it decreases. The cation exchange capacity of a soil is dependent upon the amount and type of clay in the soil and the amount of soil organic matter. Lead absorption is due to precipitation of the carbonate, fixation on organic matter, or sorption by hydrous oxides of iron and magnesium. Griffin and Shimp (1976) demonstrated that the sorption capacity of a clay for lead at a pH of 5.0 was much greater than at a pH of 4.0.

Because of the high affinity of soil for lead, the metal tends to accumulate in the upper few centimeters of soil. In a study of heavy metal mobility in soils near a zinc smelter, lead was found to be concentrated in the upper 10 cm of the soil (Scokart et al. 1983). This was due to the extremely low mobility of lead in soil. The reason that urban soils have such high lead levels is twofold. First, there are more sources of lead. But more important is the fact that the lead in the soil is so immobile that it continues to accumulate. In a study of trace metals in virgin agricultural soil profiles in Canada, Wright and others (1955) found lead to be more concentrated in the upper part of the soil profile. The lead was assumed to come from the weathering process and was concentrated in the zone where leaching was the most prevalent. This is further evidence for the very low mobility of lead in the environment.

There is one potential pathway for lead migration. If lead is sorbed onto colloidal-sized metal hydroxides, and the hydroxide moves through an aquifer as a colloidal particle, then the lead would also move. This would show up as lead in total metals analysis, which is run on an unfiltered sample. The colloidal particles, which may impart turbidity to the sample, would be digested and any sorbed lead liberated in the analysis. Colloidal-sized lead particles could also migrate with groundwater and be detected with the total lead analysis.

6.8.15 Rare Earth Elements

Rare earth elements (REEs) are increasingly important materials for modern technologies and can be found in groundwater. Although REE concentrations in groundwater can be low, they are used in investigations as tracers to indicate water movement and source, and importantly have associated radioactive pollutants in REE mining waste. There are 17 REEs, but the name "rare" is misleading as some (e.g., cerium) can be relatively abundant in the earth's crust. REE mining activity is rapidly expanding as are the economic uses of REEs. For example, REEs are used in cellular phones, laptop computer hard drives, automobile airbags and ABS brakes, medical magnetic resonance imaging (MRI), hybrid car batteries, wind turbine generators, plasma color televisions, satellite components, and communications equipment, to name a few applications. REEs have been shown to be useful in tracking and tracing groundwater (Johannessonn et al. 1997; Kreamer et al. 1996; Johannessonn 2006), and radioactive elements of uranium and thorium are commonly found in slurry tailing from REE mining.

6.9 Radioactive Isotopes

6.9.1 Introduction

Certain isotopes of elements undergo spontaneous decay, resulting in the release of energy and energetic particles and consequent formation of different isotopes. Some of these radioactive isotopes are naturally occurring and others are created by the bombardment of the Earth by cosmic radiation. Humans have created nuclear isotopes through the detonation of nuclear weapons and the construction of nuclear reactors. Table 6.6 lists the sources of environmentally important isotopes.

Radionuclides emit ionizing radiation–alpha particles, beta particles, and gamma rays–when they decay. An alpha particle is a helium nucleus with atomic mass 4 and atomic number 2. A beta particle is either a negative electron or a positron (positive electron). Gamma radiation consists of electromagnetic radiation similar to X-rays but more energetic (i.e., it has a shorter wave length). Gamma radiation is more destructive to tissue than X-rays. The primary effect of these particles is to produce ions, hence the name ionizing radiation. Alpha particles do not penetrate very far into matter due

TABLE 6.6 Sources of environmentally important radioactive isotopes.

Source	Radionuclides
Naturally occurring	^{40}K, ^{222}Rn, ^{226}Ra, $^{230,232}Th$, $^{235,238}U$
Cosmic irradiation	^{3}H, ^{7}Be, ^{14}C, ^{22}Na
Nuclear weapons tests	^{3}H, ^{90}Sr, ^{137}Cs, $^{239,240}Pu$
Mining waste—uranium, phosphate, coal	^{222}Rn ^{226}Ra, $^{230,232}Th$, $^{235,238}U$
Industrial wastes—e.g., nuclear power plants, weapons manufacturing, research and medical waste	$^{59,63}Ni$, ^{60}Co, ^{90}Sr, $^{93,99}Zr$, ^{99}Tc, ^{107}Pd, ^{129}I, ^{137}Cs, ^{144}Ce, ^{151}Sm, $^{152,154}Eu$, ^{237}Np, $^{239,240,242}Pu$, $^{241,243}Am$

Source: G. W. Gee, D. Rai, and R. J. Serne 1983. Mobility of radionuclides in soil. In D. W. Nelson et al. (ed) *Chemical Mobility and Reactivity in Soil Systems*, 203. (Madison, WI: Soil Science Society of America Spec. Publ. 11, 1983).

to their large size, but they produce a lot of ions along their short path. Beta particles penetrate to a greater depth but produce fewer ions per unit path length.

Radionuclide concentrations can be reported in terms of their mass per volume concentration (e.g., milligrams per liter). However, they are more frequently reported in terms of a standard unit of radioactivity, the **curie** (Ci). A curie is 3.7 × 10^{10} disintegrations per second. In water we use the **picocurie** (pCi), which is 1 × 10^{-12} Ci, or 3.7 × 10^{-2} disintegrations per second. In the SI system the unit of radioactivity is the **becquerel** (Bq), which is 1 disintegration per second.

Radiation doses are measured in terms of **rads**, which are a measure of the absorption by the body of ionizing radiation of any type. A rad is equivalent to 100 ergs of energy from ionizing radiation absorbed per gram of soft tissue. In the SI system the unit of dose is a **gray** (Gy), which is equal to 100 rads.

The effect of ionizing radiation depends upon the type of particle and the body tissue with which it interacts. Therefore, the absolute measurement of dose must be converted to a **dose equivalent**. The unit of dose equivalent is the **rem**. Rads are converted to rems by multiplying by a factor that depends upon the type of ionizing radiation and its biological effect. For example, with gamma radiation the factor is 1 and a rad is equal to a rem. In the SI system the unit of dose equivalent is the **seivert** (Sv), and it is equal to a gray times the dose factor. A seivert is 100 rem.

6.9.2 Adsorption of Cationic Radionuclides

The cationic radionuclides may be subjected to ion exchange and other processes that sorb the radionuclide onto mineral or organic surfaces in the soil. The following transition metals and lanthanides have large distribution coefficients and hence low mobilities in waters that are in the neutral range: ^{60}Co, ^{59}Ni, ^{63}Ni, ^{65}Zn, ^{93}Zr, ^{107}Pd, ^{110}Ag, ^{114}Ce, ^{147}Pm, ^{151}Sm, ^{152}Eu, and ^{154}Eu. Many of them do not desorb significantly. The degree of sorption is strongly related to the pH of the solution. Insoluble metal hydroxides may also be formed. Technetium (Tc) solubility depends strongly upon the Eh of the solution, because under oxidizing conditions it forms the soluble pertechnetate ion (TcO_4^-) (Gee, Rai, and Serne 1983).

^{90}Sr, ^{137}CS, and ^{226}Ra undergo cation exchange in a fashion similar to other exchangeable cations, such as Ca^{2+} and Mg^{2+}. Thorium and lead also have high distribution coefficients and limited mobility in neutral to alkaline soil. Lead is sorbed on hydrous oxides of iron, aluminum, and most likely manganese. Thorium hydroxides are of very limited solubility (Gee, Rai, and Serne 1983).

6.9.3 Uranium

Uranium occurs primarily as ^{238}U, with ^{235}U being much more rare. One of the disintegration products of ^{238}U is ^{226}Ra. This decay series ends with ^{206}Pb, a stable isotope. ^{238}U can also degrade to ^{234}U. The $^{234}U/^{238}U$ ratio is useful in tracking and dating groundwater (see Chapter 8). ^{238}U has a very long half-life, 4.5 x 10^9 years, which indicates that it is not very radioactive. The ^{235}U isotope can decay to form ^{223}Ra.

The chemistry of dissolved uranium is somewhat complex (Giridher and Langmuir 1991; Langmuir 1978). It has three valence states, +4, +5, and +6. Uranium can undergo oxidation-reduction reactions such as oxidation from the +4 to the +6 state:

$$U^{4+} + 2H_2O \rightleftharpoons UO_2^{2+} + 4H^+ + 2e^-$$

In a system with just uranium and water, stable species include (1) +4 valence: U^{4+} UOH^{3+}, and (2) +6 valence: UO_2^{2+} UO_2H^+ $(UO2)_3(OH)_5^+$ and $(UO2)_3(OH)_7^-$. The stability fields for this ions and precipitates are shown in Figure 6.14 for an aqueous solution with a total uranium activity of 10^{-6} mol/L The U(6+) species has a tendency to from a complexes with a wide variety of inorganic anions, including carbonate, hydroxide, phosphate, fluoride, and sulfate. This can be illustrated with an Eh-pH diagram of the same 10^{-6} mol/L solution of U but in contact with carbon dioxide at a partial pressure of 10^{-2} atm. This is represented by Figure 6.15. In Figure 6.14 the UO_2^{2+} formed a series of complexes with OH^-, starting with UO_2OH^+, at a pH above about 5.2. With carbon present, as in Figure 6.15, UO_2^{2+} can form a series of carbonate complexes that replace the hydroxyl complexes.

The soluble complexes of oxidized uranium depend upon the pH of the water. Most natural water contains fluoride, phosphorus, carbon dioxide, and sulfur. Figure 6.16 shows the distribution of uranyl complexes for a groundwater under standard conditions with $P_{CO2} = 10^{-2.5}$ atm, $F^- = 0.3$ mg/L, $Cl^- = 10$ mg/L, $SO_4^{2-} = 100$ mg/L, and $PO_4^- = 0.1$mg/L. In different pH ranges the most prevalent stable species include

$$UO_2^{2+}, UO_2(HPO_4)_2^{2-}, UO_2(CO_3)_2^{2-}, \text{and } UO_2(CO_3)_3^{4-}.$$

If reduced species of iron or sulfur are present, they could reduce U(6+) to U(4+) and precipitate the nearly insoluble mineral uranite, UO_2 This reduction could occur by oxidation of HS^- to SO_4^{2-}:

$$4UO_2(CO_3)_3^{4-} + HS^- + 15H^+ \rightleftharpoons 4UO_2(s) + SO_4^{2-} + 12CO_2(g) + 8H_2O$$

The same reduction could be accomplished by oxidation of ferrous iron to ferric hydroxide:

$$UO_2(CO_2)_3^{4-} + 2Fe^{2+} + 3H_2O \rightleftharpoons UO_2(s) + 2Fe(OH)_3 + 3CO_2$$

Because sulfur and iron are common in groundwater systems, under reducing conditions one could expect the formation of uranite, which would remove uranium from solution. Figures 6.14 and 6.15 show the stability field for uranite ($U0_2$). In the has a very low solubility. The primary thorium ore is monazite, which contains oxides of thorium, phosphorus, and the rare earths yttrium, lanthanum, and cerium.

The mobility of thorium is greatly enhanced if ligands are present to form complexes. Figure 6.20 shows the inorganic thorium complexes that form as a function of the pH of the solution. The solution contains 0.3 mg/L F^-, 10 mg/L Cl^-, 100 mg/L SO_4^{2-} and 0.1mg/L PO_4^{2-}. It can be seen from this figure that the most abundant aqueous species in order of increasing pH are $Th(SO_4)_2^0$, ThF_2^{2+} $Th(HPO_4)_2^0$, $Th(HPO_4)_3^{2-}$ and $Th(OH)_4^0$ However, the mobility of thorium complexes formed by organic ligands such as EDTA and citric acid are much greater than those formed by inorganic ligands (Langmuir and Herman 1980).

Adsorption of dissolved thorium increases with increasing pH above pH 2. The sorption of thorium onto clays, oxides and soil organic matter is nearly total by a pH of 6.5. Strongly complexing organic ligands such as EDTA can retard sorption or even promote desorption (Langmuir and Herman 1980). Thorium in natural waters and soil should be nearly immobile due to the low solubility of the minerals and the strong tendency for dissolved forms to be sorbed only by clays, mineral oxides, and soil organic matter.

6.9.5 Radium

Radium occurs naturally in four isotopes: ^{223}Ra, 226Ra and ^{228}Ra. ^{232}Th decays into both ^{228}Ra and ^{224}Ra, whereas ^{235}U decays to ^{223}Ra and ^{238}U disintegrates to ^{235Th}, which in turn decays to ^{226}Ra. One isotope, ^{226}Ra, has a much longer half-life than any of the others, 1599 years. Because of their short half-lives, the radium isotopes are strongly radioactive (Hem 1985).

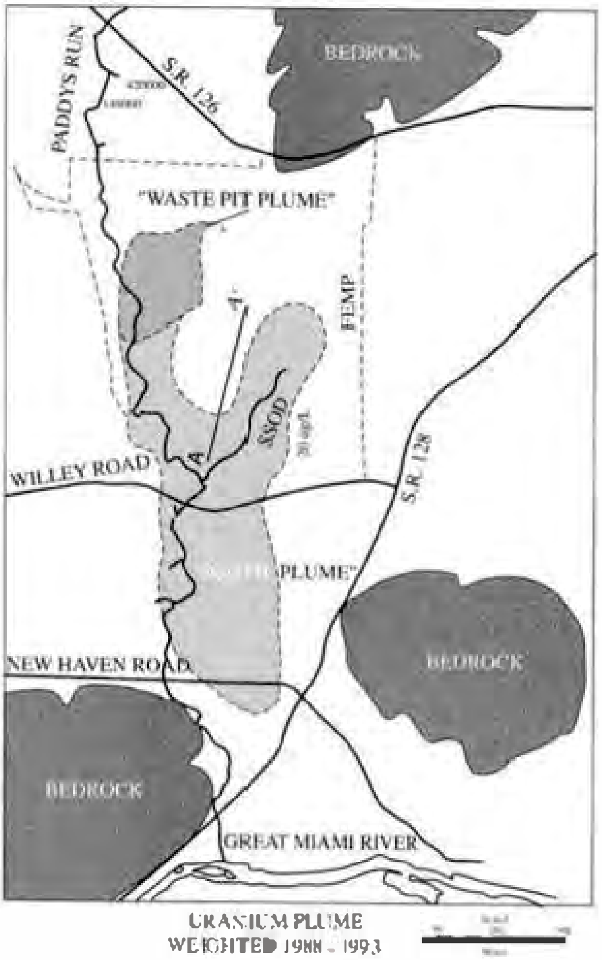
Knowledge of the aqueous chemistry of radium is summarized in IAEA (2014). It is reportedly similar in chemical behavior to barium (Hem 1985) and calcium (Kathren 1984). It is more soluble than uranium or thorium and can be bioconcentrated by plants (Brazil nuts have an especially high radium content). Radium can be strongly exchanged in the cation exchange series. According to Kathren (1984), the cation exchange sequence for soils is

$$Sr^{2+} < Ra^{2+} < Ca^{2+} < Mg^{2+} < Cs^{2+} < Rb^{2+} < K^+ < NH_4^+ < Na^+ < Li^+$$

^{228}Ra has a much shorter half-life, (5.8 yr) than ^{226}Ra. However, its parent, ^{232}Th, is more abundant in nature than ^{238}U, the parent of ^{226}Ra. As a result, both isotopes are found in groundwater. The U.S. EPA has proposed MCLs of 20 pCi/L for both ^{226}Ra and ^{228}Ra (Federal Register, July 18, 1991). Wells with high radium levels in groundwater have been discovered to be concentrated in two areas of the United States: the Piedmont and coastal plain of the Middle Atlantic states and the upper Northwestern states of Minnesota, Iowa, Illinois, Missouri, and Wisconsin (Hess et al. 1985). Table 6.7 summarizes the distribution of ^{226}Ra and ^{228}Ra in the Atlantic coastal plain and Piedmont region.

The radium content of groundwater is a function of the rock type of the aquifer. Igneous rocks, such as granites, contain the highest proportion of uranium and thorium, the parent isotopes of radium. Granitic rock aquifers and sands and sandstones derived from the weathering of granites have the potential to have high radium. Phosphate rock is also very high in uranium. Radium is not only a problem that is naturally occurring,

FIGURE 6.17 Composite plume of total dissolved uranium >0.20 µg/L for the period 1988 to 1993.



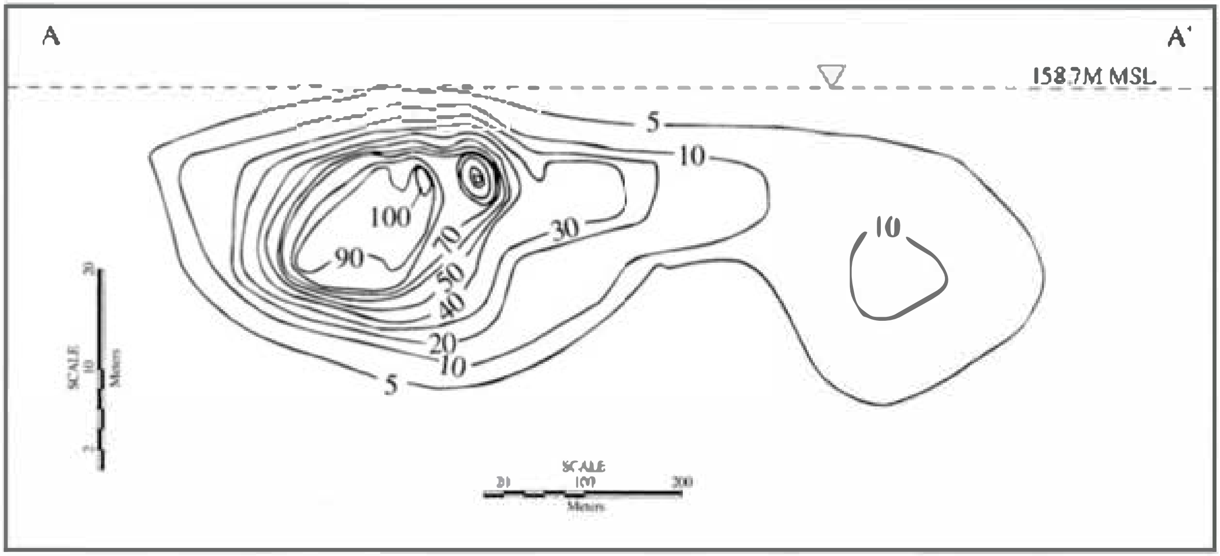
Source: W.C. Sidle and P.Y. Lee. 1996. Uranium contamination in the Great Miami Aquifer at the Fernald Environmental Management Project. Fernald Ohio. *Groundwater* 34:876-882. Used with permission.

Table 6.7 Distribution of 226Ra and 228Ra by aquifer type in the Atlantic coastal plain and Piedmont provinces.

Aquifer Type	Number of Samples	Ra-228 (pCi/L) Geometric Mean	Range	Ra-226 (pCi/L) Geometric Mean	Range
Igneous (acidic)	42	1.39	0.0–22.6	1.8	0.0-15.9
Metamorphic	75	0.33	0.0–3.9	0.37	0.0-7.4
Sand	143	1.05	0.0–17.6	1.36	0.0–25.9
Arkose	92	2.16	0.0–13.5	2.19	0.0–23.0
Quartzose	50	0.27	0.0–17.6	0.55	0.0–25.9
Limestone	16	0.06	0.0–0.2	0.12	0.0–0.3

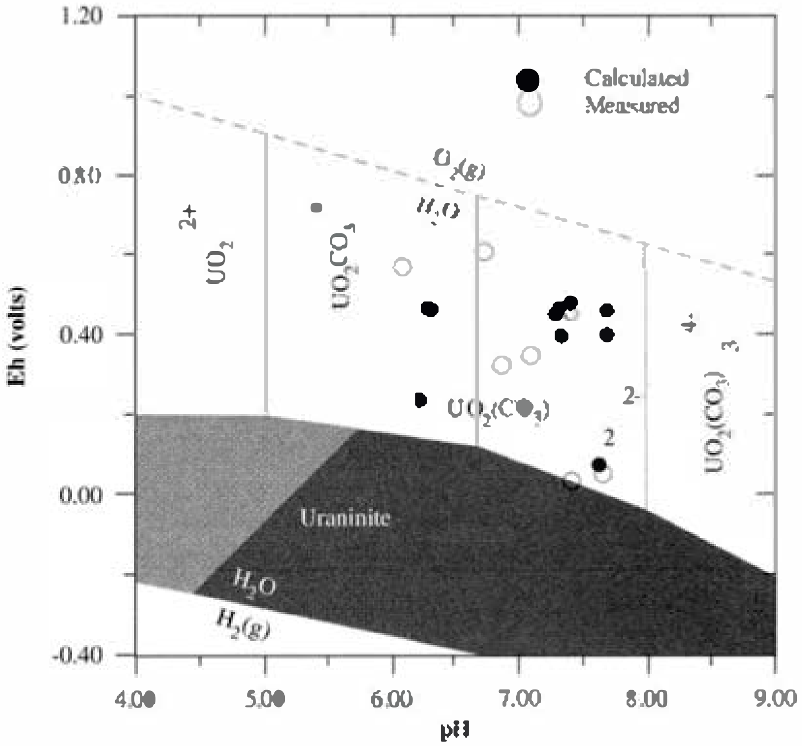
Source: C. T. Hess, J. Michel, T. R. Horton, H. M. Prichard, and W. A. Coniglio, "The occurrence of radioactivity in public water supplies in the United States," *Health Physics* 48 (1985):553–86.

FIGURE 6.18 Longitudinal profile of total dissolved uranium along line A – A′ from Figure 6.17.



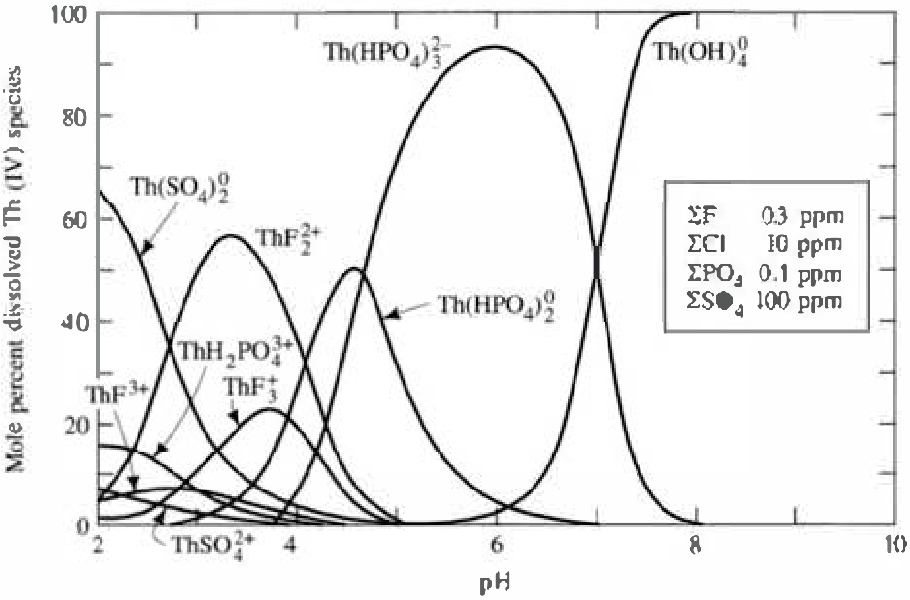
Source: W. C. Sidle and P. Y. Lee. 1996. Uranium contamination in the Great Miami Aquifer at the Fernald Environmental Management Project, Fernald Ohio. *Groundwater* 34:876-882. Used with permission.

Figure 6.19 Measured and calculated redox potential for the UO_2^{2+}/U^{4+} pair plotted on the $\Sigma U = 10^{-6}$ stability field.



Source: W. C. Sidle and P. Y. Lee. 1996. Uranium contamination in the Great Miami Aquifer at the Fernald Environmental Management Project, Fernald Ohio, *Groundwater* 34:876-882. Used with permission.

Figure 6.20 Distribution of thorium complexes as a function of pH under standard conditions for an aqueous solution containing 0.3 mg/L F^-, 10 mg/L Cl^-, 100 mg/L SO_4^{2-}, and 0.1 mg/L PO_4^{3-}.



Source: D. Langmuir and J.S. Herman. 1980. The mobility of thorium in natural waters at low temperatures. *Geochemica et Cosmochimica Acta* 44:1753–1766. Used with permission.

but there are localized areas of radium contamination from industrial operations. These are associated with uranium mill tailings as well as facilities where radioluminescent paints were prepared and used. For example, from World War I up until 1968 wrist watches with radium dials that glowed in the dark were sold in the United States.

6.9.6 Radon

There are several isotopes of radon, but ^{222}Rn is the only one that is important environmentally. The other isotopes have half-lives of less than 1 min. The half-life of ^{222}Rn is 3.8 days. ^{222}Rn is produced by the decay of ^{226}Ra, so that it is associated with rocks that are high in uranium. Radon can be associated with water that is low in dissolved ^{226}Ra, because it comes primarily from the decay of the radium in the rock. Radon is a noble gas and does not undergo any chemical reactions, nor is it sorbed onto mineral matter. Radon is lost from water by diffusion into the atmosphere and by radioactive decay through a series of short-lived daughter products to ^{210}Pb, which has a half-life of 21.8 yr.

The EPA has proposed an MCL standard of 300 pCi/L for radon in drinking water (Federal Register, November 2, 1999). However, there is also a health concern for excessive radon accumulation in homes. Radon can enter homes through emanations from the soil as well as by diffusion from tap water with a high radon content.

Owners of private water systems are most at risk from radon in drinking water. Public water-supply systems normally have storage facilities to supply water during fires. The residence time for the water in these facilities allows the radon to both diffuse and decay. Private water systems rely upon wells and usually only have a very small storage facility used to maintain pressure.

8

Site Characterization—Groundwater and Soil Monitoring

8.1 Introduction

Characterization of a potentially contaminated site involves field and laboratory analysis of subsurface properties, with a goal of building a conceptual model of contaminant source strength and configuration, and pollutant movement and transformation with time and space. This, in turn, is done to optimize monitoring strategies, and develop advantageous and cost effective remedial solutions.

The process of characterization begins with identifying the goals of characterization and remediation, and these goals can widely vary. Site characterization approaches will be quite different if the overall goal is to identify parties responsible for pollution, versus a goal of protecting public health, versus a goal of maintaining a vibrant groundwater dependent ecosystem. Further, a site can have several prioritized goals and not just one. Objectives are often linked, for example, one objective might be to minimize costs by requiring a thorough (and perhaps costly) site characterization in order to reduce potentially higher remediation costs by strategically targeting pollutants. There are many different site characterization methodologies including phased or progressive approaches and adaptive management techniques. At a site where very little is known about the nature and extent of subsurface contamination, often a first sampling step is collection and analysis for a broad range of potential contaminants, to be narrowed and focused based on the findings of those early surveys.

It must be emphasized that each site is unique and should not be addressed in a "one size fits all" or "we did it this way at the last site" boilerplate approach. Some of the seemingly smallest changes in geologic heterogeneities at different sites can radically alter subsurface fluid flow, and if unrecognized can cause inappropriate assumptions to be made and incorrect approaches to be followed. Likewise, site-specific physical, human-made features that protrude into or affect the subsurface (e.g., building footings, buried pipeline trenches backed-filled with gravel or other non-native material, groundwater pumping, surface irrigation or paving, application of chemicals at the ground surface, chronic and slow leaks versus massive leaks) all can alter how pollutants change their distribution, phase, form, and potential threat. An underlying note of caution is that the data that monitoring provides is not always representative of the complete hydrogeological picture or demonstrates contaminant distribution. Not accounting for these unique properties at each site, or blindly assuming that selected monitoring data is broadly representative of actual field conditions, can cost huge sums in misspent money, useless monitoring, ineffective remediation, lost time, and misstated risks (Nielsen 2005).

There are some general perspectives and overall guiding principles regarding monitoring and site characterization that are helpful. They include the following:

1. Resources spent on proper and thorough site characterization typically save many times their investment in reduced remedial costs.
2. Incautious monitoring installation and practices can make the original environmental problem worse by allowing cross-contamination and short-circuiting of contaminant migration.
3. It is standard to have well-defined goals for characterization and remediation before embarking on site activities.
4. It is very helpful to calculate a good mass balance of contaminants early on, including an estimate (or range of estimates) in source mass, amount retained in vadose zone, amount reaching the water table, mass dissolving into water, mass volatilizing into the gaseous phase, amount sorbing onto soils, mass transforming and/or chemically or biologically degrading, and other sources and sinks of contaminant mass.
5. Typically assessment should begin with noninvasive methods (methods that do not appreciably disturb the subsurface at a site) in order to optimize subsequent invasive methods (such as monitoring well installation).
6. Employing an "outside-in" approach where possible is advantageous to reduce equipment contamination or to prevent contaminant spreading, (e.g., drilling monitoring wells first in areas suspected of low contamination rather than "hot spots," or the practice of sampling wells deemed to be cleanest with low contamination first to reduce the possibility of cross contamination).
7. Phased approaches have benefits in allowing adjustment in monitoring strategies as more information is learned.
8. Consider early/interim remedial action as monitoring and monitoring plans are progressing (beyond just typical emergency response actions to immediate threats). Actions which are taken as monitoring plans are being completed can include: providing early source isolation, plume containment, and extraction of nonaqueous phase liquids to reduce their propensity to migrate.

There are a selection of noninvasive, or minimally invasive techniques available for initial groundwater surveys at potentially contaminated sites, and these procedures are often followed by groundwater and soil sampling. For groundwater sampling, the more invasive methods of installing monitoring wells and collecting groundwater samples have been developed with the specific intention of obtaining a representative sample of water from an aquifer (FDEP 2008; Hughes and Aarons 2014; Aller et al. 1991; NUDLC 2012; Arnold et al. 2009). These monitoring well methods minimize the potential for the introduction of contaminants into the ground through the process of installing a monitoring well. Wells and sampling devices can be constructed of materials that have a minimum tendency to leach materials into and sorb compounds from the water sample. Groundwater samples can be collected in such a manner that dissolved gases are not lost or exchanged with the atmospheric gases. Soil samples can also be collected for classification and chemical analysis.

Various methods of collecting samples of soil water are also available, as are procedures for determining the location and nature of subsurface contamination. Soil gas sampling can be done to give an indication of areas where volatile organic compounds are contained in the soil or groundwater. Many other forensic approaches help with the determination of groundwater and contaminant travel times, source location and timing, contaminant transformations and phase changes, geological formations and structures, and potential risk.

Proper site characterization can transform understanding and advance the development of effective remedial strategies. Australian guidance defines the "sound science" associated with contaminated site characterization and development of robust site conceptual models as being based on "organized investigations and observations conducted by qualified personnel using documented methods and leading to verifiable results and conclusions" (NSW 2010).

8.2 Noninvasive Measures

At the beginning of a site characterization program, noninvasive methods are employed to understand the sire without excessive perturbation of the subsurface. Although monitoring wells are usually an essential part of characterizing groundwater contamination, their installation can trigger vertical migration of pollutants, depending on the method of installation. A site characterization process typically begins with definition of objectives and a review of site specifics and history. Records of facility operations and inventories are investigated, contaminant handling practices at the site are looked into, drains and drywells are located, surface features and drainage patterns are reviewed, buried pipelines are identified, past and present employees may be interviewed, pertinent climatic data checked, existing local wells pinpointed along with associated groundwater quality data, and applicable law and regulations reviewed. As part of this process, facility records and manifests are analyzed to understand the possible mass of contaminants handled historically at the site. Agency and utility files, and regional geologic and hydrogeologic information are evaluated. An integral part of these undertakings is an initial site water balance and contaminant mass balance. Most of these undertakings are office related and not carried out directly on-site.

Air photo interpretation, surface geophysics, and quick soil and surface water survey and screening techniques are minimally invasive field techniques. Soil gas surveys are particularly useful for volatile compounds, and there are other noninvasive and informative practices useful in initial site assessment.

8.2.1 Interpretation of Aerial Photography and Remote Sensing

A review of site surface features, both present-day and historical, are easily accessible with the advent of widely available air photo libraries, such as National Aeronautics and Space Administration (NASA) World Wind and Google Earth. Many things pertinent to site characterization can be observed from visible aerial photography. This includes past and present site structures, roads and access points, possible soil staining or discoloration, the proximity of nearby creeks and streams, local wetlands and reservoirs and how these change with time, vegetative changes, urbanization, local erosion, industrial surface impoundments, and evaporation ponds. In tectonically active terrain, faults can sometimes be identified by observable surface lineaments. (Faults can be crucial to groundwater flow and contaminant movement in fractured terrain). Because of the replacement of film with digital imagery, the record of aerial photography has come to have a previously unrealized permanence. It should be noted that aerial photography displays a degree of radial distortion and without correction measurements of distance and topography are not accurate. Even so, aerial observation can provide better spatial resolution and geometric fidelity than many ground-based approaches.

The electromagnetic spectrum beyond visible light can also be quite helpful, as aerial photography provides broader spectral sensitivity than the human eye. Spectral bands or individual wavelengths can help identify many site activities. For example, near-infrared radiation (reflectance) can identify plant health, and thermal infrared (emitted spectra) can show heat sources on a property. Radar scanning can identify topographic expressions of subtle features like faults and folds often better than conventional satellite images. These radar techniques include Side-Looking Airborne Radar (SLAR) and LIDAR (a combination of the word "light" and "radar") that can identify ground uplift or subsidence, and define geomorphologic features. There are also airborne geophysical techniques that are noninvasive and help define the geological surroundings of a site. Although traditionally used for geologic resource and mineral assessment, aeromagnetic, radiometric, and gravity surveys can add important information to an understanding of field geological influences on contaminant travel.

8.2.2 The Use of Surface Geophysical Techniques for Site Characterization

Noninvasive surface geophysical techniques can advance site characterization in many ways, although some techniques are expensive, and natural and human-made surface features can interfere with their efficacy. American Standard Testing Methods' ASTM D6429-(2011)e1 is a standard guide for selection of surface geophysical methods, and Olhoeft (1992) provides a Geophysical Advisor Expert System to facilitate field decisions on appropriate geophysical methods.

Electromagnetic Surveys (EM) One surface geophysical method is an electromagnetic survey that measures the magnetic susceptibility of earth materials and their variation. An electromagnetic (EM) induction sensor can detect subsurface electrical conductivity dissimilarities, and therefore is good for locating lateral changes or discontinuities in soil or rock, and fluid filled fracture zones. These heterogeneities can be extremely important in subsurface contaminant movement, particularly for nonaqueous phase liquids (NAPLs). EM techniques can directly detect: burial trenches or pits containing drums or bulk wastes, electrically conductive plumes (particularly useful in coastal saltwater intrusion and saline landfill plumes), plume movement using time-series measurements, and utility pipes/cables (which may transport contaminants through their trench backfill and/or interfere with other geophysical techniques). Electrical conductivity variation can also be an indicator of NAPL presence.

Airborne electromagnetic surveys can explore large swaths of land, helping to delineate factors directly pertinent to contaminant hydrogeology such as large faults, paleochannels and shear zones with appreciable groundwater and/or clay gouge, and dissimilarities in the electrical conductivity of groundwater bodies. Helicopter transient electromagnetic surveys (TEM) can examine subsurface properties down to 200m depth, and have been used to identify contaminated landfill sires, model pollution and coastal hydrogeology, and optimize management of mining tailings facilities (Silvestri et al. 2009; Pellerin et al. 2010; Kirkegard et al. 2011; Christensen and Halkjaer 2014).

Direct Current Resistivity and Induced Polarization Another geophysical technique is a direct current resistivity survey that employs a constant electrical source using electrodes placed in the ground. The attenuation of voltage from between these electrodes (electrical resistance) allows calculation of depths to water tables or water-bearing horizons, freshwater/ saltwater interfaces, depth to bedrock, and stratigraphy at a sire. Like EM techniques, direct current resistivity can identify electrically anomalous plumes and burial sires for bulk wastes and drums. Fencelines, pipelines, and other surface interferences can alter DC resistivity results. A related technique is induced polarization which measures the transient electrical response. This technique has been applied to locating subsurface NAPLs and tracking active or passive remediation, particularly for surfactants that might be injected for soil flushing cleanups (Personna et al. 2013; Magill 2009).

Time Domain Reflectometry Time Domain Reflectometry or TDR measures the relationship between the velocity that an electromagnetic wave moves through and between metal rods which are pushed into the ground, and the dielectric constant of the soil through which the wave propagates. This method has been used to estimate soil water content for many years, but many other applications for contaminated soil have been developed. For example, Olchawa and Kumor (2008) have used a soil's dielectric permittivity measured with TDR to measure the content of diesel oil in soil.

Magnetometry Magnetometry measures nonuniformities in the earth's magnetic field typically caused by buried tanks and drums made of ferrous material (iron and steel) and underground pipelines and utilities. Because many industrial sites have the potential to contain leaking tanks or pipes, these surveys can help locate problem areas. Even in the absence of leaking tanks and pipes. backfill surrounding underground tanks and pipes can be a conduit for some future pollutant flow and can be identified as a potential preferred pathway for fluid migration. Also, locating buried utility features is a critical step before drilling monitoring boreholes.

Seismic Surveys Reflective and refractive seismic techniques require an energy source such as a force striking the ground which generates low-amplitude waves through the earth to surface geophones that record the arrival of these waves. The time delay of wave arrival provides information that can help calculate subsurface stratigraphy, depths to both water table and bedrock, physical and elastic properties of subsurface formations, and lateral soil/rock discontinuities. Because pollution sources can either be pooled up above, or deflected by, subsurface layers, their identification is important in developing an accurate site conceptual model.

Ground Penetrating Radar (GPR) Ground penetrating radar (GPR) in optimal circumstances also can identify depth to water table and bedrock, stratigraphy, metallic and nonmetalic buried objects, and underground tunnels and cavities. It has limitations in clayey soils because of a lack of radar penetration.

8.2.3 Rapid Noninvasive Field Surveys and Screening

If a thousand soil samples are sent to the laboratory for contaminant analysis, and only one comes back as registering detectable concentration, time and money has been wasted in site characterization. There are rapid field methods for determining the extent of soil, water, and major well contamination that can help focus and direct characterization efforts and save resources. For example, surface water sampling and analysis surveys are normally simple and quick because of easy access, and are often a first measure taken at a site suspected of contamination. Certain surface waters, such as springs, gaining reaches of streams, and wetlands, often directly reflect changes in adjacent groundwater.

Unaided Methods Some survey methods are unaided, such as when soil staining is directly visible, or inferred from directly observable problems like noxious odors, stressed or dead vegetation, and impaired or dead animals. Test pits, holes for building footings, and trenches can be an easy way to observe large cross-sections of the shallow subsurface. Pits, holes, and trenches are often available at urban and industrial sites where buildings are being put in, old underground tanks are being exhumed, or underground pipelines and utilities are being established. These open holes and trenches can provide opportunities for visible identification of contamination because of large continuous exposure of the subsurface. Direct sampling of soil and any ponded water is simple with a limited risk of vertical contaminant migration. Test pits and trenches can delineate shallow stratigraphy, waste disposal areas, grossly contaminated sites, buried pipelines and underground storage tanks. Importantly, some of these site features potentially contain health hazards (e.g., toxic gases or potential trench wall collapse), and safety measures need to always be considered in these investigations.

Colorimetric Screening Techniques Classes of contaminants, like NAPLs, can be inexpensively and immediately detected by direct visual sightings in soil and water, but can be difficult when a NAPL or another pollutant of interest is clear or colorless, at low saturation, or distributed heterogeneously. NAPLs which cannot be visually detected can be quickly discovered by a number of other simple techniques. Many NAPLs like crude oil, coal tar, creosote, and other petroleum products naturally fluoresce when exposed to ultraviolet (UV) light. The inexpensive methodology of putting a soil sample in a transparent plastic bag and placing it under a "black" (UV) light is a cost effective way to screen soils for many sorts of NAPL contamination. Also for NAPLs there are hydrophobic dyes which, when put in transparent containers with soils and shaken, give indicator colors in the presence of NAPLs. In water, hydrophobic filters or hydrophobic materials can be used to detect NAPL, or centrifugation can more clearly separate a nonaqueous phase from water. A syringe needle can also be used to extract suspected globules in a surface water or groundwater sample, and the globule can be placed in a water column to observe whether it mixes, sinks, or floats. In wells, NAPL presence can be observed in a number of ways. A simple quick method is dropping and retrieving a weighted string into a well and observing whether oil phases adhere to it. The weighted string should not be reused in another well to avoid cross-contamination. Hydrocarbon detection pastes (and water detection pastes for fuel storage tanks) can additionally help differentiate oils and water.

Immunological Surveys Another rapid field screening technique for water and soils are immunological surveys where polyclonal antibodies are mixed with soils and elicit a colorimetric response in the presence of certain pollutants. Polycyclic aromatic hydrocarbons (PAHs) have been shown to be detectable with about 5% false negatives and 5% false positives in one immunological survey (Knopp et al. 2000).

8.3 Minimally Invasive Soil Monitoring

Monitoring techniques which have minor perturbation of field site geologic materials include soil vapor monitoring, soil water sampling, and phyroscreening. Although some of these techniques penetrate the subsurface, the disturbance is minor and at shallow depths.

8.3.1 Soil Vapor Monitoring—Introduction

Soil-gas monitoring can be valuable for several reasons. Volatile organic liquids in the subsurface can partition into a vapor phase in the vadose zone and therefore be identified with soil gas measurement. A volatile organic liquid source may be pure oil phase product either adhering to a mineral surface or forming a nonaqueous phase layer on top of the capillary zone. It may also be dissolved in soil water or groundwater. The major benefit of soil gas screening is that it can locate zones of contamination. Identified locations of undissolved product present in the vadose zone can be recognized as a potentially persistent reservoir for ongoing contamination of groundwater, and infiltrating precipitation could dissolve the product in these zones and carry it down to the water table in the aqueous phase. Soil-gas monitoring can also be used to help determine the location of spills and leaks, and the horizontal extent of a layer of a volatile, nonaqueous phase liquid, such as gasoline, floating on the water table. Vapors from the gasoline can partition into the vadose zone, so that if they are detected by soil-gas monitoring in an area where product spills or leaks are not likely, this is an indication that the product may be migrating into the area. Additionally, soil-gas monitoring has been used as a screening method to evaluate the extent of a plume of groundwater contaminated with volatile organic compounds. The soil gas above the plume may contain volatile organics if the plume is at the water table.

Contaminant vapors themselves can be problematic. They can intrude into buildings and homes, sometimes with adverse health and safety implications (USEPA 2002). The restoration of a site may involve soil remediation if organic compounds are detected in the vadose zone. Soil vapor monitoring has been incorporated into guidelines for site investigation for some countries, for example Denmark (Algreen et al. 2015a). Under many conditions soil gas monitoring can be done much more quickly and inexpensively than installing groundwater monitoring wells. Soil gas monitoring is a noninvasive technique with little subsurface disturbance which can be used to optimize follow-on invasive methods such as well installation (ITRC 2007).

The boring is then unsealed; the vapor monitor is removed and sealed in a container for shipping to the lab, where it is analyzed (Kerfoot and Meyer 1986; NSW 2010).

Soil gas monitoring to find groundwater contamination plumes works best in areas where the vadose zone is comprised of dry, coarse-grained soils. The depth to water cannot be too deep, but at least 4.6 m (15 ft) is preferable. If the water table is too shallow, the concentration gradients are very steep, and a slight difference in depth of measurement may give a great difference in measured values (Marrin 1988). It is not possible to find an exact correlation between the soil gas concentration and contaminant concentration in the underlying groundwater. At best an order-of-magnitude correlation is possible (Thompson and Marrin 1987). Soil gas measurements are affected not only by the soil gas but also by the sampling technique and the soil-air permeability. After a rainfall, soil pores may be physically occluded by infiltrating rainwater and sampling may be impossible, particularly in finer soils. If there are several volatile organic compounds in the groundwater, they will partition into the vadose zone according to their individual Henry's law constants (Chapter 3). The organic compound with the greatest concentration in the soil gas may be the compound with the greatesr Henry's law constant and not the one with the greatest concentration in the groundwater. Although care must be taken when interpreting the results of a soil gas survey, these surveys are valuable screening techniques and have significant qualitative value.

Samples of indoor air in buildings are important in identifying risks from explosive or toxic vapors, but at some sites they also show a general correlation between intrusive indoor air vapor concentrations and underlying groundwater volatile organic compound (VOC) plumes. These indoor air concentrations can vary greatly seasonally or with varying barometric pressure, but still can provide useful information which mirrors groundwater concentrations. Indoor air sampling uses a vacuum-filled ampule in which a valve is released and air is drawn in. Valve release can either be rapid for a single-time sample, or can have a slow timed release that collects an integrated sample with time.

8.3.3 Soil Water Sampling—Introduction

Contamination moving from the surface toward the water table passes through the vadose zone. Monitoring of soil-water quality in the vadose zone beneath hazardous-waste land-treatment systems is required under Subtitle C of the Resource Conservation and Recovery Act in the United States. States may also require vadose-zone monitoring beneath other types of hazardous-waste facilities.

In order to determine the chemical composition and quality of soil moisture in the vadose zone, a sample must be collected. Because the soil water in the vadose zone is under tension, it cannot flow into a well under gravity the way that groundwater flows into a well. Soil water must be collected with a suction lysimeter (Wilson 1990).

8.3.4 Suction Lysimeters

A **suction lysimeter** is a porous cup located on the end of a hollow tube. The tube can be PVC or even stainless steel. The porous cup can be ceramic, nylon, PFTE, or fritted stainless steel. Tubing connects the suction lysimeter with the surface.

A suction is applied to the hollow tube and held for a period of time. If the suction is greater (more negative) than the soil-moisture tension in the soil, a potential gradient will develop from the soil to the porous cup. Soil-water will flow into the porous cup, from which it can then be directed through the tubing to the surface for collection. The flow of soil moisture can be slow, and it may be necessary to hold the vacuum overnight to supply a sufficient volume.

A vacuum lysimeter simply has a porous tip on the end of a hollow tube with a stopper that extends to the surface. The vacuum is applied to the lysimeter by means of a hand-vacuum pump attached to a small tube that extends down to the porous tip, and a sample is drawn to the surface when vacuum is applied (Figure 8.1). The practical depth of this type of sampler is about 1.8 m (6 ft) due to the awkwardness and cost of installing long tubes (Wilson 1990).

A pressure-vacuum lysimeter has a hollow tube that is about 5.08 cm (2 in.) in diameter and 0.3 m (1 ft) long. Two tubes run from the lysimeter to the surface (Figure 8.2). One of the tubes, the discharge line, extends to the bottom of the lysimeter and the other tube, the pressure-vacuum line, ends near the top. A vacuum is applied to the pressure vacuum line with a vacuum pump while the discharge line is shut off with a pinch clamp. The pressure-vacuum line is then sealed with a pinch clamp and the lysimeter is allowed to sit overnight so that the sample can be drawn into the cup. The pinch clamps are then removed. A hand-pressure pump is then attached to the pressure-vacuum line, and when pressure is applied, the water is forced up the discharge line to the surface. (A single pressure-vacuum hand pump can be used for this operation.) The maximum practical operational depth for the pressure vacuum pump is about 15 m (50 ft). At depths

FIGURE 8.1 Operation of a vacuum lysimeter.

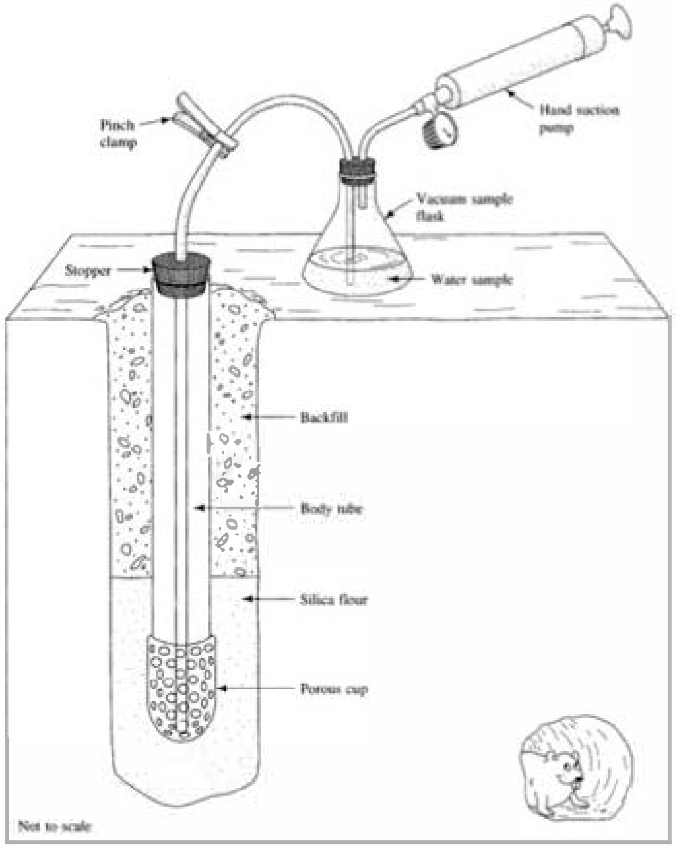
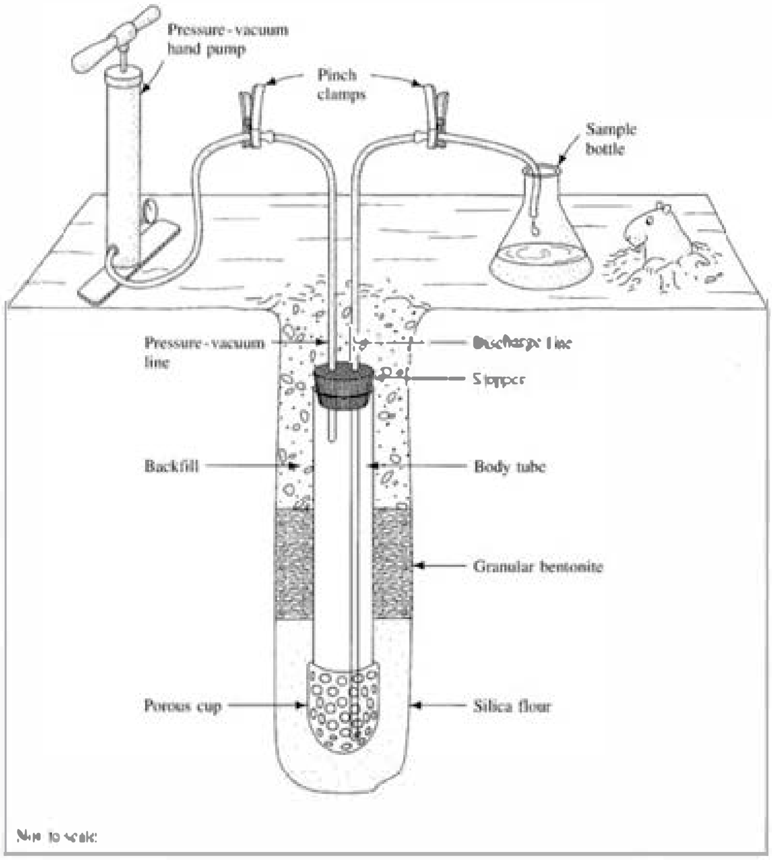


FIGURE 8.2 Operation of a pressure-vacuum lysimeter.



greater than this, the pressure needed to force the sample to the surface tends to drive it back out of the porous cup. This can be avoided by using a lysimeter with a check valve and an internal reservoir (Figure 8.3). When the vacuum is applied the water is drawn into the reservoir. When the pressure is then applied, the check valve prevents backflow into the porous cup and the sample must go to the surface.

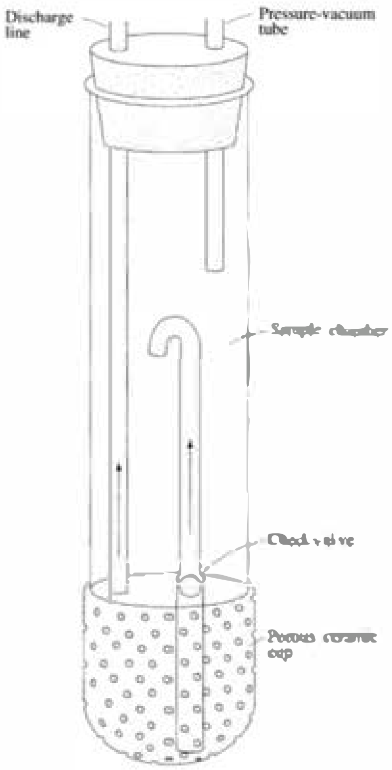
8.3.5 Installation of Suction Lysimeters

In order for suction lysimeters to work properly, they must be carefully installed (Wilson 1991). Prior to use, new porous ceramic cups should be leached with a 10% hydrochloric acid solution for 24 hours to remove dust from manufacturing. They should then be thoroughly rinsed by passing distilled water through them. The lysimeter is then pressure tested before being installed by submerging it in water and applying a pressure of 207 kpa (30 lb/in.^{2}) to test for leaks. No leaks should appear at any fittings, and air should bubble evenly through the porous cup.

The suction lysimeter is installed in an augered hole that has a greater diameter than the hollow tube. If the suction lysimeter is placed at a shallow depth, less than about 3 m (10 ft), then the access hole can typically be made by a hand auger. If it is greater than that depth, then a hollow-stem auger-drilling rig is needed to auger a hole.

The porous tip must be well bedded in slurry made of 200-mesh silica flour or native soil material that has been dried and screened to remove the fraction larger

FIGURE 8.3 Design of a pressure-vacuum lysimeter with a sample chamber and a check valve.



than coarse sand. There needs to be good hydraulic contact with the porous cup, the bedding material, and the native soil. Prior to installation the porous tip should be well hydrated by soaking in distilled water.

If a hollow-stem auger is being used, the augers should first be pulled back about 0.61 m (2 ft) to expose the native soil. A slurry made from silica flour and distilled water (0.45 kg (1 lb) of 200-mesh silica flour and 150 mL of distilled water) is put into the hole with a tremmie pipe to fill the hole with about 15.25 cm (6 in.) of slurry. The suction lysimeter is then lowered into the hole and centered. The tremmie pipe is then used carefully to place the slurry around the lysimeter up to an elevation of about 0.3 m (1 ft) above the top of the lysimeter. The unit should be held in place until the water drains from the slurry. The unit is then tested to see if it will hold a vacuum of 60 Kpa (0.6 bars). If it does, the augers are pulled back another 0.91 m (3 ft); then about 0.3 m (1 ft) of sieved native soil and 0.61 m (2 ft) of bentonite granules are added. The tremmie pipe is used to add distilled water to the bentonite to hydrate it. Finally, the augers are pulled and the borehole is backfilled with native soils that are tamped down to ensure compaction. Since a lot of distilled water was added to the soil during installation, the lysimeter needs to be purged until consistent water quality is obtained.

8.3.6 Phyto-screening

Phyto-screening is based on the ability of plants to translocate contaminants from their root zone to plant tissues above ground. Because the root zones of plants can be relatively large and their capture areas in the soil ill-defined, the method is somewhat qualitative, but potentially useful, particularly in locales with shallow groundwater contamination at large sites. Trees can draw water from groundwater, the capillary fringe, and/or pore water in the vadose zone, and therefore phyto-screening can supplement and enhance soil gas screening techniques (Algreen et al. 2015a). Often tree coring or plant tissue harvesting is used as a collection and detection method for determining the location of subsurface pollutants. Coring and use of plant tissues has been used, with certain limitations, to locate chlorinated solvents (Vroblesky, Nietch, and Morris 1999; Orchard et al. 2000; Vroblesky et al. 2004; Sorek et al. 2008; Larsen et al. 2008; Limmer et al. 2011), BTEX compounds (Algreen et al. 2015b; Wilson et al. 2013) and heavy metals (Stefanov et al. 2012; Algreen et al. 2012; 2014).

8.4 Invasive Methods - Monitoring Well Design

8.4.1 General Information

Monitoring wells are installed for a number of different purposes. During the installation of a monitoring well, a soil boring may be made or rock-core samples may be collected to determine the basic geology of the site. Prior to the design of a well, it is necessary to determine what its use will be. Some purposes of monitoring wells include:

- Measuring the elevation of the water table.
- Measuring a potentiometric water level within an aquifer, or at several depths in an aquifer.
- Collecting water samples for chemical analysis.
- Collecting samples of a nonaqueous phase liquid that are less dense than water.
- Collecting samples of a nonaqueous phase liquid that are more dense than water.
- Testing the permeability of an aquifer or aquiclude at discrete depths.
- Providing access for geophysical instruments.
- Collecting a sample of soil gas.

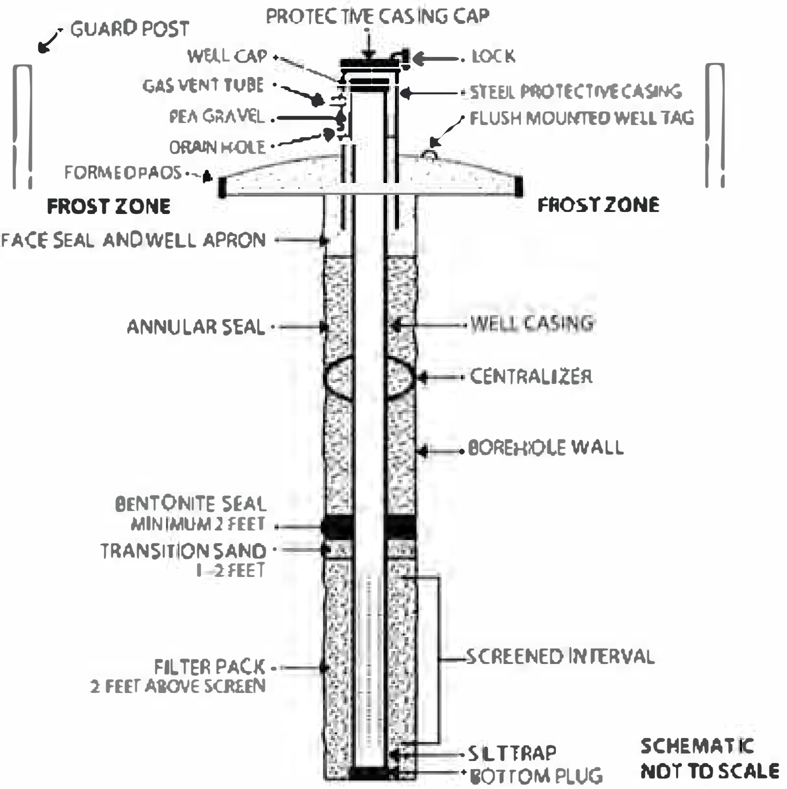
The use for which the well is intended will dictate the design. For example, if a well is to be used for the collection of water samples, the casing must be large enough to accommodate the water-sampling device. However, the diameter should not be much larger than the minimum size, because prior to the sampling of a well, stagnant water must be removed from the casing; the larger the diameter of the casing, the greater the volume of water that must be pumped and properly disposed. Some slightly more expensive characterization techniques can be well worth it for understanding a site. For example, high-resolution multilevel wells can produce orders of magnitude more data and understanding than single-screened wells. Figure 8.4 is a generalized schematic of a typical monitoring well. The following factors should be specified in the design of a monitoring well:

- Type of casing material.
- Diameter of the casing.
- If there will be a well screen, multiple screens, or an open borehole.
- If there is an open borehole, how deep the surface casing should be set. Cross connections between separate aquifers should be avoided.
- Length of casing.
- Depth of the well.
- Number of target sampling depths and screened intervals necessary in each well.
- Setting and length of the well screen(s).

- Diameter of well screen(s).
- Type of material for well screen(s).
- Slot opening of well screen.
- If an artificial filter pack (gravel pack) is necessary.
- Gradation of filter pack (gravel pack) material.
- Method of installation of well and screen.
- Material used to seal annular space between casing and borehole wall.
- Protective casing or well vault.

Monitoring network design is determined not only by intended well uses, but physical factors in the locale. Site specific influences of geography, practical consideration of surface conditions, and subsurface variability determine network monitoring design (Arnold et al. 2009). Geographical factors include natural and human-made topographic anomalies; natural and engineered surface drainage routes; areas of potential recharge and discharge such as wetlands; factors which influence the overall water balance such as weather and climatic variability; and anthropogenic features such as buildings, pavement, and pipelines. The practicalities of site accessibility and compatibility of monitoring wells with facility operations is often an important factor in well placement. Subsurface conditions also help dictate well network design. In general, more monitoring wells with closer intervals between wells, and multilevel sampling ability are required if there is complicated geology (e.g., discontinuous structures, tight folds, closely spaced

Figure 8.4 Typical monitoring well.



Source: E. Hughes and G. Aarons, 2014. *Well Design and Construction for Monitoring Groundwater at Contaminated Sites*. The California Environmental Protection Agency.

fractures, faults, solution channels), heterogeneous conditions (e.g., variable hydraulic conductivity, variable lithology), steep or variable hydraulic gradients, low dispersivity potential, high flow velocities, or if the aquifer is located near a recharge zone. Depths to water tables, confining layers, and bedrock surfaces are key in decisions about screen intervals and drilling depths. Lastly, the number and placement of wells often is based on prior application of noninvasive methods. These can include indirect methods (such as surface geophysics, soil gas where applicable, airborne remote sensing) or direct observation (such as existing wells, soil borings, test pits, and observation of local outcrops).

Common problems with groundwater monitoring systems include instances where wells are placed by regulatory mandate; where there is incomplete site data; when initial ideas on site (and regional) geology, hydrogeology, and water balance are not correct; and when incorrect assumptions are made regarding waste constituent migration. Difficulties also arise with improperly constructed wells, when they are not properly identified, or in cases when wells are not properly surveyed for location and elevation.

8.4.2 Monitoring Well Casing

All monitoring wells have a casing, whether they have a screen or terminate in an open borehole in bedrock. The casing is a piece of solid pipe that leads from the ground surface to the well screen or open borehole and is intended to keep both soil and water from entering the well other than through the screen or open borehole. Casing also prevents water from flowing from one aquifer horizon to another, provided the annular space outside the casing is properly sealed.

The diameter of the casing for a monitoring well is determined by the use for which the monitoring well is planned. If the only purpose of the monitoring well is to measure water levels, then a 2.54 cm (1 in.) inside-diameter casing is all that is needed. An electric probe to measure water level or a pressure transducer will fit inside the 2.54 cm (1 in.) casing. Figure 8.5 shows an electric probe being lowered into a 5.08 cm (2 in.) casing.

If a well is to be used to collect a groundwater sample, the diameter of the well needs to be such that standard well-sampling equipment can fit inside. The common standard for well-sampling equipment is a nominal 5.08 cm (2 in.) diameter. This can accommodate a wide variety of pumps that can withdraw water at rates of 0.03 to 0.13 or 0.19 L/s (0.5 to 2 or 3 gal./min). Specially designed borehole geophysical equipment can also fit inside a 5.08 cm diameter casing.

For some applications, monitoring wells may be intended for several functions such as measuring water levels, collecting water samples, pumping to remove contaminated water and perhaps floating nonaqueous phase liquids, and as a part of a vapor-extraction system. These wells sometimes have diameters larger than 5.08 cm (2 in.) to accommodate pumping equipment with a higher-flow capacity. The actual equipment to be used determines the casing diameter.

Casing diameter can also be influenced by the depth of the well. The deeper the well, the stronger the casing and screen must be to resist the lateral pressure at the final depth and the crushing force of the weight of the length of casing. Larger diameter casing can be made with thicker walls to have greater strength. It is easier to have a straight well with stronger casing. Straight wells are important in accommodating bailers and pumps.

The outside diameter of casing is standard; however, the inside diameter is a function of the wall thickness. Table 8.1 lists the wall thickness and inside diameter for

FIGURE 8.5 Electric probe used to measure water levels in monitoring wells.

Photo credit: Jim Labre.

TABLE 8.1 Dimensions of inside and outside diameters of well casings.

		Schedule 5		Schedule 10		Schedule 40		Schedule 80	
Pipe Size	**Outside Diameter**	**Wall Thickness**	**Inside Diameter**	**Wall Thickness**	**Inside Diameter**	**Wall Thickness**	**Inside Diameter**	**Wall Thickness**	**Inside Diameter**
Nominal 2"	2.375"	0.065"	2.245"	0.109"	2.157"	0.154"	2.067"	0.218"	1.939"
Nominal 3"	3.500"	0.083"	3.334"	0.120"	3.260"	0.216"	3.068"	0.300"	2.900"
Nominal 4"	4.500"	0.083"	4.334"	0.120"	4.260"	0.237"	4.026"	0.337"	3.826"
Nominal 5"	5.563"	0.109"	5.345"	0.134"	5.295"	0.258"	5.047"	0.375"	4.813"
Nominal 6"	6.625"	0.109"	6.407"	0.134"	6.357"	0.280"	6.065"	0.432"	5.761"

various schedules of casing. The sizes are listed in English units (inches) as many casings and screens were produced for decades in countries not yet on the metric system. Table 8.2 lists recommendations for selection of casing and screen material. Heavier-schedule casing is stronger because it has a thicker wall. The strength of a casing also depends upon the material from which it is constructed. A schedule 5 casing

TABLE 8.2 Recommendations for selection of casing and screen material.

	Do Not Use:	Use:
1	PTFE if well depth exceeds 225-375 feet (68.6-14 meters)	PVC, ABS, SS
2	PVC or ABS if well depth exceeds 1200–2000 feet (366-6 10 meters)	SS
3	SS if pH < 7.0	PVC, ABS or PTFE
4	SS if D.O. > 2 ppm	PVC, ABS or PTFE
5	SS if H_2S > 1 ppm	PVC, ABS or PTFE
6	SS if TDS > 1000 ppm	PVC, ABS or PTFE
7	SS if CO_2 > 50 ppm	PVC, ABS or PTFE
8	SS if Cl^- > 500 ppm	PVC, ABS or PTFE
9	PVC if a neat PVC solvent/softening agent* is present or if the aqueous concentration of the PVC solvent/softening agent exceeds 0.25 times its solubility in water	SS, PTFE
10	Solvent-bonded joints for PVC casings	Threaded PVC casings
11	Welding stainless joints	Threaded SS casings
12	Any PVC well casing that is not NSF-ASTM approved—D-1785 and F-480	NSF-ASTM approved PVC well casings—D-1785 and F-480
13	Any stainless steel casing that is not ASTM approved—A312	ASTM approved SS 304 and SS 316 casings—A312
14	Any ABS well casing that is not ASTM approved	ASTM approved ABS casings—F-480

*Known PVC solvents/softening agents include:
Tetrohydrofuran, cyclohexane, methyl ethyl ketone, methyl isobutyl ketone, methylene chloride, trichloromethane, 1,1-dichloroethane, 1,1,1-trichloroethane, trichloroethylene, benzene, toluene, acetone, and tetrachloroethylene.

ABS	Acrylonitrile butadiene styrene
D.O.	Dissolved oxygen
ppm	parts per million
PTFE	Polytetrafluoroethylene
PVC	Polyvinyl chloride
SS	Stainless steel
TDS	Total dissolved solids

Source: E. Hughes and G. Aarons. 2014. *Well Design and Construction for Monitoring Groundwater at Contaminated Sites*. The California Environmental Protection Agency.)

made of stainless steel is stronger than a schedule 40 casing made of polyvinyl chloride (PVC), yet leaves a greater inside diameter.

There are a number of materials used to make well casings and screens These materials vary in chemical inertness, strength, durability, ease of handling, and cost. One must always consider the intended use of the monitoring well before selecting a material. What is the chemistry of the groundwater and associated contaminants?

Will any compounds present in the groundwater react with any of the possible casing materials? How deep will the well be? What are the strength requirements? Is the well intended for a short-term monitoring project or will it remain in service for many years?

Well casings are available in a variety of materials: fluoropolymers, such as PTFE, or polytetrafluoroethylene (Teflon® is the brand name of one manufacturer of PTFE), mild steel, galvanized steel, stainless steel, polyvinyl chloride (PVC), acrylonitrile butadiene styrene (ABS), fluorinated ethylene propylene (FEP), fiberglass-reinforced epoxy (FRE), polypropylene, and fiberglass-reinforced plastic (FRP). The ideal casing material is inexpensive, strong, not subjected to degradation in the environment, and will not affect water-quality samples by either leaching chemicals into or sorbing them from the groundwater (Ranney and Parker 1997). Mild or galvanized steel is often used for water-supply well casings but is not as frequently found in monitoring wells because it may react with the groundwater to leach metals from the casing (Barcelona et al. 1983). Polypropylene, FEP, and ABS are not widely available. Most monitoring wells are made of stainless steel or PVC, with PTFE being less common. PVC casing is the least expensive. Relative casing costs for other materials, compared with PVC, are mild steel = 1.1, polypropylene = 2.1, type 304 stainless steel = 6.9, type 316 stainless steel = 11.2, and PTFE = 20.7. Type 316 stainless steel is more resistant to corrosion than type 304 under reducing conditions (Aller et al. 1991).

Stainless steel has the greatest strength, followed by mild steel. Both are also resistant to heat, but they are heavier than the plastics and are, therefore, more difficult to install. The lower strength of the plastics is compensated for by using a heavier-schedule casing than necessary with steel. Most monitoring wells are shallow enough that schedule 40 or 80 PVC has sufficient strength. PTFE is more brittle and has less wear resistance than PVC or polypropylene and is hence less durable. PTFE also has a low tensile strength and high weight per unit length, which limits its use to shallow depths. Even there, PTFE casing tends to bow under its weight when installed in monitoring wells and may not be straight and plumb. Although its nonstick properties are good in frying pans, the neat cement grout used to seal the annular space between the casing and the borehole may not bond to the PTFE casing (Nielsen 1988). Table 8.3 gives comparative strengths of casing materials.

Groundwater monitoring wells can come into contact with pure organic compounds (LNAPLs and DNAPLs) as well as highly acidic and highly basic conditions. Ranney and Parker (1997) tested six different materials that are used or could be used as monitoring well casings in order to test their resistance to pure (neat) organic chemicals and acids and bases. (Stainless steel and galvanized steel are known to be unaffected by organic compounds but susceptible to corrosion by acids and bases.) They found that PTFE and FEP were unaffected by any of the 28 different organic chemicals in which they were immersed. The other four materials—PVC, ABS, FRE, and FRP—were affected to some degree by some, or in the case of ABS, all of the 28 chemicals. This study suggests that if contact with neat organic compounds is possible, PTFE, FEP, or stainless steel casings should be considered, although some PTFE materials are slightly porous, and are deformable and "ductile" under loading.

In the selection of casing material for groundwater monitoring wells, we must consider the potential chemical reactions between the casing material and the groundwater. Ideally, casing material should neither leach matter into water nor sorb

TABLE 8.3 Comparative strengths of casing materials. Note: 1 lb = 0.454 kg and 1 lb/in² = 0.07 kg/cm².

Material	Casing Tensile Strength (lb)		Casing Collapse Strength (lb/in²)	
	2-inch diameter nominal	4-inch diameter nominal	2-inch diameter nominal	4-inch diameter nominal
Polyvinyl chloride (PVC)	7,500	22,000	307	158
PVC casing joint[b]	2,800	6,050	300	150
Stainless steel (SS)[c]	37,760	92,000	896	315
SS casing joint[b]	15,900	81,750	No data	No data
Polytetrafluoroethylene (PTFE)	3,800	No data	No data	No data
PTFE casing joints[b]	540	1,890	No data	No data
Epoxy fiberglass	22,600	56,500	330	250
Epoxy casing joints[d]	14,000	30,000	230	150
Acrylonitrile butadiene styrene (ABS)	8,830	22,000	No data	No data
ABS casing joints[d]	3,360	5,600	No data	No data

a Information provided by E.I. du Pont de Nemours & Company, Wilmington, DE.

b All joints are flush-threaded.

c Stainless steel casing materials are Schedule 5 with Schedule 40 joints; other casing materials (PVC, PTFE, epoxy, ABS) are Schedule 40.

d Joints are not flush-threaded, but are a special type that is thicker than Schedule 40.

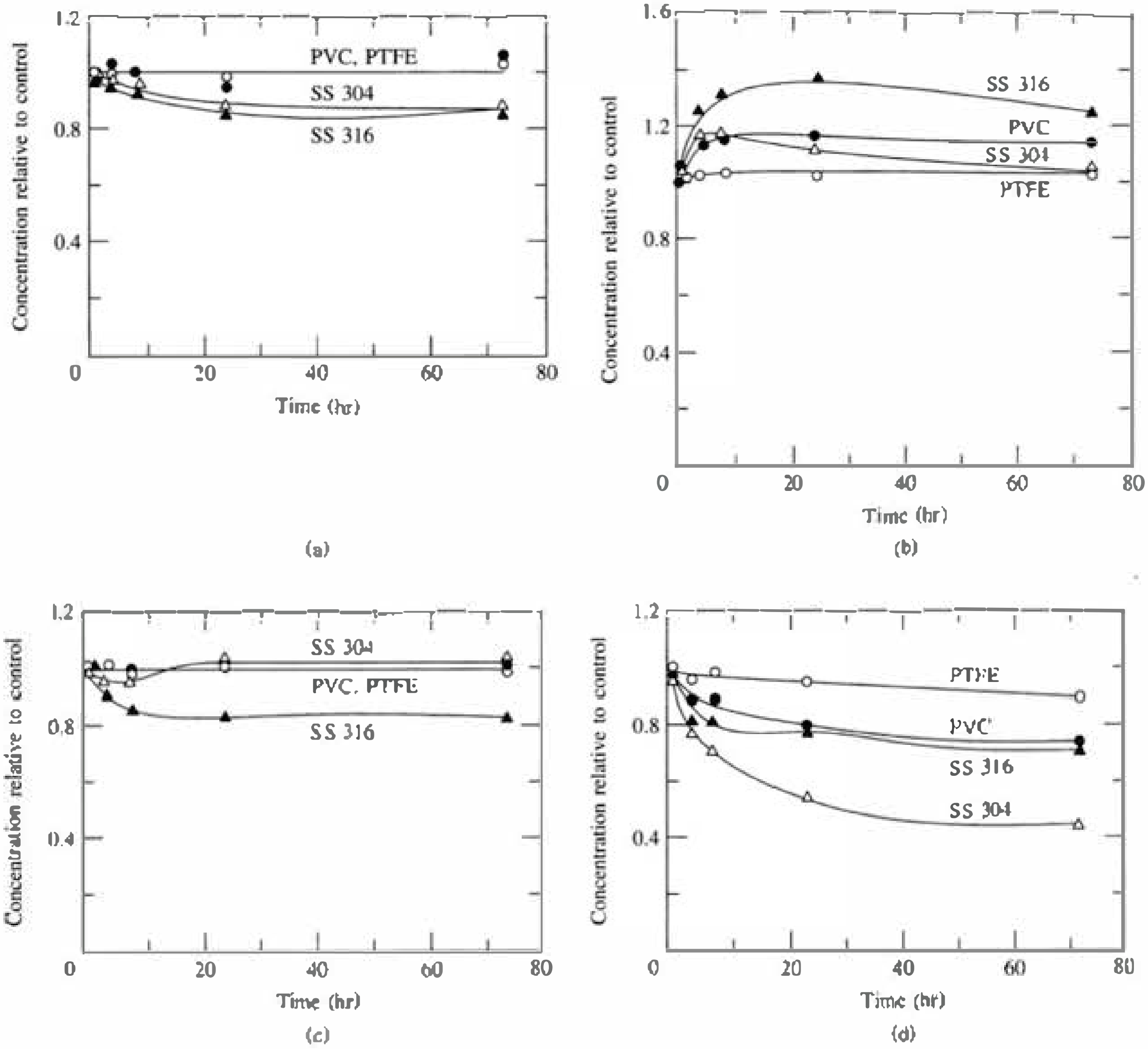
Source: E. Hughes and G. Aarons, 2014. *Well Design and Construction for Monitoring Groundwater at Contaminated Sites.* The California Environmental Protection Agency)

chemicals from water. Table 8.4 shows general recommendations for casing/ screen material selection.

Reynolds and Gillham (1985) studied the sorption from aqueous solution of five halogenated organic compounds by several polymer materials. The organic compounds used were 1,1,1-trichloroethane, 1,1,2,2-tetrachloroethane, hexachloroethane, perchloroethene, and bromoform. The materials tested were PVC, PTFE, nylon, polypropylene, polyethylene, and latex rubber. Nylon, polypropylene, polyethylene, and latex rubber rapidly absorbed all five compounds. PVC absorbed all the compounds but 1,1,1-trichloroethane, although the rate of absorption was low. PTFE absorbed all the compounds but bromoform; although the rate of adsorption of three of the four remaining compounds was low, PTFE absorbed 50% of the perchloroethylene in 8 hours.

Parker, Hewitt, and Jenkins (1990) evaluated the suitability of PVC, PTFE, stainless steel type 304 (SS 304), and stainless steel type 316 (SS 316) as casing material for monitoring metals in groundwater. They evaluated the interaction of four trace elements that are of concern in groundwater studies: arsenic, cadmium, chromium, and lead. The metals were tested at concentrations of 50 and 100 µg/L dissolved in groundwater. Figure 8.6 shows the results of this study. If the concentration relative to

FIGURE 8.6 Sorption and leaching of a. arsenic, b. cadmium, c. chromium, and d. lead by well casings made from PVC, PTFE, type 304 stainless steel, and type 316 stainless steel.

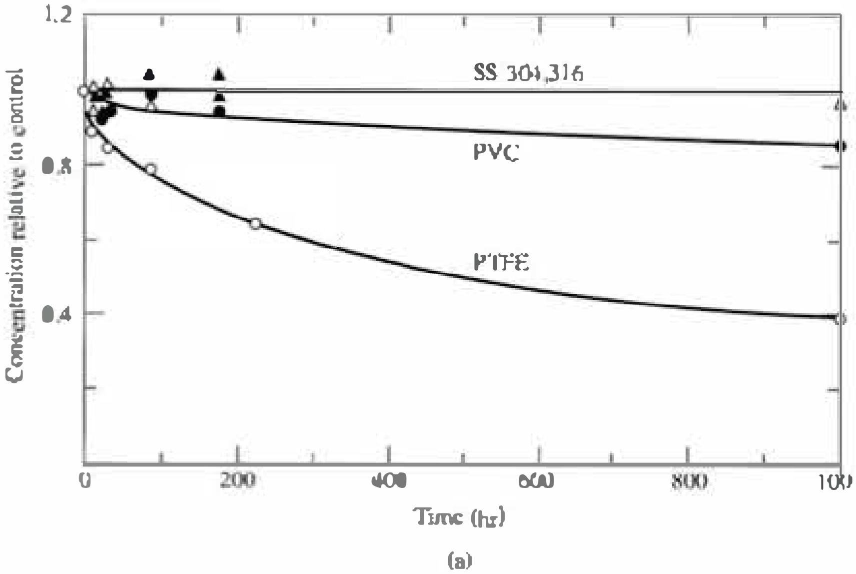


Source: L. V. Parker, A. D. Hewitt, and T. F. Jenkins. 1990. Influence of casing materials on trace-level chemicals in ground water. *Groundwater Monitoring & Remediation* 10:146–156. Used with permission.

for well casing should be used, and in the United States it should carry the designation *NSF wc*, which indicates that the casing conforms to National Sanitation Foundation Standard 14 for potable water supply (National Sanitation Foundation 1988).

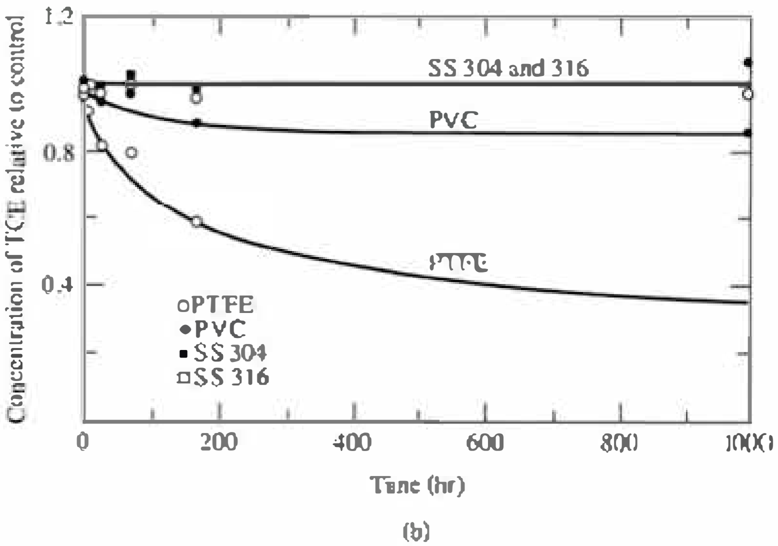
However, PVC should be avoided if organic compounds are present in the ground as nonaqueous phase liquids. Likewise, PVC casing should also never be joined with solvent-glued joints. These solvents include compounds such as methylethylketone and tetrahydrofuran and they may leach into groundwater samples. Threaded joints that are machined directly onto the PVC are the preferred method of joining casing sections and casing to screen. Joints should be flush on the inside of the casing to prevent equipment being lowered into the casing from hanging up in a projecting joint inside

FIGURE 8.7a Sorption of trichloroethylene in the part per million range from groundwater by PVC, PTFE, type 304, and type 316 stainless steel well casings.



Source: L. V. Parker, A. D. Hewitt, and T. F. Jenkins. 1990. Influence of casing materials on trace-level chemicals in ground water. *Groundwater Monitoring & Remediation* 10:146–156. Used with permission.

FIGURE 8.7b Sorption of trichloroethylene in the part per billion range from by PVC, PTFE, type 304, and type 316 stainless steel well casings.



Source: L. V. Parker and T. A. Ranney. 1994. Effect of concentration on sorption of dissolved organics by PVC, PTFE and stainless steel well casings. *Groundwater Monitoring & Remediation* 14:139–149. Used with permission.

the well, or bridging and stoppage of grout or filter pack material in the annular space outside the well.

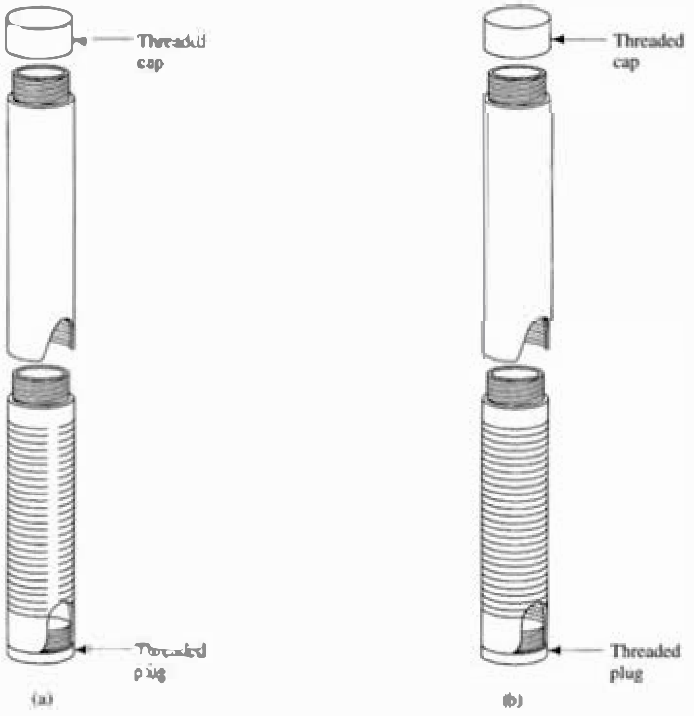
There are groundwater contaminants other than either metals or dissolved non-polar organic compounds. Many chemicals associated with agriculture are strongly polar or ionic. Papiernik, Widmer and Spalding (1996) studied the impact of using various materials to sample agricultural contaminants, including nitrate-N, atrazine, diethylatrazine, diisopropylatrazine, cyanazine, alachlor, metolachlor and butachlor. They found that other than butachlor (which is not in common use in the United States) there was no significant difference in absorption of the target by either polytetrafluoroethylene (PTFE), rigid PVC, flexible PVC, stainless steel, high density polyethylene (HDPE), or low density polyethylene (LDPE). For any of the chemicals tested, other than butachlor, any of the materials could be used. The least expensive would be HDPE, LDPE, and rigid PVC.

8.4.3 Monitoring Well Screens

If the monitoring well terminates in an unconsolidated formation, a screen is necessary to allow the water to enter while keeping the sediment out. In most monitoring well applications, the well screen is the same diameter as the casing to which it is attached by a threaded coupling. Likewise, the well screen is normally made of the same material as the casing. The considerations that go into deciding the material to use for the casing also apply to the screen. In many cases multilevel sampling will provide crucial information and multiple, isolated screened intervals are necessary.

The screen or screens will have openings to permit the water to enter. Manufactured well screen should always be used rather than hand-cut slots or drilled holes in plastic pipe. The two common screens for monitoring wells are slotted pipe, which is available in PVC and PTFE, and continuous wire wrap, which is available in stainless steel. Figure 8.8 illustrates these two screen types.

FIGURE 8.8 Slotted (a) and continuous wire-wrapped (b) monitoring well screens.



The width of the slot or wire-wrap opening is precisely controlled during the manufacture of the screen; the screen is available in a variety of opening sizes, generally ranging from 0.02 to 0635 cm (0.008 to 0.250 in.) A screen with an opening of 0.010 in. (0.0254 cm) is referred to as a 10-slot screen. Many manufacturers carry only a limited number of slot sizes in stock—for example, 10- and 20-slot. Since the casing and screen are typically ordered in advance of the well construction, the hydrogeologist usually has settled on a standard design prior to going on the job. Decisions on slot sizes are important in that too large a slot size without proper filter pack can allow sediment to enter the well during pumping. Conversely, a small slot size can inhibit nonaqueous phase liquids (NAPLs) from entering a well. NAPL must have enough thickness and fluid pressure to supplant water in small slots, overcoming capillary pressure. If well screen slots have small opening sizes, NAPL outside the well in a thin pool may not be able to enter through the screens.

8.4.4 Naturally Developed and Filter-Packed Wells

The casing and screen may be placed in the borehole and the native sediment allowed to cave around the screen. This is called a **naturally developed well** and is often used in sandy sediment with very limited amounts of silt and clay present, but is most realistic for wells with single screens. At least 90% of the sediment should be retained on a 10-slot screen before a naturally developed well is considered (Aller et al. 1991). When water is withdrawn from such a well, it may initially be cloudy due to suspended silt and clay, but the water should eventually clear as the fines near the screen are removed by a process called "well development." In a naturally developed well the slot size is selected to allow some of the fine sediment to enter the well during development; this leaves only the coarser sediment outside the screen.

In designing a water well, it is very important that the well be hydraulically effective—i.e., there should be a minimal loss of energy as the water flows into the well. As mentioned, the selection of the slot opening for naturally developed water wells is very important and is based on a grain-size distribution curve of the sediment opposite the well screen. Monitoring wells are designed to retain much more of the natural formation than water wells because they are much more difficult to develop (Driscoll 1986). Monitoring wells are not usually designed with the precision necessary for a water-supply well. The well should be hydraulically efficient as well as being as clear of silt and clay as possible. If preliminary investigations indicate that the aquifer to be monitored has reasonably coarse sand or gravel and few fines, a standard slot size may be preselected for all the monitoring wells. Ten-slot screen is frequently used under these conditions.

If the formation is cohesive—that is, has a high clay content—or if it is sandy with a high silt content, it will be necessary to use an **artificial filter pack**. Filter packs have also been referred to as "sand packs" or "gravel packs." Filter-pack material is typically medium to coarse sand that is predominately silica with no carbonates. It is mined and graded to have a specific grain-size distribution. Manufactured filter-pack material comes washed and bagged and is far preferable to native sand as artificial filter pack. The filter-pack material is placed in the borehole opposite the well screen. Its purpose is to stabilize the natural formation and keep it out of the screen. This will reduce the amount of silt and clay that enters the well when it is developed. There are also dual-screen well intake systems (pre-packs) that have a small diameter screen within a larger, second larger diameter screen, and the space in between is filled with filter pack material. Dual screen intakes are sometimes used when there is a propensity for fine-grained material to enter the well. A major disadvantage of these systems is that the two screens can compound the inhibition of NAPLs to enter a well.

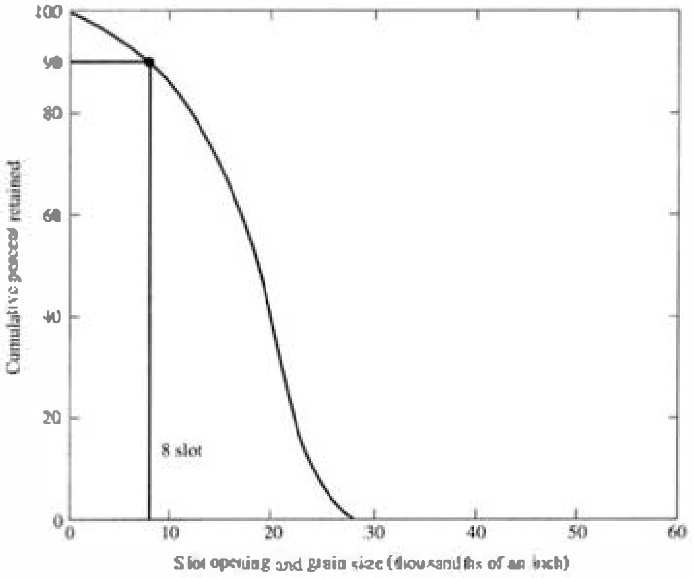
The grain size of the filter-pack material is based on the nature of the formation opposite the screen. If the formation is fine sand, then the grain-size distribution is determined. The filter pack material should have an average grain size that is twice the average grain size of the formation and have a uniformity coefficient (ratio of 40% retained size to 90% retained size) between 2 and 3 (Driscoll 1986). The screen-slot opening is then selected to retain 90% of the filter pack. The minimum practical slot size for monitoring well screens is 0.02 cm (0.008 in.) Figure 8.9 shows a grain-size distribution curve for a filter-pack material designed for an eight-slot screen. If the monitoring well is in silt or clay, all one can do is install an 8 slot screen and appropriate filter pack.

The filter-pack material should be approximately 5 to 7.5 cm (2 to 3 in.) thick. This means that a 5 cm (2 in.) diameter well screen should be installed in a borehole about 10 to 15 cm (6 to 8 in.) in diameter. The filter-pack material is normally extended 0.61 or 0.91 m (2 or 3 ft) above the top of the well screen to allow for settlement of the material during development.

8.4.5 Annular Seal

The annular space in the borehole above the filter pack must be sealed to prevent the movement of surface water downward to the filter pack. It may also be sealed to prevent vertical movement of groundwater from one zone to another or to isolate a discrete sampling zone. The seal should be made of a material that has a low permeability, bonds well to the natural formation and the casing, and expands after it has been

FIGURE 8.9 Grain-size distribution curve used to select an eight-slot screen for a monitoring well.



emplaced to ensure a tight seal. It should set up within a day or so and be durable and permanent.

Materials typically used for an annular seal are bentonite pellets, granular bentonite slurry, neat cement grout, bentonitesand slurry, and neat cement grout with a powdered bentonite additive.

Neat cement grout is a mixture of 42.5 kg (94 lb) of type I Portland cement with about 19 to 23 L (5 to 6 gal.) of water. Granular bentonite slurry is a mixture of 13.6 kg (30 lb) of untreated bentonite powder mixed with 56.7 kg (125) lb of untreated bentonite granules with 378.5 L (100 gal) of water. Bentonite-cement grout is a mixture of 2.3 kg (5 lb) of untreated powdered bentonite with 42.5 kg (94 lb) of type 1 Portland cement and 32 L (8.5 gal.) of water. Bentonitesand slurry is a mixture of 25 kg (55 lb) of untreated powdered bentonite with 378.5 L (100 gal.) of water and 10 to 25% sand by volume to make a slurry that weighs 9.6 kg/L (11 lb/gal.) All water used to make these slurries should be from a source that is fresh and known to be uncontaminated and free from floating oil.

Bentonite is a clay containing at least 85% sodium montmorillonite; it will swell to several times its original volume when thoroughly hydrated. This hydration takes place below the water table. However, bentonite has a high cation-exchange capacity and can affect the chemistry of water that comes into contact with it. Portland cement is used to make cement grout. When Portland cement cures, it is highly alkaline and can affect the pH of groundwater that comes into contact with it. Neat cement grout will shrink by at least 17% when it cures. The addition of bentonite to make a bentonite-cement grout significantly reduces the shrinkage problem. If neat cement grout or bentonite cement grout is used, the casing material should be either stainless steel or schedule 80 PVC due to the heat generated as the cement cures.

The materials available for an annular seal are not ideal. Although they can be used to make an impermeable seal, there is a chance they might affect groundwater quality in their immediate vicinity. This problem is mitigated if 0.61 m (2 ft) of fine sand is placed in the annular space above the filter-pack material or native sand opposite the screen. This keeps the annular seal material from coming into contact with the water entering the well screen.

Many hydrogeologists place a 0.61 m or 0.91 m (2 or 3 ft) layer of bentonite pellets above the fine sand if the pellets will be below the water table. The pellets will swell and keep the grout material from entering the filter-pack material. Clay pellets should not be used in the vadose zone due to lack of hydration and lack of swelling; a clay slurry should be used instead. If the top of the 0.61 m (2 ft) fine-sand seal is above the water table, then 0.61 m (2 ft) of granular bentonite may be placed prior to the addition of the annular seal.

8.4.6 Protective Casing

In order to provide physical protection for the investment in a costly monitoring well, as well as to protect from vandalism by individuals accidentally or intentionally putting foreign fluids and objects into a monitoring well, a locking protective steel casing or well vault is needed.

A protective casing extends several feet above the ground surface. It extends above the top of the monitoring well and has an inside diameter sufficiently large so that the hydrogeologist can reach inside and unscrew a cap from the monitoring well. It is set into a surface cement seal. For monitoring wells installed in freezing climates, a drain hole at the bottom of the surface casing is desirable to prevent accumulation of moisture that could freeze in the annular space between the protective casing and the monitoring well. (One of the authors has seen a stainless-steel monitoring well casing pinched shut by water that accumulated in a protective casing without a drain hole and then froze!)

In some applications, it is not practical to have a monitoring well that extends above ground—for example, in the driveway at a gas station. There are small well vaults available that can be used for protection for monitoring wells. However, they should be in places that are not going to flood; otherwise floodwaters could enter the aquifer via the monitoring well. If a well vault is used in a gas station or similar location, it should be clearly marked and should be distinctive from the fillers for underground storage tanks so that an inattentive person does not try to fill it with gasoline! A locking well cap without a vent hole should also be used.

8.4.7 Screen Length and Setting

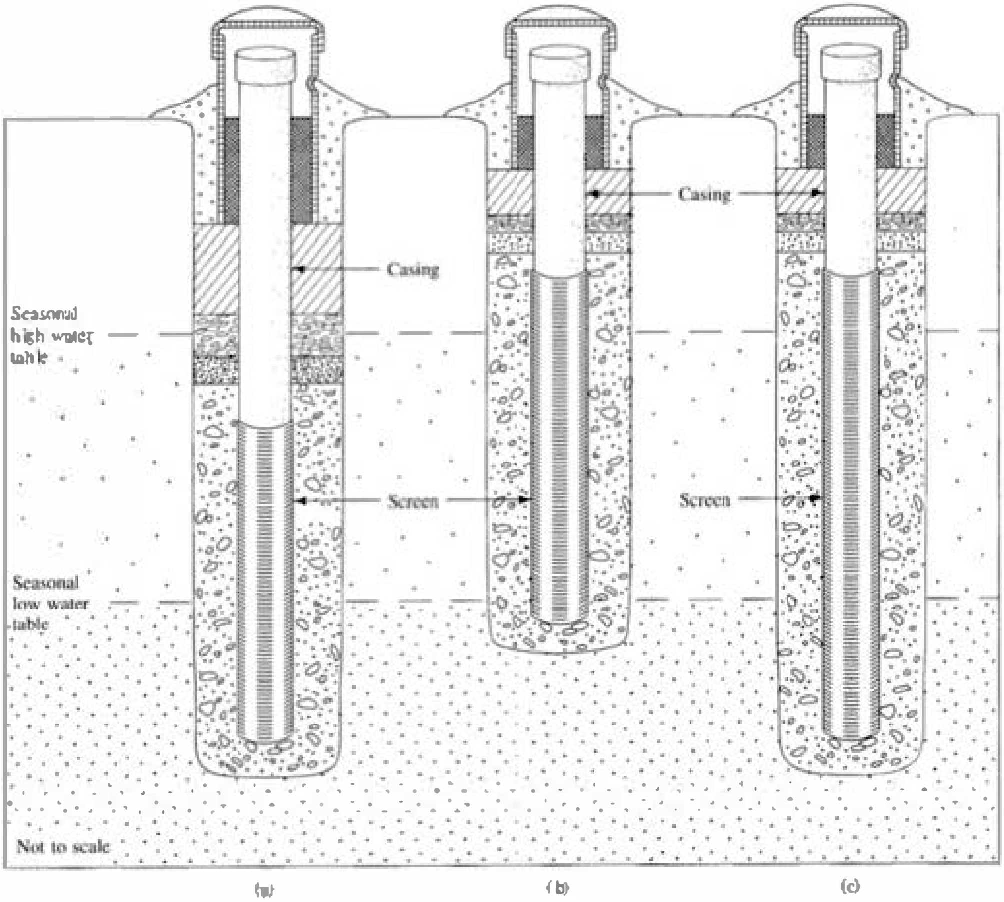
The hydrogeologist must decide on the length of the screen and the depth to which it will be set, based on the objectives of the monitoring program. Objectives could include monitoring the position of the water table, measuring the potentiometric head at some depth in the aquifer, collecting representative water samples from various depths in the aquifer, and detecting both light and dense nonaqueous phase liquids. Moreover, monitoring might be intended to detect the migration of groundwater containing contaminants into an aquifer or evaluating the effectiveness of removing contaminants from an aquifer. All might require different approaches.

To monitor the position of the water table or to detect the presence of LNAPLs, the screen must be set so that it intersects the water table. The screen must be long enough to intersect the water table over the range of annual fluctuation. In addition, the screen must be long enough so that when the water table is at its greatest depth below the land surface, there is enough of the screen remaining below the water table to contain sufficient water for a water sample. A water-table monitoring well will also be able to detect the presence of light nonaqueous phase liquids. In most applications the minimum length of the screen for a water table–monitoring well is 3 m (10 ft) with about 1.5 m (5 ft) above and 1.5 m (5 ft) below the water table. If the water table has more than 1.5 m (5 ft) of annual fluctuation, a longer well screen is needed. However, some governmental guidance specifies a maximum screen length of 3 m (10 ft) or less. Figure 8.10 shows examples of incorrect (a and b) and correct (c) placement of a multipurpose monitoring well intended to measure the position of the water table, detect floating nonaqueous phase liquids, and collect water samples from the upper part of the aquifer.

If the purpose of a monitoring well is to measure the potentiometric pressure at some depth in the aquifer, then the well is called a piezometer. A piezometer should have a relatively short screen length, 0.6 to 1.5 m (2 to 5 ft), so that the pressure that is recorded is representative of only a small vertical section of the aquifer. A piezometer can also be used to collect groundwater samples that are representative of a small vertical section of the aquifer.

Monitoring wells utilized to collect groundwater samples should be designed with respect to a specific groundwater monitoring goal. The concentration of groundwater

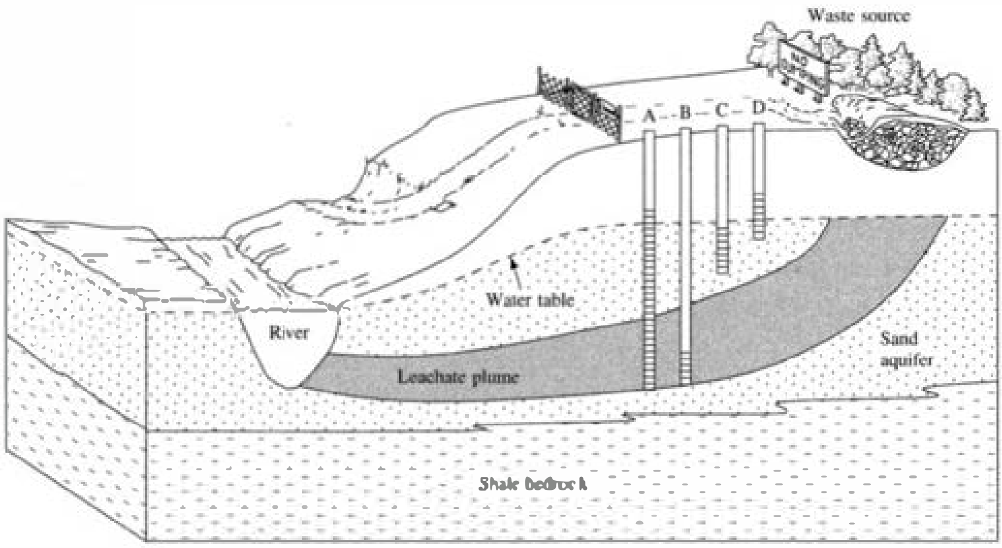
FIGURE 8.10 (a) Incorrect placement of water table-monitoring well screen. Seasonally high water table is above the top of the screen and floating, light nonaqueous phase liquids would be above the screen and not detected. (b) Incorrect placement of water table-monitoring well screen. Seasonally low water table is so far down in well that there is not enough water in well to collect a sample for chemical analysis. (The water table elevation could still be determined) (c) Correct length and placement of water table-monitoring well screen.



contaminants can vary vertically. If a monitoring well has a long well screen, it has a greater probability of intersecting a plume of contamination. However, a water sample taken from such a well may draw water from both contaminated and uncontaminated parts of the aquifer, resulting in a reported concentration that is less than that of the groundwater in the plume. This is illustrated in Figure 8.11.

The collection of such unrepresentative water samples may have serious implications for the implementation of groundwater regulations. While monitoring groundwater in order to find the actual concentration of contaminants in a plume, it may be necessary to use several monitoring wells or piezometers screened at different depths at the same location (well cluster). Alternatively, several nested wells or piezometers can be placed in a single large borehole, each well with a screened interval and surrounding filter pack at a different depth, and with impermeable grout placed in the borehole between the screened intervals of the individual wells. These clustering and nested techniques can be expensive, not only due to the initial cost of the wells but also due to the costs of multiple chemical analyses for each round of sampling. However, such

FIGURE 8.11 Effect of monitoring well-screen length on water-quality sampling. Monitoring well A is fully screened through the thickness of the aquifer. It intersects the plume of leachate but the reported concentration will be less than the actual concentration as water is withdrawn from both contaminated and uncontaminated parts of the aquifer. Piezometer B is also screened to intersect the plume of leachate. The reported concentration will be representative of the leachate. Piezometer C and water-table monitoring well D don't intersect the plume, indicating that it is deep in the aquifer.



a configuration will yield the greatest amount of information about the hydraulic head as well as the water quality, and is typically a recommended regulatory approach for groundwater monitoring. Additionally, there are multilevel monitoring wells that allow discrete vertical sampling in a single borehole, along with measurement of other hydrogeologic properties such as hydraulic conductivity and fluid pressure (head). Multilevel sampling will be discussed further in Section 8.4.9.

If a monitoring well is intended to serve as a warning that a plume of contamination is escaping from a potential source, then it should be screened in the most permeable parts of the aquifer initially to intercept rapid excursions, with the understanding that measured concentrations may be diluted and not representative of the most contaminated parts of an aquifer. Groundwater, and contaminants that it may be carrying, not only preferentially travel through the most permeable material but travel faster there as well. Hence, the leading edge of a plume of contamination will follow the most permeable pathway.

If the plume of contaminated water is following a zone or direction of high hydraulic conductivity, it may flow in a direction that is not parallel to grad *h*. This may mean that the location of the plume is not exactly down-gradient from the source. (Likewise, as has been discussed in earlier chapters, nonaqueous phase liquids can pool up and deflect off low permeability geologic layers in down-dip directions totally inconsistent with the directions of groundwater flow).

On the other hand, long term monitoring can have diffierent priorities. If an aquifer is contaminated and a monitoring well has been installed to monitor the progress of a remediation effort, the well should not be screened in the most permeable part of the aquifer. Many contaminants can become trapped in low permeability regions, and can become sequestered for long periods of time. The eventual slow release of these trapped pollutants can cause a classically observed "rebound" in aqueous concentrations long after the high permeability zones appear to have been clean. In pump and treat systems, the water will preferentially travel through and flush out the more permeable zones. A well screened in a permeable zone may indicate that the aquifer is rapidly being cleaned, but in fact less permeable zones located nearby may still have high concentrations of contaminants that have yet to be removed. Therefore in contaminant investigations, monitoring low permeability zones is also typically carried out.

In general, the concentration of a solute obtained from a monitoring well will be less than the maximum concentration present in the aquifer. The well screen provides a vertically averaged value of the solute in the aquifer over the length of the screen. If the contaminant plume is thinner than the length of the screen, then the vertically averaged concentration of the solute that is obtained from a monitoring well will be less than the solute concentration in the plume as the monitoring well will be drawing in some uncontaminated water and diluting the contaminated water. Chiang, Raven, and Dawson (1995) found that if a monitoring well is purged continuously for 24 hours prior to sampling, it will draw in uncontaminated water from the aquifer below the well screen, and the concentration of solute in the well could be as much as an order of magnitude lower than the vertically averaged solute concentration in the aquifer.

8.4.8 Summary of Monitoring Design for Single Screened Wells

Figure 8.12 illustrates a comparison of the final design of a water-table observation well and a piezometer illustrating the design elements discussed in this section for single well screen designs.

8.4.9 Multiple-level Wells and Multilevel Devices for Groundwater Monitoring

Because many field studies have suggested that most contaminant plumes exhibit significant concentration changes over small vertical distances (Smith et al. 1987; Dumble et al. 2006; Biswas et al. 2014; USDOE 2015), multilevel monitoring wells (particularly high resolution techniques) often produce orders of magnitude more information and more accurate results than single, long-screened wells. Natural hydraulic gradients within long-screened wells can create vertical flow and cross-contamination within the well, and make definition of the vertical distribution of dissolved contaminants impossible (Reilly et al. 1989; Church and Granato 1996; Elci et al. 2001; Neilsen 2005; McMillan 2014). This message has not gotten through to all municipalities, industries, and regulators, however. The U.S. Nuclear Regulatory Commission (NRC), in its 2003 NUREG 1569 Guidance (pages 5-42 and 5-43) for in situ uranium leaching operations correctly states:

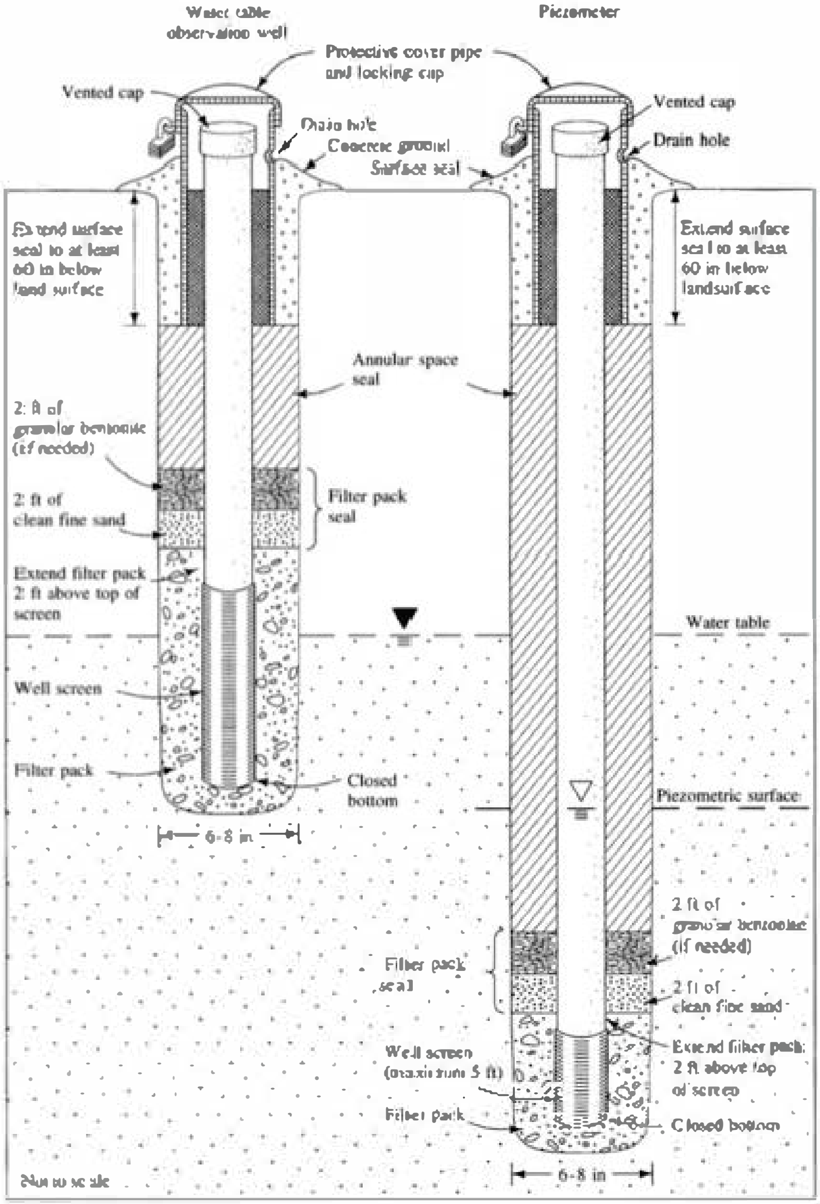
> *"Fully screened monitor wells sample the entire thickness of the aquifer. Therefore, excursions could not pass above or below the well screens. However, the concentration of the indicator parameters might be diluted and therefore may not provide timely warning that an excursion is occurring.*

But then the NRC Guidance continues:

> *"Partially screened monitor wells only sample the zone of extraction within an aquifer. These wells might miss some excursions, but would suffer less from dilution effects than fully screened wells. For most situations the staff favors fully screened monitor wells."*

In this document the U.S. Nuclear Regulatory Commission misrepresents multilevel sampling and does not recognize that high resolution multilevel monitoring: (1) is less likely to "miss" contaminant excursions than wells screened the entire aquifer

FIGURE 8.12 Construction details of a water-table observation well and piezometer.

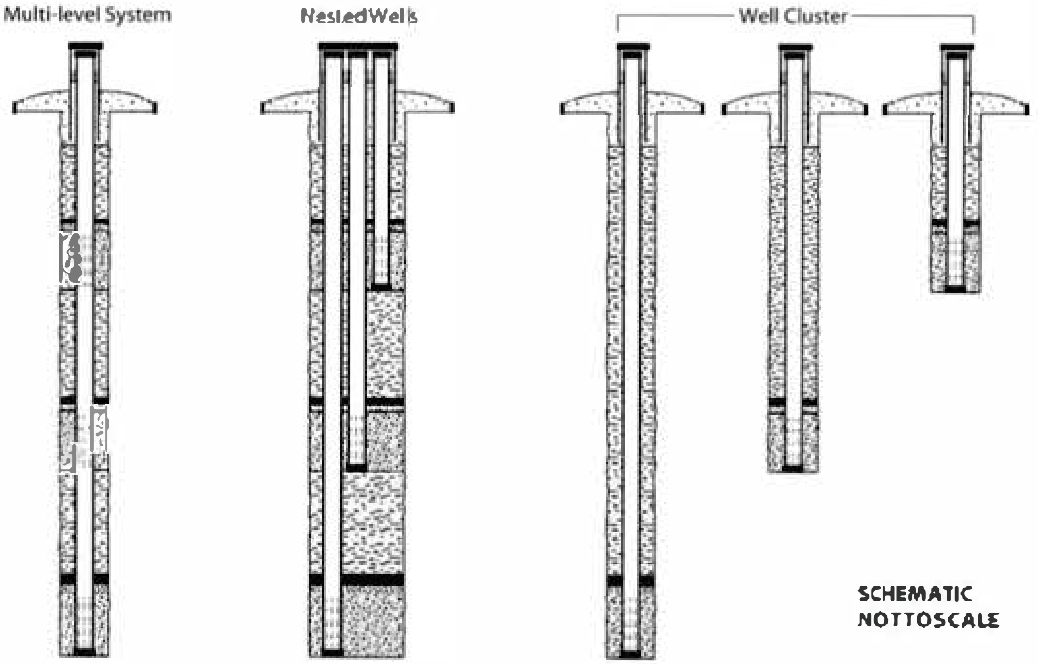


Source: Wisconsin Department of Natural Resources.

length, (2) has more possibility of accurately intercepting and quantifying excursions without bias, (3) reduces the possibility of contaminants migrating vertically within a monitoring well, (4) is many times more useful in post-mining remediation and site stabilization (both in directing cost-effective cleanup efforts and documenting their success), and (5) is much more protective of public health and ecological well-being.

Nested and Clustered Wells As mentioned in Section 8.4.7, to reduce dilution effects of long-screened wells and to preserve vertical sampling integrity, usually monitoring wells are installed in nested or clustered configurations (also called "multiple completions"), or with other types of multilevel sampling devices in a single borehole. Figure 8.13 illustrates multilevel sampling systems, nested wells, and well clusters. For nested wells, there is typically a single large borehole with several piezometers or wells placed in the same hole with screened intervals at different depths below the water table and with grout separating each different sampling depth. There has been some concern with the integrity of grout sealants in nested wells, and some criticism has been leveled at using these nested configurations. This is because of the difficulty in achieving effective and impermeable grout layers. These problems can be significant where the grout layers are thin because of many vertically close-spaced screen and grout intervals, or where there are many casing riser pipes in the nested well requiring grout to be placed effectively between the many pipes without void spaces developing. Clustered well groupings, on the other hand, sample different depths at the same locality by having several, closely spaced monitoring wells or piezometers with each in its own individual borehole. These individual wells typically can be placed within 1.5 m

FIGURE 8.13 Multilevel sampling systems, nested wells, and well clusters with above ground completion.



Source: E. Hughes and G. Aarons. 2014. *Well Design and Construction for Monitoring Groundwater at Contaminated Sites*. The California Environmental Protection Agency.

(5 ft) of each other. Under these circumstances it is possible to obtain an excellent seal to prevent vertical movement of water along the casing.

In nested wells, two or more monitoring wells or piezometers are placed in a large-diameter borehole with grout seal between screened intervals at different depths. For example, this could be done in an unconsolidated formation by (1) driving a 25.4 or 30.5 cm (10 or 12 in.) diameter casing with a cable tool rig to the depth of the bottom piezometer, (2) installing the deepest piezometer, (3) pulling back the casing and installing the filter pack and seal for the deepest piezometer, (4) pulling back the casing and grouting up to the level of the next piezometer, (5) allowing the grout to harden, (6) installing the next piezometer, (7) pulling back the casing and installing the filter pack and seal for the second piezometer, and (8) pulling back the casing and grouting up to the level of the third piezometer, etc.

Simple Manufactured Multilevel Samplers It is possible to install inexpensive multilevel sampling devices in a sandy aquifer. One early manufactured model of such a device consists of a rigid PVC tube, inside of which are multiple tubes of flexible tubing. Each tube leads from the surface and ends at a different depth. Each has a port into which a groundwater sample can be drawn. Sampling ports can be closely spaced vertically, so that very detailed vertical sampling can be accomplished. Water is withdrawn from the tubing by applying suction, so the water table had to be less than 7.6 m (25 ft) below the surface in these simple early multilevel sampling wells. These rudimentary methods include a variation by fastening a bundle of flexible tubes, each of a different length, to the outside of a rigid PVC pipe that acts as a spine. Several types of simple manufactured multilevel samplers have been developed (Pickens et al. 1978; Cherry and Johnson 1982; Ronen et al. 1986).

Barker et al. (1987) evaluated the bias in samples that can be introduced by the use of multilevel piezometers constructed out of flexible tubing. Leaching of plastics from the plastic tubing is one problem. Another problem is the sorbing of organics by the tubing. Both these problems can be minimized by using Teflon® tubing and thoroughly purging the tube prior to sampling, although Teflon® is porous and can have some minimal memory effect. Many types of flexible tubing can actually transmit organics from groundwater through the tubing wall to the sample water in the tubing. This is especially true for polyethylene tubing. Samples drawn from below an organic plume may indicate contamination, when in fact the organics are being transmitted across the plastic tubing from adjacent contaminated groundwater. This can apparently occur even with Teflon® tubing. For this reason, multilevel piezometers, designed so that the flexible tubing is exposed to groundwater, may not be appropriate for monitoring plumes of organic contaminants. If the flexible tubing is contained within a casing, such as in Figure 8.14, this should not be an issue because the tubing doesn't come into contact with the groundwater.

A simple multilevel sampler can be installed by using a hollow-stem auger. The device is constructed at the surface and lowered to the desired depth through the augers. It is not possible to develop the sampling ports, so this device is best suited for clean, sandy sediment. No filter pack or grout is used in this very simple construction. The augers are withdrawn and the native sand is allowed to slump around it. One disadvantage of this device is that it is usually not possible to measure water levels with it.

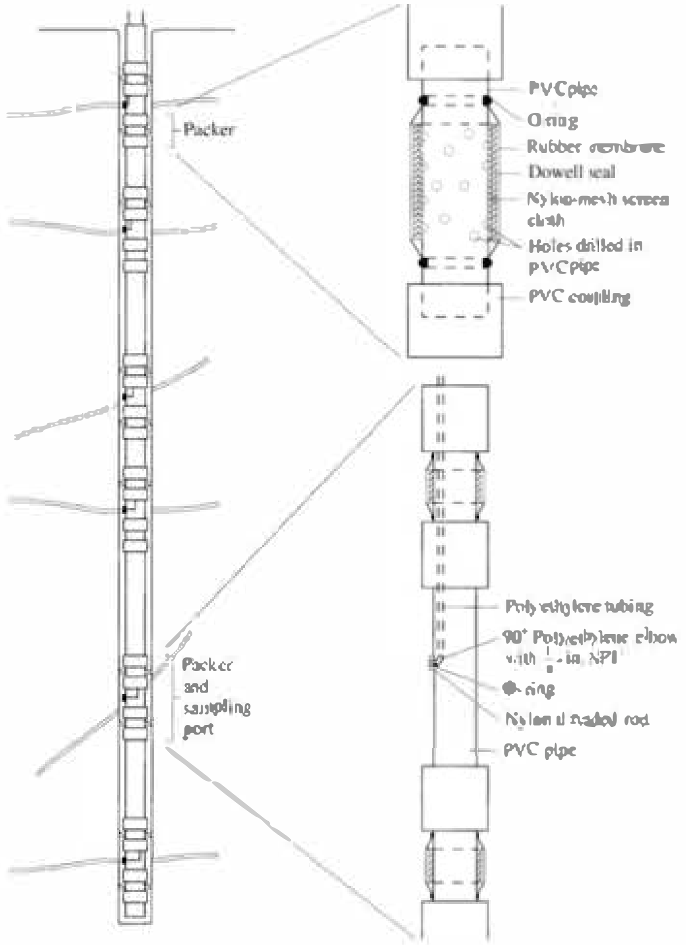
generally expensive, these multilevel wells have advantages of allowing fewer wells and subsurface disturbance at each site, collection of fluid samples without repeated purging, prevention of vertical flow within the borehole, less possibility of cross contamination with discrete depth sampling, and options for automated sampling at any number of multiple depths in a single well.

Flexible Liner Systems Another type of multilevel sampling practice employs the flexible liner system (developed by FLUTe™) and represents a significant advancement over a simple multilevel system. Similar to the simple system above, it has a series of internal tubes inside a liner which allow sampling and pressure measurement at selected intervals down hole in uncased wells. In hard rock consolidated systems, downhole television logging in uncased boreholes can identify exact locations of fractures (and other depths of interest) and tubing can be customized to sample those depths. In this system, a flexible polyurethane–coated, nylon fabric liner is emplaced with eversion (turning inside out) from a shipping reel. The liner is pressurized (pneumatically or hydraulically), inflated, and extends downward from internal pressure head. The liner deploys from the ground surface downward, creating a sealing pressure that prevents vertical flow outside the liner, and has tubing (usually made of polyvinylidene fluoride—PVDF) inside the liner from ground surface to vertically displaced subsurface ports. The system is versatile in that the inflating liner can be placed in boreholes that change direction due to directional drilling, and can move in varying diameter boreholes, such as narrow, shallow surface casing to wider uncased sections below, or narrowing or telescoping boreholes. Interestingly, this system can be modified to measure discrete depths of nonaqueous phase liquids (NAPLs) by use of a hydrophobic "ribbon" sampler. In this application, a porous, continuous, hydrophobic sleeve, that is impregnated with a powdered oil dye (Sudan IV), is deployed concurrently on the outside of the flexible liner. The hydrophobic material readily "wicks" NAPLs and when retrieved identifies depths of NAPL contamination. The hydrophobic sleeve is replaceable for additional deployments on the same flexible liner (Riha et al. 2000; USEPA 2004).

Packer Systems A type of multilevel sampler optimal in bedrock boreholes involves straddle packers, which when inflated isolate a section of a borehole for hydrological testing and sampling. In this design (Figure 8.15) packers are located above and below each sampling port; when they are inflated, they seal off that part of the borehole and are particularly effective in segregating individual fractures or groups of fractures for analysis in uncased boreholes. Packers can also be used within well casing in less consolidated material. Packers can be permanently installed, or they can be removed and reused if desired. Though designs vary, the inside of a typical single packer is a perforated pipe forming the inner packer body, covered with a porous plastic sleeve and an expansion sleeve. External to that is a gum rubber inner sheath, often enveloped in woven Kevlar® and encased in a durable gum rubber outer sheath, with the assembly secured on either end with stainless steel clamps. One type is the Solinist® Waterloo System with includes multi-purge manifold well heads and dedicated sampling pumping and transducers.

Interesting specialized variants of packer systems have been constructed for specialized applications. Packers have been used in small, bedrock boreholes in conjunction with seals created by injecting grout into a flexible cylindrical impervious fabric liner. These liners have a diameter slightly larger than the borehole, ensure that the

FIGURE 8.15 Multilevel groundwater sampling device for use in fractured rock aquifers.



Source: J. A. Cherry and P.E. Johnson. 1982. A multilevel device for monitoring in fractured rock. *Groundwater Monitoring & Remediation* 2:41–44 Used with permission.

entire borehole above a screened interval is sealed, and prevent grout from entering fractures and altering groundwater chemistry (Parker et al. 2015; Pierce et al. 2015).

8.5 Installation of Monitoring Wells

8.5.1 Decontamination Procedures

Because the purpose of drilling a monitoring well is to collect a sample of water and analyze it for very small concentrations of chemicals, it is highly desirable not to introduce any chemicals into the aquifer as a part of the well-drilling and installation procedure. The process of cleaning the equipment and supplies that will be used is called **decontamination**.

When materials are manufactured, they may become coated with substances such as grease and oil. Therefore, unless the manufacturer specifically guarantees that the article has been decontaminated and has shipped it in a well-sealed wrapper, it should be decontaminated. Equipment that has been used at a contaminated site should be assumed to be contaminated and should be decontaminated before it is used at another site. Even at the same site, if a drill rig or a bailer is used at different wells, decontamination is required to prevent cross contamination (contamination from one area being introduced into a clean area) that could occur.

There is wide variability in required and recommended decontamination procedures in the United States between the USEPA and the various states (Mickam et al. 1989). The hydrogeologist must consult with the appropriate regulatory authority to determine if a specific decontamination procedure is required. In the absence of a specific requirement, the following generic procedure should adequately clean equipment and supplies. In some cases not all the steps are required. For cleaning large equipment such as a drilling rig, a specific area must be set aside and a decontamination pad must be constructed to capture all the fluids used in the process. If the rig is contaminated, wash water from it may also become contaminated. Be careful that any solvents used aren't accidentally released to the environment. Small tools such as bailers and Shelby tubes can be cleaned in buckets set on a polyethylene sheet. Sampling pumps can be cleaned by running various wash solutions through them, as well as washing the exterior.

The following steps are used to clean drilling and soil sampling equipment including drill rig, augers, drill rod, tools, sampling tubes, etc.:

1. Use a wire brush or similar equipment to remove all dried sediment and thick accumulations of grease.
2. Wash the equipment with a soft brush and water with phosphate-free detergent.
3. In extreme conditions organic residues can be removed by washing the equipment with an organic solvent such as methanol or propanol. Don't use solvents such as trichloroethene that might be expected to be found at a hazardous waste site.
4. Clean and rinse the equipment with potable water.
5. Rinse the equipment with deionized water.

Steam cleaning with a pressure sprayer can be used in step 4 for equipment that can withstand the heat and force of the spray. After equipment has been decontaminated, it should not be placed on the ground. It can be wrapped in clean paper or aluminum foil or set on polyethylene sheets.

Sampling equipment should also be decontaminated between uses. If the equipment has not come into contact with nonaqueous-phase liquids, rinsing with potable water and washing thoroughly with phosphate-free detergent, including scrubbing the inside of tubes with a bottle brush, followed by a potable-water wash and then a deionized-water rinse, should suffice. If the equipment has come into contact with nonaqueous-phase organic liquids, then an initial solvent wash may be necessary.

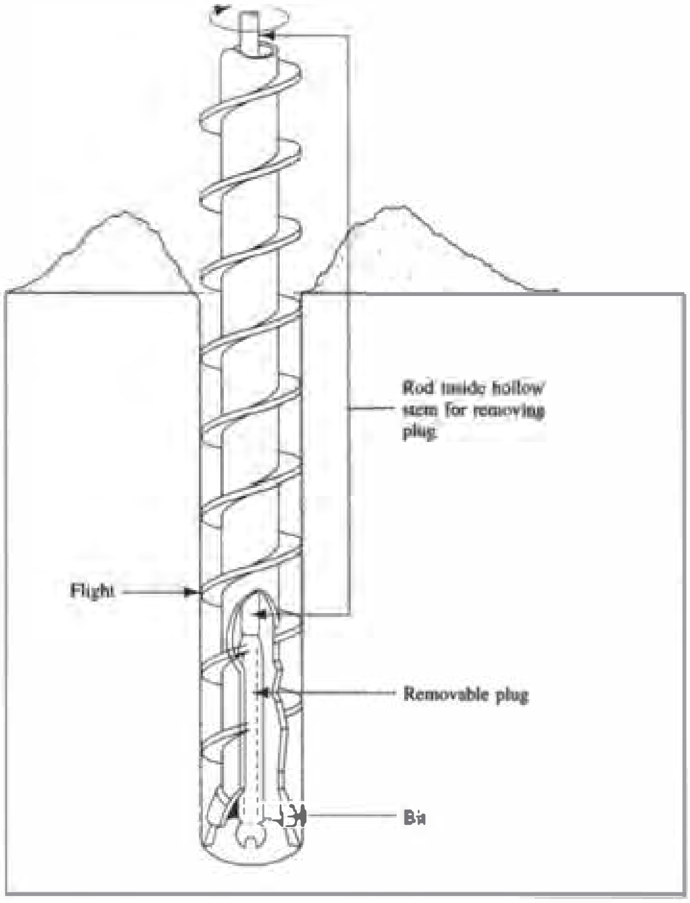
The cost of decontamination of sampling equipment and the uncertainty introduced by solvent washing has led many hydrogeologists to specify dedicated sampling equipment in each well. Disposable bailers are also available that are less expensive than the cost of labor involved in cleaning reusable bailers.

8.5.2 Methods of Drilling

There are a number of methods of drilling that are appropriate for installation of monitoring wells. When working in shallow unconsolidated formations, hollow-stem augers are commonly used. If a well is to be drilled deeper than about 30.5 m (100 ft) or into bedrock, a rotary drilling method may be appropriate. Cable-tool drilling is an excellent way of installing monitoring wells in both unconsolidated and consolidated formations, but it is slow and may be expensive. Hollow-stem augers with a bit that contains carbide teeth can also be used in weak, indurated rock. Newer techniques include sonic drilling and directional drilling.

Hollow-Stem Augers Hackett (1987; 1988) presents an authoritative discussion of all aspects of drilling with hollow-stem augers. A hollow-stem auger looks a little like a large, untapered screw (Figure 8.16). The auger flights are constructed around a hollow pipe. A drilling rig rotates the augers and a bit on the end of the auger loosens the sediment, which is then brought up to the surface by the rotating auger flights. The cuttings accumulate at the surface and must be shoveled away from the augers. Figure 8.17 pictures an auger-drilling rig. The auger is advanced into the ground as it is rotated. A plug on the end of a rod inserted through the hollow-stem may be screwed into the bit to seal the end of the opening and prevent sediment from coming up inside the hollow-stem. Alternatively, a nonretrievable plug can be placed in the end of the

FIGURE 8.16 Hollow-stem auger drill rod and bit.



Source: M. L. Scalf et al. 1981. *Manual of Ground Water Sampling Procedures.* National Water Well Association. Used with permission.

FIGURE 8.17 Hollow-stem auger drilling rig.

Photo credit: C.W. Fetter.

bit. This plug is knocked out of the end of the augers when the final depth is reached and it is no longer needed. However knock-out plugs preclude the collection of soil and water samples during drilling.

One advantage of drilling with hollow-stem augers is that drilling fluids and mud are normally not required. Circulation of drilling fluids has the potential to spread contaminants throughout the borehole. Drilling mud is a viscous liquid needed in mud-rotary drilling that can line the borehole and partially seal it. However, when drilling in formations with cohesive layers, the auger bit may smear clay from the cohesive layers so that it mixes with sand and gravel layers at the perimeter of the borehole. Auger drilling typically can advance about 15.3 to 30.5 m (50 to 100 ft) per day if samples are being taken. Occasionally, downward progress can cease if a large cobble or boulder is encountered (called auger refusal).

Augers usually come in lengths of 1.5 m (5 ft). One flight is advanced into the ground and then the drill stem is disconnected and another flight is attached to the augers in the ground. At this time samples of the formation ahead of the auger bit may be taken. The plug on the end of the bit must be removed before sampling can occur. The maximum depth at which hollow-stem auger drilling can normally be used is 45.8 m (150 ft) (Hackett 1987); as a practical matter, it rarely exceeds 30.5 m (100 ft).

Some loosely consolidated sands, called heaving sands, can enter into the borehole when the plug is being removed. This problem can be avoided by keeping the hollow stem filled with potable water when the plug is removed. The potable water should not contain any contaminants that might be found in the groundwater. If no formation sampling is planned, then a knock-out plug can be used to prevent the introduction of heaving sands into the hollow-stem during drilling. The knock-out plug can be removed after the final depth is reached by pushing down with the well casing if it is stainless steel; otherwise it will be necessary to use a rod prior to the time that the well is installed.

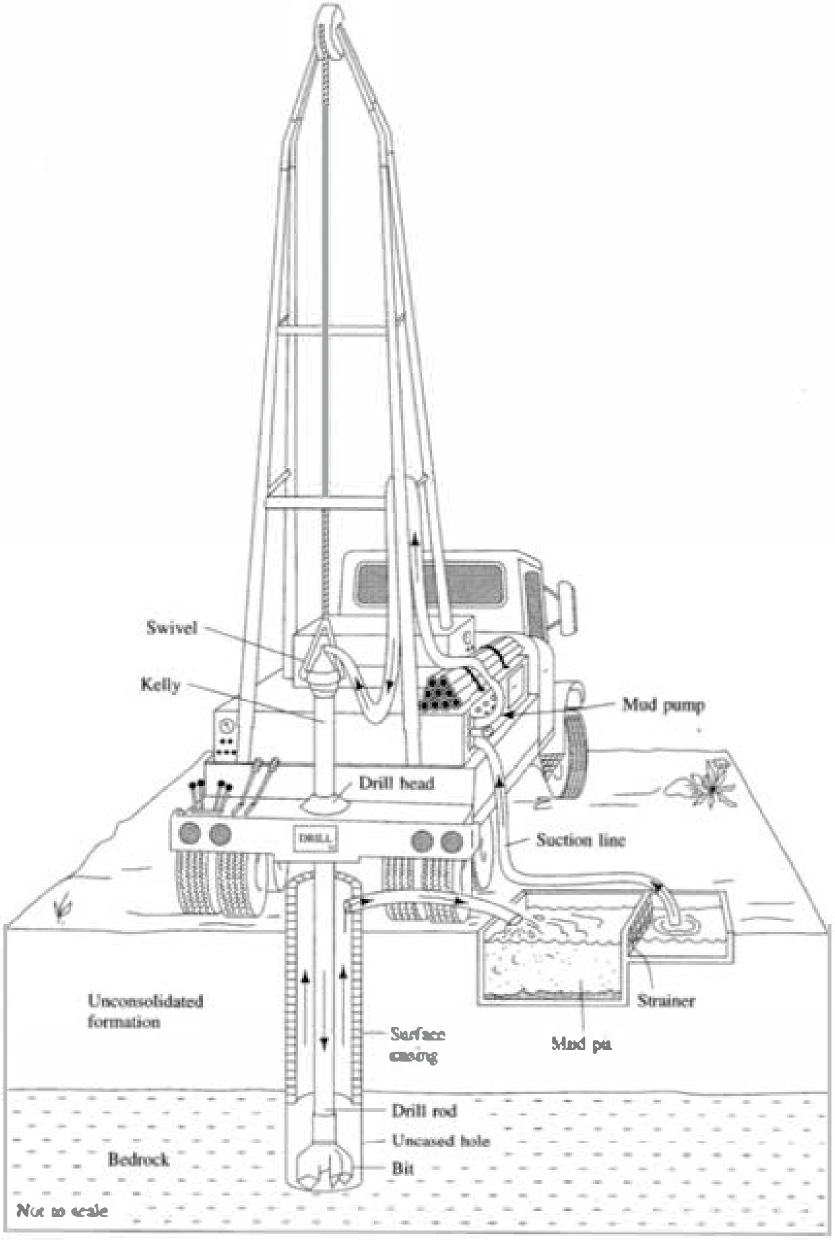
Hollow-stem auger drilling can also be used to sample water quality at various depths during drilling. At a selected horizon the plug at the end of the hollow stem is removed. A well point on the end of a rod is lowered to the bottom of the augers and then is driven ahead of the bit by hammering or hydraulic pressure. The well point is developed by pumping until clear water is obtained. A sample of groundwater at that depth is then obtained. It is best if potable water is not used in the borehole during this procedure, because it could interfere with the groundwater quality. If there is heaving sand inside the augers, the well point can be driven through it. Alternatively, a slotted hollow-stem auger can be used (sometimes called a screened hollow-stem auger or Keck auger) which allows water to flow into the stem.

Keeley and Boateng (1987) suggested a modification of the hollow-stem auger drilling technique, in which a temporary casing that is larger in diameter than the auger bit is employed. The auger is advanced several feet and then the temporary casing is driven to the depth of the auger bit by repeatedly dropping a heavy weight on the top of the casing. The advantage of this modification is that it prevents mixing of soil horizons as the augers rotate.

Mud-Rotary Drilling Mud-rotary drilling can be used in both unconsolidated and consolidated formations. It is fairly rapid, up to 30.5 m (100 ft)/day, and can be used to depths far in excess of most that might be required for groundwater-contamination studies. A heavy drilling fluid, made by mixing various additives to water, is circulated in the borehole by pumping it down the inside of hollow drill rods. The mud rises back to the surface in the annular space between the borehole wall and the drill pipe. The rising mud carries with it the drill cuttings, which settle out in a mud tank at the surface. Figure 8.18 shows the circulation pattern for mud-rotary drilling. Alternately, reverse circulation is often used where drilling fluid goes down the annular space and returns upward through the drill pipe (opposite of Figure 8.18). This method, discussed below, can allow greater upward velocities and larger, heavier cuttings can be retrieved.

One advantage of mud-rotary drilling is that the borehole will remain open after the string of drill pipe and the bit are removed. This means that a complete suite of geophysical logs can be run on the hole, which is kept open by the weight of the mud

FIGURE 8.18 Circulation of drilling fluid in mud-rotary drilling.



inside it. However, the fluid in the drilling mud can penetrate the native formations and alter the groundwater geochemistry. The coating of drilling mud on the borehole walls may be difficult to remove. This can impede the hydraulic connection between the well and the formation. Bentonite-based drilling muds may remove metals from the groundwater and affect the chemistry. Certain additives to drilling mud can also be problematic from a water quality standpoint. Because of the potential problems with drilling mud, rotary drilling may not be as suitable for groundwater contamination studies as hollow-stem augers. However, under many hydrogeologic conditions it is the only drilling method that is practical. Good well development to remove the residual drilling mud in the screen zone is very important

Air-Rotary Drilling If the monitoring well is to be installed in bedrock, then air-rotary drilling may be considered. First a surface casing needs to be installed through any unconsolidated material. Typically this is done by using mud-rotary drilling. The surface casing is large enough that the air-rotary bit can fit inside of it.

The fluid used in air rotary is compressed air, which is blown down the inside of the drill pipe. The air then blows the cuttings back up the annular space, where they accumulate around the borehole. When the water table is encountered, the air may blow groundwater out of the borehole as well. If this occurs, it is possible to determine when the water table is encountered and the relative yield of the well. However, the air may also force the water back into the formation. Air-rotary drilling using a down-hole percussion bit can drill up to 18 m (60 ft)/hr. Samples are collected as chips, which are brought to the surface with the return flow of air and water.

Air-rotary drilling is fast and can go to depths of a thousand feet of more. Because air is the drilling fluid, contamination problems are minimized. However, the drillers may want to add a foaming agent to the air (air/polymer mix) as it goes down the hole. The foam helps to float the chips to the surface, but it consists of organic chemicals such as isopropyl alcohol, ethyl alcohol, and alcohol ether sulfate, and its use should be avoided. The air compressors have air filters, which need to be in good working condition; otherwise, lubricating oil and other contaminants may be introduced into the borehole with the compressed air. Percussion hammers used for air-rotary drilling may also need lubricants.

Air-rotary drilling may introduce volatile organic compounds into the atmosphere as well as blowing contaminated dust out of the borehole.

Reverse-Rotary Drilling In reverse-rotary drilling the circulating drilling fluid drains down the annular space and then is pulled up the center of the drill stem by a suction pump located on the drill rig. Because the drilling fluid rises with a much greater velocity in reverse-rotary than in mud-rotary drilling, a much less viscous drilling fluid is used. In many cases clear water mixed with the drill cuttings is all that is necessary. This gives the reverse-rotary method an advantage over mud-rotary drilling, since it is much easier to develop the well because there is no mud wall on the borehole to break down. However, reverse-rotary drilling is more expensive than the mud-rotary method, and the minimum borehole diameter is 30.5 cm (12 in.)

Cable-Tool Drilling Cable-tool drilling is one of the oldest drilling methods and has been used widely for the installation of water wells. Although the drilling equipment is less expensive than for some other methods, the drilling is slow and overall costs may be expensive due to high labor costs.

In cable-tool drilling a heavy bit is located at the end of a tool string hanging from a cable. The drill rig repeatedly lifts and drops the hammer, which breaks up consolidated rock or loosens unconsolidated sediment. A steel casing is driven into the formation behind the bit. When the bottom of the casing fills with broken rock and sediment, the tool string and bit are removed, and a bottom-loading bailer is used to remove the accumulated cuttings. Below the water table, the groundwater and cuttings make a slurry. Above the water table, water must be added to make a slurry so that the bailer can be used. Drive casing is needed only until bedrock is reached. In most bedrock formations the hole will stay open without drive casing. Figure 8.20 shows the tools used for cable-tool drilling.

Advantages of cable-tool drilling include the fact that no drilling fluids are used and that nothing is circulated through the well. Both factors serve to limit contamination problems. It is easy to collect representative samples of the formation during bailing of the casing. Well points can be driven ahead of the casing in unconsolidated formations for the collection of water quality samples. Cable-tool drilling can be used to depths in excess of 305 m (1000 ft). This method however can be extremely slow for deep boreholes, as the tool string and bit must be removed from progressively deeper depths to allow insertion of a bailer for the removal of cuttings, the bailer must then be removed from depth, and the tool string and bit reinserted. As depths increase the time required for this process compounds.

Sonic (Vibratory) Drilling Sonic drilling uses high frequency mechanical oscillation with rotary motion to fluidize subsurface material. As soils and formational materials experience liquefaction, temporary porosity reduction and inertial effects reduce friction on the drill string and drill. The destroyed shear strength of the subsurface formations allows rapid downward advancement in most instances. Advantages include a minimal amount of formation disturbance, reduction of drill spoils and waste compared to other methods, the method can produce continuous cores, sonic does not require circulating drilling fluids, and it can be converted to air or mud rotary or cable tool percussion techniques. Its disadvantages are that the technique is not as readily available as other techniques and is generally more expensive initially.

Other Types of Drilling Other types of drilling include percussion rotary air blast (RAB), air core drilling, and diamond core drilling. RAB combines rotary fluid circulation with the percussive impacts of a pneumatic, reciprocating, piston-driven "hammer" to pulverize rock. This is an effective way to advance drilling downhole in consolidated rock and mixed consolidated/unconsolidated terrain. Like most rotary fluid circulation techniques, circulation can be lost if a large cavity is encountered such as caverns in karst areas, lava tubes in volcanic regions, or human-made features such as subsurface mine shafts. Air core drilling cannot penetrate consolidated rock as well as RAB; it normally is used on weathered regolith or other unconsolidated material. The air core method utilizes hardened steel or tungsten blades to cut into the ground, and collects a more representative sample of solid material compared to RAB. Diamond core drilling is a very slow method used in hard, consolidated rock. It produces a rock core that can be inspected. Often fracture patterns, fracture orientation and aperture size can be determined from these cores. Diamond coring for short intervals can also be used on smaller consolidated formations encountered while drilling with other methods.

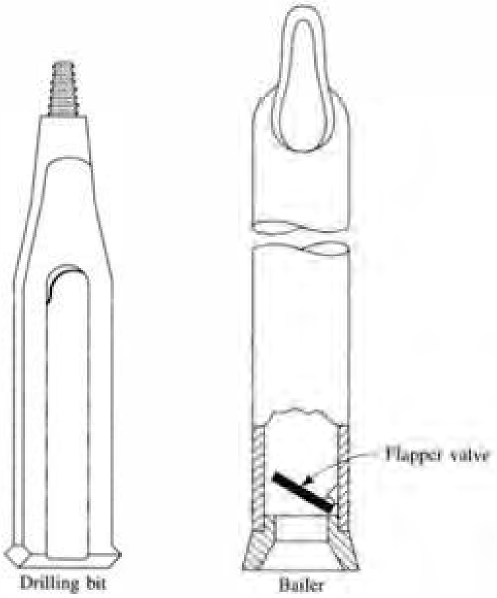
When drilling in areas with muddy or spongy soils, it may be necessary to build temporary roads, e.g., laying down a layer of crushed rocks to permit the heavy drilling equipment to reach the drilling locations without getting stuck (Figure 8.19). Alternatively, portable coring drilling machines, originally designed for mineral exploration, can be used to advantage to install hard rock monitoring wells in sites that are hard to access, in remote locations and wilderness sites, and in eco-sensitive areas. Drills, such as the Shaw Portable Core Drill and the Winkie Drill can produce small diameter holes amenable to fractured rock monitoring (Parker et al. 2015).

FIGURE 8.19 When drilling in difficult-to-access areas or where soggy soils prevent heavy drill equipment to reach the site, a portable drill rig can be used. Shown here is the installation of an 8-inch bedrock well with a portable air-rotary drill rig in a rice field in Goa, India. The drill rig is powered by pneumatic pressure provided by a truck-mounted compressor which is safely stationed on hard ground approximately 100 m (300 ft) away.

Photo credit: T. B. Boving.

Directional Drilling Directional drilling involves the placement of nonvertical boreholes. Most of the above drilling methods are able to be used in slant drilling (excepting cable tool), where in the simplest application, the mast or drill rig tower is tilted and drilling proceeds at an angle. This modification allows great horizontal access under structures such as buildings, landfills and highly contaminated areas. Drilling through a subsurface NAPL pool, for example, can be avoided in some cases. Traditional drilling methods can be difficult to control in slant drilling because of unwanted deflection, as in slant auger drilling. As slant auger drilling proceeds, cuttings which fall on the bottom side of the hole can eventually force the bit upward into a more horizontal line.

FIGURE 8.20 Tools used for cable-tool drilling.



Controlling wellbore trajectory has become more of a refined technology in recent years. Most modern directional drilling begins in a vertical direction until a desired kick off point where the well inclination is changed using drilling motors and rotary steerable systems. While the use of directional drilling is much more common in oil and gas development, its applications to contaminant hydrogeology are plentiful, particularly where surface or near-surface features or contaminant hotspots must be avoided, but geologic, hydrogeologic, and contaminant information from greater depths directly under these areas is needed.

8.5.3 Drilling in Contaminated Soil

When drilling at a contaminated site, the cuttings that are brought to the surface may be contaminated. Drilling personnel should wear appropriate protective clothing and, if necessary, use breathing apparatus. A large, heavy sheet of plastic should be placed in the work area, and the drill bit should be advanced through a hole in the center of the plastic sheet.

The cuttings augered to the surface can be collected from the plastic sheet and put into containers for proper disposal.

8.5.4 Sample Collection of Solid Material During Drilling

Samples of unconsolidated materials and rock are needed to delineate the geology of a site. They are collected by drilling **borings**. Borings may be made just for sample collection, or they may be made as a part of the process of installing a monitoring well. Borings may be made by any of the methods of drilling discussed in Section 8.5.

During the drilling process, earth materials are brought to the surface. During the augering process, soil and sediment ride up the augers; in the mud-rotary process, earth materials come up mixed with the mud; in air-rotary drilling there is a slurry of rock and water brought to the surface by air pressure; and cuttings are brought to the surface with a bailer in cable-tool drilling. In all cases the samples are disturbed, some (such as the samples on the augers) more than others. In addition, it may be difficult to tell the exact depth represented by the sample. Fine layering of sedimentary materials cannot be distinguished in such samples. An imprecise model of the geology can be constructed from these samples, but for more details, undisturbed samples should be collected.

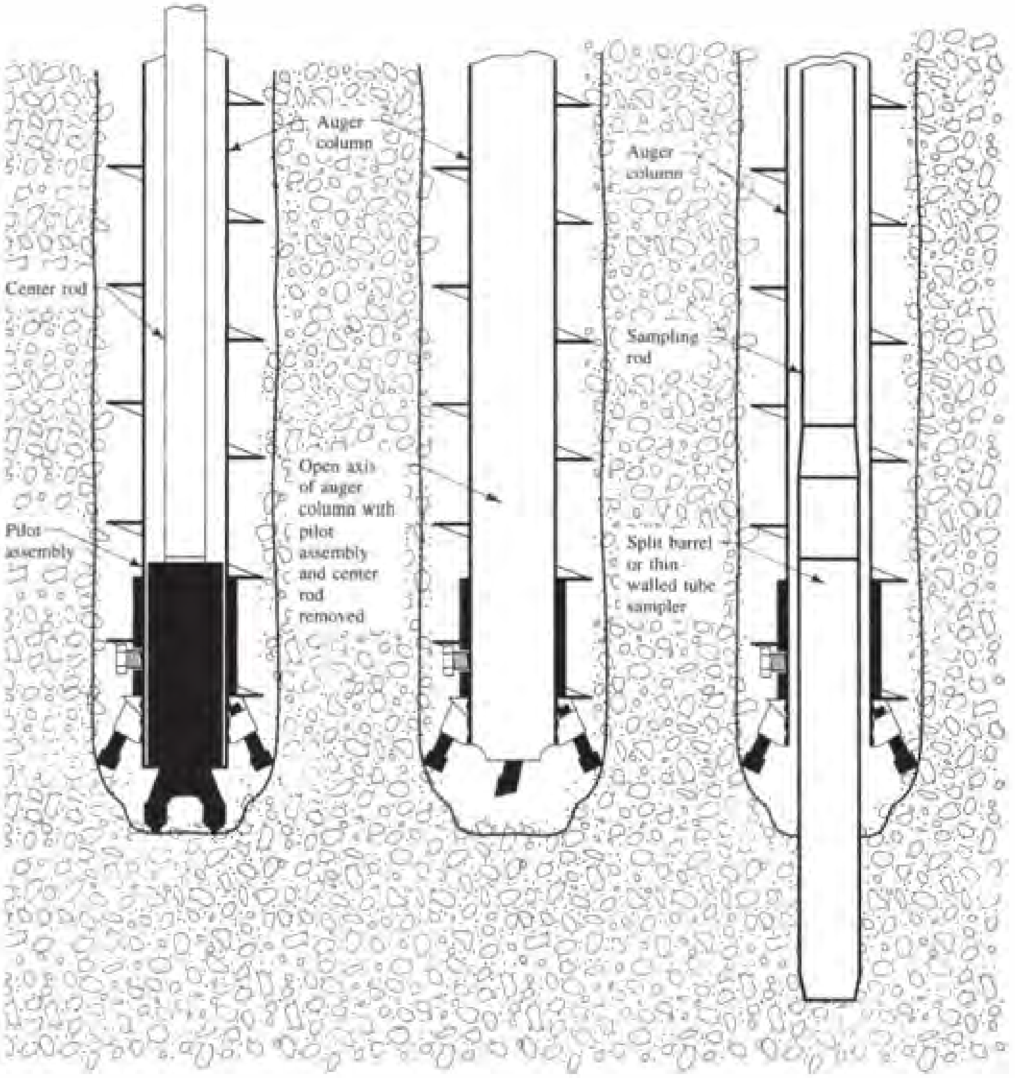
A **core sample** is collected for consolidated material by obtaining a **rock-core sample** with a special drilling bit studded with industrial diamonds as mentioned above, or for unconsolidated material with special sampling tubes that are driven into the unconsolidated formations. Interpretation of hard rock cores in consolidated, fractured media suspected of contamination has become quite advanced in the last few decades and can include field geologic core analysis, and laboratory analysis (Parker et al. 2012). The initial field analysis involves determination of the number of fractures, fracture orientation and aperture size, and fracture porosity measurement. This analysis can also observe any occluding chemical precipitates filling (or "healing") the fractures. The orientation of fractures from several core holes can be analyzed to give a three-dimensional view of fractures at a site. Combined with downhole geophysics and tomographic methods, field data can give considerable insight into a fractured rock media and the potential for contaminant movement.

Laboratory measurement of bedrock cores can quantify contaminants in the core, simulate degradation microcosms, and provide core physical, mineralogical, and microbial measurements to determine contaminant phase and mass distribution. Typically, most groundwater flow in fractured consolidated rock occurs through interconnected networks of fractures and secondary porosities, surrounded by low permeability blocks of rock. In adjacent blocks with porosity greater than 1% however, particularly in sedimentary rocks, an appreciable mass of a contaminant can move into the rock matrix. This matrix diffusion in low-permeability blocks or effectively reduces the mass flux in the surrounding fractures (Parker et al. 1997; Parker et al. 2010; Kennel 2008).

Great care must be exercised in the interpretation of rock cores or unconsolidated borings, particularly in the measurement of subsurface contamination or characterization of stratigraphy based on just a few samples. The absence of contamination in a core could be the result of preferential flow (also called "funneling," "fingering," wetting front instabilities, or Rayleigh Taylor instabilities), allowing contamination to completely bypass a boring but still be present in massive amounts. Likewise, unwarranted extrapolation of meager stratigraphic data, particularly assuming continuous layers of unvarying properties, is a common problem particularly in situations where incomplete site characterization goes unchallenged. There are two main types of sampling tubes for unconsolidated samples. Both types of tubes can be used with hollow-stem augering and mud-rotary drilling if the drill rod and bit have a provision for a sample tube to be extended through them into the formation ahead of the bit. Figure 8.21 shows the sequence for the extension of a sampler through the end of the bit of a hollow-stem auger. The sampler is driven or pushed into undisturbed formation ahead of the bit. In cable-tool drilling the drill bit is removed from the borehole and the sampler is lowered on a rod or cable.

A **Shelby tube** is a thin-walled tube that can be screwed to the end of a rod, lowered to the bottom of the drilled hole, and pressed into cohesive sediments by using hydraulic pressure reacting against the weight of the drill rig. These samples are said

FIGURE 8.21 Sequential steps for the collection of a core sample through a hollow-stem auger.



Source: G. Hackett. 1987. Drilling and constructing monitoring wells with hollow-stem augers part 1: Drilling considerations. *Groundwater Monitoring & Remediation* 7:51–62. Used with permission.

to be *undisturbed*, although they are in fact minimally disturbed. The precise method of collecting a Shelby tube sample is described in method ASTM D1587 (American Society for Testing and Materials 1983). The sample can be extruded from the Shelby tube in the lab and trimmed into a permeameter for a permeability test. Details of the microstrarigraphy can be examined as well. Shelby tube sampling does not work with noncohesive sediments.

A split-spoon sampler can be used for the collection of samples of both cohesive and noncohesive sediments. The split-spoon sampler consists of a split tube with thicker walls than a Shelby tube. The two halves are placed together and joined by screwing a circular drive shoe on the bottom and a head assembly on the top. The assembled split-spoon sampler is screwed to a rod and lowered to the bottom of the drill hole. A pipe-like weight of 63.5 kg (140 lb) is placed on the top of the rod.

The weight is repeatedly raised and dropped a distance of 76 cm (30 in.) in order to drive the split-spoon sampler into the formation. The number of blows necessary to drive the sampler every 15cm (6 in.) is recorded as the sampler is driven 46 cm (18 in.) into the formation. The more dense the formation, the greater the number of blows needed to drive it 15 cm (6 in.). The process is described by ASTM 1586 (American Society for Testing and Materials 1984).

After the split-spoon sampler is driven 46 cm (18 in.), or after refusal, it is brought to the surface and opened. Frequently, less than 46 cm (18 in.) of sediment have been collected. Fine, noncohesive sediment such as sand may fall out of the sampler as it is being retrieved. Sediment greater in diameter than one-third of the diameter of the sampler may not enter it at all. A pebble may lodge in the barrel and not allow any other sediment to enter. Sediments may compact in the sampler so that a full 18-inch sample may actually occupy less than 46 cm (18 in.) of the core barrel. The hydrogeologist examining the split-spoon sample must use his or her judgment in making a log based on the split-spoon samples. Figure 8.22 is a photograph of a split-spoon sample.

FIGURE 8.22 Hydrogeologist describing a split-spoon sample.

Photo credit: C.W. Fetter.

A standard for core samples is to collect one 46 cm (18 in.) sample every 1.5 m (5 ft). This frequency of sampling is suitable for relatively homogeneous formations. However, if the microstratigraphy of the formations is important—for example, if there are permeable sand seams in a clay formation—then continuous-core samples should be collected. Continuous cores are made by advancing the drill bit to the full depth that was sampled by a split spoon and then immediately taking another core sample of the fresh formation ahead of the previous core. Continuous-core samples can also be collected in cohesive soils by using a special core barrel that collects a 1.5 m (5 ft) long sample inside a hollow-stem auger as the auger is being advanced. If a sequence consisting of a 3-inch split spoon followed by a 6.35 cm (2.5 in.) split spoon followed by a 5 cm (2 in.) split spoon is used, 1.37 to 1.5 m (4.5 to 5 ft) of continuous sample core can be collected before the augers need to be advanced.

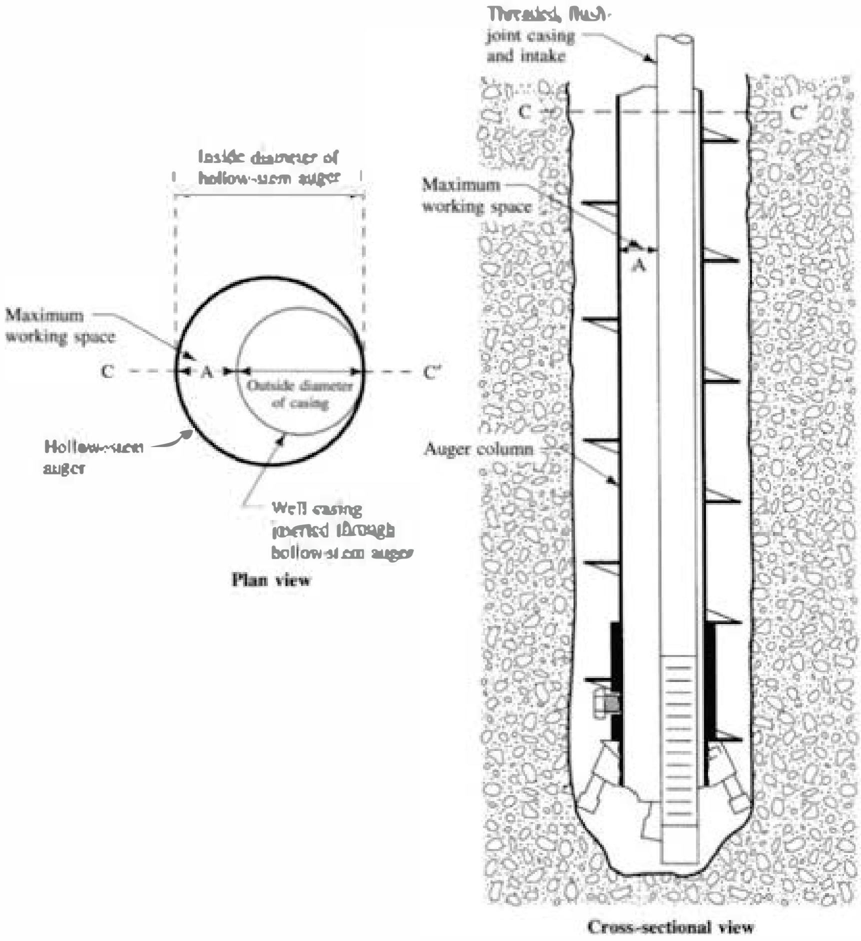
In consolidated formation a rock-core sample is collected by use of a core barrel with a diamond-studded bit. The rotating bit grinds up rock in an annular pattern, leaving an undisturbed center of rock that enters the core barrel. There is a core lifter just behind the bit to keep the core from falling out of the core barrel when the drill rods and bit are retrieved from the borehole. For shallow soil sampling, some coring and auger soil sampling devices can be operated by hand. Helical or post-hole augers gather a disturbed, near-surface sample and are superior to coring devices in rocky soils. Soil cores can be taken by hand from the ground surface with specialized coring devices that can allow sampling for VOCs and other potential contaminants. Cores are typically extruded after sampling and readied for transport or analysis. Decontamination techniques for coring equipment between samples is required to prevent cross-contamination.

8.5.5 Installation of Monitoring Wells

Following the collection of samples during the installation of borings, a monitoring well can be installed in the borehole. Boreholes drilled with mud should stay open with the drill rod removed. Hollow-stem augers are generally left in the ground and the well is installed through them, as is drive casing in cable-tool drilling. There must be a sufficient working opening inside the casing or augers. For a 5 cm (2 in.) nominal monitoring well, this means a minimum 10.8 cm (4.25 in.) opening is needed. The casing can be offset within the auger to give the largest working opening (Figure 8.23) although care must be taken to keep the well casing and screen as centrally located as possible. With a 10.8 cm (4.25 in.) inside diameter auger and a 5 cm (2 in.) nominal casing, this creates a 4.76 cm (1.875 in.) working opening.

The first step in the installation of a monitoring well is to screw the well screen to the casing and then lower the assembly through the inside of the augers or temporary casing. Prior to installation the casing and screen should be thoroughly decontaminated. The casing and screen may be wrapped in white butcher paper after it has been decontaminated and then kept wrapped until just before it is lowered into the augers. Figure 8.24 shows a 6.1 m (20 ft) casing and screen being lowered by hand. Longer casings need to be lowered on a cable using the drilling rig. In boreholes not drilled by hollow-stem augering, it is generally important to have centralizers (mechanical collars-type devices) attached to the casing/ screen combination to keep them from contacting the wellbore walls (Nielsen 2005).

FIGURE 8.23 Casing offset inside hollow-stem auger to give greatest working opening.



Source: G. Hackett. 1988. Drilling and constructing monitoring wells with hollow-stem augers part 2: Monitoring well installation. *Groundwater Monitoring & Remediation* 8:60–68. Used with permission.

Once the casing and screen have been lowered into the well, the filter-pack material needs to be placed. The volume of filter-pack material necessary to fill the annular space between the screen and casing and the borehole wall from the bottom of the borehole to a point 0.6 m (2 ft) above the top of the screen should be computed. At least this much material must be on hand before starting the filter-pack installation. A weighted measuring tape is lowered into the working opening between the casing and the hollow-stem auger and the total depth of the borehole is measured and recorded.

If the formation is cohesive and can stand open for a short while, the augers are withdrawn 0.3 or 0.6 m (1 or 2 ft) from the bottom. Filter-pack material is then poured into the working opening, and the annular space is filled to the level of the auger bit. Care should be taken that the filter-pack sand doesn't fill the space between the casing and the augers, because it can lock the casing and hollow-stem augers together. The weighted tape is used to determine the position of the top of the filter pack. The augers are then withdrawn another 0.3 to 0.6 m (1 to 2 ft), and the process is repeated until the entire filter pack is placed. Figure 8.25 illustrates what is known as the free-fall method of filter-pack emplacement.

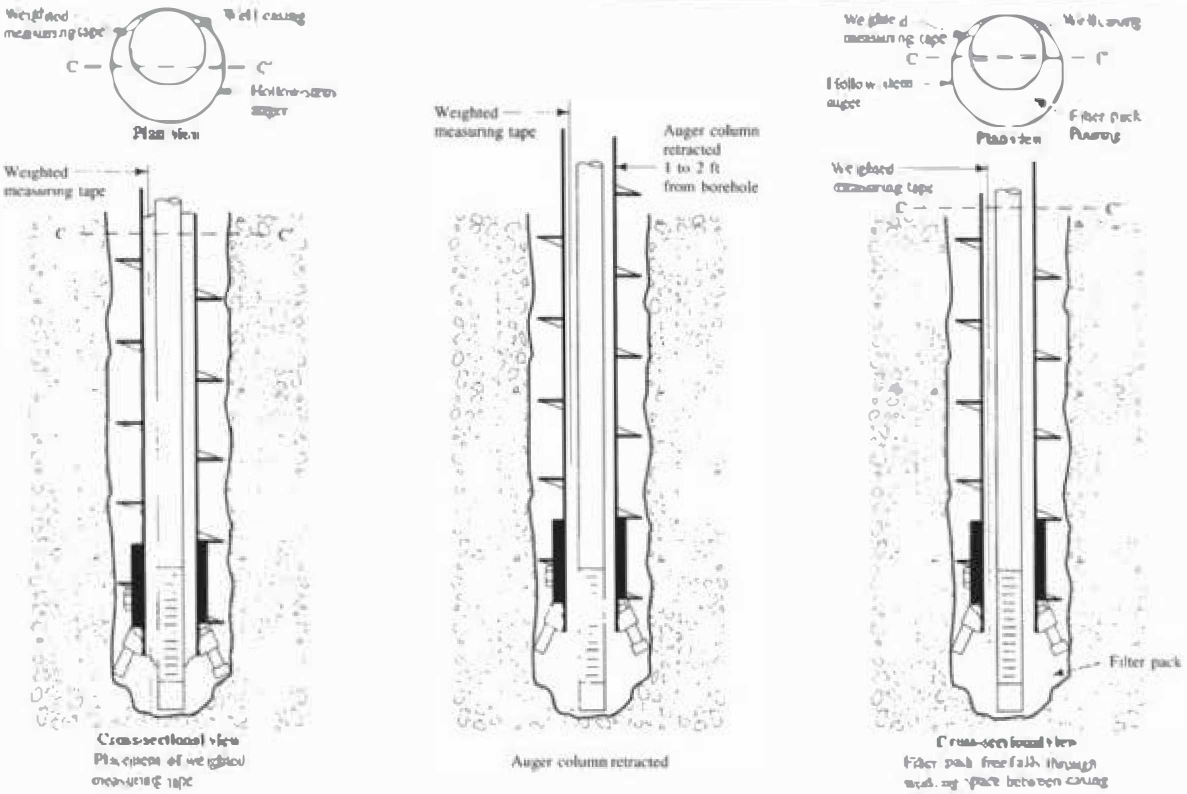
FIGURE 8.24 Lowering well screen and casing into hollow-stem augers. Note the white wrapping paper around the decontaminated casing.

Photo credit: C. W. Fetter.

When filter-pack material drops through a water column, it may separate according to size. It may also bridge the space between the casing and the auger and create a void below. To avoid these problems, a **tremmie pipe** should be used wherever possible (Figure 8.26). A tremmie pipe is a pipe that extends from the surface and through which the filter-pack sand may be poured. After the augers are withdrawn a few feet, the annular space is filled with sand being poured down the tremmie pipe. The tremmie pipe is raised as the level of sand rises. The tremmie pipe can be used to tamp down the sand, and the weighted tape is used to measure the position of the top of the filter pack.

If the formation is noncohesive, it will collapse as the augers are withdrawn. Under these conditions, the withdrawal of the augers and the addition of the filterpack

FIGURE 8.25 Free-fall method of filter-pack emplacement with a hollow-stem auger. The method also works with drive casing.



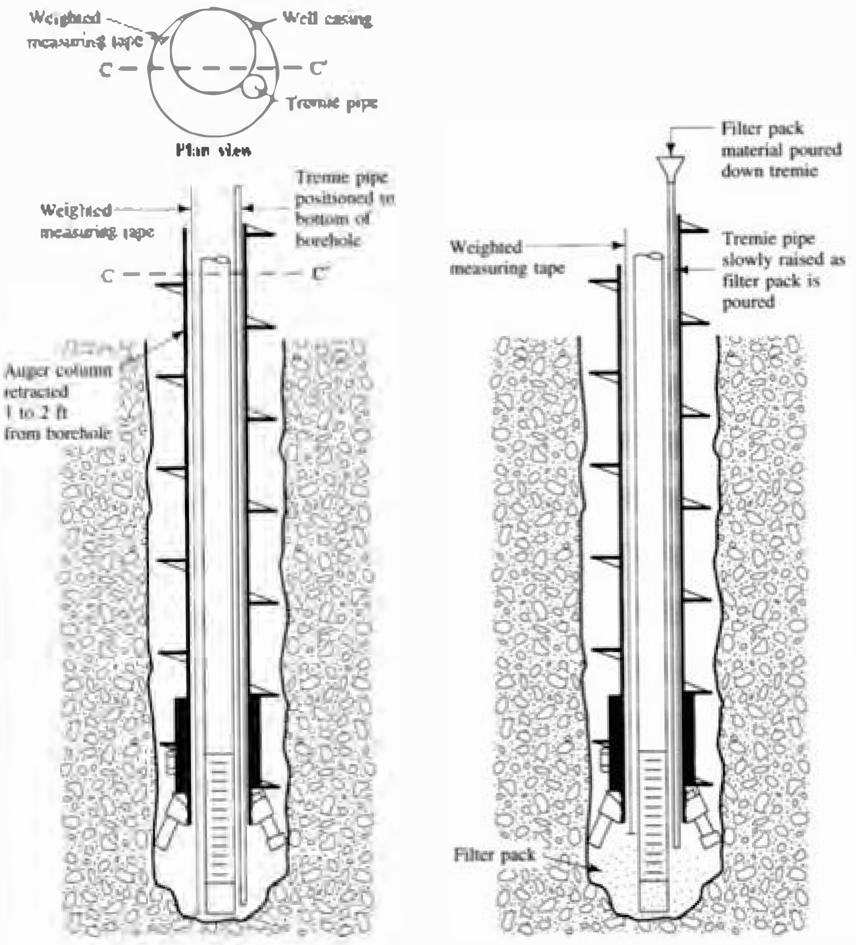
Source: G. Hackett. 1988. Drilling and constructing monitoring wells with hollow-stem augers part 2: Monitoring well installation. *Groundwater Monitoring & Remediation* 8:60–68. Used with permission.

material must occur simultaneously (Hackett 1988). A cable must be attached to the top of the auger string so that the working opening is accessible at all times. The hollow stem of the augers is filled with clean water, and a positive hydraulic head is thus maintained throughout the operation. The augers are very slowly withdrawn, and at the same time filter-pack material is added so that the top of the filter pack is within an inch or so of the bottom of the augers. This requires precise coordination of the rate of addition of filter-pack sand and the rate of withdrawal of the augers.

The final depth of the top of the filter pack is confirmed by measurement with the weighted tape. It should be 0.6 m (2 ft) above the top of the screen. The augers are then withdrawn another 0.6 m (2 ft) and 0.6 m (2 ft) of pure bentonite clay is placed by free fall through the working space. If the area is below the water table, bentonite pellets are used; if the area is above the water table, granular bentonite or slurry is used (see 8.4.5). Pellets should be dropped a few at a time so that they aren't caught in the working space as they start to swell by hydration. The weighted tape is used to confirm the final thickness of the bentonite layer after enough time has elapsed to allow the bentonite to hydrate. Bentonite pellets should not be used as grout in the vadose zone, as hydration is extremely slow even if water is poured through the pellets.

Placement of the annular seal should take place by use of a tremmie pipe. The tremmie pipe should be lowered to the top of the bentonite seal. The augers are

FIGURE 8.26 Use of a tremmie pipe for emplacement of filter-pack material.



Cross-sectional view

Weighted measuring tape and tremie pipe in retracted auger column

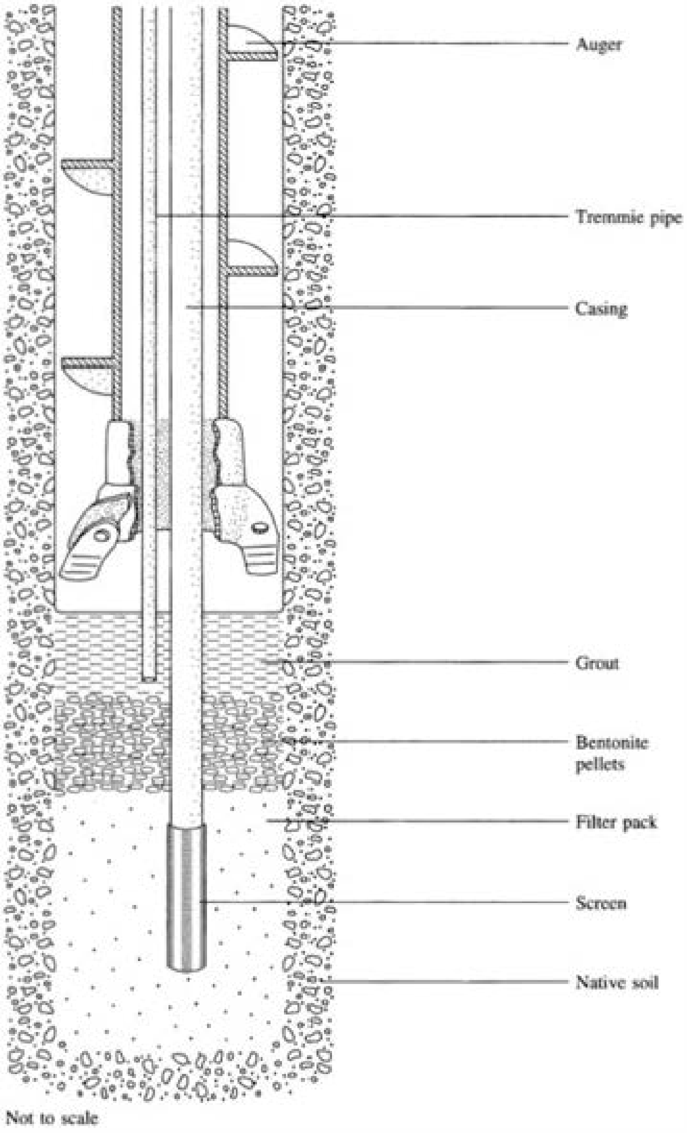
Filter pack poured through bottom-discharge tremie pipe

Source: G. Hacket; 1988. Drilling and constructing monitoring wells with hollow-stem augers part 2: Monitoring well installation. *Groundwater Monitoring & Remediation* 8:60-68. Used with permission.

withdrawn 0.6 m (2 ft) or so and the annular space is filled from the bottom with grout, which is either pumped down the tremmie pipe or is fed by gravity (Figure 8.27). The weighted tape is used to confirm the position of the top of the grout. The augers are then repeatedly withdrawn and grout is emplaced until it is brought close to the surface. The tremmie pipe can be left at the bottom until the grout is brought to the surface, or it can be raised as the augers are withdrawn. For slumping sediments, the grout must be emplaced simultaneously and at the same rate as the augers are withdrawn.

The final step is the installation of a locking protective cap. Bentonite-cement can be brought all the way to the surface. If bentonite grout or bentonite-sand grout is used, the final few feet filling the annular space must be neat cement or bentonite-cement grout. A slight mounding of the surface grout will prevent the pooling of water at the surface next to the well. The locking protective casing can be pushed into the cement grout when

FIGURE 8.27 Use of a tremmie pipe for emplacement of grout above the bentonite pellets.



it is still soft. If the grout settles overnight, its level should be brought to the surface with additional material. A stronger surface seal can be obtained if the top 0.61 m (2 ft) of the annular space is filled with concrete, as opposed to bentonite-cement grout.

8.5.6 Monitoring Well Development

Once a monitoring well is constructed, it is necessary that it undergo development. This is a process of removing fine sand, silt, and clay from the aquifer around the well screen. If drilling mud was used, then vigorous development may be needed to break down the mud pack on the borehole wall. Development is needed to create a well that ideally will not pump silt and clay when it is sampled. It also may create a zone around the well screen that is more permeable than the native soil and that stabilizes the native soil so that the fine sediments do not enter the filter pack.

Aller et al. (1991) made the following observations about monitoring well development:

1. Using compressed air for well development may alter native water chemistry, crack the casing, or blow the bottom cap off the screen.
2. Adding water to the well for flushing the well or surging can alter the groundwater chemistry, at a minimum by dilution.
3. Breaking down a mud wall left in the borehole from mud-rotary drilling is very difficult.
4. Developing a well when the screen is in a clean, homogeneous, high-permeability aquifer is relatively easy.
5. Developing a well when the screen is in a fine-grained, stratified, low-permeability formation is difficult.
6. Developing a large-diameter well is easier than developing a small-diameter well.
7. Shallow monitoring wells are easier to develop than deeper monitoring wells.
8. Monitoring wells that can be bailed dry tend to be turbid because of the steep hydraulic gradients that are developed.
9. In the final analysis, many monitoring wells cannot be developed to the point where a nonturbid, groundwater sample can be collected. This is especially true if the formation does not yield very much water, so that extensive development is not possible.

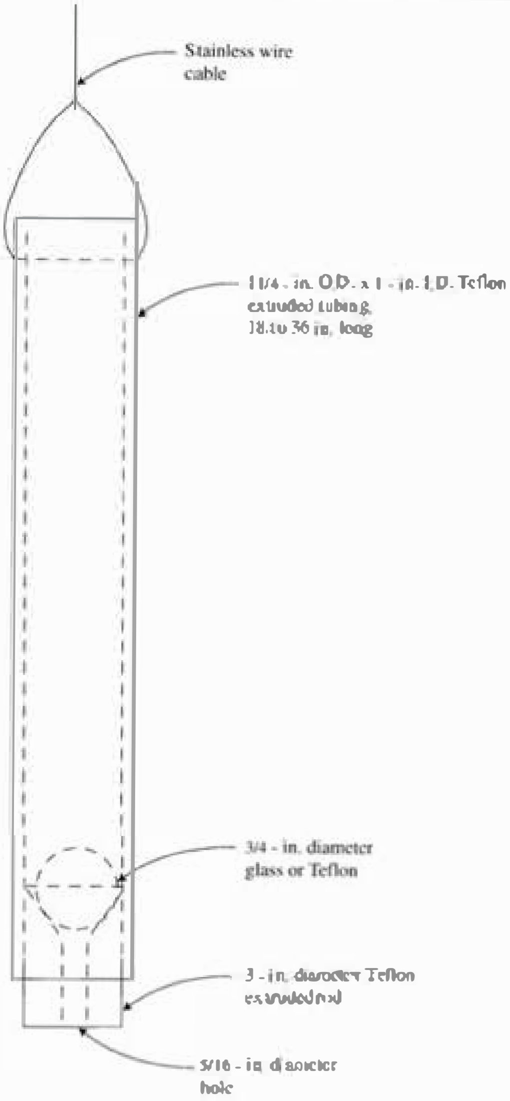
If the borehole is drilled into a stable, consolidated formation, especially if mud is used during the drilling, it may be advantageous to flush the borehole with potable, fresh water to wash out as much of the mud as possible prior to installation of the well and filter pack. This will greatly cut the time needed for well development. In some cases it will not be permissible to add water to the borehole, since this might alter the groundwater chemistry.

There are three procedures used for monitoring well development: bailing, surge block surging, and pumping/overpumping/backwashing. These may be used alone or in combination.

A bailer for a monitoring well is a section of pipe that is open on the top end and has a foot valve on the bottom end. It is attached to a line so that it can be lowered into the well. Water fills it from the bottom; then when it is raised by the line, the foot valve closes and the water inside is trapped. Figure 8.28 is a diagram of a bailer.

When developing a well by bailing, the bailer should be allowed to freefall to the water surface. When it strikes the water, a pressure wave results, which pushes water from the well screen out into the formation. After the bailer is filled with water, it is withdrawn and water from the formation enters the screen. This back-and-forth motion of water through the filter pack loosens fine sediment so that it can be drawn into the well and removed by the bailer. The bailer should be allowed to sink to the screen area so that the water that fills it contains the fine sediment that is brought into the well from the filter pack. The bailer can also be raised and lowered when it is submerged to force water to move back and forth through the screen area. Bailing can take some hours to develop a monitoring well effectively; this can translate into significant labor cost. Bailing for development can be undertaken by hand or by using a cable attached to a

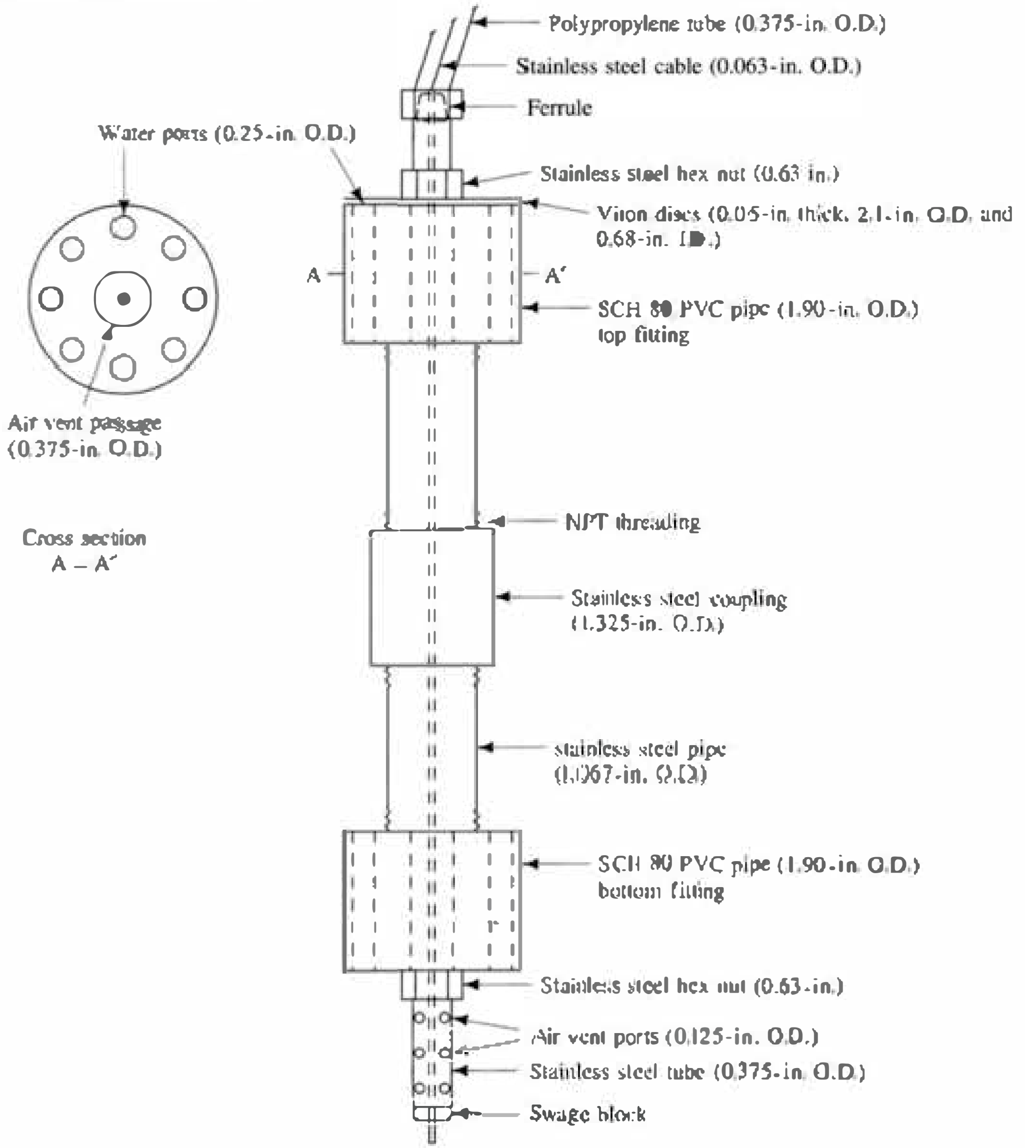
FIGURE 8.28 Diagram of a bottom-loading bailer.



power-operated drum on a drill rig or truck. Some well-development outfits have an arm that can go up and down like a walking beam to create a surging action. Care should be taken so that the surging action is not vigorous enough to collapse the well screen.

A surge block is a device that fits inside the well with a flexible gasket that is close in size to the inside diameter of the well. Figure 8.29 shows the design of a surge block for small-diameter monitoring wells. It is attached to a rod that is raised and lowered with a stroke of about 0.9 m (3 ft). Most of the water is moved up or down by the action of the surge block, although some fraction of the water bypasses the surge block. The surging is initiated with the surge block at the top of the well screen, and the block is gradually lowered until the entire screened area has been surged. Every so often the surge block is removed and the well bailed to remove the sediment that has been brought into the well. If too much sediment accumulates above the surge block, it can bind between the surge block and the casing wall and lock up the surge block. To avoid this, the surge block

FIGURE 8.29 Design of a specialized surge block for monitoring wells.



Source: R. Schalla and R. W. Landick. 1986. A new valved and air-vented surge plunger for developing small-diameter monitor wells. *Groundwater Monitoring & Remediation* 6:77–80. Used with permission.

must be removed and the well bailed frequently. Surging begins with a gentle action; as development progresses it becomes more vigorous, with a more rapid plunging action. Again, too vigorous a surging action might cause the screen to collapse.

Pumping the well can aid in development. A number of different types of pumps are suitable. However, some pumps might be damaged by the sediment that must necessarily be removed during development. The ideal pump for development is capable of a wide range of flow velocities and does not have a valve that prevents backflow. The pump intake should be in the screen zone so that it will immediately pick up sediment that is brought into the well. The pump is started at a low velocity and is shut off every so often. When it is shut down, the water in the pump column between the water surface and the pump will flow back into the well and out into the filter pack. When the pump is started again, this water will be drawn into the well and will loosen fine sediment in the filter pack. With time, the rate at which the well is pumped is increased so that the water velocity through the filter pack into the screen is increased. Eventually, the well will be overpumped—that is, pumped at a rate that is greater than the flow into the well through the well screen. There will be a rapid decrease in the water level in the well during overpumping, and it cannot be sustained for very long. Eventually the water from the well should clear. Monitoring wells should be periodically redeveloped.

8.5.7 Record Keeping During Monitoring Well Construction

Many localities have detailed record-keeping requirements for monitoring well construction. Even when detailed records aren't required by statute, they should be kept as a matter of sound professional practice. Figure 8.30 shows a one-page form that can be used to record important information on monitoring well construction. Many firms have their own forms, and many states, provinces, and regions have a required form. The form should be filled out in the field as the information is collected.

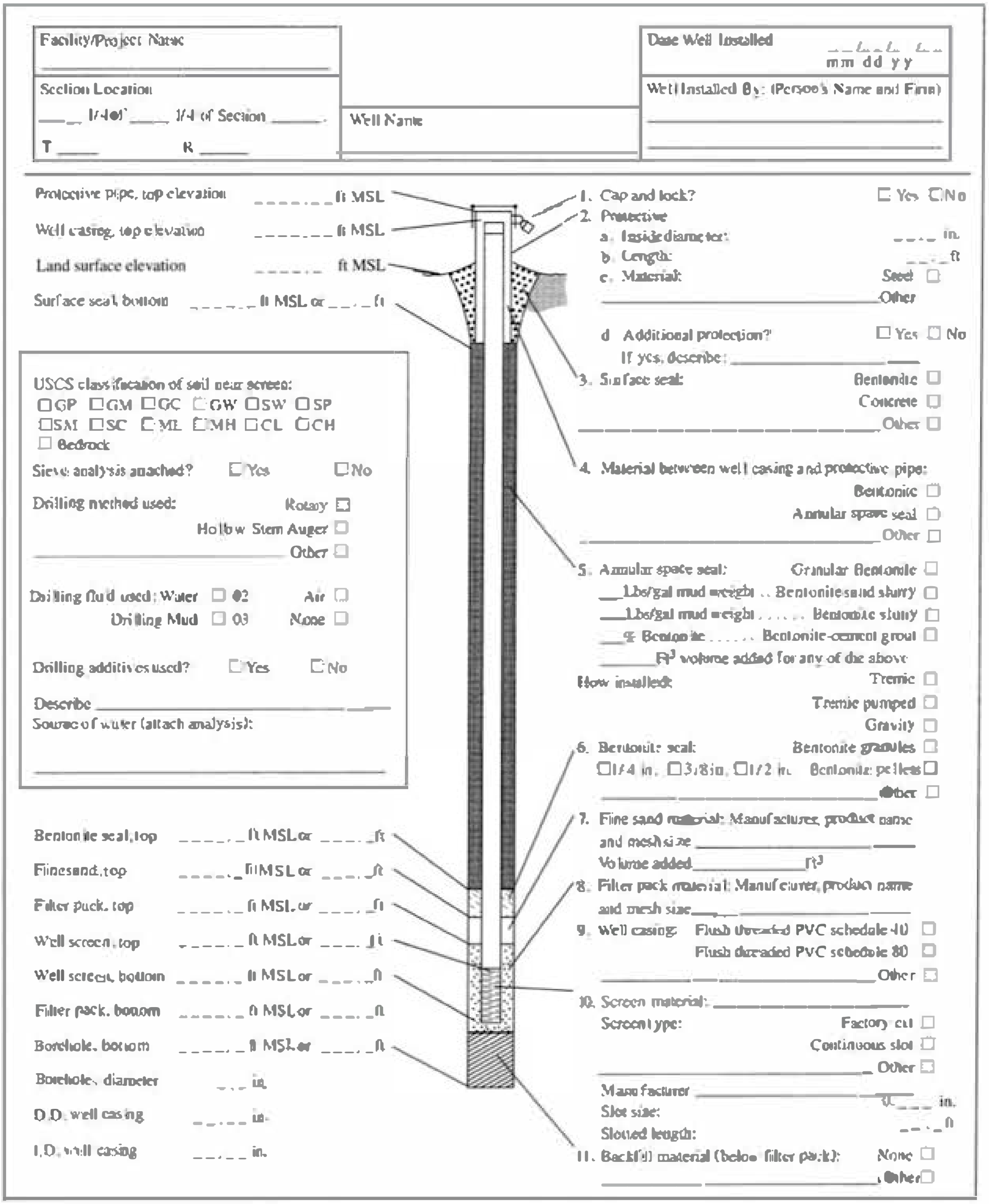
Records should also be kept of well development, including the date that it occurred, the method used, the water level at the start of development, the water level at the end of development, the time spent developing the well, and the volume of water removed. The thickness of sediment on the bottom of the well can be determined by measuring the depth to the bottom of the well with a weighted tape. This measured distance is subtracted from the measured length of the well casing and screen that was installed. The difference between the two dimensions is the thickness of sediment inside the well. This thickness should be measured and recorded both before and after development. If possible, sediment should be removed with a bottom-loading bailer.

8.5.8 Monitoring Well and Borehole Abandonment

Sometimes difficulties are encountered during the construction of a monitoring well that prevent its completion. Monitoring wells may be installed for a specific time period, after which they must be removed. Test borings may be made with no intention of using the borehole for construction of a monitoring well. In all such cases, proper abandonment of the well should be undertaken. Many countries and regions have specific well-abandonment codes. In the absence of specific requirements, monitoring wells and boreholes should be abandoned in such a manner that surface water cannot drain into the aquifer. Otherwise a direct connection for contaminated water from the surface to the aquifer can result. Nor should contaminated water or fluids be allowed to move vertically within the borehole to contaminate other depths.

If a casing and screen have been installed, they should be removed if possible. This can be accomplished by pulling if the annular seal has not been filled with a cement-type grout. If a plastic casing breaks while being pulled, it can be removed by drilling it out with hollow-stem augers. Following the removal of the casing, a tremmie pipe should be used to fill the resulting borehole from the bottom with an appropriate material, such as neat cement or bentonite grout. The grout is placed while the augers are being pulled out of the hole. Material removed from a monitoring well may be contaminated and should be properly disposed of.

FIGURE 8.30 Form for recording information about construction details of a monitoring well.



Facility/Project Name ____________________
Section Location
_____ 1/4 of _____ 1/4 of Section _____
T _____ R _____
Well Name ____________________
Date Well Installed __/__/__ mm dd yy
Well Installed By: (Person's Name and Firm) ____________________

Protective pipe, top elevation _______ ft MSL
Well casing, top elevation _______ ft MSL
Land surface elevation _______ ft MSL
Surface seal, bottom _______ ft MSL or _____ ft

USCS classification of soil near screen:
☐ GP ☐ GM ☐ GC ☐ GW ☐ SW ☐ SP
☐ SM ☐ SC ☐ ML ☐ MH ☐ CL ☐ CH
☐ Bedrock
Sieve analysis attached? ☐ Yes ☐ No
Drilling method used: Rotary ☐
Hollow Stem Auger ☐
____________________ Other ☐
Drilling fluid used: Water ☐ 02 Air ☐
Drilling Mud ☐ 03 None ☐
Drilling additives used? ☐ Yes ☐ No
Describe ____________________
Source of water (attach analysis):
____

Bentonite seal, top _____ ft MSL or _____ ft
Fine sand, top _____ ft MSL or _____ ft
Filter pack, top _____ ft MSL or _____ ft
Well screen, top _____ ft MSL or _____ ft
Well screen, bottom _____ ft MSL or _____ ft
Filter pack, bottom _____ ft MSL or _____ ft
Borehole, bottom _____ ft MSL or _____ ft
Borehole, diameter _____ in.
O.D. well casing _____ in.
I.D. well casing _____ in.

1. Cap and lock? ☐ Yes ☐ No
2. Protective
   a. Inside diameter: _____ in.
   b. Length: _____ ft
   c. Material: Steel ☐
   ____________________ Other ☐
   d. Additional protection? ☐ Yes ☐ No
   If yes, describe: ____________________
3. Surface seal: Bentonite ☐
   Concrete ☐
   ____________________ Other ☐
4. Material between well casing and protective pipe:
   Bentonite ☐
   Annular space seal ☐
   ____________________ Other ☐
5. Annular space seal: Granular Bentonite ☐
   ____ Lbs/gal mud weight . . Bentonite-sand slurry ☐
   ____ Lbs/gal mud weight . . . . . . Bentonite slurry ☐
   ____ % Bentonite . . . . . . Bentonite-cement grout ☐
   ______ Ft³ volume added for any of the above
   How installed: Tremie ☐
   Tremie pumped ☐
   Gravity ☐
6. Bentonite seal: Bentonite granules ☐
   ☐ 1/4 in. ☐ 3/8 in. ☐ 1/2 in. Bentonite pellets ☐
   ____________________ Other ☐
7. Fine sand material: Manufacturer, product name and mesh size ____________________
   Volume added ____________ ft³
8. Filter pack material: Manufacturer, product name and mesh size ____________________
9. Well casing: Flush threaded PVC schedule 40 ☐
   Flush threaded PVC schedule 80 ☐
   ____________________ Other ☐
10. Screen material: ____________________
   Screen type: Factory cut ☐
   Continuous slot ☐
   ____________________ Other ☐
   Manufacturer ____________________
   Slot size: 0.____ in.
   Slotted length: _____ ft
11. Backfill material (below filter pack): None ☐
   ____________________ Other ☐

Source: Modified from Wisconsin Department of Natural Resources.

If the casing and screen have been grouted into place, it may not be possible to remove them. If this is the case, several approaches can be used. The casing could be cut off below grade; then the screen and casing must be filled from the bottom using a tremmie pipe and an appropriate material such as neat cement or bentonite grout. If the casing is in poor condition it can be ripped or perforated with casing rippers allowing grout to be injected into the annular space. Alternatively, casing can be gun-perforated using either a device that fires steel projectiles through the casing and into the formation, or a jet type perforator that uses small shaped explosive charges to burn holes through the casing and allow grout injection (Aller et al. 1991).

Boreholes in sediments can be filled with grout or native soils mixed with bentonite. Boreholes into bedrock should be grouted with a cement-type grout.

8.6 Well Sampling

8.6.1 Introduction

After a monitoring well has been designed, installed, and developed, the next step is to collect a water sample. The water sample should be representative of the water in the formation; that is, the sampling techniques should collect water from the aquifer and not from water that has been standing in the well casing or screen. In addition, the sampling device should provide a sample that has not been altered by the sampling process and should not cause cross contamination.

8.6.2 Fluid Level and Pressure Measurement

Several devices are available for the downhole measurement of water levels, pore pressures and NAPL layers in wells or piezometers. Historically, steel tape was used to measure water levels in wells. Chalk would be applied to the tape at the expected water level depth, and then retrieved to the surface. The depth to water would be indicated on depth markings on the tape at the point where the chalk had been washed away by the water. Another historical method to measure hydraulic head is a "bubble tube" which is a pipe or tube sent downhole with a known air pressure to depths below land surface and below the water table or piezometric surface. The tube continues to bubble until it reaches a depth where the water pressure is equal to the air pressure within the tube and the depth below water surface can be calculated. This method is not used in situation where volatilization of contaminants is possible or LNAPLs are suspected in the wells.

Water levels are now often determined by electrical probes with depth demarcations which are lowered in a well or piezometer until a peeping sound indicates that the water level has been reached. For more exacting and quantitative NAPL determinations in wells, depth-discrete and transparent bailers can be sent downhole, or interface probes can be used. An interface probe is a modified electrical water level probe which has an ability to give separate acoustic and visual signals for water and NAPL in the fluid column (Mercer and Cohen 1990; Cohen and Mercer 1993). Unlike the bailer, however, interface probes cannot retrieve a NAPL sample for analysis, but only measure the vertical thickness of NAPL in a well.

Long term water level measurements are now often made with a recording transducer which measures temporal pressure changes in a well at a specified depth, which correlates to overlying water levels. Vibrating wire piezometers are useful in measuring well water levels and pore pressures for geotechnical applications.

8.6.3 Well Purging

Water that has been standing in the well has been in contact with atmospheric gases and the well casing and screen. This contact can affect the water chemistry. Oxygen can diffuse into the water and dissolved gases can volatilize or oxidize. Trace elements may be leached from the well casing. Organics may be sorbed by the well casing. In order to be sure that the water being drawn into the sampling device comes from the aquifer, the well must be purged of standing water prior to sampling. The goal of purging is to remove all the water that has been standing in the well. The volume of water that must be removed to accomplish that goal depends upon the method of purging and formation permeability.

The first step in well purging is to measure the depth of water in the well, the total well depth, and the inside diameter of the well casing. These measurements are used to compute the volume of water standing in the casing. If a well is purged by a method that withdraws water from the top of the water column, then theoretically only one well volume needs to be withdrawn. For example, purging with a bailer that is lowered slowly into the well to a depth no greater than the length of the bailer will remove water only from the top of the column. If a pump is used to purge the well, the pump intake should be as close as possible to the top of the water column. Although one well volume would theoretically remove all the standing water, good practice suggests that at least three well volumes should be removed to be sure that the standing water in the casing and screen is totally removed. This also removes water from the filter-pack area. If a well is bailed dry, or nearly so, it is not necessary to attempt to remove multiple-well volumes. As soon as the well has recovered enough to contain sufficient sample volume, the sample can be collected.

If the pump intake is lowered to the level of the screen in the well during purging, then most of the water will come from the screen area, and an area of stagnant water will develop in the water column above the pump intake. Under such conditions up to five well volumes need to be pumped to remove all of the stagnant water in the well (Gibb et al. 1981). Keeley and Boateng (1987) advocate a staged technique when purging with a pump. The pump intake is lowered to just below the water surface at the beginning of the purging process and then is gradually lowered through the water column until it is at the screen zone, when purging is complete. Purging three well volumes with this technique should be adequate.

Electrical conductivity and pH can be monitored during the well-development procedure. If they vary widely during the well-purging process, this may mean that water from different sources is being withdrawn. If these values do not stabilize, this does not necessarily mean that the stagnant water has not been withdrawn from the well. There may be instrument drift, or the water quality in the aquifer may be changing as water from different parts of the aquifer is being withdrawn. If possible, the well should be purged until it is not turbid.

The water being purged from the monitoring well may be contaminated. If so, it must be properly disposed of in a treatment facility. For this reason, purging techniques that limit the amount of water withdrawn are desirable.

8.6.4 Well-Sampling Devices

There are a large number of sampling devices available for monitoring wells. They operate under different physical principles and designs and have different applications.

Most are available in a variety of materials The following is a partial list of available devices (Nielsen and Yeates 1985; Pohlmann and Hess 1988):

1. *Open bailer*. This device is a rigid tube with an open top and either a closed bottom or a check valve on the bottom. It is attached to a line and is lowered and raised by hand. It withdraws the sample from the top of the water column.
2. *Point-source bailer*. This device has a check valve on both the top and bottom and can be lowered on a line to a given depth below the surface, where the valves can be closed by a cable. It can collect grab samples from any depth in the water column. Some bailers are intentionally disposable to prevent cross-contamination from multiple sampling, and some are transparent or translucent allowing visual identification of colored NAPLs or other compounds in the bailer.
3. *Syringe sampler*: A medical syringe, or similar device, is attached to a length of tubing and is lowered to a selected depth in the water column. A suction is applied to the tubing and the syringe, which was lowered in the "empty" position. The syringe fills as the water comes into the needle because of the vacuum being developed by the suction on the tubing.
4. *Gear-drive pump*: This device is similar to a traditional submersible electrical pump. There is a miniature electrical motor attached to the pump, which rotates a set of gears to drive the sample up the discharge line via positive displacement. A continuous flow of water under positive pressure is developed.
5. *Bladder pump*: This sampler has a rigid tube containing an internal flexible bladder. There are check valves on either end of the rigid tube. When the bladder is deflated, water enters the lower end of the tube through the check valve. When the tube is full, the bladder is inflated with an inert gas pumped down from the surface. The bottom check valve closes, the top check valve opens, and the water sample flows up the discharge line. When the bladder deflates, the water in the discharge line can't drain back into the rigid tube because of the check valve. The water is under positive pressure at all times and doesn't come into contact with the gas.
6. *Helical-rotor pump*: This pump has a submersible electrical motor. It rotates a helical rotor-stator, which drives water up the discharge line under positive pressure.
7. *Gas-drive piston pump*: A piston that pumps the water is driven up and down by gas pressure from the surface. The gas does not contact the sample.
8. *Submersible centrifugal pump*: A submersible electrical motor drives an impeller in the pump, which creates a pressure and forces the water up a discharge line.
9. *Peristaltic pump*: Unlike the others, this is a pump located at the land surface. It is a self-priming vacuum pump that can draw a water sample up tubing under suction. Loss of volatile compounds and dissolved gases may occur due to the vacuum developed.
10. *Gas-lift pump*: A constant stream of gas or air is used to force the water up a discharge tube. The water comes into contact with the gas or air and oxidation and loss of volatiles can occur.
11. *Gas-driven pump*: An inert gas is used to alternately pressurize and depressurize a sample chamber. The sample chamber has check valves to create a one-way flow

of water up a discharge line. This is similar to a bladder pump except that there is no bladder, so the gas comes into contact with the water sample.

12. *Passive samplers:* Consist of an organic phase, such as a plastic film or polymer, which accumulates contaminants from the aqueous phase or (soil) air. Passive samplers are useful for sampling the water column as well as interstitial water (ITRC 2005; USEPA 2012).

Figure 8.31 is a matrix of sampling devices and the suitable applications for collection of groundwater samples.

Pearsall and Eckhardt (1987), Yeskis et al. (1988), and Tai, Turner, and Garcia (1991) evaluated the efficacy of a number of different sampling devices in collecting representative samples of volatile organic compounds in groundwater. The first two studies were performed by withdrawing water from monitoring wells with different devices and comparing the results. The authors had no controls—that is, they did not know the actual concentration of the contaminants in the aquifer.

Yeskis et al. (1988) tested a bailer, a bladder pump, a piston pump, a submersible electric impeller pump, and a submersible electric helical stator-rotor pump. They found very little variation in the results except for the bailer. The bailer samples were in general less than half of the values obtained by the other devices. Pearsall and Eckhardt (1987) evaluated two 5 cm (2 in.) submersible helical stator-rotor pumps made of different materials, a 4-inch submersible electrical water-well pump, a cast-iron centrifugal suction pump, a peristaltic pump, and a bailer. The submersible pumps all gave similar results; the peristaltic and centrifugal suction pumps gave somewhat lower results. Silicon and PVC tubing appeared to give lower results than Teflon® tubing when used with the same pump. The bailer gave variable results, depending upon the concentration.

Tai, Turner, and Garcia (1991) built a 30.5 m (100 ft) tall, 12.7 cm (5 in.)-diameter, stainless-steel, vertical standpipe with sampling ports at various depths. They were able to use a sampling device to collect a sample from the standpipe, at the same time drawing a control sample from that depth through a sample port. They tested a Teflon® point-source bailer, a manual-driven piston pump, a motor-driven piston pump, a submersible helical-rotor pump, a peristaltic pump, and a bladder pump. Teflon® tubing was used to convey samples to the surface from the pumps. Because they had control samples, they were able to calculate a percent recovery for each sampling device. Table 8.5 shows the percent recovery for each sampling device at different depths. Examination of this table shows that the submersible pump, the peristaltic pump, and the bladder pump all had excellent recoveries, ranging from 98.5 to 100.5%. The other three devices were not as accurate, with the bailer having the lowest recovery.

The low recovery using the bailer was probably due to agitation of the sample as it was being transferred from the bailer to a 40 mL sample bottle for volatile organic analysis. Although it is a simple piece of equipment, an experienced operator is needed for correct use of a bailer.

On the basis of available research (Parker 1994) the piston pump, the bladder pump, and the electrical submersible helical-rotor pump appear to be the best devices for the collection of water samples containing volatile organic compounds. Peristaltic pumps are also suitable for metals and semivolatile organics if used with a rheostat to

FIGURE 8.31 Matrix showing applications of a number of groundwater sampling devices.

Portable Sampling Devices					Ground Water Parameters													
					Inorganic							Organic				Radioactive		Biol.
	Device	Approximate Maximum Sample Depth	Minimum Well Diameter	Sample Delivery Rate or Volume	EC	pH	Redox	Major Ions	Trace metals	Nitrate, Fluoride	Dissolved Gases	Non volatile	Volatile	TOC	TOX	Radium	Gross Alpha & Beta	Coliform Bacteria
Grab	Open bailer	no limit	½ in.	Variable	•			•	•	•		•				•		•
	Point-source bailer	no limit	½ in.	Variable	•	•	•	•	•	•		•	•	•	•	•		•
	Syringe sampler	no limit	1½ in.	0.01–0.2 gal	•	•	•	•	•	•		•				•	•	•
Positive displacement (submersible)	Gear-drive	200 ft	2 in.	0–0.5 g/min									•					
	Bladder pump	400 ft	1½ in.	0–2 g/min	•	•	•	•	•	•	•	•	•	•	•	•	•	•
	Helical rotor	160 ft	2 in.	0–1.2 g/min	•	•	•	•	•	•	•	•	•	•	•	•	•	
	Piston pump (gas-drive)	500 ft	1½ in.	0–0.5 g/min	•			•	•	•		•				•	•	
	Centrifugal	variable	3 in.	variable	•			•		•						•	•	
Suction lift	Peristaltic	26 ft	½ in.	0.01–0.3 g/min	•			•		•		•				•		•
Gas contact	Gas lift	variable	1 in.	Variable														
	Gas-drive	150 ft	1 in.	0.2 g/min	•			•		•		•				•		

Source: K.F. Pohlmann and J.W. Hess. 1988. Generalized ground water sampling device matrix. *Groundwater Monitoring & Remediation* 8:8 2-84. Used with permission.

TABLE 8.5 Percent recovery of sampling devices compared with control samples.

	Water Depth					
	17.5 ft		54 ft		92 ft	
Sampler	Low[a] Conc.	High[b] Conc.	Low[a] Conc.	High[b] Conc.	Low[a] Conc.	High[b] Conc.
Submersible pump	97.8	99.7	99.5	98.5	100.1	100.1
Peristaltic pump	97.7	98.7	98.7	98.5	97.7	100.0
Bladder pump		101.5		100.5		99.9
Teflon bailer	93.9	96.3	92.4	93.9	92.7	91.4
Manual-driven piston pump	102.2	—	102.5	101.1	102.3	103.5
Motor-driven piston pump	97.4	96.8	99.8	98.4	100.9	100.7

Source: Tai et al. 1991.

create a low pumping rate. A bailer is acceptable if used properly with a minimum of agitation so as not to create splashing in the well and loss of volatiles. Bailers should have a bottom-emptying device. Such a bailer should be able to recover 90% of the volatile organics in the water.

Parker and Ranney (1996) examined the effect on using various rigid and flexible tubing used in water sampling devices on trace-level dissolved-organic compounds present in groundwater. They found that fluorinated ethylene propylene (FEP), FEP-lined polypropylene and polyvinylidine fluoride (PVDF) were the least absorptive of the rigid tubing. In addition, they do not leach constituents into water. Of these, PVDF is the least expensive. Where a flexible tubing is necessary, such as the head of a peristaltic pump, fluoroelastomer tubing and a copolymer of vinylidine fluoride and hexafluoropropylene were much less sorptive than the other flexible tubing. They also leached the fewest constituents into the water. The copolymer is less expensive than the fluoroelastomer.

Wherever possible, dedicated sampling equipment should be used in each well. This prevents the possibility of cross contamination between wells. It also eliminates the cost of decontaminating the equipment between wells and the possibility of interference from solvents used for decontamination. Inexpensive disposable bailers are available and may be an acceptable sampling device for many studies where the cost of dedicated sampling equipment in each well is not justified.

8.6.5 Methods of Collecting a Groundwater Sample Without Drilling a Well

The installation of a monitoring well is a costly proposition, generally in the range of $5,000 to over $15,000 USD for shallow wells in unconsolidated materials. Moreover, the process can be disruptive to the property owner and can damage lawns and crops. At some sites there may be limited knowledge about the direction of groundwater movement and the existence and location of contaminated groundwater. The hydrogeologist may find it desirable to perform some type of screening investigation prior to the installation of permanent monitoring wells. During the screening the hydrogeologist may try to find the location and depth of groundwater contamination. There are devices that one can use to collect a groundwater sample without installing a monitoring well. These devices, as well as a standard sandpoint piezometer, can be used during the installation of a test boring.

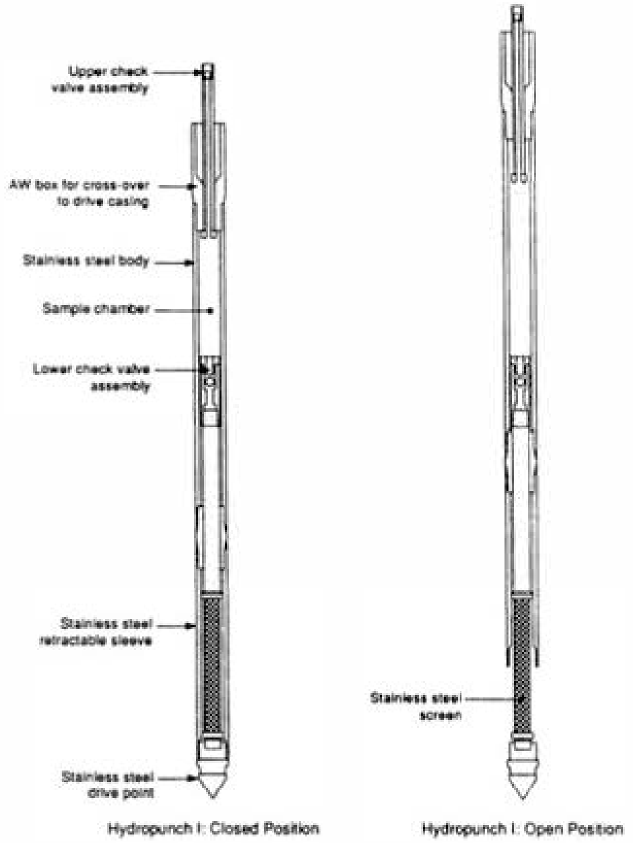
These methods all allow the collection of discrete samples in a vertical profile which gives one the ability to construct a vertical-concentration profile similar to that of a multilevel sampler. However, they have a drawback in that the samples cannot be replicated at a future date because the sampler is withdrawn after use.

The HydroPunch™ is one such device, a direct-push sampler, that can be used to collect a groundwater sample from a discrete depth in the earth (Edge and Cordry 1989). It consists of a pointed sampling probe that is attached to a hollow drill rod. The rod is pushed into the earth by the hydraulic ram of a drilling machine or cone penetrometer rig, or is driven into the earth by the dropping of a weight using a drilling machine. Such a device will obviously only work in unconsolidated materials. Moreover, HydroPunch I™ cannot be used in very coarse sediment. As a general rule, if a 2-inch split-spoon sampler cannot be driven into the earth, then the HydroPunch I™ will most likely be damaged if an attempt is made to drive it. A sturdier HydroPunch II™ has been made which can be used with cone penetometers or in conjunction with drill rigs. When the probe has been advanced to the target depth, the drive pipe is retracted about 1.5 ft (0.5 m). This raises a shield on the probe which exposes a stainless steel well screen that is 10 in. (25 cm) long. The probe has to be pushed at least five feet below the water table to completely fill the sampler. Hydrostatic pressure in the aquifer forces water to flow into the screen where it will rise into the probe until it reaches equilibrium with the hydrostatic pressure in the aquifer. Figure 8.32 illustrates the HydroPunch™ in both the closed and open positions. The screen openings in the HydroPunch™ are relatively large, and although water will enter relatively rapidly, the sample may be turbid. A check valve in the probe prevents water from draining back out of the screen and the entire assembly is withdrawn from the ground in order to retrieve the groundwater sample.

The BAT Enviroprobe™ is another type of discrete depth sampler (Mines et al. 1993). It is manufactured by Hogentogler & Co. Inc. of Columbia, Maryland. It is also pushed or driven into the earth to the desired depth by a drilling or cone penetrometer rig. When the drive pipe to which the probe is attached is pulled back about 1 ft. (0.3 m), a stainless steel sleeve is moved upward which exposes a 4-inch (10 cm) long screen. Figure 8.33 shows the BAT Enviroprobe™ in both a closed and an open position. There is a septum on the top of the screen which prevents groundwater from rising higher than the screen. The sample is collected by lowering a device with a double-ended hypodermic needle with an evacuated glass vial, which also contains a septum. The hypodermic needle penetrates both septa, and the water can move from the screen zone into the evacuated vial. The vial containing the groundwater sample is then withdrawn. Should this not contain sufficient sample volume, additional vials can be lowered through the riser pipe.

In the case of both the HydroPunch™ and the BAT Enviroprobe™, the water entering the screen is formation water and there is no need to either develop the well or purge it prior to sampling. This reduces the cost as the sample collection is quicker and also there is no contaminated purge and development water to dispose. Zemo et al. (1995) field-tested both the HydroPunch™ and BAT Enviroprobe™ and found that there was no statistically significant difference in trichloroethylene concentration found in

FIGURE 8.32 Closed and open position of the HydroPunch™ probe.



Source: Zemo et al. 1995. Field comparison of analytical results from discrete depth ground water samplers. *Ground Water Monitoring & Remediation* 15:133–141. Used with permission.

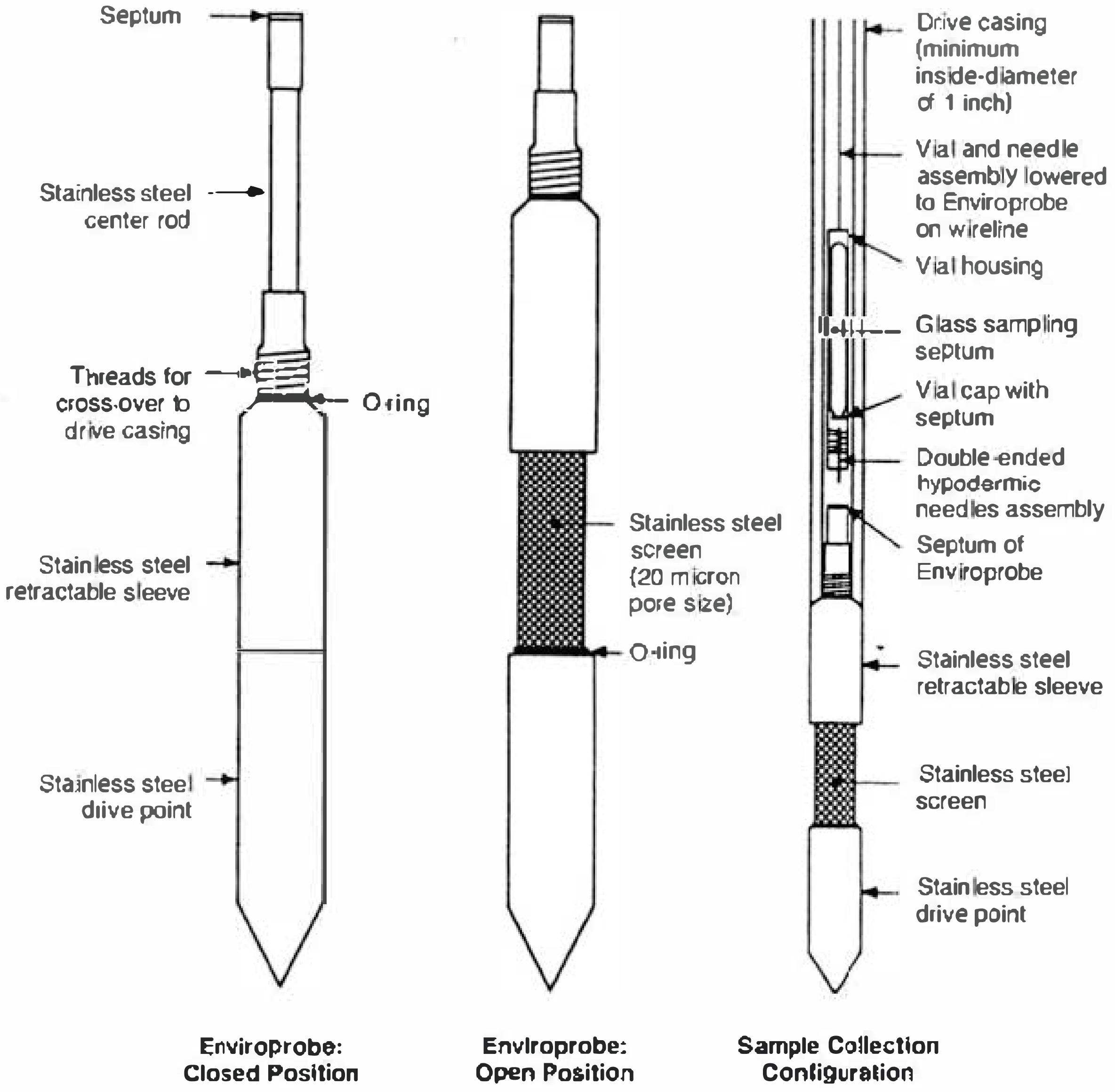
groundwater samples collected from either probe. However, they did find that there was a difference in chlorobenzene concentration. They were unable to determine why such a difference should exist.

If the unconsolidated material is too coarse for the sampling probes to be pushed very far into the earth, then they can be used with a hollow-stem auger drilling rig. The drilling rig is used to install a test boring. At selected depths, either probe can be advanced within the augers and ahead of the drill bit to collect a groundwater sample. This approach has the distinct advantage of gathering stratigraphic data along with water-quality data. In the absence of a specific sampling probe, a standard 2-foot long sandpoint piezometer can be driven ahead of the drill bit to collect a water sample. In this case a bailer is used to collect the groundwater sample. After the water sample has been collected, the device is withdrawn from the borehole and the augers advanced.

8.6.6 Low-Flow Purging of Monitoring Wells

An important advance in contaminant hydrogeology field methods is the development of micropurging or low-flow purging techniques (Puls and Paul 1995). The purging techniques presented in section 8.6.3 are designed to remove all of the stagnant water in both the screen and the casing above the screen. The micropurging technique withdraws

FIGURE 8.33 Closed and open position of the BAT Enviroprobe™ probe.



Source: Zemo et al. 1995. Field comparison of analytical results from discrete-depth ground water samplers. *Ground Water Monitoring & Remediation* 15:133–141. Used with permission.

water directly from the screen zone at a rate that is less than the recharge rate from the aquifer into the screen. The stagnant water in the casing does not mix with the fresh water entering the screen (Powell and Puls 1993). This purging rate is less than 1 L per minute; a suggested rate is only 100 mL/min. At this rate there is minimal drawdown in the pumping well and the water chemistry of the purged water tends to reach a constant value within one-half of a casing volume (Barcelona, Wehrmann, and Varljen 1994).

Micropurging is accomplished by using either a dedicated bladder or submersible pump with the intake set in the center of a well screen or a peristaltic pump with the end of the sample tubing set in the screen zone (Kearl et al. 1994). If a dedicated pump is not used, the pump should be placed in the well at least 24-hours prior to the time that the sample is collected. The purge rate should be about 100 mL/min, although somewhat higher rates could be used for very permeable formations. Two volumes of water contained in the pump and the tubing should be removed prior to collecting the sample. This will be much less than the volume of water in only one well casing. Samples do not need to be field filtered.

One of the problems that arises when sampling groundwater for metals occurs when the water sample is turbid. The turbidity is due to suspended mineral grains. These particles may contain sorbed metals. Some U.S EPA programs and some U.S. state agencies prohibit the filtration of samples used for metal analysis as it is known that metals can travel in the groundwater with colloids (Puls and Powell 1992). However, turbidity in a sample can be caused by the process of lowering sampling instruments into the monitoring well (Kearl, Korte, and Cronk 1992) or by high screen-entrance velocities developed when significant drawdown occurs during purging. Micropurging techniques utilizing dedicated sampling equipment in each well will provide a sample with the least amount of artificially introduced turbidity. This will provide the best sample for use in determining total metals.

Kearl et al. (1994) compared samples collected by micropurging with samples collected by traditional purge and sample techniques. For most inorganic analytes and all organic analytes, there was no statistically significant difference between the two methods.

In addition to the ability to collect a nonturbid sample, there are other advantages of the micropurging technique. In some monitoring wells located in low permeability formations, traditional purging may withdraw most or all of the water from the well. This means that one must wait for a day or more for the well to recover enough water to yield a sample. This means that the sampled water was still stagnant for a period of time before being withdrawn. With a micropurging technique, a very low pumping rate could draw fresh formation water into the screen zone without much lowering of the water level in the casing.

There are two variable costs associated with groundwater sampling: personnel time and the expense of disposing of the contaminated purge water (Schilling 1995). With dedicated pumping equipment, the time for micropurging is generally less than that needed for traditional purge and sampling, hence the cost will be lower. The amount of contaminated water which must be disposed is much less in micropurging, hence the cost will be less.

While the impact of turbidity in a groundwater sample can have a significant effect on the concentration of metals in the sample, the same is not true for at least some chlorinated solvents. Paul and Puls (1997) examined the impact of sample turbidity on the concentration of trichloroethylene, cis-1,2-dichlorethylene and vinyl chloride. In both field and laboratory samples they found that solids entrained in the sample had no significant impact on the measured concentration of any of the three compounds. On this basis they concluded that turbidity in the sample does not appear to be of significance when sampling for VOC analysis. They did note that if the turbidity was the result of sample agitation that factor might result in loss of volatiles.

8.6.7 Sampling Frequency

Groundwater sampling is carried out commensurate with efforts to understand the nature and extent of groundwater contamination, predict future movement, ensure that harmful excursions of pollutants do not occur, facilitate remediation, and other goals pertinent to site characterization. Many regulatory agencies specify and sometimes codify periodic time frames for sampling of monitoring well arrays, such as monthly, quarterly, or annual sampling. These periodic samplings have the benefits of allowing practitioners to predict many costs in advance, and look for long-term trends in water quality. From a regulatory standpoint this makes sense, although natural events that can alter water quality are not always periodic. For example, in karst systems great changes in subsurface water quality can occur during pulse flow events, and perhaps in many cases the best monitoring strategies for cave systems include sampling immediately before, during, and after intense rainfall and infiltration. Regulatory monitoring requirements are sometimes wrongly viewed as the maximum effort necessary to understand and deal effectively with groundwater contamination, particularly if monitoring costs are to be minimized. In reality, although standardized monitoring intervals make regulatory expectations clear, a one-size-fits-all sampling frequency is not always the best way to understand subsurface contamination at a particular site. Long-term costs are typically reduced with a clear understanding of contaminant distribution and movement, and sometimes this necessitates more frequent, strategic sampling before remedial action and site closure is attempted.

8.7 Other Site Characterization Methods and Groundwater Contamination Forensics

8.7.1 Introduction

Site characterization is much more than just identifying groundwater pollutants and measuring their occurrence in the subsurface. A challenge is that many well-defined characterization goals and objectives require a deep understanding of a site's geology, an understanding of groundwater travel times, knowledge of the chemical characteristics of potential contaminants, and awareness of logistical and safety concerns, just to name a few necessities. These complex objectives are often resolved by geologic testing, detailed environmental chemistry analysis, and environmental forensics.

There are many wide-ranging applications of site characterization techniques and groundwater forensics that support a robust understanding of source water protection, the potential for contaminant movement and transformation, groundwater vulnerability, and the integrity of aquitards or barriers which are relied upon to isolate waste. Numerous monitoring and characterization techniques have been, and continue to be developed, adding to the arsenal of methodologies to characterize subsurface contamination, and many of these methods rely on probes to be driven into the subsurface, measurements to be taken from boreholes, or samples to be taken from wells. In some cases contamination can be suspected based on field conditions. Field observations for NAPLs illustrate this point. For example, if DNAPL chemical concentrations in groundwater increase with depth in a pattern inconsistent with advective groundwater flow, or increase counter to a hydraulic gradient, there is support for the possibility of DNAPL being spread in its free phase. Other indicators of free-phase NAPL include situations where the aqueous concentration of NAPL compounds in groundwater is greater than 1% of the pure phase (for a single NAPL compound) or effective solubility limit (for NAPL mixtures). Note that the opposite is not true; concentrations below 1% may or may not be associated with free-phase NAPL. In soils where NAPL concentrations are greater than 10,000mg/kg (1% of soil mass) free phase can be suspected. Other qualitative signs of free-phase NAPL include erratic concentrations of NAPL chemicals in groundwater, soil, and soil gas; rebound of elevated dissolved NAPL concentrations after a pumping system is turned off; the presence of DNAPL chemicals in groundwater that is older than potential release dates; and observed deterioration of pumps and well components.

Quantitative methods can often be used as evidence in legal proceedings and the field of environmental forensics is based on efforts to distinguish pollutant sources (Morrison and Murphy 2006). Environmental forensics is defined by Hester and Harrison (2008) as "a combination of analytical and environmental chemistry, which is useful in the court room context. It therefore involves field analytical studies and both data interpretation and modeling connected with the attribution of pollution events to their causes." There are a vast number of techniques to determine the source and pathways of groundwater contamination that fall into the realm of forensic hydrogeology.

8.7.2 Borehole Geophysics and Downhole Techniques

Many geophysical techniques originally developed for oil and gas exploration are often used in drilled boreholes to define subsurface geology and hydrogeology, directly identify pollutants, and/or understand the potential movement and distribution of contamination. Downhole logging approaches will "ground truth" surface geophysical techniques and results can be directly compared to borehole cuttings or core samples. Like borehole cuttings and core, downhole geophysics provides vertically continuous data, but geophysical methods sample a greater subsurface volume with relatively little bias. As more boreholes are logged at a site and cross-borehole techniques are used, 3-dimensional imaging techniques (tomography) can assist visualization of contaminants and subsurface geological structures, faults, and formations (Obiadi et al. 2012). Downhole surveys have assumed great importance in contaminant site surveys because the specific site characteristics and heterogeneities in porous media and fractured rock can profoundly influence the distribution and the potential for remediation for a host of contaminants. Borehole geophysics can provide information directly applicable to site characterization, including delineation of hydrogeologic properties, subsurface water quality, and determination of a well's construction, status, and condition.

Physical, Visual, and Acoustic Borehole Geophysics Several techniques can measure the physical, visual, or acoustic properties of boreholes. One of the most straightforward downhole techniques is television (TV) logging where a color optical image is made of the borehole walls. This is particularly effective in identifying and characterizing fractures in hard rock materials, but can also identify lithology, water level, cascading water from perched zones (which could transmit contamination vertically), well construction failure, and water quality indicators such as suspended particles, gases, and chemical precipitates. TV logging can be viewed real-time and/or be stored and archived, and cameras and focal lengths can be adjusted to view either straight downhole, angled, or side-looking for inspection of borehole walls. An extension of TV logging is acoustic televiewer logging which records a photographic, digital image of the acoustic reflectivity of the borehole, oriented magnetically. These televiewer logs are used in water or mud-filled open holes, and can identify geologic contacts between different strata, and fault location, strike, and dip. Televiewers use a rotating transducer which can transmit and receive many samples per revolution and have azimuthal information from magnetometers on the device. This acoustic or sonic logging can help determine the porosity of a rock, aid in identification of lithology, facilitate estimation of secondary porosity and fracturing, and help assess rock permeability. Seismic logging, which transmits sound at lower frequencies, can be extended to cross-borehole tomography where images of seismic velocity between boreholes is generated, and geologic and hydrologic properties between the boreholes can be better understood.

Another type of physical downhole measurement is a caliper log which measures the varying diameter of an uncased borehole. Variable borehole diameter can indicate the potential for material to fracture or slough away from the walls and into a borehole, and therefore be a sign of media which may transport contamination. Alternatively, hydrogeologically transmissive zones can be directly identified with flowmeter monitoring. Vertical flowmeter testing in a single hole involves moving a flow measuring device up and down a hole during pumping or during nonpumping times, pinpointing zones of high and low groundwater transmissivity. Single-hole flow metering can also measure the rate and direction of vertical flow which can cause pollutants to migrate, and show relative vertical hydraulic gradients. In cross-hole flowmeter profiling, a flowmeter is placed in one hole while water is added or withdrawn from another borehole at a constant rate, allowing calculation of transmissivities, head differences, or storage coefficient between the boreholes. Packer systems (see section 8.4.9) can further isolate individual fractures and/or test hydrologic properties at individual depths between holes. Impeller flowmeters (rotameters, spinners) are most commonly used for these measurements, but have less resolution than heat-pulse or electromagnetic flowmeters. Vertical measurement of water temperature in a borehole can also be useful. These temperature measurements can define hydrostratigraphic layers, vertical flow, and water-bearing zones. Vertical borehole flow is implied by temperature gradients that are inconsistent with the regional geothermal gradient which is typically about 2.5°C per 100 m (1°F per 70 ft.). Distributed temperature sensing (DTS) has been used in boreholes to delineate hydrostratigraphic heterogeneities by synoptically profiling temperature distribution changes from thermal dilution tests. These tests do not disturb the fluid column (Leaf, Hart, and Bahr 2012).

Gamma and Neutron Logging Other borehole logging techniques are useful in site characterization. Downhole gamma logging records the amount of natural gamma radiation emitted by a formation in the vicinity of a borehole. Specific sources of gamma emission are potassium-40 (^{40}K) and daughter products of uranium and thorium decay series which are common in clays and shale. This is because these geologic materials contain weathered products from potassium feldspar and mica, and are apt to concentrate uranium and thorium. Importantly, clay and shale typically have low permeability and are barriers to contaminant flow. Another technique, neutron logging, measures the amount of water in any particular vertical section of borehole. Energetic or "fast" neutrons are sent out into the formation surrounding the borehole usually from an Americium Beryllium (Am-Be) or Plutonium Beryllium (Pu-Be) source, and these neutrons are slowed down by collision with hydrogen ions associated with water. The returning "slow" neutrons are measured by a detector and indicate water bearing strata in the vadose zone, and water-filled porosity below the water table.

Electrical Techniques in Borehole Geophysics Several borehole electrical techniques are available for site characterization. These include single point resistance logs, normal-resistivity logs, spontaneous-potential logs, electromagnetic induction logs, and fluid-resistivity logs. Single point resistance logs measure the electrical resistance between selected points in the borehole and an electrical ground on the surface, and are useful for understanding lithology, water quality and the amount of fracturing in hard rocks. Interpretation involves identifying zones of increasing resistance associated with small diameter boreholes, whereas lower resistance is related to saline water, large borehole diameter, and highly fractured media. Normal-resistivity logs record the resistance to electrical flow immediately outside an open, uncased borehole, and interpretation generally is similar to that of single point resistance measurement. Normal-resistivity logs typically involve deployment of a string of vertically displaced electrodes in a single hole.

Electromagnetic-induction (EM) logs also measure electrical conductivity or resistivity immediately outside a borehole and are excellent for indicating porosity, permeability, clay content, and total dissolved solids in fluids. Further, EM and other electrical techniques are proficient in identifying landfill leachate and saline water intrusion. EM borelog techniques are designed to optimize readings outside the borehole and minimize influence of the borehole and borehole fluids. Conversely, fluid-resistivity logs are geared toward examining borehole fluids, particularly the dissolved salt and solid concentrations.

Other Borehole Geophysical Techniques One versatile monitoring procedure for organic compounds is laser induced fluorescence (LIF) that uses laser light to excite fluorescent molecules in petroleum products. The excitation is specific for PAH compounds, but nearly all petroleum products contain some PAHs. LIF field measurements utilize a direct push logging arrangement which allows vadose zone and aquifer material to be examined at depth below ground surface. Further, LIF can distinguish different NAPLs in the subsurface using the intensity of the fluorescence in the media, its spectral signature, and the lag time between the laser pulse and emission of fluorescence. The laser light is transmitted down and uphole by two separate fiber optic threads, and the signal is processed and analyzed in real time.

Fiber optic chemical sensors (FOCS) are a variant of LIF and have been developed using a sensor for analysis of soil, air, or water that records changes in light absorbance, reflectance, fluorescence, and light polarization of the medium. Unlike LIF which just uses fiber optics to transport light down and uphole, FOCS uses the fiber optic cable as an integral part of the sensor. Specifically, part of the fiber optic cladding is removed from the cable in the sensor and replaced with a chemically selective layer that, when placed in the sample media, reacts with a specific analyte of interest. Raman spectroscopy is used to identify specific metals and organic chemicals. The detection limits are typically in the ppm range for VOCs.

8.7.3 Water Quality Indicators of Groundwater Provenance and Movement—Tracers

Beyond sampling water for contaminant concentrations and conducting geophysical surveys for defining subsurface geology, there are many other methodologies and water-quality indicators pertinent to site characterization. The chemical mixtures in measured contaminants and certain characteristic compounds (or "tracers") can be key indicators of pollutant source, travel pathways, and transformation. Tracer techniques for groundwater can be divided into water quality surrogates that are either (1) chemicals added to aquifer systems or to potential contaminants in regions where subterranean flow is expected to be rapid, or (2) "environmental tracers" which are groundwater quality changes which have occurred over longer periods of time in groundwater. The former includes dyes and chemicals intentionally added to track movement and flow, and the latter refers to "natural or anthropogenic compounds or isotopes that are widely distributed in the near-surface environment of the Earth, such that variations in their abundances can be used to determine pathways and timescales of environmental processes" (Cook and Böhlke 2000).

Payne et al. (2008) and Suthersan et al. (2014) present guidance for tracer selection, tracer test design, and data interpretation. An optimal groundwater tracer is highly detectable, mimics either groundwater or pollutant movement, is chemically stable for a desired length of time, has little background concentration in the groundwater being investigated, is not sorbed or filtered by the geologic media, and does not have adverse health or ecological effects (Davis et al. 1980). Conservative compounds that are not sorbed or retarded in their flow are particularly useful and these include chloride, bromide, iodide, nitrate, sulfate, and boron. These compounds can reflect groundwater origins with less ambiguity than other dissolved species, because they are often present in groundwater and some, like boron, are relatively unaffected by evaporation or chemical reactions (Barth 1998; Bassett et al., 1995; Vengosh 1998).

Dyes and Injected Tracers, Artificially Introduced Tracers In many fast-flowing (e.g., karst, carbonate rock, and caves) groundwater systems, tracer dyes can be released to track direction and travel times of flow. Optimal systems typically transmit water and pollutants quickly, which is advantageous because a long waiting time for the re-emergence of injected tracers is not favorable. Tracers can be artificially injected into wells, sinkholes, caverns, and disappearing streams in karst terrain. Popular tracer dyes include fluorescent dyes such as fluorescein which was developed over 145 years ago, pyranine, lissamine FF, photine CU, amino G acid (7-amino 1,3 napthalene disulphonic acid), optical brightners, and a variety of rhodamine dyes. A downside of some of these dyes is that some have negative health effects. Dyes can be used either qualitatively by visual observation, or collected with adsorbing devices to quantitatively measure flow. A simple adsorption apparatus involves placement of a charcoal packet along expected pathway of subterranean flow. More sensitive devices include filter fluorometers and spectrofluorometers which can determine specific fluorescent wavelengths, quantify flow more accurately, and distinguish background fluorescence and other interferences. In addition to the tracing of natural waters, dyes can help determine pipeline leaks. Nonpolar fuel dyes can be added to demarcate different fuel types and are required in some countries. This can help distinguish the individual impacts of multiple fuel leaks of similar types, but from different sources.

Things other than dyes can be injected as tracers of groundwater flow. A common tracer for groundwater is chloride (Cl^-) which is a component of common table salt. Care must be used when using ionic tracers so that the concentration of salts added to groundwater does not change its density and subsequently impact natural groundwater flow. A more unusual tracer that has been used in cave systems is a signal emitting float which has a delayed explosion. The seismic signals emitted from these generated impulses can help locate subsurface passages. Other tracers that have been used with varying degrees of success include silicic acid, boric acid, phosphoric acid, acetic acid, alcohols including ethanol, sugars (sucrose, maltose, dextrose, glucose), and glycerol (Davis et al. 1985). Each of these tracers has disadvantages: acid can react with aquifer material, sugars decompose rapidly, and alcohols tend to be absorbed onto organic material (which can actually be used to advantage by measuring partitioning into suspected organic contaminants).

Tracers developed for contaminant hydrogeology include a class of compounds called partitioning tracers. These newer methods involve circulating a suite of tracer compounds, not just a single tracer, in the subsurface to measure how some tracers are slowed by contaminant mass, particularly a mass of nonaqueous phase liquids. Partioning tracers measure groundwater flow and the mass of a stagnant immiscible liquid pollutant blocking groundwater's path by observing the differential tracer retardation. The underlying principles of this tracer method have been discussed in Chapter 3.

Scientific developments include the study of colloidal tracers and smaller, nanoparticle tracers. These colloidal tracers have included yeasts, bacteriophages (viruses), fluorescent latex microspheres, bacteria (living and dead), spores (Lycopodium and vegetative spores), and other nanoparticles (Davis et al. 1980; McKay et al. 2000; Zhang et al. 2015). Solid tracers are larger than dissolved aqueous tracers and have the negative possibility of being sieved or filtered through porous media and small-aperture fractured media. Larger particle tracers do, however, have the positive quality of not being absorbed in the rock matrix. Occasionally, solid tracers have been observed to move faster than average groundwater velocity—this has been explained by the notion that larger particles move through larger pore spaces or fracture apertures where groundwater velocities are higher than average (Zhao 2015).

Gases can be used as tracers of vapor migration, and of liquid migration by injection and dissolution of gases into groundwater. Inert radioactive tracer gases have been considered, such as xenon (^{133}Xe) and radon (^{222}Rn), particularly in identifying groundwater/surface water interaction, bur health concerns and a short half-life for radon are inhibitory (Xie et al. 2016). Noble gases of helium, neon, argon, krypton, and xenon are other potential tracers as their natural background in the environment is low. Chloroflourocarbons (CFCs or Freon® compounds), also have low environmental background and have been used for both groundwater and gaseous tracer experiments (Thompson et al. 1974, Weeks et al. 1982; Kreamer et al. 1990).

Environmental Tracers Environmental tracers which show water-quality patterns and changes do not have to be injected by site investigators, and are directly relevant to understanding a contaminated site. Some of these tracer signals arise due to natural flluctuations in local, regional, or global conditions, while others reflect anthropogenic influences and activities. Some take advantage of short term changes. For example, diurnal temperature fluctuations can be used to define gaining and losing reaches of streams. Probes placed in bottom sediments of streams that show daily temperature variation can be associated with losing reaches as water, affected by daily conditions, infiltrates. Conversely, steady temperatures in stream bottom sediments can be indicative of a gaining groundwater contribution to a stream through the sediments, as most groundwater is typically more constant in temperature. Other tracer signals arise from longer-term changes in climate, recharge differences, or substances that humans introduced into the environment decades ago. Compounds and isotopes that have leaked into the atmosphere from human activities (e.g., chlorofluorocarbons from refrigerants, radionuclides from testing of nuclear weapons) return through rainfall to the vadose zone and groundwater, and allow dating of groundwater age, whereas pharmaceuticals, personal care products, and specific compounds in some foods (e.g., caffeine) are not readily removed by sewage treatment and become tracers of wastewater release into the environment.

The source of a pollutant strongly influences its chemical makeup, and chemical differences from dissimilar sources can be used to trace and track environmental contamination. Biogenic gaseous mixtures containing methane are typically "dry" which means a higher concentration of methane and light hydrocarbons, whereas thermogenic gases and those from pipelines have less light 2 to 4 carbon compounds (C2s to C4s) and are "wet" with a higher concentration of 5 carbon (C5) and higher molecular weight compounds. Landfill gases are often approximately half methane and half carbon dioxide with an absence of oxygen. Natural gas derived from dewatering of coal layers, an extraction process whose retrieved product is called "coal seam gas" or "coal bed methane," is typically higher in methane than natural gas extracted from other sources and is therefore sometimes called "sweet gas." Crude oil and coal from different regions of the world have different chemical constituents which can be tracked, for example differences in the amount of sulfur compounds designates different quality of crude oil. The petroleum industry has noted that uptake of sulfur into plants is possible. Because different isotopes of sulfur can fractionate in different ways, the transport and fate of sulfur bearing compounds can be further tracked. Also, natural gas in pipelines in municipal and urban settings typically has noxious smelling mercaptan added so that leaks of this normally odorless gas are readily noticeable and are often reported. The added gases which allow leak detection and tracking sometimes have descriptive names like Cadaverine and Putrescine.

Human sewage and animal waste have a host of associated compounds and microbes which can be used to track their contamination in groundwater systems. Bacterial indicators, like Escherichia coli (*E.coli*) are useful, but often can be filtered out in porous media, whereas bacteriophages and human viruses are smaller and can travel farther. When microbes occur in groundwater they can indicate source by phenotype, genotype, and speciation (some microbes are more associated with human waste and others with ruminant species). Some genera and species of bacteria studied as indicators differentiating human from other mammalian waste include: *E.coli*, relative amounts of fecal streptococci and fecal staphylococci, *Bacteroides* spp., *Rhodococcus coprophilus* (animal herbivores), *Clostridium perfringens, Bifidobacterium adolescentis* (human), and *Bifidobacterium thermophilum* (animal). Other tracers of human and animal waste include: sterols, steroid estrogens (found in human sewage outfall), fatty acids and lipids, surfactants and detergents, caffeine (human ingestion and sewage outfall), triclosan (an antibacterial and antifungal agent found in hand soaps, body washes, toothpastes, and some cosmetics—sewage outfall), and sewage/septic tank related nonylphenol ethoxylate metabolites (Swartz et al. 2006).

Ionized substances have been used both as artificially injected tracers and measured as natural environmental tracers indicating source. There are a large number of ions which can be tracked and traced, and these substances do not decompose with time. Historically, those chemical species with high concentrations, easy detection, and low sorption have been the most popular. This includes negatively charged anion species which are repelled by negatively charged clay surfaces and therefore resist sorption. Traditional tracer ions include Cl^-, Br^-, Li^+, NO_3^-, NH_4^+, $SO_4^=$, Mg^{++}, K^+, B, and I^-. Of these, Cl^- and Br^- are the most popular. Organic anions have been used as tracers, including benzoate Metal complexes with chelating agents have been used to track groundwater flow, balancing the need for a detectable tracer with the potentially negative health effects of mobilizing a heavy metal pollutant (Davis et al. 1980). With the advent of Inductively Coupled Plasma Mass Spectrometers (ICP-MS) investigations of naturally occurring trace elements to identifying groundwater pathways increased (Stetzenbach et al. 1994; Kreamer et al. 1996; Johannessen et al. 1997).

Impottantly, CFCs have also been used for dating recharge from precipitation, because the first wide use Freon® refrigerants began after 1930, and subsequently increasing amounts of gaseous CFCs leaked into the atmosphere and mixed with precipitation, eventually infiltrating the ground surface and recharging groundwater. CFCs were also used as aerosol spray can propellants, but because they contribute to ozone layer depletion in the atmosphere, their use has been phased out under the Montreal Protocol. CFCs are greenhouse gases with an approximate residence time in the atmosphere of 65 to 130 years and their abundance or absence in groundwater is an indicator of groundwater age. The ratio of CFCs to SF_6 (sulfur hexafluotide) has a groundwater dating age range of about 1 to 40 years.

8.7.4 Water Quality Indicators of Groundwater Provenance and Movement—Groundwater Composition, Compound Ratios, Daughter Products, Degradation Indicators, and Other Indicator Compounds

A considerable number of methods to track, trace, and date groundwater contamination rely on looking at the changing composition of pollutant compounds, associated chemicals, and differences in the chemical nature of multiple sources. Identifying and utilizing compositional differences is a powerful tool in understanding groundwater and contaminant flow.

Inorganic Indicators One of the simplest ways to distinguish different sources and transformation of contaminants is by analyzing groundwater chemical quality and compound ratios. Significant analytical chemistry advancements have been, and continue to be, made since major anions and cations were first measured in groundwater, but these ions, and the ratios between these ions (particularly the more mobile anions) continues to be a source of groundwater definition. Piper, Stiff, and Maucha diagrams visually portray the major ionic components of water quality and can indicate groundwater provenance. Ratios of ions can also be used to distinguish waters. For example, a common anion comparison used to trace groundwater has been the Cl^-/Br^- ratio. Davis et al. (1998) report on many of the uses and applications of this ratio, including determining the origin and evolution of salt water and brines, and studying salt in potable groundwater. Factors which can affect this ratio include distance from the ocean, dry lake beds, or other sources of salt, including pollution (Davis et al. 2004; Alcala and Custodio 2008). These ratios have been used to track septic tank pollution in the United States (Katz et al. 2011). Other useful ratios are total inorganic carbon to total organic carbon ratios, and carbon to nitrogen ratios.

Mining operations for various metals often can have more than one metallic species that can enter groundwater, or mobilizing agents and additives associated with the particular extraction method and target metal. These other species and additives can often be used to track the influence of mining operations on groundwater systems. Several metals, metalloids, and nonmetals can often be found together in metal extraction and mining (e.g., it is possible to observe combinations of uranium, copper, arsenic, gold, silver, vanadium, sulfur, thorium, lead, zinc, or others from some precious metal operations). Other types of mining undertakings have other potential tracers released into the environment. *In situ* leach mining typically uses an injected lixiviant to dissolve and mobilize extractable metals, and these lixiviants can be used as one indicator of potential contaminant migration, with the cautionary note that while a rapidly moving lixiviant can give early warning of potentially slower-moving contamination, the disappearance of the lixiviant does not necessarily indicate the disappearance of the spectrum of potential groundwater contaminants at a mining site. Metals can also be used as surrogate tracers for energetic compounds, that is propellants, explosives, and pyrotechnics (PEP) compounds. For propellants and some fuels particularly linked with the rocket fuel oxidizer perchlorate, Cr^{+3}, Cr^{+6}, Cu^{+2}, and Zn have been evaluated as surrogates. Surrogate compounds in fireworks and flares include Na, K, Ba, Cu^{+3}, Sb, Sr, Al, As, and Cr^{+5} (Motzer 2001).

Organic Indicators Organic compounds, particularly mixtures of organic chemicals, have a wide range of sources, additives, and degradation products which can be tracked in groundwater (Chapter 7). The differing rates of degradation of the compounds in subsurface organic mixtures produce changes in the ratios of those compounds and of generated daughter compounds. Many organic mixtures have unique source compositions and all eventually weather and transform with time. Hydrocarbon fuels in particular have different compositions, depending on fuel type and additives. These differences serve as distinguishing features when several different fuels have leaked or have been spilled. Fuels and oils normally consist of mixtures of hundreds of compounds, and different fuel types have different dominant ranges in the number of their carbon atoms. Crude oil has compounds that range from having one or two carbon atoms (C1 and C2) to compounds with close to sixty (C60). Crude is fractionally distillated to establish different types of hydrocarbon products, and different additives are put in for these varied purposes. Gasoline for cars (petrol) and small airplanes (aviation gas or AV-gas) typically have light hydrocarbons predominantly ranging from the 4 carbon compounds (C4) to about the 11 or 12 carbon range (C11 to C12). Kerosene is a heavier fuel with approximately the C8 to C17 compounds, diesel fuels are roughly in the C8 to C24 range, the jet fuel JP-4 is about C5 to C14, and JP-8 and Jet-A approximately C8 to C18. Stoddard solvent, which was used in the past as a dry cleaning fluid, has a typical petroleum distillate fractions of C7 to C12, heavy fuel oils are generally between C8 and C50, bunker fuel used in ships are approximately C10 to C26, and lubricating oils are even heavier with carbon numbers around the C14 to C50 range. Other residuum from crude distillation often have more than 20 carbon atoms in their constituent compounds, with waxes ranging approximately from C20 to

Darrah et al. 2013). Recently, examining methane in concert with noble gases in stream beds has been used to identify thermogenic methane fluxes from groundwater overlying regions of shale gas development (Heilweil et al. 2015). Methane isotopes as well as dissolved organic carbon and tritium have been use to evaluate connectivity between aquifers and underlying coal seam gas operations (Iverach et al. 2015).

Quantifying the uptake of nutrient compounds during biodegradation and the resultant production of daughter products and residuals are ways to monitor the rates of transformation of organics. Petroleum degradation is normally an aerobic process which uses oxygen and produces carbon dioxide; by monitoring the extent of change in these compounds one can calculate the rate of biodegradation and, importantly, determine whether the plume is moving faster than the rate of natural or augmented pollutant attenuation.

Harmful compounds can have additives or impurities which are not only good tracers in the environment, but they can be pollutants in their own right. Chlorinated solvents have several stabilizers. For trichloroethene (TCE), 1,4 dioxane is an important stabilizer used to facilitate transport and storage in aluminum containers. It is itself considered a solvent with negative health effects. The ratios of the chlorine-35 to chlorine-37 can be another way to fingerprint chlorinated solvents. Another example of mixtures and impurities is polychlorinated biphenyls (PCBs) which are never a pure, single compound, but mixtures of PCBs by the nature of their manufacture. PCBs can also have co-contaminants of polychlorinated dibenzofurans and polychlorinated naphthalenes. The nature of the mixtures can be a good source of differentiation, and the disparity in the degradation rates of contaminants, additives, impurities, and inert compounds can indicate age and source.

Historically, pesticides were mixed with some hydrocarbon fuels to apply them to crops. Many of these pesticides have comingled substances (some inert) and trace substances (e.g., dioxins and furans) which can help fingerprint their spatial distribution at a site. Like PCBs above, the source and age of pesticide releases can be established by comparing the ratio of inert and degrading compounds.

8.7.5 Water Quality Indicators of Groundwater Provenance and Movement—Isotopic Identification of Pollution Sources and Groundwater Pathways

The measurement and evaluation of stable, radioactive, and radiogenic isotopes has played an important role in hydrologic and geologic investigations, and are equally consequential in the characterization of contaminated sites. Because physical, chemical, or biological transformation of a contaminant can alter the compound's original isotopic ratios (fractionation), transformation processes can often be distinguished from contaminant dilution (which typically does not alter these ratios). The mathematics of Rayleigh distillation to quantify isotopic fractionation accompanying phase changes and chemical reactions are well known, and make available numerical estimates of the magnitude of isotopic change. The analytical detection of isotopes in groundwater and vapors is rapidly advancing, with the required sample volumes becoming smaller, and analyses becoming faster, less expensive, and routine. From older methods like scintillation counting of radioisotopes which required large volumes of water, through isotope ratio mass spectrometry advances, to new analytic techniques such as Laser Isotope Ratio Infrared Spectrometry IRIS, which can be portable and field deployable, the analytical chemistry underpinnings of contaminant surveys has increased the ability of the contaminant hydrogeologist to assess a site and its properties. Accelerator mass spectrometry (AMS) can sometimes separate atomic isobars (for example nitrogen-14 from carbon-14) and makes possible the detection of many isotopes, including many that are long-lived. AMS has been applied to the analysis of many isotopes including ^{36}Cl, ^{10}Be, ^{14}C, ^{3}H, ^{129}I, ^{26}Al, ^{236}U, ^{240}Pu, and ^{210}Pb.

Applications of isotope hydrology to challenges of groundwater movement and source are numerous, diverse, and are used worldwide. Isotope hydrology has been used to ascertain renewable and nonrenewable, deep groundwater in Syria (Al-Charideh and Kattaa 2016), the origin of groundwater in the Negev Desert (Vengosh et al. 2007), preferential flow along faults in Germany (Gumm et al. 2016), altered spring flow quality in Grand Canyon National Park in the United States (Ingraham, Zukosky, and Kreamer 2001), assessment of fluid inclusions at the proposed nuclear waste repository at Yucca Mountain, Nevada, as evidence of a hypogene paleohydrogeological event (Dublyansky and Spötl, 2010), baseline measurement and assessment of methane concentrations of a well in Alberta, Canada (Humez et al. 2016), and has been employed for countless other assessments at locales around the globe.

Tracing Groundwater and Pollution with Isotopes More than fifty years ago, paleoclimatologists and environmental geochemists began using the stable isotopes of hydrogen and oxygen to track meteoric water movement on the environment (Craig 1961; Dansgaard 1964). An equation showing the average relationship between these isotopes was established (the global meteoric water line) and variations due to temperature, seasonality, precipitation and recharge altitude, latitudinal relationships, and paleo-effects were key in understanding global water movement, including groundwater source and pathway. Because surface waste impoundments (ponds, pits, and lagoons) have the potential to partially evaporate water, then have the remaining surface water leak into the subsurface, isotopic fractionation during evaporation of water is particularly important to contaminant site characterization studies. Evaporated water has a lighter isotopic composition, enriching the remaining liquid with heavier isotopes which can often be tracked into the subsurface, distinguished from background groundwater isotopic signatures, and used to establish mixing ratios of leaked, contaminated water to natural background groundwater signatures. For very old groundwater, past climatic change can be observed and contribute to studies of aquifer isolation and aquitard or aquiclude integrity. Aquitard integrity and the origin of pore water has been investigated in Canada for mining operations and potential nuclear waste storage by comparing Pleistocene age versus modern stable isotope ratios, below and above thick aquitards (Hendry et al. 2013; Hendry et al. 2015). The stable isotopes of water are hydrogen and deuterium, and oxygen-16 and oxygen-18.

The stable isotopes of nitrogen (nitrogen 14 and 15) in concert with those of oxygen have been used to discern anthropogenic sources of nitrate, nitrite, and ammonium in groundwater These contaminant sources can include septic tank effluent or wastewater, animal manure, and mineral fertilizers, and can often be distinguished by isotopic ratios. Because there is some overlap and ambiguity between isotopic composition in wastewater and animal manure, and denitrification processes in the subsurface can result in fractionation after nitrate release, additional indicators can be used to help tell different sources apart. Distinguishing co-contaminants from agriculture can include herbicides, pesticides, and major ions and trace elements from soil amendments. From wastewater, co-contaminants can include pharmaceutical compounds, residuals from personal care products, caffeine, and artificial sweeteners. Some animal feeds contain unique inorganic additives as well. Relatively conservative stable isotopes of boron (10 and 11) have also been used to make a distinction between wastewater and animal manure (Eppich et al. 2012). In China, stable isotopes of hydrogen, and oxygen and sulfur have been used to delineate the sources of anthropogenic nitrate and sulfate groundwater pollution (Li er al. 2006). Sulfate isotopic values indicated much of the pollution came from recharge of air pollutants from the combustion of coal, with some contribution of sulfur additives in fertilizer.

Mining residuals and mineral waste products can be distinguished by isotopic analysis. In uranium oxides, stable isotopes of oxygen can help distinguish anthropogenic mining activities from natural background as can activity ratios of uranium-234 to uranium-238. $^{234}U/^{238}U$ ratios are close to 1, (secular equilibrium) near uranium mining outfall, whereas naturally occurring uranium background in groundwater often has a higher ratio, particularly in old groundwater. Conversion of ^{238}U to ^{234}U can further be examined by its concurrent production of alpha particles, ^{4}He. Another isotope, uranium-236 is dominantly anthropogenic, is found in spent nuclear fuels and some reprocessed uranium, and can therefore help trace nuclear waste leaks. Plutonium (Pu) is also of human manufacture, and while trace amounts can be found in nature (parts per trillion in groundwater) larger concentrations of this fissile material indicate contaminant excursion. A potential nuclear waste product and tracer is technetium-99 which is the most significant long-lived fission product of uranium.

Other mining and industrial by-products, including metals and salts, can be characterized with isotopic analysis, sometimes in conjunction with other approaches. For example, stable isotopic analysis of chromium species in groundwater can give a picture of the natural reduction of mobile and harmful Cr(VI) to less problematic Cr(III). It can also characterize the extent and rate of Cr reduction during remedial activities. Another industrially produced compound which has been found in groundwater, and is an endocrine disruptor in humans, is perchlorate. Perchlorate has some naturally occurring salts, but is mostly generated by industrial processes especially for the production of rocket fuel oxidizers. Tracking the compound in the environment bas included measurement of the oxygen and chlorine isotopes of perchlorate itself as well as other isotopic ratios and attendant compounds. Other useful isotopic analyses for perchlorate tracking are stable isotopes of strontium, nitrogen, and tritium, and isotopic ratios of $^{37}Cl/^{35}Cl$, $^{87}Sr/^{86}Sr$, and $^{16}O/^{17}O$. Some of perchlorate's additional surrogates in groundwater that can assist in source identification and age dating include: nitrates, sodium, chlorides, strontium, phosphate, metals, and nitroglycerins (Morrison and Murphy 2006). These methods can help determine whether perchlorate in the environment is natural or synthetic.

Isotopes and Groundwater Dating Isotopes are also used for characterizing the fate and transport of organic compounds. Processes affecting dense chlorinated solvents and other volatile organic compounds can be evaluated using chlorine isotopes which are fractionated during biodegradation, but are unaffected by dilution and dispersion. MTBE biodegradation can be analyzed with isotopic analysis, the difference between production methane from natural, shallow biodegradation versus leaks from pipelines or production wells can be ascertained. When a compound such as trichloroethene is discovered at a site, compound specific isotopic analysis can help determine whether it is a daughter product of previously spilled tetrachloroethene, or a leak in and of itself.

Site characterization involves understanding groundwater flow and travel times. Isotopic techniques are pivotal in age dating of groundwater, and there are different approaches depending on groundwater's suspected residence times. Relatively young groundwater is often dated by using radionuclides released into the atmosphere during past nuclear weapons testing. For example, tritium (^3H), with a half-life of 12.4 years, with its decay product ^3He, provides a useful tracer of recently recharged groundwater. When calculating groundwater age from tritium, adjustments to $^3H/^3He$ ratios must be made if there is terrigenic helium in the groundwater from the earth's mantle or crust. Tritium to helium-3 ratios are most effective at dating groundwater 0.5 to approximately 40 years old. Another dating technique for modern groundwater 10 years old or younger uses krypton-85, which is produced by nuclear reprocessing and has a similar half-life to tritium, and comparable dating range as well. Nuclear bomb-pulse chlorine-36 is also used to date young groundwater recharged after the 1950s, but in lower, natural concentrations in deep systems can also be used to evaluate submodern groundwater that is 50,000 to a million years old. Methods for dating submodern groundwater (>1,000 years since recharge) include radiocarbon dating (carbon-14). The amount of ^{14}C (half-life 5,730 years) in groundwater can indicate when it was last in contact with the atmosphere, but care must be taken to account for uncertainties due to potential groundwater interaction with carbon from other sources, such as the "dead" carbon in limestones and other carbonate rocks which has no ^{14}C. In optimal conditions ^{14}C can be used to date groundwater about 1,000 to 40,000 years old and can sometimes be used in concert with argon-39 (half-life 269 years). Silicon-32 has the beneficial aspect for groundwater dating of having a half-life of 140 years which allows it to fill a gap between tritium and carbon-14 dating, but its loss and interaction with solid phase silica in an aquifer and analytical difficulties have limited its use. Uranium isotopic ratios are also a useful groundwater dating tool. $^{234}U/^{238}U$ ratios (called uranium isotope disequilibrium) typically increase with groundwater age and can be used to give approximate ages from 10,000 to one million years old. Some isotopes with long half-lives have the potential to date very old groundwater with applications for understanding the isolation of deep contaminant burial, nuclear storage, or deep waste injection. These include iodine-129 (half-life 15.7×10^6 years), krypton-81 (half-life 2.29×10^5 years), and Xeon-139 (half-life 2.165×10^{21} years).

8.7.6 Water Quality Indicators of Groundwater Condition—Microbial testing and Genome Sequencing

Studying subsurface microbiology at contaminated waste sites allows groundwater professionals to calculate the rate of natural attenuation of pollutants, the efficacy of amendments added to groundwater to enhance contaminant breakdown, and the

8.8 Summary

Site characterization involves goal setting and outcome definition, use of noninvasive techniques, followed by strategic application of invasive methods of investigation. In order to collect data for groundwater contamination studies, it is usually necessary to install monitoring wells. Such wells can permit one to measure water levels, collect water samples for analysis, and detect the presence of nonaqueous phase liquids.

Monitoring-well design considers the type and diameter of casing and screen, the material from which the casing and screen is constructed, and whether the well will have an artificial-filter pack or be naturally developed. The annular space between the casing and the borehole must be properly sealed, and the well needs a protective covering. Monitoring wells may be installed by hollow-stem auger drilling, mud-rotary drilling, air-rotary drilling, reverse-rotary drilling, and cable-tool drilling. The equipment used for monitoring-well installation and the material used for the well must be properly decontaminated. Once installed, the well needs to be developed to remove fine material from the area outside the well screen. Water-table wells are installed to monitor the water table and piezometers are used to monitor formations below the water table. Frequently, a water-table well and several piezometers are installed at the same location to form a nest of wells to sample the formations at different depths. Multilevel monitoring devices may be used to collect samples from very closely-spaced vertical intervals.

There are a number of sampling devices that have been developed to withdraw water samples from monitoring wells. These include bailers, bladder pumps, stator-rotor pumps, piston pumps, and peristaltic pumps. The ability of these devices to collect an unbiased sample varies with the design, technique used, and material from which they are constructed. Prior to sampling a well, it is necessary to purge it to remove stagnant water from the casing. Micropurging techniques result in a water quality sample that is as free of turbidity as possible and at a lower cost than traditional purge and sample techniques due to a shorter time to collect the sample and reduced costs for disposal of contaminated purge water. Soil water must be collected through the use of a suction lysimeter. These are installed in boreholes above the water table. Soil gas vapor can be sampled through active probes that withdraw soil gas samples for analysis or passive devices that sorb soil gas onto activated charcoal devices. Monitoring soil gas can indicate areas where the soil has been contaminated and requires remediation. It can also be used to delineate areas where shallow groundwater is contaminated by volatile organic compounds and where there is a layer of a volatile, nonaqueous phase liquid floating on the top of the capillary zone. Phyto-screening, surface geophysics, and aerial photographic interpretation are other noninvasive or low impact characterization techniques that are appropriate at many sites.

There are a host of chemical and microbial analysis technologies that assist interpretation of the source, movement, and transformation of subsurface contaminants. Differences in source chemistry, generation of daughter compounds, and comparison of compound ratios lend themselves naturally to environmental forensic investigations. Chemical compound transformation, the utilization and uptake of nutrient compounds, varying chemical compound ratios, and changes in subsurface microbial communities all can be indicators of bioremediation and compound attenuation. Geophysics, groundwater dating, and borehole core analysis can define the geologic provenance and flow constraints which affect pollutants.

9

Site Remediation

9.1 Introduction

Since the early 1980s groundwater scientists and engineers have developed a number of techniques for both containing and remediating soil and groundwater contamination. In the United States this has been driven by federal legislation including the Resource and Conservation and Recovery Act (RCRA) and the Comprehensive Environmental Response, Compensation and Liability Act (CERCLA). The Hazardous and Solid Waste Amendments of RCRA address the storage of liquids in underground tanks. Individual states have also passed environmental regulations that may be triggered when property is sold. Regulations associated with these laws dictate when it is necessary to evaluate if a site is contaminated, and if it is, what must be done to remediate the contaminated soil and groundwater. Even in the absence of a specific regulatory requirement, many potential property buyers will require the seller to demonstrate that a property is not contaminated. This may take the form of a Phase I Environmental Study, which involves a detailed review of the historical uses of the property and a review of state records to determine if there is a likelihood of a potentially contaminating activity in the past. This may be followed by a Phase II Environmental Study, where several soil borings are drilled and one or more groundwater monitoring wells are installed. These investigations are for the protection of the buyer and the financing institution because if the property is found to be contaminated after purchase, the new owner would be responsible for some or all of the cleanup costs (Phase III).

In general, remediation of a site must address two issues. If there is an ongoing source of contamination, control of the source will be necessary. There is no point in remediating the environment if new contamination is being released to the soil or groundwater. Examples of sources include landfills, mine tailings piles, leaking underground storage tanks, pipelines, septic tanks, and sewer lines. In addition to primary sources, such as those listed above, there can be secondary sources of contamination due to contaminants which have already been released to the environment. These secondary sources include nonaqueous phase liquids (NAPLS) which may be trapped in the vadose zone, floating on the water table or trapped below the water table. Once the primary source has been removed or isolated, then secondary sources must be identified and isolated. Only after that has occurred is treatment of contaminated soil and groundwater effective.

The final goal of a remediation program for contaminated soils and groundwater is generally subject to approval of a state or federal regulatory agency. In almost all cases it will be impossible to completely remove all contamination so that the site returns to a pristine condition. After all, many contaminated sites have been the locus of industrial activities for decades; indeed, some sites in the eastern United States or in Europe have been used by one industry or another for centuries. In the United States of America, state agencies or the U.S. Environmental Protection Agency may have numerical standards for the soil and groundwater that must be met after site remediation. Similarly, in the European Union, the European Environment Agency (EEA) works together with national agencies on defining what are "good" and "poor" quality water bodies (Water Framework Directive 2000/60/EC of the European Parliament and of the Council). Many other countries have modeled their environmental standards on EPA or European regulations. These standards are generally based on anticipated future land use. Soil remediation standards for future residential land use will be more stringent than those for industrial use. Groundwater standards may be based on drinking water Maximum Contaminant Levels (MCLs).

The application of very stringent standards may result in the expenditure of large amounts of money to reduce extremely small or even nonexistent risks (Viscusi and Hamilton 1996). As much as everyone would like to live in a pristine environment, it simply is not practicable in the post-industrial world. There are limited funds available for environmental cleanup; we should expend those funds in a manner that is most effective in terms of reducing real risks. This has led to the concept of risk based corrective actions (RBCA). Rather than cleaning up all sites to a set standard, a risk assessment of the site is made, and risks to specific receptors are addressed. For example, if the groundwater is saline and not used as a drinking-water source, it may not be really necessary to remove a chlorinated solvent to the drinking-water standard.

Contaminant hydrogeologists in collaboration with engineers, chemists, biologists, modelers, and many other experts have developed some very powerful methods of removing contamination from soil and groundwater. However, these methods are not capable of totally removing all contamination. A zero contamination strategy is not possible, even if we were willing to commit unlimited funds.

In this chapter we will examine a number of source zone and groundwater plume remedial techniques, some proven and some experimental. Table 1 provides an overview of some of the most common technologies and their applicability and development status. There are a few textbooks (e.g., Suthersan et al. 2017) and a number of public domain resources that can guide us in the discussion of these remediation technologies. For instance, the Interstate Technology and Regulatory Council (ITRC) makes available documents ranging from technical overviews and case studies of innovative remediation technologies to technical and regulatory guidance documents for applying cleanup technologies (www.itrcweb.org/guidance). Similarly, the Federal Remediation Technologies Roundtable (FRTR) provides access to a remediation technology screening matrix for screening potentially applicable technologies for a remediation project, including a long list of technology descriptions (www.frtr.gov/scrntools.htm). The National Academies of Sciences, Engineering, and Medicine—National Research Council (NRC) publishes periodic reports on the state-of-the-art in the remediation of contaminated sites (http://www.nap.edu/topic). The Strategic Environmental Research and Development Program (SERDP) is an environmental science and technology program, planned and executed by the U.S. Department

TABLE 9.1 Common and innovative contaminant remediation technologies.

Technology	Application	Development Status
Pump-and-Treat (P&T)	(Source Zone) / Plume / Containment	Established
Physical Containment	Source Zone / Plume	Established
Solidification/Stabilization	Source Zone	Established
Soil Vapor Extraction / Air Sparging	Unsaturated Zone; Source Zone / Plume	Established
Bioremediation and Monitored Natural Attenuation (MNA)	Source Zone / Plume	Innovative / Established
Permeable Reactive Barrier	Source Zone / Plume	Innovative / Established
Chemically Enhanced Flushing	Source Zone	Established
Thermal Treatment	Source Zone / Unsaturated Zone	Innovative / Established
In Situ Oxidation	Source Zone / Plume	Innovative / Established
Phytoremediation	Plume / Unsaturated Zone / Containment	Innovative / Established

Note: The boundary between what is a conventional and innovative technology is fluid.

Source: Modified after NRC 2013.

of Defense (DOD), Department of Energy, and the EPA and others. Together with another U.S. DOD program, the Environmental Security Technology Certification Program (ESTCP), these programs support the development and demonstration of the latest remediation technologies. They also provide access to documents describing innovative, cost-effective, and sustainable environmental cleanup solutions, including for the treatment of DNAPL source zones or groundwater plumes (www.serdp-estcp.org). Funded by the European Union, the EUGRIS (European Groundwater and Contaminated Land Remediation Information System) is an openly available information platform for contaminated land and groundwater information (www.eugris.info/index.asp). While there are many more resources available to students as well as practitioners, one of the largest depositories of information about contaminated site characterization and remediation technologies is maintained by the U.S. EPA (www.clu-in.org). Currently, the website includes information on several hundred field-scale remediation technology demonstration projects.

9.2 Source-Control Measures

9.2.1 Solid Waste

Solid waste may have been buried in an unsecure landfill, placed in an open excavation or old quarry, or simply spread on the land surface. If contaminants continue to be leached from these sources by infiltrating precipitation, or even groundwater if the solid wastes have been buried below the water table, then a source-control measure is necessary before groundwater remediation is attempted. If the source continues to leach contaminants, then groundwater remediation may be futile.

Source-control measures include physical removal of the waste and transportation to a secure landfill or incinerator, construction of impermeable covers or low-permeability caps to eliminate or minimize infiltration of precipitation, and construction of physical barriers around the waste source.

9.2.2 Removal and Disposal

If the source is removed, then wastes can no longer migrate from it. Solid waste that has been spread on the land surface can easily be removed by conventional earthmoving equipment. Waste that has been buried in a landfill can also be exhumed and transported to a secure landfill. A hazardous-waste landfill was operated near Wilsonville, Illinois, USA, from 1976 to 1981. Hazardous wastes, including liquids, were buried in drums that were placed in 26 trenches, each approximately 3.3 m to 6.5 m (10 to 20 ft) deep, 15 to 30 m (50 to 100 ft) wide, and 53 m to 122 m (175 to 400 ft) long. In 1981, it was found that hazardous wastes had migrated up to 16.7 m (50 ft) from the trenches over a 3-year period, a rate 100 to 1000 times greater than predicted prior to construction of the landfill. Following a court order, the site owner exhumed and removed all the drums and transported them to a more secure landfill. The process took 4 years and many millions of dollars (Herzog et al. 1989).

Excavation and removal of hazardous materials must be done in a manner that protects the health and safety of workers and the public. The materials may be hazardous if one comes into contact with them, they give off toxic or dangerous vapors, or if ingestion of these materials would be harmful. The risk of moving material as opposed to leaving it in place must always be evaluated prior to a removal action.

Furthermore, the final disposition must be environmentally sound. In at least one case, spent solvents were moved from an abandoned hazardous-waste site to a solvent-recycling facility. The latter facility eventually went bankrupt and became a hazardous-waste site itself. Under CERCLA, the courts have found that the generator of hazardous wastes is responsible for their cleanup and disposal costs if the disposal-site operator becomes bankrupt. In this case, the generator had to pay twice for the disposal of wastes. This policy is known as "cradle-to-grave" and is designed to ensure that hazardous waste is controlled from the time it is generated until its ultimate disposal. The EPA defines hazardous waste as "waste with properties that make it dangerous or potentially harmful to human health or the environment" (U.S. EPA 2016). In regulatory terms, an RCRA hazardous waste falls into two categories: (1) waste specifically listed by EPA and (2) characteristic waste which exhibits one or more of the following: ignitability, corrosivity, reactivity, or toxicity. These four waste characteristics are communicated in many different ways, including Material Safety Data Sheets (MSDS) or by hazard labels. For instance, the NFPA 704 chemical hazard label standard uses a diamond-shaped diagram of symbols and numbers to indicate the degree of hazard associated with a particular chemical or material (Figure 9.1). You probably have seen this or similar signs posted in laboratories or other places where potentially hazardous materials are being stored. In any given state, the EPA or the state hazardous waste regulatory agency enforces hazardous waste laws and most universities have hazardous waste offices to ensure compliance with those laws.

FIGURE 9.1 The NFPA 704 chemical hazard label. Each quadrant is labeled with its respective color and hazard.

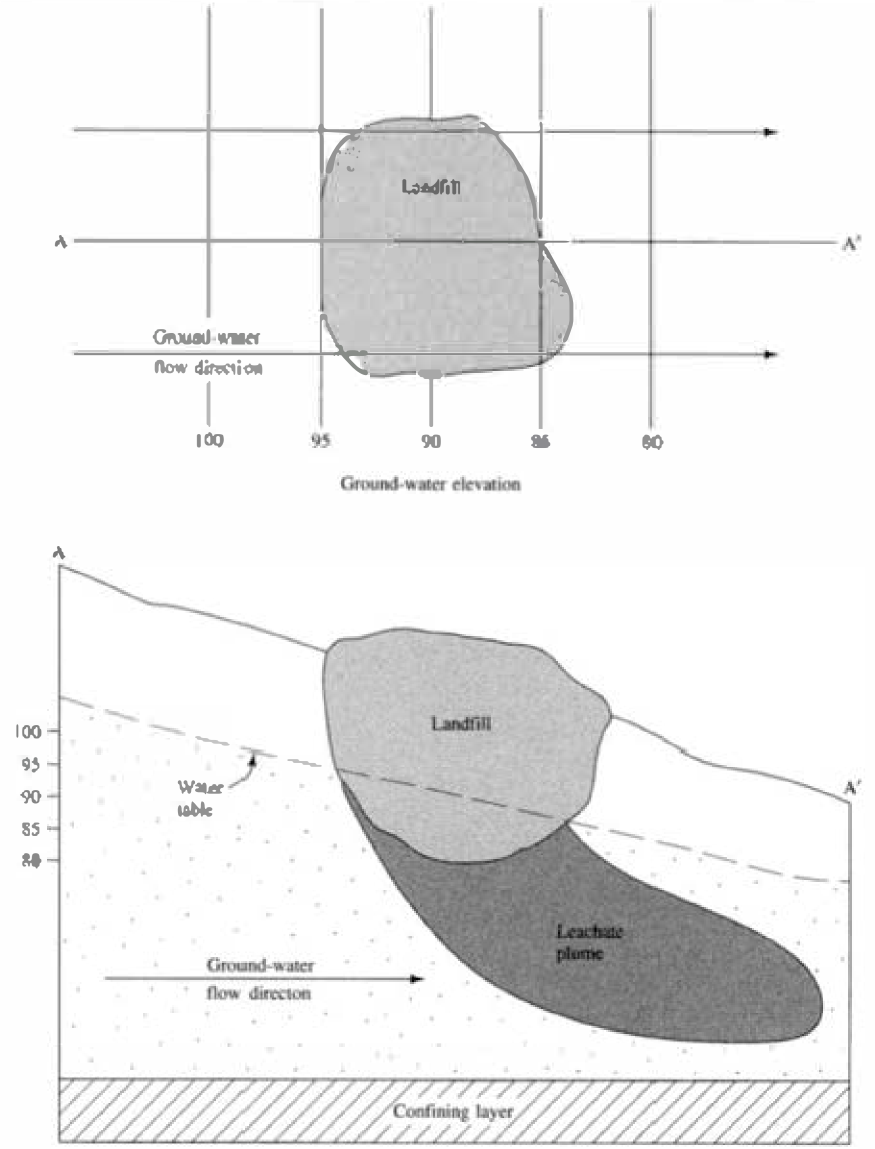
Soil contaminated with organic compounds may be remediated by excavation and incineration. This is a technique that has been proposed for highly refractory organic compounds, such as PCBs and some pesticides. The organic matter of the soil is incinerated while a supplemental fuel is burned in the incinerator. Incineration converts the waste into ash, flue gas, and heat. While the heat can be utilized for beneficial purposes, there is concern about toxic compounds that might accumulate in the ash and gaseous emissions of the incinerator plant. The appropriate disposal of the ash and the filtration of the flue gas add significant cost to the waste incineration and make this process expensive. Compounds with a high BTU (heat) value, such as hydrocarbons, can also be incinerated. This is less costly, since supplemental fuel is not needed. However, permits are needed for incineration, and these may be difficult to obtain from state and local authorities.

9.2.3 Containment

If the waste cannot economically or technically be excavated, then it may be possible to contain it. If the waste is below the water table, flowing groundwater can pass through it and create leachate as illustrated in Figure 9.2a. Such buried waste can be surrounded by a **groundwater cutoff** wall. The purpose of the groundwater cutoff wall is to divert groundwater flow from passing through the waste so that it cannot form leachate (Lynch et al. 1984; Need and Costello 1984). The cutoff wall needs to be deep enough to key into an impermeable layer so that groundwater cannot pass under the wall, which is referred to as encapsulation. Note that the term encapsulation is not only used to describe the isolation of an area of waste, but is used also to describe the different measure of surrounding an individual container with impermeable material.

There are several ways that cutoff walls can be used (U.S. EPA 1998). The wall can extend all around the waste (Figure 9.2b). If this is done, the groundwater will flow around the wall and be diverted from the waste. The water table will rise on the upgradient

FIGURE 9.2a Top view and cross section of a landfill that was constructed with an excavation that extends below the water table. Groundwater can flow through the waste and create leachate.

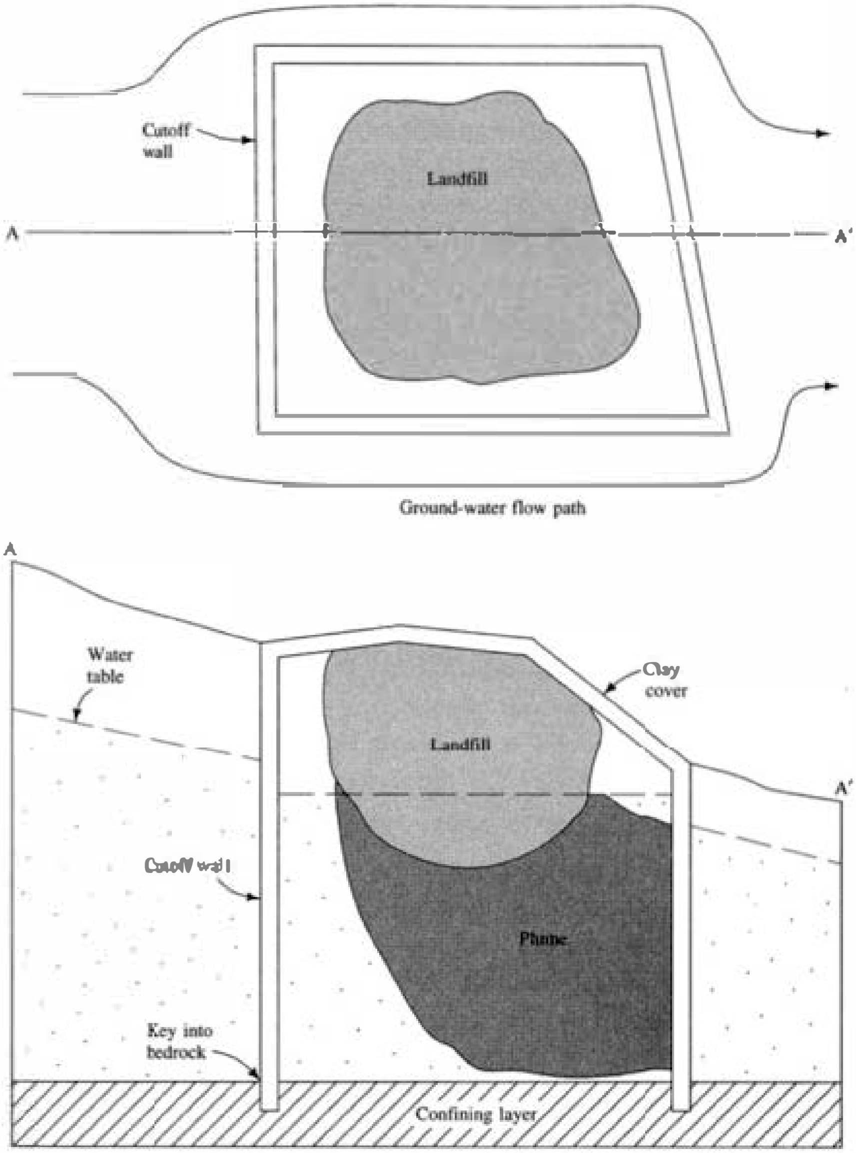


wall and fall on the downgradient wall. If there is no recharge or flow through the cutoff walls, the water table within the cutoff walls will be flat. However, there is generally leakage through the cover or cutoff walls, so some extraction wells will be needed for added hydraulic control within the cutoff walls to prevent build-up of water within walls.

If the cutoff walls are extended far enough to surround both the waste body and the plume of contamination, then remediation may proceed without worry that it will spread further. One of the problems that have arisen with the remediation of groundwater is that the plume may spread rapidly, whereas legal action to assess blame for the plume proceeds through the courts with glacial speed. If a cutoff wall is installed as an emergency action, then the plume can wait until the courts have spoken.

Cutoff walls have also been used to stop the spread of a contaminant plume. At the Rocky Mountain Arsenal near Denver, Colorado, USA, a cutoff wall was constructed

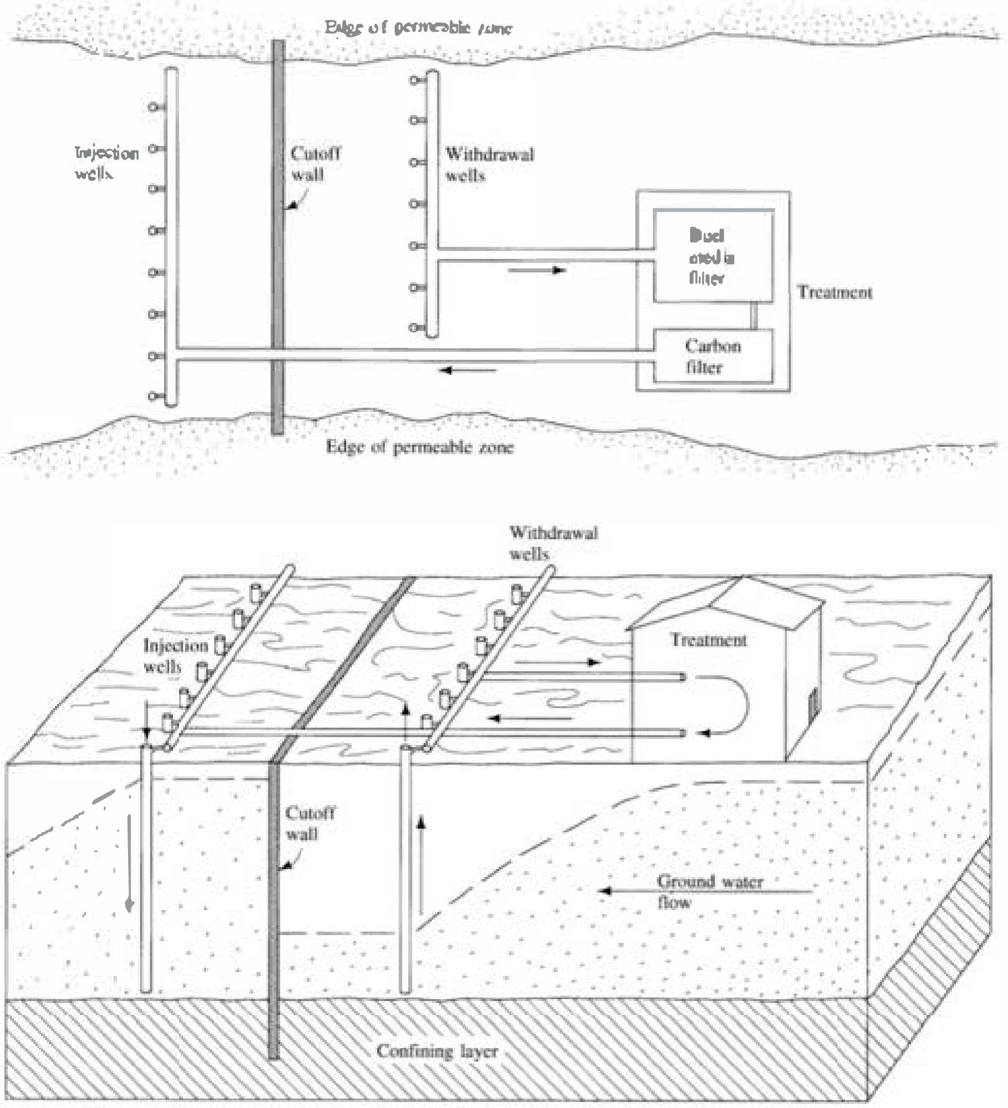
FIGURE 9.2b Top and side view of a cutoff wall that completely surrounds the landfill in (a), opposite page. Cutoff wall is keyed into underlying low-permeability formation.



across a bedrock valley containing higher-permeability, unconsolidated deposits that acted as a pathway for a contaminant plume. The contaminated water is pumped from the upgradient side of the cutoff wall, treated to remove the contamination, and injected into the aquifer on the downgradient side of the cutoff wall (U.S. EPA 1998). This system is illustrated in Figure 9.3.

A number of different types of materials have been suggested for use in cutoff walls (Pearlman 1999). Most are constructed of soil-bentonite slurries, but concrete and concrete/polymer mixtures are also used particularly in regions of topographic relief. A trench is excavated with an excavator or backhoe. The trench is held open by a slurry of bentonite and water. The slurry acts in the same manner as the drilling mud that holds open a borehole. The bentonite slurry penetrates into the more permeable formations and forms a low-permeability filter cake. As the working end of the trench

FIGURE 9.3 Cutoff wall used with extraction and injection wells at the Rocky Mountain Arsenal, Denver, Colorado, to isolate and treat a plume of contaminated groundwater.



is built around the site, the opposite end of the trench is back-filled with a soil-bentonite slurry. The soil-bentonite slurry has a very low permeability and minimizes the movement of most groundwater through it. The trench is typically 1 m (2 to 3 ft) wide and can be up to 18.3 m (60 ft) deep if excavated with a backhoe or up to 36.5 m (120 ft) deep if dug with a clamshell shovel (Need and Costello 1984). While expensive, technology to install cutoff walls as deep as 122 m (400 ft) is available (Valkenburg 1991). Preconstruction design studies are needed to determine if the waste that is to be contained is compatible with the bentonite-soil slurry.

A grout curtain may also be constructed as a cutoff barrier. Grout is injected into the earth through a borehole. The grout is liquid when injected but eventually hardens into an impermeable material. This approach was used to contain radioactive water at the Fukushima nuclear power plant disaster site in Japan, according to the company in charge for the site remediation (www.tepco.co.jp). Other construction methods include steel-sheet piling, bored pile walls and, as temporary solution, artificial ground freezing. The selection of a cut-off barrier construction method will depend on the desired depth of wall, ground conditions, and geometry of wall.

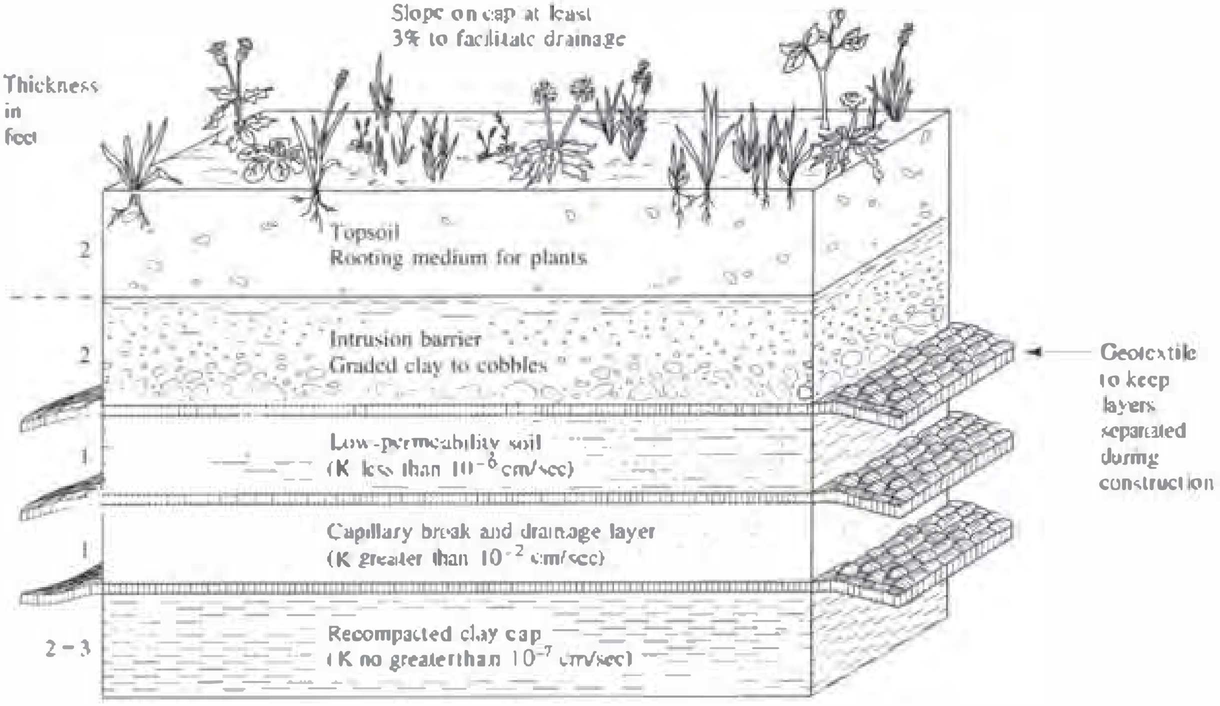
If contaminated material can be immobilized or its solubility reduced through a chemical reaction, this process is called stabilization. Similarly, if the contaminated material can be encapsulated to form a solid and to restrict its migration by decreasing the surface area exposed to leaching, that process is referred to as solidification. **Solidification/Stabilization** is an established technology that has been used for decades to address a variety of *in situ* and *ex situ* solid and liquid wastes. Typically, the contaminated material is treated with an inorganic or organic binder, such as cement, fly ash, lime, soluble silicates or asphalt, epoxide, polyesters, and polyethylene (U.S. EPA 2000).

In most cases it will also be necessary to construct a cover over the waste material to prevent the infiltration of precipitation. If the waste material is above the water table, a cover without a slurry wall might be all that is needed. For a waste material buried below the water table, a low-permeability cover is needed in association with a slurry wall. In the absence of a cover, the infiltrating water will fill the area within the slurry wall like a bathtub.

Covers may be constructed of native soils, synthetic membranes, or a combination of both. Covers are typically sloped in order to promote runoff of precipitation. It may even be necessary to bring in fill material to create the necessary elevation at the center of the cover to form the needed slope.

A multilayer cover constructed of natural materials might have the following elements, starting from the surface (Figure 9.4): (1) 0.6 m (2 ft) of topsoil as a rooting medium for vegetation with shallow roots, such as grass or crown vetch, which is

FIGURE 9.4 Typical design of a multilayer cap for a landfill that is constructed of natural soil materials.



needed to prevent erosion; (2) a 0.6 m (2 ft) thick compacted layer of cobbles mixed with clay to stop burrowing animals from breaching the cap; (3) a 0.3 m (1 ft) thick low-permeability zone to separate the cobble layer from the next-lower zone; (4) a 0.3 m (1 ft) thick layer of very permeable sand, which acts as a capillary break to the movement of soil moisture and provides for lateral drainage of any infiltrating precipitation; and (5) a bottom layer that consists of 0.6 to 1 m (2 to 3 ft) of recompacted clay with a maximum permeability less than 10^{-7} cm/sec (8.5 × 10^{3} ft/d) to act as a final barrier to groundwater recharge. Geotextile fabric would be needed between several of the layers to keep the materials from mixing during construction and to distribute the stresses evenly. Figure 9.4 shows the details of this design. Erosion of the soil and penetration of the cover by tree roots are the main concerns for the long-term integrity of this design.

Synthetic geomembranes can also be used in cover designs as low-permeability layers. One advantage of using native soil materials is that their long-term performance is assured, whereas the long-term behavior of plastic membranes, and those made of other materials has not been tested for all types of soil, climatic, and contaminant mixture scenarios. However, for many applications, plastic membrane covers are suitable. They can easily be installed so that monitoring and extraction wells extend through the cap.

Infiltration of precipitation into the ground can also be reduced by paving the surface with a material such as asphalt. However, an asphalt seal is more permeable than a multilayer cover and would require extensive maintenance to seal cracks that form. Diversion ditches and drains might be used to prevent surface runoff from entering an area where it can infiltrate into the soil and come into contact with buried waste material.

There are alternative cover designs that are increasingly being used for waste disposal sites and hazardous waste landfills. For instance, the evapotranspiration (ET) cover system relies on the properties of one or more vegetated soil layers to store water until it is either transpired through vegetation or evaporated from the soil surface (e.g., Hauser et al. 2001). Compared to conventional land fill covers, ET cover systems are less costly to construct. However, ET cover systems are mostly limited to areas that have arid or semi-arid climates, such as the southwestern United States (U.S. EPA 2003; 2011).

9.2.4 Hydrodynamic Isolation

Hydraulic controls can also be used to isolate a zone where the groundwater has been contaminated. An extraction well positioned at the leading edge of a contaminant plume can be used to stabilize the position of the plume or contain it (Figure 9.5). The plume-stabilization well will pump contaminated water, which may require treatment before disposal. It will prevent the encroachment of the plume of contamination to uncontaminated parts of the aquifer. With the contamination thus isolated, work on source control and other remediation measures can progress at the most expedient pace.

The downgradient limit of the capture zone is called the stagnation point. Figure 9.6 shows a water table profile along the y-axis. It can be seen that the stagnation point forms a groundwater divide between flow toward the well and flow in the regional direction. The stagnation point and the capture zone are also shown for an LNAPL spill in Figure 9.7. Note that there is a maximum quantity of water that can be pumped from a single extraction well. If the plume is wider than the capture zone developed by the maximum pumping rate, then multiple extraction wells are needed. One concern with multiple extraction wells is that their capture zones must overlap,

FIGURE 9.5 Plume-stabilization well used to isolate plume of contaminated groundwater.

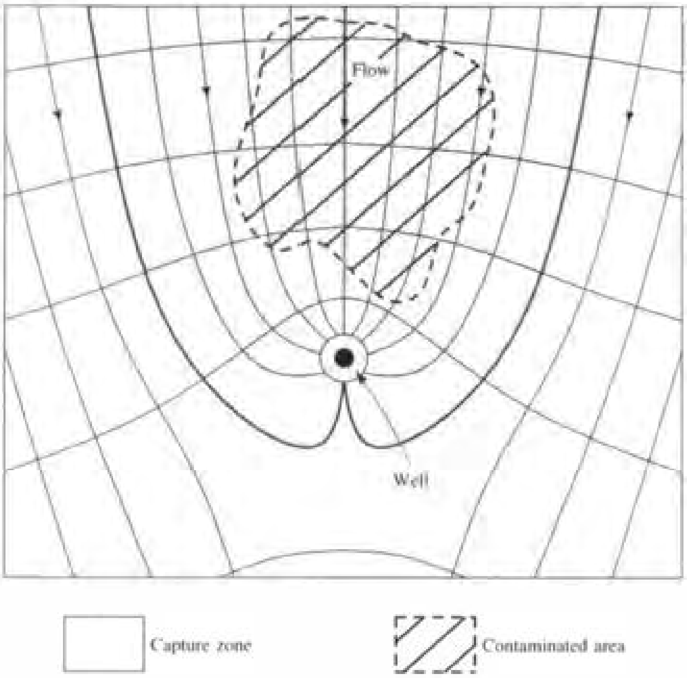
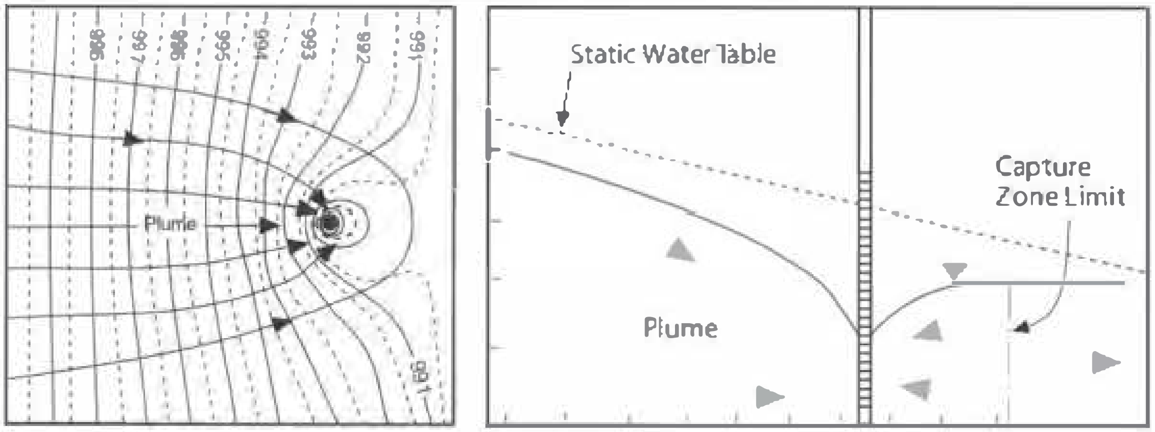


FIGURE 9.6 Example of plume stabilization by a well which is used to hydraulically contain a plume of contaminated groundwater. Shown are plan view and cross sections.

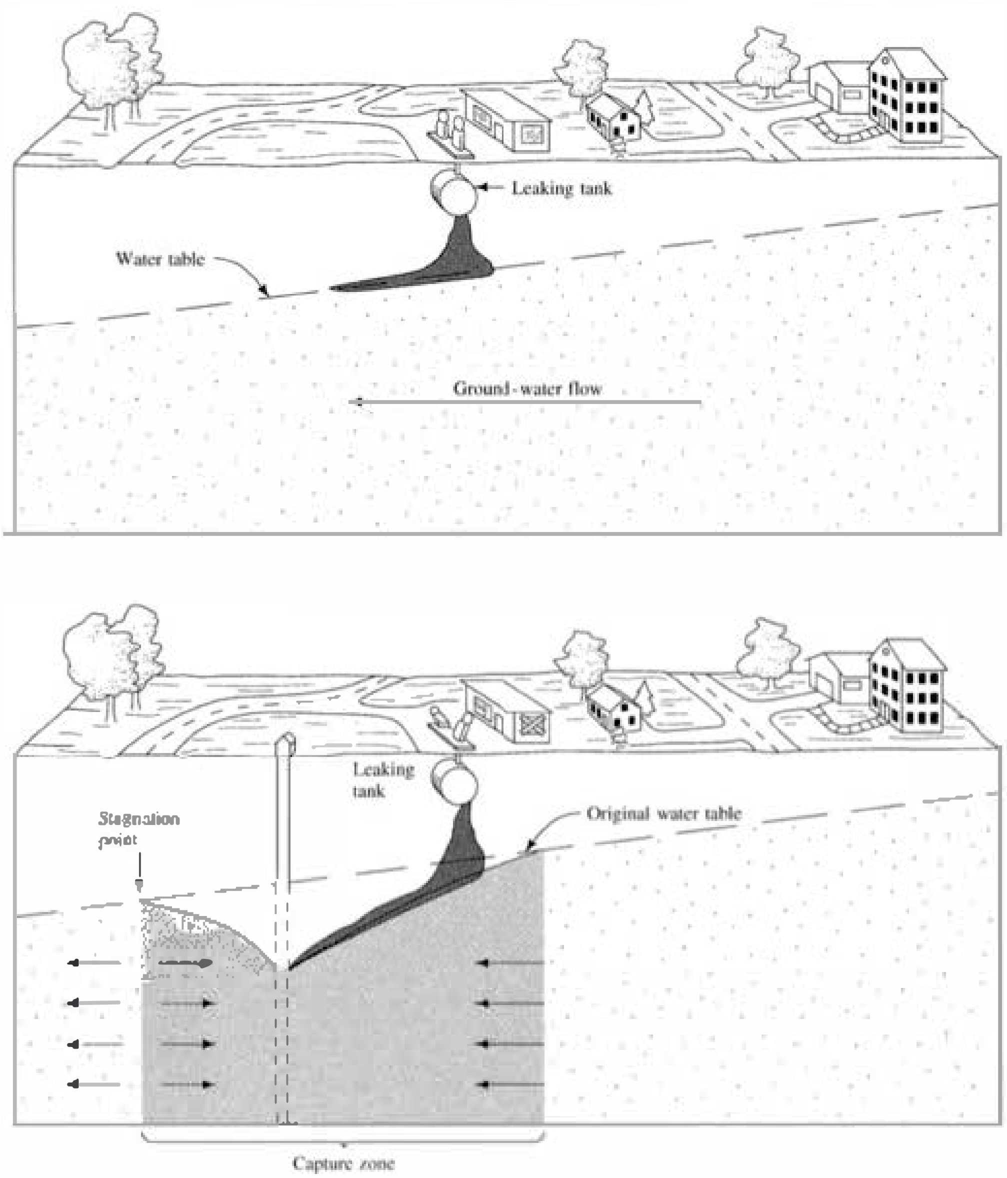


Source: After Cohen et al. 1993; as cited in U.S. EPA 1995. Report EPA/625/R95/005.

or groundwater flow can pass between them. These considerations illustrate why contaminant hydrogeologists regularly rely on groundwater models as an important aide in designing remediation systems.

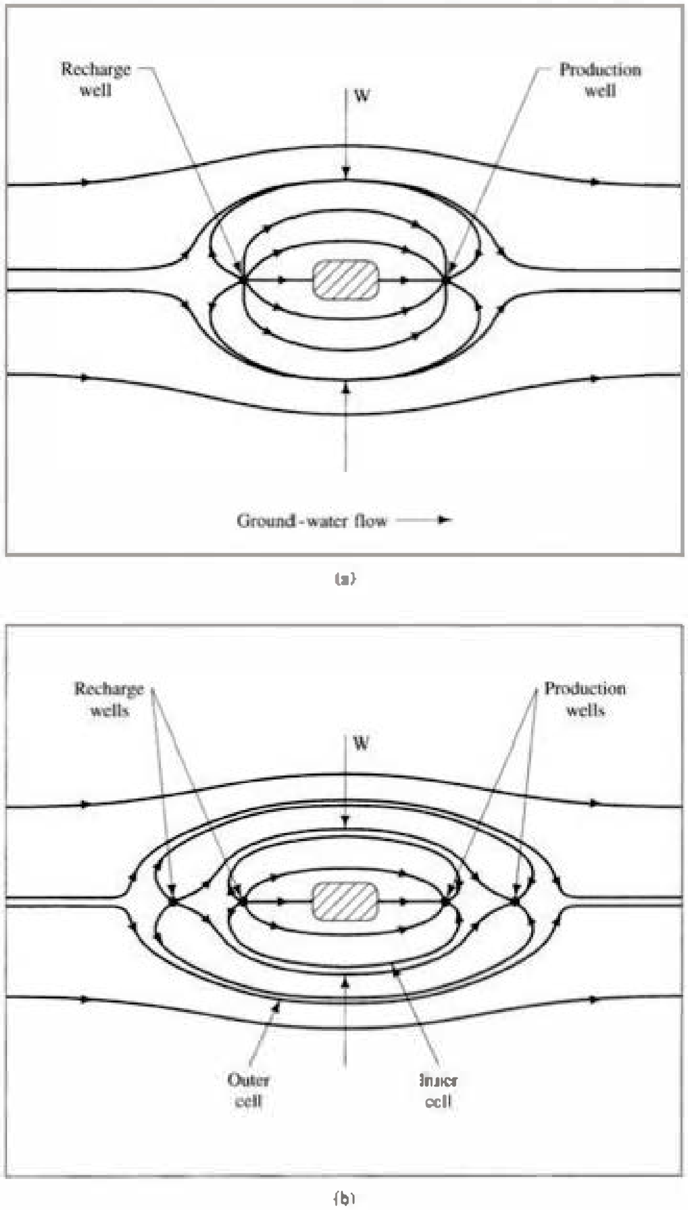
Wilson (1984) described the use of a pair of injection and withdrawal wells to create a hydraulic isolation zone around a plume of gasoline contamination. The withdrawal well draws contaminated water to it; the water is then reinjected into the ground upgradient of the position of the plume (Figure 9.8a). The withdrawn water may be treated prior to injection, or nutrients can be added to promote bioremediation. In addition, treatment systems may need periodic maintenance necessitating a shutdown.

FIGURE 9.7 Cross section along the *x* axis showing the cone of depression for a single extraction well superimposed on the regional water table.



With a reinjection system the untreated water can still be injected and the downgradient plume-stabilization well can be kept pumping. Otherwise, if the plume-stabilization well is shut down, the plume might be able to spread beyond its hydraulic boundary. Care must be exercised to minimize smearing of LNAPLs by reducing rigorous pumping that results in great fluctuations of the water table. Wilson (1984) also described a double-cell hydraulic containment system with two pairs of injection and production wells, as shown in Figure 9.8b. This system provides further isolation of the plume and also creates a smaller inner cell so that the production well that is pumping contamination will pump a smaller volume of water, which will lower treatment costs. With two injection and pumping wells, there is a possibility of shutting down one well periodically for maintenance and still having the system operational.

FIGURE 9.8 Plan view of (a) single-cell and (b) double-cell hydraulic containment of contaminated groundwater.



(a)

(b)

Source: J. L. Wilson. 1984. Proceedings of the Fourth National Symposium and Exposition on Aquifer Restoration and Ground Water Monitoring, 65–70. National Water Well Association. Used with permission.

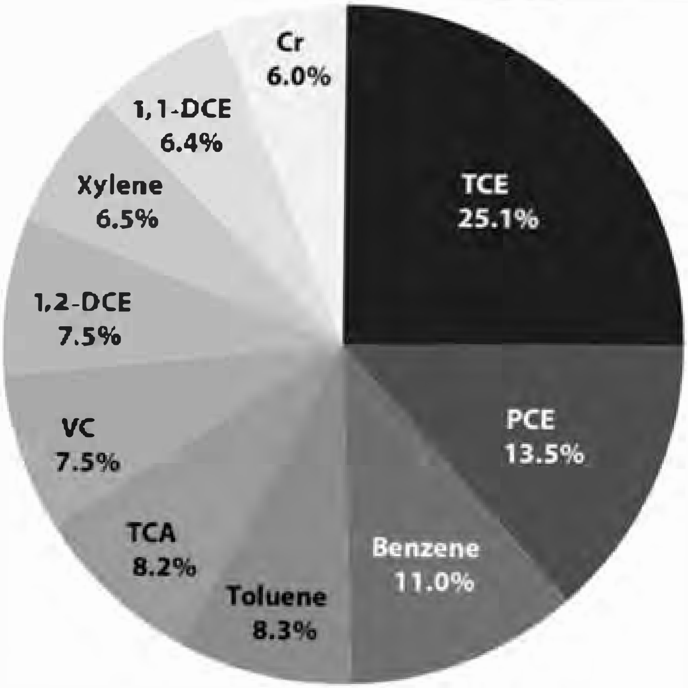
9.3 Pump-and-Treat Systems

9.3.1 Overview

For a long time, almost all groundwater remediation was based on extraction wells or drains that were usually accompanied by treatment of the extracted water before discharge (Mackay and Cherry 1989). The extraction of groundwater that contains dissolved inorganic and organic chemicals removes the contaminants from the subsurface so that the contaminated groundwater can be treated at the surface. This remediation approach is known as Pump-and-Treat (P&T). The advantage of the P&T method is that conventional methods of wastewater treatment can be employed. Pump-and-treat was the sole remedy at 56% (485 of 877 sites) of National Priority List (NPL) sires in the United States between fiscal years 1982 and 2005, representing the most common groundwater remedial action during that period (U.S. EPA 2007). Figure 9.9 provides an overview of the 10 most frequently treated contaminants using P&T technology. P&T systems also are frequently used to treat metals and metalloids, including chromium (U.S. EPA 2007). There are, however, a number of disadvantages that limit the usefulness of this technology to emergency responses, plume containment in combination with source-control measures, or treatment of highly water soluble compounds Since the early 1990s many highly efficient groundwater treatment technologies have been devised and tested so that contaminated site managers now have alternatives to the P&T technologies. Not surprisingly, by 2011 only 22% of groundwater remedies at NPL sites were P&T based (U.S. EPA 2013).

Depending on the efficacy of treatment and regulatory requirements, the treated water can be discharged to a receiving water body, passed to a publicly owned wastewater treatment plant for further treatment and dilution, or reinjected into the ground. Often the disposal of the treated wastewater requires state and local permits or regulatory approval. Discharge to a publicly owned wastewater treatment plant may require local permits for industrial discharge and there might be pretreatment standards. Water

FIGURE 9.9 Contaminants treated most commonly by pump-and-treat systems: trichloroethene (TCE); tetrachloroethene (PCE); 1,1,1-trichloroethane (TCA); 1,2-dichloroethene (1,2-DCE); 1,1-dichloroethene (1,1-DCE), vinyl chloride (VC), and chromium (Cr).



Source: U.S. EPA 2007.

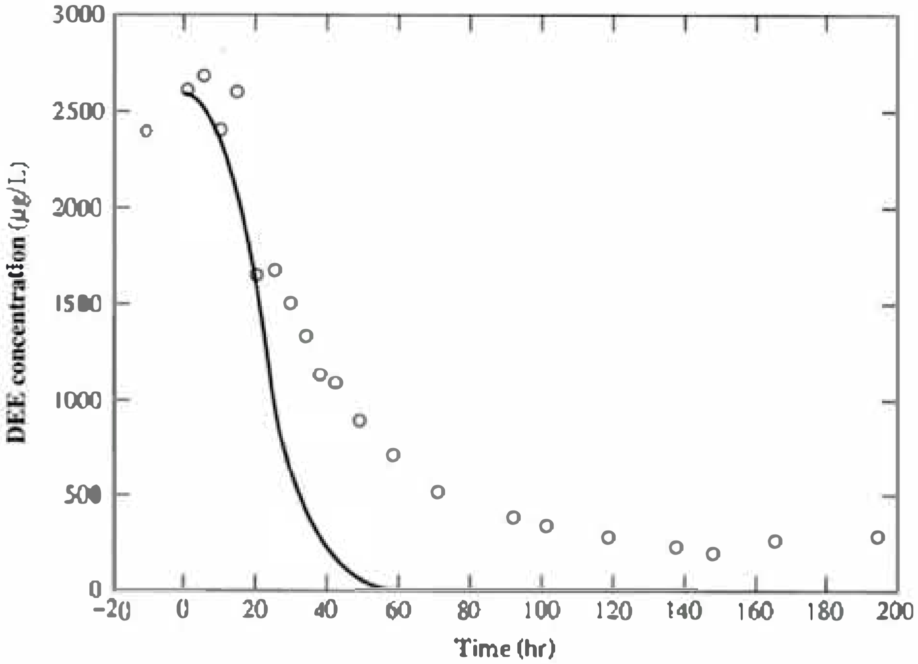
discharged to a surface-water body in the United States requires state permits, including a National Pollutant Discharge Elimination System (NPDES) permit. Many states provinces, and regions require a permit to inject water into the ground and there may be concentration limits specified as a part of the permit. If there are NAPLs present, the situation is much more complex than if all contaminants are in a dissolved form. As long as an NAPL is present, it will partition between the NAPL phase and the dissolved phase Thus, as contaminated water is withdrawn from the aquifer for treatment, the clean water that is drawn into the aquifer eventually becomes contaminated with pollutants partitioning from the remaining NAPL. If some of the NAPL is mobile, it may be captured by pumping. LNAPLs that are floating on the water table are relatively easy to locate and remove if the LNAPL has not been smeared vertically However, DNAPLs that sink to the bottom of the aquifer are very difficult even to locate, much less recover (Mackay and Cherry 1989; Freeze and Cherry 1989). Because considerable amounts of residual NAPL will remain even if the mobile NAPL is removed, a great many years may be required for pump-and-treat systems to remove all the residual NAPL by partitioning into the recoverable dissolved phase In the case of contamination by DNAPLs especially in fractured rock aquifers, it may be very difficult or impossible to remediate a contaminated aquifer (Mackay and Cherry 1989; Freeze and Cherry 1989; National Academies of Sciences, Engineering, and Medicine 2015).

If the dissolved phase sorbs onto the mineral matter of the soil, that phase may desorb as the contaminated water is flushed from the pores. The greater the distribution coefficient, the more slowly the sorbed phase will be released and the longer it will take to remediate the aquifer. The kinetics of desorption dictate that many pore volumes of uncontaminated water might be needed to remove completely the sorbed phase of both organic and inorganic contaminants. Whiffin and Bahr (1984) noted that the observed rate at which organic compounds desorbed from an aquifer was slower than the rate predicted by transport equations that assumed equilibrium conditions between the sorbed phase and the dissolved phase (Figure 9.10). The advection-dispersion equation results were initially fairly accurate; however, when the concentration dropped to about half the initial concentration, the actual rate of removal was slower than the predicted rate

The discrepancy between the Whiffin and Bahr (1984) model and the observations in the field are related to contaminant residence time in the subsurface and diffusion transport processes. Hence, in heterogeneous media, some contaminants can be sequestered for long periods of time, despite active pumping. Contaminants that have been in the ground for a long period of time have been able to diffuse into the less permeable zones of porous media aquifers or into the bedrock matrix of fractured rock aquifers. Pump-and-treat systems are inefficient in removing these contaminants, because the majority of the water being removed by pumping will come from the most permeable zones of the aquifer. In alternating layers of sand and clay, the contaminated water will penetrate the fine clay, which has very limited permeability, from the highly permeable sands over time. Some of the contamination will remain in the dissolved phase, some will partition onto the surface of the clay lens and associated soil organic carbon and some will diffuse into the clay lens. The fine sediment will have a larger surface area per unit volume of the aquifer than the coarse sediment and thus will sorb more contamination.

These mass transport limitations have been illustrated by Mackay and Cherry (1989) (Figure 9.11). Figure 9.11a shows contamination residing in homogenous aquifer

FIGURE 9.10 Measured desorption values for diethyl ether for water pumped from a purge well (open circles) versus calculated desorption curve based on advection-dispersion equation (solid line).



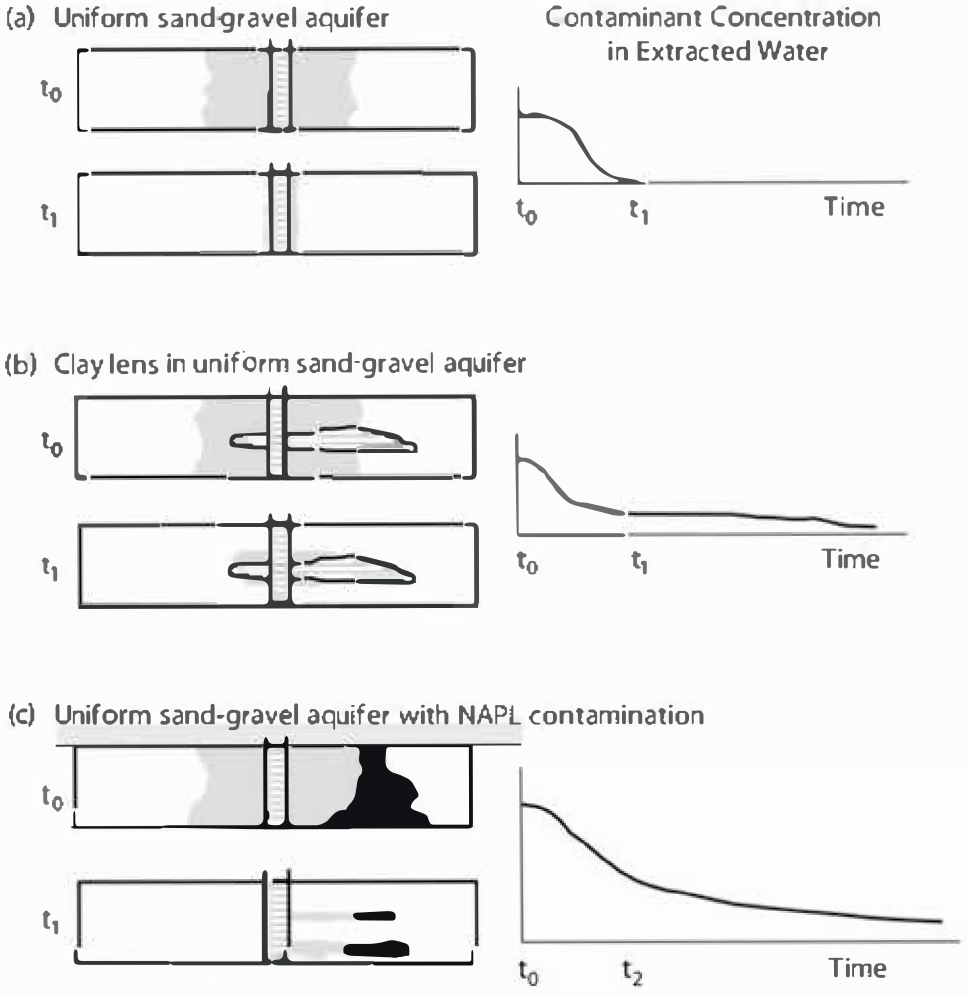
Source: R. B. Whiffin and J. M. Bahr. 1984. Proceedings of the Fourth National Symposium and Exposition on Aquifer Restoration and Ground Water Monitoring, 75-81. National Water Well Association. Used with permission.

composed of uniform sand. During the time interval t_0 to t_1, the contamination is effectively flushed out. However, if the porous media is heterogeneous and the aquifer consists of sand with an interbedded clay lens, the concentration in the effluent from the extraction well is still elevated at t_1 (Figure 9.11b). Water removed by pumping will come primarily from the sandy material. The contaminated water in the pores of sand will be fairly quickly removed; perhaps only a few pore volumes of water will need to be flushed through to accomplish this. Contaminants sorbed onto the sand grains will be removed by partitioning into the clean water that then occupies the pores in the coarse sand layers.

Meanwhile, the contaminated water occupying the pores of the clay lens will be flushed from this layer very slowly. It will take the movement of many pore volumes of water through the sand to flush just a few pore volumes of water through the much less permeable clay layer. Hence, it will take much longer to remove the contaminants that are desorbing from the fine sediments after the contaminated pore water is removed from the sand.

There will be an initial rapid decline in the concentration of contaminants in the water being removed by a pump-and-treat system. This decline represents the removal of the contaminated water contained in the larger pores of the aquifer. Initially, when the larger pores in the sandy material are being flushed, the drop in concentration will be rapid. Flushing the much smaller pores in the clay will take much more time and, the rate at which the concentration declines will decrease. The concentration will eventually approach somewhat constant value, which represents a steady state condition where the rate at which the contaminants are being removed by the pump-and-treat

FIGURE 9.11 Hypothetical examples of contaminant removal during pump-and-treat treatment. Gray areas indicate sorbed and dissolved contaminants (uniform initial distribution). Lined shapes indicate clay lens. Black areas indicate NAPL.

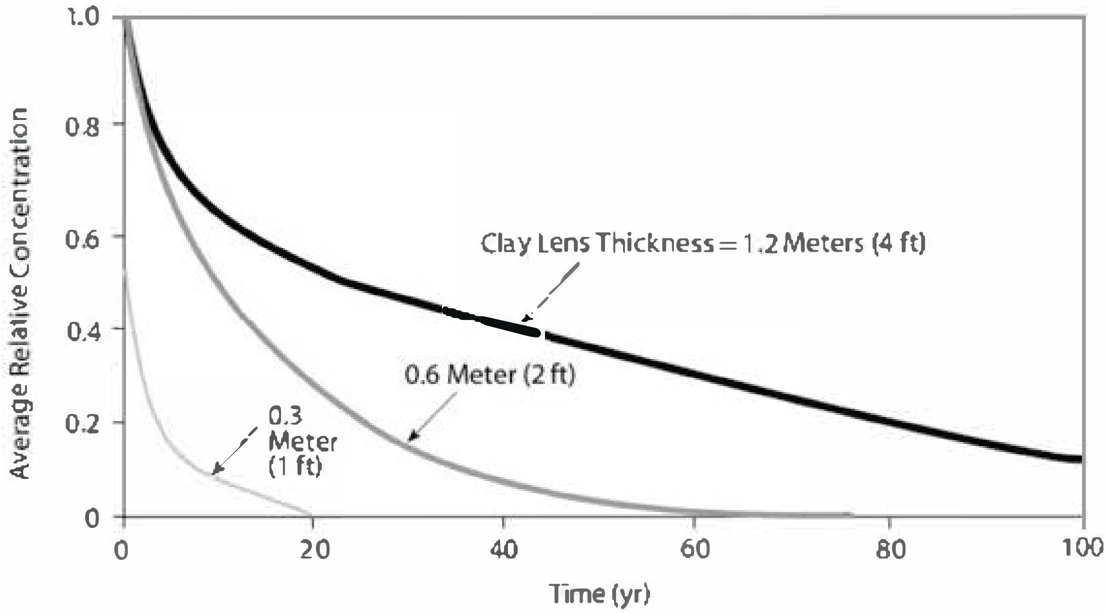


Source: Modified after Mackay and Cherry 1989.

system is equal to the rate at which they are being released into the groundwater by diffusion desorption and/or partitioning from residual NAPLs (Figure 9.11c). The resulting long period of slow release of contaminants to the groundwater is called the **tailing** phase of the remediation.

During the tailing phase in the remediation process contaminant mass is still being removed from the aquifer, but the groundwater is not becoming any cleaner. The concentration at which this occurs may be higher than the cleanup goals for the remediation. It may take many years of pumping at this stage to reduce the amount of sorbed contaminants and/or the residual NAPLs sufficiently for the groundwater quality to improve to a point where it meets cleanup goals. Figure 9.12 depicts how the slow, diffusion-controlled release of contamination from material of low hydraulic permeability (clay) can determine the length of the remediation period. For instance, it would take about 10 years to reduce the TCE concentration by 90% if the clay lens is 0.3 m (1 ft) thick. The time increases to almost 40 years for a lens 0.6 m (2 ft) thick and to over

FIGURE 9.12 The effect of matrix diffusion on the average relative trichloroethene (TCE) concentrations in clay lenses of varying thickness as a function of time.



Source: U.S.EPA 1996.

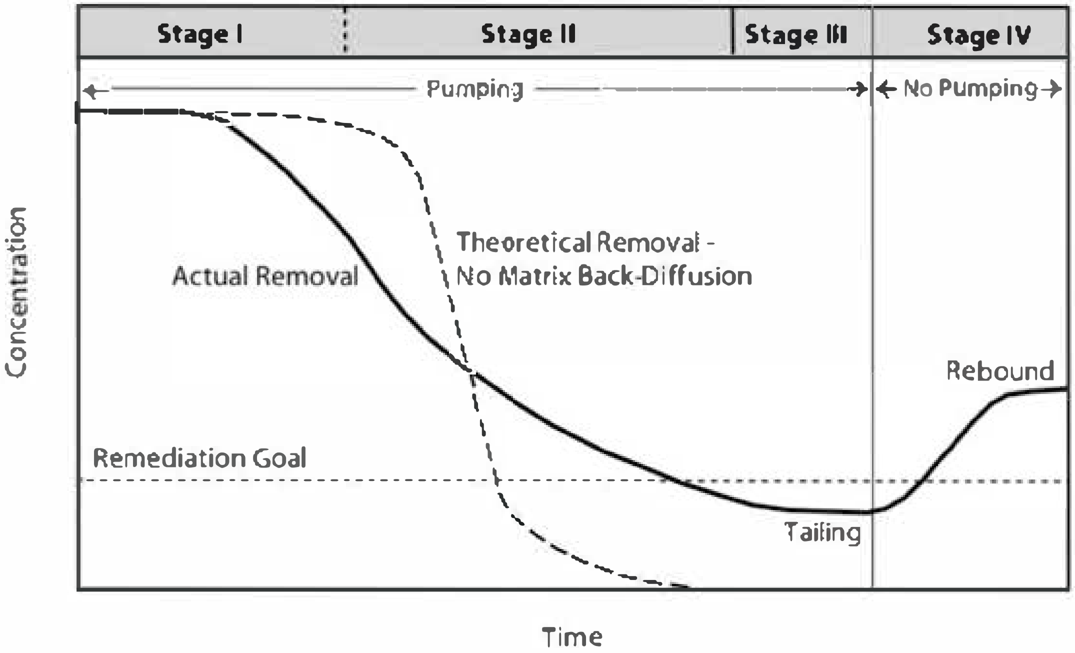
100 years for a lens 1.2 m (4 ft) in thickness. These simulations show that it may take decades or longer to significantly lower the contaminant concentration in clay lenses.

A study of pump-and-treat cleanup at 16 sites in the United States where the groundwater was contaminated with organics revealed that if the initial concentration of contamination was high (>1000 μg/L), pumping could achieve reductions of contaminant concentrations of 90 to 99% before leveling occurred. At sites where the initial concentration was less than 1000 μg/L, leveling occurred before a 90% reduction was accomplished (Doty and Travis 1991). Moreover, if remediation is halted before the sorbed phase is completely removed, the dissolved concentration will eventually rebound and rise above the level detected at the end of the remedial period as additional material desorbs to come to equilibrium with the dissolved phase. Typically, the rebound of the dissolved contaminant concentration is quick, i.e., can occur within a few days after the pumping ceased.

The effects of rebound and tailing on the progress of P&T treatment are illustrated in Figure 9.13. It must be noted that these effects are not solely limited to P&T systems, but also affect other, more innovative groundwater treatment technologies that rely on chemically-enhanced flushing processes to remove contamination from low-permeability material.

Figure 9.13 illustrates the multiple stages in remediation of a contaminated aquifer or soil. Early during the treatment (Stage I), there is rapid removal of contaminant mass and concentrations drop quickly. Stage I transitions into Stage II which represents the diffusion-controlled period as the concentration graph attains an asymptotic shape. During the tailing stage (Stage III), the rate of mass removal slows because the site geology controls the rate at which the remaining contamination is released. The impact of matrix diffusion is illustrated by the dashed line curve, which shows the theoretical removal expected in

FIGURE 9.13 Stages in the remediation of a contaminated aquifer or soil.



Source: Modified after U.S. EPA 1996.

the absence of diffusion from low-permeability domains into higher permeable zones. Remediation efforts continue until a pre-determined clean up goal has been reached. In some cases, that remediation goal may be higher than the pollutant specific standard, like the maximum contaminant level (MCL) defined by the U.S. EPA. When at one point the pumping stops, it is likely that the slow, diffusion-controlled release of contaminants from low-permeability domains results in an increase in the dissolved phase concentration. This is Stage IV, the rebound stage. Should the rebound result in groundwater concentrations higher than the cleanup standard, remediation must continue. Under these circumstances, it may be necessary to periodically turn on the pump(s) until the residual concentration drops beneath the remediation goal again. Such a treatment scheme is known as **pulsed pumping** (U.S. EPA 1996). Another option is to vary the pumping rates or turn injection wells into extraction wells and vise-versa. This **adaptive pumping** approach limits the development of stagnation zones, which are parts of the aquifer that are not, or only minimally, flushed if the extraction/injection scheme was static.

Figure 9.13 illustrates an aquifer where the contaminant is in the dissolved phase or is sorbed onto soil particles. If there is an undissolved phase (DNAPL) present, then the release of contaminant into the flushing water will be controlled by the solubility of the DNAPL. More soluble DNAPLs, such as trichloroethylene, which has a solubility of 1100 mg/L, will become dissolved much more rapidly than low-solubility NAPLs, such as coal tar or creosote. However, as the DNAPL will tend to form pools on the top of low-permeability layers, the flushing liquid will only come in contact with the top of the DNAPL pool and little dissolution will actually occur (Johnson and Pankow 1992). As a result, pump-and-treat will be inefficient for mass removal in the case of DNAPLs. In spite of this inefficiency pumping still is viable as a means of plume containment.

Pump-and-treat methods have been shown to be effective in removing a large amount of more soluble contaminant mass from the aquifer during the initial phase of pumping. They are also useful in halting the spread of a plume of contamination, i.e., plume containment. However, if the contaminant concentration in the aquifer is still above the cleanup goal once a pump-and-treat project reaches the stage where the contaminant release is diffusion controlled, decades of additional pumping might be required before the aquifer is "clean." This does not mean that the pump-and-treat approach failed, it only means that it was an unrealistic expectation to attain complete remediation of an aquifer with pump-and-treat as the only remedy. The shortcomings of conventional pump-and-treat schemes have led to the development of many innovative remediation technologies, which will be discussed in greater detail later in this chapter.

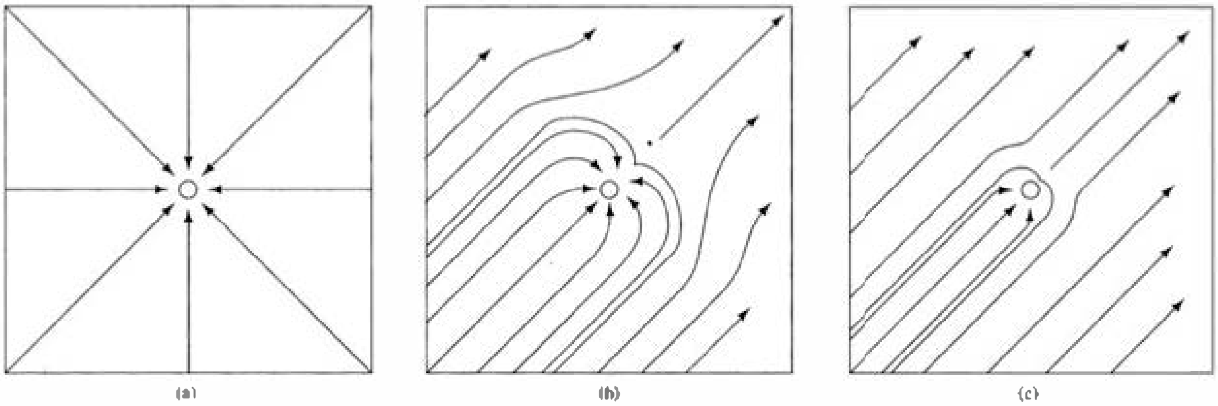
9.3.2 Capture Zones

In order to capture a plume of contaminated water, it is necessary to have one or more pumping wells located downgradient of the source area. Each well will have what is known as a **capture zone**, which is the area contributing flow to that particular well.

If the water table is flat, there is no regional flow. The capture zone of a well is radially symmetrical, centered on the well and extending as far as the edge of the cone of depression (see Figure 9.14a). If there is a slope to the water table, the groundwater flows and the capture zone are asymmetrical, with the greatest extent in the upgradient direction (Figure 9.14b). As the groundwater velocity increases, the width of the capture zone decreases for a given pumping rate (see Figure 9.14c).

The shape of the capture zone is a function of the average linear groundwater velocity, the quantity of the water being pumped from the aquifer, and the distribution of hydraulic conductivity. The upgradient extent of the capture zone depends upon the length of time over which the pumping occurs. The Wellhead Protection Area (WHPA) program was developed by the U.S. EPA that may be used to delineate capture zone. It is a semi-analytical groundwater flow simulation program that can account for multiple pumping and injection wells and delineates the area contributing flow to those wells.

FIGURE 9.14 (a) Flow lines toward a well in an aquifer with no water table gradient; (b) flow lines toward a well and the capture zone with uniform flow to the upper right of the figure; (c) flow lines toward a well and the capture zone with uniform flow to the upper right at a rate 10 times the rate of (b).



WHPA is applicable to homogeneous aquifers exhibiting two-dimensional, steady groundwater flow in an areal plane and appropriate for evaluating multiple aquifer types (i.e., confined, leaky confined, and unconfined) (U.S. EPA 1993).

If the hydrogeology is not homogeneous or if more complex geologic or contaminant transport problems have to be accounted for, there are a number of sophisticated models available today. For instance, FLOWPATH II is a 2-D finite difference, steady-state groundwater flow model for calculation of wellhead protection zones, hydraulic heads, groundwater velocities, time related path lines, capture zones, water balances, and steady state drawdown distributions. Another model is PATH3D, which can help delineating contaminant capture zones or wellhead protection zones or can be used to evaluate the effectiveness of groundwater remedial scenarios under complex hydrogeological conditions. There are a number of other noteworthy programs and the Integrated Groundwater Modeling Center (IGWMC) at the Colorado School of Mines in Golden, CO, USA, provides reviews and links to many of those models.

9.3.3 Computation of Capture Zones

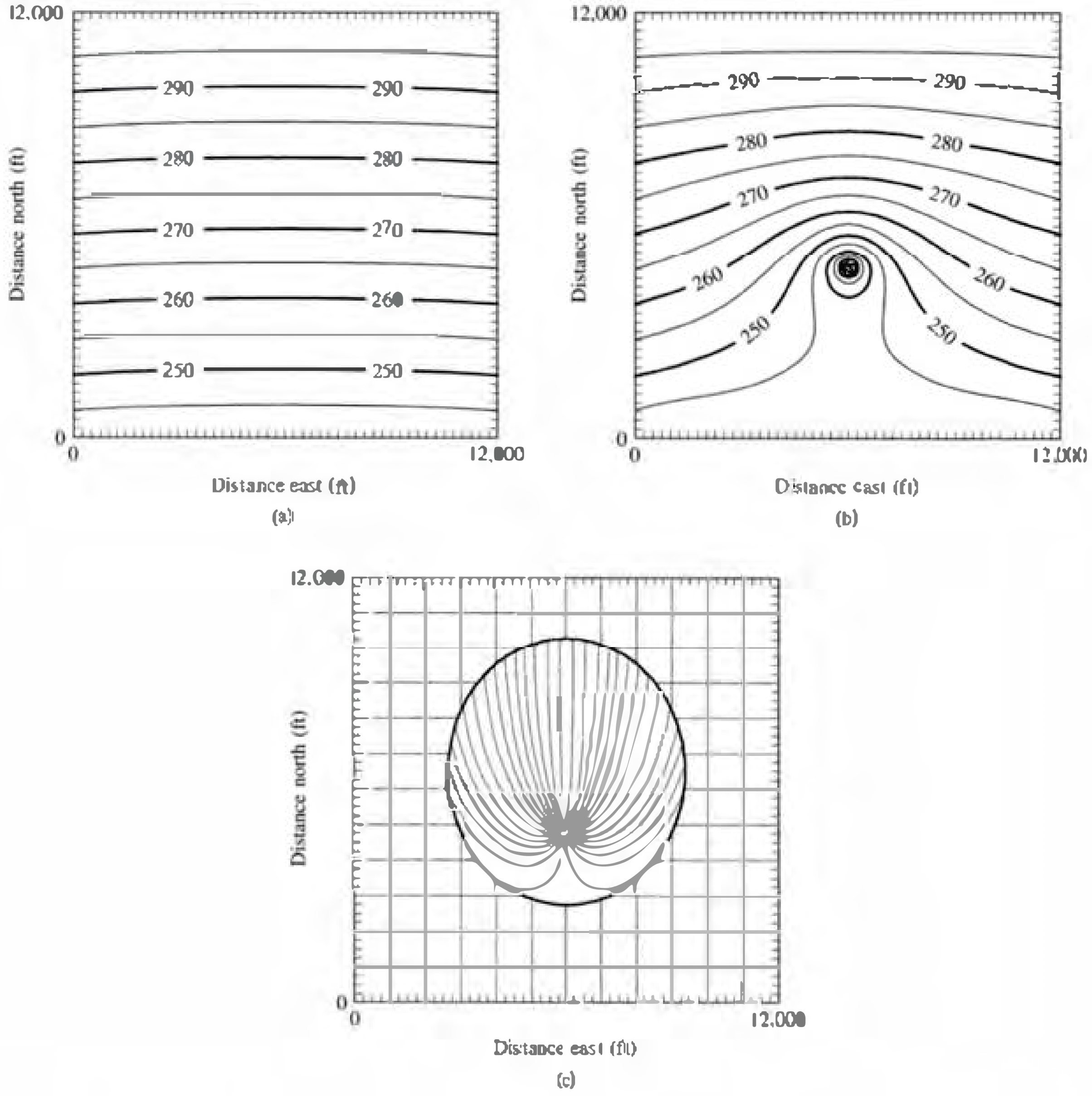
The effect of aquifer heterogeneity was illustrated by Shafer (1987). Figure 9.15a shows the initial hydraulic head for a homogeneous, isotropic, unconfined aquifer. The hydraulic-head distribution after 20 years of pumping from a single well is shown in Figure 9.15b. During this time period, the cone of depression has not spread all the way to the upgradient end of the diagram. The extent of the capture zone is shown superimposed on the model grid in Figure 9.15c. Figure 9.16a shows the distribution of hydraulic conductivity in nonhomogeneous aquifer with the same initial head distribution as the one in Figure 9.15a. In contrast to the homogenous system, the hydraulic head distribution in the nonhomogeneous aquifer with one well pumping is not symmetric and the shape of the 20-year capture zone is irregular (Figures 9.16b and c). The nonsymmetric, irregularly shaped capture zone reflects the heterogeneous distribution of the hydraulic conductivity in the nonhomogeneous aquifer. This example illustrates that ignoring aquifer heterogeneity can lead to incomplete capture of a contaminant plume.

9.3.4 Optimizing Withdrawal-Injection Systems

The rate at which groundwater restoration can be accomplished by pump-and-treat systems depends in part on how many pore volumes of water can be withdrawn from the contaminated zone. If the entire plume falls within the capture zone of one or more withdrawal wells, then we know that the plume will not spread and eventually maximum feasible restoration will occur. However, by increasing the rate (number of pore volumes of water per year) at which contaminated water is pumped, the restoration time can be decreased. For optimal conditions we also want to minimize the volume of contaminated water that is pumped, because that also must be treated.

Satkin and Bedient (1988) used a contaminant-transport model to investigate the use of various pumping and injection patterns to remediate a plume of contamination. They examined the effectiveness of seven different well patterns for various combinations of hydraulic gradient, maximum drawdown, and aquifer dispersivity. The patterns are shown on Figure 9.17.

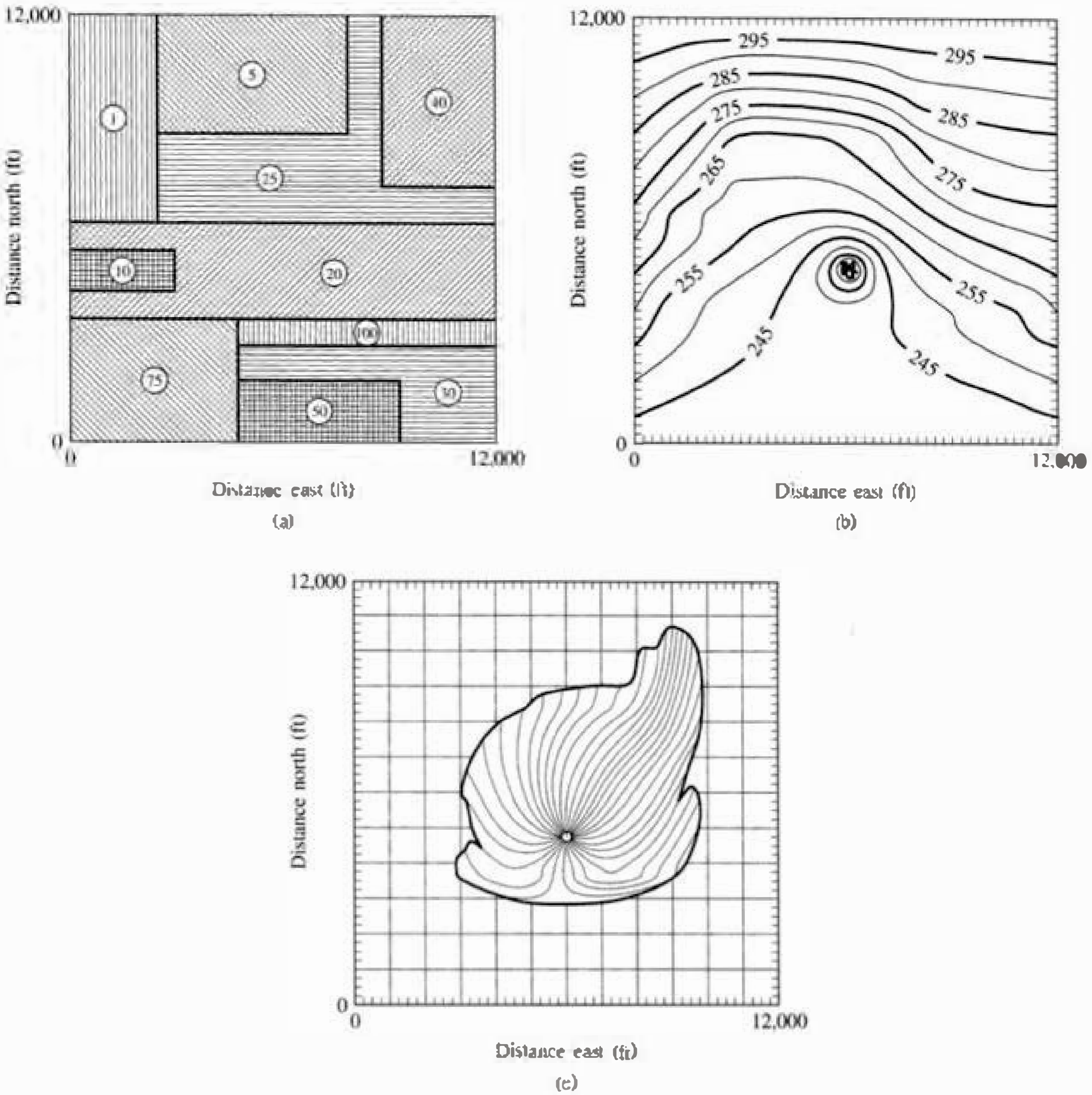
FIGURE 9.15 (a) Hydraulic head distribution with no wells pumping (b) Hydraulic head distribution in a homogeneous, isotropic aquifer with one well pumping. (c) Shape of the 20-year capture zone based on hydraulic head distribution of Figure 9.15b.



Source: J. M. Shafer. 1987. Reverse pathline calculation of time-related capture zones in nonuniform flow. *Groundwater* 25:283-289. Used with permission.

If a single pumping well is used, it must be placed so that the capture zone encompasses the plume. The closer the well can be to the center of mass of the contaminant, the faster the contamination can be removed. If the plume can be captured by a single withdrawal well, then multiple pumping wells aligned along the axis of the plume will increase the rate of cleanup over a single well by pumping a greater volume of water. The use of pumping wells without injection wells may create a problem if there isn't a receiving body of water in which to dispose of treated groundwater.

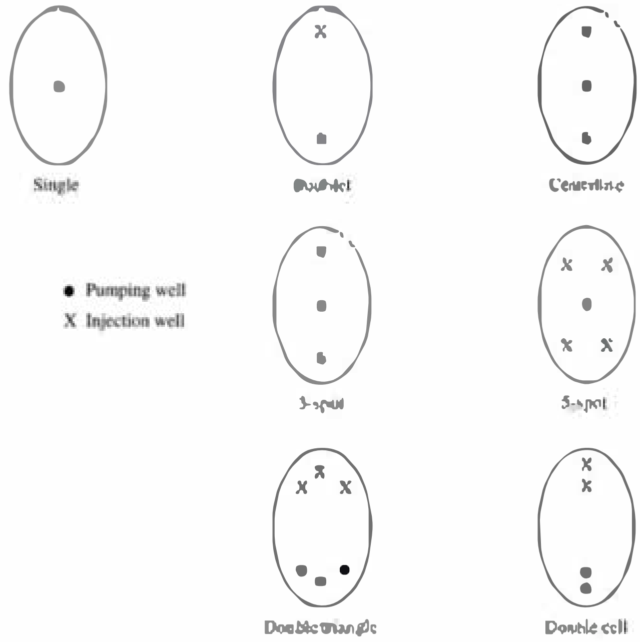
FIGURE 9.16 (a) Distribution of hydraulic conductivity in nonhomogeneous aquifer with the initial head distribution of Figure 9.15a. (b) Hydraulic head distribution in the nonhomogeneous aquifer with one well pumping. (c) Shape of the 20-year capture zone based on hydraulic head distribution of Figure 9.16b.



Source: J. M. Shafer. 1987. Reverse pathline calculation of time-related capture zones in nonuniform flow. *Groundwater* 25:283–289. Used with permission.

If injection wells are used in combination with withdrawal wells, cleanup time can be reduced, because steeper hydraulic gradients can be created. These steeper gradients will produce more water flowing to the withdrawal well(s) than occurs if extraction wells alone are used. We have already seen how a system of a downgradient withdrawal well in conjunction with an upgradient injection well can be used to create a circulation cell

FIGURE 9.17 Possible patterns for extraction and extraction-injection well systems.



Source: R. L. Satkin and P. B. Bedient. 1988. Effectiveness of various aquifer restoration schemes under variable hydrogeologic conditions. *Groundwater* 26:488–498. Used with permission.

to isolate the plume. This is called a doublet on Figure 9.17. Other injection-withdrawal combinations tested included the double cell and double triangle, which are variations of the doublet. Two patterns tested were based on one extraction well and multiple injection wells: the three-spot and the five-spot. When injection wells are used in conjunction with extraction wells, the treated water is disposed via reinjection. However, groundwater injection wells are prone to clogging and may need periodic maintenance (Fetter 1994). Additionally, states, provinces, or regions may have water-quality standards for any water that is reinjected; many locales require a permit for injection wells.

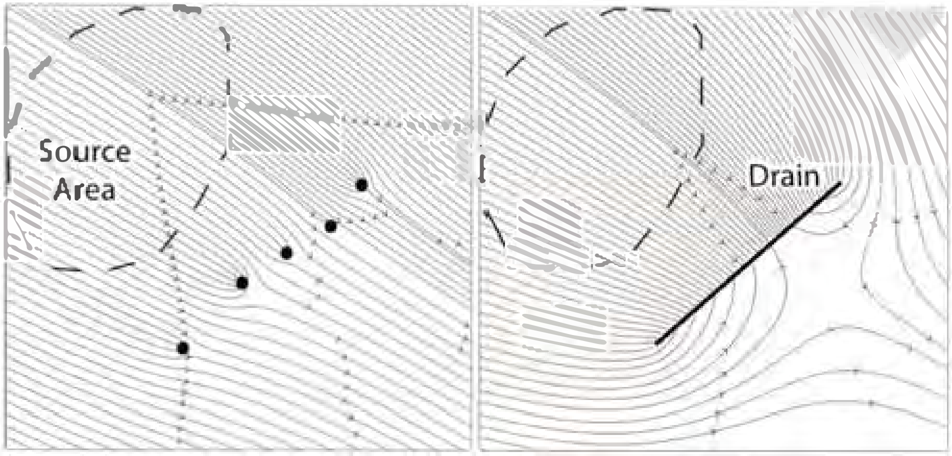
Satkin and Bedient (1988) found that the best well pattern for cleanup was highly site-specific. They also found that even with the same well pattern, variation in the placement of the wells yielded different cleanup times. When the hydraulic gradient is low, the doublet, double cell, and three-spot patterns were very effective. Under conditions of high hydraulic gradient, the centerline was most effective. In this pattern the downgradient injection well, which must be located beyond the leading edge of the plume, creates a hydraulic barrier to further migration of the plume. The five-spot pattern was not found to be very effective under any conditions.

9.3.5 Permanent Plume Stabilization

Decades of experience with pump-and-treat technology showed that in most cases it is not feasible or even technically possible to fully remediate a badly contaminated aquifer by pump-and-treat technology. This is especially true if the source cannot be located and removed, for example, if there are nonbiodegradable residual DNAPLs present in a fractured rock aquifer. For such aquifiers the only feasible technology might well is insufficient to prevent the plume from growing. Pumping at the source zone and downgradient improved the situation but some contaminated groundwater still escaped downgradient. Only the installation of a mid-gradient well prevented the escape of contaminated groundwater. The modeling results underline the importance of source control pumping and the establishment of sufficiently large downgradient capture zones to prevent continued offsite migration of contaminated groundwater.

A different approach to plume containment is to construct a **French drain** perpendicular to the direction of the plume migration. Such a drain system is typically constructed by excavating a ditch to the maximum depth of the plume and back filling it with gravel or other highly permeable material. Embedded at the base of the trench is a horizontal perforated pipe that connects to a vertical well. Contaminated water intercepted by the trench is collected by the pipe and then pumped to the surface for further treatment. As shown in Figure 9.19, a French drain may provide more effective plume containment than a series of extraction wells (Cohen et al. 1997). These drain systems are limited to comparably shallow plumes in unconsolidated material because digging deep trenches (>>30 m or >100 ft) is typically cost prohibitive and often not feasible, particularly if the sediment is unstable and prone to caving. Constructing French drains in bedrock is generally possible, but typically too expensive.

Figure 9.19 Compared to a line of conventional pump-and-treat wells (left), a plume emanating from an up gradient source zone can be effectively intercepted by a trench drain constructed perpendicular to the main axis of groundwater flow (right).



Source: Cohen et al. 1997.

9.4 Treatment of Extracted Groundwater

9.4.1 Overview

It is often necessary to withdraw water during site remediation projects and that water must be treated *ex situ* according to the type of contamination. Different types of treatment are needed for water contaminated with heavy metals or that is contaminated by dissolved organic compounds. Similarly, the treatment approach will be different for compounds that are volatile versus those that are not, or those pollutants that can be chemically or physically destroyed or converted into non-toxic compounds versus those that cannot. Most of the treatment techniques that are used were developed for wastewater and have been adapted to contaminated groundwater. Generally, there are two types of treatment approaches (1) separation and (2) destruction technologies. Examples for the former include adsorption to granular activated carbon (GAC), or air stripping. Destruction technologies include, for instance, UV oxidation and other advanced oxidation processes or biological treatment methods. These and other *ex situ* treatment technologies for contaminated groundwater are described in detail on the Federal Remediation Technologies Roundtable (FRTR) or EUGRIS websites and other online information depositories introduced in Section 9.1. Some of these treatment technologies require the contaminated matrix, soil or groundwater, to be transported to the treatment facility; others can be easily set up on the contaminated site. The treatment methods for contaminated soil and sediment are not covered in this chapter.

The design of a treatment system must be cost effective. To this end the designer must consider the trade-off between capital costs and operating costs. Extraction systems can be designed by the hydrogeologist to withdraw the maximum volume of water in the shortest period of time. This yields the fastest, but not necessarily the most cost-effective cleanup of the aquifer. The size of the treatment plant is dictated by the maximum rate by which water will be pumped for treatment. The capital costs for the treatment plant include the treatment vessels, pumps, piping, and tanks. The greater the flow rate at which contaminated water is pumped through the treatment system, the larger these items must be and the greater the initial capital costs.

Operating costs include the electricity to run the plant, the cost of chemicals, the labor to operate the plant, and the cost of repairs. Some of the operating costs will be continuous no matter how long the project lasts (e.g., the cost of chemicals used to treat the water). If the same total volume of water is treated, the same amount of chemicals will be needed, no matter how long or short the treatment period. Other costs, such as labor, depend primarily upon the length of time of the operation. If the total volume of contaminated water is treated over a very short period of time, there will be high initial capital costs for the large-capacity plant and low operating costs because of the short time period. If the same volume of water is pumped over a longer period of time, the capital costs will be lower, since a smaller treatment plant is needed, but the operating costs will be higher. The smallest treatment plant possible is that needed to treat the quantity of water generated by the minimum pumping rate, which is just high enough to capture the plume. There will be some optimum treatment rate that minimizes the combined capital and operating costs.

9.4.2 Treatment of Inorganic Contaminants

The majority of inorganic contamination needing treatment consists of metals, which can be removed by precipitation or adsorption. Often the treatment involves mixing of reactive agent(s) into the extracted contaminated water. Many metal hydroxides precipitate at a specific alkaline pH value. For these metals, adjustment of pH by adding lime can cause precipitation of the metal hydroxide, which is removed via a clarifier followed by filtration. Ferrous iron can be removed by aeration to create ferric iron, which will precipitate at a slightly alkaline pH. Hexavalent chromium must first be reduced to the trivalent state by lowering the pH to 3 and then adding a reducing agent such as sulfur dioxide. The trivalent chromium can then be precipitated as a hydroxide by raising the pH above the neutral value. Arsenic can be coprecipitated with iron by adding dissolved iron at a pH of 5 to 6 and then raising the pH with lime to between 8 and 9. Arsenic also adsorbs to activated alumina.

Inorganic compounds can be removed by ion exchange. This process uses a resin to adsorb and retain anionic or cationic contaminants from groundwater. In place of the toxic ions, the resin releases benign anions or cations, such as chloride and calcium. When the resin becomes saturated after all of the resin's functional groups have been occupied, it needs to be recharged before reuse, or possibly disposed and replaced. This treatment approach is used commonly for nitrate, which cannot be removed by precipitation. Ion exchange has also been used for removing radiogenic isotopes, like uranium (Botha, Bester, and Hardwick 2009). Inorganic contaminants can also be removed by reverse osmosis and electro dialysis. In reverse osmosis, water is pressured to flow through a semi-porous membrane. While the water molecule passes through the membrane, many molecules and ions cannot and are retained on the membrane surface In case of electro dialysis, flow through a membrane is induced by an electric potential and because the membranes are cation- or anion-selective, either positive ions or negative ions will flow through and can be exchanges for benign ions. This method has been used to remove radium, uranium, arsenic, nitrate, perchlorate, and hardness from drinking water (U.S. EPA 2015) or to remove cooper, chromium and arsenic from chromated copper arsenate (CCA) treated timber waste water (Ribeiro, Mateus, and Ottosen 2000).

9.4.3 Treatment of Dissolved Organic Contaminants

Many of the organic contaminants found in groundwater are volatile. They can be stripped from the water by exposing the water to a flow of air. This is accomplished in an air-stripping tower (Figure 9.20). The tower is a tall cylinder filled with an inert packing material, typically made of polypropylene. The packing material is designed to have a very high porosity and a large total surface area. The contaminated water is sprayed into the top of the tower onto the packing material. A blower attached to the bottom of the tower forces air up the tower at the same time that the water, which was broken up into droplets by the spray nozzles, trickles down the packing material. The volatile organic chemicals vaporize from the water into the air and are expelled out of the top of the tower. Care must be taken that emissions from the air-stripping tower do not create an air-pollution problem. For this reason, the exhaust from the air stripper is typically treated by sorption onto activated carbon or a thermal treatment unit, as can be the case for gasoline type vapors. For typical air stripping towers 4.6 to 6 m (15 to 20 ft) in height and containing conventional packing, removal efficiencies of VOC are around 99%. The removal efficiencies can be improved by adding a second air stripper in series with the first, heating the contaminated water, or changing the configuration of packing material (FTRC 2015). A potential problem with air stripping is biological fouling, which describes the buildup of biofilms growing on the inside of the air stripping tower. If not attended to, biofouling can lead to decreasing treatment and eventually clogging of the system. Another common problem with air strippers is precipitation of iron or other minerals. Typically, if the treated groundwater contains more than 5 mg/liter iron or its hardness is greater than 800 mg/liter (FRTR 2015), it becomes likely that mineral precipitates will build up inside the stripper tower. Mechanical filters, such as sand beds, might be needed to filter the precipitated iron from the wastewater stream

An uncontaminated, confined sand aquifer that was 1.5 m (5 ft) thick was instrumented with a line of injection and extraction wells located 6 m apart. The direction of groundwater flow from the injection to the extraction wells was parallel to the regional hydraulic gradient. Intermediate sampling wells were placed at distances of 1, 2.2, and 4 m (3 to 12 ft) from the injection wells. Depending upon the injection and withdrawal rates, travel times from the injection wells to the withdrawal wells were from 20 to 42 hr. When oxygenated water was injected into the aquifer prior to the biostimulation experiments, the oxygen was transported to the extraction wells with little loss.

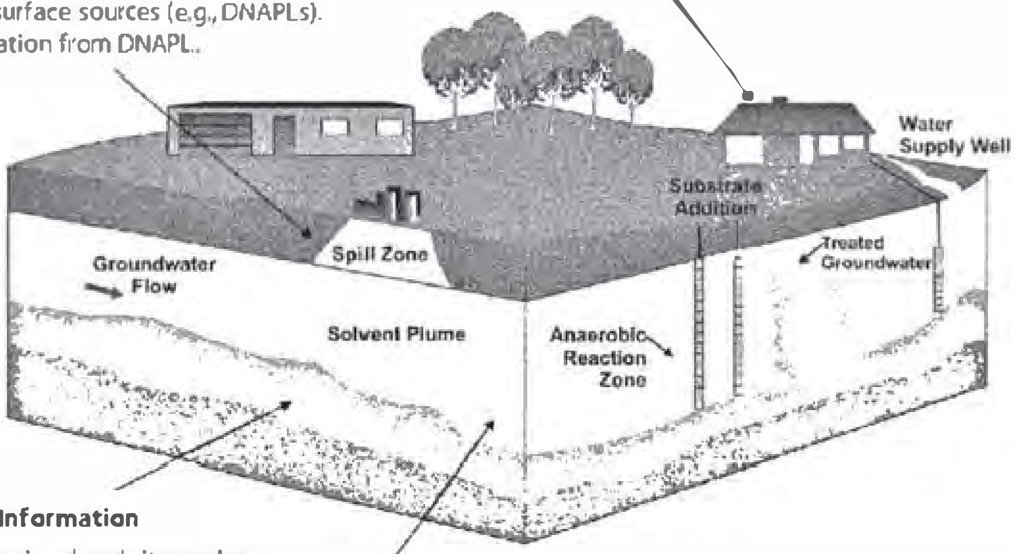
The compounds that were selected for study were vinyl chloride (VC), *trans*-1, 2-dichloroethene (t-DCE), cis-1, 2-Dichloroethene (c-DCE), and trichloroethene (TCE). When these were injected prior to biostimulation, they were retarded in the rank order of TCE > t-DCE > c-DCE > VC. It was found that with a long period of injection prior to biostimulation, the sorption capacity of the aquifer could be saturated with respect to TCE, t-DCE, and c-DCE. After 1000 hr. of injection, the concentration of these compounds in the monitoring well located 1 m (~3 ft) from the injection well was found to be 90 to 95% of the injected concentration.

After the aquifer reached steady-state concentrations of the organic halides, it was biostimulated by injecting alternating pulses of dissolved oxygen and methane, along with continuous injection of the organic halides. The methane acted as the primary substrate (electron donor) for the growth of indigenous methane-utilizing bacteria, while the oxygen was the electron acceptor. The organic halides were degraded by cometabolism, a process by which the methantrophic bacteria that are utilizing the methane produce enzymes that are able to degrade the chlorinated ethenes. During the biostimulation experiments, decreases in concentration of both methane and the organic halides were observed. Within 2 m (6 ft) of travel through the aquifer, VC was reduced by 90 to 95%, t-DCE by 80 to 90%, c-DCE by 45 to 55%, and TCE by 20 to 30%. Residence times in the aquifer were only 1 to 2 days for this amount of biodegradation. It took about three weeks for the biostimulation experiment to reach these steady-state rates of reduction. An intermediate degradation product, *trans*-dichloroethene epoxide, was detected. When the injection of methane was halted, the concentration of the epoxide quickly decreased and the concentration of the halogenated ethenes slowly increased. However, when the rate of methane addition was increased beyond a certain concentration, it was shown to reduce the rate of transformation of VC and tDCE. Thus, while methane was necessary for stimulating *in situ* aerobic biotransformation, there appears to be an optimal concentration beyond which it inhibits the process.

9.11 Conceptual Site Models

The bioremediarion approach serves as an example for the complexity of the biochemical and hydrogeologic interactions and their dependency on aquifer characteristics and the physical/chemical properties of the contaminant(s). Failure to understanding these conditions can determine the success or failure of site cleanup activities. Therefore, the development of a conceptual model of the site is an essential part of the site remediation process. Such a model is referred to as a conceptual site model (CSM). A CSM develops during the course of a site investigation. Elements of a CSM include at minimum a conceptualization of the processes that determine contaminant releases, contaminant migration, and the relationship between contaminant sources and receptors. The CSM is used to integrate all site information and data and to determine whether data gaps exist and whether additional information needs to be collected at the site. The model is used furthermore to facilitate the selection of remedial alternatives and to evaluate the effectiveness of remedial actions in reducing the exposure of environmental receptors to contaminants (ASTM 2014). The CSM should be maintained and refined as new information and data is collected from the initial assessment through site closeout. Different types of CSM are common, including text documents and pictorial and graphical depictions of current and future site conditions. Parsons Corporation (2004) provides an example of the elements of a graphical CSM (Figure 9.38). Typical CSM information needs and other elements of a CSM for sites contaminated with unexploded ordnance and/or other hazardous, toxic, and radioactive waste is provided by the U.S. Army Corp of Engineers (2012).

FIGURE 9.38 Elements of a Conceptual Site Model.



Risk Assessment

- Current and potential receptors.
- Completed pathways?

Contaminant Source Information

- Location and nature of previous contaminant sources.
- Locations of subsurface sources (e.g., DNAPLs).
- Flux of contamination from DNAPL.

Hydrogeological Information

- Description of regional and site geology.
- Stratigraphy that may provide preferential pathways for, or barriers to, contaminant transport.
- Depth to ground water.
- Hydraulic gradients (horizontal and vertical).
- Hydraulic conductivity (degree of heterogeneity).
- Groundwater / surface water interactions.

Contaminant Distribution, Transport, and Fate Parameters

- Phase distribution of contaminant (gaseous, aqueous, sorbed, free-phase DNAPL or residual DNAPL) in the unsaturated and saturated zones.
- Spatial distribution of subsurface contaminants.
- Temporal trends in contaminant concentrations.
- Contaminant natural attenuation processes (destructive and nondestructive).
- Geochemical indicators (aerobic / anaerobic).

Source: Parsons Corporation 2004.

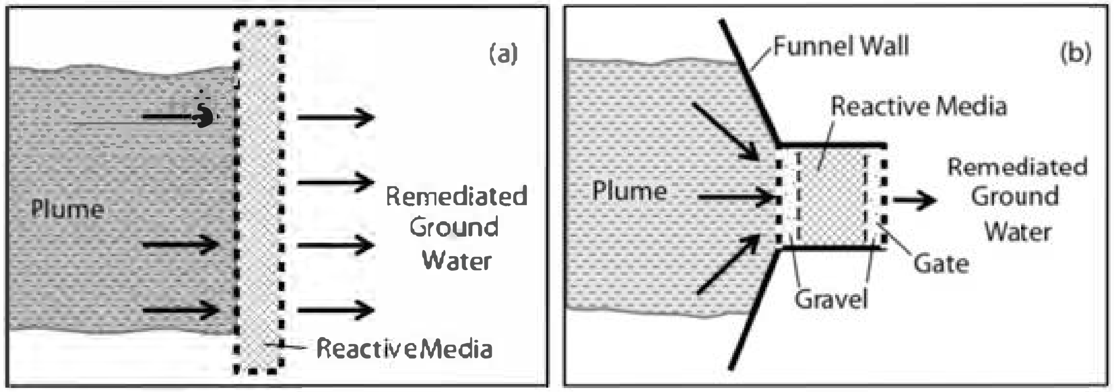
■ 9.12 Permeable Reactive Barriers

A permeable reactive barrier (PRB) is a subsurface emplacement of reactive materials through which a dissolved contaminant plume must move as it flows, typically under natural gradient conditions. Treated water exits on the other side of the PRB. This *in* *situ* method for remediating dissolved-phase contaminants in groundwater combines a passive chemical or biological treatment zone with subsurface fluid flow management (U.S. EPA 2015d). The purpose of a PRB is to intercept a contaminant plume and prevent it from migrating to downgradient receptors, such as drinking water wells.

The concept of placing reactive materials in the path of a plume was developed based on observations by Reynolds et al. (1990). The authors noticed that at their field site concentration of dissolved chlorinated compounds were systematically lower in wells with galvanized iron casing compared to wells constructed from non-metallic pipe material. Laboratory experiments showed that metallic or zero valent iron (ZVI) reacted with the chlorinated compounds and degraded them to non-toxic products, such as ethane and ethane (Gillham and O'Hannesin 1994). The first field trial of a PRB was carried out by Gillham and O'Hannesin on the Canadian Air Force Base Borden, Ontario in 1991. A trench of up to 6 m (20 ft) in length and 2.5 m (8 ft) deep was excavated and backfilled with a mix of 22% of granular iron from a local foundry and 78% coarse sand. The total volume of the reactive matrix was 20 m^3. The groundwater flow velocity in the unconfined sandy aquifer at the site was 9 cm/day (0.3 ft/day). The groundwater concentration of TCE was 258 mg/L and 68 mg/L for PCE. After installation, approximately 90% of the TCE and 86% of the PCE were removed within this proto-type PRB system, with no measurable decrease in performance over the first five year duration of the test. All degradation intermediates, including *cis*-1,2-DCE, were degraded within the reactive barrier. Changes in water chemistry indicated that calcium carbonate was precipitating within the reactive material. However, the clogging caused by the precipitates was inconsequential for the performance of the system within the five year study period. The authors concluded that full removal would have been achieved by increasing the amount of ZVE (O'Hannesin and Gillham 1998). Since these early trials, more than 200 reactive barriers have been installed and PRB technology is now an accepted practice for groundwater remediation, particularly for the treatment of dissolved chlorinated VOC plumes (ITRC 2011).

In situ PRB systems are typically constructed by digging a continuous trench perpendicular to the flow direction of a groundwater plume (Figure 9.39). After excavation, the trench is backfilled with a mix of reactive material and coarse sand and gravel, which provides the mix with a hydraulic permeability and porosity that is greater than the surrounding natural sediments. The length and depth of the PRB is determined by the dimensions of the groundwater plume, i.e., the trench must be large enough to capture the entire plume in both horizontal and vertical direction. If possible, the trench is anchored in a less permeable stratum, such as a clay layer, to prevent the plume from diving under the treatment system. In some cases, funnel-and-gate PRB systems have been installed in which an impermeable barrier blocks the advancing plume and redirects (funnels) the flow of contaminated groundwater through an opening (gate) in the wall and into a PRB system (ITRC 2005a). A funnel-and-gate system is depicted in Figure 9.39. The length of PRB systems is limited by site conditions and typically ranges from a few meters to a few hundred meters. The depth, however, is limited by the equipment available to excavate the trench. Trenches excavated with conventional equipment, such a back hoes or chain trencher, are comparably shallow (10 to 15 m or 33 to ~50 ft). Depths of 20 m (66 ft) or more can be achieved by caisson installation or cofferdam/sheet pile methods. Alternatively, the reactive material can be mixed *in situ* into the treatment zone or slurries of reactive materials can be directly injected into the subsurface. The cost of constructing the trench and backfilling it with reactive material is the major cost driver of this remediation technology.

FIGURE 9.39 Permeable reactive barrier (PRB) designs (map view). (a) Continuous trench and (b) Funnel-and-gate systems.



The thickness of the PRB wall is a critical design parameter. It depends on hydrogeologic factors, (such as groundwater flow velocities and flow directions which may change over the seasons), the strength and chemical make-up of the source zone including which contaminants are present and how much mass of dissolved contaminant must be treated, and the reactivity of the PRB material, including the geochemical conditions that can influence the reactive material, such as the pH of the groundwater. The reactivity of the material inside a PRB can be quantified in terms of a reaction rate constant or the half-life time of the contaminant coming in contact with the reactive material. Because some contaminants, including PCE and TCE, undergo sequential degradation, which involves the production of toxic intermediates, such as vinyl chloride, reaction rates for each compounds need to be taken into consideration. If the flow-through thickness and contaminant residence time inside the PRB is underestimated, still-contaminated water will emerge on the downgradient side of the wall. It is therefore not surprising that extensive laboratory and field tests are required to ensure the field performance of a PRB system. A lot of practical information about the proper installation of PRB systems has been accumulated over the past two decades and many PRB installations manuals and guidance documents are available on the internet, including Gavaskar et al. (2000) and ITRC (2011).

Zero-valent iron based PRBs are most commonly used for the *in situ* treatment of chlorinated aliphatic VOC, such as PCE and TCE. The reactions involved in the degradation of chlorinated VOC by metallic iron (Fe^0) within a PRB are abiotic in nature. Zero valent iron is a mild reductant and can react with dissolved oxygen (Eqn. 9.1) and to some extent with water (Eqn. 9.2):

$$2Fe^0_{(S)} + 4H^+_{(aq)} + O_{2(aq)} \rightarrow 2Fe^{2+}_{(aq)} + 2H_2O \quad \textbf{(9.1)}$$

$$Fe^0_{(S)} + 2H_2O \rightarrow Fe^{2+}_{(aq)} + H_{2(aq)} + 2OH^-_{(aq)} \quad \textbf{(9.2)}$$

These two equations illustrate the corrosion (=oxidation) of iron when coming in contact with oxygen or water. The two electrons released during the oxidation of iron can be readily accepted by chlorinated hydrocarbons, which are degraded via reductive dehalogenation, as shown in Equation 9.3

$$\begin{array}{lll} Fe^0 \rightarrow Fe^{2+} + 2e^- & & \text{Oxidation} \\ RCl + 2e^- + H^+ \rightarrow RH + Cl^- & & \text{Reduction} \\ \hline Fe^0 + RCl + H^+ \rightarrow Fe^{2+} + RH + Cl^- & & \text{Net Reaction} \qquad (9.3) \end{array}$$

The products of the reductive dechlorination reaction are chloride (Cl^-), ferrous iron (Fe^{2+}), less chlorinated hydrocarbons, and hydrogen. Dechlorination of chloroethenes and chloroethanes is complete with ethene and ethane as the final carbon-containing compounds, respectively (Orth and Gillham 1996; Fennelly and Roberts 1998). The corrosion of the iron can generate large amounts of iron oxides and (oxy)hydroxide precipitates, which may eventually decrease the porosity and permeability of the reactive material within the PRB; particularly at the upgradient side of the barrier. However, these iron precipitates can convert to magnetite, which does not passivate the reactive surface of the iron. Also, field experiences from many PRB sites indicate that the loss of permeability due to precipitation is a relatively slow process that takes decades to cause significant changes in the hydraulic performance of the system. If installed properly, it is therefore likely that the dechlorination reaction is sustainable for many years of PRB operation (EPA 1998).

The degradation of chlorinated hydrocarbons by ZVI is a stepwise process during which intermediates are produced, such as *cis*-1,2-dichloroethene, vinyl chloride or chloroacetylene in cases where the parent compound is TCE or PCE. The degradation reactions are typically described using pseudo first-order kinetics with respect to the halogenated hydrocarbon, with the rate constant relatively insensitive to the initial hydrocarbon concentration (IRTC 2011).

$$C = C_0^{-k't}$$

or:

$$\ln\left(\frac{C}{C_0}\right) = -k't$$

where C_0 and C are the concentrations of the chlorinated compound of the influent and at time t, respectively. The pseudo-first order rate constant is k, which equals the first order rate constant, k, when the concentration of the iron remains constant. Dehalogenation rates vary for the different halogenated contaminants. The primary determinant of degradation rate is the iron surface area, i.e., the surface area of iron per unit volume of pore water. For this reason, some PRB designs are based on nanoscale iron particles, which have larger surface areas and higher surface reactivity compared to conventional granular iron. Nanoscale iron particles range in size from approximately 10 to 100 nm and have a high iron content (>99.5% Fe) (Zhang 2003).

The reaction rates can be enhanced further by coating the iron particles with metallic catalyst, such as palladium (Li and Farrel 2000). One advantage of nanoscale iron particles is that slurries of these particles can be injected directly into the treatment zone. This approach alleviates the need of excavating a trench and back-filling it with mixes of ZVI and highly permeable sand/gravel materials.

Dissolved chlorinated compounds were the first groundwater contaminants treated by *in situ* PRB systems using metallic iron as the reactive material. Since then, the list of ZVI treatable compounds has rapidly expanded and now includes many other organic and inorganic contaminants (Table 9.2). For instance, metallic iron can transform explosives, such as TNT (Johnson and Tratnyek 2008), and pesticides, e.g., Lindane (U.S. EPA 2002) or can immobilize inorganic ions, such as arsenic (VI) and chromium (VI). Particularly metals that occur as anions exhibit a high degree of mobility because anions do not readily sorbed to the predominantly negatively-charged aquifer materials. For example, chromium (VI) is usually speciated as chromate, CrO_4^{2-}, which is a known carcinogen. The anion is comparably soluble under typical near-neutral pH and only slightly negative Eh conditions in typical aquifers. However, when reduced to trivalent Cr(III), relatively non-toxic and little soluble precipitates are formed. The immobilization of Cr(VI) by iron is a two-step process: first, Cr(VI) is reduced to Cr(III) (Eqn. 9.4). Subsequently, the Cr(III) precipitates as Fe(III) oxyhydroxide (Eqn. 9.5) (U.S. EPA 1998):

$$CrO_4^{2-} + Fe^0 + 8H^+ \rightarrow Fe^{3+} + Cr^{3+} + 4H_2O \quad \textbf{(9.4)}$$

$$(1-x)Fe^{3+} + (x)Cr^{3+} + 2H_2O \rightarrow Fe_{(1-x)}Cr_xOOH_{(s)} + 3H^+ \quad \textbf{(9.5)}$$

The mechanisms of Cr(VI) reduction by Fe(0) and their effects on the pH and Eh conditions of the system have been described by Powell et al. (1995) and Powell and Puls (1997). At some sites, Cr(VI) occurs together with other contaminants, such as TCE. Research has shown that it is possible to simultaneously treat both chromium and TCE with ZVI (U.S. EPA 1998).

While ZVI remains the most widely used reactive material used in PRB systems, an increasing number of new reactive materials and variations of the PRB based treatment approach are being developed and tested. These advances are greatly expanding the number of treatable groundwater contaminants. They also make it possible to apply this technology to hydrogeologic environments other than the unconsolidated aquifers for which PRB was initially developed. For example, a fractured bedrock aquifer comprised of shale and siltstone is contaminated with PCE at a manufacturing plant in northern New Jersey, USA (U.S. EPA 2011b). The main source area is located in shallow bedrock to a depth of approximately 13 m (42.5 ft) below ground surface, with some contamination in deeper parts of the aquifer. The lateral extent of the PCE plume is approximately 25 m (80 ft) by 37 m (120 ft). The plume was approximately 1.2 km (4,000 ft) in length prior to treatment. A pump-and-treat system and later, an enhanced bioremediation system were installed for containment of the PCE plume. After observing some reduction of contaminant flux, a nanoscale zero-valent iron injection was proposed as a more aggressive strategy. Before the injection of the nanoscale particles into the bedrock, the hydraulic communication within the fracture network was improved by hydrofracturing. This technology involves applying

TABLE 9.2 Common environmental contaminants that can be transformed by ZVI, including bimetallic and nanoscale iron particles.

Chlorinated methanes	**Chlorinated ethenes/ethanes**	**Chlorinated benzenes**	**Trihalomethanes**
Carbon tetrachloride (CCl_4)	Tetrachloroethere (C_2Cl_4)	Hexachlorobenzene (C_6Cl_6)	Bromoform ($CHBr_3$)
Chloroform ($CHCl_3$)	Trichloroethene (C_2HCl_3)	Pentachlorobenzene (C_6HCl_5)	Dibromochloromethane ($CHBr_2Cl$)
Dichloromethane (CH_2Cl_2)	*cis*-Dichloroethene ($C_2H_2Cl_2$)	Tetrachlorobenzenes ($C_6H_2Cl_4$)	Dichlorobromomethane ($CHBrCl_2$)
Chloromethane (CH_3Cl)	*trans*-Dichloroethene ($C_2H_2Cl_2$)	Trichlorobenzenes ($C_6H_3Cl_3$)	
	1,1-Dichloroethene ($C_2H_2Cl_2$)	Dichlorobenzenes ($C_6H_4Cl_2$)	
	Vinyl chloride (C_2H_3Cl)	Chlorobenzene (C_6H_5Cl)	
	1,1,1-trichloroethane ($C_2H_3Cl_3$)		
	1,1,2-trichloroethane ($C_2H_3Cl_3$)		
	1,1-dichloroethane ($C_2H_4Cl_2$)		
Otherpolychlorinated hydrocarbons	Pesticides	Organic dyes	Other organic contaminants
Dioxins	DDT ($C_{14}H_9Cl_5$)	Orange II ($C_{16}H_{11}N_2NaO_4S$)	TNT ($C_7H_5N_3O_6$)
Pentachlorophenol (C_6HCl_5O)	Lindane ($C_6H_6Cl_6$)	Chrysoidine ($C_{12}H_{13}ClN_4$)	RDX ($C_3H_6N_6O_6$)
PCBs		Tropaeolin O ($C_{12}H_9N_2NaO_5S$)	N-nitrosodimethylamine (NOMA) ($C_4H_{10}N_{20}$)
		Acid Orange	
		Acid Red Arsenic (AsO_3^{-4})	
Heavy metal ions	Radiogenic ions	Inorganic ions	
Mercury (Hg^{2+})	Uranium (U VI)	Perchlorate (ClO^{-4})	
Nickel (Ni^{2+})	Technetium (Tc VII)	Nitrate (NO^{-3})	
Silver (Ag^{+})		Dichromate ($Cr_2O_2^{-7}$)	
Cadmium (Cd^{2+})		Selenium (Se IV)	
		Arsenic (As VI)	

Source: Modified after Zhang 2003 and U.S. EPA 1998.

high hydrostatic pressures to the well wall until the solid bedrock fractures. The newly opened fractures permit enhanced injection and farther reach of the nanoparticle slurry into the bedrock. Following hydrofracturing, approximately 800 pounds of nanoscale iron particles was delivered through four injection wells. Performance monitoring of the ZVI injection indicated significant impacts on source area geochemistry, including increased pH levels (~9) and low ORP values (-500 mV). Although it is likely that the iron particles did not reach all contaminated areas of the bedrock aquifer, it appears that amount of injected iron was sufficient to control both the primary PCE source and any back diffusion from the shale and siltstone matrix.

Innovative reactive materials for PRB include surfactant-modified zeolites, metal hydroxides or carbonates, organoclays, peat moss, mulch, compost and agricultural waste products (Thiruvenkatachari et at. 2008). Zeolites are clay minerals that have an elevated permeability (for a clay) and a high capacity for cation exchange. When coated with non-ionic surfactants, the surface of the zeolites becomes more hydrophobic, which makes it attractive to non-polar organic compounds. When modified with cationic surfactants, the zeolite surface has a positive charge and hence a greater affinity for anions, such as dissolved chromate (Bowman 2003; Misaelides 2011). Surfactant modified zeolites retain some of their cation ion exchange capacity. Peat moss has an affinity for both heavy metal ions, such as nickel or uranium and anions, e.g., chromate. Compounds like mulch or agricultural waste products used in PRBs are intended to be long-term sources of organic carbon or, in case of compost, serve as a source of nutrients (IRTC 2011). For instance, Lu et al. (2008) investigated the performance of pilot-scale permeable reactive barrier filled with plant mulch that was installed at Altus Air Force Base in Oklahoma, USA in 2002. The barrier was 139 m long (~450 ft), 7 m deep (~2 m), and 0.5 m (1.6 ft) wide and was constructed to treat trichloroethylene (TCE) contamination in groundwater emanating from a landfill. Data from over four years' monitoring indicated that the PRB stimulated TCE degradation to cis-DCE and vinyl chloride. Ongoing biodegradation reactions were corroborated by the detection of TCE degrading bacteria DNA (*Dehalococcoides*) and the detection of vinyl chloride within and downgradient of the PRB.

Systems like the one described by Lu et al. (2008) are also called biowalls or bio barriers. These *in situ* biowalls use solid low-cost organic materials, such as mulch or compost, to stimulate anaerobic degradation of chlorinated solvents, energetic (e.g., perchlorate) and explosive compounds (e.g., TNT, anions (nitrate and sulfate), and heavy metals (e.g., chromium and cadmium). Biowall materials can be amendment with, for example, emulsified vegetable oil, to stimulate both biotic and abiotic degradation processes. This permits to optimize biowall performance based on the type of contaminant(s) present and the desired degradation pathway(s) to be stimulated (Air Force Center for Engineering and the Environment 2008). Typically, biowalls stimulate anaerobic degradation processes, including reductive dechlorination and biotic anaerobic oxidation, and therefore are most often used for treating dissolved chlorinated compounds like PCE and TCE and their degradation products (DCE isomers and vinyl chloride). According to the ITRC (2011), an advantage of biological PRB systems over purely abiotic systems, such a ZVI, is that the treatment processes may extend downgradient of the constructed treatment zone due to migration of soluble organic carbon, enabling the effects of anaerobic degradation beyond the biowall. In addition, the biowall system can be amended with specific bacteria (bioaugmentation) to target one or multiple contaminants and accelerate their degradation. A drawback is that the longevity of biowalls is anticipated to be shorter than that of ZVI walls and replenishment of organic substrate may be required.

The geochemistry of the solution inside a PRB system and downgradient can be adjusted by materials to buffer pH (e.g., limestone gravel) or to adjust the redox potential and further stimulate abiotic biogeochemical transformation processes (e.g., addition of reactive iron sulfite minerals, such as pyrite or mackinawite). The redox conditions in the treatment zone can also be manipulated by injecting sodium dithionite solution. The dithionate reduces ferric iron (Fe III) that is naturally present in the aquifer material to ferrous iron (Fe II). The presence of Fe(II) in the treatment zone can reduce, for example, soluble Cr(VI) to Cr(III) precipitates (Naftz et al. 2002). Also, the injection of oxidants, like hydrogen peroxide (H_2O_2) or potassium permanganate ($KMnO_4$) into the PRB can create strongly oxidizing conditions that are suitable for the *in situ* chemical oxidation and destruction of many organic contaminants, including BETX and other petroleum hydrocarbons (Thiruvenkatachari et at. 2008). Finally, sorbing barriers systems have been developed which use granular activated carbon or ion exchange materials. However, these systems have a limited live time and need to be replacement when the capacity of the sorbent is exhausted.

There now are a great variety of the reactive materials and amendments that permit tailoring the PRB treatment to specific contaminants, including once that cannot be treated with the original ZVI approach, e.g., BTEX compounds. Barriers of different chemistries may also be placed sequentially which further increases the treatment options for contaminated site managers. It is likely that future research into PRB system will further enhance the applicability of this remediation approach.

9.13 Chemically-Enhanced *In Situ* Flushing

Some chemicals, such as surface active agents (surfactants), complexing agents (cyclodextrins) or cosolvenrs (alcohols), can increase the solubility of otherwise slightly soluble hydrophobic organic contaminants, such as petroleum hydrocarbons or chlorinated solvents. In case of some metals or ionic organic contaminants, a similar solubility enhancing effect can be achieved by injecting acidic, basic, or reducing solutions. When injected into the aquifer and flushed through the contaminated source zone, these solubility enhancing agents increase the aqueous phase concentration of the contaminants, sometimes by orders of magnitude. After its passage through the treatment zone, the flushing solution is extracted and treated at the surface. Therefore, in its most basic form, chemically-enhanced flushing technology can be considered an enhancement of pump-and-treat in which water is the flushing solution. Compared to P&T, chemically-enhanced flushing is a much more aggressive and relatively rapid treatment approach with treatment durations often an order or two magnitudes shorter than P&T (ITRC 2009a).

In situ flushing is considered a mature remediation technology. The chemically-enhanced flushing approach is used predominantly to remediate source zones, particularly residual NAPL compounds. It is less well suited for the treatment of dissolved plumes or contaminants residing in the unsaturated zone. Flushing is most efficient in relatively homogeneous and permeable (hydraulic conductivity $>10^{-3}$ cm/sec) soil the biowall system can be amended with specific bacteria (bioaugmentation) to target one or multiple contaminants and accelerate their degradation. A drawback is that the longevity of biowalls is anticipated to be shorter than that of ZVI walls and replenishment of organic substrate may be required.

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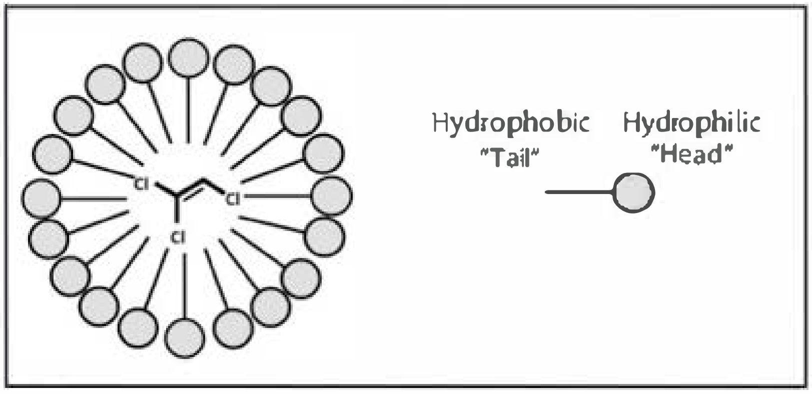
(Naval Facilities Engineering Command 2002). Heterogeneous aquifer conditions, including fractured bedrock aquifers, typically stand in the way of effectively flooding the treatment zone because lower permeable zones may be by-passed. Chemically-enhanced flushing is sometimes used in combination with other *in situ* remediation technologies, such as bioremediation or *in situ* oxidation (e.g., Dugan et al. 2010). Although their effect on the solubility of contaminants is similar, there are major differences between surfactant, cosolvent, or complexing agents. The following sections provide a brief overview of these agents. One disadvantage is that field applications typically have limited areal extent. For further readings, there have been a great number of papers, books, and manuals written about these flushing agents (e.g., Keuper et al. 1997; Lowe et al. 1999; Ward et al. 2000; Boving and Brusseau 2000; Naval Facilities Engineering Command 2002; 2003; ITRC 2003; Pennel et al. 2014).

9.13.1 Surfactant Enhanced *In Situ* Flushing

Surfactants are amphiphilic organic molecules that have both hydrophobic and hydrophilic moieties. When dissolved in water, surfactant molecules tend to cluster together and form micelles (Figure 9.40). These micelles aggregate when a specific threshold, known as critical micellar concentration (CMC), is exceeded. In water, the hydrophilic "heads" of the dissolved surfactant molecules point towards the aqueous phase, assuring that surfactants are highly water soluble. The hydrophobic "tails" of the surfactant molecule project inside the micelle. The "heads" and "tails" of surfactant molecules are typically separated by hydrocarbon chains. The non-polar core of these micelles attracts equally non-polar compounds, like TCE or other chlorinated solvents. This partitioning of hydrophobic contaminants into the micelle structure is the basis of the surfactant enhanced flushing technology, which is also referred to as Surfactant Enhanced Aquifer Remediation (SEAR). The enhancement of contaminant solubility is directly proportional to the concentration of the surfactant above the CMC.

Surfactants also reduce the interfacial tension between the aqueous and NAPL phases. At very low interfacial tensions, larger globules of NAPL spontaneously break

FIGURE 9.40 Surfactants are amphiphilic compounds; they have both hydrophobic and hydrophilic moieties. Above the critical micelle concentration, surfactant molecules aggregate into micelles. Hydrophobic contaminants (TCE shown here) can partition into the hydrophobic interior of the micelle.



up into tiny droplets of about 5 to 50 nm in radius. At that point, the system consists of water, NAPL droplets and surfactants and is called a **microemulsion**. The reduction in interfacial tension and formation of microemulsions can be exploited to **mobilize** NAPL. Relative to surfactant enhanced solubilization, NAPL mobilization can remove more contaminant mass in less time. But, in case of DNAPL, there is greater risk of uncontrolled downward movement, as DNAPL is being physically displaced by the surfactant solution. When injecting surfactant solution with the primary purpose of inducing mobilization, it is therefore necessary to prevent vertical DNAPL migration. This can either be achieved by having competent bedrock or a capillary barrier underlying the treatment zone or by manipulating the density the DNAPL, for example, by co-injection of cosolvents. Because of the risk of vertical displacement, mobilization flooding should only be considered when there is a high degree of certainty that the flushing solution can be recovered. In general, a surfactant flushing system can be tailored to remove contaminants either primarily by solubilization or primarily by mobilization (Pope 2015). Under appropriate site conditions, removal rates as high as 98.5% of the original DNAPL mass have been reported (Londergan et al. 1997). A number of very well documented field tests have demonstrated that *in situ* flushing can achieve these high removal percentages in months, and sometimes even days (EPA 2000).

Surfactants are produced at industrial scales and are one of the most widely used chemicals. Many different kinds of surfactants have been developed for a large number of applications, including detergents, fire-fighting agents (see Chap. 5) or pharmaceuticals and cosmetics. Depending on the charge of their polar heads, surfactant can be non-ionic, cationic or anionic. For most remediation applications, non-ionic or anionic surfactants are preferred because they do not sorb as strongly to the charged surfaces of natural minerals (i.e., clays) as cationic surfactants. Also, they are generally less toxic than cationic surfactants.

Case Study: Hill Air Force Base, Utah.

The Hill Air Force Base is located near Ogden, Utah, USA. The test site was used continuously from 1967 until 1975 for base-wide disposal of spent degreasing fluids and other solvents. At the site, DNAPL pooled within the topographic lows of a clay aquitard approximately 15 to 17 m (50 to 56 ft) below ground surface. The DNAPL was composed of approximately 70% TCE, 10% PCE, 5% TCA with other minor volatile organic constituents. In addition, there was a significant oil and grease fraction entrained in the DNAPL. The groundwater contaminants included PCE, TCE, TCA, DCE and trace heavy metals. The depth to groundwater was 8.3 m (27 ft). The unconfined aquifer consists of alluvial sands and gravel. The deposits are highly heterogeneous and are underlain by a thick uniform and continuous clay layer. The effective porosity of the aquifer is 20% and its hydraulic conductivity is 6×10^{-3} to 5×10^{-2} cm/sec (17 ft/day to 146 ft/day).

Prior to the surfactant flooding, a DNAPL source-recovery system was installed. Partitioning interwell tracer tests (PITT) were conducted pre- and post- surfactant flooding to characterize the DNAPL distribution and to demonstrate the removal efficiency of the surfactant treatment. The flushing solution injected into the treatment zone consisted of 8% an anionic surfactant (Aerosol MA-801) and 4% isopropyl alcohol. About 0.7% of sodium chloride was added to adjust the ionic strength of the mixture. The solution decreased the interfacial tension between the surfactant solution and the DNAPL to 0.02 dynes/cm. About 2.4 pore volumes of the flushing solution were injected during a 3 day period, followed by 5.5 days compounds by self-sustaining smoldering processes (Switzer et al. 2009; Pironi et al. 2009). This approach is commercialized as self-sustaining treatment for active remediation (STAR) technology.

ISTT field applications are growing in number, partially because clean up goals can be achieved quickly, often within days or weeks. ESTCP (2010) provides a critical evaluation of 182 ISTT applications conducted between 1988 and 2007. Of those 182 applications, 87 used electrical resistance heating, 46 steam-based heating, 26 conductive heating, and 23 other heating technology applications. Measured in terms of reducing contaminant concentration and mass flux from the treatment zone, improvements ranged from less than 10 to over 1000 times. Overall, the electrical resistance heating and thermal conductive heating variants of ISTT are less affected by heterogeneous and low-permeability lithologies (EPA 2014a), which is why *in situ* thermal technology performance appears less hindered by the geologic stratification and mass-transfer resistances that limit other *in situ* remediation technologies (Triplett Kingston, Dahlen, and Johnson 2010).

9.15 *In situ* Chemical Oxidation (ISCO)

In situ chemical oxidation (ISCO) refers to a groundwater remediation technology that relies on the chemical oxidation of a wide variety of dissolved contaminants by strong oxidants, such as permanganate (MnO_4^-), hydrogen peroxide (H_2O_2), ozone (O_3), catalyzed hydrogen peroxide (Fenton oxidation), persulfate ($S_2O_8^{2-}$), peroxone (H_2O_2 and O_3), or percarbonate. The reactive species and other properties of common oxidants are summarized in Table 9.4. Relative to each other, ozone and persulfate are stronger oxidants than permanganate and hydrogen peroxide. Fenton's reagent produces a variety of oxidizing species of different strengths.

An ISCO treatment system is similar to *in situ* enhanced flushing systems, except that generally no extraction well(s) is required. A solution of the oxidant in water is prepared on the site and then injected into the subsurface. Vertical injection wells and direct push probes are the most common delivery methods. As the oxidant solution moves through the treatment zone it comes into contact with the contaminant and degrades it into benign compounds, including carbon dioxide and water. The oxidant concentration and the amount of oxidant mass injected into the treatment zone must be determined beforehand based on the initial soil and groundwater contaminant concentrations. Also, natural organic matter (NOM) or reduced minerals, carbonate, and other free radical scavengers in the subsurface can reduce the amount of oxidant available to degrade the target compounds. Thus, the amount of ISCO reagent that can be potentially wasted on oxidant consuming compounds must be included into the oxidant dose calculations. This natural oxidant demand is an important ISCO design parameter and failure to consider it will influence the treatment performance and cost of the ISCO system. However, there is little advantage in an "over injection of oxidant" approach because there is the potential to enhance the release and migration of the target contaminants, generate excessive heat, and form undesired by-products, including precipitates (NRC 2005b; IRTC 2005; Siegrist et al. 2011).

Oxidizing agents like sodium or potassium permanganate, persulfate and percarbonate are solids, whereas hydrogen peroxide is a liquid and ozone is a gas. Because

TABLE 9.4 Common oxidants and their most important oxidant reactions, including persistence and electrode potentials of the reactive species involved. Reduction potential is negative.

Oxidant	Reactive Species	Reactions	Persistence⁺	Electrode Potential (Eh)
Permanganate	Permanganate ion (MnO_4^-)	$MnO_4^- + 4H^+ + 3e^- \rightarrow MnO_{2(solid)} + 2H_2O$ ($3.5 < pH < 12$)	>3 months	1.7 V
Hydrogen peroxide	Hydrogen peroxide (H_2O_2)	$H_2O_2 + 2H^+ + 2e^- \rightarrow 2H_2O$	min.-hrs	1.8 V
Ozone	Ozone (O_3)	$O_3 + 2H^+ + 2e^- \rightarrow O_2 + 2H_2O$	min.-hrs	2.1 V
	Hydroxyl radical ($\cdot OH$)	$2O_3 + 3H_2O \rightarrow 4O_2 + 2\cdot OH + 2H_2O$		2.8 V
Fenton's (catalyzed hydrogen peroxide)		$Fe_2^+ + H_2O_2 \rightarrow Fe^{3+} + \cdot OH + OH^-$ (initiation rxn)		
	Hydroxyl radical ($\cdot OH$)	$2\cdot OH + 2H^+ + 2e^- \rightarrow 2H_2O$		2.8
	Perhydroxyl radical ($\cdot OH_2$)	$\cdot OH_2 + 2H^+ + 2e^- \rightarrow 2H_2O$		1.7
	Superoxide radical ($\cdot O_2$)	$\cdot O_2 + 4H^+ + 3e^- \rightarrow 2H_2O$		−2.4 V
	Hydroperoxide anion (HO_2^-)	$HO_2^- + H_2O + 2e^- \rightarrow 3OH^-$		-0.9 V
Persulfate ($S_2O_8^{2-}$)	Persulfate ($S_2O_8^{2-}$)	$S_2O_8^{2-} + 2e^- \rightarrow 2\cdot SO_4^{2-}$ (initiation rxn)	hrs-weeks	2.1 V
	Sulfate radical ($\cdot SO_4^-$)	$\cdot SO_4^- + e^- \rightarrow SO_4^{2-}$		2.6V
Activated Persulfate ($S_2O_8^{2-}$)		$S_2O_8^{2-} + Heat^* \rightarrow 2\cdot SO_4^-$ (initiation rxn)	min-weeks	2.1 V
	Sulfate radical ($\cdot SO_4^-$)	$2\cdot SO_4^- + 2H_2O \rightarrow 2HSO_4^- + 2\cdot OH$		2.6V
	Hydroxyl radical ($\cdot OH$)	$2\cdot OH + 2H^- + 2e^- \rightarrow 2H_2O$		2.8 V

⁺ Literature values and estimates.

* Other persulfate activators: Fe^{2+}, elevated pH >10.5 and peroxone (H_2O_2 and O_3).

Source: Huling and Pivetz (2006); ITRC 2005b.

ozone is inherently unstable, it must be produced at the site immediately before injection into subsurface. Permanganate salts might be delivered to the site in form of an aqueous solution. Most oxidants are hazardous chemicals that must be handled properly by trained field personnel.

ISCO treatment is applicable to variety of contaminants; however, chlorinated solvents are by far the most commonly treated ones. In an analysis of ISCO field applications and performance data, Krembs et al. (2010) found that of 223 sites analyzed, 70% treated chloroethenes and 8% chloroethanes. Other commonly treated contaminants include chlorobenzenes, BTEX and other petroleum hydrocarbons, incl. PAH and gasoline additives (MTBE). About 54% of sites contained NAPL. In general, fuel-related compounds, particularly MTBE, can be treated more effectively relative to chlorinated compounds. However, a number of organic compounds (e.g., PCB or perfluorinated flame retardants) are resistant or even impossible to treat with currently existing ISCO methods. Therefore, the development of advanced oxidation processes is an area of ongoing research.

ISCO is a comparably aggressive contaminant mass-reduction technology and primarily applied to NAPL source zones and groundwater plumes with high dissolved contaminant concentrations. ISCO has been implemented at sites with varied subsurface conditions, ranging from unconsolidated permeable and homogeneous materials to fractured bedrock environments. Generally, ISCO is a relative rapid treatment process that can achieve treatment goals within weeks or months. However, a comparably small percentage of ISCO treatments met pre-defined remediation goals, such as maximum contaminant levels (MCL) (Krembs et al. 2010). This may signify that remediation practitioners overestimated the performance of ISCO or underestimated the impact of site conditions on this technology.

Of the ISCO projects reviewed by Krembs et al. (2010), 89% combined the use of ISCO with other *in situ* remediation technologies. For instance, ISCO has been coupled with surfactants/cosolvents enhanced DNAPL removal, either in sequence or simultaneously (Dugan et al. 2010). Similarly, Eberle et al. (2017) reports on a pilot-scale field project where activated persulfate oxidant was used in combination with cyclodextrin, an enhanced solubilization agent discussed in Section 9.12. The advantage of combining the two treatment approaches is that the enhanced solubilization agent increases the mass of contaminant in solution and thereby makes it available for destruction by the oxidizing agent. This *in situ* "treatment train" approach, when performed as designed, can eliminate the need for extracting and *ex situ* treatment of contaminated liquids. Also, there is ample field site evidence that microbial populations are not permanently reduced by ISCO. In fact, it appears that microbial populations even flourish after ISCO treatment, which permits coupling ISCO with enhanced bioremediation or monitored natural attenuation (MNA) technologies (NRC 2005).

■ 9.16 Phytoremediation

Phytoremediation is a set of technologies that rely on plants and their associated microorganisms to sequester, extract, or degrade toxic compounds in groundwater, soils, sediment and surface water. Because it is a natural process, phytoremediation can be an effective remediation method for a variety of sites and contaminants, at a reduced rate. A large number of plants have been evaluated for potential use in phytoremediation applications. The selection of one or more plant species is based on factors such as ability to extract or degrade the contaminants of concern, adaptation to local climates, high biomass, depth root structure, compatibility with soils, growth rate, ease of planting and maintenance, and ability to take up large quantities of water through the roots (U.S. EPA 2012c). Recent developments in transgenic plant research may lead to a greater selection of plant varieties or the treatment of contaminants currently not possible (Lee 2013). The duration of the treatment generally depends on the type and initial contaminant concentration, its distribution within the treatment zone, plant selection and their growth rate, hydrogeologic and climatologic conditions, and other site characterisrics.

Phytoremediarion has become an alternative to other, more aggressive cleanup technologies because of relatively low capital costs and the inherently aesthetic nature of planted sites. However, this treatment technology is not a "Do something quick and cheap in the fiield and then walk away" approach. Like any remediation system, phytoremediation requires significant operation, maintenance, and monitoring for several years after planting. For instance, plants may require irrigation, fertilization, weed and pest control or replanting (ITRC 2009).

9.17 Summary

There is great interest in developing effective and efficient methods of remediating contaminated soils and groundwater in order to meet the mandates of public concern and federal legislation such as RCRA and CERCLA in the United States.

In order to have a successful remediation, it is necessary to first isolate or remove the source of the contamination. Sources can include hazardous wastes spread on the land or improperly buried in the earth, leaking landfills, leaking underground storage tanks, or soils that have become contaminated by accidental spills and leaks. If it is not possible to remove sources, they can be isolated by physical barriers, such as slurry walls and impermeable covers or by hydrodynamic barriers created by pumping and injection wells.

While not very effective, contaminated groundwater can be pumped from the ground and treated. Pump-and-treat technologies can be effectively used to hydraulically control plumes. Before initiating a pump-and-treat program, any mobile NAPL present should be removed. Floating NAPLs can be removed by multi-phase extraction pumps located in wells. Residual NAPL and contaminants sorbed onto mineral surfaces and soil organic carbon will slowly partition into the clean groundwater that replaces the contaminated groundwater removed by pumping. This will greatly prolong the period of time that it takes to remediate the aquifer. If all the residual contamination is not removed from the aquifer, the concentration of contaminants will increase after the termination of a pump-and-treat operation. It may be impossible to remediate sites contaminated with DNAPLs by conventional pump-and-treat methods. Such aquifers might require permanent plume-stabilization wells to prevent the spread of the plume, or need to be remediated with more advanced technologies.

Water that is extracted from the aquifer can be treated to remove both organic and inorganic contaminants. Methods of treatment of dissolved organics include air stripping and carbon absorption. Underground tanks that are leaking should be removed and replaced. Soil and groundwater remediation is frequently necessary after a leaking tank has been removed.

Vadose zone soil contaminated by residual volatile organic compounds (VOC) can be remediated by soilvapor extraction systems. Air, containing organic vapors, is drawn from the soil pores via SVE wells in the vadose zone and replaced with fresh air. Some methods exist that combine pumping water for treatment with soil vapor extraction to treat contaminated soil and groundwater simultaneously.

Soil and groundwater contaminated by organic compounds may be amenable to bioremediation by both aerobic and anaerobic microbes. Electron acceptors and/or donor may be added to the soil or aquifer to encourage microbial activity. *In situ* bioremediation and related monitored natural attenuation (MNA) processes have the advantage of treating the contaminants dissolved in soil and groundwater at the same time as residual contaminants in the soil.

Permeable Reactive Barriers (PRB) are linear structures placed in the path of an advancing groundwater plume. Reactive materials inside the PRB, such as metallic iron, interact with the dissolved contaminants and degrade or immobilize them. PRBs are passive treatment systems because no pumping is required.

Chemically-enhanced *in situ* flushing technology relies on chemicals that enhance the solubility and, in some case, mobility of NAPL compounds in the subsurface. The primary objective of this remediation technology is to remove the maximum amount of contaminant with a minimum amount of chemicals and in minimal time while maintaining hydraulic control over the injected chemicals and contaminant. This approach requires injection and extraction wells with above ground treatment of the extracted liquids.

During thermal *in situ* treatment, heat is delivered to the treatment zone to volatize, displace, or destroy amendable contaminants in the subsurface. Convection and conduction heat sources have been tested and found effective for remediating a variety of contaminants, including some that are not treatable with other methods. However, high temperature necessary to destroy those compounds can also affect the soil properties. Thermal treatment is typically combined with SVE systems to capture volatilized compounds. New approaches include subsurface controlled, contaminant burning, or smoldering techniques.

In situ oxidation relies on strong oxidants that, when injected into the treatment zone, degrade organic contaminants. This aggressive remediation approach typically does not require the extraction of contaminated liquids from the subsurface and is applicable to a large number of organic compounds.

Phytoremediation takes advantage of green plants and their ability to take up, transform or volatilize a number of metal and organic contaminants. While limited to relatively low soil and groundwater contaminant concentrations, and typically requiring many growing seasons to achieve clean up goals, phytoremediation is a green technology.

While great advances have been made in the field of remediation over the past decades, many contaminants and site-settings, particularlly fractured bedrock aquifiers, remain difficult or impossible to treat with current methods. Hence, this topic will remain an area of active research for many years.

Chapter Notation

B	Uniform thickness of a confined aquifer
Bgs	Below ground surface
C	Concentration
Co	Initial concentration
U	Regional specific discharge (Darcy velocity)
Q	Pumping rate of plume-capture well
d	Distance between extraction wells
k	Pseudo-first order rate contestant
x	Distance along the x axis
y	Distance along the y axis
$h_0—h$	Drawdown
T	Aquifer transmissivity
S	Aquifer storativity
R	Radius of a pumping well
t	Time since pumping began

References

ADAC. 2015. Entwicklung der Tankstellenanzahl seit 1965 in Deutschland. Accessed September 3, 2015 from https://www.adac.de/infotestrat/tanken-kraftstoffe-und-antrieb/probleme-tankstelle/anzahl-tankstellen-markenverteilung/default.aspx

Air Force Center for Engineering and the Environment (AFCEE). 2008. Technical Protocol for Enhanced Anaerobic Bioremediation Using Permeable Mulch Biowalls and Bioreactors. Available from https://clu-in.org/download/techfocus/prb/Final-Biowall-Protocol-05-08.pdf

American Petroleum Institute (API). 2007. API 2007. Technical Protocol for Evaluating the Natural Attenuation of MtBE. API Publication 4761. 186 pp.

Standard Practice for Environmental Site Assessments: Phase I Environmental Site Assessment Process. Accessed September 13, 2015 at http://www.astm.org/Standards/E1527.htm

ASTM. 2014. ASTM E1689—95 Standard Guide for Developing Conceptual Site Models for Contaminated Sites. Available from http://www.astm.org/Standards/E1689.htm

Ardito, C. P., and J. F. Billings. 1990. "Alternative remediation strategies: The subsurface volatilization and ventilation system." In *Proceedings of Petroleum Hydrocarbons and Organic Chemicals in Ground Water: Prevention, Detection and Restoration*, 281–96. Dublin, Ohio: National Water Well Association.

Bainchi-Mosquera, G. C., R. M. Allen-King, and D. M. Mackay. 1994. Enhancing degradation of dissolved benzene and toluene using a solid oxygen-releasing compound. *Ground Water Monitoring and Remediation* 14:120–128.

Belochini, F., A. Dell'Anno, L. DeProrpis, S. Ubaldini, F. Cerrone, and R. Danovaro. 2009. Auto- and heterotrophic acidophilic bacteria enhance the bioremediation efficiency of sediments contaminated by heavy metals. *Chemosphere* 74:1321–1326.

Blake, S. B., and R. W. Lewis. 1982. "Underground oil recovery." *Proceedings of the Second National Symposium on Aquifer Restoration and Ground Water Monitoring* 69–76. Dublin, OH: National Water Well Association.

Borden, R. C., R. T. Goin, and C.-M. Kao. 1997. Control of BTEX migration using a biologically enhanced permeable barrier. *Ground Water Monitoring and Review* 17:70–80.

Botha, M., L. Bester, and E. Hardwick. 2009. Removal of uranium from mine water using ion exchange at Driefontein Mine. In *Abstracts of the International Mine Water Conference 19th–23rd October 2009*, Pretoria, South Africa.

Bowman, R. S. 2003. Applications of surfactant-modified zeolites to environmental remediation. *Microporous and Mesoporous Materials* 61:43–56.

Boving, T. B., and J. E. McCray. 2000. Cyclodextrin-enhanced remediation of organic and metal contaminants in porous media and groundwater. *Remediation Journal* 10:59–83.

Boving, T. B., and M. L. Brusseau. 2000. Solubilization and removal of residual trichloroethene from porous media: Comparison of several solubilization agents. *Journal of Contaminant Hydrology* 42:51–67.

Boving, T. B., J. E. McCray, W. J. Blanford, and M. L. Brusseau. 2004. "Cyclodextrin enhanced remediation at NAB Little Creek, Virginia Beach, VA: Cost and performance assessment."

DOCUMENT

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TITLE 35: ENVIRONMENTAL PROTECTION
SUBTITLE G: WASTE DISPOSAL
CHAPTER I: POLLUTION CONTROL BOARD
SUBCHAPTER j: COAL COMBUSTION WASTE SURFACE IMPOUNDMENTS

PART 845
STANDARDS FOR THE DISPOSAL OF COAL COMBUSTION RESIDUALS IN SURFACE IMPOUNDMENTS

SUBPART A: GENERAL PROVISIONS

SUBPART B: PERMITTING

SUBPART C: LOCATION RESTRICTIONS

SUBPART D: DESIGN CRITERIA

SUBPART E: OPERATING CRITERIA

SUBPART F: GROUNDWATER MONITORING AND CORRECTIVE ACTION

SUBPART G: CLOSURE AND POST-CLOSURE CARE

SUBPART H: RECORDKEEPING

SUBPART I: FINANCIAL ASSURANCE

AUTHORITY: Implementing Sections 12, 22, and 22.59 of the Environmental Protection Act [415 ILCS 5/12, 22, and 22.59] and authorized by Sections 22.59, 27, and 28 of the Environmental Protection Act [415 ILCS 5/22.59, 27, and 28].

SOURCE: Adopted in R20-19 at 45 Ill. Reg. 5884, effective April 21, 2021.

SUBPART A: GENERAL PROVISIONS

Section 845.100 Scope and Purpose

a) This Part establishes criteria for determining which CCR surface impoundments do not pose a reasonable probability of adverse effects on health or the environment. CCR surface impoundments failing to satisfy any of the requirements of this Part are considered open dumps, which are prohibited under Section 21(a) of the Act.

b) This Part applies to owners and operators of new and existing CCR surface impoundments, including any lateral expansions of CCR surface impoundments that dispose of or otherwise engage in solid waste management of CCR generated from the combustion of coal at electric utilities and independent power producers. Unless otherwise provided in this Part, these requirements also apply to CCR surface impoundments located off-site of the electric utility or independent power producer.

c) This Part also applies to inactive CCR surface impoundments at active and inactive electric utilities or independent power producers, regardless of the fuel currently used at the facility to produce electricity.

d) Except as provided in Section 845.170, inactive CCR surface impoundments are subject to all the requirements of this Part applicable to existing CCR surface impoundments.

e) This Part does not apply to wastes, including fly ash, bottom ash, boiler slag, and flue gas desulfurization materials generated at facilities that are not part of an electric utility or independent power producer, such as manufacturing facilities, universities, and hospitals. This Part also does not apply to fly ash, bottom ash, boiler slag, and flue gas desulfurization materials generated primarily from the combustion of fuels (including other fossil fuels) other than coal, for the purpose of generating electricity unless the fuel burned consists of more than 50% coal on a total heat input or mass input basis, whichever results in the greater mass feed rate of coal.

f) This Part does not apply to the beneficial use of CCR.

g) This Part does not apply to CCR placement at active or abandoned underground or surface coal mines.

h) This Part does not apply to landfills that receive CCR.

i) If a CCR surface impoundment has completed an Agency-approved closure before April 21, 2021, this Part does not require the owner or operator of the CCR surface impoundment to resubmit to the Agency any closure plan, closure report, or closure certification for that completed closure.

j) Upon completion of an Agency-approved closure, the CCR surface impoundment is considered a CCR surface impoundment that has completed closure for purposes of fee applicability under Section 22.59(j) of the Act.

Section 845.110 Applicability of Other Regulations

a) Compliance with the requirements of this Part does not affect the need for the owner or operator of a CCR surface impoundment, or lateral expansion of a CCR surface impoundment, to comply with all other applicable federal, state, tribal, or local laws or other requirements.

b) Any CCR surface impoundment or lateral expansion of a CCR surface impoundment is subject to the following requirements:

    1) Illinois Endangered Species Protection Act [520 ILCS 10] and 40 CFR 257.3-2.

2) Surface Water

A) A facility must not cause a discharge of pollutants into waters of the United States that is in violation of the requirements of the National Pollutant Discharge Elimination System (NPDES) under section 402 of the Clean Water Act.

B) A facility must not cause a discharge of dredged material or fill material to waters of the United States that is in violation of the requirements under section 404 of the Clean Water Act, as amended.

C) A facility or practice must not cause non-point source pollution of waters of the United States that violates applicable legal requirements implementing an areawide or statewide water quality management plan that has been approved by USEPA under section 208 of the Clean Water Act, as amended.

D) Definitions of the terms "discharge of dredged material", "point source", "pollutant", and "waters of the United States" can be found in the Clean Water Act, as amended (33 USC 1251 et seq.) and implementing regulations, specifically 33 CFR 323 (42 FR 37122, July 19, 1977).

E) Except as in compliance with the provisions of the Act, Board regulations, and the CWA, and the provisions and conditions of the NPDES permit issued to the discharger, the discharge of any contaminant or pollutant by any facility into the waters of the State from a point source or into a well will be unlawful.

3) Rivers, Lakes and Streams Act [615 ILCS 5/23 and 23(a)] and 17 Ill. Adm. Code 3702.

Section 845.120 Definitions

Except as stated in this Section, or unless a different meaning of a word or term is clear from the context, the definition of words or terms in this Part will be the same as that applied to the same words or terms in the Environmental Protection Act:

"1000-year flood" means a flood of magnitude (or greater) of 1 in 1000 probability of occurring in any given year.

"Act" means the Illinois Environmental Protection Act [415 ILCS 5].

"Active facility" or "active electric utility" or "independent power producer" means any facility, subject to the requirements of this Part, that is in operation on or after October 19, 2015. An electric utility or independent power producer is in operation if it is generating electricity that is provided to electric power transmission systems or to electric power distribution systems on or after October 19, 2015. An off-site CCR surface impoundment is in operation if it is accepting or managing CCR on or after October 19, 2015.

"Active life" or "in operation" means the period of operation beginning with the initial placement of CCR in the CCR surface impoundment and ending at completion of closure activities in accordance with Subpart G.

"Agency" means the Illinois Environmental Protection Agency.
"Aquifer" means a geologic formation, group of formations, or portion of a formation capable of yielding usable quantities of groundwater to wells or springs.

"Area-capacity curves" means graphic curves that readily show the reservoir water surface area, in acres, at different elevations from the bottom of the reservoir to the maximum water surface, and the capacity or volume, in acre-feet, of the water contained in the reservoir at various elevations.

"Areas susceptible to mass movement" means those areas of influence (i.e., areas characterized as having an active or substantial possibility of mass movement) where, because of natural or human-induced events, the movement of earthen material at, beneath, or adjacent to the CCR surface impoundment may result in the downslope transport of soil and rock material by means of gravitational influence. Areas of mass movement include, but are not limited to, landslides, avalanches, debris slides and flows, soil fluctuation, block sliding, and rock fall.

"Beneficial use of CCR" means CCR that meets the definition of "coal combustion by-product" in Section 3.135 of the Act [415 ILCS 5/3.135] and the definition of "beneficial use of CCR" in 40 CFR 257.53, incorporated by reference in Section 845.150.

"Board" means Illinois Pollution Control Board.

"Certified laboratory" means any laboratory certified under Section 4(o) of the Act or certified by USEPA for the specific constituents to be examined.

"Closed" for purposes of this Part means placement of CCR in a CCR surface impoundment has stopped, and the owner or operator has completed closure of the CCR surface impoundment and has initiated post-closure care in accordance with Subpart G.

"*Coal combustion residuals*" or "*CCR*" *means fly ash, bottom ash, boiler slag, and flue gas desulfurization materials generated from burning coal for the purpose of generating electricity by electric utilities and independent power producers*. [415 ILCS 5/3.142]

"CCR fugitive dust" means solid airborne particulate matter that contains or is derived from CCR, emitted from any source other than a stack or chimney.

"CCR storage pile" means any temporary accumulation of solid, non-flowing CCR placed on the land that is designed and managed to control releases of CCR to the environment. CCR contained in an enclosed structure is not a CCR storage pile. Examples of control measures to control releases from CCR storage piles include: periodic wetting, application of surfactants, tarps, or wind barriers to suppress dust; tarps or berms for preventing contact with precipitation and controlling run-on/run-off; and impervious storage pads or geomembrane liners for soil and groundwater protection.

"*CCR surface impoundment*" or "*impoundment*" *means a natural topographic depression, man-made excavation, or diked area, which is designed to hold an accumulation of CCR and liquids, and the surface impoundment treats, stores, or disposes of CCR.* [415 ILCS 5/3.143]

"Dike" means an embankment, berm, or ridge of either natural or man-made materials used to prevent the movement of liquids, sludges, solids, or other materials.

"Displacement" means the relative movement of any two sides of a fault measured in any direction.

"Disposal" means the discharge, deposit, injection, dumping, spilling, leaking, or placing of any solid waste as defined in section 1004(27) of the Resource Conservation and Recovery Act into or on any land or water or into any well so that the solid waste, or constituent thereof, may enter the environment or be emitted into the air or discharged into any waters, including groundwater. For purposes of this Part, disposal does not include the beneficial use of CCR.

"Downstream toe" means the junction of the downstream slope or face of the CCR surface impoundment with the ground surface.

"Enclosed structure" means:

> A completely enclosed, self-supporting structure that is designed and constructed of manmade materials of sufficient strength and thickness to support itself, the CCR, and any personnel and heavy equipment that operate within the structure, and to prevent failure due to settlement, compression, or uplift; climatic conditions; and the stresses of daily operation, including the movement of heavy equipment within the structure and contact of that equipment with containment walls;
>
> The structure has containment walls that are designed to be sufficiently durable to withstand any movement of personnel, CCR, and handling equipment within the structure;

> The structure is designed and operated to ensure containment and prevent fugitive dust emissions from openings, such as doors, windows and vents, and the tracking of CCR from the structure by personnel or equipment.

"Exceedance of the groundwater protection standard" means:

> For existing CCR surface impoundments and inactive CCR surface impoundments:
>
> an analytical result with a concentration greater than the numerical value of the constituents listed in Section 845.600(a), in a down gradient well; or
>
> when the up gradient background concentration of a constituent exceeds the numerical value listed in Section 845.600(a), an analytical result with a concentration at a statistically significant level above the up gradient background concentration, in a down gradient well.
>
> For new CCR surface impoundments and lateral expansions of existing CCR surface impoundments, an analytical result with a constituent concentration at a statistically significant level above the up gradient background concentration, in a down gradient well.

"Existing CCR surface impoundment" means a CCR surface impoundment in which CCR is placed both before and after October 19, 2015, or for which construction started before October 19, 2015 and in which CCR is placed on or after October 19, 2015. A CCR surface impoundment has started construction if the owner or operator has obtained the federal, State, and local approvals or permits necessary to begin physical construction and a continuous on-site, physical construction program had begun before October 19, 2015.

"Facility" means all contiguous land, and structures, other appurtenances, and improvements on the land, used for treating, storing, disposing of, or otherwise conducting solid waste management of CCR. A facility may consist of several treatment, storage, or disposal operational units (e.g., one or more landfills, surface impoundments, or combinations of them).

"Factor of safety" or "safety factor" means the ratio of the forces tending to resist the failure of a structure to the forces tending to cause that failure, as determined by accepted engineering practice.

"Fault" means a fracture or a zone of fractures in any material along which strata on one side have been displaced with respect to that on the other side.

"Flood hydrograph" means a graph showing, for a given point on a stream, the discharge, height, or other characteristic of a flood as a function of time.

"Free liquids" means liquids that readily separate from the solid portion of a waste under ambient temperature and pressure.

"Groundwater" means water below the land surface in a zone of saturation.

"Hazard potential classification" means the possible adverse incremental consequences that result from the release of water or stored contents due to failure of the diked CCR surface impoundment or mis-operation of the diked CCR surface impoundment or its appurtenances. The hazardous potential classifications include Class 1 and Class 2, defined as follows:

> Class 1 CCR surface impoundment means a diked surface impoundment where failure or mis-operation will probably cause loss of human life.
>
> Class 2 CCR surface impoundment means a diked surface impoundment where failure or mis-operation results in no probable loss of human life, but can cause economic loss, environmental damage, disruption of lifeline facilities, or impact other concerns.

"Height" means the vertical measurement from the downstream toe of the CCR surface impoundment at its lowest point to the lowest elevation of the crest of the CCR surface impoundment, not including spillways.

"Holocene" means the most recent epoch of the Quaternary period, extending from the end of the Pleistocene Epoch, at 11,700 years before present, to present.

"Hydraulic conductivity" means the rate at which water can move through a permeable medium (i.e., the coefficient of permeability).

"Inactive CCR surface impoundment" means a CCR surface impoundment in which CCR was placed before but not after October 19, 2015 and still contains CCR on or after October 19, 2015. Inactive CCR surface impoundments may be located at an active facility or inactive facility.

"Inactive Closed CCR surface impoundment" means an inactive CCR surface impoundment that completed closure before October 19, 2015 with an Agency-approved closure plan.

"Inactive facility" or "inactive electric utilities or independent power producers" means any facility that is not in operation on or after October 19, 2015.

"Incised CCR surface impoundment" means a CCR surface impoundment that is constructed by excavating entirely below the natural ground surface, holds an accumulation of CCR entirely below the adjacent natural ground surface, and does not consist of any constructed diked portion.

"Inflow design flood" means the flood hydrograph that is used in the design or modification of the CCR surface impoundment and its appurtenant works.

"In operation" means the same as "active life".

"Karst terrain" means an area where karst topography, with its characteristic erosional surface and subterranean features, is developed as the result of dissolution of limestone, dolomite, or other soluble rock. Characteristic physiographic features present in karst terrains include, but are not limited to, dolines, collapsed shafts (sinkholes), sinking streams, caves, seeps, large springs, and blind valleys.

"Lateral expansion" means a horizontal or vertical expansion of the waste boundaries of an existing CCR surface impoundment made after October 19, 2015.

"Liquefaction factor of safety" means the factor of safety (safety factor) determined using analysis under liquefaction conditions.

"Lithified earth material" means all rock, including all naturally occurring and naturally formed aggregates or masses of minerals or small particles of older rock that formed by crystallization of magma or by induration of loose sediments. This term does not include man-made materials, such as fill, concrete, and asphalt, or unconsolidated earth materials, soil, or regolith lying at or near the earth surface.

"Maximum horizontal acceleration in lithified earth material" means the maximum expected horizontal acceleration at the ground surface as depicted on a seismic hazard map, with a 98% or greater probability that the acceleration will not be exceeded in 50 years, or the maximum expected horizontal acceleration based on a site-specific seismic risk assessment.

"New CCR surface impoundment" means a CCR surface impoundment or lateral expansion of an existing or new CCR surface impoundment that first receives CCR or starts construction after October 19, 2015. A new CCR surface impoundment has started construction if the owner or operator has obtained the federal, State, and local approvals or permits necessary to begin physical construction and a continuous on-site, physical construction program had begun after October 19, 2015.

"Operator" means the person or persons responsible for the overall operation of a CCR surface impoundment.

"Outermost damage zone of a fault" means the volume of deformed wall rocks around a fault surface that results from the initiation, propagation, interaction and build-up of slip along faults.

"Owner" means the person or persons who own a CCR surface impoundment or part of a CCR surface impoundment.

"Poor foundation conditions" means those areas where features exist which indicate that a natural or human-induced event may result in inadequate foundation support for the structural components of an existing or new CCR surface impoundment. For example, failure to maintain static and seismic factors of safety, as required in Section 845.460, would cause a poor foundation condition.

"Probable maximum flood" means the flood that may be expected from the most severe combination of critical meteorologic and hydrologic conditions that are reasonably possible in the drainage basin.

"Qualified person" means a person or persons trained to recognize specific appearances of structural weakness and other conditions that are disrupting, or have the potential to disrupt, the operation or safety of the CCR surface impoundment by visual observation and, if applicable, to monitor instrumentation.

"Qualified professional engineer" means an individual who is licensed under the Professional Engineering Practice Act of 1989 [225 ILCS 325] to practice one or more disciplines of engineering and who is qualified by education, technical knowledge and experience to complete the engineering analyses and make the specific technical certifications required under this Part.

"Recognized and generally accepted engineering practices" means engineering maintenance or operation activities based on established codes, widely accepted standards, published technical reports, or a practice widely recommended throughout the industry. These practices generally detail approved ways to perform specific engineering, inspection, or mechanical integrity activities.

"Retrofit" means to remove all CCR and contaminated soils and sediments from the CCR surface impoundment, and to ensure the surface impoundment complies with the requirements in Section 845.410.

"Run-off" means any rainwater, leachate, or other liquid that drains over land from any part of a CCR surface impoundment or lateral expansion of a CCR surface impoundment.

"Run-on" means any rainwater, leachate, or other liquid that drains over land onto any part of a CCR surface impoundment or lateral expansion of a CCR surface impoundment.

"Sand and gravel pit" or "quarry" means an excavation for the extraction of aggregate, minerals or metals. The term sand and gravel pit and/or quarry does not include subsurface or surface coal mines.

"Seismic factor of safety" means the factor of safety (safety factor) determined using analysis under earthquake conditions using the peak ground acceleration for a seismic event with a 2% probability of exceedance in 50 years, equivalent to a return period of approximately 2,500 years, based on the U.S. Geological Survey (USGS) seismic hazard maps for seismic events with this return period for the region where the CCR surface impoundment is located.

"Seismic impact zone" means an area having a 2% or greater probability that the maximum expected horizontal acceleration, expressed as a percentage of the earth's gravitational pull (g), will exceed 0.10 g in 50 years.

"Slope protection" means engineered or non-engineered measures installed on the upstream or downstream slope of the CCR surface impoundment to protect the slope against wave action or erosion, including rock riprap, wooden pile, concrete revetments, vegetated wave berms, concrete facing, gabions, geotextiles, or fascines.

"Solid waste management" or "management" means the systematic administration of the activities that provide for the collection, source separation, storage, transportation, processing, treatment, or disposal of solid waste.

"Static factor of safety" means the factor of safety (safety factor) determined using analysis under the long-term, maximum storage pool loading condition, the maximum surcharge pool loading condition, and the end-of-construction loading condition.

"Structural components" means liners, leachate collection and removal systems, final covers, run-on and run-off systems, inflow design flood control systems, and any other component used in the construction and operation of the CCR surface impoundment that is necessary to ensure the integrity of the surface impoundment and ensure that the contents of the surface impoundment are not released into the environment.

"Temporary accumulation" means an accumulation on the land that is neither permanent nor indefinite. To demonstrate that the accumulation on the land is temporary, all CCR must be removed from the pile at the site. The entity engaged in the activity must have a record in place, such as a contract, purchase order, facility operation and maintenance, or fugitive dust control plan, documenting that all the CCR in the pile will be completely removed according to a specific timeline.

"Unstable area" means a location that is susceptible to natural or human-induced events or forces capable of impairing the integrity of that area, including structural components of some or all the CCR surface impoundment that are responsible for preventing releases from the surface impoundment. Unstable areas can include poor foundation conditions, areas susceptible to mass movements, and karst terrains.

"Uppermost aquifer" means the geologic formation nearest the natural ground surface that is an aquifer, as well as lower aquifers that are hydraulically interconnected with this aquifer within the facility's property boundary. Upper limit is measured at a point nearest to the natural ground surface to which the aquifer rises during the wet season.

"Waste boundary" means a vertical surface located at the hydraulically downgradient limit of the CCR surface impoundment. The vertical surface extends down into the uppermost aquifer.

"Wetlands" means those areas that are inundated or saturated by surface or groundwater at a frequency and duration sufficient to support, and that under normal circumstances do support, a prevalence of vegetation typically adapted for life in saturated soil conditions. Wetlands generally include swamps, marshes, bogs, and similar areas.

Section 845.130 Surface Impoundment Identification

The owner or operator of a CCR surface impoundment must place on, or immediately adjacent to, the CCR surface impoundment a permanent identification marker at least six feet high showing the identification number of the CCR surface impoundment assigned by the Agency, the name associated with the CCR surface impoundment and the name of the owner or operator of the CCR surface impoundment. The owner or operator must maintain the marker at all times an operating permit is required under this Part.

Section 845.140 Right of Inspection

The owner or operator of a CCR surface impoundment must allow the Agency and its duly authorized representatives to perform inspections in accordance with the Agency's authority under the Act, including:

a) Entering, at reasonable times, the facility where CCR surface impoundments are located or where any activity is to be conducted under a permit issued under this Part;

b) Having access to and copying at reasonable times any records required to be kept under the terms and conditions of a permit of this Part;

c) Inspecting at reasonable times, including during any hours of operation:

  1) Equipment constructed or operated under a permit issued under this Part;

  2) Equipment or monitoring methodology; or

  3) Equipment required to be kept, used, operated, calibrated and maintained under a permit issued under this Part;

d) Obtaining and removing, at reasonable times, samples of any raw or finished water, discharge or emission of pollutants;

e) Entering, at reasonable times, to use any photographic, recording, testing, monitoring or other equipment for the purpose of preserving, testing, monitoring or recording any raw or finished water, activity, discharge or emission authorized by a permit.

Section 845.150 Incorporations by Reference

a) For purposes of this Part, the Board incorporates the following material by reference:

1) Non-Regulatory Government Publications and Publications of Recognized Organizations and Associations:

Association for the Advancement of Cost Engineering (AACE), 726 East Park Avenue #180, Fairmont, WV 26554, (304) 296-8444, web.aacei.org.

"Cost Estimate Classification System — As Applied in Engineering, Procurement, and Construction for the Process Industries", TCM Framework: 7.3 – Cost Estimating and Budgeting. March 6, 2009, AACE International Recommended Practice No. 18R-97.

NTIS. National Technical Information Service, 5285 Port Royal Road, Springfield VA 22161, (703) 605-6000, www.ntis.gov.

"Test Methods for Evaluating Solid Waste, Physical/Chemical Methods", USEPA Publication No. SW-846, as amended by Updates I, II, IIA, IIB, III, IIIA, and IIIB (Doc. No. 955-001-00000-1) (available online at https://www.epa.gov/hw-sw846/sw-846-compendium).

2) Code of Federal Regulations, Available from the Superintendent of Documents, U.S. Government Publishing Office, Washington, DC 20401, (202) 783-3238, https://www.ecfr.gov, https:/www.govinfo.gov/app/collection/cfr, or https://www.federalregister.gov:

40 CFR 257.53 (2019) (Definition of “beneficial use of CCR”)

40 CFR 257.103(f)(1)(x) (85 Fed. Reg. 53563-64 (Aug. 28, 2020)) (Preparation of Semi-Annual Progress Reports)

b) This Section incorporates no later editions or amendments.

Section 845.160 Severability

If any provision of this Part or its application to any person or under any circumstances is adjudged invalid, that adjudication must not affect the validity of this Part as a whole or of any portion not adjudged invalid.

Section 845.170 Inactive Closed CCR Surface Impoundments

a) Among the provisions of this Part, only the following apply to inactive closed CCR surface impoundments:

  1) All of Subpart A: General Provisions;

  2) The following Sections of Subpart B (Permitting):

    A) Section 845.200;

    B) Section 845.210;

    C) Section 845.220(a), (c), and (f)(1);

    D) Section 845.230(c) and (d)(4);

    E) Section 845.250;

    F) Section 845.270;

    G) Section 845.280;

    H) Section 845.290;

  3) The following Section of Subpart G (Closure and Post-Closure Care): Section 845.780(b), (d), and (e); and

  4) All of Subpart I (Financial Assurance).

b) When a prior release from an inactive closed CCR surface impoundment has caused an exceedance of the groundwater quality standards in 35 Ill. Adm. Code 620, and the owner or operator has not completed remediation of the release before completing closure, the owner or operator must initiate or continue corrective action under an operating permit issued under this Part.

c) When a release from an inactive closed CCR surface impoundment causes an exceedance of the groundwater quality standards in 35 Ill. Adm. Code 620, and the Agency has not concurred with an alternative source demonstration, the owner or operator of an inactive closed CCR surface impoundment must initiate an assessment of corrective measures that prevents further releases, remediates any releases, and restores the affected area. The owner or operator of the inactive closed CCR surface impoundment must develop a corrective action plan and obtain a construction permit consistent with subsection (a)(2) before performing any corrective action to remediate any releases and to restore the affected area, including the final cover system, groundwater monitoring system, groundwater collection trench, extraction wells, slurry walls, or any construction related to corrective action.

SUBPART B: PERMITTING

Section 845.200 Permit Requirements and Standards of Issuance

a) Permit Requirements

1) No person may construct, install, or modify a CCR surface impoundment or related treatment or mitigation facilities, including corrective action measures under Subpart F, without a construction permit issued by the Agency under this Part.

2) Except as provided in Section 845.230(d), no person may operate a CCR surface impoundment without an operating permit issued by the Agency under this Part. For purposes of this Part, a CCR surface impoundment starts operation upon initial receipt of CCR.

3) No person may perform corrective action at a CCR surface impoundment without obtaining a construction permit for corrective action and modifying the facility's operating permit, or modifying the facility's operating permit when the approved corrective action does not require the modification of the CCR surface impoundment or the installation or modification of related treatment or mitigation facilities.

4) Except as provided in Section 22.59(e) of the Act, no person may close a CCR surface impoundment without obtaining a construction permit for closure issued by the Agency under this Part.

5) A CCR surface impoundment must maintain an operating permit until:

A) The completion of post-closure care when the CCR surface impoundment is closed with a final cover system; or

B) The completion of groundwater monitoring under Section 845.740(b) when the CCR surface impoundment is closed by removal.

6) The Agency may issue a joint construction and operating permit.

b) Standards for Issuance

1) Except as provided in subsection (b)(2), the Agency may not issue any construction or operating permit required by this Part unless the applicant submits adequate proof that the CCR surface impoundment will be constructed, modified or operated so as not to cause a violation of the Act or Board rules.

2) The existence of a violation of the Act, Board regulation, or Agency regulation will not prevent the issuance of a construction or operating permit under this Part if:

   A) The applicant has been granted a variance or an adjusted standard from the regulation by the Board;

   B) The permit application is for construction, installation, or operation of equipment to alleviate or correct a violation; or

   C) The permit application is for construction, installation, or operation of equipment necessary to restore, protect or enhance the environment.

3) *In granting permits, the Agency may impose reasonable conditions specifically related to the applicant's past compliance history with the Act as necessary to correct, detect, or prevent noncompliance. The Agency may impose such other conditions as may be necessary to accomplish the purpose of the Act and as are not inconsistent with this Part.* [415 ILCS 5/39(a)]

4) *In making its determinations on permit applications under this* Part*, the Agency may consider prior adjudications of noncompliance with the Act by the applicant that involved a release of a contaminant into the environment*. [415 ILCS 5/39(a)]

Section 845.210 General Provisions

a) All permit applications must be made on the forms prescribed by the Agency and must be mailed or delivered to the address designated by the Agency on the forms. The Agency must provide a dated, signed receipt upon request. The Agency's record of the date of filing must be deemed conclusive unless a contrary date is proved by a dated, signed receipt.

b) Required Signatures of Owners or Operators

   1) All permit applications must contain the name, address, email address and telephone number of the operator, or duly authorized agent, and the

property owner to whom all inquiries and correspondence must be addressed.

2) All permit applications must be signed by the owner, operator or a duly authorized agent of the operator.

3) An application submitted by a corporation must be signed by a principal executive officer of at least the level of vice president, or his or her duly authorized representative, if that representative is responsible for the overall operation of the facility described in the application form. In the case of a partnership or a sole proprietorship, the application must be signed by a general partner or the proprietor, respectively. In the case of a publicly owned facility, the application must be signed by either the principal executive officer, ranking elected official, or other duly authorized employee.

c) Legal Description. All permit applications must contain a legal description of the facility boundary and a description of the boundaries of all units included in the facility.

d) Previous Assessments, Investigations, Plans and Programs

1) The Agency may approve the use of any hydrogeologic site investigation or characterization, groundwater monitoring well or system, or groundwater monitoring plan, bearing the seal and signature of an Illinois Licensed Professional Geologist or Licensed Professional Engineer, completed before April 21, 2021 to satisfy the requirements of this Part.

2) For existing CCR surface impoundments, the owner or operator of the CCR surface impoundment may use a previously completed location restriction demonstration required by Section 845.300 (Placement Above the Uppermost Aquifer), Section 845.310 (Wetlands), Section 845.320 (Fault Areas), Section 845.330 (Seismic Impact Zones), and Section 845.340 (Unstable Areas) provided that the previously completed assessments meet the applicable requirements of those Sections.

3) For existing CCR surface impoundments, the owner or operator of the CCR surface impoundment may use a previously completed assessment to serve as the initial assessment required by Section 845.440 (Hazard Potential Classification Assessment), Section 845.450 (Structural Stability Assessment) and Section 845.460 (Safety Factor Assessment) provided that the previously completed assessment:

A) Was not completed more than five years ago; and

B) Meets the applicable requirements of those Sections.

4) For inactive closed CCR surface impoundments, the owner or operator of the CCR surface impoundment may use a post-closure care plan previously approved by the Agency.

e) The Agency must mail all notices of final action by certified mail, postmarked with a date stamp and with return receipt requested. Final action must be deemed to have taken place on the postmarked date that the notice is mailed.

f) Violation of any permit condition or failure to comply with the Act or regulations promulgated under the Act must be grounds for enforcement action as provided in the Act, including revocation of a permit.

g) Issuance of a permit under this Part does not relieve the applicant of the obligation to obtain other permits required by law.

h) The owner or operator must place in the facility's operating record all permit applications submitted to the Agency and all permits issued under this Part (see Section 845.800(d)(1)).

i) Agency Listserv

1) For each facility subject to this Part, the Agency must create and maintain a listserv. Each listserv must include the email addresses of all interested persons who notify the Agency in writing—either directly under subsection (i)(2) or through the facility owner or operator under Section 845.220(a)(9) or 845.240(f)(4)—of their respective email addresses and that they would like to receive emails of notices concerning the facility.

2) The Agency’s webpage must specify how interested persons may notify the Agency in writing of their respective email addresses and that they would like to be added to the Agency’s listserv for a facility subject to this Part.

3) When this Part requires that the Agency email a notice to the listserv for a facility, the Agency must do so within the timeframe specified, concurrently with other required means of disseminating the notice, or otherwise in a timely manner. When this Part requires an owner or operator to request that the Agency email a notice to the listserv for the facility, the Agency must do so within two business days after receiving the request from the owner or operator.

Section 845.220 Construction Permits

a) All construction permit applications must contain the following information and documents.

1) Design and Construction Plans (Construction History)

  A) Identifying Information

    i) The name and address of the person or persons owning or operating the CCR surface impoundment;

    ii) The name associated with the CCR surface impoundment; and

    iii) The identification number of the CCR surface impoundment if one has been assigned by the Agency.

  B) A statement of the purpose for which the CCR surface impoundment is being used, how long the CCR surface impoundment has been in operation, and the types of CCR that have been placed in the CCR surface impoundment.

  C) The name and size in acres of the watershed within which the CCR surface impoundment is located.

  D) A description of the physical and engineering properties of the foundation and abutment materials on which the CCR surface impoundment is constructed.

  E) A statement of the type, size, range, and physical and engineering properties of the materials used in constructing each zone or stage of the CCR surface impoundment; the method of site preparation and construction of each zone of the CCR surface impoundment; and the approximate dates of construction of each successive stage of construction of the CCR surface impoundment.

  F) At a scale that details engineering structures and appurtenances relevant to the design, construction, operation, and maintenance of the CCR surface impoundment, detailed dimensional drawings of the CCR surface impoundment, including a plan view and cross-sections of the length and width of the CCR surface impoundment, showing all zones, foundation improvements, drainage provisions, spillways, diversion ditches, outlets, instrument locations, and slope protection, in addition to the normal operating pool surface elevation and the maximum pool surface elevation following peak discharge from the inflow design flood, the expected maximum depth of CCR within the CCR surface impoundment, and any identifiable natural or manmade features that could adversely affect operation of the CCR surface impoundment due to malfunction or mis-operation.

G) A description of the type, purpose, and location of existing instrumentation.

H) Area-capacity curves for the CCR surface impoundment.

I) A description of each spillway and diversion design features and capacities and calculations used in their determination.

J) The construction specifications and provisions for surveillance, maintenance, and repair of the CCR surface impoundment.

K) Any record or knowledge of structural instability of the CCR surface impoundment.

2) Narrative Description of the Facility. The permit application must contain a written description of the facility with supporting documentation describing the procedures and plans that will be used at the facility to comply with the requirements of this Part. The descriptions must include, but are not limited to, the following information:

A) The types of CCR expected in the CCR surface impoundment, including a chemical analysis of each type of expected CCR;

B) An estimate of the maximum capacity of each surface impoundment in gallons or cubic yards;

C) The rate at which CCR and non-CCR waste streams currently enter the CCR surface impoundment in gallons per day and dry tons;

D) The estimated length of time the CCR surface impoundment will receive CCR and non-CCR waste streams; and

E) An on-site transportation plan that includes all existing and planned roads in the facility that will be used during the operation of the CCR surface impoundment.

3) Site Location Map. All permit applications must contain a site location map on the most recent United States Geological Survey (USGS) quadrangle of the area from the 7 ½ minute series (topographic), or on another map whose scale clearly shows the following information:

A) The facility boundaries and all adjacent property, extending at least 1000 meters (3280 feet) beyond the boundary of the facility;

B) All surface waters;

C) The prevailing wind direction;

D) The limits of all 100-year floodplains;

E) All-natural areas designated as a Dedicated Illinois Nature Preserve under the Illinois Natural Areas Preservation Act [525 ILCS 30];

F) All historic and archaeological sites designated by the National Historic Preservation Act (16 USC 470 et seq.) and the Illinois Historic Sites Advisory Council Act [20 ILCS 3410]; and

G) All areas identified as critical habitat under the Endangered Species Act of 1973 (16 USC 1531 et seq.) and the Illinois Endangered Species Protection Act [520 ILCS 10].

4) Site Plan Map. The application must contain maps, including cross-sectional maps of the site boundaries, showing the location of the facility. The following information must be shown:

A) The entire facility, including any proposed and all existing CCR surface impoundment locations;

B) The boundaries, both above and below ground level, of the facility and all CCR surface impoundments or landfills containing CCR included in the facility;

C) All existing and proposed groundwater monitoring wells; and

D) All main service corridors, transportation routes, and access roads to the facility.

5) A narrative description of the proposed construction of, or modification to, a CCR surface impoundment and any projected changes in the volume or nature of the CCR or non-CCR waste streams.

6) Plans and specifications fully describing the design, nature, function and interrelationship of each individual component of the facility.

7) A new groundwater monitoring program or any modification to an existing groundwater monitoring program that includes but is not limited to the following information:

A) A hydrogeologic site investigation meeting the requirements of Section 845.620, if applicable;

B) Design and construction plans of a groundwater monitoring system meeting the requirements of Section 845.630; and

C) A proposed groundwater sampling and analysis program that includes selection of the statistical procedures to be used for evaluating groundwater monitoring data (see Sections 845.640 and 845.650).

8) The signature and seal of a qualified professional engineer.

9) Certification that the owner or operator of the CCR surface impoundment completed the public notification and public meetings required under Section 845.240, a summary of the issues raised by the public, a summary of any revisions, determinations, or other considerations made in response to those issues, and a list of interested persons in attendance who would like to be added to the Agency's listserv for the facility.

b) New Construction. In addition to the requirements in subsection (a), all construction permit applications to build a new CCR surface impoundment, lateral expansion of a CCR surface impoundment, or retrofit an existing CCR surface impoundment must also contain the following information and documents:

1) Plans and specifications that demonstrate the proposed CCR surface impoundment will meet the location standards in the following Sections:

A) Section 845.300 (Placement Above the Uppermost Aquifer);

B) Section 845.310 (Wetlands);

C) Section 845.320 (Fault Areas);

D) Section 845.330 (Seismic Impact Zones); and

E) Section 845.340 (Unstable Areas and Floodplains).

2) Plans and specifications that demonstrate the proposed CCR surface impoundment will meet the following design criteria:

A) The CCR surface impoundment will have a liner meeting the liner requirements of Section 845.400(b) or (c);

B) The CCR surface impoundment will have a leachate collection system meeting the requirements of Section 845.420; and

C) The CCR surface impoundment, if not incised, will be constructed with slope protection, as required by Section 845.430.

3) CCR fugitive dust control plan (see Section 845.500(b)).

4) Preliminary written closure plan (see Section 845.720(a)).

5) Initial written post-closure care plan, if applicable (see Section 845.780(d)).

c) Corrective Action Construction. In addition to the requirements in subsection (a), all construction permit applications that include any corrective action performed under Subpart F must also contain the following information and documents:

1) Corrective action plan (see Section 845.670);

2) Groundwater modeling, including:

A) The results of groundwater contaminant transport modeling and calculations showing how the corrective action will achieve compliance with the applicable groundwater standards;

B) All modeling inputs and assumptions;

C) Description of the fate and transport of contaminants with the selected corrective action over time; and

D) Capture zone modeling, if applicable;

3) Any necessary licenses and software needed to review and access both the models and the data contained within the models required by subsection (c)(2);

4) Corrective action groundwater monitoring program, including identification of revisions to the groundwater monitoring system for corrective action; and

5) Any interim measures necessary to reduce the contaminants leaching from the CCR surface impoundment, and/or potential exposures to human or ecological receptors, including an analysis of the factors specified in Section 845.680(a)(3).

d) Closure Construction. In addition to the requirements in subsection (a), all construction permit applications for closure of the CCR surface impoundment under Subpart G must contain the following information and documents:

1) Closure prioritization category , if applicable (see Section 845.700(g));

2) Final closure plan (see Section 845.720(b)), including the closure alternatives analysis required by Section 845.710;

3) Groundwater modeling, including:

A) The results of groundwater contaminant transport modeling and calculations showing how the closure will achieve compliance with the applicable groundwater standards;

B) All modeling inputs and assumptions;

C) Description of the fate and transport of contaminants, with the selected closure over time;

D) Capture zone modeling, if applicable; and

E) Any necessary licenses and software needed to review and access both the model and the data contained within the model.

4) Proposed schedule to complete closure; and

5) Post-closure care plan specified in Section 845.780(d), if applicable.

e) *Owners or operators of CCR surface impoundments who submitted a closure plan to the Agency before May 1, 2019, and who complete closure before July 30, 2021, shall not be required to obtain a construction permit for closure under subsection (d)*. [415 ILCS 5/22.59(e)]

f) A single construction permit application may be submitted for new construction, corrective action, and closure if the construction is related to the same multi-phased project. The permit application for a project with multiple phases must contain all information required by subsections (a), (b), (c), and (d), as applicable.

g) Duration of Construction Permits

1) For any construction permit that is not for the closure or retrofit of the CCR surface impoundment, the construction permit must be issued for fixed terms not to exceed 3 years.

2) For any construction permit for the closure or retrofit of a CCR surface impoundment, the construction permit must be issued for an initial fixed term expiring within the timeframe approved by the Agency in the construction permit or five years, whichever is less. The Agency may renew a construction permit for closure or retrofit in two-year increments under Section 845.760(b).

Section 845.230 Operating Permits

The operating permit applications must contain the following information and documents:

a) Initial operating permit for a new CCR surface impoundment and any lateral expansion of a CCR surface impoundment.

1) A demonstration that the CCR surface impoundment, as built, meets the location standards in the following Sections:

A) Section 845.300 (Placement Above the Uppermost Aquifer);

B) Section 845.310 (Wetlands);

C) Section 845.320 (Fault Areas);

D) Section 845.330 (Seismic Impact Zones); and

E) Section 845.340 (Unstable Areas and Floodplains);

2) Certification from a qualified professional engineer that the composite liner, or if applicable, the alternative composite liner, has been constructed in accordance with the requirements of Section 845.400(b) or (c);

3) Certification from a qualified professional engineer that the leachate collection system has been constructed in accordance with the requirements of Section 845.420, if applicable;

4) Evidence that the permanent markers required by Section 845.130 have been installed;

5) Documentation that the CCR surface impoundment, if not incised, will be operated and maintained with one of the forms of slope protection specified in Section 845.430;

6) Initial hazard potential classification assessment and accompanying certification (see Section 845.440(a)(2));

7) Initial Emergency Action Plan and accompanying certification (see Section 845.520(e));

8) Initial structural stability assessment and accompanying certification (see Section 845.450(c));

9) Initial safety factor assessment and accompanying certification (see Section 845.460(b));

10) Fugitive dust control plan and accompanying certification (see Section 845.500(b)(7));

11) Initial inflow design flood control system plan and accompanying certification (see Section 845.510(c)(3));

12) Proposed groundwater monitoring program, including a minimum of eight independent samples for each background and downgradient well (see Section 840.650(b));

13) Preliminary written closure plan (see Section 845.720(a));

14) Initial written post-closure care plan, if applicable (see Section 845.780(d));

15) An analysis of the chemical constituents found within the CCR to be placed in the CCR surface impoundment;

16) An analysis of the chemical constituents of all waste streams, chemical additives, and sorbent materials entering or contained in the CCR surface impoundment; and

17) A certification that the owner or operator meets the financial assurance requirements of Subpart I.

b) Renewal Operating Permit

1) Documentation that the CCR surface impoundment, if not incised, is being operated and maintained with one of the forms of slope protection specified in Section 845.430;

2) Emergency Action Plan certification if the plan was amended (see Section 845.520);

3) Fugitive dust control plan certification if the plan was amended (see Section 845.500(b)(7));

4) Any significant changes to the design and construction plans compiled under subsection (d)(2)(A) or Section 845.220(a)(1);

5) A statement that the groundwater monitoring has been conducted under an Agency approved groundwater monitoring program;

6) Written preliminary closure plan, if amended (see Section 845.720(a)); and

7) Written post-closure care plan, if amended (see Section 845.780(d)).

c) Post-Closure Care Operating Permit

The owner or operator of a CCR surface impoundment conducting post-closure care under Section 845.780 must maintain an operating permit until the completion of post-closure care. Any changes to the post-closure care plan, groundwater monitoring system, groundwater sampling and analysis program, and groundwater monitoring program must be submitted to the Agency in an operating permit application.

d) Initial Operating Permit for Existing, Inactive and Inactive Closed CCR Surface Impoundments

1) The owner or operator of an existing, inactive or inactive closed CCR surface impoundment who has not completed post-closure care must submit an initial operating permit application to the Agency by October 31, 2021;

2) The initial operating permit application for existing or inactive CCR surface impoundments that have not completed an Agency approved closure before July 30, 2021, must contain the following information and documents on forms prescribed by the Agency:

A) The history of construction specified in Section 845.220(a)(1);

B) An analysis of the chemical constituents found within the CCR to be placed in the CCR surface impoundment;

C) An analysis of the chemical constituents of all waste streams, chemical additives and sorbent materials entering or contained in the CCR surface impoundment;

D) A demonstration that the CCR surface impoundment, as built, meets, or an explanation of how the CCR surface impoundments fails to meet, the location standards in the following Sections:

    i) Section 845.300 (Placement Above the Uppermost Aquifer);

    ii) Section 845.310 (Wetlands);

    iii) Section 845.320 (Fault Areas);

    iv) Section 845.330 (Seismic Impact Zones); and

    v) Section 845.340 (Unstable Areas);

E) Evidence that the permanent markers required by Section 845.130 have been installed;

F) Documentation that the CCR surface impoundment, if not incised, will be operated and maintained with one of the forms of slope protection specified in Section 845.430;

G) Initial Emergency Action Plan and accompanying certification (see Section 845.520(e));

H) Fugitive dust control plan and accompanying certification (see Section 845.500(b)(7));

I) Groundwater Monitoring Information:

    i) A hydrogeologic site characterization (see Section 845.620);

    ii) Design and construction plans of a groundwater monitoring system (see Section 845.630);

    iii) A groundwater sampling and analysis program that includes selection of the statistical procedures to be used for evaluating groundwater monitoring data (see Section 845.640); and

    iv) Proposed groundwater monitoring program that includes a minimum of eight independent samples for each background and downgradient well (see Section 845.650(b));

J) Preliminary written closure plan (see Section 845.720(a));

K) Initial written post-closure care plan, if applicable (see Section 845.780(d));

L) The certification required by Section 845.400(h), or a statement that the CCR surface impoundment does not have a liner that meets the requirements of Section 845.400(b) or (c);

M) History of known exceedances of the groundwater protection standards in Section 845.600, and any corrective action taken to remediate the groundwater;

N) A certification that the owner or operator meets the financial assurance requirements of Subpart I;

O) Hazard potential classification assessment and accompanying certification (see Section 845.440(a)(2));

P) Structural stability assessment and accompanying certification (see Section 845.450(c));

Q) Safety factor assessment and accompanying certification (see Section 845.460(b));

R) Inflow design flood control system plan and accompanying certification (see Section 845.510(c)(3));

S) Safety and health plan (see Section 845.530); and

T) For CCR surface impoundments required to close under 845.700, the proposed closure priority categorization required by Section 845.700(g).

3) The initial operating permit application for an existing or inactive CCR surface impoundment where an Agency approved closure has been completed before July 30, 2021, and where the impoundment is not an inactive closed CCR surface impoundment, must contain the following information and documents on forms prescribed by the Agency:

A) The history of construction specified in Section 845.220(a)(1);

B) Evidence that the permanent markers required by Section 845.130 have been installed;

C) Documentation that the CCR surface impoundment, if not incised, will be operated and maintained with one of the forms of slope protection specified in Section 845.430;

D) Emergency Action Plan certification (see Section 845.520(e));

E) Groundwater monitoring information:

i) A hydrogeologic site characterization meeting the requirements of Section 845.620;

ii) Design and construction plans of a groundwater monitoring system meeting the requirements of Section 845.630;

iii) A groundwater sampling and analysis program that includes selection of the statistical procedures to be used for evaluating groundwater monitoring data (see Section 845.640); and

iv) Proposed groundwater monitoring program that includes a minimum of eight independent samples for each background and downgradient well (see Section 845.650(b));

F) Written post-closure care plan, if applicable (see Section 845.780(d));

G) History of known exceedances of the groundwater protection standards in Section 845.600, and any corrective action plan taken to remediate the groundwater.

4) The initial operating permit application for inactive closed CCR surface impoundments must contain the following information:

A) Evidence that the permanent markers required by Section 845.130 have been installed;

B) Groundwater monitoring program;

C) Written post-closure care plan (see Section 845.780(d)); and

D) History of known exceedances of the groundwater quality standards in 35 Ill. Adm. Code 620, whether the owner or operator has obtained a groundwater management zone, and any corrective action taken to remediate the groundwater.

e) Operating permits must be issued for fixed terms not to exceed five years.

Section 845.240 Pre-Application Public Notification and Public Meeting

a) At least 30 days before the submission of a construction permit application, the owner or operator of the CCR surface impoundment must hold at least two public meetings to discuss the proposed construction, with at least one meeting to be held after 5:00 p.m. in the evening. Any public meeting held under this Section must be located at a venue that is accessible to persons with disabilities, and the owner or operator must provide reasonable accommodations upon request.

b) The owner or operator must prepare and circulate a notice explaining the proposed construction project and any related activities and the time and place of the public meeting. At least 30 days before the public meeting, the owner or operator of the CCR surface impoundment must:

1) Mail or hand-deliver the notice to the Agency and all residents within a one-mile radius from the facility boundary;

2) Post the notice to the owner's or operator's publicly accessible Internet site under Section 845.810;

3) Post the notice in conspicuous locations throughout villages, towns, or cities within 10 miles of the facility, or use appropriate broadcast media (such as radio or television);

4) Request that the Agency email the notice to the Agency's listserv for the facility; and

5) Include in the notice the owner's and operator's contact information, the internet address where the information in Section 845.240(e) will be posted, and the date on which the information will be posted to the site.

c) When a proposed construction project or any related activity is located in an area with a significant proportion of non-English speaking residents, the notification must be circulated, or broadcast, in both English and the appropriate non-English language, and the owner or operator must provide translation services during the public meetings required by Section 845.240(a), if requested by non-English speaking members of the public.

d) The owner or operator of the CCR surface impoundment must prepare documentation recording the public meeting and place the documentation in the facility's operating record as required by Section 845.800(d)(2).

e) At least 30 days before a public meeting, the owner or operator of the CCR surface impoundment must post on the owner's or operator's publicly accessible internet site all documentation relied upon in making a tentative construction permit application.

f) At the public meeting, the owner or operator of the CCR surface impoundment must:

1) Present its decision-making process for the construction permit application, including, when applicable, the corrective action alternatives and the closure alternatives considered. The presentation must include a comparison of projected groundwater impacts for each alternative considered and an objective comparison of the pros and cons of each alternative considered;

2) Include a question/answer portion of the meeting to allow the public to ask questions. There must be representatives from the owner or operator present who are qualified and knowledgeable enough to answer the questions posed by the public.

3) If there are questions posed by the public at the hearing that cannot be answered in person or if there are subsequent questions posed by the public following the meeting, the owner or operator of the facility must respond to those questions in writing within a reasonable timeframe and post the response on the facility's CCR website required by Section 845.810; and

4) Explain that the Agency is creating a listserv for the facility, compile a list of interested persons in attendance—and their respective email addresses—who would like to be added to the listserv, and transmit that list to the Agency with the permit application.

g) Within 14 days after the public meetings required by Section 845.240, the owner or operator must distribute a general summary of the issues raised by the public, as well as a response to those issues or comments raised by the public. If these comments resulted in a revision, change in a decision, or other considerations or determination, a summary of these revisions, changes and considerations must be included in the summary. The summary must be distributed to any attendee who requests a copy at the public meeting.

h) This Section does not apply to applications for minor modifications as described in Section 845.280(d).

Section 845.250 Tentative Determination and Draft Permit

Following the receipt of a complete application for a construction permit, operating permit, or joint construction and operating permit, the Agency must prepare a tentative determination.

a) The tentative determination must include at least the following:

1) A statement regarding whether the permit is to be issued or denied; and

2) If the determination is to issue the permit, a draft permit and a brief description of any conditions contained in the permit.

b) Upon tentative determination to issue or deny the permit:

1) If the determination is to issue the permit, the Agency must notify the applicant in writing of the content of the tentative determination and draft permit and of its intent to circulate public notice of issuance in accordance with Section 845.260;

2) If the determination is to deny the permit, the Agency must notify the applicant in writing of the tentative determination and of its intent to circulate public notice of denial, in accordance with Section 845.260. In the case of denial, notice to the applicant must include a statement of the reasons for denial, as required by Section 39(a) of the Act.

c) The documents supporting the Agency's tentative decision to issue or deny a permit must be made part of the Agency's record.

Section 845.260 Draft Permit Public Notice and Participation

a) The Agency must post a notification that it has received a permit application on the Agency's webpage and must email the notice to the Agency's listserv for the applicant's facility.

b) Public Notice of Draft Permit

1) Not earlier than 15 days following the Agency's notification to the applicant of its tentative decision under Section 845.250 to issue or deny the permit application, the Agency must circulate public notice of the completed application for the permit in a manner designed to inform interested and potentially interested persons of the construction, modification, operation or closure of a CCR surface impoundment and of the proposed determination to issue or deny the permit.

2) The contents of public notice of completed applications for permits must include at least the following:

A) Name, address, and telephone number of the Agency;

B) Name and address of the applicant;

C) Brief description of the applicant's activities or operations that result in the construction, operation, modification or closure of a CCR surface impoundment;

D) A statement of the tentative determination to issue or deny the permit;

E) A brief description of the procedures for the formulation of final determinations, including the procedures for submitting comments and the expiration date of the comment period;

F) Address and telephone number of Agency premises at which interested persons may obtain further information and request a copy of the permit application and related documents;

G) A translation of the public notice into the appropriate language or languages will be made if the Agency determines that a project is located within one mile of a significant population of non-English speaking residents;

H) A brief description of how members of the public can request a public hearing under Section 845.260(d); and

I) A brief description of how members of the public can request being added to the Agency's listserv for the facility.

3) Procedures for the circulation of public notice required under this Section must include at least the following concurrent actions:

A) Posting on the Agency's webpage and all the Agency's social media outlets;

B) Mailing the notice to the clerk of the nearest city, town or village requesting further posting in conspicuous locations throughout the city, town or village;

C) Requiring the applicant to post the notice near the entrance to the applicant's premises; and

D) Emailing the notice to the Agency's listserv for the facility.

c) Public Comment Period

1) The Agency must accept written comments from interested persons on the draft permit determination for 45 days following the circulation of the public notice under subsection (b).

2) All comments must be submitted to the Agency and to the applicant.

3) The Agency must keep all timely submitted comments and consider them in the formulation of its final determination with respect to the permit application.

4) The period for comment may be extended at the discretion of the Agency.

d) Public Hearing

1) The Agency must hold a public hearing on the issuance or denial of a draft permit whenever the Agency determines that there exists a significant degree of public interest in the proposed permit.

2) Within the 45-day public comment period, any person, including the applicant, may submit to the Agency a request for a public hearing, which must include the reasons why a hearing is warranted.

3) Hearings held under this Section must be held in the geographical area in which the CCR surface impoundment is located. When determining the hearing location, consideration must be given to facilitating attendance of interested or affected persons and organizations and to accessibility of hearing sites to public transportation.

e) Notice of Public Hearing

1) The Agency must issue notice of a public hearing not less than 30 days before the date of the hearing, under the procedures for the circulation of public notice in subsection (b)(3).

2) The contents of the public notice for the public hearing must include at least the following:

A) Name, address, and telephone number of the Agency;

B) Name and address of each applicant whose application will be considered at the hearing;

C) Brief description of the applicant's activities or operations that result in the construction, operation, modification or closure of a CCR surface impoundment;

D) Information regarding the time and location of the hearing;

E) The purpose of the hearing;

F) A concise statement of the issues to be considered at the hearing;

G) Address and telephone number of premises at which interested persons may obtain further information and request a copy of the draft permit and related documents; and

H) A statement that the hearing will be conducted in accordance with this Section.

I) A translation of the public notice into the appropriate language or languages will be made if the Agency determines that a project is located within one mile of a significant population of non-English speaking residents.

f) When the Agency receives written comments or holds a public hearing under this Section, the Agency must prepare a responsiveness summary that includes:

1) An identification of the public participation activity conducted;

2) Description of the matter on which the public was consulted;

3) An estimate of the number of persons present at the hearing;

4) A summary of all significant comments, criticisms, and suggestions, whether written or oral, submitted during the public comment period, at the hearing, or during the time the hearing record was open;

5) The Agency's response to all significant comments, criticisms, and suggestions; and

6) A statement of Agency action, including, when applicable, the issuance or denial of the permit.

Section 845.270 Final Permit Determination and Appeal

a) The Agency must not make a final permit determination until the public participation process in Section 845.260 has concluded.

b) After the consideration of any comments that may have been received, the Agency may either issue or deny the permit.

c) The Agency must provide a notice of the issuance or denial of the permit to the applicant, to any person who provides comments or an email address to the Agency during the public notice period or a public hearing, and to any person on the Agency's listserv for the facility. The Agency must post its final permit determination and, if a public hearing was held, the responsiveness summary, to the Agency's website. The notice must briefly indicate any significant changes that were made from the terms and conditions of the draft permit.

d) In the case of denial, the Agency must inform the applicant of the reasons for denial, as required by Section 39(a) of the Act.

e) Appeal

1) If the Agency refuses to grant, or grants with conditions, a permit under this Part, the applicant may petition the Board to appeal the Agency's final decision under Section 40 of the Act.

2) *If the Agency grants or denies a permit under this Part, a third party, other than the permit applicant or Agency, may appeal the Agency's decision as provided under federal law for CCR surface impoundment permits.* [415 ILCS 5/40(g)]

3) All appeals must be filed with the Board within 35 days after the final action is served on the applicant.

Section 845.280 Transfer, Modification and Renewal

a) No permit is transferable from one person to another except as approved by the Agency. Approval must be granted only if a new owner or operator seeking transfer of a permit can demonstrate the ability to comply with all applicable financial requirements of Subpart I.

b) Agency Initiated Modification. The Agency may modify a permit under the following conditions:

1) Discovery of a typographical or calculation error;

2) Discovery that a determination or condition was based upon false or misleading information;

3) An order of the Board issued in an action brought under Title VII, VIII, IX or X of the Act; or

4) Promulgation of new statutes or regulations affecting the permit.

c) The owner or operator of a CCR surface impoundment may initiate modification to its permit by application submittal to the Agency at any time after the permit is approved and before the permit expires.

d) The Agency may make minor modifications to a permit without following the public notice procedures of Section 845.260. Minor modifications may only:

1) Correct typographical errors;

2) Require more frequent monitoring or reporting by the permittee, including the installation of additional groundwater monitoring wells;

3) Allow for a change in ownership or operational control of a facility when the Agency determines that no other change in the permit is necessary, provided that a written agreement containing a specific date for transfer of permit responsibility, coverage, and liability between the current and new permittees has been submitted to the Agency;

4) Change the construction schedule, which does not impact the scheduled date of completion; or

5) Require electronic reporting requirements.

e) An application for renewal of a permit must be filed with the Agency at least 180 days before the expiration date of the existing permit unless the Agency grants a waiver of this requirement. The Agency may grant a waiver of the 180-day requirement only if:

1) The permittee submits a written request to the Agency at least 60 days before the expiration of the permit;

2) The permittee's written request includes the reasonably justifiable causes for not meeting the 180-day requirement; and

3) The permittee's written request includes a date by which the permittee will submit the renewal application.

f) Any Agency decision to deny a waiver request must be made within 21 days after receipt of the waiver request (see subsection (e)(1)).

g) The terms and conditions of an expiring permit remain effective and enforceable against the permittee until the Agency takes final action on the pending permit renewal application, only if the permittee has submitted a timely application under subsection (e) and the Agency, through no fault of the permittee, does not issue a new permit by the expiration date of the previous permit.

Section 845.290 Construction Quality Assurance Program

a) The following must be constructed according to a Construction Quality Assurance (CQA) program:

1) The construction of a new CCR surface impoundment, or the lateral expansion of an existing CCR surface impoundment;

2) The retrofit of an existing CCR surface impoundment;

3) Installation of a groundwater collection system and discharge system;

4) Installation of the groundwater monitoring system; and

5) Installation of the final cover system.

b) The CQA program must meet the following requirements:

1) The owner or operator of the CCR surface impoundment must designate a CQA officer who is a qualified professional engineer.

2) At the end of each week of construction, until construction is complete, a summary report must be prepared either by the CQA officer or under the supervision of the CQA officer. The report must include descriptions of the weather, locations where construction occurred during the previous week, materials used, results of testing, inspection reports, and procedures used to perform the inspections. The CQA officer must review and approve the report. The owner or operator of the CCR surface impoundment must place the weekly reports in the facility's operating record (see Section 845.800(d)(3)).

3) The CQA officer must certify the following, when applicable:

A) The bedding material contains no undesirable objects;

B) The final closure plan or corrective action plan approved by the construction permit has been followed;

C) The anchor trench and backfill are constructed to prevent damage to a geosynthetic membrane;

D) All tears, rips, punctures, and other damage are repaired;

E) All geosynthetic membrane seams are properly constructed and tested in accordance with the manufacturer's specifications;

F) Any groundwater collection system is constructed to intersect the water table;

G) Any groundwater collection system is properly constructed to slope toward extraction points, and the extraction equipment is properly designed and installed;

H) Appropriate operation and maintenance plans for the groundwater collection system and extraction and discharge equipment are provided;

I) Proper filter material consisting of uniform granular fill, to avoid clogging, is used in construction;

J) The filter material, as placed, possesses structural strength adequate to support the maximum loads imposed by the overlying materials and equipment used at the facility;

K) CCR stabilization; and

L) Site restoration, if any.

4) The CQA officer must supervise and be responsible for all inspections, testing and other activities required to be implemented as part of the CQA program under this Section.

5) The CQA officer must be present to provide supervision and assume responsibility for performing all inspections of the following activities, when applicable:

A) Compaction of the subgrade and foundation to design parameters;

B) Application of final cover, including installation of the geomembrane; and

C) Installation of the groundwater collection system and discharge system.

6) If the CQA officer is unable to be present as required by subsection (b)(5), the CQA officer must provide the following in writing:

A) The reasons for his or her absence;

B) A designation of a person who must exercise professional judgment in carrying out the duties of the CQA officer-in-absentia; and

C) A signed statement that the CQA officer assumes full responsibility for all inspections performed and reports prepared by the designated CQA officer-in-absentia during the absence of the CQA officer.

7) The CQA program must ensure, at a minimum, that construction materials and operations meet design specifications.

SUBPART C: LOCATION RESTRICTIONS

Section 845.300 Placement Above the Uppermost Aquifer

a) Existing and new CCR surface impoundments, and all lateral expansions of CCR surface impoundments, must be constructed with a base that is located at least 1.52 meters (five feet) above the upper limit of the uppermost aquifer, or must demonstrate that there will not be an intermittent, recurring, or sustained hydraulic connection between any portion of the base of the CCR surface impoundment and the uppermost aquifer due to normal fluctuations in groundwater elevations (including the seasonal high water table).

b) The owner or operator of the CCR surface impoundment must obtain a certification from a qualified professional engineer stating that the demonstration meets the requirements of subsection (a).

c) The owner or operator of an existing CCR surface impoundment must complete the demonstration required by subsection (a) and submit the completed demonstration, along with a qualified professional engineer's certification, to the Agency in the facility's initial operating permit application.

d) The owner or operator of a new CCR surface impoundment or a lateral expansion of a CCR surface impoundment must submit plans and specifications in a construction permit application that demonstrate the CCR surface impoundment will be constructed under subsection (a). Upon completion of construction, the owner or operator must obtain a certification from a qualified professional engineer that the CCR surface impoundment or lateral expansion was constructed in accordance with the requirements in subsection (a) and submit the certification to the Agency in the facility's initial operating permit application.

Section 845.310 Wetlands

a) Existing and new CCR surface impoundments, and all lateral expansions of CCR surface impoundments, must not be located in wetlands unless the owner or operator demonstrates the following:

    1) When applicable under section 404 of the Clean Water Act, Interagency Wetlands Policy Act of 1989 [20 ILCS 830] and Rivers, Lakes, and Streams Act [615 ILCS 5], or other applicable State wetlands laws, a clear and objective rebuttal of the presumption that an alternative to the CCR surface impoundment is reasonably available that does not involve wetlands.

    2) The construction and operation of the CCR surface impoundment will not cause or contribute to any of the following:

        A) A violation of any applicable State or federal water quality standard;

    B) A violation of any applicable toxic effluent standard or prohibition under section 307 of the Clean Water Act;

    C) Jeopardize the continued existence of endangered or threatened species or result in the destruction or adverse modification of a critical habitat, protected under the Endangered Species Act of 1973 (16 USC 1531 et seq.) and the Illinois Endangered Species Protection Act [520 ILCS 10]; and

    D) A violation of any requirement under the Marine Protection, Research, and Sanctuaries Act of 1972 (16 USC 1431 and 33 USC 1401) for the protection of a marine sanctuary.

3) The CCR surface impoundment will not cause or contribute to significant degradation of wetlands by addressing all the following factors:

    A) Erosion, stability, and migration potential of native wetland soils, muds and deposits used to support the CCR surface impoundment;

    B) Erosion, stability, and migration potential of dredged and fill materials used to support the CCR surface impoundment;

    C) The volume and chemical nature of the CCR;

    D) Impacts on fish, wildlife, and other aquatic resources and their habitat from release of CCR;

    E) The potential effects of catastrophic release of CCR to the wetland and the resulting impacts on the environment; and

    F) Any additional factors, as necessary, to demonstrate that ecological resources in the wetland are sufficiently protected.

4) To the extent required under section 404 of the Clean Water Act or applicable State wetlands laws, steps have been taken to attempt to achieve no net loss of wetlands (as defined by acreage and function) by first avoiding impacts to wetlands to the maximum extent reasonable as required by subsections (a)(1) through (3), then minimizing unavoidable impacts to the maximum extent reasonable, and, finally, offsetting remaining unavoidable wetland impacts through all appropriate and reasonable compensatory mitigation actions (e.g., restoration of existing degraded wetlands or creation of man-made wetlands); and

5) Sufficient information is available to make a reasoned determination with respect to the demonstrations in subsections (a)(1) through (4).

b) The owner or operator of the CCR surface impoundment must obtain a certification from a qualified professional engineer stating that the demonstration meets the requirements of subsection (a).

c) The owner or operator of an existing CCR surface impoundment must complete the demonstration required by subsection (a) and submit the completed demonstration, along with the qualified professional engineer's certification, to the Agency with the facility's initial operating permit application.

d) The owner or operator of a new CCR surface impoundment or a lateral expansion of a CCR surface impoundment must submit plans and specifications in a construction permit application that demonstrate the CCR surface impoundment will be constructed under subsection (a). Upon completion of construction, the owner or operator must obtain a certification from a qualified professional engineer that the CCR surface impoundment or lateral expansion was constructed in accordance with the requirements in subsection (a) and submit the certification to the Agency in the facility's initial operating permit application.

Section 845.320 Fault Areas

a) Existing and new CCR surface impoundments, and all lateral expansions of CCR surface impoundments, must not be located within 60 meters (200 feet) of the outermost damage zone of a fault that has had displacement in Holocene time unless the owner or operator demonstrates that an alternative setback distance of less than 60 meters (200 feet) will prevent damage to the structural integrity of the CCR surface impoundment.

b) The owner or operator of the CCR surface impoundment must obtain a certification from a qualified professional engineer stating that the demonstration meets the requirements of subsection (a).

c) The owner or operator of an existing CCR surface impoundment must complete the demonstration required by subsection (a) and submit the completed demonstration, along with the qualified professional engineer's certification, to the Agency with the facility's initial operating permit application.

d) The owner or operator of a new CCR surface impoundment or a lateral expansion of a CCR surface impoundment must submit plans and specifications in a construction permit application that demonstrate the CCR surface impoundment will be constructed under subsection (a). Upon completion of construction, the owner or operator must obtain a certification from a qualified professional engineer that the CCR surface impoundment or lateral expansion was constructed in accordance with the requirements in subsection (a) and submit the certification to the Agency in the facility's initial operating permit application.

Section 845.330 Seismic Impact Zones

a) Existing and new CCR surface impoundments, and all lateral expansions of CCR surface impoundments, must not be located in seismic impact zones unless the owner or operator demonstrates that all structural components, including liners, leachate collection and removal systems, and surface water control systems, are designed to resist the maximum horizontal acceleration in lithified earth material for the site.

b) The owner or operator of the CCR surface impoundment must obtain a certification from a qualified professional engineer stating that the demonstration meets the requirements of subsection (a).

c) The owner or operator of an existing CCR surface impoundment must complete the demonstration required by subsection (a) and submit the completed demonstration, along with the qualified professional engineer's certification, to the Agency with the facility's initial operating permit application.

d) The owner or operator of a new CCR surface impoundment or a lateral expansion of a CCR surface impoundment must submit plans and specifications in a construction permit application that demonstrate the CCR surface impoundment will be constructed under subsection (a). Upon completion of construction, the owner or operator must obtain a certification from a qualified professional engineer that the CCR surface impoundment or lateral expansion was constructed in accordance with the requirements of subsection (a) and submit the certification to the Agency in the facility's initial operating permit application.

Section 845.340 Unstable Areas and Floodplains

a) An existing or new CCR surface impoundment, or any lateral expansion of a CCR surface impoundment, must not be located in an unstable area unless the owner or operator demonstrates that recognized and generally accepted engineering practices have been incorporated into the design of the CCR surface impoundment to ensure that the integrity of the structural components of the CCR surface impoundment will not be disrupted.

b) The owner or operator must consider all the following factors, at a minimum, when determining whether an area is unstable:

  1) On-site or local soil conditions, including liquefaction, that may result in significant differential settling;

  2) On-site or local geologic or geomorphologic features; and

  3) On-site or local human-made features or events (both surface and subsurface).

c) An existing or new CCR surface impoundment, or any lateral expansion of a CCR surface impoundment, must not be located in a floodplain unless the owner or operator demonstrates that recognized and generally accepted engineering practices have been incorporated into the design of the CCR surface impoundment to ensure that the CCR surface impoundment will not restrict the flow of the base flood, reduce the temporary water storage capacity of a floodplain, or result in washout of CCR, so as to pose a hazard to human life, wildlife, or land or water resources. For purposes of this subsection (c):

  1) Base flood means a flood that has a 1 percent or greater chance of recurring in any year or a flood of a magnitude equaled or exceeded once in 100 years on average within the time of historical river level records.

  2) Floodplain means the lowland and relatively flat areas adjoining inland and coastal waters, including flood-prone areas of offshore islands, which are inundated by the base flood.

  3) Washout means the carrying away of CCR by waters of the base flood.

d) The owner or operator of the CCR surface impoundment must obtain a certification from a qualified professional engineer stating that the demonstration meets the requirements of subsections (a) and (c).

e) The owner or operator of an existing CCR surface impoundment must complete the demonstration required by subsections (a) and (c) of this Section and submit the completed demonstration, along with a qualified professional engineer's certification, to the Agency with the facility's initial operating permit application.

f) The owner or operator of a new CCR surface impoundment, or a lateral expansion of a CCR surface impoundment, must submit plans and specifications in a construction permit application that demonstrate the CCR surface impoundment will be constructed under subsections (a)and (c). Upon completion of construction, the owner or operator must obtain a certification from a qualified professional engineer that the CCR surface impoundment or lateral expansion was constructed in accordance with the requirements in subsections (a) and (c) and submit the certification to the Agency in the facility's initial operating permit application.

Section 845.350 Failure to Meet Location Standards

a) An owner or operator of an existing CCR surface impoundment who fails to demonstrate compliance with the requirements of this Subpart is subject to the requirements of Section 845.700.

b) An owner or operator of a new CCR surface impoundment, or any lateral expansion of a CCR surface impoundment, who fails to make the demonstration showing compliance with the requirements of this Subpart is prohibited from placing CCR in the CCR surface impoundment.

SUBPART D: DESIGN CRITERIA

Section 845.400 Liner Design Criteria for Existing CCR Surface Impoundments

a) An existing CCR surface impoundment is considered to be an existing lined surface impoundment if it has been constructed with either a composite liner that meets the requirements of subsection (b) or an alternative composite liner that meets the requirements of subsection (c).

b) Composite Liner

1) A composite liner must consist of two components: the upper component consisting of, at a minimum, a 30-mil geomembrane liner, and the lower component consisting of at least a two-foot layer of compacted soil with a hydraulic conductivity of no more than 1×10^{-7} centimeters per second (cm/sec). The geomembrane liner components consisting of high-density polyethylene (HDPE) must be at least 60 mil. The geomembrane liner or upper liner component must be installed in direct and uniform contact with the compacted soil or lower liner component.

2) The composite liner must be:

A) Constructed of materials that have appropriate chemical properties and sufficient strength and thickness to prevent failure due to pressure gradients (including static head and external hydrogeologic forces), physical contact with the CCR or leachate to which they are exposed, climatic conditions, the stress of installation, and the stress of daily operation;

B) Constructed of materials that provide appropriate shear resistance of the upper and lower component interface to prevent sliding of the upper component, including on slopes;

C) Placed upon a foundation or base capable of providing support to the liner and resistance to pressure gradients above and below the liner to prevent failure of the liner due to settlement, compression, or uplift; and

D) Installed to cover all surrounding earth likely to be in contact with the CCR or leachate.

c) Alternative Composite Liner

1) An alternative composite liner must consist of two components: the upper component consisting of, at a minimum, a 30-mil geomembrane liner, and a lower component, that is not a geomembrane, with a liquid flow rate no greater than the liquid flow rate of two feet of compacted soil with a hydraulic conductivity of no more than 1×10^{-7} cm/sec. The geomembrane liner components consisting of high-density polyethylene (HDPE) must be at least 60 mil. If the lower component of the alternative liner is compacted soil, the geomembrane liner must be installed in direct and uniform contact with the compacted soil.

2) The liquid flow rate through the lower component of the alternative composite liner must be no greater than the liquid flow rate through two feet of compacted soil with a hydraulic conductivity of 1×10^{-7} cm/sec. The hydraulic conductivity for the two feet of compacted soil used in the comparison must be no greater than 1×10^{-7} cm/sec. The hydraulic conductivity of any alternative to the two feet of compacted soil must be determined using recognized and generally accepted methods.

3) The liquid flow rate comparison must be made using the following equation, which is derived from Darcy's Law for gravity flow through porous media.

$$Q/A = q = k ((h/t)+1)$$

Where:
Q = flow rate (cubic centimeters/second)
A = Surface area of the liner (squared centimeters)
q = flow rate per unit area (cubic centimeters/ second/squared centimeter)
k = hydraulic conductivity of the liner (centimeters /second)
h = hydraulic head above the liner (centimeters); and
t = thickness of the liner (centimeters)

4) The alternative composite liner must meet the requirements specified in subsection (b).

d) The hydraulic conductivity of the compacted soil must be determined using recognized and generally accepted methods.

e) The owner or operator of an existing CCR surface impoundment that has not completed an Agency approved closure before July 30, 2021 must submit an initial operating permit application under Section 845.230 that demonstrates whether the CCR surface impoundment was constructed with either of the following:

1) A composite liner that meets the requirements of subsection (b); or

2) An alternative composite liner that meets the requirements of subsection (c).

f) A CCR surface impoundment is considered to be an unlined CCR surface impoundment if either:

1) The owner or operator of the CCR surface impoundment determines that the CCR surface impoundment is not constructed with a liner that meets the requirements of subsection (b) or (c); or

2) The owner or operator of the CCR surface impoundment fails to document whether the CCR surface impoundment was constructed with a liner that meets the requirements of subsection (b) or (c).

g) All unlined CCR surface impoundments are subject to the requirements of Section 845.700.

h) The owner or operator of the CCR surface impoundment must obtain a certification from a qualified professional engineer attesting that the CCR surface impoundment meets the requirements of subsection (a) and submit the certification to the Agency in the facility's initial operating permit application.

Section 845.410 Liner Design Criteria for New CCR Surface Impoundments and Any Lateral Expansion of a CCR Surface Impoundment

a) New CCR surface impoundments and lateral expansions of existing and new CCR surface impoundments must be designed, constructed, operated, and maintained with either a composite liner or an alternative composite liner that meets the requirements of Section 845.400(b) or (c).

b) Any liner specified in this Section must be installed to cover all surrounding earth likely to be in contact with CCR. Dikes must not be constructed so as to damage the composite liner.

c) Before construction, the owner or operator must obtain certification from a qualified professional engineer that the design of the composite liner or, if applicable, the design of an alternative composite liner complies with the requirements of this Section and submit this certification to the Agency in the facility's construction permit application.

d) Upon completion of construction, the owner or operator must obtain a certification from a qualified professional engineer that the composite liner or, if applicable, the alternative composite liner has been constructed in accordance with the requirements of this Section and submit this certification to the Agency in the facility's initial operating permit application.

Section 845.420 Leachate Collection and Removal System

A new CCR surface impoundment must be designed, constructed, operated and maintained with a leachate collection and removal system. The leachate collection and removal system must be designed, constructed, operated, and maintained to collect and remove leachate from the leachate collection system of the CCR surface impoundment during its active life and post-closure care period.

a) The leachate collection and removal system must:

  1) Be placed above the liner required by Section 845.400 or Section 845.410;

  2) Have placed above it a filter layer that has a hydraulic conductivity of at least 1×10^{-5} cm/sec;

  3) Have a bottom slope of three percent or more towards the collection pipes;

  4) Be constructed of:

    A) Granular drainage materials with a hydraulic conductivity of 1×10^{-1} cm/sec or more and a thickness of 24 inches or more above the crown of the collection pipe; or

    B) Synthetic drainage materials with a transmissivity of 6×10^{-4} m^2/sec or more;

  5) Be constructed of materials that are chemically resistant to CCR and any non-CCR waste managed in the CCR surface impoundment and the leachate expected to be generated, and of sufficient strength and thickness to prevent collapse under the pressures exerted by overlying waste and any waste cover materials and equipment used at the CCR surface impoundment;

  6) Be designed, constructed and operated with collection pipes at the base of the granular material to prevent clogging with fines during the active life and post-closure care period;

  7) Have collection pipes

    A) Designed such that leachate is collected at a sump and is pumped or flows out of the CCR surface impoundment;

    - B) With slopes that allow flow from all points within the CCR surface impoundment to the sump or drain outlet; and

    - C) Large enough to conduct periodic cleaning;

  - 8) Have a protective layer or other means of deflecting the force of CCR pumped into the CCR surface impoundment;

  - 9) Be designed and operated to minimize clogging during the active life and post-closure care period; and

  - 10) At a minimum, the leachate collection and removal system must be operated to remove free liquids from the CCR surface impoundment at the time of closure and during post closure care.

- b) The owner or operator must obtain certification from a qualified professional engineer that the design of the leachate collection system complies with the requirements of this Section and submit this certification to the Agency in the facility's construction permit application.

- c) Upon completion, the owner or operator must obtain a certification from a qualified professional engineer that the leachate collection system has been constructed in accordance with the requirements of this Section and submit this certification to the Agency in the facility's initial operating permit application.

Section 845.430 Slope Maintenance

The slopes and pertinent surrounding areas of the CCR surface impoundment must be designed, constructed, operated, and maintained with one of the forms of slope protection specified in subsection (a) that meets all the performance standards of subsection (b).

- a) Slope protection must consist of one of the following:

  - 1) A vegetative cover consisting of grassy vegetation;

  - 2) An engineered cover consisting of a single form or combination of forms of engineered slope protection measures; or

  - 3) A combination of the forms of cover specified in subsection (a)(1) or (a)(2).

- b) Any form of cover for slope protection must meet the following performance standards:

1) The cover must be installed and maintained on the slopes and pertinent surrounding areas of the CCR surface impoundment;

2) The cover must provide protection against surface erosion, wave action, and adverse effects of rapid drawdown;

3) The cover must be maintained to allow for the observation of, and access to, the slopes and pertinent surrounding areas during routine and emergency events;

4) Woody vegetation must be removed from the slopes or pertinent surrounding areas. Any removal of woody vegetation with a diameter greater than ½ inch must be directed by a person familiar with the design and operation of the CCR surface impoundment and in consideration of the complexities of removal of a tree or shrubbery, who must ensure the removal does not create a risk of destabilizing the CCR surface impoundment or otherwise adversely affect the stability and safety of the CCR surface impoundment or personnel undertaking the removal; and

5) The height of vegetation must not exceed 12 inches.

Section 845.440 Hazard Potential Classification Assessment

a) Hazard Potential Classification Assessments

1) The owner or operator of the CCR surface impoundment must conduct an initial and annual hazard potential classification assessment of the CCR surface impoundment. The owner or operator must document the hazard potential classification of each CCR surface impoundment as either a Class 1 or Class 2 CCR surface impoundment. The owner or operator must also document the basis for each hazard potential classification.

2) The owner or operator of the CCR surface impoundment must obtain a certification from a qualified professional engineer stating that the initial hazard potential classification and each annual classification was conducted in accordance with the requirements of this Section.

3) Timeframe for Submission of the Hazard Potential Classification Assessments and Certifications

A) The owner or operator of a new CCR surface impoundment must submit the initial hazard potential classification assessment certification with the initial operating permit application before the initial receipt of CCR in the surface impoundment.

B) The owner or operator of an existing CCR surface impoundment must submit the initial hazard potential classification assessment certification with its first annual inspection report required by Section 845.540(b).

C) The owner or operator of a CCR surface impoundment must submit the annual hazard potential classification assessment certification each year with the annual inspection required by Section 845.540(b).

D) The owner or operator of a CCR surface impoundment must place each hazard potential classification assessment in the facility's operating record (see Section 845.800(d)(4)).

b) The requirements of this Section apply to all CCR surface impoundments, except for those CCR surface impoundments that are incised CCR surface impoundments. If an incised CCR surface impoundment is subsequently modified (e.g., a dike is constructed) such that the CCR surface impoundment no longer meets the definition of an incised CCR surface impoundment, the CCR surface impoundment is subject to the requirements of this Section.

Section 845.450 Structural Stability Assessment

a) The owner or operator of a CCR surface impoundment must conduct initial and annual structural stability assessments and document whether the design, construction, operation, and maintenance of the CCR surface impoundment is consistent with recognized and generally accepted engineering practices for the maximum volume of CCR and CCR wastewater that can be impounded in the CCR surface impoundment. The assessment must, at a minimum, document whether the CCR surface impoundment has been designed, constructed, operated, and maintained with:

1) Stable foundations and abutments;

2) Adequate slope protection to protect against surface erosion, wave action, and adverse effects of sudden drawdown;

3) Dikes mechanically compacted to a density sufficient to withstand the range of loading conditions in the CCR surface impoundment;

4) Slope protection consistent with Section 845.430;

5) A single spillway or a combination of spillways configured as specified in subsection (a)(5)(A). The combined capacity of all spillways must be designed, constructed, operated, and maintained to adequately manage

flow during and following the peak discharge from the event specified in subsection (a)(5)(B).

A) All spillways must be either:

i) Of non-erodible construction and designed to carry sustained flows; or

ii) Earth- or grass-lined and designed to carry short-term, infrequent flows at non-erosive velocities where sustained flows are not expected.

B) The combined capacity of all spillways must adequately manage flow during and following the peak discharge from a:

i) Probable maximum flood for a Class 1 CCR surface impoundment; or

ii) 1000-year flood for a Class 2 CCR surface impoundment.

6) Hydraulic structures underlying the base of the CCR surface impoundment or passing through the dike of the CCR surface impoundment that maintain structural integrity and are free of significant deterioration, deformation, distortion, bedding deficiencies, sedimentation, and debris that may negatively affect the CCR surface impoundment; and

7) For CCR surface impoundments with downstream slopes that can be inundated by the pool of an adjacent water body, such as a river, stream or lake, downstream slopes that maintain structural stability during low pool of the adjacent water body or sudden drawdown of the adjacent water body.

b) The annual assessment described in this Section must identify any structural stability deficiencies associated with the CCR surface impoundment in addition to recommending corrective measures. If a deficiency or a release is identified during the periodic assessment, the owner or operator of the surface impoundment must submit to the Agency a construction permit application including documentation detailing proposed corrective measures and must obtain any necessary permits from the Agency as soon as feasible.

c) The owner or operator of the CCR surface impoundment must obtain a certification from a qualified professional engineer stating that the initial structural stability assessments and each annual assessment thereafter was conducted in accordance with the requirements.

d) Timeframe for Submission of Structural Stability Assessment

1) The owner or operator of a new CCR surface impoundment must submit the initial structural stability assessment certification with the initial operating permit application before the initial receipt of CCR in the surface impoundment.

2) The owner or operator of an existing CCR surface impoundment must submit the initial structural stability assessment certification with its first annual inspection report required by Section 845.540(b).

3) The owner or operator of a CCR surface impoundment must submit the annual structural stability assessment certification each year with the annual inspection required by Section 845.540(b).

4) The owner or operator of a CCR surface impoundment must place each structural stability assessment in the facility's operating record (see Section 845.800(d)(5)).

e) The requirements of this Section apply to all CCR surface impoundments, except for those CCR surface impoundments that are incised CCR surface impoundments. If an incised CCR surface impoundment is subsequently modified (e.g., a dike is constructed) such that the CCR surface impoundment no longer meets the definition of an incised CCR surface impoundment, the CCR surface impoundment is subject to the requirements of this Section.

Section 845.460 Safety Factor Assessment

a) The owner or operator of a CCR surface impoundment must conduct an initial and annual safety factor assessment for each CCR surface impoundment and document whether the calculated factors of safety for each CCR surface impoundment achieve the minimum safety factors specified in this Section for the critical cross-section of the embankment. The critical cross-section is the cross section anticipated to be the most susceptible of all cross-sections to structural failure based on appropriate engineering considerations, including loading conditions. The safety factor assessments must be supported by appropriate engineering calculations.

1) For new CCR surface impoundments, the calculated static factor of safety under the end-of-construction loading condition must equal or exceed 1.30. The assessment of this loading condition is only required for the initial safety factor assessment and is not required for subsequent assessments.

2) The calculated static factor of safety under the long-term, maximum storage pool loading condition must equal or exceed 1.50.

3) The calculated static factor of safety under the maximum surcharge pool loading condition must equal or exceed 1.40.

4) The calculated seismic factor of safety must equal or exceed 1.00.

5) For dikes constructed of soils that have susceptibility to liquefaction, the calculated liquefaction factor of safety must equal or exceed 1.20.

b) The owner or operator of the CCR surface impoundment must obtain a certification from a qualified professional engineer stating that the initial safety factor assessment and each annual assessment thereafter was conducted in accordance with the requirements of this Section.

c) Timeframe for Submission of the Safety Factor Assessment

1) The owner or operator of a new CCR surface impoundment must submit the initial safety factor assessment certification with the initial operating permit application before the initial receipt of CCR in the surface impoundment.

2) The owner or operator of an existing CCR surface impoundment must submit the initial safety factor assessment certification with its first annual inspection report required by Section 845.540(b).

3) The owner or operator of a CCR surface impoundment must submit the annual safety factor assessment certification each year with the annual inspection required by Section 845.540(b).

4) The owner or operator of a new CCR surface impoundment must place each safety factor assessment in the facility's operating record as required by Section 845.800(d)(6).

d) Failure to Document Minimum Safety Factors

1) For new CCR surface impoundments, until the date an owner or operator of a CCR surface impoundment documents that the calculated factors of safety achieve the minimum safety factors specified in this Section, the owner or operator is prohibited from placing CCR in the CCR surface impoundment.

2) An owner or operator of the CCR surface impoundment who either fails to complete a timely safety factor assessment or fails to demonstrate minimum safety factors as required by this Section is subject to the requirements of Section 845.700.

e) The requirements of this Section apply to all CCR surface impoundments, except for those CCR surface impoundments that are incised CCR surface impoundments. If an incised CCR surface impoundment is subsequently modified (e.g., a dike is constructed) such that the CCR surface impoundment no longer meets the definition of an incised CCR surface impoundment, the CCR surface impoundment is subject to the requirements of this Section.

SUBPART E: OPERATING CRITERIA

Section 845.500 Air Criteria

a) The owner or operator of a CCR surface impoundment, or any lateral expansion of a CCR surface impoundment, must adopt measures that will effectively minimize CCR from becoming airborne at the facility, including CCR fugitive dust originating from CCR surface impoundments, roads, and other CCR management and material handling activities.

b) CCR Fugitive Dust Control Plan. The owner or operator of the CCR surface impoundment must prepare and operate in accordance with a CCR fugitive dust control plan as specified in this subsection (b). This requirement applies in addition to, not in place of, any applicable standards under the Occupational Safety and Health Act (29 USC 15), including 29 CFR 1910.1018, 29 CFR 1910.1024, 29 CFR 1910.1025, 29 CFR 1910.1027, and 1910.1053, or any other State or federal law.

1) The CCR fugitive dust control plan must identify and describe the CCR fugitive dust control measures the owner or operator will use to minimize CCR from becoming airborne at the facility. The owner or operator must select, and include in the CCR fugitive dust control plan, the CCR fugitive dust control measures that are most appropriate for site conditions, along with an explanation of how the measures selected are applicable and appropriate for site conditions. Examples of control measures that may be appropriate include: locating CCR inside an enclosure or partial enclosure; operating a water spray or fogging system; reducing fall distances at material drop points; using wind barriers, compaction, or vegetative covers; establishing and enforcing reduced vehicle speed limits; paving and sweeping roads; covering trucks transporting CCR; reducing or halting operations during high wind events; or applying a daily cover.

2) The CCR fugitive dust control plan must include procedures to log every complaint from members of the public received by the owner or operator involving CCR fugitive dust events at the facility. The owner or operator must:

A) Include for each logged complaint the date of the complaint, the date of the incident, the name and contact information of the complainant, if given, and all actions taken to assess and resolve the complaint; and

B) Submit quarterly reports to the Agency no later than 14 days from the end of the quarter of all complaints received in that quarter, including the information required by subsection (b)(2)(A).

3) The CCR fugitive dust control plan must include a description of the procedures the owner or operator will follow to periodically assess the effectiveness of the control plan.

4) The owner or operator of a CCR surface impoundment must prepare an initial CCR fugitive dust control plan for the facility by October 31, 2021, or by initial receipt of CCR in any CCR surface impoundment at the facility if the owner or operator becomes subject to this Part after October 31, 2021.

5) Amendment of the Plan. The owner or operator of a CCR surface impoundment subject to the requirements may amend the written CCR fugitive dust control plan at any time provided the revised plan is submitted to the Agency. The owner or operator must amend the written plan whenever there is a change in conditions that would substantially affect the written plan in effect, such as the construction and operation of a new CCR surface impoundment.

6) The owner or operator must place the initial and any amendments to the fugitive dust control plan in the facility's operating record as required by Section 845.800(d)(7). The most recent fugitive dust control plan must be placed in the facility's operating record and available on the owner's or operator's CCR website before submitting a permit application under this Part.

7) The owner or operator must obtain a certification from a qualified professional engineer that the initial CCR fugitive dust control plan, or any subsequent amendment of it, meets the requirements of this Section.

c) Annual CCR Fugitive Dust Control Report. The owner or operator of a CCR surface impoundment must prepare an annual CCR fugitive dust control report that includes a description of the actions taken by the owner or operator to control CCR fugitive dust and the four quarterly fugitive dust complaint reports submitted under subsection (b)(2)(B). The annual CCR fugitive dust control report must be submitted as a part of the annual consolidated report required by Section 845.550.

Section 845.510 Hydrologic and Hydraulic Capacity Requirements for CCR Surface Impoundments

a) The owner or operator of an existing or new CCR surface impoundment or any lateral expansion of a CCR surface impoundment must design, construct, operate, and maintain an inflow design flood control system as specified in subsections (a)(1) and (2).

  1) The inflow design flood control system must adequately manage flow into the CCR surface impoundment during and following the peak discharge of the inflow design flood specified in subsection (a)(3).

  2) The inflow design flood control system must adequately manage flow from the CCR surface impoundment to collect and control the peak discharge resulting from the inflow design flood specified in subsection (a)(3).

  3) The inflow design flood, at a minimum, is:

    A) For a Class 1 CCR surface impoundment, as determined under Section 845.440(a), the probable maximum flood;

    B) For a Class 2 CCR surface impoundment, as determined under Section 845.440(a), the 1000-year flood; or

    C) For an incised CCR surface impoundment, the 25-year flood.

b) Discharge from the CCR surface impoundment must be handled in accordance with the surface water requirements in Section 845.110(b)(3) and 35 Ill. Adm. Code Subtitle C.

c) Inflow Design Flood Control System Plan

  1) Content of the Plan. The owner or operator must prepare initial and annual inflow design flood control system plans for the CCR surface impoundment. These plans must document how the inflow design flood control system has been designed and constructed to meet the requirements of this Section. Each plan must be supported by appropriate engineering calculations.

  2) Amendment of the Plan. The owner or operator of the CCR surface impoundment may amend the written inflow design flood control system plan at any time. The owner or operator must amend the written inflow design flood control system plan whenever there is a change in conditions that would substantially affect the written plan in effect.

  3) The owner or operator must obtain a certification from a qualified professional engineer stating that the initial and periodic inflow design flood control system plans meet the requirements of this Section.

4) Timeframe for Plan Submission

A) The owner or operator of a new CCR surface impoundment must submit to the Agency the initial inflow design flood control system plan certification with the initial operating permit application before the initial receipt of CCR in the surface impoundment.

B) The owner or operator of an existing CCR surface impoundment must submit the initial inflow design flood control system plan certification with its first annual inspection report required by Section 845.540(b).

C) The owner or operator of a CCR surface impoundment must submit the annual inflow design flood control system plan certification each year with the annual inspection required by Section 845.540(b).

D) The owner or operator of a new CCR surface impoundment must place each inflow design flood control system plan in the facility's operating record (see Section 845.800(d)(8)).

Section 845.520 Emergency Action Plan

a) The owner or operator of a CCR surface impoundment must prepare and maintain a written Emergency Action Plan (EAP). The owner or operator must place the EAP and any amendment of the EAP in the facility's operating record (see Section 845.800(d)(9)).

b) At a minimum, the EAP must:

1) Define the events or circumstances involving the CCR surface impoundment that represent a safety emergency, along with a description of the procedures that will be followed to detect a safety emergency in a timely manner;

2) Define responsible persons, their respective responsibilities, and notification procedures for a safety emergency involving the CCR surface impoundment;

3) Provide contact information of emergency responders;

4) Include a map that delineates the downstream area that would be affected if a CCR surface impoundment fails and a physical description of the CCR surface impoundment; and

5) Include provisions for an annual face-to-face meeting or exercise between representatives of the owner or operator of the CCR surface impoundment and the local emergency responders.

c) The owner or operator of a CCR surface impoundment must prepare an initial Emergency Action Plan for the facility by October 31, 2021, or by initial receipt of CCR in any CCR surface impoundment at the facility if the owner or operator becomes subject to this Part after October 31, 2021.

d) Amendment of the Plan

1) The owner or operator of a CCR surface impoundment may amend the written EAP at any time.

2) The owner or operator must amend the written EAP whenever there is a change in conditions that would substantially affect the EAP in effect.

3) The written EAP must be evaluated, at a minimum, every five years to ensure the information required in this Section is accurate.

e) The owner or operator of the CCR surface impoundment must obtain a certification from a qualified professional engineer stating that the written EAP, and any subsequent amendment of the EAP, meets the requirements of this Section.

f) Activation of the EAP. The EAP must be implemented once events or circumstances involving the CCR surface impoundment that represent a safety emergency are detected, including conditions identified during any structural stability assessments, annual inspections, and inspections by a qualified person. The owner or operator of the CCR surface impoundment must submit records documenting all activations of the EAP to the Agency and place the documentation in the facility's operating record as required by Section 845.800(d)(10).

g) The owner or operator of a CCR surface impoundment must document the annual face-to-face meeting or exercise between representatives of the owner or operator of the CCR surface impoundment and the local emergency responders as required by subsection (b)(5). The owner or operator of the CCR surface impoundment must place this documentation in the facility's operating record as required by Section 845.800(d)(11).

Section 845.530 Safety and Health Plan

a) The owner or operator of the CCR surface impoundment must develop a Safety and Health Plan and ensure that employees, contract workers, and third-party contractors are informed regarding the Safety and Health Plan. The owner or operator must conduct ongoing worker hazard analyses and ensure employees, contract workers, and third-party contractors are aware of those analyses. The plan must be updated as needed based on the worker hazard analyses, but at least annually. The plan, and all amendments to the plan, must be placed in the facility's operating record as required by Section 845.800(d)(12), and on the owner's or operator's publicly accessible internet site.

b) For worker exposure safety, in addition to all other applicable local, State and federal requirements, the owner or operator of the CCR surface impoundment, for all chemical constituents identified in the CCR under Sections 845.230(a)(15) and 845.230(d)(2)(C), must:

1) Consider the recommendations in the most recent "NIOSH Pocket Guide to Chemical Hazards", Department of Human Health and Services, Centers for Disease Control and Prevention, National Institute for Occupational Safety and Health (available at cdc.gov/niosh/npg/default.html);

2) Implement the Occupational Safety and Health Administration regulations in Chapter 17 of Title 29 of the Code of Federal Regulations for all hazards not otherwise classified as defined in 29 CFR 1910.1200(c); and

3) Provide safety data sheets (Globally Harmonized System of Classification and Labeling of Chemicals adopted by OSHA) or create a facility-specific safety data sheet under 29 CFR 1910.1200(g).

c) The Safety and Health Plan must include a personnel training program that meets the following minimum requirements:

1) Employees, contract workers, and third-party contractors must successfully complete a training program that informs them of the hazards at the facility to ensure compliance with the requirements of this Part. The facility must maintain an outline of the training program used (or to be used) at the facility and a brief description of training program updates.

2) At a minimum, the training program must be designed to ensure that employees, contract workers, and third-party contractors understand and are able to respond effectively to the following:

A) Procedures for using, inspecting, repairing, and replacing facility emergency and monitoring equipment;

B) Communications or alarm systems;

C) Response to fires or explosions;

D) Response to a spill or release of CCR;

E) The training under the Occupational Safety and Health Standards in 29 CFR 1910.120, 29 CFR 1926.65, and the OSHA 10-hour or 30-hour construction safety training;

F) Information about chemical hazards and hazardous materials identified in subsection (b); and

G) The use of engineering controls, administrative controls, and personal protective equipment.

d) Employees, contract workers, and third-party contractors must successfully complete the program required in subsection (c) before undertaking any activity to construct, operate or close a CCR surface impoundment.

e) Employees, contract workers, and third-party contractors must take part in an annual review of the initial training required in subsection (c).

f) The owner or operator of the CCR surface impoundment must perform, at a minimum, the following hazard communication activities:

1) Post signs at the facility identifying the hazards of CCR, including dust inhalation when handling CCR;

2) Post signs at the facility identifying unstable CCR areas that may make operation of heavy equipment hazardous; and

3) Post signs at the facility where the CCR surface impoundment is located identifying safety measures and necessary precautions, including the proper use of personal protective equipment.

Section 845.540 Inspection Requirements for CCR Surface Impoundments

a) Inspections by a Qualified Person.

1) All CCR surface impoundments and any lateral expansion of a CCR surface impoundment must be examined by a qualified person as follows:

A) At intervals not exceeding seven days and after each 25-year, 24-hour storm, inspect for the following:

i) Any appearances of actual or potential structural weakness and other conditions that are disrupting, or have the potential to disrupt, the operation or safety of the CCR surface impoundment;

ii) Deterioration, malfunctions or improper operation of overtopping control systems, where present;

iii) Sudden drops in the level of the CCR surface impoundment's contents;

iv) Erosion that creates rills, gullies, or crevices six inches or deeper, other signs of deterioration including failed or eroded vegetation in excess of 100 square feet, or cracks in dikes or other containment devices; and

v) Any visible releases;

B) At intervals not exceeding seven days, inspect the discharge of all outlets of hydraulic structures that pass underneath the base of the CCR surface impoundment or through the dike, of the CCR surface impoundment, for abnormal discoloration, flow or discharge of debris or sediment; and

C) At intervals not exceeding 30 days, monitor all CCR surface impoundment instrumentation.

2) The owner or operator must prepare a report for each inspection that includes the date of the inspection, condition of the CCR surface impoundment, any repairs made to the CCR surface impoundment, and the date of the repair. The results of the inspection by a qualified person must be recorded in the facility's operating record as required by Section 845.800(d)(13).

3) The owner or operator of a CCR surface impoundment must initiate the inspections required by subsection (a) by April 30, 2021, or by initial receipt of CCR in a CCR surface impoundment if the owner or operator becomes subject to this Part after April 30, 2021. The inspections required by subsection (a) must continue until the completion of closure by removal or the completion of post-closure care.

4) If a 25-year, 24-hour storm is identified more than 48 hours before the next scheduled weekly inspection, an additional inspection must be conducted within 24 hours after the end of the identified storm event, before the scheduled seven-day inspection.

b) Annual Inspections By a Qualified Professional Engineer.

1) The CCR surface impoundment must be inspected on an annual basis by a qualified professional engineer to ensure that the design, construction,

operation, and maintenance of the CCR surface impoundment is consistent with recognized and generally accepted engineering standards. The inspection must, at a minimum, include:

A) A review of available information regarding the status and condition of the CCR surface impoundment, including files available in the operating record (e.g., CCR surface impoundment design and construction information required by Sections 845.220(a)(1) and 845.230(d)(2)(A), previous structural stability assessments required under Section 845.450, the results of inspections by a qualified person, and results of previous annual inspections);

B) A visual inspection of the CCR surface impoundment to identify signs of distress or malfunction of the CCR surface impoundment and appurtenant structures;

C) A visual inspection of any hydraulic structures underlying the base of the CCR surface impoundment or passing through the dike of the CCR surface impoundment for structural integrity and continued safe and reliable operation;

D) The annual hazard potential classification certification, if applicable (see Section 845.440);

E) The annual structural stability assessment certification, if applicable (see Section 845.450);

F) The annual safety factor assessment certification, if applicable (see Section 845.460); and

G) The inflow design flood control system plan certification (see Section 845.510(c)).

2) Inspection Report. The qualified professional engineer must prepare a report following each inspection that addresses the following:

A) Any changes in geometry of the impounding structure since the previous annual inspection;

B) The location and type of existing instrumentation and the maximum recorded readings of each instrument since the previous annual inspection;

C) The approximate minimum, maximum, and present depth and elevation of the impounded water and CCR since the previous annual inspection;

D) The storage capacity of the impounding structure at the time of the inspection;

E) The approximate volume of the impounded water and CCR at the time of the inspection;

F) Any appearances of an actual or potential structural weakness of the CCR surface impoundment, in addition to any existing conditions that are disrupting or have the potential to disrupt the operation and safety of the CCR surface impoundment and appurtenant structures; and

G) Any other changes that may have affected the stability or operation of the impounding structure since the previous annual inspection.

3) By January 31 of each year, the inspection report must be completed and included with the annual consolidated report required by Section 845.550.

4) Frequency of Inspections. The owner or operator of the CCR surface impoundment must conduct the inspection required by subsections (b)(1) and (2) on an annual basis. The deadline for conducting a subsequent inspection is based on the date of conducting the previous inspection.

5) If a deficiency or release is identified during an inspection, the owner or operator must submit to the Agency documentation detailing proposed corrective measures and obtain any necessary permits from the Agency.

Section 845.550 Annual Consolidated Report

a) By January 31 of each year, the owner or operator of the CCR surface impoundment must prepare an annual consolidated report for the preceding calendar year that includes the following:

1) Annual CCR fugitive dust control report (see Section 845.500(c));

2) Annual inspection report (see Section 845.540(b)), including:

A) Annual hazard potential classification certification, if applicable (see Section 845.440);

B) Annual structural stability assessment certification, if applicable (see Section 845.450);

C) Annual safety factor assessment certification, if applicable (see Section 845.460); and

D) Inflow design flood control system plan certification (see Section 845.510(c)).

3) Annual Groundwater Monitoring and Corrective Action Report (see Section 845.610(e)).

b) The owner or operator of the CCR surface impoundment must submit the annual consolidated report to the Agency in addition to placing the annual consolidated report in the facility's operating record as required by Section 845.800(d)(14).

SUBPART F: GROUNDWATER MONITORING AND CORRECTIVE ACTION

Section 845.600 Groundwater Protection Standards

a) For existing CCR surface impoundments and for inactive CCR surface impoundments:

1) The groundwater protection standards at the waste boundary must be:

A) Antimony: 0.006 mg/L

B) Arsenic: 0.010 mg/L

C) Barium: 2.0 mg/L

D) Beryllium: 0.004 mg/L

E) Boron: 2 mg/L

F) Cadmium: 0.005 mg/L

G) Chloride: 200 mg/L

H) Chromium: 0.1 mg/L

I) Cobalt: 0.006 mg/L

J) Fluoride: 4.0 mg/L

K) Lead: 0.0075 mg/L

L) Lithium: 0.04 mg/L

M) Mercury: 0.002 mg/L

N) Molybdenum: 0.1 mg/L

O) pH: 6.5-9.0 units

P) Selenium: 0.05 mg/L

Q) Sulfate: 400 mg/L

R) Thallium: 0.002 mg/L

S) Total Dissolved Solids: 1200 mg/L

T) Radium 226 and 228 combined: 5 pCi/L

2) For constituents with a background concentration higher than the levels identified in subsection (a)(1), the background concentration must be the groundwater protection standard.

b) For new CCR surface impoundments, the groundwater protection standards at the waste boundary must be background for the constituents listed in subsection (a)(1), calcium, and turbidity.

c) The owner or operator of a CCR surface impoundment may not obtain alternative groundwater quality standards in 35 Ill. Adm. Code 620.450(a)(4) for the constituents in subsections (a) and (b) before the end of post-closure care under Section 845.780, when closing with a final cover system, or before the end of groundwater monitoring under Section 845.740(b), when closing by removal.

Section 845.610 General Requirements

a) All CCR surface impoundments and lateral expansions of CCR surface impoundments are subject to the groundwater monitoring and corrective action requirements of this Subpart.

b) Required Submissions and Agency Approvals for Groundwater Monitoring

1) Existing CCR Surface Impoundments. The owner or operator of an existing CCR surface impoundment must submit the following to the Agency in an initial operating permit application:

A) A hydrogeologic site characterization meeting the requirements of Section 845.620;

B) Design and construction plans of a groundwater monitoring system meeting the requirements of Section 845.630;

C) A groundwater sampling and analysis program that includes selection of the statistical procedures to be used for evaluating groundwater monitoring data as required by Section 845.640; and

D) A monitoring program that includes a minimum of eight independent samples for each background and downgradient well as required by Section 845.650(b).

2) New CCR Surface Impoundments. The owner or operator of a new CCR surface impoundment and all lateral expansions of a CCR surface impoundment must submit the information required in subsections (b)(1)(A) through (C) in a construction permit application, and the information required in subsection (b)(1)(D) in an operating permit application.

3) All owners and operators of CCR surface impoundments must:

A) Conduct groundwater monitoring under a monitoring program approved by the Agency under this Subpart;

B) Evaluate the groundwater monitoring data for statistically significant levels over background levels for the constituents listed in Section 845.600 after each sampling event;

C) Determine compliance with the groundwater protection standards in Section 845.600 after each sampling event; and

D) Submit all groundwater monitoring data to the Agency and any analysis performed under subsections (b)(3)(B) and (b)(3)(C) within 60 days after completion of sampling, and place the groundwater monitoring data in the facility's operating record as required by Section 845.800(d)(15).

c) Once the groundwater monitoring system and the groundwater monitoring program have been established at the CCR surface impoundment as required by this Subpart, the owner or operator must conduct groundwater monitoring and, if necessary, corrective action throughout the active life and post-closure care period of the CCR surface impoundment or the time period specified in Section 845.740(b) when closure is by removal.

d) If a CCR surface impoundment has a release, the owner or operator must immediately take all necessary measures to control all sources of the release to reduce or eliminate, to the maximum extent feasible, further releases of contaminants into the environment. The owner or operator of the CCR surface impoundment must comply with all applicable requirements of Sections 845.660, 845.670, and 845.680.

e) Annual Groundwater Monitoring and Corrective Action Report

1) The owner or operator of the CCR surface impoundment must prepare and submit to the Agency an annual groundwater monitoring and corrective action report as a part of the annual consolidated report required by Section 845.550.

2) For the preceding calendar year, the annual report must document the status of the groundwater monitoring and corrective action plan for the CCR surface impoundment, summarize key actions completed, including the status of permit applications and Agency approvals, describe any problems encountered, discuss actions to resolve the problems, and project key activities for the upcoming year.

3) At a minimum, the annual groundwater monitoring and corrective action report must contain the following information, to the extent available:

A) A map, aerial image, or diagram showing the CCR surface impoundment, all background (or upgradient) and downgradient monitoring wells, including the well identification numbers, that are part of the groundwater monitoring program for the CCR surface impoundment, and a visual delineation of any exceedances of the groundwater protection standards;

B) Identification of any monitoring wells that were installed or decommissioned during the preceding year, along with a narrative description of why those actions were taken;

C) A potentiometric surface map for each groundwater elevation sampling event required by Section 845.650(b)(2);

D) In addition to all the monitoring data obtained under this Subpart, a summary including the number of groundwater samples that were collected for analysis for each background and downgradient well, and the dates the samples were collected;

E) A narrative discussion of any statistically significant increases over background levels for the constituents listed in Section 845.600; and

F) Other information required to be included in the annual report as specified in this Subpart.

4) A section at the beginning of the annual report must provide an overview of the current status of groundwater monitoring program and corrective action plan for the CCR surface impoundment. At a minimum, the summary must:

A) Specify whether groundwater monitoring data shows a statistically significant increase over background concentrations for one or more constituents listed in Section 845.600;

B) Identify those constituents having a statistically significant increase over background concentrations and the names of the monitoring wells associated with the increase;

C) Specify whether there have been any exceedances of the groundwater protection standards for one or more constituents listed in Section 845.600;

D) Identify those constituents with exceedances of the groundwater protection standards in Section 845.600 and the names of the monitoring wells associated with the exceedance;

E) Provide the date when the assessment of corrective measures was initiated for the CCR surface impoundment;

F) Provide the date when the assessment of corrective measures was completed for the CCR surface impoundment;

G) Specify whether a remedy was selected under Section 845.670 during the current annual reporting period, and if so, the date of remedy selection; and

H) Specify whether remedial activities were initiated or are ongoing under Section 845.780 during the current annual reporting period.

Section 845.620 Hydrogeologic Site Characterization

a) The owner or operator of the CCR surface impoundment must design and implement a hydrogeologic site characterization.

b) The hydrogeologic site characterization must include, but is not limited to, the following:

1) Geologic well logs/boring logs;

2) Climatic aspects of the site, including seasonal and temporal fluctuations in groundwater flow;

3) Identification of nearby surface water bodies and drinking water intakes;

4) Identification of nearby pumping wells and associated uses of the groundwater;

5) Identification of nearby dedicated nature preserves;

6) Geologic setting;

7) Structural characteristics;

8) Geologic cross-sections;

9) Soil characteristics;

10) Identification of confining layers;

11) Identification of potential migration pathways;

12) Groundwater quality data;

13) Vertical and horizontal extent of the geologic layers to a minimum depth of 100 feet below land surface, including lithology and stratigraphy;

14) A map displaying any known underground mines beneath a CCR surface impoundment;

15) Chemical and physical properties of the geologic layers to a minimum depth of 100 feet below land surface;

16) Hydraulic characteristics of the geologic layers identified as migration pathways and geologic layers that limit migration, including:

    A) Water table depth;

    B) Hydraulic conductivities;

    C) Effective and total porosities;

    D) Direction and velocity of groundwater flow; and

E) Map of the potentiometric surface;

17) Groundwater classification under 35 Ill. Adm. Code 620; and

18) Any other information requested by the Agency that is relevant to the hydrogeologic site characterization.

Section 845.630 Groundwater Monitoring Systems

a) Performance Standard. The owner or operator of a CCR surface impoundment must install a groundwater monitoring system that consists of a sufficient number of wells, installed at appropriate locations and depths, to yield groundwater samples that:

1) Accurately represent the quality of background groundwater that has not been affected by leakage from a CCR surface impoundment. A determination of background quality may include sampling of wells that are not hydraulically upgradient of the CCR management area where:

A) Hydrogeologic conditions do not allow the owner or operator of the CCR surface impoundment to determine what wells are hydraulically upgradient; or

B) Sampling at other wells will provide an indication of background groundwater quality that is demonstratively as representative or more representative than that provided by the upgradient wells; and

2) Accurately represent the quality of groundwater passing the waste boundary of the CCR surface impoundment. The downgradient monitoring system must be installed at the waste boundary that ensures detection of groundwater contamination. All potential contaminant pathways must be monitored.

b) The number, spacing, and depths of monitoring system wells must be determined based upon site-specific technical information identified in the hydrogeologic site characterization conducted under Section 845.620.

c) The groundwater monitoring system must include a sufficient number of monitoring wells necessary to meet the performance standards specified in subsection (a) based on the site-specific information specified in subsection (b). The groundwater monitoring system must contain:

1) A minimum of one upgradient and three downgradient monitoring wells; and

2) Additional monitoring wells as necessary to accurately represent the quality of background groundwater that has not been affected by leakage from the CCR surface impoundment and the quality of groundwater passing the waste boundary of the CCR surface impoundment.

d) Multiunit Groundwater Monitoring System

1) The owner or operator of multiple CCR surface impoundments may install a multiunit groundwater monitoring system instead of separate groundwater monitoring systems for each CCR surface impoundment.

2) The multiunit groundwater monitoring system must be equally as capable of detecting monitored constituents at the waste boundary of the CCR surface impoundment as the individual groundwater monitoring system specified in subsections (a) through (c) for each CCR surface impoundment, based on the following factors:

A) Number, spacing, and orientation of each CCR surface impoundment;

B) Hydrogeologic setting;

C) Site history; and

D) Engineering design of the CCR surface impoundment.

e) Monitoring wells must be properly constructed in a manner consistent with the standards of 77 Ill. Adm. Code 920.170.

1) The owner or operator must document and include in the facility's operating record the design, installation, development, and decommissioning of any monitoring wells, piezometers and other measurement, sampling, and analytical devices. The qualified professional engineer must be given access to this documentation when completing the groundwater monitoring system certification required by subsection (g).

2) The monitoring wells, piezometers, and other measurement, sampling, and analytical devices must be operated and maintained so that they perform to the design specifications throughout the life of the monitoring program.

f) The owner or operator of a new CCR surface impoundment must submit a construction permit application containing documentation showing that the groundwater monitoring system is designed to meet the requirements of this Section. The owner or operator of all CCR surface impoundments must submit an operating permit application containing documentation showing that the groundwater monitoring system has been constructed to meet the requirements of this Section.

g) The owner or operator must obtain a certification from a qualified professional engineer stating that the groundwater monitoring system has been designed and constructed to meet the requirements of this Section. If the groundwater monitoring system includes the minimum number of monitoring wells specified in subsection (c)(1), the certification must document the basis supporting this determination. The certification must be submitted to the Agency with the appropriate permit application.

Section 845.640 Groundwater Sampling and Analysis Requirements

a) The groundwater monitoring program must include consistent sampling and analysis procedures that are designed to ensure monitoring results that provide an accurate representation of groundwater quality at the background and downgradient wells required by Section 845.630. The owner or operator of the CCR surface impoundment must develop a sampling and analysis program that includes procedures and techniques for:

1) Sample collection;

2) Sample preservation and shipment;

3) Analytical procedures;

4) Chain of custody control; and

5) Quality assurance and quality control.

b) The groundwater monitoring program must include sampling and analytical methods that are appropriate for groundwater sampling and that accurately measure constituents and other monitoring parameters in groundwater samples. For purposes of this Subpart, the term "constituent" refers to both constituents and other monitoring parameters listed in Section 845.600.

c) The owner or operator must perform the following each time ground water is sampled:

1) Measure groundwater elevations in each well before purging;

2) Determine the rate and direction of groundwater flow; and

3) Measure groundwater elevations in wells that monitor the same CCR management area within a time period short enough to avoid temporal

variations in groundwater flow that could preclude accurate determination of groundwater flow rate and direction.

d) The owner or operator of the CCR surface impoundment must establish background groundwater quality in a hydraulically upgradient or background well for each of the constituents listed in Section 845.600. Background groundwater quality may be established at wells that are not located hydraulically upgradient from the CCR surface impoundment if it meets the requirements of Section 845.630(a)(1).

e) The number of samples collected when conducting monitoring (for both downgradient and background wells) must be consistent with the statistical procedures chosen under subsection (f) and the performance standards under subsection (g). The sampling procedures must be those specified by Section 845.650(a) through (c).

f) Statistical Methods

1) The owner or operator of the CCR surface impoundment must select one of the statistical methods specified in subsection (f)(1) to be used in evaluating groundwater monitoring data for each specified constituent. The statistical test chosen must be conducted separately for each constituent in each monitoring well.

A) A parametric analysis of variance followed by multiple comparison procedures to identify statistically significant evidence of contamination. The method must include estimation and testing of the contrasts between each compliance well's mean and the background mean levels for each constituent.

B) An analysis of variance based on ranks followed by multiple comparison procedures to identify statistically significant evidence of contamination. The method must include estimation and testing of the contrasts between each compliance well's median and the background median levels for each constituent.

C) A tolerance or prediction interval procedure, in which an interval for each constituent is established from the distribution of the background data and the level of each constituent in each compliance well is compared to the upper tolerance or prediction limit.

D) A control chart approach that gives control limits for each constituent.

E) Another statistical test method that meets the performance standards of subsection (g).

2) The owner or operator of the CCR surface impoundment must obtain a certification from a qualified professional engineer stating that the selected statistical method is appropriate for evaluating the groundwater monitoring data for the CCR surface impoundment. The certification must include a narrative description of the statistical method selected to evaluate the groundwater monitoring data. The certification must be submitted to the Agency with the appropriate permit application.

3) The owner or operator of the CCR surface impoundment must submit the following to the Agency in an operating permit application:

A) Documentation of the statistical method chosen; and

B) The qualified professional engineer certification required by subsection (f)(2).

g) Any statistical method chosen under subsection (f) must comply with the following performance standards, as appropriate, based on the statistical test method used:

1) The statistical method used to evaluate groundwater monitoring data must be appropriate for the distribution of constituents. Normal distributions of data values must use parametric methods. Non-normal distributions must use non-parametric methods. If the distribution of the constituents is shown by the owner or operator of the CCR surface impoundment to be inappropriate for a normal theory test, then the data must be transformed or a distribution-free (non-parametric) theory test must be used. If the distributions for the constituents differ, more than one statistical method may be needed.

2) If an individual well comparison procedure is used to compare an individual compliance well constituent concentration with background constituent concentrations or a groundwater protection standard, the test must be done at a Type I error level of at least 0.01 for each testing period. If a multiple comparison procedure is used, the Type I experiment wise error rate for each testing period must be at least 0.05; however, the Type I error of at least 0.01 for individual well comparisons must be maintained. This performance standard does not apply to tolerance intervals, prediction intervals, or control charts.

3) If a control chart approach is used to evaluate groundwater monitoring data, the specific type of control chart and its associated constituent values must be such that this approach is at least as effective as any other

approach in this Section for evaluating groundwater data. The constituent values must be determined after considering the number of samples in the background database, the data distribution, and the range of the concentration values for each constituent of concern.

4) If a tolerance interval or a prediction interval is used to evaluate groundwater monitoring data, the levels of confidence and, for tolerance intervals, the percentage of the population that the interval must contain, must be such that this approach is at least as effective as any other approach in this Section for evaluating groundwater data. These constituents must be determined after considering the number of samples in the background database, the data distribution, and the range of the concentration values for each constituent of concern.

5) The statistical method must account for data below the limit of detection with one or more statistical procedures at least as effective as any other approach in this Section for evaluating groundwater data. Any practical quantitation limit that is used in the statistical method must be the lowest concentration level that can be reliably achieved within specified limits of precision and accuracy during routine laboratory operating conditions that are available to the facility. For the constituents identified in Section 845.600(a)(1), the practical quantitation limit must be less than the groundwater protection standards.

6) If necessary, the statistical method must include procedures to control or correct for seasonal and spatial variability as well as temporal correlation in the data.

h) The owner or operator of the CCR surface impoundment must determine whether there is a statistically significant increase over background values for each constituent in Section 845.600.

1) In determining whether a statistically significant increase has occurred, the owner or operator must compare the groundwater quality of each constituent at each monitoring well designated under Section 845.630(a)(2) or (d)(1) to the background value of that constituent, according to the statistical procedures and performance standards specified by subsections (f) and (g).

2) Within 60 days after completing sampling and analysis, the owner or operator must determine whether there has been a statistically significant increase over background for any constituent at each monitoring well.

i) The owner or operator must measure total recoverable metals concentrations in measuring groundwater quality. Measurement of total recoverable metals captures both the particulate fraction and dissolved fraction of metals in natural waters. Groundwater samples must not be field filtered before analysis.

j) All groundwater samples taken under this Subpart must be analyzed by a certified laboratory using Test Methods for Evaluating Solid Waste, Physical/Chemical Methods, SW-846, incorporated by reference in Section 845.150.

Section 845.650 Groundwater Monitoring Program

a) The owner or operator of a CCR surface impoundment must conduct groundwater monitoring consistent with this Section. At a minimum, groundwater monitoring must include groundwater monitoring for all constituents with a groundwater protection standard in Section 845.600(a), calcium, and turbidity. The owner or operator of the CCR surface impoundment must submit a groundwater monitoring plan to the Agency with its operating permit application.

b) Monitoring Frequency

1) The monitoring frequency for all constituents with a groundwater protection standard in Section 845.600(a), calcium, and turbidity must be at least quarterly during the active life of the CCR surface impoundment and the post-closure care period or period specified in Section 845.740(b) when closure is by removal except as allowed in subsection (b)(4).

A) For existing CCR surface impoundments, a minimum of eight independent samples from each background and downgradient well must be collected and analyzed for all constituents with a groundwater protection standard listed in Section 845.600(a), calcium, and turbidity within 180 days after April 21, 2021.

B) For new CCR surface impoundments, and all lateral expansions of CCR surface impoundments, a minimum of eight independent samples for each background well and downgradient well must be collected and analyzed for all constituents with a groundwater protection standard listed in Section 845.600(a), calcium, and turbidity during the first 180 days of sampling.

2) The groundwater elevation monitoring frequency must be monthly.

3) Measurement of water elevation within the CCR surface impoundment must be conducted each time the groundwater elevations are measured (see subsection 845.650(b)(2)) before dewatering for closure.

4) After completion of five years of monitoring under this Part, the owner or operator of a CCR surface impoundment may ask the Agency for approval

of a semiannual monitoring frequency by demonstrating all of the following:

A) The groundwater monitoring effectiveness will not be compromised by the reduced frequency of monitoring;

B) Sufficient data has been collected to characterize groundwater;

C) The groundwater monitoring schedule currently does not show any statistically significant increasing trends; and

D) The concentrations of constituents monitored under Section 845.650(a) at the down-gradient monitoring wells are below the applicable groundwater protection standards of Section 845.600.

5) If, after an Agency approval of a semiannual monitoring frequency under subsection (b)(4), a statistically significant increasing trend is detected or an exceedance above the GWPS is detected, the monitoring must revert to a quarterly frequency.

c) The number of samples collected and analyzed for each background well and downgradient well during subsequent quarterly sampling events must be consistent with Section 845.640 and must account for any unique characteristics of the site; but must include at least one sample from each background and downgradient well.

d) If one or more constituents are detected, and confirmed by an immediate resample, to be in exceedance of the groundwater protection standards in Section 845.600 in any sampling event, the owner or operator must notify the Agency which constituent exceeded the groundwater protection standard and place the notification in the facility's operating record as required by Section 845.800(d)(16). The owner or operator of the CCR surface impoundment also must:

1) Characterize the nature and extent of the release and any relevant site conditions that may affect the remedy ultimately selected. The characterization must be sufficient to support a complete and accurate assessment of the corrective measures necessary to effectively clean up all releases from the CCR surface impoundment under Section 845.660. The owner or operator of the CCR surface impoundment must submit the characterization to the Agency and place the characterization in the facility's operating record as required by Section 845.800(d)(16). Characterization of the release includes the following minimum measures:

A) Install additional monitoring wells necessary to define the contaminant plumes;

B) Collect data on the nature and estimated quantity of material released, including specific information on the constituents listed in Section 845.600 and the levels at which they are present in the material released;

C) Install at least one additional monitoring well at the facility boundary in the direction of contaminant migration and sample this well in accordance with subsections (a) and (b); and

D) Sample all wells in accordance with subsections (a) and (b) to characterize the nature and extent of the release.

2) Notify all persons who own the land or reside on the land that directly overlies any part of the plume of contamination if contaminants have migrated off-site as indicated by sampling of wells in accordance with subsection (d)(1). The owner or operator must send notifications made under this subsection (d)(2) to the Agency and place the notifications in the facility's operating record (see Section 845.800(d)(16)).

3) Except as provided in subsection (e), within 90 days after the detected exceedance of the groundwater protection standard, initiate an assessment of corrective measures (see Section 845.660).

e) Alternative Source Demonstration (ASD). The owner or operator of a CCR surface impoundment may, within 60 days after the detected exceedance of the groundwater protection standard, submit a demonstration to the Agency that a source other than the CCR surface impoundment caused the contamination and the CCR surface impoundment did not contribute to the contamination, or that the exceedance of the groundwater protection standard resulted from error in sampling, analysis, statistical evaluation, natural variation in groundwater quality, or a change in the potentiometric surface and groundwater flow direction. Either type of ASD must include a report that contains the factual or evidentiary basis for any conclusions and a certification of accuracy by a qualified professional engineer.

1) The owner or operator must place the ASD on the facility's publicly accessible Internet site (CCR website) under Section 845.810 within 24 hours after the submission to the Agency.

2) Within two business days after receiving the ASD, the Agency must email a notice to its listserv for the facility that the ASD is available to view on the facility's CCR website.

3) Members of the public may submit to the Agency written comments on the ASD within 14 days after the Agency provides notice under subsection (e)(2).

4) The Agency must provide a written response to the owner and operator either concurring or not concurring with the ASD within 30 days after receiving the ASD. The Agency must also mail or email its response to each person who timely submitted a written public comment under subsection (e)(3) and supplied a mailing or email address.

5) If the Agency concurs with the ASD, the owner or operator must continue monitoring as required by this Section. The owner or operator must also include the ASD in the annual groundwater monitoring and corrective action report required by Section 845.610(e).

6) If the Agency does not concur with the ASD, the owner or operator must initiate the assessment of corrective measures under Section 845.660.

7) If the Agency does not concur with the ASD, the owner or operator may petition the Board for review of the Agency's non-concurrence under 35 Ill. Adm. Code 105. The filing of a petition for review under subsection (e)(7) does not automatically stay any requirements of this Part as to the owner or operator, including the 90-day deadline to initiate an assessment of corrective measures (see Section 845.660(a)(1)).

Section 845.660 Assessment of Corrective Measures

a) Unless the Agency has concurred with an alternative source demonstration made under Section 845.650(e), the owner or operator must initiate an assessment of corrective measures to prevent further releases, to remediate any releases, and to restore the affected area.

1) The assessment of corrective measures must be initiated within 90 days after finding that any constituent listed in Section 845.600 has been detected in exceedance of the groundwater protection standards in Section 845.600, at the downgradient waste boundary or immediately upon detection of a release of CCR from a CCR surface impoundment.

2) The assessment of corrective measures must be completed and submitted to the Agency within 90 days after initiation of assessment of corrective measures, unless the owner or operator demonstrates to the Agency the need for additional time to complete the assessment of corrective measures due to site-specific conditions or circumstances. The owner or operator must submit this demonstration, along with a certification from a qualified professional engineer attesting that the demonstration is accurate, to the Agency within 60 days after initiating an assessment of corrective

measures. The Agency must either approve or disapprove the demonstration within 30 days. The 90-day deadline to complete the assessment of corrective measures may be extended for no longer than 60 days. The owner or operator must also include the Agency approved demonstration in the annual groundwater monitoring and corrective action report required by Section 845.610(e), in addition to the certification by a qualified professional engineer.

b) The owner or operator of the CCR surface impoundment must continue to monitor groundwater in accordance with the monitoring program as specified in Section 845.650.

c) The assessment under subsection (a) must include an analysis of the effectiveness of potential corrective measures in meeting all the requirements and objectives of the corrective action plan, as described by Section 845.670, addressing at least the following:

1) The performance, reliability, ease of implementation, and potential impacts of appropriate potential remedies, including safety impacts, cross-media impacts, and control of exposure to any residual contamination;

2) The time required to begin and complete the corrective action plan; and

3) The institutional requirements, such as State or local permit requirements or other environmental or public health requirements that may substantially affect implementation of the corrective action plan.

d) The owner or operator of the CCR surface impoundment must discuss the results of the corrective measures assessment, at least 30 days before the selection of remedy, in a public meeting with interested and affected parties (see Section 845.240).

e) When the owner or operator of a CCR surface impoundment is completing closure and corrective action simultaneously, the owner or operator may combine the corrective measures assessment required by this Section and the closure alternatives analysis required by Section 845.710 into one assessment of alternatives.

Section 845.670 Corrective Action Plan

a) The owner or operator must prepare a semi-annual report describing the progress in selecting a remedy and developing a corrective action plan. The semi-annual report must be submitted to the Agency and placed in the operating record as required by Section 845.800(d)(17).

b) Within one year after completing the assessment of corrective measures as specified in Section 845.660, and after completion of the public meeting in Section 845.660(d), the owner or operator of the CCR surface impoundment must submit, in a construction permit application to the Agency, a corrective action plan that identifies the selected remedy. This requirement applies in addition to, not in place of, any applicable standards under any other State or federal law.

c) The corrective action plan must meet the following requirements:

1) Be based on the results of the corrective measures assessment conducted under Section 845.660;

2) Identify a selected remedy that at a minimum, meets the standards listed in subsection (d);

3) Contain the corrective action alternatives analysis specified in subsection (e); and

4) Contain proposed schedules for implementation, including an analysis of the factors in subsection (f);

d) The selected remedy in the corrective action plan must:

1) Be protective of human health and the environment;

2) Attain the groundwater protection standards specified in Section 845.600;

3) Control the sources of releases to reduce or eliminate, to the maximum extent feasible, further releases of constituents listed in Section 845.600 into the environment;

4) Remove from the environment as much of the contaminated material that was released from the CCR surface impoundment as is feasible, taking into account factors such as avoiding inappropriate disturbance of sensitive ecosystems; and

5) Comply with standards for management of wastes as specified in Section 845.680(d).

e) Corrective Action Alternatives Analysis. In selecting a remedy that meets the standards of subsection (d), the owner or operator of the CCR surface impoundment must consider the following evaluation factors:

1) The long- and short-term effectiveness and protectiveness of each potential remedy, along with the degree of certainty that the remedy will prove successful based on consideration of the following:

A) Magnitude of reduction of existing risks;

B) Magnitude of residual risks in terms of likelihood of further releases due to CCR remaining following implementation of a remedy;

C) The type and degree of long-term management required, including monitoring, operation, and maintenance;

D) Short-term risks that might be posed to the community or the environment during implementation of a remedy, including potential threats to human health and the environment associated with excavation, transportation, and re-disposal of contaminants;

E) Time until groundwater protection standards in Section 845.600 are achieved;

F) The potential for exposure of humans and environmental receptors to remaining wastes, considering the potential threat to human health and the environment associated with excavation, transportation, re-disposal, containment, or changes in groundwater flow;

G) The long-term reliability of the engineering and institutional controls, including an analysis of any off-site, nearby destabilizing activities; and

H) Potential need for replacement of the remedy.

2) The effectiveness of the remedy in controlling the source to reduce further releases based on consideration of each of the following potential factors:

A) The extent to which containment practices will reduce further releases; and

B) The extent to which treatment technologies may be used.

3) The ease or difficulty of implementing each potential remedy based on consideration of the following types of factors:

A) Degree of difficulty associated with constructing the technology;

B) Expected operational reliability of the technologies;

C) Need to coordinate with and obtain necessary approvals and permits from other agencies;

D) Availability of necessary equipment and specialists; and

E) Available capacity and location of needed treatment, storage, and disposal services.

4) The degree to which community concerns are addressed by each potential remedy.

f) The owner or operator must specify, as part of the corrective action plan, a schedule for implementing, of and completing, remedial activities. The schedule must require the completion of remedial activities within a reasonable time, taking into consideration the factors in this subsection (f). The owner or operator of the CCR surface impoundment must consider the following factors in determining the schedule of remedial activities:

1) Extent and nature of contamination, as determined by the characterization required under Section 845.650(d);

2) Reasonable probabilities of remedial technologies achieving compliance with the groundwater protection standards established by Section 845.600 and other objectives of the remedy;

3) Availability of treatment or disposal capacity for CCR managed during implementation of the remedy;

4) Potential risks to human health and the environment from exposure to contamination before completion of the remedy;

5) Resource value of the aquifer, including:

A) Current and future uses, including potential residential, agricultural, commercial industrial and ecological uses;

B) Proximity and withdrawal rate of users;

C) Groundwater quantity and quality;

D) The potential impact to the subsurface ecosystem, wildlife, other natural resources, crops, vegetation, and physical structures caused by exposure to CCR constituents;

E) The hydrogeologic characteristic of the facility and surrounding land; and

F) The availability of alternative water supplies; and

6) Other relevant factors.

Section 845.680 Implementation of the Corrective Action Plan

a) Within 90 days after the Agency's approval of the corrective action plan submitted under Section 845.670, the owner or operator must initiate corrective action. Based on the schedule approved by the Agency for implementation and completion of corrective action, the owner or operator must:

1) Establish and implement a corrective action groundwater monitoring program that:

A) At a minimum, meets the requirements of the monitoring program under Section 845.650;

B) Documents the effectiveness of the corrective action remedy; and

C) Demonstrates compliance with the groundwater protection standard under subsection (c).

2) Implement the corrective action remedy approved by the Agency under Section 845.670; and

3) Take any interim measures necessary to reduce the contaminants leaching from the CCR surface impoundment, and/or potential exposures to human or ecological receptors. Interim measures must, to the greatest extent feasible, be consistent with the objectives of, and contribute to the performance of, any remedy that may be required by Section 845.670. The following factors must be considered by an owner or operator in determining whether interim measures are necessary:

A) Time required to develop and implement a final remedy;

B) Actual or potential exposure of nearby populations or environmental receptors to any of the constituents listed in Section 845.600;

C) Actual or potential contamination of sensitive ecosystems or current or potential drinking water supplies;

D) Further degradation of the groundwater that may occur if remedial action is not initiated expeditiously;

E) Weather conditions that may cause any of the constituents listed in Section 845.600 to migrate or be released;

F) Potential for exposure to any of the constituents listed in Section 845.600 as a result of an accident or failure of a container or handling system; and

G) Other situations that may pose threats to human health and the environment.

b) If the Agency or an owner or operator of the CCR surface impoundment determines, at any time, that compliance with the requirements of Section 845.670(d) is not being achieved through the remedy selected, the owner or operator must implement other methods or techniques that could feasibly achieve compliance with the requirements. These methods or techniques must receive approval by the Agency before implementation.

c) Corrective action must be considered complete when:

1) The owner or operator of the CCR surface impoundment demonstrates compliance with the groundwater protection standards established by Section 845.600 has been achieved at all points within the plume of contamination that lies beyond the waste boundary;

2) Compliance with the groundwater protection standards has been achieved by demonstrating that concentrations of constituents listed in Section 845.600 have not exceeded the groundwater protection standards for a period of three consecutive years, using the statistical procedures and performance standards in Section 845.640(f) and (g); and

3) All actions required to complete the remedy have been satisfied.

d) All CCR managed under a remedy approved by the Agency under Section 845.670, or an interim measure required under subsection (a)(3), must be managed in a manner that complies with this Part.

e) Upon completion of the corrective action plan, the owner or operator must submit to the Agency a corrective action completion report and certification.

1) The corrective action completion report must contain supporting documentation, including:

A) Any engineering and hydrogeology reports, including, monitoring well completion reports and boring logs, all CQA reports, certifications, and designations of CQA officers-in-absentia required by Section 845.290;

B) A written summary of the implementation of the corrective action plan as stated in the construction permit and this Part;

C) Groundwater monitoring data demonstrating compliance with subsection (c);

D) Any remedial actions completed under subsection(d);

E) Documentation showing compliance with the selected remedy requirements of Section 845.670(b); and

F) Any other information relied upon by the qualified professional engineer in making the closure certification.

2) The corrective action completion certification must include a statement from a qualified professional engineer attesting that the corrective action plan has been completed in compliance with the requirements of subsection (c).

3) The owner or operator must place the corrective action completion report and certification in the facility's operating record as required by Section 845.800(d)(18).

SUBPART G: CLOSURE AND POST-CLOSURE CARE

Section 845.700 Required Closure or Retrofit of CCR Surface Impoundments

a) Required Closure. The owner or operator of the following CCR surface impoundments must stop placing CCR or non-CCR waste streams in the CCR surface impoundment and must initiate closure of the CCR surface impoundment:

1) An existing CCR surface impoundment that has not demonstrated compliance with any of the following location restrictions:

A) Uppermost aquifer location (see Section 845.300);

B) Wetlands (see Section 845.310);

C) Fault areas (see Section 845.320);

D) Seismic impact zones (see Section 845.330); or

E) Unstable areas and floodplains (see Section 845.340).

2) The owner or operator of any CCR surface impoundment that has failed to complete the initial or any subsequent annual safety factor assessment required by Section 845.460 or that has failed to document the calculated factors of safety for the CCR surface impoundment to achieve the minimum safety factors specified in Section 845.460(a).

b) Required Closure or Retrofit. The owner or operator of an existing unlined CCR surface impoundment, as determined under Section 845.400(f), must stop placing CCR and non-CCR waste streams into that CCR surface impoundment and either retrofit or close the CCR surface impoundment in accordance with the requirements of Subpart G. The owner or operator of a CCR surface impoundment electing to retrofit must submit, in accordance with the schedule in subsection (h), the written preliminary retrofit plan under subsection 845.770(a)(3) and a construction permit application to retrofit under Section 845.770;

c) Beginning on April 21, 2021, the owner or operator of the CCR surface impoundment required to close under subsection (a), or electing to close under subsection (b), must immediately take steps to categorize the CCR surface impoundment under subsection (g) and to comply with the closure alternatives analysis requirements in Section 845.710. Within 30 days after April 21, 2021, the owner or operator must send the category designation, including a justification for the category designation, for each CCR surface impoundment to the Agency for review. The owner or operator of the CCR surface impoundment must submit a construction permit application containing a final closure plan under the schedule in subsection (h).

d) Timeframes for Closure

1) Except as provided in subsection (d)(2), the owner or operator must stop placing CCR and non-CCR waste streams in the impoundment and initiate closure within six months after failing to complete any of the demonstrations listed in subsection (a).

2) For CCR surface impoundments required to close under subsection (a)(1) or electing to close under subsection (b):

A) If, on April 21, 2021, the owner or operator of a CCR surface impoundment has not satisfied an alternative closure requirement of 40 CFR 257.103 that allows for the continued receipt of CCR or non-CCR waste streams, the owner or operator must not place CCR or non-CCR waste streams into the CCR surface impoundment after April 21, 2021.

B) If, by November 30, 2020, the owner or operator of a CCR surface impoundment has submitted a complete demonstration to USEPA seeking an alternative deadline to stop receiving waste or complete closure under 40 CFR 257.103(f), the deadline to stop receiving waste will be tolled until USEPA issues a decision. If USEPA determines that a submission is incomplete, an owner or operator must immediately stop receiving waste and comply with all applicable deadlines of Section 845.700(d)(1).

C) If USEPA disapproves the requested alternative deadline to stop receiving waste and complete closure, the owner or operator of the CCR surface impoundment must immediately stop receiving waste and initiate closure within six months after the USEPA denial of the extension and will be subject to Section 845.760(a).

D) If, USEPA approves a demonstration that alternative disposal capacity is infeasible under 40 CFR 257.103(f)(1), the owner or operator must stop placing CCR or non-CCR waste streams into the CCR surface impoundment by the end of the initial time extension approved under 40 CFR 257.103 or once alternative capacity becomes available, whichever is sooner. In no case may the owner or operator of the CCR surface impoundment place CCR or non-CCR waste streams into an eligible CCR surface impoundment after October 15, 2024, or into any other CCR surface impoundment subject to closure under Section 845.700(a) or (b) after October 15, 2023.

E) If USEPA approves a demonstration for permanent cessation of coal-fired power boilers by a certain date under 40 CFR 257.103(f)(2), the owner or operator must:

  i) For CCR surface impoundments that are 40 acres or smaller, stop operation of the coal-fired boiler and complete closure by October 17, 2023; or

  ii) For CCR surface impoundments that are larger than 40 acres, stop operation of the coal-fired boiler and complete closure by October 17, 2028.

F) The USEPA's decision to approve or deny the demonstration requesting an alternative deadline to initiate closure must, within 30 days be submitted to the Agency and placed in the facility’s operating record as required by Section 845.800(d)(19).

G) Failure to remain in compliance with any of the requirements of this Part will result in the automatic loss of authorization under subsections (d)(2)(D) and (d)(2)(E).

H) The owner or operator of the CCR surface impoundment with a USEPA-approved extension will not be given extensions of the timeframes for completion of closure under Section 845.760(c).

e) Semi-Annual Reports. The owner or operator of a CCR surface impoundment closing under the time frames in subsections (d)(2)(B) and (d)(2)(C) must prepare semi-annual reports consistent with the requirements in 40 CFR 257.103(f)(1)(x), incorporated by reference in Section 845.150, until the owner or operator has initiated closure.

f) An owner or operator of a CCR surface impoundment required to close under this Section must prepare the notification required under Section 845.730(d) that the CCR surface impoundment is closing under this Section.

g) Closure Prioritization

1) The owner or operator of a CCR surface impoundment required to close under this Section must assign the CCR surface impoundment to one of the following categories. Category 1 has the highest priority for closure. Category 7 has the lowest priority for closure.

A) Category 1 includes CCR surface impoundments that have impacted an existing potable water supply well or that have impacted groundwater quality within the setback of an existing potable water supply well.

B) Category 2 includes CCR surface impoundments that are an imminent threat to human health or the environment or have been designated by the Agency under subsection (g)(5).

C) Category 3 includes CCR surface impoundments located in areas of environmental justice concern, as determined by the Agency under subsection (g)(6).

D) Category 4 includes inactive CCR surface impoundments that have an exceedance of the groundwater protection standards in Section 845.600.

E) Category 5 includes existing CCR surface impoundments that have exceedances of the groundwater protection standards in Section 845.600.

F) Category 6 includes inactive CCR surface impoundments that are in compliance with the groundwater protection standards in Section 845.600.

G) Category 7 includes existing CCR surface impoundments that are in compliance with the groundwater protection standards in Section 845.600.

2) If a CCR surface impoundment can be categorized in more than one category, the owner or operator of the CCR surface impoundment must assign the CCR surface impoundment the highest priority category.

3) Whenever an owner or operator of a CCR surface impoundment has more than one CCR surface impoundment that must close under this Section, the owner or operator must close the CCR surface impoundments in order of priority.

4) If the CCR surface impoundment meets the criteria for Category 1, the owner or operator must take immediate steps to mitigate the impact to any existing potable water supply. The owner or operator of the CCR surface impoundment, must act to replace the water supply with a supply of equal or better quality and quantity within 30 days after notice that the impact has occurred.

5) The Agency may designate a CCR surface impoundment as a Category 2 surface impoundment when:

A) The CCR surface impoundment has failed to document that the calculated factors of safety for the CCR surface impoundment achieve the minimum safety factors specified in Section 845.460(a);

B) The CCR surface impoundment has not demonstrated compliance with the location restrictions in Subpart C;

C) The owner or operator has been enjoined under Section 43 of the Act;

D) An exceedance of the groundwater protection standards in Section 845.600 has migrated off-site; or

E) The Agency finds that an emergency condition exists creating an immediate danger to public health or welfare, or the environment.

6) For purposes of, and only for, this Part, areas of environmental justice concern are identified as any area that meets either of the following:

A) Any area within one mile of a census block group where the number of low-income persons is twice the statewide average, where low income means the number or percent of a census block group's population in households where the household income is less than or equal to twice the federal poverty level; or

B) Any area within one mile of a census block group where the number of minority persons is twice the statewide average, where minority means the number or percent of individuals in a census block group who list their racial status as a race other than white alone or list their ethnicity as Hispanic or Latino.

7) For purposes of subsection (g)(6), if any part of a facility falls within one mile of the census block group, the entire facility, including all its CCR surface impoundments, must be considered an area of environmental justice concern.

8) The Agency may designate a CCR surface impoundment as another Category when site-specific conditions contradict the designations provided by the owner or operator in subsection (c) and the categories in subsection (g)(1).

h) Application Schedule

1) Category 1, Category 2, Category 3, and Category 4 CCR surface impoundment owners or operators must submit either a construction permit application containing a final closure plan or a construction permit application to retrofit the CCR surface impoundment in accordance with the requirements of this Part by February 1, 2022.

2) Category 5 CCR surface impoundment owners or operators must submit either a construction permit application containing a final closure plan or a construction permit application to retrofit the CCR surface impoundment in accordance with the requirements of this Part by August 1, 2022.

3) Category 6 and Category 7 CCR surface impoundment owners or operators must submit either a construction permit application containing a final closure plan or a construction permit application to retrofit the CCR surface impoundment in accordance with the requirements of this Part by August 1, 2023.

4) Owners or operators consolidating one or more CCR surface impoundments for closure must meet the application schedule of the highest priority CCR surface impoundment.

5) If the Agency denies a construction permit application submitted under this Section, the owner and operator must submit a revised construction permit application addressing all deficiencies identified by the Agency. The revised construction permit application for closure must be submitted

to the Agency within 90 days after the Agency's denial if the Agency's denial is not appealed under Section 845.270. If the Agency's denial is appealed and upheld, the owner or operator must submit a revised construction permit application for closure within 90 days after a final decision by the Board is rendered. The owner or operator of the CCR surface impoundment must discuss the owner's or operator's proposed response to all deficiencies identified by the Agency in a public meeting with interested and affected parties held under Section 845.240.

Section 845.710 Closure Alternatives

a) Closure of a CCR surface impoundment, or any lateral expansion of a CCR surface impoundment, must be completed either by leaving the CCR in place and installing a final cover system or through removal of the CCR and decontamination of the CCR surface impoundment, as described in Sections 845.720 through 845.760.

b) Before selecting a closure method, the owner or operator of each CCR surface impoundment must complete a closure alternatives analysis. The closure alternatives analysis must examine the following for each closure alternative:

1) The long- and short-term effectiveness and protectiveness of the closure method, including identification and analyses of the following factors:

A) The magnitude of reduction of existing risks;

B) The magnitude of residual risks in terms of likelihood of future releases of CCR;

C) The type and degree of long-term management required, including monitoring, operation, and maintenance;

D) The short-term risks that might be posed to the community or the environment during implementation of a closure, including potential threats to human health and the environment associated with excavation, transportation, and re-disposal of contaminants;

E) The time until closure and post-closure care or the completion of groundwater monitoring under Section 845.740(b) is completed;

F) The potential for exposure of humans and environmental receptors to remaining wastes, considering the potential threat to human health and the environment associated with excavation, transportation, re-disposal, containment or changes in groundwater flow;

G) The long-term reliability of the engineering and institutional controls, including an analysis of any off-site, nearby destabilizing activities; and

H) Potential need for future corrective action of the closure alternative.

2) The effectiveness of the closure method in controlling future releases based on analyses of the following factors:

A) The extent to which containment practices will reduce further releases; and

B) The extent to which treatment technologies may be used.

3) The ease or difficulty of implementing a potential closure method based on analyses of the following types of factors:

A) Degree of difficulty associated with constructing the technology;

B) Expected operational reliability of the technologies;

C) Need to coordinate with and obtain necessary approvals and permits from other agencies;

D) Availability of necessary equipment and specialists; and

E) Available capacity and location of needed treatment, storage, and disposal services.

4) The degree to which the concerns of the residents living within communities where the CCR will be handled, transported and disposed of are addressed by the closure method.

c) In the closure alternatives analysis, the owner or operator of the CCR surface impoundment must:

1) Analyze complete removal of the CCR as one closure alternative, along with the modes for transporting the removed CCR, including by rail, barge, low-polluting trucks, or a combination of these transportation modes;

2) Identify whether the facility has an onsite landfill with remaining capacity that can legally accept CCR, and, if not, whether constructing an onsite landfill is possible; and

3) Include any other closure method in the alternatives analysis if requested by the Agency.

d) The analysis for each alternative completed under this Section must:

1) Meet or exceed a class 4 estimate under the AACE Classification Standard, incorporated by reference in Section 845.150, or a comparable classification practice as provided in the AACE Classification Standard;

2) Contain the results of groundwater contaminant transport modeling and calculations showing how the closure alternative will achieve compliance with the applicable groundwater protection standards;

3) Include a description of the fate and transport of contaminants with the closure alternative over time, including consideration of seasonal variations; and

4) Assess impacts to waters in the State.

e) At least 30 days before submission of a construction permit application for closure, the owner or operator of the CCR surface impoundment must discuss the results of the closure alternatives analysis in a public meeting with interested and affected parties (see Section 845.240).

f) After completion of the public meeting under subsection (e), the owner or operator of a CCR surface impoundment must select a closure method and submit a final closure plan to the Agency under Section 845.720(b). All materials demonstrating completion of the closure alternatives analysis specified in this Section must be submitted with the final closure plan.

g) The selected closure method must meet the requirements and standards of this Part, ensure the protection of human health and the environment, and achieve compliance with the groundwater protection standards in Section 845.600.

Section 845.720 Closure Plan

a) Preliminary Written Closure Plan

1) Content of the Preliminary Closure Plan. The owner or operator of a new CCR surface impoundment or an existing CCR surface impoundment not required to close under Section 845.700 must prepare a preliminary written closure plan that describes the steps necessary to close the CCR surface impoundment at any point during the active life of the CCR surface impoundment consistent with recognized and generally accepted engineering practices. The preliminary written closure plan must include, at a minimum, the following:

A) A narrative description of how the CCR surface impoundment will be closed in accordance with this Part.

B) If closure of the CCR surface impoundment will be accomplished through removal of CCR from the CCR surface impoundment, a description of the procedures to remove the CCR and decontaminate the CCR surface impoundment in accordance with Section 845.740.

C) If closure of the CCR surface impoundment will be accomplished by leaving CCR in place, a description of the final cover system, designed in accordance with Section 845.750, and the methods and procedures to be used to install the final cover. The closure plan must also discuss how the final cover system will achieve the performance standards specified in Section 845.750.

D) An estimate of the maximum inventory of CCR ever on-site over the active life of the CCR surface impoundment.

E) An estimate of the largest area of the CCR surface impoundment ever requiring a final cover (see Section 845.750), at any time during the CCR surface impoundment's active life.

F) A schedule for completing all activities necessary to satisfy the closure criteria in this Section, including an estimate of the year in which all closure activities for the CCR surface impoundment will be completed. The schedule should provide sufficient information to describe the sequential steps that will be taken to close the CCR surface impoundment, including identification of major milestones such as coordinating with and obtaining necessary approvals and permits from other agencies, the dewatering and stabilization phases of CCR surface impoundment closure, or installation of the final cover system, and the estimated timeframes to complete each step or phase of CCR surface impoundment closure. When preparing the preliminary written closure plan, if the owner or operator of a CCR surface impoundment estimates that the time required to complete closure will exceed the timeframes specified in Section 845.760(a), the preliminary written closure plan must include the site-specific information, factors and considerations that would support any time extension sought under Section 845.760(b).

2) The owner or operator of the CCR surface impoundment must submit the preliminary written closure plan to the Agency with its initial operating permit application. The owner or operator of the CCR surface

impoundment must submit the most recently amended preliminary closure plan to the Agency with each operating permit renewal application. The owner or operator must place preliminary and amended preliminary written closure plans in the facility's operating record as required by Section 845.800(d)(20).

3) Amendment of a Preliminary Written Closure Plan.

A) The owner or operator may amend the preliminary written closure plan at any time.

B) The owner or operator must amend the preliminary written closure plan whenever:

i) There is a change in the operation of the CCR surface impoundment that would substantially affect the written closure plan in effect; or

ii) Before closure activities have started, unanticipated events necessitate a revision of the written closure plan.

C) The owner or operator must amend the closure plan at least 60 days before a planned change in the operation of the facility or CCR surface impoundment, or within 60 days after an unanticipated event requires the need to revise an existing written closure plan.

4) The owner or operator of the CCR surface impoundment must obtain and submit with its initial and renewal operating permit applications a written certification from a qualified professional engineer that the initial and any amendment of the preliminary written closure plan meets the requirements of this Part.

b) Final Closure Plan

1) The owner or operator of a CCR surface impoundment must submit to the Agency, as a part of a construction permit application for closure, a final closure plan. The plan must be submitted before the installation of a final cover system or removal of CCR from the surface impoundment for the purpose of closure.

2) Except as otherwise provided in Section 22.59 of the Act, the owner or operator of a CCR surface impoundment must not close a CCR surface impoundment without a construction permit issued under this Part.

3) The final closure plan must identify the proposed selected closure method, and must include the information required in subsection (a)(1) and the closure alternatives analysis specified in Section 845.710.

4) If a final written closure plan revision is necessary after closure activities have started for a CCR surface impoundment, the owner or operator must submit a request to modify the construction permit within 60 days following the triggering event.

5) The owner or operator of the CCR surface impoundment must obtain and submit with its construction permit application for closure a written certification from a qualified professional engineer that the final written closure plan meets the requirements of this Part.

Section 845.730 Initiation of Closure

Initiation of closure activities. Except as provided for in this Section, the owner or operator of a CCR surface impoundment must initiate closure of the CCR surface impoundment within the applicable timeframes specified in either subsection (a) or (b). For purposes of this Section, closure of the CCR surface impoundment has been initiated if the owner or operator has stopped placing waste in the CCR surface impoundment and has submitted to the Agency a construction permit application under Section 845.220(d).

a) Known Final Receipt. The owner or operator must initiate closure of the CCR surface impoundment within 30 days after the date on which the CCR surface impoundment either:

1) Receives the known final placement of waste, either CCR or any non-CCR waste stream; or

2) Removes the known final volume of CCR from the CCR surface impoundment for the purpose of beneficial use of CCR.

b) Temporarily Idled CCR Surface Impoundments.

1) Except as provided by subsection (b)(2), the owner or operator must initiate closure of a CCR surface impoundment that has not received CCR or any non-CCR waste stream, or is no longer removing CCR for the purpose of beneficial use, within two years after the last receipt of waste or within two years after the last removal of CCR material for the purpose of beneficial use.

2) Notwithstanding subsection (b)(1), the owner or operator of the CCR surface impoundment may secure an additional two years to initiate closure of the idle surface impoundment if the Agency approves the owner's or operator's written demonstration that the CCR surface

impoundment will continue to accept wastes or will start removing CCR for the purpose of beneficial use. The documentation must be supported by, at a minimum, the information specified in this subsection (b)(2). The owner or operator may obtain two-year extensions, provided the owner or operator continues to be able to demonstrate that there is reasonable likelihood that the CCR surface impoundment will accept wastes in the foreseeable future or will remove CCR from the surface impoundment for the purpose of beneficial use. The owner or operator must place each Agency approved demonstration, if more than one time extension is sought, in the facility's operating record as required by Section 845.800(d)(21) before the end of any two-year period.

A) Information documenting that the CCR surface impoundment has remaining storage or disposal capacity or that the CCR surface impoundment can have CCR removed for the purpose of beneficial use; and

B) Information demonstrating that that there is a reasonable likelihood that the CCR surface impoundment will resume receiving CCR or non-CCR waste streams in the foreseeable future or that CCR can be removed for the purpose of beneficial use. The narrative must include a best estimate as to when the CCR surface impoundment will resume receiving CCR or non-CCR waste streams. The situations listed in this subsection (b)(2)(B) are examples of situations that would support a determination that the CCR surface impoundment will resume receiving CCR or non-CCR waste streams in the foreseeable future.

  i) Normal plant operations include periods during which the CCR surface impoundment does not receive CCR or non-CCR waste streams, such as the alternating use of two or more CCR surface impoundments whereby, at any point in time, one CCR surface impoundment is receiving CCR while CCR is being removed from a second CCR surface impoundment after its dewatering.

  ii) The CCR surface impoundment is dedicated to a coal-fired boiler surface impoundment that is temporarily idled (e.g., CCR is not being generated) and there is a reasonable likelihood that the coal-fired boiler will resume operations in the future.

  iii) The CCR surface impoundment is dedicated to an operating coal-fired boiler (i.e., CCR is being generated); however, no CCR is being placed in the CCR surface impoundment because the CCR is being entirely diverted to beneficial uses, but there is a reasonable likelihood that the CCR surface impoundment will again be used in the foreseeable future.

iv) The CCR surface impoundment currently receives only non-CCR waste streams and those non-CCR waste streams are not generated for an extended period of time, but there is a reasonable likelihood that the CCR surface impoundment will again receive non-CCR waste streams in the future.

3) In order to obtain additional time extensions to initiate closure of a CCR surface impoundment beyond the two years provided by subsection (b)(1), the owner or operator of the CCR surface impoundment must submit the demonstration required by subsection (b)(2) to the Agency for review and approval. The written documentation must include the following statement signed by the owner or operator or an authorized representative:

> I certify under penalty of law that I have personally examined and am familiar with the information submitted in this demonstration and all attached documents, and that, based on my inquiry of those individuals immediately responsible for obtaining the information, I believe that the submitted information is true, accurate, and complete. I am aware that there are significant penalties for submitting false information, including the possibility of fine and imprisonment.

c) The timeframes specified in subsections (a) and (b) do not apply to an owner or operator of a CCR surface impoundment closing the CCR surface impoundment as required by Section 845.700:

d) By the date the owner or operator initiates closure of a CCR surface impoundment, the owner or operator must prepare a notification of intent to close a CCR surface impoundment. The notification must be placed in the facility's operating record as required by Section 845.800(d)(21).

Section 845.740 Closure by Removal

a) Closure by Removal of CCR. An owner or operator may elect to close a CCR surface impoundment by removing all CCR and decontaminating all areas affected by releases of CCR from the CCR surface impoundment. CCR removal and decontamination of the CCR surface impoundment are complete when all CCR and CCR residues, containment system components such as the impoundment liner and contaminated subsoils, and CCR impoundment structures and ancillary equipment have been removed. Closure by removal must be completed before the completion of a groundwater corrective action under Subpart F.

b) After closure by removal has been completed, the owner or operator must continue groundwater monitoring under Subpart F for three years after the completion of closure or for three years after groundwater monitoring does not show an exceedance of the groundwater protection standard established under Section 845.600, whichever is longer.

c) The owner or operator of a CCR surface impoundment removing CCR during closure must responsibly handle and transport the CCR consistent with this subsection.

1) Transportation

A) Manifests

i) When transporting CCR off-site by motor vehicle, manifests must be carried as specified in 35 Ill. Adm. Code 809. For purposes of this Part, coal combustion fly ash that is removed from a CCR surface impoundment is not exempt from the manifest requirement.

ii) When transporting CCR off-site by any other mode or method, including trains or barges, manifests must be carried specifying, at a minimum, the following information: the volume of the CCR; the location from which the CCR was loaded onto the mode of transportation and the date the loading took place; and the location where the CCR is being taken and the date it will be delivered.

B) The owner or operator of a CCR surface impoundment from which CCR is removed and transported off-site must develop a CCR transportation plan, which must include:

i) Identification of the transportation method selected, including whether a combination of transportation methods will be used;

ii) The frequency, time of day, and routes of CCR transportation;

iii) Any measures to minimize noise, traffic, and safety concerns caused by the transportation of the CCR;

iv) Measures to limit fugitive dust from any transportation of CCR;

v) Installation and use of a vehicle washing station;

vi) A means of covering the CCR for any mode of CCR transportation, including conveyor belts; and

vii) A requirement that, for transport by motor vehicle, the CCR is transported by a permitted special waste hauler under 35 Ill. Adm. Code 809.201.

2) The owner or operator of a CCR surface impoundment must develop and implement onsite dust controls, which must include:

A) A water spray or other commercial dust suppressant to suppress dust in CCR handling areas and haul roads; and

B) Handling of CCR to minimize airborne particulates and offsite particulate movement during any weather event or condition.

3) The owner or operator of a CCR surface impoundment must provide the following public notices:

A) Signage must be posted at the property entrance warning of the hazards of CCR dust inhalation; and

B) When CCR is transported off-site, a written notice explaining the hazards of CCR dust inhalation, the transportation plan, and tentative transportation schedule must be provided to units of local government through which the CCR will be transported.

4) The owner or operator of the surface impoundment must take measures to prevent contamination of surface water, groundwater, soil and sediments from the removal of CCR, including the following:

A) CCR removed from the surface impoundment may only be temporarily stored, and must be stored in a lined landfill, CCR surface impoundment, enclosed structure, or CCR storage pile.

B) CCR storage piles must:

i) Be tarped or constructed with wind barriers to suppress dust and to limit stormwater contact with storage piles;

ii) Be periodically wetted or have periodic application of dust suppressants;

iii) Have a storage pad, or a geomembrane liner, with a hydraulic conductivity no greater than 1 x 10^{-7} cm/sec, that is properly sloped to allow appropriate drainage;

iv) Be tarped over the edge of the storage pad where possible;

v) Be constructed with fixed and mobile berms, where appropriate, to reduce run-on and run-off of stormwater to and from the storage pile, and minimize stormwater-CCR contact; and

vi) Have a groundwater monitoring system that is consistent with the requirements of Section 845.630 and approved by the Agency.

C) The owner or operator of the CCR surface impoundment must incorporate general housekeeping procedures such as daily cleanup of CCR, tarping of trucks, maintaining the pad and equipment, and good practices during unloading and loading.

D) The owner or operator of the CCR must minimize the amount of time the CCR is exposed to precipitation and wind.

E) The discharge of stormwater runoff that has contact with CCR must be covered by an individual National Pollutant Discharge Elimination System (NPDES) permit. The owner or operator must develop and implement a Stormwater Pollution Prevention Plan (SWPPP) in addition to any other requirements of the facility's NPDES permit. Any construction permit application for closure must include a copy of the SWPPP.

d) At the end of each month during which CCR is being removed from a CCR surface impoundment, the owner or operator must prepare a report that:

1) Describes the weather, precipitation amounts, the amount of CCR removed from the CCR surface impoundment, the amount and location of CCR being stored on-site, the amount of CCR transported offsite, the implementation of good housekeeping procedures required by subsection (c)(4)(C), and the implementation of dust control measures; and

2) Documents worker safety measures implemented. The owner or operator of the CCR surface impoundment must place the monthly report in the facility's operating record as required by Section 845.800(d)(23).

e) Upon completion of CCR removal and decontamination of the CCR surface impoundment under subsection (a), the owner or operator of the CCR surface impoundment must submit to the Agency a completion of CCR removal and decontamination report and a certification from a qualified professional engineer that CCR removal and decontamination of the CCR surface impoundment has been completed in accordance with this Section. The owner or operator must place the CCR removal and decontamination report and certification in the facility's operating record as required by Section 845.800(d)(32).

f) Upon completion of groundwater monitoring required under subsection (b), the owner or operator of the CCR surface impoundment must submit to the Agency a completion of groundwater monitoring report and a certification from a qualified professional engineer that groundwater monitoring has been completed in accordance with this Section. The owner or operator must place the groundwater monitoring report and certification in the facility's operating record as required by Section 845.800(d)(24).

Section 845.750 Closure with a Final Cover System

Closure Performance Standard When Leaving CCR in Place:

a) The owner or operator of a CCR surface impoundment must ensure that, at a minimum, the CCR surface impoundment is closed in a manner that will:

1) Control, minimize or eliminate, to the maximum extent feasible, post-closure infiltration of liquids into the waste and releases of CCR, leachate, or contaminated run-off to the ground or surface waters or to the atmosphere;

2) Preclude the probability of future impoundment of water, sediment, or slurry;

3) Include measures that provide for major slope stability to prevent the sloughing or movement of the final cover system during the closure and post-closure care period;

4) Minimize the need for further maintenance of the CCR surface impoundment; and

5) Be completed in the shortest amount of time consistent with recognized and generally accepted engineering practices.

b) Drainage and Stabilization of CCR Surface Impoundments. The owner or operator of a CCR surface impoundment or any lateral expansion of a CCR surface impoundment must meet the requirements of this subsection (b) before installing the final cover system required by subsection (c).

1) Free liquids must be eliminated by removing liquid wastes or solidifying the remaining wastes and waste residues.

2) Remaining wastes must be stabilized sufficiently to support the final cover system.

c) Final Cover System. If a CCR surface impoundment is closed by leaving CCR in place, the owner or operator must install a final cover system that is designed to minimize infiltration and erosion, and, at a minimum, meets the requirements of this subsection (c). The final cover system must consist of a low permeability layer and a final protective layer. The design of the final cover system must be included in the preliminary and final written closure plans required by Section 845.720 and the construction permit application for closure submitted to the Agency.

1) Standards for the Low Permeability Layer. The low permeability layer must have a permeability less than or equal to the permeability of any bottom liner system or natural subsoils present, or a hydraulic conductivity no greater than 1 x 10^{-7} cm/sec, whichever is less. The low permeability layer must be constructed in accordance with the standards in either subsection (c)(1)(A) or (c)(1)(B), unless the owner or operator demonstrates that another low permeability layer construction technique or material provides equivalent or superior performance to the requirements of either subsection (c)(1)(A) or (c)(1)(B) and is approved by the Agency.

A) A compacted earth layer constructed in accordance with the following standards:

i) The minimum allowable thickness must be 0.91 meter (three feet); and

ii) The layer must be compacted to achieve a hydraulic conductivity of 1 x 10^{-7} cm/sec or less and minimize void spaces.

B) A geomembrane constructed in accordance with the following standards:

i) The geosynthetic membrane must have a minimum thickness of 40 mil (0.04 inches) and, in terms of hydraulic flux, must be equivalent or superior to a three-foot layer of soil with a hydraulic conductivity of 1 x 10^{-7} cm/sec;

ii) The geomembrane must have strength to withstand the normal stresses imposed by the waste stabilization process; and

iii) The geomembrane must be placed over a prepared base free from sharp objects and other materials that may cause damage.

2) Standards for the Final Protective Layer. The final protective layer must meet the following requirements, unless the owner or operator demonstrates that another final protective layer construction technique or material provides equivalent or superior performance to the requirements of this subsection (c)(2) and is approved by the Agency.

A) Cover the entire low permeability layer;

B) Be at least three feet thick, be sufficient to protect the low permeability layer from freezing, and minimize root penetration of the low permeability layer;

C) Consist of soil material capable of supporting vegetation;

D) Be placed as soon as possible after placement of the low permeability layer; and

E) Be covered with vegetation to minimize wind and water erosion.

3) The disruption of the integrity of the final cover system must be minimized through a design that accommodates settling and subsidence.

4) The owner or operator of the CCR surface impoundment must obtain and submit with its construction permit application for closure a written certification from a qualified professional engineer that the design of the final cover system meets the requirements of this Section.

d) This subsection specifies the allowable uses of CCR in the closure of CCR surface impoundments closing under Section 845.700. Notwithstanding the prohibition on further placement in Section 845.700, CCR may be placed in these surface impoundments, but only for purposes of grading and contouring in the design and construction of the final cover system, if:

1) The CCR placed was generated at the facility and is located at the facility at the time closure was initiated;

2) CCR is placed entirely above the elevation of CCR in the surface impoundment, following dewatering and stabilization (see subsection (b));

3) The CCR is placed entirely within the perimeter berms of the CCR surface impoundment; and

4) The final cover system is constructed with either:

   A) A slope not steeper than 5% grade after allowance for settlement; or

   B) At a steeper grade, if the Agency determines that the steeper slope is necessary, based on conditions at the site, to facilitate run-off and minimize erosion, and that side slopes are evaluated for erosion potential based on a stability analysis to evaluate possible erosion potential. The stability analysis, at a minimum, must evaluate the site geology; characterize soil shear strength; construct a slope stability model; establish groundwater and seepage conditions, if any; select loading conditions; locate critical failure surface; and iterate until minimum factor of safety is achieved.

Section 845.760 Completion of Closure Activities

a) Except as provided for in subsection (b), the owner or operator must complete closure of existing and new CCR surface impoundments, and any lateral expansion of a CCR surface impoundment, within the timeframe approved by the Agency in the final closure plan, or within five years of obtaining a construction permit for closure, whichever is less.

b) Extensions of Closure Timeframes

   1) The timeframes for completing closure of a CCR surface impoundment specified under subsection (a) may be extended if the owner or operator has demonstrated to the Agency that it was not feasible to complete closure of the CCR surface impoundment within the required timeframes due to factors beyond the facility's control.

   2) The demonstration must include a narrative explaining the basis for additional time.

   3) The owner or operator must submit the demonstration to the Agency with a renewal construction permit application for closure.

   4) Factors that may support a demonstration include:

      A) Complications stemming from the climate and weather, such as unusual amounts of precipitation or a significantly shortened construction season;

B) Time required to dewater a surface impoundment due to the volume of CCR contained in the CCR surface impoundment or the characteristics of the CCR in the surface impoundment;

C) Statement that the geology and terrain surrounding the CCR surface impoundment will affect the amount of material needed to close the CCR surface impoundment; or

D) Time required or delays caused by the need to coordinate with and obtain necessary approvals and permits from the Agency or other agencies.

c) Maximum Time Extensions

1) CCR surface impoundments of 40 acres or smaller that are not closing by removal may extend the time to complete closure by no longer than two years.

2) CCR surface impoundments larger than 40 acres that are not closing by removal may extend the timeframe to complete closure of the CCR surface impoundment multiple times, in two-year increments. For each two-year extension sought, the owner or operator must substantiate the factual circumstances demonstrating the need for the extension. No more than a total of five two-year extensions may be obtained for any CCR surface impoundment.

3) CCR surface impoundments that are closing by removal may extend the time to complete closure multiple times, in two-year increments. For each two-year extension sought, the owner or operator must substantiate the factual circumstances demonstrating the need for the extension. In no instance may the time allowed for closure by removal be extended beyond the completion of a groundwater corrective action as required by Section 845.680(c)(1).

d) In order to obtain an additional time extension to complete closure of a CCR surface impoundment beyond the times provided by subsection (a), the owner or operator of the CCR surface impoundment must include with the demonstration required by subsection (b) the following statement signed by the owner or operator or an authorized representative:

> I certify under penalty of law that I have personally examined and am familiar with the information submitted in this demonstration and all attached documents, and that, based on my inquiry of those individuals immediately responsible for obtaining the information, I believe that the submitted information is true, accurate, and complete. I am aware that

there are significant penalties for submitting false information, including the possibility of fine and imprisonment.

e) Upon completion of all closure activities required by this Part and approved in the final closure plan, the owner or operator of the CCR surface impoundment must submit to the Agency a closure report and a closure certification.

1) The closure report must contain supporting documentation, including:

A) Engineering and hydrogeology reports, including monitoring well completion reports and boring logs, all CQA reports, certifications, and designations of CQA officers-in-absentia required by Section 845.290;

B) Photographs, including time, date and location information of the photographs, of the final cover system and groundwater collection system, if applicable, and any other photographs relied upon to document construction activities;

C) A written summary of closure requirements and completed activities as stated in the closure plan and this Part; and

D) Any other information relied upon by the qualified professional engineer in making the closure certification.

2) The closure certification must include a statement from a qualified professional engineer that closure has been completed in accordance with the Agency-approved final closure plan and the requirements of this Section.

3) The owner or operator must place the closure report and certification in the facility's operating record as required by Section 845.800(d)(24).

f) Within 30 days after the Agency's approval of the closure report and closure certification submitted under subsection (e), the owner or operator must prepare a notification of closure of the CCR surface impoundment. The notification must include the certification by a qualified professional engineer required by subsection (e)(2). The owner or operator must place the notification in the facility's operating record as required by Section 845.800(d)(25).

g) If an owner or operator of a CCR surface impoundment has completed closure of the CCR surface impoundment before April 21, 2021, the owner or operator must notify the Agency of the completed closure by September 30, 2021, if that notification has not previously been submitted.

h) Deed Notations

1) Following closure of a CCR surface impoundment, the owner or operator must record a notation on the deed to the property, or some other instrument that is normally examined during title search.

2) The notation on the deed must in perpetuity notify any potential purchaser of the property that:

   A) The land has been used as a CCR surface impoundment; and

   B) Its use is restricted under the post-closure care requirements as provided by Section 845.780(d)(1)(C) or groundwater monitoring requirements in Section 845.740(b).

3) Within 30 days after recording a notation on the deed to the property, the owner or operator must submit to the Agency a notification stating that the notation has been recorded. The owner or operator must place the notification in the facility's operating record as required by 845.800(d)(26).

Section 845.770 Retrofitting

Retrofit of a CCR surface impoundment must be completed in accordance with the requirements of this Section.

a) To retrofit an existing CCR surface impoundment, the owner or operator must:

   1) First remove all CCR, including any liners except as specified in subsection (a)(4), as necessary, and contaminated soils and sediments from the CCR surface impoundment;

   2) Comply with the requirements in Sections 845.410 and 845.420; and

   3) Within 30 days after April 21, 2021, the owner or operator electing to retrofit a CCR surface impoundment under this Section must submit a written preliminary retrofit plan to the Agency and post the written preliminary retrofit plan in the facility's operating record as required by Section 845.800(d)(27). The written preliminary retrofit plan must include a prioritization categorization under Section 845.700(g) and the expected construction permit application date under Section 845.700(h); and

   4) An owner or operator may request the Agency to approve the use of an existing competent geomembrane liner as a supplemental liner by submitting visual inspection, and analytical testing results to demonstrate that the existing liner is not contaminated with CCR constituents.

b) A CCR surface impoundment undergoing a retrofit remains subject to all other requirements of this Part, including the requirement to conduct any necessary corrective action.

c) Written Retrofit Plan

1) Content of the Plan. The owner or operator must prepare a written retrofit plan that describes the steps necessary to retrofit the CCR surface impoundment consistent with recognized and generally accepted engineering practices. The written retrofit plan must include, at a minimum, all the following information:

A) A narrative description of the specific measures that will be taken to retrofit the CCR surface impoundment in accordance with this Section.

B) A description of the procedures to remove all CCR, liners as necessary, and contaminated soils and sediments from the CCR surface impoundment.

C) An estimate of the maximum amount of CCR and other contaminated materials that will be removed as part of the retrofit operation.

D) An estimate of the largest area of the CCR surface impoundment that will be affected by the retrofit operation.

E) A schedule for completing all activities necessary to satisfy the retrofit criteria in this Section, including an estimate of the year in which retrofit activities of the CCR surface impoundment will be completed.

2) The owner or operator must submit the written retrofit plan with the construction permit application and must obtain a construction permit before retrofitting a CCR surface impoundment.

3) Amendment of a Written Retrofit Plan.

A) The owner or operator may submit a permit modification application to amend the initial or any subsequent written retrofit plan at any time.

B) The owner or operator must seek to amend the written retrofit plan whenever:

i) There is a change in the operation of the CCR surface impoundment that would substantially affect the written retrofit plan in effect; or

ii) unanticipated events necessitate a revision of the written retrofit plan either before or after retrofit activities have started.

C) The owner or operator must seek to amend the retrofit plan at least 60 days before a planned change in the operation of the facility or CCR surface impoundment, or within 60 days after an unanticipated event requires the revision of an existing written retrofit plan. If a written retrofit plan needs to be revised after retrofit activities have started for a CCR surface impoundment, the owner or operator must submit a request to modify the construction permit within 60 days following the triggering event.

4) The owner or operator of the CCR surface impoundment must obtain a written certification from a qualified professional engineer that the activities outlined in the written retrofit plan, including any amendment of the plan, meet the requirements of this Section.

d) By the date the owner or operator submits a construction permit application to the Agency to retrofit a CCR surface impoundment, the owner or operator must prepare a notification of intent to retrofit a CCR surface impoundment. The owner or operator has completed the notification when it has been placed in the facility's operating record as required by Section 845.800(d)(28).

e) When activities related to retrofitting the CCR surface impoundment include the removal of CCR from the surface impoundment, the handling and removal of CCR must be performed in a manner consistent with the requirements of Section 845.740.

f) Deadline for Completion of Activities Related to the Retrofit of a CCR Surface Impoundment. Any CCR surface impoundment that is being retrofitted must complete all retrofit activities within the timeframe approved by the Agency in the retrofit plan, or within five years after obtaining a construction permit, whichever is less. The same procedures specified for the extension closure timeframes in Section 845.760(b) apply to extension of retrofit timeframes.

g) Upon completion of all retrofit activities required by this Part and approved by the Agency in a construction permit, the owner or operator of the CCR surface impoundment must submit to the Agency a retrofit completion report and certification.

1) The retrofit completion report must contain supporting documentation, including:

   A) Engineering and hydrogeology reports, including monitoring well completion reports and boring logs, all CQA reports, certifications, and designations of CQA officers-in-absentia required by Section 845.290;

   B) Photographs, including time, date and location information of the photographs, of the liner system and leachate collection system, and any other photographs relied upon to document construction activities;

   C) A written summary of retrofit requirements and completed activities as stated in the construction permit and this Part; and

   D) Any other information relied upon by the qualified professional engineer in making the closure certification.

2) The retrofit certification must include a statement from a qualified professional engineer that retrofit has been completed in accordance with the retrofit plan specified in subsection (c) and the requirements of this Part.

3) The owner or operator must place the retrofit completion report and certification in the facility's operating record as required by Section 845.800(d)(29).

h) Within 30 days after the Agency's approval of the retrofit completion report and certification submitted under subsection (g), the owner or operator must prepare a notification of completion of retrofit activities. The notification must include the certification by a qualified professional engineer as required by subsection (g)(2). The owner or operator has completed the notification when it has been placed in the facility's operating record as required by Section 845.800(d)(30).

i) At any time after the initiation of a CCR surface impoundment retrofit, the owner or operator may stop the retrofit and seek to initiate closure of the CCR surface impoundment in accordance with the requirements of this Subpart G. The owner or operator of the CCR surface impoundment must obtain an approved construction permit for closure.

Section 845.780 Post-Closure Care Requirements

a) Applicability

1) Except as provided by subsection (a)(2), this Section applies to the owners or operators of CCR surface impoundments who have completed an Agency approved closure.

2) An owner or operator of a CCR surface impoundment that elects to close a CCR surface impoundment by removing CCR as provided by Section 845.740 is not subject to the post-closure care criteria of this Section.

b) Post-closure Care Maintenance Requirements. Following closure of the CCR surface impoundment, the owner or operator must conduct post-closure care for the CCR surface impoundment, which must consist of at least the following:

1) Maintaining the integrity and effectiveness of the final cover system, including making repairs to the final cover as necessary to correct the effects of settlement, subsidence, erosion, or other events, and preventing run-on and run-off from eroding or otherwise damaging the final cover;

2) If the CCR surface impoundment is subject to the design criteria of Section 845.420, maintaining the integrity and effectiveness of the leachate collection and removal system and operating the leachate collection and removal system in accordance with the requirements of Section 845.420; and

3) Maintaining the groundwater monitoring system and monitoring the groundwater in accordance with the requirements of Subpart F.

c) Post-closure Care Period

1) Except as provided by subsection (c)(2), the owner or operator of the CCR surface impoundment must conduct post-closure care for 30 years.

2) At the end of the 30-year post-closure care period, the owner or operator of the CCR surface impoundment must continue to conduct post-closure care until the groundwater monitoring data shows the concentrations are:

A) Below the groundwater protection standards in Section 845.600; and

B) Not increasing for those constituents over background, using the statistical procedures and performance standards in Section 845.640(f) and (g), provided that:

i) Concentrations have been reduced to the maximum extent feasible; and

ii) Concentrations are protective of human health and the environment.

d) Written Post-closure Care Plan

1) Content of the Plan. The owner or operator of a CCR surface impoundment must prepare a written post-closure care plan that includes, at a minimum, the information specified in this subsection (d)(1).

A) A description of the monitoring and maintenance activities required in subsection (b) for the CCR surface impoundment and the frequency at which these activities will be performed;

B) The name, address, telephone number, and email address of the person or office to contact about the facility during the post-closure care period; and

C) A description of the planned uses of the property during the post-closure care period. Post-closure use of the property must not disturb the integrity of the final cover, liners, or any other component of the containment system, or the function of the monitoring systems unless necessary to comply with the requirements of this Part. Any other disturbance is allowed if the owner or operator of the CCR surface impoundment demonstrates that disturbance of the final cover, liner, or other component of the containment system, including any removal of CCR, will not increase the potential threat to human health or the environment. The demonstration must be certified by a qualified professional engineer and must be submitted to the Agency.

2) Deadline to Prepare the Initial Written Post-closure Care Plan. The owner or operator of a CCR surface impoundment must submit to the Agency an initial written post-closure care plan consistent with the requirements specified in subsection (d)(1), with its initial operating permit application.

3) Amendment of a Written Post-closure Care Plan.

A) The owner or operator may submit an operating permit modification application to amend the initial or any subsequent written post-closure care plan developed under subsection (d)(1) at any time.

B) The owner or operator must seek to amend the written closure care plan whenever:

i) There is a change in the operation of the CCR surface impoundment that would substantially affect the written post-closure care plan in effect; or

ii) unanticipated events necessitate a revision of the written post-closure care plan, after post-closure activities have started.

C) The owner or operator must seek to amend the written post-closure care plan at least 60 days before a planned change in the operation of the facility or CCR surface impoundment, or within 60 days after an unanticipated event requires the need to revise an existing written post-closure care plan. If a written post-closure care plan is revised after post-closure activities have started for a CCR surface impoundment, the owner or operator must submit a request to modify the operating permit within 30 days following the triggering event.

4) The owner or operator of the CCR surface impoundment must obtain a written certification from a qualified professional engineer that the initial, and any amendment of the, written post-closure care plan meets the requirements of this Section.

e) Upon the completion of the post-closure care period, the owner or operator of the CCR surface impoundment must submit a request to the Agency to terminate post-closure care. The request must include a certification by a qualified professional engineer verifying that post-closure care has been completed in accordance with the post-closure care plan specified in subsection (d) and the requirements of this Section.

f) Notification of Completion of Post-closure Care Period. Within 30 days after the Agency's approval of the owner's or operator's request to terminate post-closure care, the owner or operator must prepare a notification of completion of post-closure care and must place the notification in the facility's operating record as required by Section 845.800(d)(31).

SUBPART H: RECORDKEEPING

Section 845.800 Facility Operating Record

a) Each owner or operator of a CCR surface impoundment subject to the requirements of this Part must maintain files of all information required by this Section in a written operating record at the facility.

b) Unless specified otherwise, each file must be retained for at least three years past the date the Agency approved the owner's or operator's request to terminate post-closure care, when closure is with a final cover system, or the completion of groundwater monitoring under Section 845.740(b), when closure is by removal.

c) An owner or operator of more than one CCR surface impoundment subject to the provisions of this Part may comply with the requirements of this Section in one recordkeeping system provided the system identifies each file by the name and identification number of each CCR surface impoundment. The files may be maintained on microfilm, on a computer, on computer disks, on a storage system accessible by a computer, on magnetic tape disks, or on microfiche.

d) Unless otherwise required below, the owner or operator of a CCR surface impoundment must place the following information, as it becomes available, in the facility's operating record:

1) Copies of all permit applications and permits issued under this Part;

2) Documentation recording the public meetings held under Section 845.240;

3) Weekly CQA reports under Section 845.290(b);

4) Hazard potential classification assessments for CCR surface impoundments (see Section 845.440(a)(3)(D));

5) Structural stability assessments for CCR surface impoundments (see Section 845.450(d)(4));

6) Safety factor assessments for CCR surface impoundments (see Section 845.460(c)(4));

7) The CCR fugitive dust control plan and any subsequent amendment of the plan (see Section 845.500(b)(6)), except that only the most recent fugitive dust control plan must be maintained in the facility's operating record, irrespective of the time requirement specified in subsection (b);

8) Inflow design flood control system plans for CCR surface impoundments (see Section 845.510(c)(4)(D));

9) Emergency Action Plan (see Section 845.520(a)), except that only the most recent EAP must be maintained in the facility's operating record irrespective of the time requirement specified in subsection (b);

10) Documentation prepared by the owner or operator recording all activations of the EAP (see Section 845.520(f));

11) Documentation prepared by the owner or operator recording the annual face-to-face meeting or exercise between representatives of the owner or

operator of the CCR surface impoundment and the local emergency responders (see Section 845.520(g));

12) Safety and Health Plan (see Section 845.530(a));

13) Documentation recording the results of each inspection and instrumentation monitoring by a qualified person (see Section 845.540(a)(2));

14) Annual consolidated report (see Section 845.550), which contains the following:

    A) The annual CCR fugitive dust control report (see Section 845.500(c));

    B) The annual inspection report (see Section 845.540(b)(3)); and

    C) The annual groundwater monitoring and corrective action report (see Section 845.610(e));

15) All groundwater monitoring data submitted to the Agency and any analysis performed (see Section 845.610(b)(3)(D));

16) Within 30 days after detecting one or more monitored constituents above the groundwater protection standard, the notifications required by Section 845.650(d) and (e);

17) The semi-annual report describing the progress in selecting and designing the remedy (see Section 845.670(a));

18) Within 30 days after completing the corrective action plan, the notification required by Section 845.680(e);

19) USEPA-approved or denied demonstration as required by Section 845.700(d)(2)(F);

20) The preliminary written closure plan and any amendment of the plan (see Section 845.720(a)) except that only the most recent closure plan must be maintained in the facility's operating record, irrespective of the time requirement specified in subsection (b);

21) The written demonstrations, including the certification required by Section 845.730(b)(3), for a time extension for initiating closure (see Section 845.730(b)(2));

22) The notification of intent to close a CCR surface impoundment (see Section 845.730(d));

23) The monthly reports for closure by removal (see Section 845.740(d));

24) The closure report and certification (see Section 845.760(e)(3)), or the completion of groundwater monitoring report and certification (see Section 845.740(f));

25) The notification of completion of closure of a CCR surface impoundment (see Section 845.760(f));

26) The notification recording a notation on the deed (see Section 845.760(h));

27) The preliminary written retrofit plan for a CCR surface impoundment (see Section 845.770(a)(3));

28) The notification of intent to initiate retrofit of a CCR surface impoundment (see Section 845.770(d));

29) The retrofit completion report and certification (see Section 845.770(g)(3));

30) The notification of completion of retrofit activities (see Section 845.770(h));

31) The notification of completion of post-closure care period (see Section 845.780(f));

32) The completion of CCR removal and decontamination report and certification (see Section 845.740(e)); and

33) The most current cost estimates (see Section 845.940(d)).

Section 845.810 Publicly Accessible Internet Site Requirements

a) Each owner or operator of a CCR surface impoundment subject to the requirements of this Part must maintain a publicly accessible Internet site (CCR website) containing the information specified in this Section. The owner's or operator's website must be titled "Illinois CCR Rule Compliance Data and Information".

b) An owner or operator of more than one CCR surface impoundment subject to the provisions of this Part may comply with the requirements of this Section by using the same Internet site for multiple CCR surface impoundments, provided the CCR website clearly delineates information by the name and identification number of each CCR surface impoundment.

c) Unless otherwise required in this Section, the information required to be posted to the CCR website must be made available to the public on the CCR website until 3 years after post-closure care (when closure is with a final cover system) or the completion of groundwater monitoring under Section 845.740(b) (when closure is by removal).

d) Unless otherwise required in this Section, the information must be posted to the CCR website within 14 days after placing the pertinent information required by Section 845.800 in the operating record.

e) The owner or operator must place all the information specified under Section 845.800(d) on the owner's or operator's CCR website.

f) The owner or operator must place all the information specified in Section 845.240(e) on the owner's or operator's CCR website at least 30 days before the public meeting.

g) The owner or operator must notify the Agency of the web address of the publicly accessible Internet site, including any change to the web address. The Agency must maintain a list of these web addresses on the Agency's website.

SUBPART I: FINANCIAL ASSURANCE

Section 845.900 General Provisions

a) This Subpart provides procedures by which the owner or operator of a CCR surface impoundment subject to this Part provides financial assurance satisfying the requirements of Section 22.59(f) of the Act.

b) The owner or operator must provide financial assurance to ensure the following:

1) Completion of closure;

2) Completion of post-closure care, if applicable; and

3) Remediation of releases from a CCR surface impoundment.

c) The owner or operator must maintain financial assurance equal to or greater than the current cost estimates always calculated under Section 845.930, except as otherwise provided by Section 845.910.

d) Financial assurance must be provided, by a trust agreement, a surety bond guaranteeing payment, a surety bond guaranteeing payment or performance, or an irrevocable letter of credit (see Section 845.950). The owner or operator must provide financial assurance to the Agency within the timeframes in Section 845.950(c).

e) This Subpart does not apply to the State of Illinois, its agencies and institutions, any unit of local government, or any not-for-profit electric cooperative as defined in Section 3.4 of the Electric Supplier Act [220 ILCS 30].

f) The Agency is authorized to enter into contracts and agreements necessary to carry out the purposes of this Subpart and of Section 22.59(f) of the Act. Neither the State, nor the Director of the Agency, nor any State employee will be liable for any damages or injuries arising out of, or resulting from, any action taken under this Part.

g) The Agency may sue in any court of competent jurisdiction to enforce its rights under financial instruments. The filing of an enforcement action before the Board is not a condition precedent to such an Agency action, except when this Subpart or the terms of the instrument provide otherwise.

h) The Agency must have the authority to approve or disapprove any financial assurance mechanism posted or submitted under this Subpart.

i) The following Agency actions may be appealed to the Board as a permit denial under Section 845.270(e) and Section 22.59(f)(3) of the Act:

  1) A refusal to accept financial assurance tendered by the owner or operator;

  2) A refusal to release the owner or operator from the requirement to maintain financial assurance;

  3) A refusal to release excess funds from a trust;

  4) A refusal to approve a reduction in the penal sum of a bond; and

  5) A refusal to approve a reduction in the amount of a letter of credit.

j) An owner or operator must notify the Agency by certified mail of the beginning of a voluntary or involuntary proceeding under Title 11 of the United States Code (Bankruptcy) naming any of the owners or operators as debtor, within 10 days after the proceeding starts.

k) An owner or operator that fulfills the requirements of Section 845.960, 845.970, 845.980, or 845.990 by obtaining a trust fund, surety bond, or letter of credit will be deemed to be without the required financial assurance in the event of bankruptcy of the trustee or issuing institution, or a suspension or revocation of the authority of the trustee institution to act as trustee or of the institution issuing the surety bond or letter of credit to issue those instruments. The owner or operator must establish alternative financial assurance within 60 days after such an event.

Section 845.910 Upgrading Financial Assurance

a) The owner or operator must increase the total amount of financial assurance to equal or exceed the current cost estimate within 60 days after either of the following occurrences:

1) An increase in the current cost estimate; or

2) A decrease in the value of a trust fund.

b) The owner or operator of a CCR surface impoundment must make annual adjustments for inflation if required under Section 845.930 or 845.940.

Section 845.920 Release of Financial Institution and Owner or Operator

a) The Agency must release a trustee, surety, or other financial institution when:

1) An owner or operator substitutes alternative financial assurance such that the total financial assurance for the CCR surface impoundment is equal to or greater than the current cost estimate, without counting the amounts to be released; or

2) The Agency releases the owner or operator from the requirements of this Subpart under subsection (b).

b) The Agency must release an owner or operator of a CCR surface impoundment from the requirements of this Subpart under the following circumstances:

1) Completed Closure. In the Agency's approval of the closure report and certification under Section 845.760, the Agency must notify the owner or operator in writing that it is no longer required by this Subpart to maintain financial assurance for closure of the CCR surface impoundment.

2) Completed Post-Closure Care. In the Agency's approval of the owner's or operator's request to terminate post-closure care under Section 845.780, the Agency must notify the owner or operator in writing that it is no longer required by this Subpart to maintain financial assurance for post-closure care of the CCR surface impoundment.

3) Completed Corrective Action. In the Agency's approval of the corrective action completion report and certification under Section 845.680, the Agency must notify the owner or operator in writing that it is no longer

required by this Subpart to maintain financial assurance for corrective action.

Section 845.930 Cost Estimates

a) The owner or operator must prepare and submit to the Agency, for approval, written cost estimates for:

   1) The total costs for closure and post-closure care;

   2) Preliminary corrective action costs; and

   3) The total costs of the corrective action plan for remediation of any releases from a CCR surface impoundment.

b) Written Cost Estimate for Closure and Post-closure

   1) The owner or operator must have a detailed written estimate, in current dollars, of the cost of closing the CCR surface impoundment in accordance with this Part and providing post-closure care on an annual basis, when required, in accordance with this Part. The cost estimate is the total cost for closure and post-closure care.

   2) The cost estimate must equal the cost of final closure and post-closure care at the point in the CCR surface impoundment's active life when the extent and manner of its operation would make closure and post-closure care the most expensive.

   3) The cost estimate must be based on the assumption that the Agency will contract with a third party at the appropriate prevailing wages, under the Prevailing Wage Act [820 ILCS 130], if applicable, to implement the closure and post-closure care plans. A third party is a party who is neither a parent nor a subsidiary of the owner or operator.

   4) The cost estimate may not be reduced by allowance for the salvage value of facility structures or equipment, for the resale value of land, for the sale of CCR or its beneficial reuse if permitted by the Agency under this Part, or for other assets associated with the facility at the time of partial or final closure.

   5) The owner or operator must not incorporate a zero cost for CCR, if permitted by the Agency under this Part, that might have economic value.

   6) The cost estimate must, at a minimum, include all costs for all activities necessary to close the CCR surface impoundment and provide post-closure care in accordance with all requirements.

7) The post-closure care portion of the cost estimate must, at a minimum, be based on the following elements:

A) Maintaining the integrity and effectiveness of the final cover system, including making repairs to the final cover as necessary to correct the effects of settlement, subsidence, erosion, or other events, and preventing run-on and run-off from eroding or otherwise damaging the final cover;

B) If the CCR surface impoundment is subject to the design criteria of Section 845.420, maintaining the integrity and effectiveness of the leachate collection and removal system and operating the leachate collection and removal system in accordance with the requirements of Section 845.420; and

C) Maintaining the groundwater monitoring system and monitoring the groundwater in accordance with the requirements of this Part.

c) Cost Estimate for Corrective Action

1) Preliminary Corrective Action Cost Estimate. An owner or operator of a CCR surface impoundment with a release that has caused an exceedance of the groundwater protection standard in Section 845.600, or groundwater quality standard in 35 Ill. Adm. Code 620, must provide a preliminary corrective action cost estimate that is equal to 25% of the costs calculated under subsection (b).

2) Corrective Action Cost Estimate. The owner or operator must provide to the Agency a detailed written estimate, in current dollars, of the cost of hiring a third party at the appropriate prevailing wages, under the Prevailing Wage Act, if applicable, to implement the approved corrective action plan in accordance with this Part. The corrective action cost estimate must account for the total costs of corrective action activities as described in the approved corrective action plan for the entire corrective action period.

3) The owner or operator must annually adjust the cost estimates in this subsection (c) for inflation (see Section 845.940(a)) until the approved corrective action plan is completed.

4) The owner or operator must increase the corrective action cost estimates in this subsection (c) and the amount of financial assurance provided if changes in the corrective action plan or CCR surface impoundment conditions increase the maximum costs of corrective action.

5) The owner or operator may reduce the amount of the corrective action cost estimate, upon Agency approval, if the cost estimate exceeds the maximum remaining costs of corrective action.

Section 845.940 Revision of Cost Estimates

a) During the active life of the CCR surface impoundment, the owner or operator must adjust the cost estimates for closure, post-closure care, and corrective action for inflation on an annual basis. The adjustments must occur within 60 days before the anniversary date of the establishment of the financial instruments used to comply with Section 845.950. The adjustment may be made by recalculating the maximum costs of closure, post-closure care, or corrective action in current dollars, or by using an inflation factor derived from the annual Implicit Price Deflator for Gross National Product (Deflator) as published by the U.S. Department of Commerce in its Survey of Current Business (Table 1.1.9) (see subsections (a)(1) and (a)(2)). The inflation factor is the result of dividing the latest published annual Deflator by the Deflator for the previous year.

1) The first adjustment is made by multiplying the cost estimate by the inflation factor. The result is the adjusted cost estimate.

2) Subsequent adjustments are made by multiplying the latest adjusted cost estimate by the latest inflation factor.

b) During the active life of the CCR surface impoundment, the owner or operator must revise the cost estimate within 30 days after the Agency has approved a request to modify the corrective action plan, closure plan, or post-closure care plan, if the change in the modified plan increases the cost of corrective action, closure or post-closure care. The revised cost estimate must be adjusted for inflation (see subsection (a)).

c) At least 60 days before submitting any closure plan to the Agency, the owner or operator must revise the cost estimate if the selected closure method increases the estimated closure or post-closure care costs.

d) The owner or operator must keep the most current cost estimates in the facility's operating record during the operating life of the CCR surface impoundment.

Section 845.950 Mechanisms for Financial Assurance

a) The owner or operator of a CCR surface impoundment must use any of the mechanisms listed in this subsection (a) to provide financial assurance for closure and post-closure care, and for corrective action at a CCR surface impoundment. An owner or operator of a CCR surface impoundment must also meet the requirements of subsections (b), (c), and (d). The mechanisms are as follows:

1) A trust fund (see Section 845.960);

2) A surety bond guaranteeing payment (see Section 845.970);

3) A surety bond guaranteeing performance (see Section 845.980); or

4) An irrevocable letter of credit (see Section 845.990).

b) The owner or operator of a CCR surface impoundment must ensure that the language of the mechanisms listed in subsection (a), when used for providing financial assurance for closure, post-closure, and corrective action, is consistent with the forms prescribed by the Agency and satisfies the following:

1) The amount of funds assured is sufficient to cover the costs of closure, post-closure care, and corrective action; and

2) The funds will be available in a timely fashion when needed.

c) The owner or operator of a CCR surface impoundment must provide financial assurance utilizing one or more of the mechanisms listed in subsection (a) within the following timeframes:

1) An owner or operator of an existing CCR surface impoundment must provide financial assurance to the Agency for closure and post-closure care within 60 days after April 21, 2021;

2) An owner or operator of a new CCR surface impoundment must provide financial assurance to the Agency for closure and post-closure care at least 60 days before the date of initial receipt of CCR in the CCR surface impoundment.

3) In the case of corrective action required by this Part, the owner or operator of the CCR surface impoundment must provide preliminary financial assurance for corrective action no later than when the owner or operator initiates an assessment of corrective measures under Section 845.650(d)(3). The preliminary financial assurance for corrective action must be maintained until replaced with financial assurance based on the cost estimate of the corrective action. The owner or operator of the CCR surface impoundment must provide financial assurance based on the approved corrective action plan to the Agency within 60 days after either the Agency's approval or April 21, 2021, whichever is later.

d) The owner or operator must provide continuous financial assurance coverage until the owner or operator is released from the financial assurance requirements of this Subpart under Section 845.920(b).

e) Use of Multiple Financial Assurance Mechanisms. An owner or operator may satisfy the requirements of this Subpart by establishing more than one financial mechanism per CCR surface impoundment. These mechanisms are limited to trust funds, surety bonds guaranteeing payment, and letters of credit. The mechanisms must be as specified in Sections 845.960, 845.970, and 845.990, as applicable, except that it is the combination of mechanisms, rather than the single mechanism, that must provide financial assurance for an aggregate amount at least equal to the current cost estimate for closure, post-closure care, and corrective action, except that mechanisms guaranteeing performance, rather than payment, may not be combined with other instruments. The owner or operator may use any or all the mechanisms to provide financial assurance for corrective action, closure and post-closure care.

f) Use of a Financial Assurance Mechanism for Multiple CCR Surface Impoundments in Illinois. An owner or operator may use a financial assurance mechanism specified in this Subpart to meet the requirements of this Subpart for more than one CCR surface impoundment located in Illinois. Evidence of financial assurance submitted to the Agency must include a list showing, for each CCR surface impoundment, the identification number (see Section 845.130), name, address and the amount of funds assured by the mechanism. The amount of funds available through the mechanism must be at least the sum of funds that would be available if a separate mechanism had been established and maintained for each CCR surface impoundment. The amount of funds available to the Agency must be enough to close and provide post-closure care for all of the owner's or operator's CCR surface impoundments. In directing funds available through a single mechanism for the closure and post-closure care of any single CCR surface impoundment covered by that mechanism, the Agency must direct only that amount of funds designated for that CCR surface impoundment, unless the owner or operator agrees to the use of additional funds available under that mechanism.

Section 845.960 Trust Fund

a) An owner or operator may satisfy the requirements of this Subpart by establishing a fully funded trust fund that conforms to the requirements of this Section and submitting to the Agency an original signed duplicate of the trust agreement.

b) The trustee must be an entity that has the authority to act as a trustee and of whom either of the following is true:

1) It is an entity whose trust operations are examined by the Illinois Department of Financial and Professional Regulation under the Illinois Banking Act [205 ILCS 5]; or

2) It is an entity that complies with the Corporate Fiduciary Act [205 ILCS 620].

c) The trust agreement must be on forms prescribed by the Agency. The trust agreement must be updated within 60 days after a change in the amount of the current closure, post-closure, and corrective action cost estimates covered by the agreement.

d) The trust fund must be fully funded from the date that the trust agreement becomes effective.

e) The trustee must evaluate the trust fund annually, as of the day the trust was created or on such earlier date as may be provided in the agreement. The trustee must notify the owner or operator and the Agency of the value within 30 days after the evaluation date.

f) If the owner or operator of a CCR surface impoundment establishes a trust fund after having used one or more alternative mechanisms specified in this Subpart, the trust fund must be fully funded and established according to the specifications of this Section.

g) Release of Excess Funds

 1) If the value of the financial assurance is greater than the total amount of the current cost estimate, the owner or operator may submit a written request to the Agency for a release of the amount in excess of the current cost estimate.

 2) Within 60 days after receiving a request from the owner or operator for a release of funds, the Agency must instruct the trustee to release to the owner or operator the funds as the Agency specifies in writing to be in excess of the current cost estimate.

h) Reimbursement for Closure, Post-closure Care, and Corrective Action Expenses

 1) After initiating corrective action, closure, or post-closure care an owner or operator, or any other person authorized to perform corrective action, closure, or post-closure care, may request reimbursement for closure, post-closure care, or corrective action expenditures by submitting itemized bills to the Agency.

 2) Within 60 days after receiving the itemized bills for closure, post-closure care, or correction action activities, the Agency must determine whether the expenditures are in accordance with the closure, post-closure care, or corrective action plan. The Agency must instruct the trustee to make reimbursement in amounts the Agency specifies in writing as expenditures made in accordance with the closure, post-closure care, or corrective action plan.

3) If the Agency determines, based on information available to it, that the cost of closure and post-closure care or corrective action will be greater than the value of the trust fund, it must withhold reimbursement of amounts it determines are necessary to preserve the fund in order to accomplish closure and post-closure care or corrective action until it determines that the owner or operator is no longer required to maintain financial assurance for closure and post-closure care or corrective action. If the fund is inadequate to pay all claims, the Agency must pay claims according to the following priorities:

    A) Persons with whom the Agency has contracted to perform closure, post-closure care, or corrective action activities (first priority);

    B) Persons who have completed closure, post-closure care, or corrective action authorized by the Agency (second priority);

    C) Persons who have completed work that furthered the closure, post-closure care, or corrective action (third priority);

    D) The owner or operator and related business entities (last priority).

Section 845.970 Surety Bond Guaranteeing Payment

a) An owner or operator may satisfy the requirements of this Subpart by obtaining a surety bond that conforms to the requirements of this Section and submitting the bond to the Agency.

b) The surety company issuing the bond must, at a minimum, be among those listed as acceptable sureties on federal bonds in Circular 570 of the U.S. Department of the Treasury. Circular 570 is available on the Internet from the following website: https://fiscal.treasury.gov/surety-bonds/circular-570.html.

c) The surety bond must be on forms prescribed by the Agency.

d) Any payments drawn from or made under the bond will be placed in the Coal Combustion Residual Surface Impoundment Financial Assurance Fund within the State Treasury.

e) Conditions

    1) The bond must guarantee that the owner or operator will:

        A) Provide closure and post-closure care in accordance with the approved closure and post-closure care plans and, if the bond is a corrective action bond, provide corrective action in accordance with this Part; and

B) Provide alternative financial assurance, as specified in this Subpart, and obtain the Agency's written approval of the assurance provided within 90 days after receipt by both the owner or operator and the Agency of a notice from the surety that the bond will not be renewed for another term.

2) The surety will become liable on the bond obligation when, during the term of the bond, the owner or operator fails to perform as guaranteed by the bond. The owner or operator fails to perform when the owner or operator:

A) Abandons the CCR surface impoundment;

B) Is adjudicated bankrupt;

C) Fails to initiate closure of the CCR surface impoundment or post-closure care or corrective action when ordered to do so by the Board under Title VIII of the Act (Enforcement), or when ordered to do so by a court of competent jurisdiction;

D) Notifies the Agency that it has initiated closure or corrective action, or initiates closure or corrective action, but fails to close the CCR surface impoundment or provide post-closure care or corrective action in accordance with the Agency-approved closure and post-closure care or corrective action plans;

E) For a corrective action bond, fails to implement or complete corrective action at a CCR surface impoundment in accordance with Section 845.670; or

F) Fails to, within 90 days after receipt by both the owner or operator and the Agency of a notice from the surety that the bond will not be renewed for another term:

i) Provide alternative financial assurance, as specified in this Subpart; and

ii) Obtain the Agency's written approval of the assurance.

3) If the owner or operator does not establish alternative financial assurance, as specified in this Subpart, and obtain written approval of that alternative assurance from the Agency within 90 days after receipt by both the owner or operator and the Agency of a notice of nonrenewal from the surety (see subsection (g)(2)), the Agency must draw on the bond. During the last 30

days of a notice of nonrenewal, the Agency must draw on the bond if the owner or operator has failed to provide alternative financial assurance, as specified in this Section, and obtain from the Agency written approval of that assurance.

f) Penal Sum

1) The penal sum of the bond must be in an amount at least equal to the current cost estimate.

2) Whenever the current cost estimate decreases, the penal sum may be reduced to the amount of the current cost estimate following written approval by the Agency.

3) Whenever the current cost estimate increases to an amount greater than the penal sum, the owner or operator, within 90 days after the increase, must either cause the penal sum to be increased to an amount at least equal to the current cost estimate and submit evidence of that increase to the Agency or obtain other financial assurance, as specified in this Subpart, to cover the increase and submit evidence of the alternative financial assurance to the Agency.

g) Term

1) The bond must be issued for a term of at least one year and must not be cancelable during that term.

2) The surety bond must provide that, on the current expiration date and on each successive expiration date, the term of the surety bond will be automatically extended for a period of at least one year unless, at least 120 days before the current expiration date, the surety notifies both the owner or operator and the Agency by certified mail of a decision not to renew the bond. Under the terms of the surety bond, the 120 days will begin on the date when both the owner or operator and the Agency have received the notice, as evidenced by the return receipts.

3) The Agency must release the surety by providing written authorization for termination of the bond to the owner or operator and the surety when either of the following occurs:

A) An owner or operator substitutes alternative financial assurance, as specified in this Subpart; or

B) The Agency releases the owner or operator from the requirements of this Subpart in accordance with Section 845.920(b).

h) Cure of Default and Refunds

1) The Agency must release the surety if, after the surety becomes liable on the bond, the owner or operator or another person provides financial assurance for closure and post-closure care of the CCR surface impoundment or corrective action at a CCR surface impoundment; unless the Agency determines that the closure, post-closure care, or corrective action plan, or the amount of substituted financial assurance, is inadequate to provide closure and post-closure care or implement corrective action in compliance with this Part.

2) After closure and post-closure care have been completed in accordance with the plans and requirements of this Part or after the completion of corrective action at a CCR surface impoundment in accordance with this Part, the Agency must refund any unspent money that was paid into the Coal Combustion Residual Surface Impoundment Financial Assurance Fund by the surety, subject to appropriation of funds by the Illinois General Assembly.

Section 845.980 Surety Bond Guaranteeing Performance

a) An owner or operator may satisfy the requirements of this Subpart by obtaining a surety bond that conforms to the requirements of this Section and submitting the bond to the Agency.

b) The surety company issuing the bond must, at a minimum, be among those listed as acceptable sureties on federal bonds in Circular 570 of the U.S. Department of the Treasury. Circular 570 is available on the Internet from the following website: https://fiscal.treasury.gov/surety-bonds/circular-570.html.

c) The surety bond must be on forms prescribed by the Agency.

d) Any payments made under the bond will be placed in the Coal Combustion Residual Surface Impoundment Financial Assurance Fund within the State Treasury.

e) Conditions

1) The bond must guarantee that the owner or operator will:

A) Provide closure and post-closure care in accordance with the approved closure and post-closure care plans and, if the bond is a corrective action bond, provide corrective action in accordance with this Part; and

B) Provide alternative financial assurance, as specified in this Subpart, and obtain the Agency's written approval of the assurance provided within 90 days after receipt by both the owner or operator and the Agency of a notice from the surety that the bond will not be renewed for another term.

2) The surety will become liable on the bond obligation when, during the term of the bond, the owner or operator fails to perform as guaranteed by the bond. The owner or operator fails to perform when the owner or operator:

A) Abandons the CCR surface impoundment;

B) Is adjudicated bankrupt;

C) Fails to initiate closure of the CCR surface impoundment or post-closure care or corrective action when ordered to do so by the Board under Title VIII of the Act (Enforcement), or when ordered to do so by a court of competent jurisdiction;

D) Notifies the Agency that it has initiated closure or corrective action, or initiates closure or corrective action, but fails to close the CCR surface impoundment or provide post-closure care or corrective action in accordance with the Agency-approved closure and post-closure care or corrective action plans;

E) For a corrective action bond, fails to implement or complete corrective action at a CCR surface impoundment in accordance with Section 845.670; or

F) Fails to, within 90 days after receipt by both the owner or operator and the Agency of a notice from the surety that the bond will not be renewed for another term:

i) Provide alternative financial assurance, as specified in this Subpart; and

ii) Obtain the Agency's written approval of the assurance.

3) Upon failure of the owner or operator to perform as guaranteed by the bond, the surety must have the option of:

A) providing closure and post-closure care in accordance with the approved closure and post-closure care plans;

B) carrying out corrective action in accordance with the corrective action plan; or

C) paying the penal sum.

f) Penal Sum

1) The penal sum of the bond must be in an amount at least equal to the current cost estimate.

2) Whenever the current cost estimate decreases, the penal sum may be reduced to the amount of the current cost estimate following written approval by the Agency.

3) Whenever the current cost estimate increases to an amount greater than the penal sum, the owner or operator, within 90 days after the increase, must either cause the penal sum to be increased to an amount at least equal to the current cost estimate and submit evidence of that increase to the Agency or obtain other financial assurance, as specified in this Subpart, and submit evidence of the alternative financial assurance to the Agency.

g) Term

1) The bond must be issued for a term of at least one year and must not be cancelable during that term.

2) The surety bond must provide that, on the current expiration date and on each successive expiration date, the term of the surety bond will be automatically extended for a period of at least one year unless, at least 120 days before the current expiration date, the surety notifies both the owner or operator and the Agency by certified mail of a decision not to renew the bond. Under the terms of the surety bond, the 120 days will begin on the date when both the owner or operator and the Agency have received the notice, as evidenced by the return receipts.

3) The Agency must release the surety by providing written authorization for termination of the bond to the owner or operator and the surety when either of the following occurs:

A) An owner or operator substitutes alternative financial assurance, as specified in this Subpart; or

B) The Agency releases the owner or operator from the requirements of this Subpart in accordance with Section 845.920(b).

h) Cure of Default and Refunds

1) The Agency must release the surety if, after the surety becomes liable on the bond, the owner or operator or another person provides financial assurance for closure and post-closure care of the CCR surface impoundment or corrective action at a CCR surface impoundment; unless the Agency determines that the closure, post-closure care, or corrective action plan, or the amount of substituted financial assurance, is inadequate to provide closure and post-closure care or implement corrective action in compliance with this Part.

2) After closure and post-closure care have been completed in accordance with the plans and requirements of this Part or after the completion of corrective action at a CCR surface impoundment in accordance with this Part, the Agency must refund any unspent money that was paid into the Coal Combustion Residual Surface Impoundment Financial Assurance Fund by the surety, subject to appropriation of funds by the Illinois General Assembly.

i) The surety will not be liable for deficiencies in the performance of closure, post-closure care, or corrective action by the owner or operator after the Agency releases the owner or operator from the requirements of this Subpart.

Section 845.990 Letter of Credit

a) An owner or operator may satisfy the requirements of this Subpart by obtaining an irrevocable standby letter of credit that conforms to the requirements of this Section and submitting the letter to the Agency.

b) The issuing institution must be an entity that has the authority to issue letters of credit and:

1) Whose letter of credit operations are regulated by the Illinois Department of Financial and Professional Regulation under the Illinois Banking Act [205 ILCS 5]; or

2) Whose deposits are insured by the Federal Deposit Insurance Corporation.

c) Forms

1) The letter of credit must be on forms prescribed by the Agency.

2) The letter of credit must be accompanied by a letter from the owner or operator, referring to the letter of credit by number, the name and address of the issuing institution, and the effective date of the letter, and providing the following information: the name and address of the CCR surface impoundment, the identification number (see Section 845.130), and the

amount of funds assured by the letter of credit for closure and post-closure care of the CCR surface impoundment, or for corrective action at the CCR surface impoundment.

d) Any amounts drawn by the Agency under the letter of credit will be deposited in the Coal Combustion Residual Surface Impoundment Financial Assurance Fund within the State Treasury.

e) Conditions on Which the Agency Must Draw on the Letter of Credit:

1) The Agency must draw on the letter of credit if the owner or operator fails to perform closure or post-closure care in accordance with the approved closure and post-closure care plans or fails to perform corrective action at a CCR surface impoundment in accordance with this Part.

2) The Agency must draw on the letter of credit if the owner or operator:

A) Abandons the CCR surface impoundment;

B) Is adjudicated bankrupt;

C) Fails to initiate closure of the CCR surface impoundment or post-closure care or corrective action when ordered to do so by the Board under Title VIII of the Act (Enforcement), or when ordered to do so by a court of competent jurisdiction;

D) Notifies the Agency that it has initiated closure or corrective action, or initiates closure or corrective action, but fails to provide closure and post-closure care or corrective action in accordance with the Agency-approved closure and post-closure care or corrective action plans;

E) For a corrective action letter of credit, fails to implement or complete corrective action at a CCR surface impoundment in accordance with Section 845.670; or

F) Fails to, within 90 days after receipt by both the owner or operator and the Agency of a notice from the surety that the bond will not be renewed for another term:

i) Provide alternative financial assurance, as specified in this Subpart; and

ii) Obtain the Agency's written approval of the assurance.

3) If the owner or operator does not establish alternative financial assurance,

as specified in this Subpart, and obtain written approval of that alternative assurance from the Agency within 90 days after receipt by both the owner or operator and the Agency of a notice of expiration from the issuing institution (see subsection (g)(2)), the Agency must draw on the letter of credit. During the last 30 days of a notice of expiration, the Agency must draw on the letter of credit if the owner or operator has failed to provide alternative financial assurance, as specified in this Section, and obtain from the Agency written approval of that assurance.

f) Amount

1) The letter of credit must be issued in an amount at least equal to the current cost estimate.

2) Whenever the current cost estimate decreases, the amount of credit may be reduced to the amount of the current cost estimate following written approval by the Agency.

3) Whenever the current cost estimate increases to an amount greater than the amount of the credit, the owner or operator, within 90 days after the increase, must either cause the amount of the credit to be increased to an amount at least equal to the current cost estimate and submit evidence of that increase to the Agency or obtain other financial assurance, as specified in this Subpart, to cover the increase and submit evidence of the alternative financial assurance to the Agency.

g) Term

1) The letter of credit must be issued for a term of at least one year and must be irrevocable during that term.

2) The letter of credit must provide that, on the current expiration date and on each successive expiration date, the letter of credit will be automatically extended for a period of at least one year unless, at least 120 days before the current expiration date, the issuing institution notifies both the owner or operator and the Agency by certified mail of a decision not to extend the letter of credit for another term. Under the terms of the letter of credit, the 120 days will begin on the date when both the owner or operator and the Agency have received the notice, as evidenced by the return receipts.

3) The Agency must return the letter of credit to the issuing institution for termination when either of the following occurs:

A) An owner or operator substitutes alternative financial assurance, as specified in this Subpart; or

B) The Agency releases the owner or operator from the requirements of this Subpart in accordance with Section 845.920(b).

h) Cure of Default and Refunds

1) The Agency must release the financial institution if, after the Agency is allowed to draw on the letter of credit, the owner or operator or another person provides financial assurance for closure and post-closure care of the CCR surface impoundment or corrective action at a CCR surface impoundment; unless the Agency determines that the closure, post-closure care, or corrective action plan, or the amount of substituted financial assurance, is inadequate to provide closure and post-closure care or implement corrective action in compliance with this Part.

2) After closure and post-closure care have been completed in accordance with the plans and requirements of this Part or after the completion of corrective action at a CCR surface impoundment in accordance with this Part, the Agency must refund any unspent money that was drawn and paid into the Coal Combustion Residual Surface Impoundment Financial Assurance Fund by the financial institution, subject to appropriation of funds by the Illinois General Assembly.

DOCUMENT
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Region 4 **U.S. Environmental Protection Agency** **Laboratory Services & Applied Science Division** **Athens, Georgia**	
Operating Procedure	
Title: Pore Water Sampling	ID: LSASDPROC-513-R5
Issuing Authority: Field Services Branch Supervisor	
Effective Date: April 22, 2023	Review Due Date: May 12, 2024
Method Reference: N/A	SOP Author: Mel Parsons

Purpose

The purpose of this operating procedure is to describe the methods and considerations to be used when obtaining a pore water sample from soil or sediment.

Scope/Application

This document describes procedures generic to all pore water sampling methods to be used by field personnel when collecting and handling samples in the field. On the occasion that Laboratory Services and Applied Science Division (LSASD) personnel determine that any of the procedures described in this section are inappropriate, inadequate or impractical and that another procedure must be used to obtain a pore water sample, the variant procedure will be documented in the field logbook, along with a description of the circumstances requiring its use. Mention of trade names or commercial products in this operating procedure does not constitute endorsement or recommendation for use.

TABLE OF CONTENTS

1 General Information

1.1 Documentation/Verification

This procedure was prepared by persons deemed technically competent by LSASD management, based on their knowledge, skills and abilities and has been tested in practice and reviewed in print by a subject matter expert. The official copy of this procedure resides on the LSASD local area network (LAN). The Document Control Coordinator is responsible for ensuring the most recent version of the procedure is placed on the LAN and for maintaining records of review conducted prior to its issuance.

1.2 General Precautions

1.2.1 Safety

Proper safety precautions must be observed when collecting pore water samples. Refer to the LSASD Safety, Health and Environmental Management Program Procedures and Policy Manual (most recent version) and any pertinent site-specific Health and Safety Plans (HASP) for guidelines on safety precautions. These guidelines, however, should only be used to complement the judgment of an experienced professional. When using this procedure, minimize exposure to potential health hazards through the use of protective clothing, eye wear and gloves. Address chemicals that pose specific toxicity or safety concerns and follow any other relevant requirements, as appropriate.

1.2.2 Procedural Precautions

The following precautions should be considered when collecting pore water samples:

- Special care must be taken not to contaminate samples. This includes storing samples in a secure location to preclude conditions which could alter the properties of the sample. Samples shall be custody sealed during long-term storage or shipment.

- Collected samples are in the custody of the sampler or sample custodian until the samples are relinquished to another party.

- If samples are transported by the sampler, they will remain under his/her custody or be secured until they are relinquished.

- Shipped samples shall conform to all U.S. Department of Transportation (DOT) rules of shipment found in Title 49 of the Code of Federal Regulations (49 CFR parts 171 to 179), and/or International Air Transportation Association (IATA) hazardous materials shipping requirements found in the current edition of IATA's Dangerous Goods Regulations.

- Documentation of field sampling is done in a bound logbook. Chain-of-custody documents shall be filled out and remain with the samples until custody is relinquished.

- All shipping documents, such as bills of lading, will be retained by the project leader and stored in a secure place.

1.2.3 Records

Information generated or obtained by LSASD personnel will be organized and accounted for in accordance with LSASD records management procedures found in LSASD Operating Procedure for Control of Records, LSASDPROC-002 (most recent version). Field notes, recorded in a bound field logbook, will be generated, as well as chain-of-custody documentation, in accordance with LSASD Operating Procedure for Logbooks, LSASDPROC-010 (most recent version), and LSASD Operating Procedure for Sample and Evidence Management, LSASDPROC-005 (most recent version).

2 Sampling Methodology

2.1 General

The pore water sampling techniques and equipment described in this procedure are designed to minimize effects on the chemical and physical integrity of the sample. If the procedures in this section are followed, a representative sample of the pore water should be obtained.

2.2 Collection Considerations

The physical location of the investigator when collecting a sample may dictate the equipment to be used. Wading is the preferred method for reaching the sampling location, particularly if the stream has a noticeable current (i.e., is not impounded). However, wading may disrupt bottom sediments causing biased results; therefore, the sampler should enter the area downstream of the sampling location and collect the sample facing upstream. If the stream is too deep to wade, the pore water sample may be collected from a platform such as a boat or by SCUBA diving. If sampling from a boat or in water deeper than the length of the sampler, extensions may be utilized. If SCUBA diving, all diving activity must be conducted in accordance with EPA’s Diving Safety Manual, current version.

2.3 Summary of Procedure

Pore water is collected using a pore water extracting device (Figure 1). The most common type used by LSASD is the PushPoint™ sampler (M.H.E. Products 2003), made out of stainless-steel tubing. The sampling end of the pore water device is inserted into the sediment to the desired depth, and pore water is extracted using a syringe or peristaltic pump. The device is suitable for use only in fine-grained material (no gravel or cobble). Other similar devices may be used providing that the integrity of the sample is maintained, and no ambient surface water is allowed in contact with the sample.

2.4 Sampling Equipment

A PushPoint™ or similar sampler typically consists of a pointed tubular stainless-steel tube with a screened zone at one end and a sampling port at the other. The pointed end with the screened zone consists of a series of very fine interlaced machined slots to allow pore water to enter the sampler.

A removable guard rod adds rigidity to the sampler during sediment insertion. The length of the screened zone will depend on the site-specific study design. Depending on the data quality objectives (DQO) of the study, filters may be placed over the screened zone if additional screening is needed. Pore water is collected through the opposite end of the device by connecting flexible tubing and using a syringe or peristaltic pump to extract the sample. Teflon® tubing is the preferred tubing to be used for collecting pore water samples. However, other tubing may be used, depending upon the DQOs for the specific application.

There are many modifications that can be incorporated into the procedure to satisfy data quality objectives for a specific application. The procedures discussed in the following sections provide guidance on the basic operation of pore water sampling devices and issues to consider when collecting pore water.

An alternative system is available in LSASD inventory for use in soft sediments in water deeper than wading depth. A well screen and short riser approximately ¾” in diameter are threaded to fasten to the bottom of a custom flange. Internal threads on the screen accept a tubing adapter. The accompanying rimmed flange has a coupling with both top and bottom threads. The well screen is screwed into the bottom of the flange and Teflon® tubing is attached to the tubing adapter threaded into the well screen. For deployment, the tubing is then inserted through a PVC pipe or well casing which is then screwed into the upper threads of the flange. The entire assembly can be deployed in water up to ten feet of depth from a well anchored boat.

2.5 Pore Water Sampler Deployment Considerations

It is critical in the collection of pore water to avoid surface water intrusion. Water will flow in a path of least resistance. If space is created around the sides of the sampling end of the pore water device during deployment, surface water may flow down the outside of the device to the screened area and into the intended sample. Therefore, the pore water device should be used with a sampling flange (Figure 2), especially when collecting pore water near the sediment-surface water interface. If pore water is collected from deep in sediments, a flange may not be necessary. When inserted though the flange, the body of the pore water device should form a watertight seal to eliminate surface water intrusion during sample collection. Flanges should include an outer vertical cutting ring to enhance sealing. Flange systems can be augmented by flexible plastic sheeting of appropriate material. The sheeting can be weighted to conform to a stream bottom by objects obtained from other areas of the stream away from the sampling location. Several of the flanges in LSASD inventory have a threaded nut and washer to facilitate sealing the flange to a polyethylene sheet.

The flange can be made of any material that will not cross contaminate the intended sample. If both inorganic and organic analyses are required, the flange should be made of inert material such as stainless steel or Teflon®. The size of the flange depends on the volume of pore water to be collected. If large volumes of pore water are to be collected, use a large flange size. A useful estimate can be made for planning by taking the required water volume, tripling it to assume 33% porosity, and then calculating the dimensions of a cylinder of this volume, based upon the penetration depth of the sampler. The flange should cover at least this estimated volume. If it is not practical to use a large flange, then multiple devices may be deployed, and smaller volumes can be collected from several devices for a composite sample. If multiple devices are deployed, they should be spaced an appropriate distance apart so they will not interfere with one another.

In general, the volume of pore water that can be collected at a given location is limited. Collecting large volumes of pore water will ultimately result in the collection of water from the overlying water body. Often, minimum required volumes must be negotiated with the laboratory to limit the volumes withdrawn.

Where significant differences in parameters such as pH or conductivity exist between the surface water and pore water, a check can be made at the end of sampling to assess whether surface water intrusion has occurred by measuring the pore water parameters at the beginning and conclusion of sampling. Fluorescent dye tracing can also be used for this purpose.

2.6 Pore Water Collection

The flange is first placed at the desired sampling point with the push-point removed to allow any water to escape from under the flange. The flange rim should be carefully worked into the soil or sediment until the flange is flush with the surface. The pore water device should then be inserted through the compression adapter on the flange and into the soil or sediment as carefully as possible (Figure 2). When the sampler is inserted to the desired depth, the compression adapter should be tightened. The push-point's guard rod can then be withdrawn. Do not reinsert the guard rod into the sampler for any reason until the sampler has been cleaned (particles rolled between the two metal surfaces will lock the parts together and permanently damage the sampler.)

When deploying the pore water device, care must be taken not to disturb the sampling area. If the sampler is wading, the sampler should lean out and insert the pore water device as far as possible away from where the sampler is standing to reduce potential effects of the sampler on the integrity of the pore water sample. Depth of penetration of the pore water device depends on the objectives of the specific investigation.

After the pore water device has been successfully deployed, attach the sample tubing to the sampling port of the pore water device. Short pieces of Silastic® tubing can be used to splice Teflon® sample tubing to a push-point sampler, taking care to butt the tubing to the sampler at the center of the splice. Then attach the other end of the tubing to a sample withdrawing device, such as a syringe or a peristaltic pump (according to LSASD Operating Procedure for Pump Operation, LSASDPROC-203). Before collecting a pore water sample, be sure to purge out all air and surface water from the pore water sampler and sample tubing with the appropriate amount of pore water. This step can be accomplished by calculating the volume of the sampler and attached tubing and pumping this volume plus an additional 10 percent of pore water through the sampler and tubing prior to collecting the sample. If utilizing a syringe for collection, a three-way valve with a side syringe must be utilized for the surface water purge in order not to cross contaminate the sampling syringe.

2.6.1 Peristaltic Pump/Vacuum Jar Collection

The peristaltic pump/vacuum jug can be used for sample collection of organic or inorganic samples because it allows for the sample to be collected without coming in contact with the pump head tubing, maintaining the integrity of the sample. This is accomplished by placing a Teflon® transfer cap assembly onto the neck of a pre-cleaned standard 1-liter amber glass container (Figure 3). Teflon® tubing (¼-inch O.D.) connects the container to both the pump and the sample source. The pump creates a vacuum in the container, thereby drawing the sample into the container without it coming into contact with the pump head tubing.

Because the sample is exposed to a vacuum and is agitated as it enters the vacuum jug, this method cannot be used for collection of samples for volatile organic compounds. An alternative method for collecting volatile organics involves filling the Teflon® tubing with sample by running the pump for a short period of time. Once the tubing is full of water, the tubing is removed from the pore water sampler and, then pinched off at the pump in order to maintain the vacuum while it is being disconnected from the pump head tubing. The water is then allowed to carefully drain, by gravity, into the sample vials. Alternatively, without disconnecting the tubing from the pump head, the contained sample can be pushed out of the tubing, into the sample vials, by reversing the peristaltic pump at very low speed. Great care must still be taken with this method in order not to agitate the sample during the transfer process or to transfer water that has been in contact with the Silastic® tubing into the vials.

Because pore water is typically collected from an anaerobic environment, it is preferable, especially when collecting samples for nutrient analysis, to maintain the integrity of the sample by minimizing exposure to air. This can be accomplished by purging the sample container with an inert gas such as nitrogen or argon prior to sampling. In addition, if analyzing for nutrients or metals, the container can be pre-preserved in order to minimize exposure of the sample to ambient conditions.

An alternative, when collecting samples for metals, nutrients, or other sample analyses not affected by Silastic® tubing and when exposure to air is not a concern, is to collect the sample directly from the discharge of the pump head tubing after an adequate purge has been demonstrated. When collecting samples in this manner, there are several considerations of which to be aware. The pump head tubing (Silastic®, etc.) must be changed after each sample and a rinsate blank must be collected from a representative piece of the pump head tubing (only one blank per investigation). Also, precautions must be taken to ensure that the end of the discharge tubing is not allowed to touch the ground or other surface to ensure the integrity of samples collected in this manner.

2.6.2 Syringe

An alternative to using the pump and vacuum container is to use a syringe as the mechanism to draw the pore water through the sampling device. The tubing from the sampling port of the pore water device can be directly attached to a syringe with a three-way valve and a side syringe and the pore water sample can be manually withdrawn. The valve is first switched to the side syringe, which is used for purging air and any ambient surface water in the system prior to sampling. The volume to be purged is determined by the length and diameter of the sampling device and attached tubing. Once the sampler has been purged, the valve is switched to the sampling syringe and the sample is drawn into the syringe. The syringe can be used as the final sample container or the pore water can be transferred to another container, depending on project objectives and analytical requirements. This is the best method to use if the sample is to be collected underwater by SCUBA diving.

2.7 Quality Control

If possible, a control or background sample should be collected from a location not affected by the possible contaminants of concern and submitted with the other samples. In streams or other bodies of moving water, the control sample should be collected upstream of the sampled area. For impounded bodies of water, particularly small lakes or ponds, it may be difficult or inappropriate to obtain an unbiased control from the same body of water from which the samples are collected. In these cases, it may be appropriate to collect a background sample from a similar impoundment located near the sampled body of water if there is a reasonable certainty that the background location has not been impacted. Equipment blanks should be collected if equipment is field cleaned and reused on-site or, if necessary, to document that low- level contaminants were not introduced by pumps, bailers or other sampling equipment.

2.8 Specific Sampling Equipment Quality Assurance Techniques

All equipment used to collect pore water samples shall be cleaned as outlined in the LSASD Operating Procedure for Field Equipment Cleaning and Decontamination, LSASDPROC-205 (most recent version) or LSASD Operating Procedure for Field Equipment Cleaning and Decontamination at the FEC, LSASDPROC-206 (most recent version) and repaired, if necessary, before being stored at the conclusion of field studies. Cleaning procedures utilized in the field or field repairs shall be thoroughly documented in field records.

3 Special Sampling Considerations

3.1 Volatile Organic Compounds (VOC)

Pore water samples for VOC analysis must be collected in 40 ml glass vials with Teflon® septa. The vial may be either preserved with concentrated hydrochloric acid or they may be unpreserved. Preserved samples have a two-week holding time, whereas, unpreserved samples have only a seven day holding time. During most sampling events, preserved vials are used due to their extended holding time. In some situations, however, it may be necessary to use unpreserved vials. For example, if the surface water sample contains a high concentration of dissolved calcium carbonate, there may be an effervescent reaction between the hydrochloric acid and the water, producing large numbers of fine bubbles. This will render the sample unacceptable. In this case, unpreserved vials should be used, and arrangements must be confirmed with the laboratory to ensure that they can accept the unpreserved vials and meet the shorter sample holding times.

Samples for VOC analysis must be collected using either stainless steel or Teflon® equipment. Samples should be collected with as little agitation or disturbance as possible. The vial should be filled so that there is a meniscus at the top of the vial and absolutely no bubbles or headspace should be present in the vial after it is capped. After the cap is securely tightened, the vial should be inverted and tapped on the palm of one hand to see if any undetected bubbles are dislodged. If a bubble or bubbles are present, the vial should be refilled. Care should be taken not to flush any preservative out of the vial during topping off. If, after attempting to refill and cap the vial, bubbles are still present, a new vial should be obtained, and the sample should be re-collected.

3.2 Dissolved Metals Sample Collection

If a dissolved metals pore water sample is to be collected, an in-line filtration should be used. The use of disposable, high-capacity filter cartridges (barrel-type) or membrane filters in an in-line filter apparatus is preferred. The high-capacity, barrel-type filter is preferred due to the higher surface area associated with this configuration.

Potential differences could result from variations in filtration procedures used to process water samples for the determination of trace element concentrations. A number of factors associated with filtration can substantially alter "dissolved" trace element concentrations; these include filter pore size, filter type, filter diameter, filtration method, volume of sample processed, suspended sediment concentration, suspended sediment grain-size distribution, concentration of colloids and colloidally-associated trace elements, and concentration of organic matter. Therefore, consistency is critical in the comparison of short-term and long-term results. Further guidance on filtration may be obtained from Section 4.7.3 of the LSASD Groundwater Sampling Procedure (LSASDPROC-301).

3.3 Special Precautions for Pore Water Sampling

- A clean pair of new, non-powdered, disposable latex gloves will be worn each time a different location is sampled, and the gloves should be donned prior to handling sampling equipment. The gloves should not come in contact with the media being sampled and should be changed any time during sample collection when their cleanliness is compromised.
- All background or control samples shall be collected and placed in separate ice chests or shipping containers. Sample collection activities shall proceed progressively from the least suspected contaminated area to the most suspected contaminated area. Samples of waste or highly contaminated media must not be placed in the same ice chest as environmental (i.e., containing low contaminant levels) or background samples.
- If possible, one member of the field sampling team should take all the notes and photographs, fill out tags, etc., while the other members collect the samples.
- Samplers must use new, verified, certified clean disposable equipment, or pre-cleaned non-disposable equipment. Non-disposable equipment should be pre-cleaned according to procedures contained in LSASD Operating Procedure for Field Equipment Cleaning and Decontamination (LSASDPROC-205), for collection of samples for trace metals or organic compound analyses.

3.4 Sample Handling and Preservation Requirements

- Pore water will typically be collected using a peristaltic pump and placed directly into sampling containers. In some cases, a syringe may be used to collect the pore water and then either left in the syringe as the sample container or transferred into an appropriate container.
- During sample collection, if transferring the sample from a collection device, make sure that the device does not come in contact with the sample containers.
- Place the sample into appropriate, labeled containers. Samples collected for VOC analysis must not have any headspace (see Section 3.1).
- All samples requiring preservation must be preserved as soon as practically possible, soon after sample collection. If pre-preserved VOA vials are used, these will be preserved with concentrated hydrochloric acid prior to departure for the field investigation. For all other chemical preservatives, LSASD will use the appropriate chemical preservative generally stored in an individual single-use vial as described in the LSASD Operating Procedure for Field Sampling Quality Control (LSASDPROC-011). The adequacy of sample preservation will be checked after the addition of the preservative for all samples, except for the samples collected for VOC analysis. If it is determined that a sample is not acceptably preserved, additional preservative should be added to achieve adequate preservation. Preservation requirements for surface water samples are found in

the USEPA Laboratory Services Branch *Laboratory Operations and Quality Assurance Manual* (LOQAM).

Figure 1. Pore Water Sampling Device

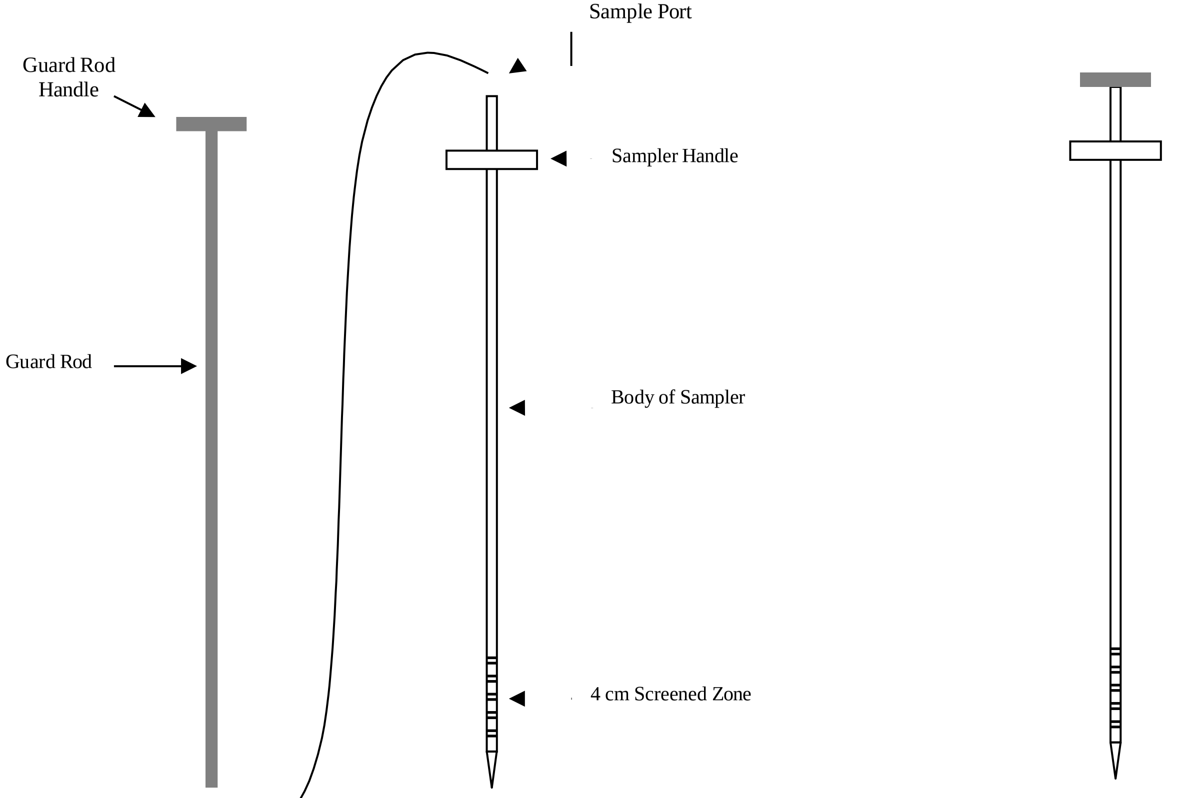
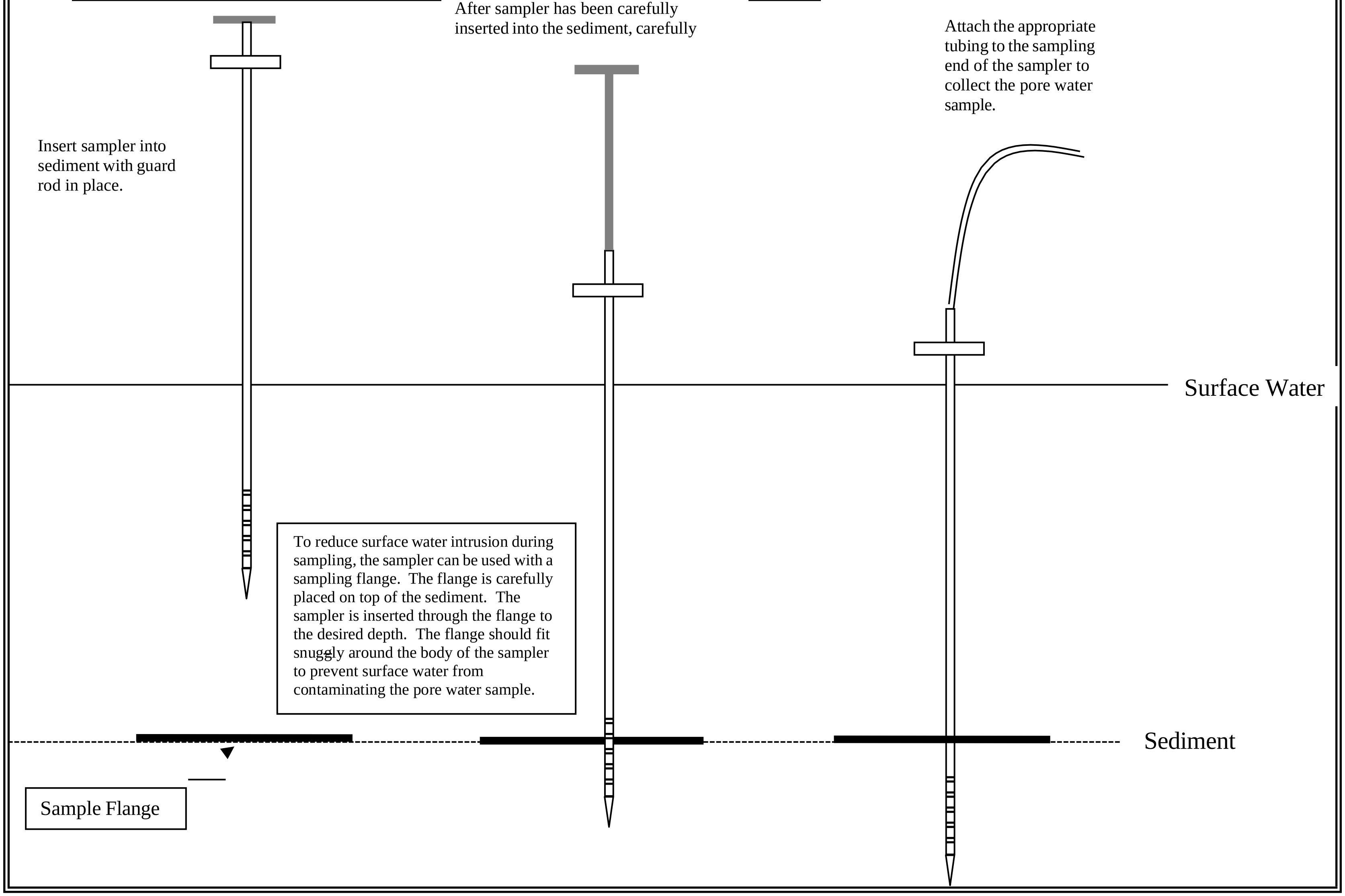


Figure 1A. Disassembled Device

Figure 1B. Assembled Device

Actual length and width of device will vary, depending on sampling needs and site conditions.
Note: cm = centimeter

Figure 2. Pore Water Sampler Deployment Using a Sampling Flange



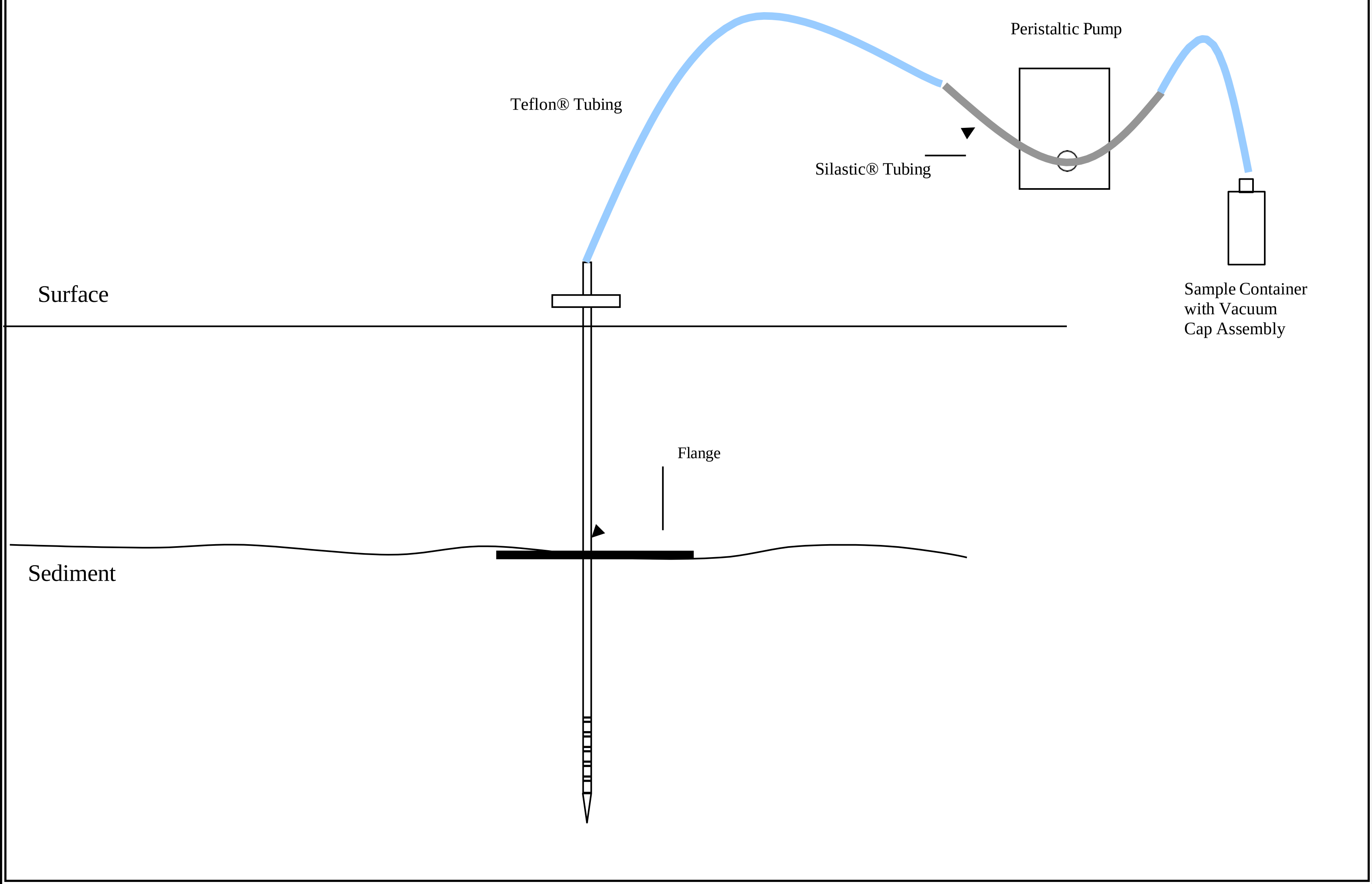
Insert sampler into sediment with guard rod in place.

After sampler has been carefully inserted into the sediment, carefully

Attach the appropriate tubing to the sampling end of the sampler to collect the pore water sample.

To reduce surface water intrusion during sampling, the sampler can be used with a sampling flange. The flange is carefully placed on top of the sediment. The sampler is inserted through the flange to the desired depth. The flange should fit snuggly around the body of the sampler to prevent surface water from contaminating the pore water sample.

Figure 3. Pore Water Sampler Deployment Using a Peristaltic Pump to Sample



References

International Air Transport Authority (IATA). Dangerous Goods Regulations, Most Recent Version.

M.H.E. Products. 2003. PushPoint Sampler (US Pat. # 6,470,967) Operators Manual and Applications Guide, Version 2.01. East Tawas, MI. http://www.mheproducts.com

LSASD Operating Procedure for Control of Records, LSASDPROC-002, Most Recent Version.

LSASD Operating Procedure for Sample and Evidence Management, LSASDPROC-005, Most Recent Version.

LSASD Operating Procedure for Logbooks, LSASDPROC-010, Most Recent Version.

LSASD Operating Procedure for Surface Water Sampling, LSASDPROC-201, Most Recent Version.

LSASD Operating Procedure for Pump Operation, LSASDPROC-203, Most Recent Version.

LSASD Operating Procedure for Field Equipment Cleaning and Decontamination, LSASDPROC-205, Most Recent Version.

LSASD Operating Procedure for Field Equipment Cleaning and Decontamination at the FEC, LSASDPROC-206, Most Recent Version.

LSASD Operating Procedure for Groundwater Sampling, LSASDPROC-301, Most Recent Version.

LSASD Operating Procedure for Potable Water Supply Sampling, LSASDPROC-305, Most Recent Version.

Title 49 Code of Federal Regulations, Pts. 171 to 179, Most Recent Version.

USEPA LSBLOQAM. Laboratory Services Branch Laboratory Operations and Quality Assurance Manual Region 4, Laboratory Services and Applied Science Division, Athens, GA. Most Recent Version.

USEPA SHEMP Safety, Health and Environmental Management Program Procedures and Policy Manual. Laboratory Services and Applied Science Division, Region 4, Athens, GA. Most Recent Version.

LSASD Operating Procedure for Field Sampling Quality Control, LSASDPROC-011, Most Recent Version.

USEPA. 2016. Diving Safety Manual, current version. US Environmental Protection Agency, Washington, DC.

Revision History

The top row of this table shows the most recent changes to this controlled document. For previous revision history information, archived versions of this document are maintained by the LSASD Document Control Coordinator on the LSASD local area network (LAN).

History	Effective Date
Replaced Chief with Supervisor; General formatting revisions.	April 22, 2023
LSASDPROC-513-R4, Pore Water Sampling, *replaces SESDPROC-513-R3.* Laboratory Services and Applied Science Division replaces Science and Ecosystem Support Division **Title Page:** Changed the Field Quality Manager from Hunter Johnson to Stacie Masters. **General:** Corrected typographical, grammatical, and/or editorial errors. Added language to clarify some procedures.	May 13, 2020
SESDPROC-513-R3, Pore Water Sampling, replaces SESDPROC-513-R2. **General:** Corrected any typographical, grammatical, and/or editorial errors. **Title Page:** Changed the Field Quality Manager from Bobby Lewis to Hunter Johnson. Updated cover page to represent SESD reorganization. John Deatrick was not listed as the Supervisor of the Field Services Branch	December 16, 2016
SESDPROC-513-R2, Pore Water Sampling, *replaces SESDPROC-513-R1.*	February 28, 2013
SESDPROC-513-R1, Pore Water Sampling, *replaces SESDPROC-513-R0.*	January 29, 2013
SESDPROC-513-R0, Pore Water Sampling, *Original Issue*	February 05, 2007

DOCUMENT
12

Rees, Jeromy

From: Diers, Stefanie
Sent: Thursday, November 2, 2023 7:52 AM
To: Dunaway, Lynn; Terranova, Sara
Cc: Summers, Michael; Hunt, Lauren; Bierwagen, Justin; Mullenax, Heather; Garee, Matthew J.; Sofat, Sanjay
Subject: RE: Joppa AS

Thanks. Sara and I will review and follow up with questions we have.

From: Dunaway, Lynn <LYNN.DUNAWAY@Illinois.gov>
Sent: Wednesday, November 1, 2023 3:40 PM
To: Diers, Stefanie <Stefanie.Diers@Illinois.gov>; Terranova, Sara <Sara.Terranova@Illinois.gov>
Cc: Summers, Michael <Michael.Summers@Illinois.gov>; Hunt, Lauren <Lauren.Hunt@Illinois.gov>; Bierwagen, Justin <Justin.Bierwagen@Illinois.gov>; Mullenax, Heather <Heather.Mullenax@Illinois.gov>; Garee, Matthew J. <Matthew.Garee@Illinois.gov>; Sofat, Sanjay <Sanjay.Sofat@Illinois.gov>
Subject: Joppa AS

Mike and I have both reviewed this and Mike asked me to send this along to you.

As filed, the Recommendation allows a 6-year temp. AS to allow sampling (5 years) and modeling/reporting (1 year) to prove monitored natural attenuation (MNA) will work.
USEPA has been very non-receptive to MNA demonstrations at other sites around the country.
Therefore, IEPA needs to amend the Rec to withdraw the Alt Standard suggested or not amend in which case Joppa maybe subject to USEPA enforcement. (Note: This was where the upper management decision came in, considering our goal to get primacy)

IEPA also asked for source monitoring, Joppa did install and has been doing total metals monitoring, but is not done yet, so the ask would be:
Please provide the groundwater sampling and analysis results for total metals at site wells listed in the Attachment B from Ramboll and Associates dated December 19, 2022 for 8 quarters of groundwater sampling along with the precipitation, infiltration and leaching analysis. [Note: unlikely that they have completed this at this time since we are just under two years since the submittal of our recommendation]

IEPA also asked for CCR characterization. Joppa provided 6 CCR samples with analysis. The issue is that there are roughly 5 million cubic yards of CCR in Joppa West, so the ask would be:
Please provide further CCR solids sampling and analysis to include a minimum of 1 sample location per 10% of the total cubic yards of CCR, with 3 samples collected from each location: one (1) from the upper 1/3 of the CCR by depth from ground surface, one (1) from the middle 1/3 of the CCR by depth from ground surface, and one (1) from the bottom 1/3 of the CCR by depth from ground surface. This would 30 samples over the entire Joppa West site. The SPLP analysis in accordance with SW846 using the lowest pH on site of 3.5.

DOCUMENT
13

Rees, Jeromy

From: Summers, Michael
Sent: Wednesday, November 1, 2023 3:32 PM
To: Hunt, Lauren; Dunaway, Lynn
Cc: Mullenax, Heather; Garee, Matthew J.; Bierwagen, Justin
Subject: RE: Joppa West Adjusted Standard Recommendation Meeting follow up

Added to clarify for lawyers in red

From: Hunt, Lauren <Lauren.Hunt@Illinois.gov>
Sent: Wednesday, November 1, 2023 3:22 PM
To: Dunaway, Lynn <LYNN.DUNAWAY@Illinois.gov>; Summers, Michael <Michael.Summers@Illinois.gov>
Cc: Mullenax, Heather <Heather.Mullenax@Illinois.gov>; Garee, Matthew J. <Matthew.Garee@Illinois.gov>; Bierwagen, Justin <Justin.Bierwagen@Illinois.gov>
Subject: RE: Joppa West Adjusted Standard Recommendation Meeting follow up

Final draft for Lynn to pass on:

As filed, the Recommendation allows a 6-year temp. AS to allow sampling (5 years) and modeling/reporting (1 year) to prove monitored natural attenuation (MNA) will work.
USEPA has been very non-receptive to MNA demonstrations at other sites around the country.
Therefore, IEPA needs to amend the Rec to withdraw the Alt Standard suggested or not amend in which case Joppa maybe subject to USEPA enforcement. (Note: This was where the upper management decision came in, considering our goal to get primacy)

IEPA also asked for source monitoring, Joppa did install and has been doing total metals monitoring, but is not done yet, so the ask would be:
Please provide the groundwater sampling and analysis results for total metals at site wells listed in the Attachment B from Ramboll and Associates dated December 19, 2022 for 8 quarters of groundwater sampling along with the precipitation, infiltration and leaching analysis. [Note: unlikely that they have completed this at this time since we are just under two years since the submittal of our recommendation]

IEPA also asked for CCR characterization. Joppa provided 6 CCR samples with analysis. The issue is that there are roughly 5 million cubic yards of CCR in Joppa West, so the ask would be:
Please provide further CCR solids sampling and analysis to include a minimum of 1 sample location per 10% of the total cubic yards of CCR, ~~and~~ with ~~one-third of the~~ 3 samples collected from each location: ~~must be~~ one (1) from the upper 1/3 of the CCR by depth from ground surface, ~~one-third collected~~ one (1) from the middle 1/3 of the CCR by depth from ground surface, and ~~one-third collected~~ one (1) from the bottom 1/3 of the CCR by depth from ground surface. This would 30 samples over the entire site. The SPLP analysis in accordance with SW846 using the lowest pH on site of 3.5. ~~the samples must be spread out as follows:~~

Lauren I. Hunt, M.S.
(she/they/he)
Environmental Protection Geologist III
Illinois Environmental Protection Agency
Bureau of Water
Groundwater Section
1021 N. Grand Avenue
PO Box 13
Springfield, IL 62702
D: 217-524-9048

C: 309-361-0037
Lauren.hunt@illinois.gov
Hours: 8:30 am to 5:30 pm Tuesday through Friday
8:30 am to 4 pm Mondays and alternating Mondays off
Working remotely Mondays and Fridays.

From: Dunaway, Lynn <LYNN.DUNAWAY@Illinois.gov>
Sent: Wednesday, November 1, 2023 3:11 PM
To: Summers, Michael <Michael.Summers@Illinois.gov>; Hunt, Lauren <Lauren.Hunt@Illinois.gov>
Cc: Mullenax, Heather <Heather.Mullenax@Illinois.gov>; Garee, Matthew J. <Matthew.Garee@Illinois.gov>; Bierwagen, Justin <Justin.Bierwagen@Illinois.gov>
Subject: RE: Joppa West Adjusted Standard Recommendation Meeting follow up

How about something like this:

1 sample per 10% of the volume with one-third of the samples being collected as follows:
upper 1/3 of the CCR by depth from ground surface,
middle 1/3 of the CCR by depth from ground surface, and
bottom 1/3 of the CCR by depth from ground surface.

From: Summers, Michael <Michael.Summers@Illinois.gov>
Sent: Wednesday, November 1, 2023 2:43 PM
To: Dunaway, Lynn <LYNN.DUNAWAY@Illinois.gov>; Hunt, Lauren <Lauren.Hunt@Illinois.gov>
Cc: Mullenax, Heather <Heather.Mullenax@Illinois.gov>; Garee, Matthew J. <Matthew.Garee@Illinois.gov>; Bierwagen, Justin <Justin.Bierwagen@Illinois.gov>
Subject: RE: Joppa West Adjusted Standard Recommendation Meeting follow up

Do we have an rational for 50,000 cubic yards? If its 5 million cubic yards and one sample per 50,000 would equal 100 samples. is this an amount we want to look at?

When using a volume are we likely to run into a “disagreement” with the site on how actual large the site is? Would it be more appropriate to base sample on the surface area of the site. Or since we do have volumes (ie depth estimates) we could do a percentage of the entire volume. It is easily quantifiable, no argument on the size of the facility. Something like a shallow, mid-point and deep (3) samples collected per acre? 3 Per every 5 acres of surface area? take a look at what is a reasonable number of samples to characterize the site.

If we to end up asking for a set number of samples, we still need to make sure that various depth are mentioned in the request for samples to adequately characterize the site.

From: Dunaway, Lynn <LYNN.DUNAWAY@Illinois.gov>
Sent: Wednesday, November 1, 2023 11:54 AM
To: Hunt, Lauren <Lauren.Hunt@Illinois.gov>; Summers, Michael <Michael.Summers@Illinois.gov>
Cc: Mullenax, Heather <Heather.Mullenax@Illinois.gov>; Garee, Matthew J. <Matthew.Garee@Illinois.gov>; Bierwagen, Justin <Justin.Bierwagen@Illinois.gov>
Subject: RE: Joppa West Adjusted Standard Recommendation Meeting follow up

For the attorneys I would break this out more like this:

As filed, the Recommendation allows a 6-year temp. AS to allow sampling (5 years) and modeling/reporting (1 year) to prove monitored natural attenuation (MNA) will work.
USEPA has been very non-receptive to MNA demonstrations at other sites around the country.

Therefore, IEPA needs to amend the Rec to withdraw the Alt Standard suggested or not amend in which case Joppa maybe subject to USEPA enforcement. (Note: This was where the upper management decision came in, considering our goal to get primacy)

IEPA also asked for source monitoring, Joppa did install and has been doing total metals monitoring, but is not done yet, so the ask would be:
Please provide the groundwater sampling and analysis results for total metals at site wells listed in the Attachment B from Ramboll and Associates dated December 19, 2022 for 8 quarters of groundwater sampling along with the precipitation, infiltration and leaching analysis. [Note: unlikely that they have completed this at this time since we are just under two years since the submittal of our recommendation]

IEPA also asked for CCR characterization. Joppa provided 6 CCR samples with analysis. The issue is that there are roughly 5 million cubic yards of CCR in Joppa West, so the ask would be:
Please provide further CCR solids sampling and analysis to include a minimum of 1 sample per 50,000? cubic yards of CCR and SPLP analysis in accordance with SW846 using the lowest pH on site of 3.5. [Note: Mike I'll let you weigh in on volume of CCR per sample that is appropriate.

From: Hunt, Lauren <Lauren.Hunt@Illinois.gov>
Sent: Wednesday, November 1, 2023 11:31 AM
To: Dunaway, Lynn <LYNN.DUNAWAY@Illinois.gov>; Summers, Michael <Michael.Summers@Illinois.gov>
Cc: Mullenax, Heather <Heather.Mullenax@Illinois.gov>; Garee, Matthew J. <Matthew.Garee@Illinois.gov>; Bierwagen, Justin <Justin.Bierwagen@Illinois.gov>
Subject: Joppa West Adjusted Standard Recommendation Meeting follow up

Hi Mike and Lynn.
Please review the following for Sara and Stefanie:

1. Please provide the groundwater sampling and analysis results for total metals at site wells listed in the Attachment B from Ramboll and Associates dated December 19, 2022 for 8 quarters of groundwater sampling along with the precipitation, infiltration and leaching analysis. [unlikely that they have completed this at this time since we are just under two years since the submittal of our recommendation].
2. Please provide further CCR solids sampling and analysis to include a minimum of 1 sample per 50,000? cubic yards of CCR and SPLP analysis in accordance with SW846 using the lowest pH on site of 3.5. [Current status is 6 total samples for approximately 5 million cubic yards (or 103.5 acres and 30 feet deep).]

Please note: EEI shows that the hydraulic conductivities are downward from the CCR unit through the UCU (Upper confining unit) into the Upper Aquifer (UA). Total solids CCR samples show that the CCR contains all of the constituents in 845.600 whereas the surrounding formations do not contain some of those and generally contain less of the 845.600 constituents than the CCR where present.

Thanks. Lauren

Lauren I. Hunt, M.S.
(she/they/he)
Environmental Protection Geologist III
Illinois Environmental Protection Agency
Bureau of Water
Groundwater Section
1021 N. Grand Avenue
PO Box 13
Springfield, IL 62702
D: 217-524-9048
C: 309-361-0037

Lauren.hunt@illinois.gov
Hours: 8:30 am to 5:30 pm Tuesday through Friday
8:30 am to 4 pm Mondays and alternating Mondays off
Working remotely Mondays and Fridays.

DOCUMENT

14

Rees, Jeromy

From: Voelker, Brian <Brian.Voelker@vistracorp.com>
Sent: Friday, December 1, 2023 1:52 PM
To: EPA.CCR.Part845.Coordinator; EPA.CCR.Part845.Notify; Hunt, Lauren; EPA.BOW.GWS.CCR
Cc: Morris, Phil; Fuller, Rhys; Modeer, Victor; Cravens, Stuart; Davies, Sam; Mitchell, David
Subject: [External] Vermilion Power Plant NEAP ASD submittal notice

As a courtesy this email is to provide notice that an ASD for the Vermilion New EAST Pond was submitted/delivered to IEPA via FedEx on November 10, 2023, to the address provided below.

Illinois Environmental Protection Agency
Bureau of Water Permit Section #15
1021 North Grand Avenue East
P.O. Box 19276
Springfield, IL 62794

It was also placed on the Luminant CCR public website, and you can access a copy there. The link below will take you to the website.
https://www.luminant.com/ccr/illinois-ccr/?dir=il-ccr%2FVermilion%2F2023

Please let me know if you have questions or concerns.

Thanks,
Brian

DOCUMENT
15

Rees, Jeromy

From: Seif, Josiah
Sent: Tuesday, December 5, 2023 9:17 AM
To: EPA.BOW.GWS.CCR; Hunt, Lauren; MacDonna, Keegan
Cc: Summers, Michael; Dunaway, Lynn; Rompot, Derek
Subject: Vermilion Power Plant New East Ash Pond received on December 1st 2023.

ASD For the **Vermilion Power Plant New East Ash Pond** was received on December 1st 2023. It was misplaced and just arrived today, 12/5 to permits. The document has been scanned to the N:Drive, Listserve has been notified and hard copy has been placed in the Impoundment. If you have any questions, please feel free to ask.

Thank you,

Josiah M. Seif

Josiah M. Seif
CCR Office Coordinator
Bureau of Water
Illinois Environmental Protection Agency
217-782-0610
Josiah.Seif@illinois.gov

DOCUMENT
16

Luminant

Dynegy Midwest Generation, LLC
1500 Eastport Plaza Drive
Collinsville, IL 62234

December 1, 2023

Illinois Environmental Protection Agency
DWPC – Permits MC#15
Attn: 35 I.A.C. § 845.650(e) Alternative Source Demonstration Submittal
1021 North Grand Avenue East
P.O. Box 19276
Springfield, IL 62794-9276

Re: Vermilion Power Plant New East Ash Pond; IEPA ID # W1838000002-04

Dear Mr. LeCrone:

In accordance with Title 35 of the Illinois Administrative Code (35 I.A.C.) Section (§) 845.650(e), Dynegy Midwest Generation, LLC (DMG) is submitting this Alternative Source Demonstration (ASD) for exceedances observed from the Quarter 2 2023 sampling event at the Vermilion Power Plant New East Ash Pond, identified by Illinois Environmental Protection Agency (IEPA) ID No. W1838000002-04.

This ASD is being submitted within 60 days from the date of determination of an exceedance of a groundwater protection standard (GWPS) for constituents listed in 35 I.A.C. § 845.600. As required by 35 I.A.C. § 845.650 (e)(1), the ASD was placed on the facility's website within 24 hours of submittal to the agency.

One hard copy is provided with this submittal.

RECEIVED
DEC 1 2023
IEPA/CAS

Sincerely,

Dianna Tickner

Dianna Tickner
Sr. Director – Decommission and Demolition

Enclosures
Alternate Source Demonstration, Quarter 2 2023, New East Ash Pond Vermilion Power Plant

Intended for
Dynegy Midwest Generation, LLC

Date
December 1, 2023

Project No.
1940103649-014

35 I.A.C. § 845.650(E): ALTERNATIVE SOURCE DEMONSTRATION

NEW EAST ASH POND
VERMILION POWER PLANT
OAKWOOD, ILLINOIS
IEPA ID: W1838000002-04

RAMBOLL Bright ideas. Sustainable change.

CERTIFICATIONS

I, Eric J. Tlachac, a qualified professional engineer in good standing in the State of Illinois, certify that the information in this report is accurate as of the date of my signature below. The content of this report is not to be used other than for its intended purpose and meaning, or for extrapolations beyond the interpretations contained herein.

Eric J. Tlachac

Eric J. Tlachac
Qualified Professional Engineer
062-063091
Illinois
Ramboll Americas Engineering Solutions, Inc.
Date: December 1, 2023

ERIC J. TLACHAC
062-063091

I, Brian G. Hennings, a professional geologist in good standing in the State of Illinois, certify that the information in this report is accurate as of the date of my signature below. The content of this report is not to be used other than for its intended purpose and meaning, or for extrapolations beyond the interpretations contained herein.

Brian G. Hennings
Professional Geologist
196-001482
Illinois
Ramboll Americas Engineering Solutions, Inc.
Date: December 1, 2023

BRIAN G. HENNINGS
196.001482

CONTENTS

TABLES (IN TEXT)

FIGURES (IN TEXT)

FIGURES (ATTACHED)

APPENDICES

ACRONYMS AND ABBREVIATIONS

35 I.A.C.	Title 35 of the Illinois Administrative Code
ASD	Alternative Source Demonstration
BCU	Bedrock Confining Unit
CCR	coal combustion residuals
DMG	Dynegy Midwest Generation, LLC
E001	Event 1
EPRI	Electric Power Research Institute
GMP	Groundwater Monitoring Plan
GWPS	groundwater protection standard
HCR	Hydrogeologic Site Characterization Report
ISGS	Illinois State Geological Survey
IQR	interquartile range
LOE(s)	line(s) of evidence
mg/L	milligrams per liter
Middle Fork	Middle Fork of the Vermilion River
NAVD88	North American Vertical Datum of 1988
NEAP	New East Ash Pond
PCA	principal component analysis
Ramboll	Ramboll Americas Engineering Solutions, Inc.
SEP	sequential extraction procedure
SI	surface impoundment
SSL	statistically significant level
TDS	total dissolved solids
TU	tritium units
UCU	Upper Confining Unit
UU	Upper Unit
VPP	Vermilion Power Plant

1. INTRODUCTION

Under Title 35 of the Illinois Administrative Code (35 I.A.C.) § 845.650(e), within 60 days from the date of determination of an exceedance of a groundwater protection standard (GWPS) for constituents listed in 35 I.A.C. § 845.600, an owner or operator of a coal combustion residuals (CCR) surface impoundment (SI) may complete a written demonstration that a source other than the CCR SI caused the contamination and the CCR SI did not contribute to the contamination, or that the exceedance of the GWPS resulted from error in sampling, analysis, statistical evaluation, natural variation in groundwater quality, or a change in the potentiometric surface and groundwater flow direction (Alternative Source Demonstration [ASD]).

This ASD has been prepared on behalf of Dynegy Midwest Generation, LLC (DMG) by Ramboll Americas Engineering Solutions, Inc (Ramboll), to provide pertinent information pursuant to 35 I.A.C. § 845.650(e) for the Vermilion Power Plant (VPP) New East Ash Pond (NEAP) (*i.e.,* Site) located near Oakwood, Illinois.

The most recent quarterly sampling event (Event 1 [E001]) was completed on June 29, 2023, and analytical data were received on August 3, 2023. In accordance with 35 I.A.C. § 845.610(b)(3)(C), comparison of statistically derived values with the GWPSs described in 35 I.A.C. § 845.600 to determine exceedances of the GWPS was completed by October 2, 2023, within 60 days of receipt of the analytical data (Ramboll, 2023). The statistical comparison identified the following GWPS exceedances at compliance groundwater monitoring wells:

- Chloride at wells 35D and 70D
- Lithium at wells 35D and 70D
- Sulfate at wells 35D and 70S
- Total dissolved solids (TDS) at wells 35D and 70S

Pursuant to 35 I.A.C. § 845.650(e), the lines of evidence (LOE) presented in **Section 3** demonstrate that sources other than the NEAP are the cause of the chloride, lithium, sulfate, and TDS GWPS exceedances at **wells 35D and 70D** listed above and the NEAP has not contributed to the exceedances.

This ASD was completed by December 1, 2023, within 60 days of determination of the exceedances (October 2, 2023), as required by 35 I.A.C. § 845.650(e). This ASD has been completed in conformance with guidance provided in the Electric Power Research Institute (EPRI) guidance for development of ASDs at CCR sites (EPRI, 2017), and the United States Environmental Protection Agency (USEPA)'s Solid Waste Disposal Facility Criteria: Technical Manual (USEPA, 1993).

Sulfate and TDS GWPS exceedances at **well 70S** will be addressed in accordance with 35 I.A.C. § 845.660.

2. BACKGROUND

2.1 Site Location and Description

The former VPP is located four miles northeast of the Village of Oakwood in Vermilion County. The NEAP lies in the bottomlands of the Middle Fork of the Vermilion River (Middle Fork) and is bordered to the west by bluffs, to the south by unimproved DMG land, and to the north and east by the Middle Fork. Several underground coal mines and one surface mine were historically operated both beneath the NEAP and in the vicinity of the VPP.

2.2 Description of New East Ash Pond CCR Unit

The NEAP is a 29-acre inactive, unlined CCR SI constructed overtop a thick shale formation using berms constructed with a low-permeability clay core and cutoff walls keyed into the underlying shale formation.

The original East Ash Pond (1989 pond footprint) was constructed in 1989 and expanded in 2002 to form the present-day NEAP. The 1989 pond footprint was built overtop a thick shale formation which is greater than 80 feet thick in the vicinity of the ash ponds. The earthen berms on the north, east, and south sides of the 1989 pond footprint were constructed with a low-permeability clay core and cutoff walls keyed into the underlying shale formation. The cutoff walls extended approximately 8 feet into the underlying shale. A natural earthen bluff composed of low-permeability native clays formed the west side of the 1989 pond footprint.

New berms were constructed to expand the capacity of the 1989 pond footprint in 2002, forming the footprint of the present-day NEAP. The new berms raised the height of the original berms and were constructed with clay liners keyed into the underlying clay core. A cutoff trench backfilled with low permeability fill was placed along the western side slope of the enlarged NEAP. The low-permeability materials surrounding the footprint of the present-day NEAP form the existing containment system. The secondary pond was not expanded or modified as part of the 2002 NEAP expansion. The VPP ceased operations in 2011 when the power plant was retired.

2.3 Geology and Hydrogeology

2.3.1 Site Hydrogeology

Significant site investigation has been completed at the VPP to fully characterize the geology, hydrogeology, and groundwater quality as provided in the October 2021 operating permit application (Geosyntec, 2021), the January 2022 construction permit application (Geosyntec, 2022), and the Hydrogeologic Site Characterization Report (HCR; Ramboll, 2021a). These materials are incorporated herein. A site conceptual model has been developed and is discussed below.

In addition to the CCRs present in the NEAP, there are three different types of unlithified material present above the bedrock, which were categorized into hydrostratigraphic units in this report as follows:

- **Upper Unit (UU):** includes mixed Quaternary alluvial deposits of the Cahokia Alluvium described as sand with occasional layers of silty clay. The alluvial sand is generally a fine to medium sand that contains silts, clays, and gravels in varying amounts. This unit is present outside of the NEAP and in the bottomlands of the Middle Fork.

- **Upper Confining Unit (UCU):** consists of predominantly low permeability silty and clayey diamictons (glacial till) of the Wedron Formation with intermittent sand layers and lenses. This unit is present outside of the NEAP and along the western bluff of the Middle Fork.
- **Bedrock Confining Unit (BCU):** lowermost unit identified at the site and underlies all unlithified deposits. This unit occurs within Pennsylvanian shale which is the uppermost lithified unit at the Site.

None of the hydrostratigraphic units described above have been identified as an aquifer. However, the Upper Unit and BCU have been identified as potential migration pathways (PMPs).

Groundwater flow direction and gradients toward the Middle Fork have not changed significantly since the hydrogeologic study of the NEAP was completed in 2003 (Ramboll, 2021a; Kelron, 2003), and recent data supports the existing conceptual site model. A bedrock potentiometric surface map for June 19, 2023, is presented in **Figure 1**.

2.3.2 Regional Bedrock Geology

Regional investigations of the Illinois Basin have identified bedrock (specifically brines within the bedrock formations) as a source of chloride in groundwater (Kelley et al, 2012; Panno et al, 2018). Studies by Cartwright (1970) and Siegel (1989) indicate that groundwater migrates toward the center of the Illinois Basin and discharges upward through overlying confining units. The "Saline groundwater and brines can be brought near or to the land surface by natural conditions, such as migrating up prominent fractures and/or faults in bedrock, or by anthropogenic activities, such as exploration for and exploitation of petroleum. The mixing of upward-migrating saline groundwater with fresh groundwater from shallow aquifers can make groundwater from private wells undrinkable and can present a very expensive problem for municipalities (Panno and Hackley, 2010). Illinois State Geological Survey reporting includes 31 chloride results from available water samples (including some samples from VPP) which range from 2.1 to 30,269 milligrams per liter (mg/L) with mean value of 1,689 mg/L and median of 13 mg/L (Illinois State Geological Survey [ISGS] 2002). The report also concludes that water from the wells completed in shale contained higher concentrations of aluminum, barium, bromide, boron, chloride, fluoride, iron, lithium, potassium, sodium, and strontium. Tritium and carbon-14 age dating has demonstrated that groundwater from the bedrock is significantly older than that from the shallow Quaternary deposits (Kelron, 2003; ISGS, 2002).

2.4 Groundwater and NEAP Monitoring

The monitoring system for the NEAP was established in the Groundwater Monitoring Plan (GMP; Ramboll, 2021b) and consists of monitoring wells installed in the UU, UCU, and BCU, including background monitoring wells 10 and 22, located west of the NEAP, and compliance monitoring wells 16A, 16B, 35S, 35D, 70S, 70D, 71S and 71D (**Figure 1**). NED1 (installed in CCR) is used to collect porewater samples and monitor water levels within the NEAP.

3. LINES OF EVIDENCE THAT POTENTIAL GROUNDWATER PROTECTION STANDARD EXCEEDANCES ARE NOT RELATED TO THE NEAP

As allowed by 35 I.A.C. § 845.650(e), this ASD demonstrates that sources other than the NEAP (the CCR unit) caused the exceedances at 35D (chloride, lithium, sulfate, and TDS) and 70D (chloride and lithium) and the NEAP did not contribute to the exceedances. Specifically, the following LOEs conclude that the chloride and lithium exceedances at 35D and 70D are due to groundwater interactions with the bedrock, and that the sulfate exceedance at 35D is due to influence from historic coal mining activities. LOEs supporting this ASD include the following:

1. The ionic composition of bedrock groundwater is different than the ionic composition of porewater and consistent with published observations for Pennsylvanian Bedrock.
2. Concentrations of chloride in the NEAP porewater are lower than those observed in the groundwater.
3. A bedrock solids and geochemical evaluation identified naturally occurring shales as the source of lithium and chloride exceedances at 35D and 70D.
4. A bedrock solids and geochemical evaluation identified naturally occurring coal seams as the source of the sulfate exceedance at 35D due to regional upward vertical hydraulic gradients in the shale bedrock.
5. Isotopic analysis of groundwater from the bedrock and overlying Quaternary deposits indicate that bedrock groundwater is between 13,000 and 35,000 years older than groundwater in the Quaternary deposits; and bedrock groundwater is isolated from the groundwater in the quaternary deposits.

These LOEs are described and supported in greater detail below.

Since the major contributors to TDS are chloride and sulfate at 70D and 35D (respectively), the LOEs that apply to chloride and sulfate also apply to TDS. **Figure A** (on the following page) shows boxplots summarizing the relative contribution of each major ion to TDS in groundwater from wells 35D and 70D since 2021. Box plots graphically represent the range of a given dataset using lines to construct a box where the lower line, midline, and upper line of the box represent the values of the first quartile, median, and third quartile values, respectively. The minimum and maximum values of the dataset (excluding outliers) are illustrated by whisker lines extending beyond the first and third quartiles of (*i.e.*, below and above) the box plot. The interquartile range (IQR) is the distance between the first and third quartiles. Outliers (values that are at least 1.5 times the IQR away from the edges of the box) are represented by single points plotted outside of the range of the whiskers. **Figure A** shows that chloride has the greatest contribution to TDS concentrations at 70D (median of 42 percent) and sulfate has the greatest contribution to TDS at 35D (median of 42 percent).

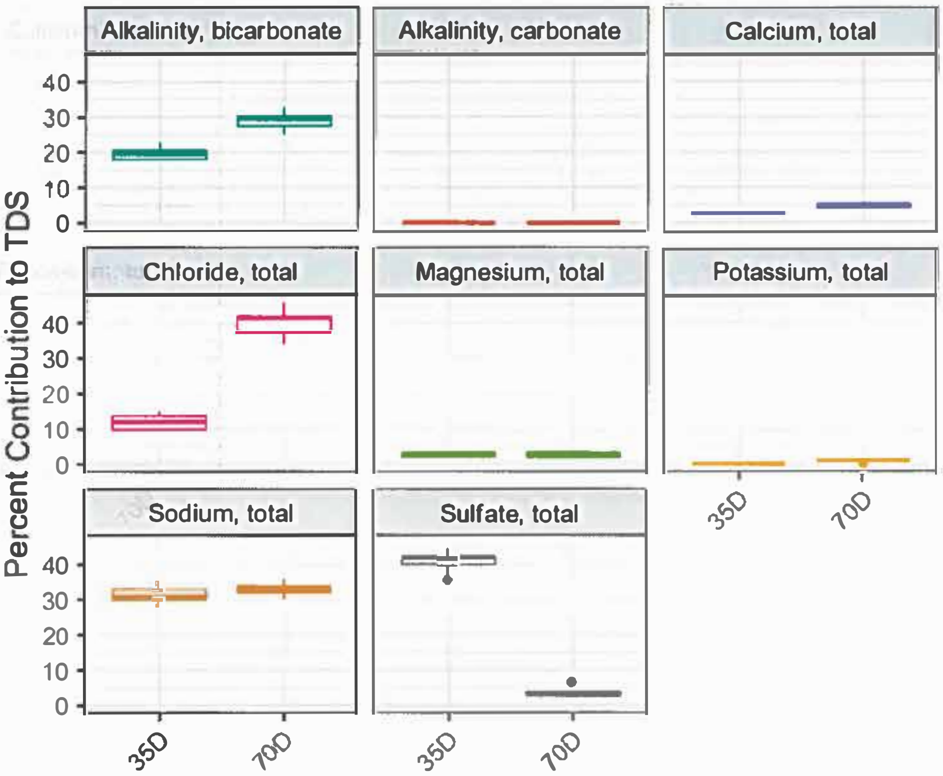


Figure A. Contribution of each major ion to TDS at wells 35D and 70D.

3.1 LOE #1: The Ionic Composition of Bedrock Groundwater is Different Than the Ionic Composition of Porewater and Consistent with Published Observations for Pennsylvanian Bedrock

Piper diagrams graphically represent ionic composition of aqueous solutions. A Piper diagram displays the position of water samples with respect to their major cation and anion content on the two lower triangular portions of the diagram, providing the information which, when combined on the central, diamond-shaped portion of the diagram, identify composition categories or groupings (hydrochemical facies). **Figure B** below is a Piper diagram that displays the ionic composition of samples collected from the bedrock background and bedrock compliance wells associated with the NEAP (sampled June 20 and 29, 2023), and porewater sampling location associated with the NEAP (sampled August 17, 2021).

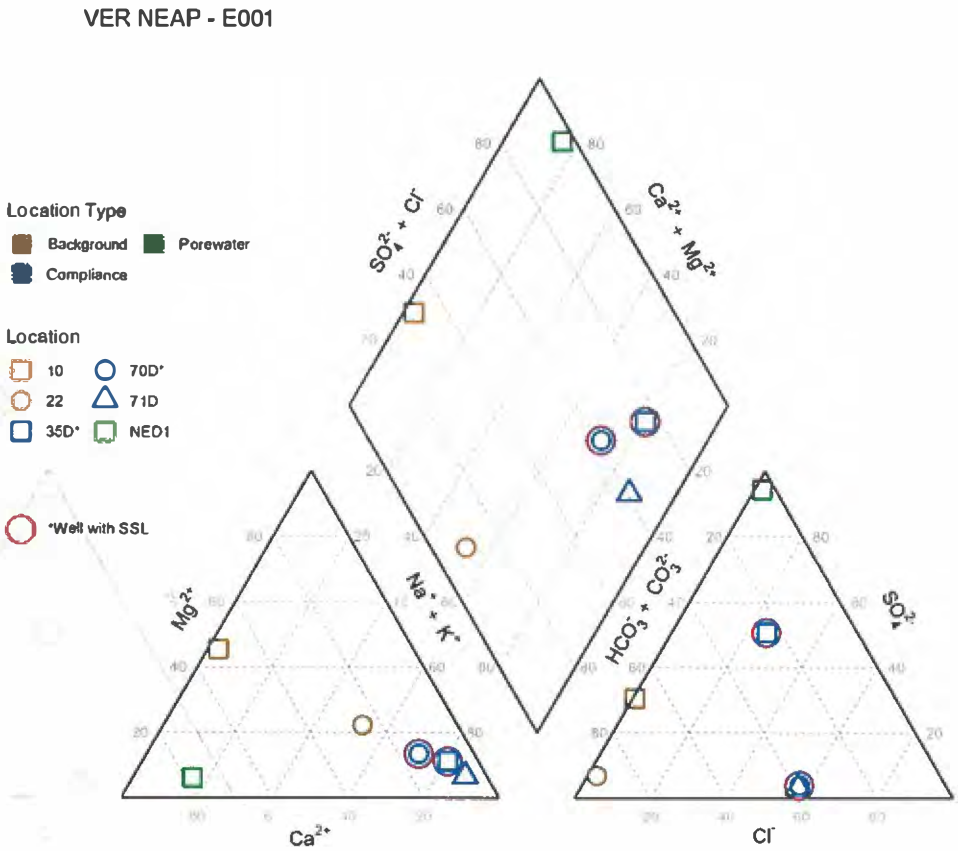


Figure B. Piper Diagram. Shows ionic composition of samples of bedrock groundwater (collected June 20 and 29, 2023) and porewater associated with the NEAP (collected on August 17, 2021).

It is evident from the piper diagram (**Figure B**) that porewater from the NEAP (green symbol) is primarily in the calcium-sulfate hydrochemical facies, while the bedrock groundwater samples (blue symbols) are in the sodium-chloride hydrochemical facies. The background BCU sample (brown symbol) is in the sodium-bicarbonate hydrochemical facies. The background BCU sample is collected from well 22, which is screened at from 556 to 576 feet North American Vertical Datum 1988 (NAVD88), and wells 35D and 70D are screened at lower elevations (536 to 546 feet NAVD88 and 541 to 551 feet NAVD88, respectively). Groundwater from deeper in Pennsylvanian aquifers tends to be more dominant in chloride, and groundwater may change from a sodium-bicarbonate to a sodium-chloride facies over small changes in depth (Lloyd and Lyke 1995). Therefore, compliance groundwater samples have a different ionic composition than porewater and a composition relative to background that is consistent with expected changes due to screen depth, indicating that NEAP porewater is not the source of CCR constituents detected in wells 35D or 70D.

3.2 LOE #2: Concentrations of Chloride in the NEAP Porewater are Lower than Those Observed in the Groundwater

A box plot of chloride concentrations in compliance monitoring wells 35D and 70D and porewater well NED1 is provided in **Figure C** on the following page. Chloride concentrations are lower in

NEAP porewater samples[1] collected during 2021 than in compliance groundwater samples collected from wells 35D and 70D from 2021 to 2023. The maximum concentration of chloride detected in NEAP porewater (44 mg/L) is lower than the minimum concentration of chloride in 35D (199 mg/L) or 70D (317 mg/L). In addition, median concentrations of chloride in wells 35D and 70D are 15 and 27 times greater, respectively, than the median chloride of 25 mg/L in NEAP porewater. Therefore, the NEAP cannot be the source of the elevated chloride concentrations observed in 35D and 70D.

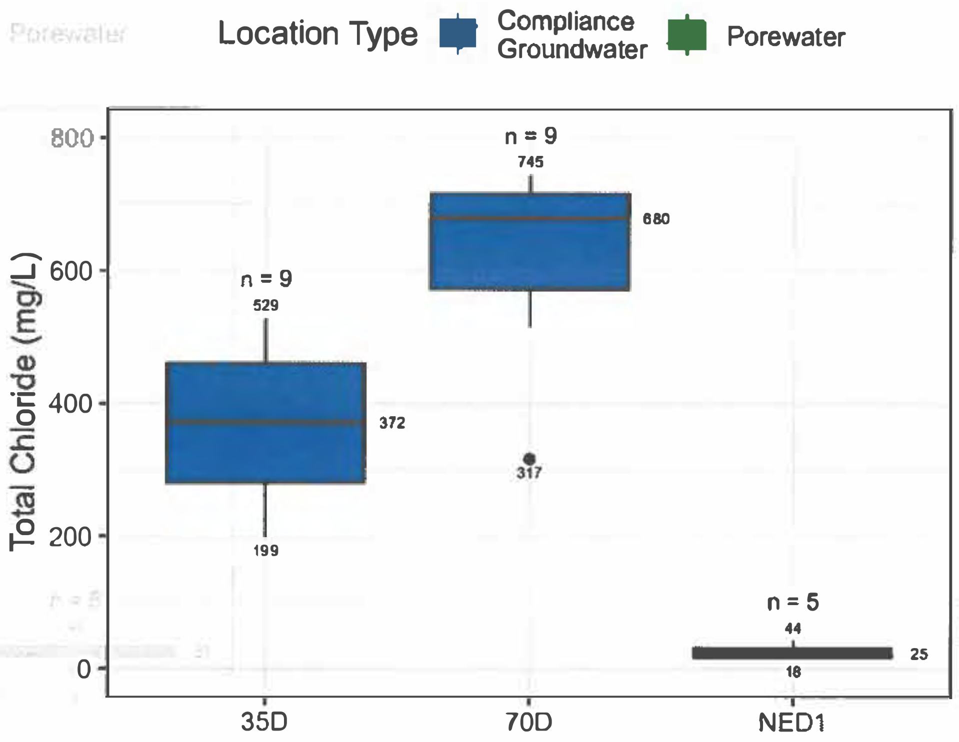


Figure C. Chloride Box Plot. The sample size (n), maximum, median, and minimum values are noted.

3.3 LOE #3: A Bedrock Solids and Geochemical Evaluation Identified Naturally Occurring Shales as the Source of Lithium and Chloride Exceedances at 35D and 70D

Appendix A presents the results of additional analysis performed in 2023 by Geosyntec. Their evaluation of site-specific solid phase compositions and geochemical conditions, multivariate statistical analyses, and literature review of Pennsylvanian-aged shale bedrock groundwaters identified naturally occurring lithium and chloride associated with shales as the alternative source of these constituents to the groundwater at 35D and 70D based on the following observations:

---

[1] CCR porewater most accurately represents the mobile constituents associated with the waste management activity within the CCR SI (EPRI, 2017). The composition of CCR porewater accumulated at the base of the CCR unit, which is derived from, and represents contact with, CCR material above and around the well screen, is the truest representation of mobile constituents throughout the CCR SI.

- Sequential extraction procedure (SEP) analyses demonstrated that much of the lithium in the solid phase is associated with the fractions which correlate to primary minerals such as micas and clay minerals, as well as the fractions associated with sulfides and oxide minerals.
- Geochemical conditions in the groundwater support desorption or dissolution of the sulfide and iron oxide mineral phases that host lithium.
- X-ray diffraction confirmed the presence of abundant micas and clay minerals, which host native lithium, in the shale bedrock.
- Groundwater chloride concentrations observed in Pennsylvanian-age shale bedrock aquifers are comparable to or higher than those observed at wells 35D and 70D.
- Principal component analysis (PCA) shows that BCU well groundwater is distinct from CCR porewater.

3.4 LOE #4: A Bedrock Solids and Geochemical Evaluation Identified Naturally Occurring Coal Seams as the Source of the Sulfate Exceedance at 35D Due to Regional Upward Vertical Hydraulic Gradients in the Shale Bedrock

Appendix A presents an evaluation of the geochemistry at 35D in the context of previously reported site conditions. This data demonstrates that elevated sulfate concentrations at 35D are the result of influence from a major coal seam in the bedrock based on the following observations:

- The coal seam mined near the site has been previously characterized and contains both iron sulfide minerals and siderite (FeCO3), which is evidence of rapid oxidation of the iron sulfide minerals.
- The groundwater chemistry at 35D suggests that siderite and the iron oxide mineral ferrihydrite are in a state of dynamic equilibrium, consistent with weathering of pyrite to siderite to ferrihydrite.
- Oxidation of sulfide minerals releases sulfate to the groundwater.
- Strong upward groundwater hydraulic gradients are present within the bedrock that provide hydraulic connection between the coal seam the bedrock that well 35D is screened.

3.5 LOE #5: Isotopic Analysis of Groundwater from the Bedrock and Overlying Quaternary Deposits Indicate that Bedrock Groundwater is Between 13,000 and 35,000 years Older Than Groundwater in the Quaternary Deposits; and, Bedrock Groundwater is Isolated from the Groundwater in the Quaternary Deposits

In 2002 ISGS and Dynegy collected groundwater samples from 8 monitoring wells and tested the samples for carbon-14 and hydrogen-3 (tritium) (ISGS, 2002). Six of the monitoring wells (25, 26, 27, 28, 29, and 30) were located adjacent to the NEAP (**Figure 2**). Wells 26 and 28 had well screens that intersected Quaternary deposits of the UU and the remaining wells were screened in shallow shale bedrock. Results of the testing are presented in Table 11 of the ISGS report included below as **Table A** and on **Figure 2**.

Table A. Isotopic Data from ISGS Sampled Wells (Table 11 from ISGS, 2002)

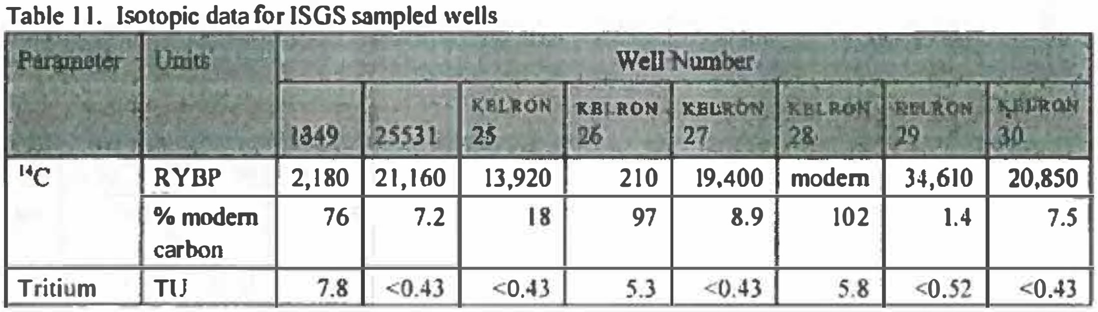


Table 11. Isotopic data for ISGS sampled wells

Parameter	Units	Well Number							
		1349	25531	KBLRON 25	KBLRON 26	KBLRON 27	KBLRON 28	KBLRON 29	KBLRON 30
^{14}C	RYBP	2,180	21,160	13,920	210	19,400	modern	34,610	20,850
	% modern carbon	76	7.2	18	97	8.9	102	1.4	7.5
Tritium	TU	7.8	<0.43	<0.43	5.3	<0.43	5.8	<0.52	<0.43

^{14}C = carbon-14

RYBP = Radiocarbon Years Before Present

TU = tritium units

Tritium is generated in the atmosphere and decays in the isolated subsurface. Water with tritium concentrations greater than 5 tritium units (TU) is considered to be recent, while water with nondetectable tritium concentrations is considered to be greater than 50 years old (ISGS, 2002). Groundwater collected from shallow Quaternary deposits is recent (TU>5), while groundwater from the shallow bedrock is older (no tritium detected). The tritium results are consistent with the carbon-14 results, which indicate that the shallow bedrock wells contain an inorganic carbon signature substantially older than that from wells screened in the Quaternary deposits. Groundwater collected from wells screened in shallow bedrock in the vicinity of the NEAP (wells 25, 27, 29, and 30) had estimated ages ranging from 13,920 to 34,610 years based on carbon-14 age dating. This is in contrast to groundwater collected from wells 26 and 28 (screened in the Quaternary deposits) which had estimated ages of less than 210 years. These results indicated to ISGS that the wells that "draw water from the bedrock are either only slightly connected to or completely isolated from the local groundwater flow system [overlying Quaternary deposits]".

In addition to the spatial location of the wells tested for carbon-14 and tritium relative to the NEAP, the elevations of the well screens and lithology of the age dated wells overlap with the well screen elevations and lithology of wells 35D and 70D which contain the GWPS exceedances (**Table B**) with the exception of MW30, which is screened at a lower elevation than all of the other wells.

Table B. Summary of Bedrock Well Screen Elevations and Lithology

Well ID	Screen Elevation (feet NAVD88)	Lithology
MW35D – exceedance well	546 to 536	shale bedrock
MW70D – exceedance well	550 to 540	shale bedrock
MW25	560 to 540	shale bedrock
MW27	557 to 537	shale bedrock
MW29	558 to 538	shale bedrock
MW30	519 to 499	shale bedrock

This data demonstrates that bedrock groundwater in the vicinity of the NEAP is isolated from the overlying Quaternary deposits and the NEAP is not the source of exceedances to the GWPS in bedrock compliance wells 35D and 70D.

4. CONCLUSIONS

Based on these five LOEs, it has been demonstrated that the NEAP is not the source of the chloride, lithium, sulfate, and TDS GWPS exceedances in wells 35D and 70D and has not contributed to exceedances identified during the first quarterly sampling event. The chloride and lithium exceedances are due to groundwater interactions with the bedrock, and the sulfate exceedance is due to influence from historic coal mining activities. Because the major contributors to TDS are chloride and sulfate, LOEs that apply to chloride and sulfate also apply to TDS.

1. The ionic composition of bedrock groundwater is different than the ionic composition of porewater and consistent with published observations for Pennsylvanian Bedrock.
2. Concentrations of chloride in the NEAP porewater are lower than those observed in the groundwater.
3. A bedrock solids and geochemical evaluation identified naturally occurring shales as the source of lithium and chloride exceedances at 35D and 70D.
4. A bedrock solids and geochemical evaluation identified naturally occurring coal seams as the source of the sulfate exceedance at 35D due to regional upward vertical hydraulic gradients in the shale bedrock.
5. Isotopic analysis of groundwater from the bedrock and overlying Quaternary deposits indicate that bedrock groundwater is between 13,000 and 35,000 years older than groundwater in the Quaternary deposits; and, bedrock groundwater is isolated from the groundwater in the quaternary deposits.

This information serves as the written ASD prepared in accordance with 35 I.A.C. § 845.650(e), demonstrating that the chloride, lithium, sulfate, and TDS exceedances observed at wells 35D and 70D during the first quarterly sampling event were not due to the NEAP and are attributable to natural groundwater interactions with bedrock and historic coal mining. Therefore, assessment of corrective measures is not required for these constituents at the NEAP.

5. REFERENCES

Cartwright, K., 1970. Groundwater discharge in the Illinois Basin as suggested by temperature anomalies. Water Resources Research 6, No. 3: 912-918.

Electric Power Research Institute (EPRI), 2017. Guidelines for Development of Alternative Source Demonstrations at Coal Combustion Residual Sites. EPRI, Palo Alto, CA. 3002010920.

Geosyntec Consultants (Geosyntec), 2021. Initial Operating Permit Application, Vermilion Power Plant, New East Ash Pond, Oakwood Illinois, October 2021.

Geosyntec Consultants (Geosyntec), 2022. Construction Permit Application, Vermilion Power Plant, New East Ash Pond, Oakwood Illinois, January 2022.

Geosyntec Consultants (Geosyntec), 2023. Technical Memorandum: Evaluation of Alternative Sources within Aquifer Solids, Vermilion Power Plant – New East Ash Pond. October 26, 2023.

Illinois Administrative Code, Title 35, Subtitle G, Chapter I, Subchapter J, Part 845: Standards for The Disposal Of Coal Combustion Residuals In Surface Impoundments, effective April 21, 2021.

Illinois State Geological Survey (ISGS), 2002. *The Geochemistry of Groundwater from the Shallow Bedrock in Central Vermilion County, Illinois.* Open-File Series Report 2002-4.

Kelley, Walton R., Samuel V. Panno, and Keith Hackley, 2012. The Sources, Distribution, and Trends of Chloride in the Waters of Illinois. Prairie Research Institute. University of Illinois at Urbana-Champaign. March 2012.

Kelron Environmental (Kelron), 2003. *Regional and Local Hydrogeology and Geochemistry, Vermilion Power Plant, Illinois.* Dynegy Midwest Generation, LLC, November 2003.

Lloyd, O. B., and W. L. Lyke, 1995. Ground Water Atlas of the United States – Illinois, Indiana, Kentucky, Ohio, Tennessee. HA-730K. United States Geological Survey.

Panno, S.V., and K.C. Hackley, 2010. Geologic influences on water quality. In *Geology of Illinois*, ed. D.R. Kolata and C.K. Nimz, 337-350. Champaign, Illinois: Illinois State Geological Survey.

Panno, S.V., Askari, Z., Kelly, W.R., Parris, T.M. and Hackley, K.C., 2018. Recharge and Groundwater Flow Within an Intracratonic Basin, Midwestern United States. Groundwater, 56: 32-45.

Ramboll Americas Engineering Solutions, Inc. (Ramboll), 2021a. *Hydrogeologic Site Characterization Report, New East Ash Pond, Vermilion Power Plant, Oakwood, Illinois*. October 25, 2021.

Ramboll Americas Engineering Solutions, Inc. (Ramboll), 2021b. *Groundwater Monitoring Plan, New East Ash Pond, Vermilion Power Plant, Oakwood, Illinois.* October 25, 2021.

Ramboll Americas Engineering Solutions, Inc. (Ramboll), 2021c. *History of Potential Exceedances, New East Ash Pond, Vermilion Power Plant, Oakwood, Illinois.* October 25, 2021.

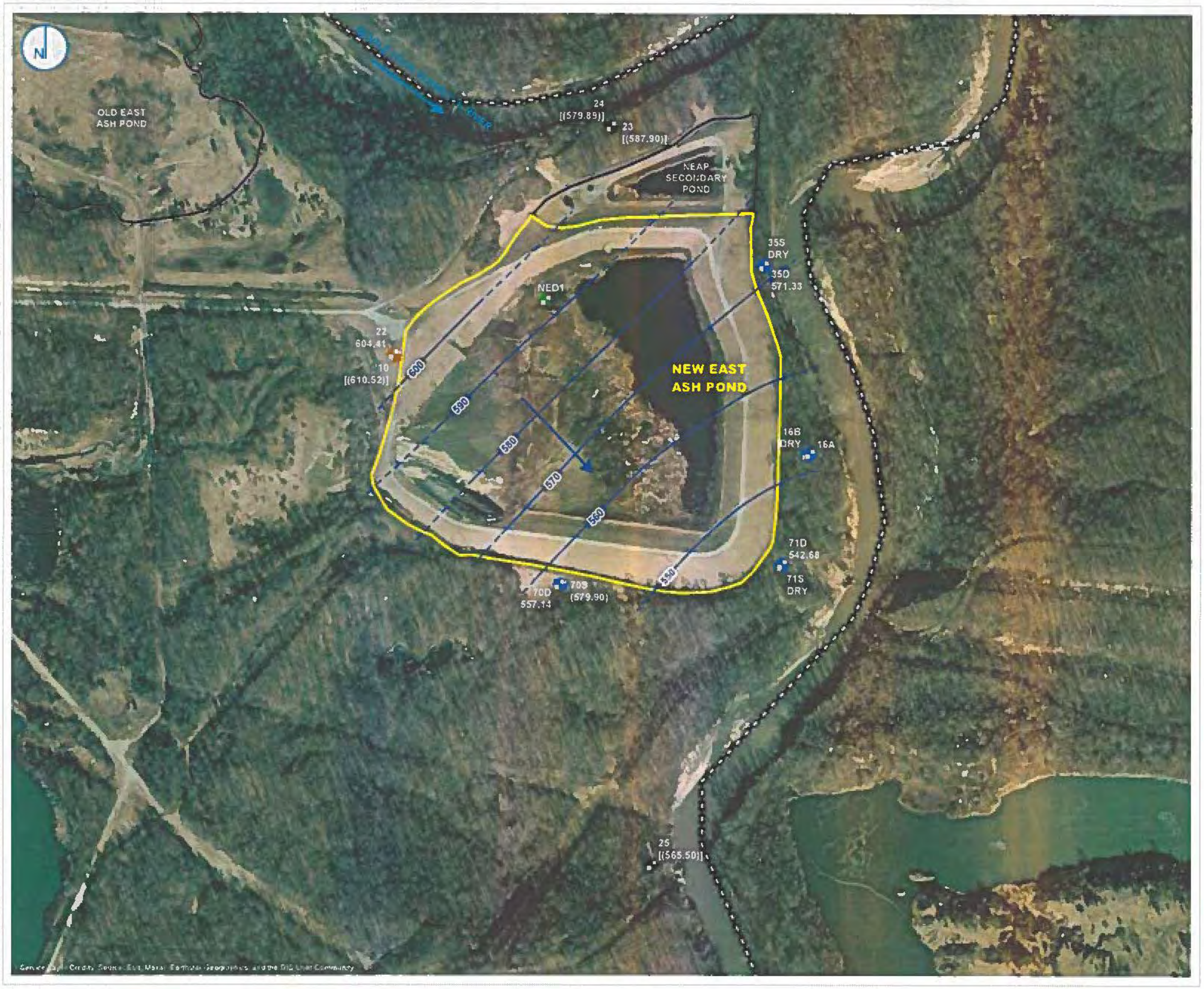
Ramboll Americas Engineering Solutions, Inc. (Ramboll), 2021d. *Hydrogeologic Site Characterization Report, North Ash Pond and Old East Ash Pond, Vermilion Power Plant, Oakwood, Illinois*. October 25, 2021.

Ramboll Americas Engineering Solutions, Inc. (Ramboll), 2023. *35 I.A.C. § 845.610(B)(3)(D) Groundwater Monitoring Data and Detected Exceedances: Quarter 2, 2023. New East Ash Pond (NEAP), Vermilion Power Plant, Oakwood, Illinois*. October 2, 2023.

Siegel, D.I., 1989. Geochemistry of the Cambrian-Ordovician Aquifer System in the Northern Midwest, U.S. Geological Survey Professional Paper 1405-D, 76p.

United States Environmental Protection Agency (USEPA), 1993. Solid Waste Disposal Facility Criteria: Technical Manual EPA530-R-93-017. Solid Waste and Emergency Response (5305). November 1993.

FIGURES



NOTES:
1. ELEVATIONS IN PARENTHESES WERE NOT USED FOR CONTOURING.
2. ELEVATIONS IN BRACKETS WERE OBTAINED OUTSIDE OF THE 24 HOUR PERIOD FROM INITIATION OF DEPTH TO GROUNDWATER MEASUREMENTS BUT WITHIN THE SAME SAMPLING EVENT.
3. ELEVATION CONTOURS SHOWN IN FEET, NORTH AMERICAN VERTICAL DATUM OF 1988

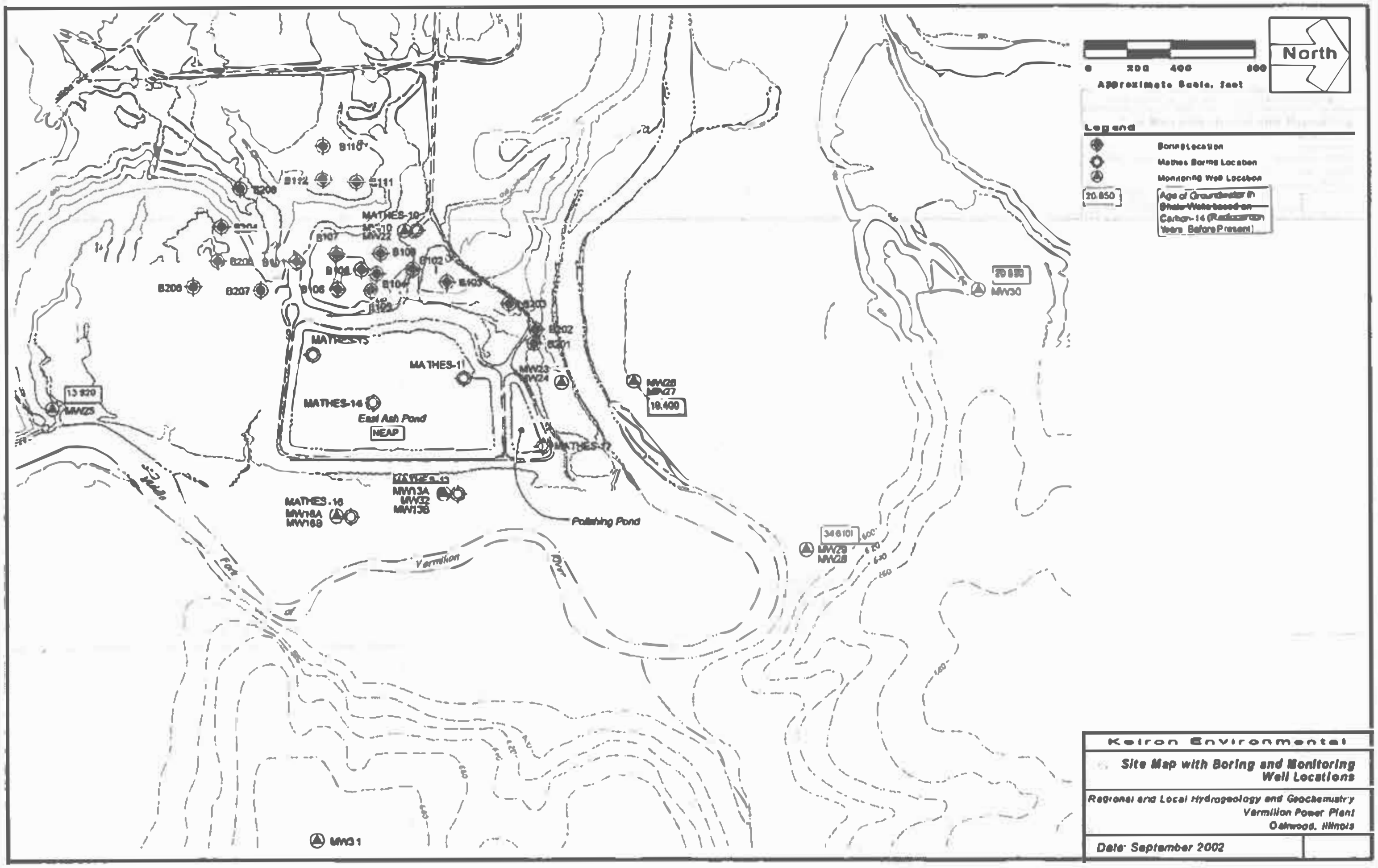
**POTENTIOMETRIC SURFACE MAP
JUNE 19, 2023**

ALTERNATIVE SOURCE DEMONSTRATION
NEW EAST ASH POND
VERMILION POWER PLANT
OAKWOOD, ILLINOIS

FIGURE 1

RAMBOLL AMERICAS
ENGINEERING SOLUTIONS, INC.

RAMBOLL



MONITORING WELL LOCATION MAP WITH RESULTS OF CARBON-14 AGE DATING

ALTERNATIVE SOURCE DEMONSTRATION
NEW EAST ASH POND
VERMILION POWER PLANT
OAKWOOD, ILLINOIS

FIGURE 2

RAMBOLL AMERICAS
ENGINEERING SOLUTIONS, INC.

RAMBOLL

APPENDICES

APPENDIX A
GEOSYNTEC CONSULTANTS, 2023. TECHNICAL MEMORANDUM: EVALUATION OF ALTERNATIVE SOURCES WITHIN AQUIFER SOLIDS, VERMILION POWER PLANT - NEW EAST ASH POND. OCTOBER 26, 2023.

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TECHNICAL MEMORANDUM

Date:	November 30, 2023
To:	Brian Voelker, Dynegy Midwest Generation, LLC
Copies to:	Stu Cravens and Phil Morris, Dynegy Midwest Generation, LLC Eric Tlachac and Brian Hennings, Ramboll
From:	Allison Kreinberg and Ryan Fimmen, PhD, Geosyntec Consultants
Subject:	Evaluation of Alternative Sources within Bedrock Solids Vermilion Power Plant – New East Ash Pond

This document serves as an Appendix to the December 1, 2023, Alternative Source Demonstration (ASD) for the Vermilion Power Plant New East Ash Pond (NEAP) (Site) for the Quarter 2 2023 sampling event completed to fulfill the requirements of Title 35 of the Illinois Administrative Code (35 I.A.C.) § 845.650(e) (VER NEAP E001 ASD). A previous Evaluation of Potential Groundwater Protection Standard (GWPS) Exceedances prepared by Ramboll Americas Engineering Solutions, Inc. (Ramboll) in January 2022 concluded that the potential GWPS exceedances of chloride, lithium, and total dissolved solids (TDS) at downgradient monitoring wells 35D and 70D could be attributed to sources other than the NEAP (Ramboll 2022). Geosyntec Consultants, Inc. (Geosyntec) has completed a review of geochemical and site conditions at the Site to evaluate the influence of the solid-phase mineralogy and geochemistry of the bedrock confining unit potential migration pathway ("bedrock") on groundwater composition. Using additional evidence from laboratory analyses and statistical evaluations, this technical memorandum demonstrates that naturally occurring lithium and chloride associated with bedrock underlying the Site is a source of lithium, chloride, and total dissolved solids (TDS) to Site groundwater. Additionally, this memorandum provides evidence that sulfate concentrations at well 35D can be attributed to the weathering of sulfur-bearing minerals within the coal seams in the Site lithology.

SITE CONDITIONS

Site geology consists primarily of unlithified alluvial and glacial deposits overlying shale bedrock that contains a major coal seam mined in the region. The alluvial deposits consist of the Cahokia Alluvium composed primarily of sand with occasional layers of silty clay and the Upper Till Unit (Wedron Formation and Glasford Formation Till) consisting of clay and silty clay with occasional sand lenses. The Cahokia Alluvium comprises the Upper Unit (UU) at the NEAP and is generally 10 to 25 feet thick. Below this unit is the Upper Confining Unit (UCU) that is comprised of the lower permeability Wedron and Glasford Formations. The UCU is of variable thickness, ranging from up to 100 feet west of the NEAP and absent east of the NEAP (Ramboll 2021).

The Bedrock Confining Unit (BCU), typically greater than 80 feet thick, consists of the Pennsylvanian-age Shelburn Formation, which is primarily a low permeability shale with thin limestone, sandstone, and coal beds. The top of the shale unit in the vicinity of the NEAP is described as highly weathered and decomposed. This unit contains the Danville (No. 7) Coal, which was encountered near the NEAP at approximately 80 to 100 feet below ground surface (ft bgs). Wells 35D and 70D are both screened within the BCU.

Groundwater within the BCU exhibits an upward hydraulic gradient and high dissolved mineral content (Ramboll 2021). Previous isotopic analyses by Kelron Environmental (Kelron) suggest that groundwater in the BCU is significantly older than the recent groundwater in the overlying unlithified deposits by approximately 13,000 to 35,000 radiocarbon years before present (Kelron 2003). Additional information regarding Site hydrogeology and stratigraphy is provided in the ASD prepared by Ramboll.

BEDROCK SOLIDS EVALUATION

Geosyntec reviewed the results of analyses completed on solid phase samples collected from the Site to evaluate if lithium and chloride concentrations in groundwater at wells 35D and 70D in excess of the GWPS could be derived from the native weathered shale bedrock lithology.

Samples were collected from soil borings advanced in June 2023 near two locations: compliance well 35D and compliance well 70D (**Figure 1**). Due to access limitations and health and safety considerations at the Site, the boring locations were adjusted in the field and are approximately 200-250 feet offset from the original well locations. Differences in ground surface elevations and bedrock dip were considered during drilling and sample selection so that the sampled intervals correspond with the well screen interval. Boring locations and well screen intervals are shown in the cross sections provided in **Attachment 2**. The material sampled for geochemical characterization is consistent with the material present in the well screens (gray weathered shale).

The field boring log for these soil borings are provided as **Attachment 2**. Soil boring logs and well construction logs for 35D and 70D are also included in **Attachment 2**. Two samples were collected from the boring near well 35D (VER-35), and three samples were collected from the boring near well 70D (VER-70) at various depths.

All samples were submitted for analysis of mineralogy via X-ray diffraction (XRD), and two samples from VER-35 (55-60 ft bgs and 60-63 ft bgs) and one sample from well VER-70[1] (75-80 ft bgs) were submitted for analyses of total lithium and lithium distribution within the bedrock using sequential extraction procedure (SEP). SEP is an analytical technique that uses progressively stronger reagents to solubilize metals from specific phases within the solid matrix and is used to infer associations between constituents and different classes of solids (Tessier et al. 1979). These classes of solids are identified based on their solubility under different reagents; the reagents are provided in **Attachment 3**. Analysis of chloride by SEP was not performed due to the high solubility of the chloride ion in solution.

Results for total and SEP analyses of lithium in these samples are presented in **Table 1** and the analytical laboratory reports are provided as **Attachment 3**. As a first step to evaluate data quality in an SEP analysis, the sum of individual extraction steps from the SEP was compared to the total lithium concentration. The sum of the SEP procedure is not expected to be exactly equal to the total metals analysis but should generally be consistent with the total metals analysis. The total lithium concentrations ranged from 39 micrograms per gram of material (µg/g) to 42 µg/g in the shale samples. The summed concentrations of lithium from the SEP analyses ranged from 45.3 to 50.8 µg/g. The results were generally consistent between the total metals analyses and the summed SEP steps, indicating good metals recovery and data quality. These results are also consistent with previous samples collected at the Site (31.1-33.3 mg/kg, Ramboll 2021) and within the Danville coal (5.5-89 mg/kg, USGS 2002).

The results presented in **Table 1** demonstrate that lithium is associated with multiple solid phase components. The majority of the lithium was released via leaching steps associated with two reactive solid phase components: metal oxides (between 24 and 28%) and sulfides (between 28 and 31%). Lithium associated with oxides and sulfides may be mobilized via desorption or dissolution of these phases in the event of geochemical changes to the system due to the relative instability of oxide and sulfide minerals.

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[1] Two samples from the unlithified units from VER-70 (30-40 ft bgs) and (41-42 ft bgs) are excluded from subsequent results tables and discussion to emphasize findings associated with shale lithologies in support of an assessment of naturally occurring lithium in bedrock.

Eh-pH diagrams were generated using groundwater data for well 35D (**Figure 2**) and well 70D (**Figure 3**) to evaluate groundwater conditions at these wells relative to the thermodynamic stability of iron oxide and iron sulfide minerals. As indicated on **Figures 2** and **3**, groundwater chemistry at both monitoring wells generally favor thermodynamic stability of the iron oxide phase. However, multiple samples from well 35D plot within the three-phase stability boundary between amorphous iron oxide $Fe(OH)_3$(ppd), the iron carbonate mineral siderite, and aqueous Fe^{2+} (**Figure 2**), indicating that groundwater at this well is experiencing dynamic equilibrium conditions in which chemical reactions between these phases may occur. Groundwater from well 70D indicates a preference for iron oxide phases ($Fe(OH)_3$(ppd)), although groundwater chemistry at this well may be trending towards iron carbonate (siderite) stability (**Figure 3**). Iron sulfide minerals such as pyrite are not predicted to be in a stable phase at either well; therefore, any existing sulfidic minerals within the bedrock would be expected to undergo oxidative dissolution. Lithium associated with the sulfide solid phase component (**Table 1**) would then become mobilized due to dissolution/desorption processes and resulting in an increase in aqueous lithium in groundwater. Similarly, dissolution of iron oxides would occur under variable equilibrium conditions and result in an increase in aqueous lithium in groundwater.

Notable abundances (31 to 37%) of lithium were also found to be associated with the final extraction of the analysis, which is typically considered to be associated with residual metals which are immobile and not readily soluble. The abundance of lithium within this residual fraction indicates association with inseparable primary mineral phases such as clay minerals (Tessier et al., 1979). Clay minerals are known to be common sorbents for naturally occurring lithium (Starkey 1982). Lithium is known to leach from lithium-hosting igneous rocks and micas through weathering processes. Mineral weathering reactions occurring in micas may result in lithium-rich micas transforming directly to illitic clays, and then to mixed-layer and smectite clays. The lithium within these primary minerals either becomes incorporated directly into the crystal structures of the clay minerals or is transported in water and later concentrated in brines through evaporation (Ronov et al. 1970). Lithium-enriched brines constitute a common origin of lithium in clay minerals, as eroded fine-grained materials (i.e., detrital clays) deposited in these brines are capable of hosting lithium within vacant sites in the octahedral layers comprising part of their crystal structures (Schultz 1969). Field lithologic descriptions of the samples from VER-35 and VER-70 indicate that the samples collected from these two locations consist of weathered shale, which is comprised primarily of mica and clay minerals that are known to be hosts of natural lithium.

Mineralogical analyses were completed using XRD to evaluate whole rock mineralogy and determine the abundance of iron oxide minerals, iron sulfide minerals, clay minerals, and micas within the bedrock solids. Whole rock mineralogy results are provided in **Table 2**. Sample mineralogy consists predominantly of quartz, mica (muscovite), feldspars (albite and microcline), and clay minerals (illite, chlorite, and kaolinite) (**Table 2**). Of these minerals, muscovite and clays are known hosts of natural lithium within their crystal structures and comprise natural sources of lithium in the system (Zawidzki 1976; Starkey 1982). As indicated in **Table 2**, these minerals are present at large abundances in samples from well 35D and well 70D (between 43.0 to 47.4%), indicating that these lithium-host minerals occur in the BCU and constitute a natural source of aqueous lithium to groundwater.

While iron oxides were not identified via XRD, they are likely present in the system. Amorphous $Fe(OH)_3$(ppd), which is thermodynamically favored to form at the Eh and pH measured in groundwater (**Figures 2 and 3**), cannot be identified via XRD due to its lack of crystalline structure. However, the SEP results identified an abundance of iron in the leaching step associated with non-crystalline oxides (step 3; **Attachment 3**), and iron oxides are often present on clay surfaces due to the relationship between their surface charges (Ohtsubo 1989). As discussed above, the XRD analysis identified the presence of clay minerals within the shale (**Table 2**, **Attachment 4**). Thus, weathering reactions involving iron oxides likely constitute an additional natural source of aqueous lithium to groundwater.

As discussed above, the shale bedrock material consists predominantly of micas and clays which are known hosts of lithium within their crystal structures. The weathered nature of the shale bedrock material suggests that chemical weathering processes are likely occurring, the result of which supports the occurrence of weathering reactions involving metal oxide and sulfide minerals, as well as alteration reactions between mica and clay minerals and between different types of clay minerals. These reactions all represent processes by which lithium associated with the native geologic materials may become mobilized, contributing aqueous lithium to groundwater.

Similar to lithium, chloride occurs naturally within shale bedrock, which likely contributes to elevated chloride in groundwater. Because of the high solubility of chloride, it is not feasible to determine phase associations through SEP; however, studies within the region have found that groundwater chloride concentrations comparable to or higher than those observed at wells 35D and 70D are often found within the Pennsylvanian-aged shale bedrock. The mean chloride concentration in Pennsylvanian bedrock aquifers in the area reported by the Illinois State Geological Survey (ISGS) is 1,689 mg/L and a chloride maximum concentration of 30,269 mg/L was reported (ISGS 2002). Chloride concentrations observed in wells 35D and 70D are 251 mg/L and 492 mg/L, respectively. A USGS summary found that water within the upper parts of the Pennsylvanian-aged bedrock is generally similar throughout the Illinois and Indiana basins. This water is influenced by the interaction with the variable interbedded rock types present in the bedrock; it can vary from a sodium bicarbonate to a sodium chloride type within a few feet of change in depth (Lloyd and Lyke 1995).

Furthermore, seeps with high naturally occurring salinity (i.e., brines) are known to occur in southern Illinois. Samples of seeps and shallow wells affected by brine in Illinois had highly variable chloride concentrations ranging from ~100 mg/L up to more than 15,000 mg/L (Panno, et al. 2005). These results suggest that contact with Pennsylvanian-aged bedrock can result in natural variability in the reported chloride concentrations in groundwater at ranges consistent with those observed at the site.

STATISTICAL EVALUATION OF GROUNDWATER COMPOSITION

Advanced statistical analyses were employed to evaluate the similarity or dissimilarity among different groundwater samples or groups based on a broad suite of analytes. Dimensional reduction techniques, such as principal component analysis (PCA), are especially effective in identifying the analytes responsible for statistical differences between samples and revealing underlying patterns related to environmental factors, contamination sources, or other natural characteristics of the Site. Clustering methods were further utilized to group samples based on their combined chemical composition through maximizing intra-group similarity and minimizing inter-group similarity.

PCA is often used to simplify large datasets with multiple variables by creating new uncorrelated variables known as principal components (PCs). The PCs are linear combinations of the original variables; the first few PCs typically capture most of the variation within the dataset. Factor loadings are calculated based on the correlation between PCs and the original variables. As such, variables with notably higher positive or negative factor loadings are main drivers of similarity or dissimilarity and clustering of samples. Factor scores are calculated based on the correlation between the combined chemical composition of each sample and the PCs. Samples with similar chemical compositions show similar factor scores and tend to cluster together on a PCA plot.

In this study, the dataset used for PCA included 62 groundwater samples collected in 2021 and 2023 from upgradient wells (10 and 22), downgradient wells (70S, 71S, 70D, 71D, 16A, and 35D) and a porewater well (NED1).[2] PCA requires that input variables have similar scales of measurement and variances. As such, data were standardized by mean-centering and scaling to unit variance prior to performing PCA. Data were further square transformed to reduce the skewness of dataset. The fraction of total variation explained by each PC is shown in **Figure 4a**, with the first two PCs accounting for approximately 80 percent [%] of the total variation in the datasets. Additionally, the quality of representation of each variable is presented in **Figure 4b**. As

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[2] Analytes included in the PCA include alkalinity, boron, calcium, pH, barium, chloride, and fluoride. The complete dataset used for PCA analysis is provided with this submission as **Attachment 5**.

illustrated in the figure, the first dimension is dominated by alkalinity, boron, and calcium, while the second dimension is dominated by fluoride, chloride, and barium.

PCA results are often visualized using biplots where samples are projected on to the first two PCs (i.e., factor scores), and factor loadings are represented as vectors. The closer the data points are on the graph, the greater the similarity in their chemical composition. The result from this study is shown on **Figure 5**, where the samples acquired from BCU are orange, UCU and UU are shades of blue, and the porewater samples are gray. The biplot suggests that porewater samples cluster relatively separately from the BCU, UCU, and UU samples. Additionally, the chemical signatures of groundwater samples from the BCU are different than combined group of UCU and UU samples, whereas the composition of upgradient samples from the UCU are similar to those from downgradient UU locations. Upgradient well 22 clusters more closely with the shallower UCU and UU wells. The PCA results indicate that the composition of the BCU groundwater samples is statistically different than that from the porewater, suggesting that the porewater is not the source of elevated lithium, chloride, and TDS to Site groundwater.

Furthermore, the factor loadings, represented as vectors on the biplot, suggest that constituents such as boron and carbonate alkalinity are responsible for the chemical signature of the porewater cluster. In contrast, chloride is one of the drivers for the distinct chemical composition of the BCU cluster.

Clustering was further explored using Ward's hierarchical clustering method, a distance measure employed in agglomerative algorithms and commonly applied in hydrogeochemical studies. The analysis was performed on a scaled and centered dataset. The results from clustering (**Figure 6**), align with findings from the PCA (**Figure 5**) and supported the distinction between porewater samples from downgradient and upgradient groundwater samples from BCU, UCU and UU. Furthermore, the distinct clustering of the BCU samples relative to the clustering of the UCU/UU samples suggests that chemical composition of groundwater samples is primarily influenced by their lithography rather than their relative locations to the CCR unit (i.e., upgradient or downgradient). These results support the conclusion that downgradient locations with lithium and chloride exceedances are not affected by the CCR unit, and their geochemistry is instead influenced by the native lithology.

SULFATE EVALUATION

Elevated sulfate concentrations have been observed in well 35D that are inconsistent with other BCU wells at the Site, as indicated by exceedances of the GWPS for sulfate at well 35D and not at other BCU wells. The PCA results shown in **Figure 5** indicate that for parameters other than sulfate (which was not included in the parameters evaluated in the PCA), the groundwater chemistry from well 35D is similar to overall bedrock groundwater chemistry. As described above and in greater detail in the Site Hydrogeologic Characterization Report (Ramboll 2021), the BCU contains a major coal seam that has been mined in the vicinity of the NEAP. Samples of this coal were collected and analyzed by Kelron and the ISGS, and XRD results indicate that the coal contains up to 10% iron sulfide, primarily pyrite and marcasite (FeS_2) (Mehnert 2002). Pyrite and especially marcasite are unstable under oxidizing conditions and will readily undergo oxidative dissolution to form dissolved iron and sulfate. This mechanism of sulfate mobilization is further supported by the observation of the iron carbonate mineral siderite ($FeCO_3$), which was described as a "needle-like white precipitate above the coal in the core" which "is undoubtedly the result of this rapid oxidation" (Mehnert 2002). Siderite is also identified in the bedrock samples collected from borings VER-35 and VER-70 at concentrations ranging from 4.9 to 5.4 weight percent (**Table 2**).

Figure 2 shows the iron thermodynamic stability diagram for the well 35D groundwater. Groundwater pH and ORP data are plotted within the iron stability field, which illustrates that under these conditions, siderite and ferrihydrite are in a state of dynamic equilibrium. The weathering of pyrite to siderite to ferrihydrite would result in an increase in aqueous sulfate concentrations.

Furthermore, strong upward vertical hydraulic gradients are present within the BCU (Kelron 2003; Ramboll 2021). While it is estimated that the coal seam is deeper than the screened interval at well 35D, an upward vertical gradient would cause sulfate generated from sulfide oxidation in the coal to influence the groundwater composition at 35D. **Figure 7** shows the locations where coal and void space were observed during exploratory drilling for the historic coal mine (Kelron 2003). In boring locations B201 and B202, artesian conditions were observed, with water geysering more than 30 feet above ground surface at an estimated flow rate of greater than 100 gallons per minute when the fractured shale was penetrated as the borings were advanced (Kelron 2003). These field observations indicate that the high hydraulic head within the coal seam can influence overlying formations.

As noted above, isotopic analyses of tritium (^3H) and radiocarbon (^{14}C) suggest that the bedrock groundwater is significantly older than the shallower groundwater at the Site (Kelron 2003). Tritium concentrations in the groundwater from the overlying unlithified deposits are between 5.3 and 5.8 tritium units and can be classified as "recent water". Tritium concentrations in the bedrock were non-detect. The age of the bedrock groundwater ranges from approximately 13,000 to 35,000 years before present as determined by radiocarbon dating. The lack of influence from recent water within the bedrock groundwater system provides further evidence that it is isolated from the shallow groundwater and that the elevated sulfate observed in 35D is due to natural variations in sulfur-bearing minerals in the bedrock.

CONCLUSION

Naturally occurring lithium, chloride, and sulfate associated with minerals in the BCU and the coal seam in the vicinity of the NEAP at the Site were identified as alternative sources of these constituents to Site groundwater. Solid-phase samples collected near compliance wells 35D and 70D contained lithium, and SEP analyses demonstrated that much of the lithium in the solid phase is associated with the fractions which correlate to primary minerals such as micas and clay minerals, as well as the fractions associated with sulfides and oxide minerals. XRD identified abundant micas and clay minerals hosted in the shale bedrock that are the source of lithium in Site groundwater. Elevated chloride concentrations in groundwater are observed in the region that originate from Pennsylvanian-aged shale bedrock and brine migration over time. Elevated sulfate concentrations at 35D are associated with the oxidative dissolution of iron sulfide minerals present in coal seams within the bedrock and transported through upward hydraulic gradients within the BCU. Advanced statistical methods demonstrate that groundwater geochemical signatures from the BCU, the UCU, and the UU are distinctly different from that of the porewater based on a combination of parameters.

The alternative source of lithium and chloride observed in wells 35D and 70D is the shale bedrock. The alternative source of sulfate observed in well 35D is the coal seams within the BCU. These elevated chloride and sulfate concentrations are the dominant contributors of elevated TDS values at 70D and 35D, respectively (VER NEAP E001 ASD). This information serves as the written ASD demonstrating that the GWPS exceedances for lithium, chloride, and TDS at well 70D and for lithium, chloride, sulfate, and TDS at 35D were not due to the NEAP CCR unit.

REFERENCES

Kelron. 2003. *Regional and Local Hydrogeology and Geochemistry, Vermilion Power Plant, Illinois.* Dynegy Midwest Generation, LLC, November.

Lloyd, O. B., and W. L. Lyke. 1995. *Ground Water Atlas of the United States – Illinois, Indiana, Kentucky, Ohio, Tennessee*. HA-730K. United States Geological Survey.

Mehnert, E. and Dreher, G. B. 2002. *The Geochemistry of Groundwater from the Shallow Bedrock in Central Vermilion County, Illinois.* Illinois State Geological Survey. Open-File Series Report 2002-4.

Ohtubo. 1989. “Interaction of Iron Oxides with Clays.” *Clay Science*, 7: 227-242.

Ramboll. 2021. *Hydrogeologic Site Characterization Report – Vermilion Power Plant New East Ash Pond.* Ramboll Americas Engineering Solutions, Inc. October.

Ramboll. 2022. *Evaluation of Potential Groundwater Protection Standard Exceedances – New East Ash Pond*. Vermilion Power Plant, Oakwood, Illinois. Ramboll Americas Engineering Solutions, Inc. January.

Ronov, A. B., Migdisov, A. A., Voskresenskaya, N. T., and Korzina, G. A. 1970. "Geochemistry of Lithium in the Sedimentary Cycle." *Geochemistry International* 7: 75-102.

Schultz, L. G. 1969. "Lithium and Potassium Adsorption, Dehydroxylation Temperature, and Structural Water Content of Aluminous Smectites." *Clays and Clay Minerals* 17(3): 115-150.

Starkey, H.C., 1982. *The Role of Clays in Fixing Lithium* (No. 1278). US Government Printing Office.

Tessier, A., P. G. C. Campbell, and M. Bisson. 1979. "Sequential extraction procedure for the speciation of particulate trace metals." *Analytical Chemistry* 5(7): 844–851.

USGS. 2002. *Characterization of the Quality of Coals from the Illinois Basin.* Resource Assessment of the Springfield, Herron, Danville, and Baker Coals in the Illinois Basin. Professional Paper 1625-D. United Stats Geological Survey. March.

Zawidzki, P. 1976. "Lithium Distribution in Micas and its Bearing on the Lithium Geochemistry of Granitoids." *Arch. Mineral* 32: 95-152

TABLES

Geosyntec Consultants, Inc.

Table 1 - Lithium SEP Results Summary
Vermilion Power Plant - New East Ash Pond

Soil Boring Location		**VER-35**		**VER-35**		**VER-70**	
Sample Depth (ft bgs)		**(55-60)**		**(60-63)**		**(75-80)**	
Location		**Downgradient**		**Downgradient**		**Downgradient**	
Field Boring Log Description		**Weathered Shale**		**Highly Weathered Shale**		**Highly Weathered Shale**	
Total Lithium		42		39		42	
SEP Results							
SEP Fraction	**SEP Reagent**	**Concentration**	**% of Total**	**Concentration**	**% of Total**	**Concentration**	**% of Total**
Exchangeable Metals Fraction	$MgSO_4$	<10	--	<10	--	<11	--
Metals Bound to Carbonates Fraction	Sodium acetate, acetic acid	0.56 J	1%	0.62 J	1%	<8.3	--
Non-crystalline Materials Fraction	Ammonium oxalate (pH 3)	0.52 J	1%	0.74 J	2%	0.41 J	1%
Metals Bound to Metal Hydroxide Fraction	Hydroxylamine HCl and acetic acid	13	28%	12	27%	12	24%
Bound to Organic Material Fraction	5% sodium hypochlorite (pH 9.5)	4.1 J	9%	3.9 J	9%	4.4 J	9%
Metals Bound to Acid/Sulfide Fraction	HNO_3, HCl, and H_2O	13	28%	14	31%	15	30%
Residual Metals Fraction	HF, HNO_3, HCL, and H_3BO_3	15	33%	14	31%	19	37%
SEP Total		46.2	100%	45.3	100%	50.8	100%

Notes:
SEP - sequential extraction procedure
ft bgs - feet below ground surface
All results shown in microgram of lithium per gram of soil (µg/g).
Total lithium was analyzed using aqua regia digest, ICP-MS
Non-detect values are shown as less than the reporting limit.
The lithium fraction associated with each SEP phase is shown.
% of total lithium is calculated from the sum of the SEP fractions.

Table 2 - Summary of X-Ray Diffraction Analysis
Vermillion Power Plant - New East Ash Pond

Geosyntec Consultants, Inc.

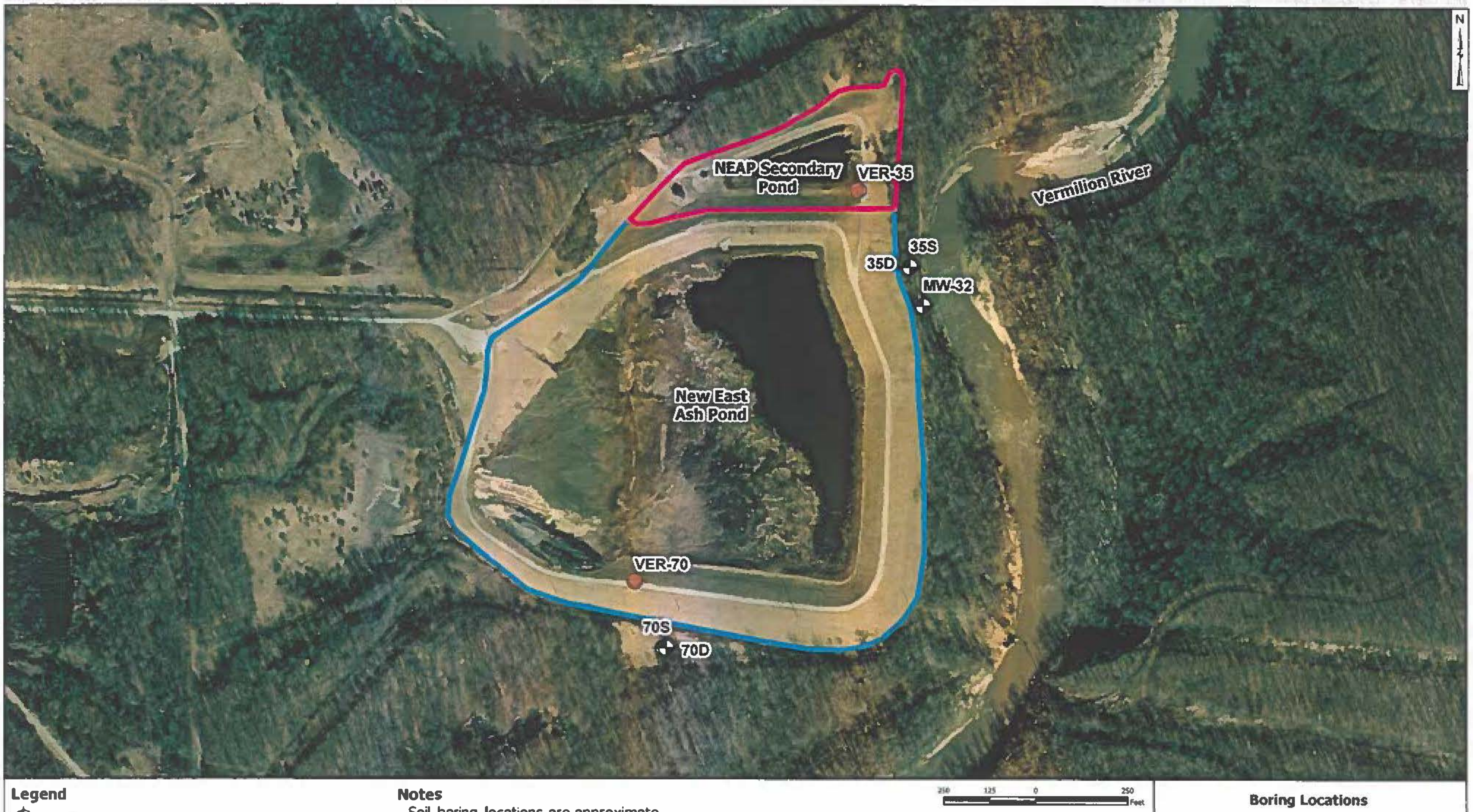
Field Boring Location			VER-35	VER-35	VER-70
Sample Depth (ft bgs)			(55-60)	(60-63)	(75-80)
Location			Downgradient	Downgradient	Downgradient
Field Boring Log Description			Weathered Shale	Highly Weathered Shale	Highly Weathered Shale
Mineral/Compound	**Formula**	**Mineral Type**	**(wt %)**	**(wt %)**	**(wt %)**
Quartz	SiO_2	Silicate	38.5	38.1	35.0
Muscovite	$KAl_2(AlSi_3O_{10})(OH)_2$	Mica	23.4	23.0	27.0
Albite	$NaAlSi_3O_8$	Feldspar	12.6	12.6	11.5
Illite	$K(Al,Mg,Fe)_2(Si,Al)_4O_{10}(OH)_2$	Clay	7.1	8.0	5.2
Chlorite	$(Fe,(Mg,Mn)_5,Al)(Si_3Al)O_{10}(OH)_8$	Clay	6.9	6.8	7.7
Kaolinite	$Al_2Si_2O_5(OH)_4$	Clay	5.6	5.4	7.5
Siderite	$FeCO_3$	Carbonate	4.9	5.0	5.4
Microcline	$KAlSi_3O_8$	Feldspar	1.0	1.1	0.70
Clay Minerals Total			19.6	20.2	20.4
Clays + Muscovite Total			43.0	43.2	47.4

Notes

Sample depth is shown in feet below ground surface (ft bgs).

wt %: percentage by weight

FIGURES



Legend
- ⌖ Monitoring Well
- ● Boring Location
- ▭ New East Ash Pond (NEAP)
- ▭ NEAP Secondary Pond

Notes
- Soil boring locations are approximate.
- Only select monitoring well locations are shown.
- Ash pond boundaries are approximate.

Boring Locations

Dynegy Midwest Generation
Vermilion Site
Oakwood, Illinois

Geosyntec
consultants

Columbus, Ohio
October 2023

Figure
1

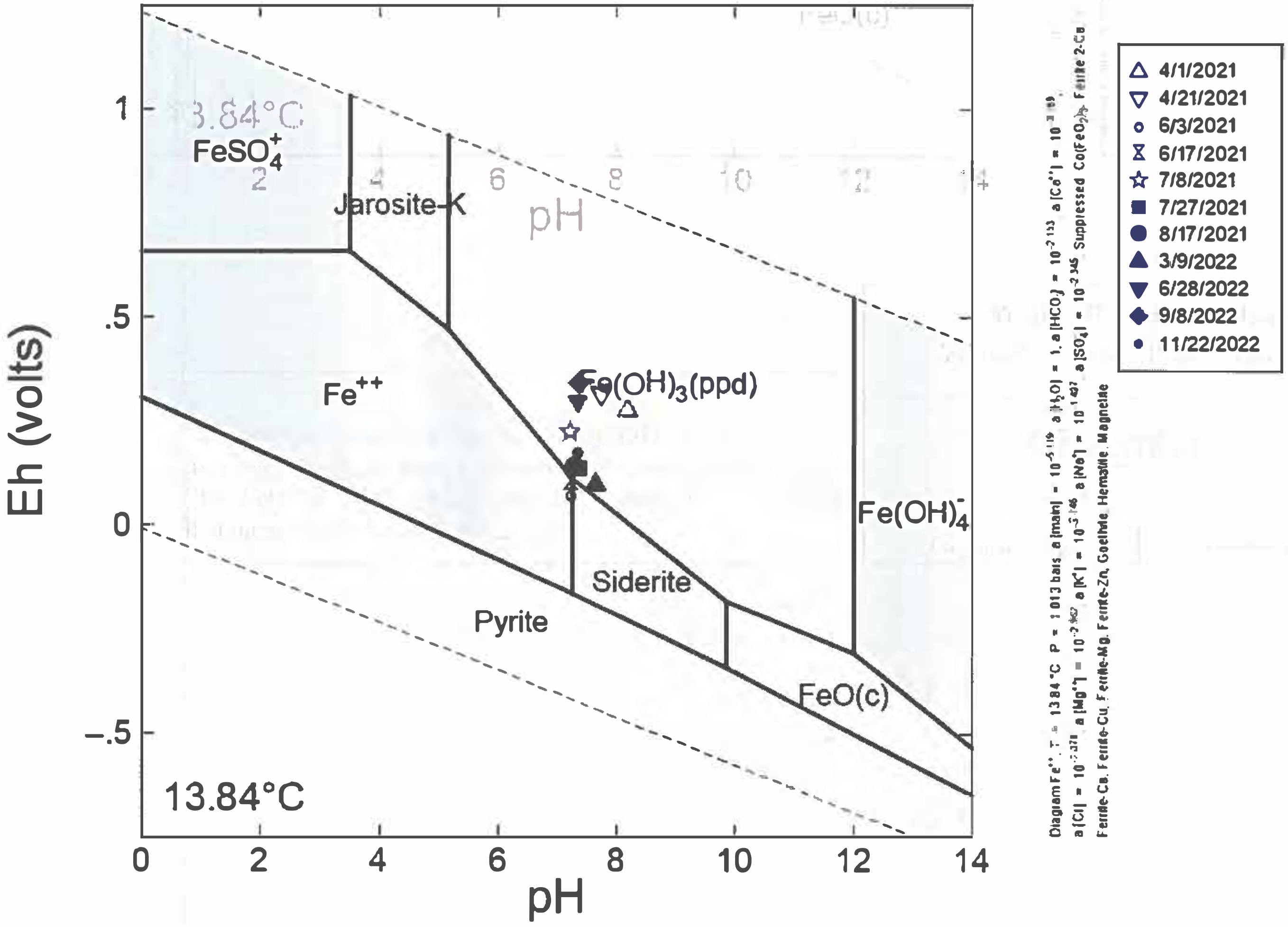


Diagram Fe^{++}, T = 13.84 °C, P = 1.013 bars, a [main] = $10^{-5.119}$, a [H_2O] = 1, a [HCO_3^-] = $10^{-2.133}$, a [Ca^{++}] = $10^{-3.189}$, a [Cl^-] = $10^{-2.378}$, a [Mg^{++}] = $10^{-2.962}$, a [K^+] = $10^{-3.146}$, a [Na^+] = $10^{-1.497}$, a [SO_4^{--}] = $10^{-2.345}$. Suppressed: $Ca(FeO_2)_2$, Ferrite-2-Ca, Ferrite-Ca, Ferrite-Cu, Ferrite-Mg, Ferrite-Zn, Goethite, Hematite, Magnetite

Notes:

1. Iron stability diagram with groundwater sampling results from well 35D.
2. Activities of constituents were calculated from average values for well 35D groundwater.

Fe – iron, pyrite – FeS_2, siderite – $FeCO_3$, $Fe(OH)_3$(ppd) – precipitated ferrihydrite, Eh – oxidation reduction potential (converted from field measurements using + 0.2 volts)

Well 35D Iron Stability Diagram

Vermilion Power Plant – New East Ash Pond

Geosyntec consultants

Columbus, Ohio

October 2023

Figure

2

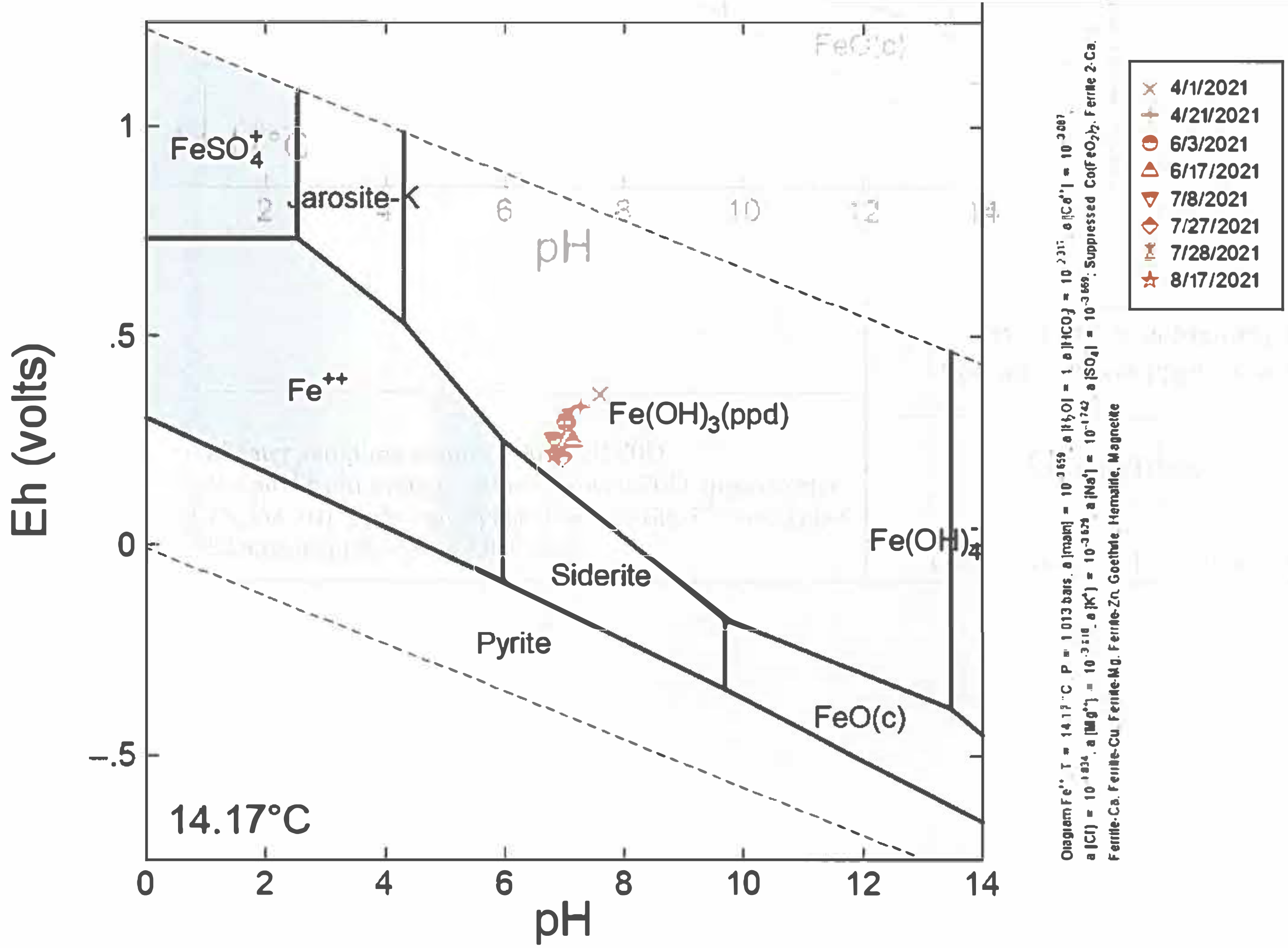


Diagram Fe^{++}, T = 14.17 °C, P = 1.013 bars, a [main] = $10^{-3.659}$, a [H$_2$O] = 1, a [HCO$_3^-$] = $10^{-2.311}$, a [Ca^{++}] = $10^{-3.087}$, a [Cl$^-$] = $10^{-1.834}$, a [Mg^{++}] = $10^{-3.518}$, a [K$^+$] = $10^{-3.679}$, a [Na$^+$] = $10^{-1.742}$, a [SO$_4^{--}$] = $10^{-3.669}$; Suppressed: Co(FeO$_2$)$_2$, Ferrite-2-Ca, Ferrite-Ca, Ferrite-Cu, Ferrite-Mg, Ferrite-Zn, Goethite, Hematite, Magnetite

Notes:
1. Iron stability diagram with groundwater sampling results from well 70D.
2. Activities of constituents were calculated from average values for well 70D groundwater.
Fe – iron, pyrite – FeS$_2$, siderite – FeCO$_3$, Fe(OH)$_3$(ppd) – precipitated ferrihydrite, Eh – oxidation reduction potential (converted from field measurements using + 0.2 volts)

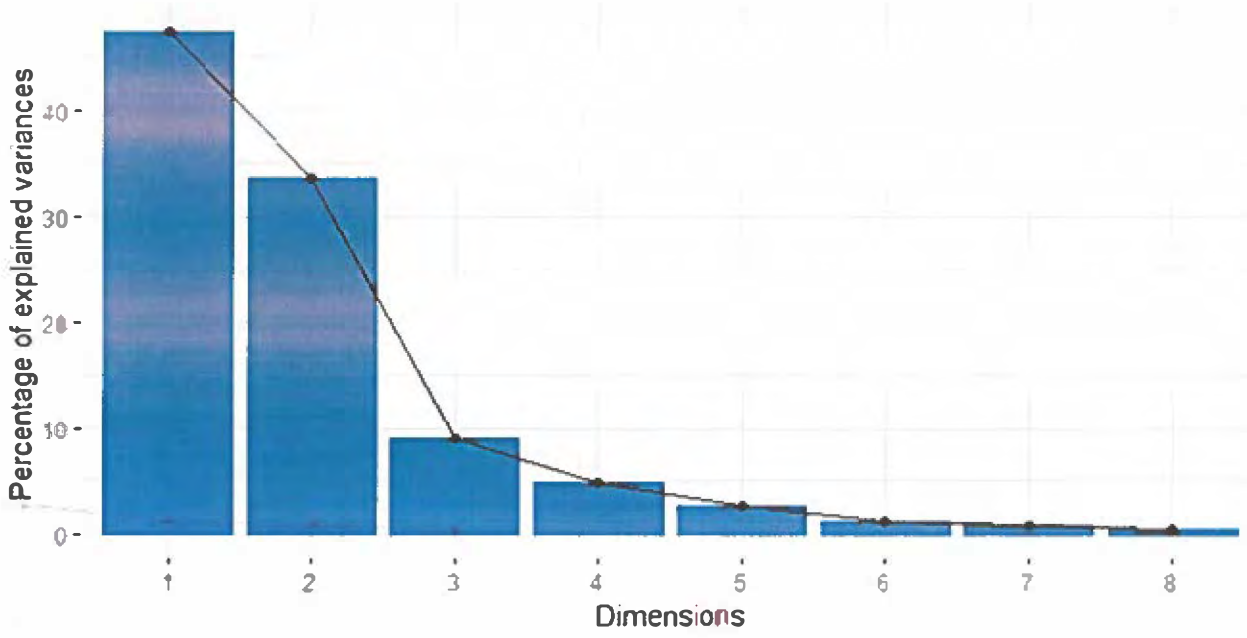
Well 70D Iron Stability Diagram
Vermilion Power Plant – New East Ash Pond

Geosyntec consultants

Figure
3

Columbus, Ohio

October 2023



Notes:
1. Samples collected from upgradient wells 10 and 22, downgradient wells 70S, 71S, 16, 35D, 70D, and 71D, and porewater well NED1 were included in the evaluation.

PCA Analysis - Quality of Representation of Principal Components

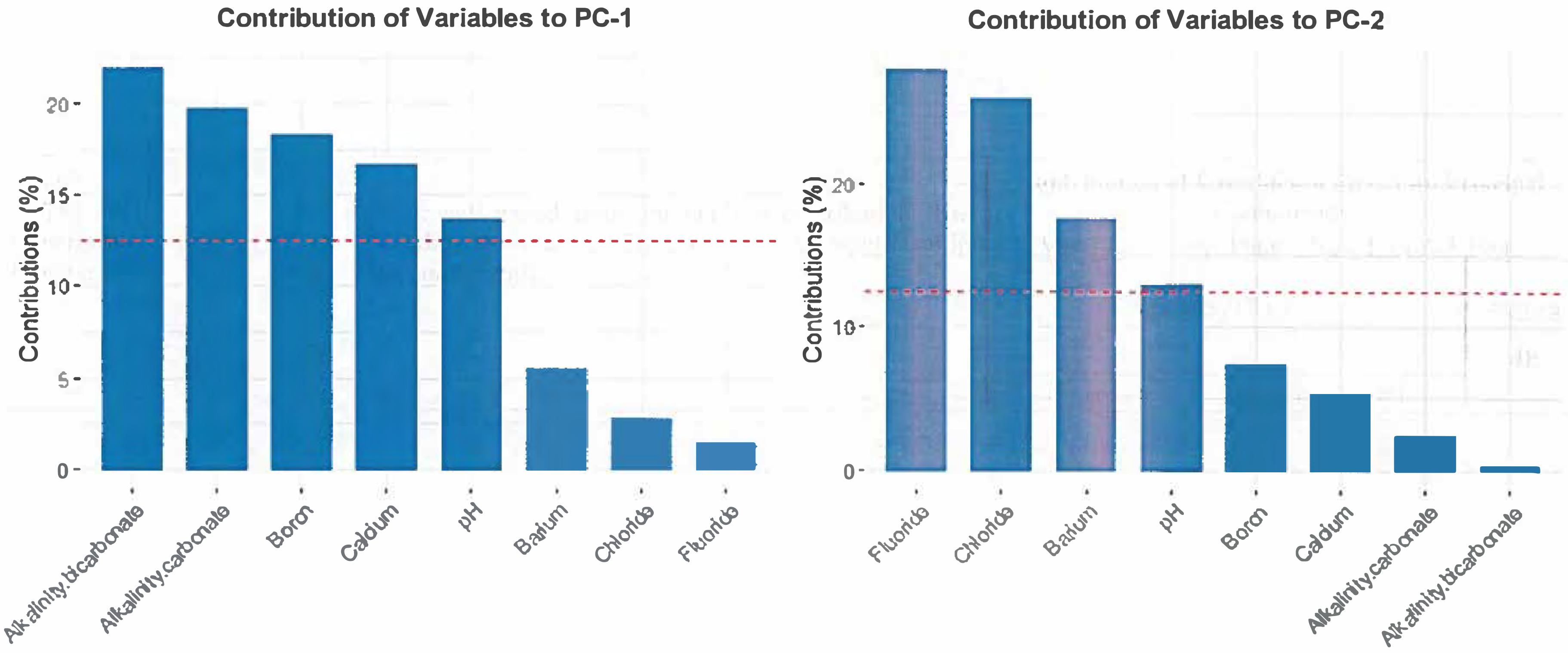
Vermilion Power Plant – New East Ash Pond

Geosyntec consultants

Columbus, Ohio

October 2023

Figure 4a



Contribution of Variables to PC-1

Contribution of Variables to PC-2

Notes:

1. The dashed red line represents the anticipated value for uniform contribution. The constituents with a contribution exceeding the reference line are considered significant in its contribution to each PC (principal component).

Contribution of Variables to First Two Principal Components

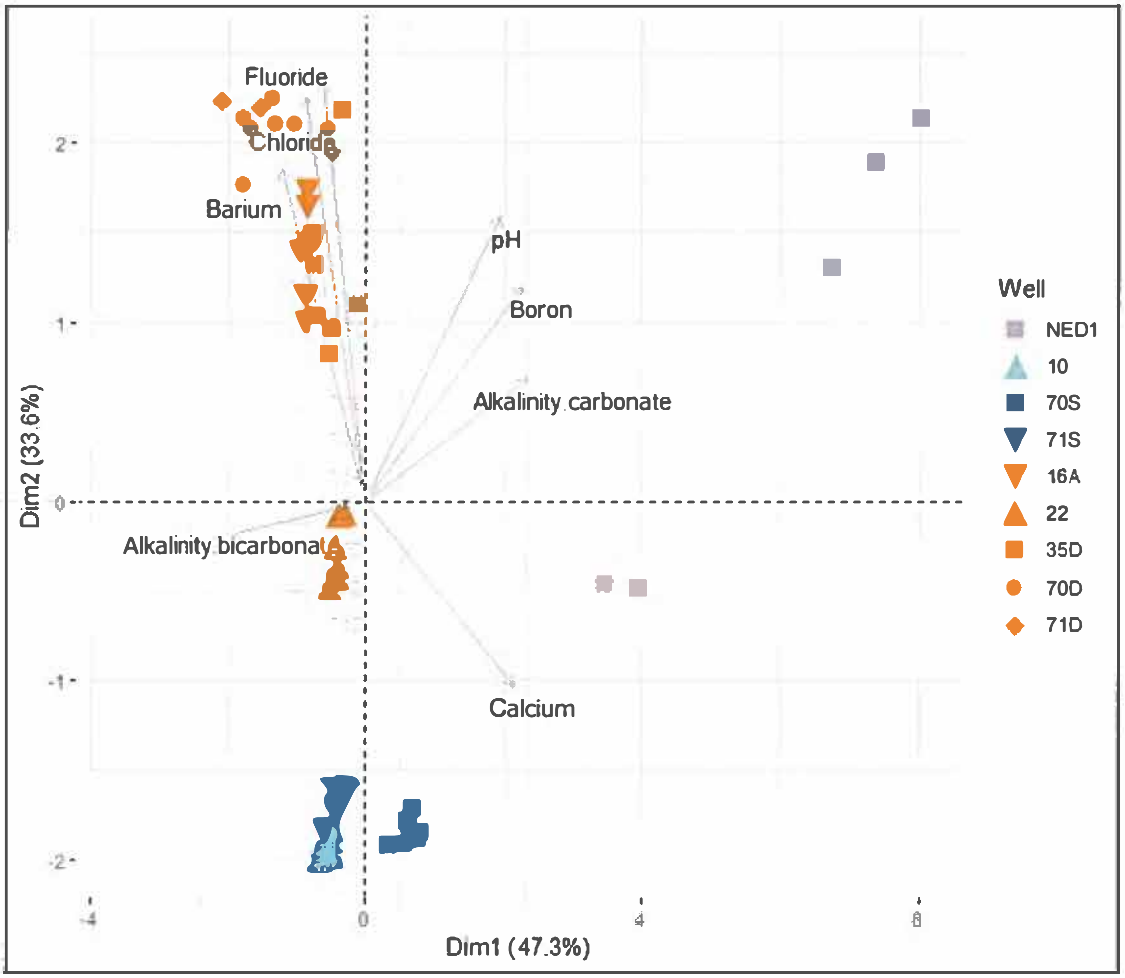
Vermilion Power Plant – New East Ash Pond

Geosyntec consultants

Figure 4b

Columbus. Ohio

October 2023



Notes:

1. The arrows signify the correlations between the constituents and the principal components.
2. Datapoints are colored based on hydrostratigraphic unit of sampling locations as follows:
   -Bedrock Confining Unit (BCU) wells: 16A, 22, 35D, 70D, 71D,
   -Upper Confining Unit (UCU) well: 10
   -Upper Unit (UU) wells: 70S, 71S
   -Coal Combustion Residual (CCR) well: NED

Principal Component Analysis Biplot

Vermilion Power Plant – New East Ash Pond

Geosyntec consultants

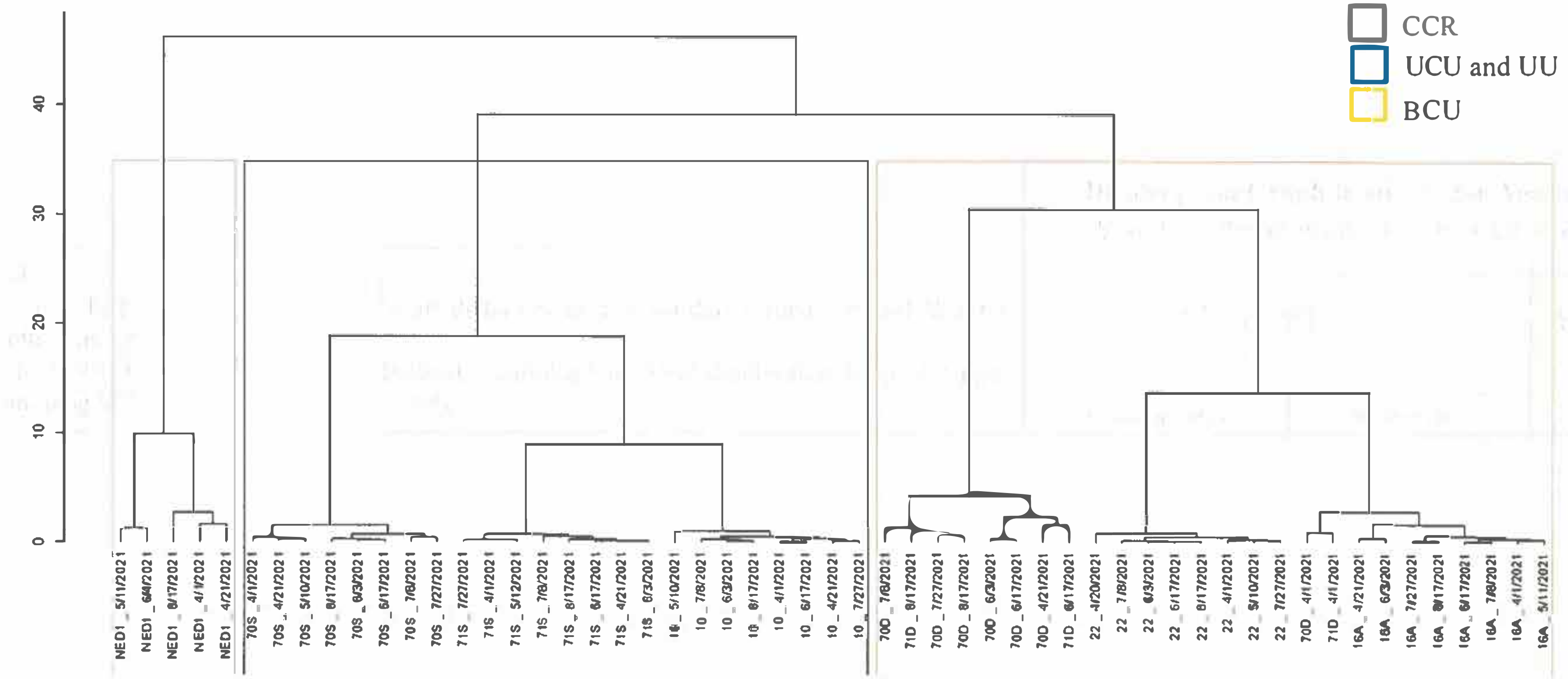
Figure

5

Columbus, Ohio

October 2023

Vistra - Groundwater Compliance - Documents\General\2023_Data_Gap_Assessment\Baldwin\2023-09 CI and F ASD Report



Notes:

1. The cluster analysis used Euclidean distances as the similarity measure and Ward's method as the clustering algorithm.
2. BCU, CCR, UCU and UU refer to Bedrock Confining Unit, Coal Combustion Residual, Upper Confining Unit, and Upper Unit, respectively.

Dendrogram Graph from Cluster Analysis

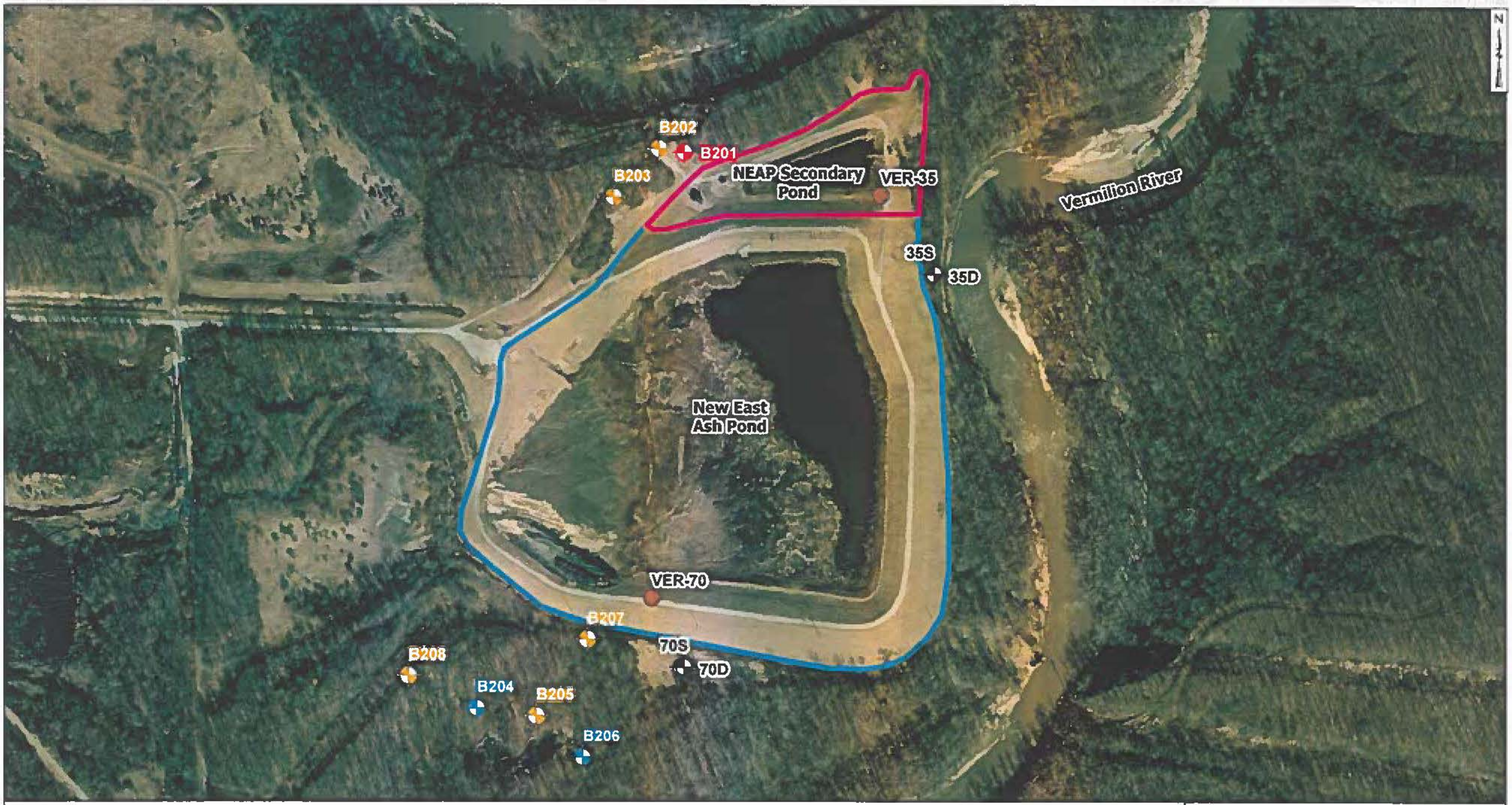
Vermilion Power Plant – New East Ash Pond

Geosyntec consultants

Columbus, Ohio

October 2023

Figure
6



Legend

2001 borings which identified:

- 🟠 Coal
- 🔴 Void Space
- 🔵 Coal & Void Space
- ⌖ Monitoring Well
- ● Boring Location
- ▭ New East Ash Pond (NEAP)
- ▭ NEAP Secondary Pond

Notes

- Soil boring locations are approximate.
- Ash pond boundaries are approximate.

Coal and Void Locations

Dynegy Midwest Generation
Vermilion Site
Oakwood, Illinois

Geosyntec consultants

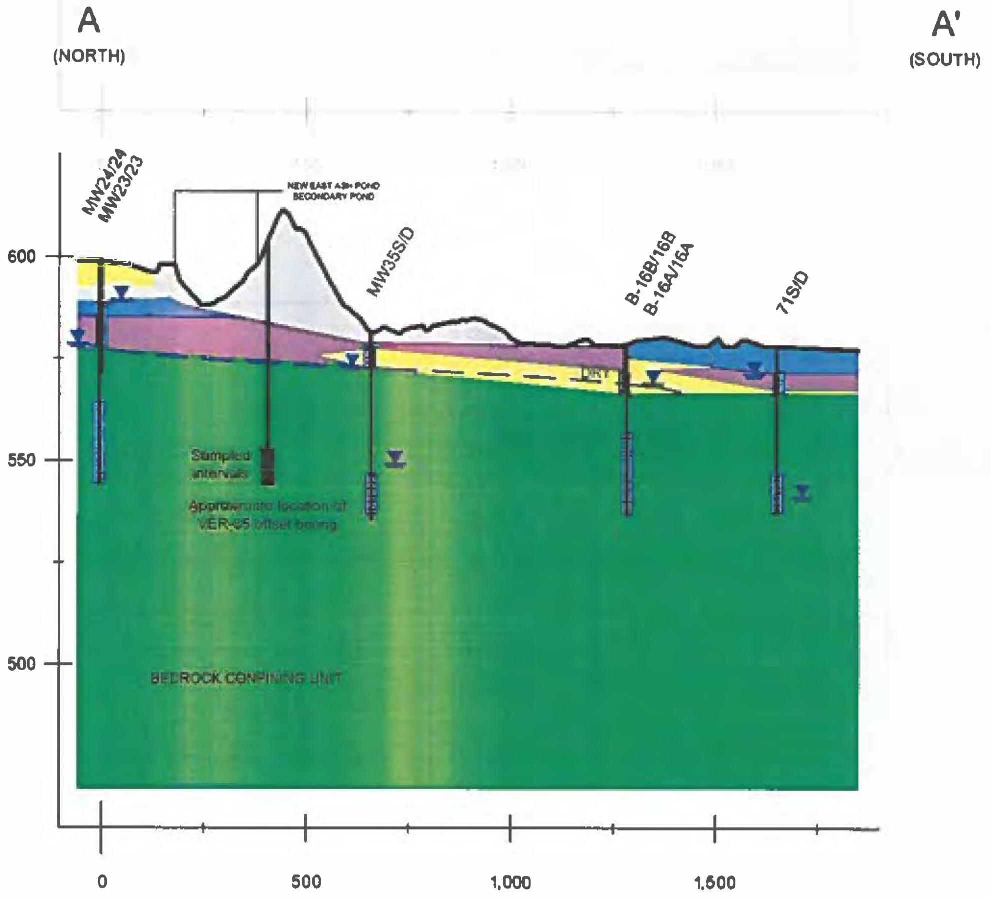
Columbus, Ohio

October 2023

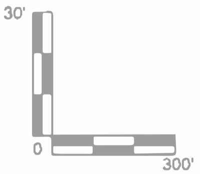
Figure 7

ATTACHMENT 1

Cross Sections



NOTES
1. This profile was developed by interpolation between widely spaced boreholes. Only at the borehole location should it be considered as an approximately accurate representation and then only to the degree implied by the notes on the borehole logs.
2. Scale is approximate.
3. Vertical scale is exaggerated 10X.
4. Groundwater elevations measured on March 29, 2021
5. PMP = Potential Migration Pathway



LEGEND

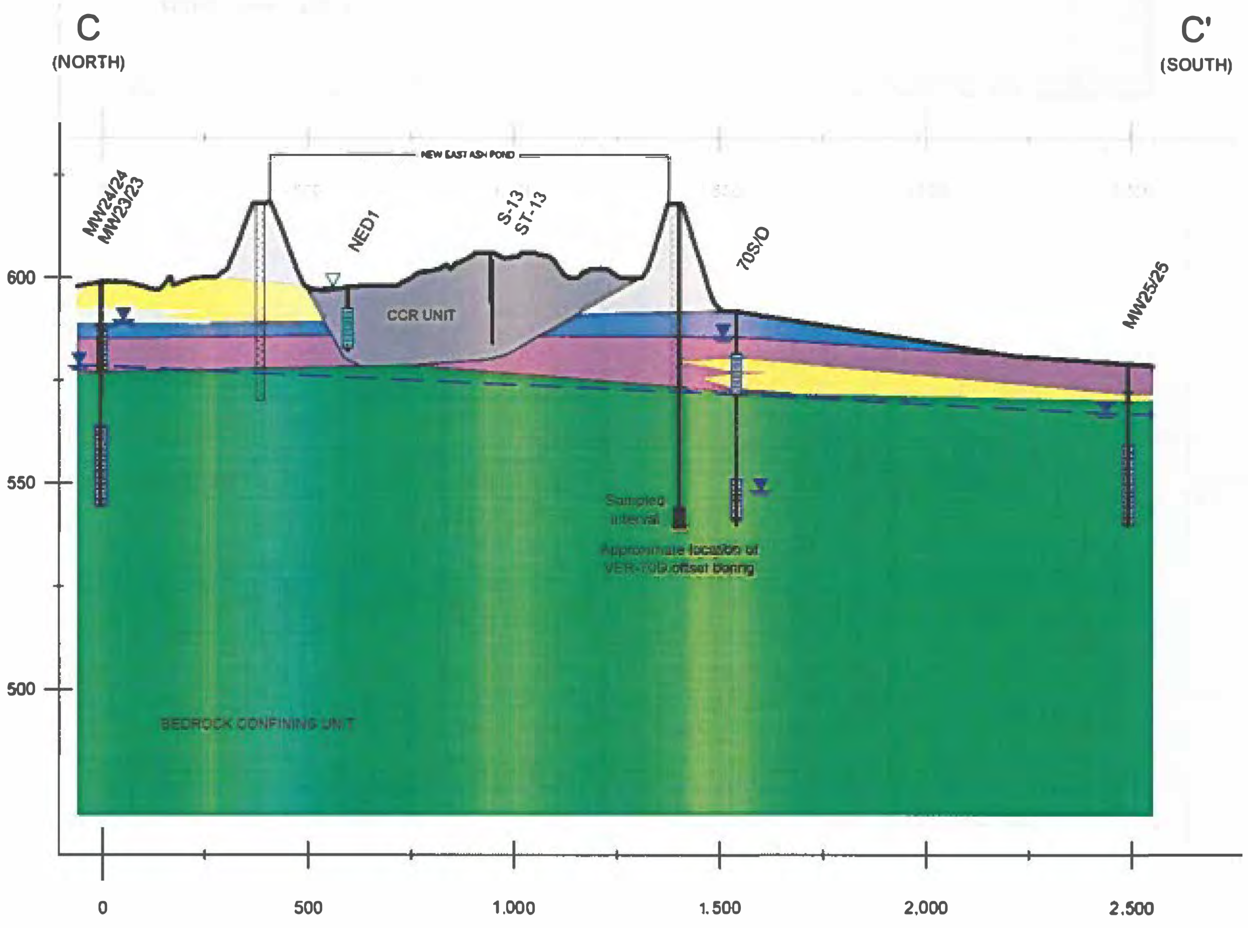
- ☐ FILL
- 🟪 CLAY(CL/CH)
- ☐ TILL (CL/CH)
- 🟦 SILT (ML)
- 🟨 SAND (SP/SM/SW)
- ☐ GRAVEL (GP/GW)
- 🟩 BEDROCK / WEATHERED BEDROCK (INTERBEDDED SHALE, LIMESTONE, SANDSTONE, V LITTLE SS)
- WELL SCREEN INTERVAL
- BEDROCK CONFINING UNIT POTENTIOMETRIC SURFACE
- BEDROCK CONFINING UNIT / PMP GROUNDWATER / OTHER GROUNDWATER / SURFACE WATER ELEVATION(S)

GEOLOGIC CROSS SECTION
A-A'

HYDROGEOLOGIC SITE CHARACTERIZATION REPORT
NEW EAST ASH POND
VERMILION POWER PLANT
OAKWOOD, ILLINOIS

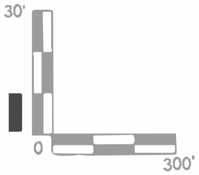
FIGURE 2-9

RAMBOLL AMERICAS
ENGINEERING SOLUTIONS, INC



NOTES

1. This profile was developed by interpolation between widely spaced boreholes. Only at the borehole location should it be considered as an approximately accurate representation and then only to the degree implied by the notes on the borehole logs.
2. Scale is approximate.
3. Vertical scale is exaggerated 10X.
4. Groundwater elevations measured on March 29, 2021
5. PMP = Potential Migration Pathway



LEGEND

▨	COAL COMBUSTION RESIDUALS (CCR)
☐	FILL
🟪	CLAY (CL/CH)
☐	TILL (CL/CH)
🟦	SILT (ML)
🟨	SAND (SP/SM/SW)
☐	GRAVEL (GP/GW)
🟩	BEDROCK / WEATHERED BEDROCK (INTERBEDDED SHALE, LIMESTONE, SANDSTONE, V LITTLE SS)
▤	WELL SCREEN INTERVAL
— —	BEDROCK CONFINING UNIT POTENTIOMETRIC SURFACE
▽	POREWATER ELEVATION
▼	BEDROCK CONFINING UNIT / PMP GROUNDWATER / OTHER GROUNDWATER / SURFACE WATER ELEVATION(S)
⁝	CLAY CORE KEYED 8-FT INTO BEDROCK

GEOLOGIC CROSS SECTION
C-C'

HYDROGEOLOGIC SITE CHARACTERIZATION REPORT
NEW EAST ASH POND
VERMILION POWER PLANT
OAKWOOD, ILLINOIS

FIGURE 2-11

RAMBOLL AMERICAS
ENGINEERING SOLUTIONS, INC

ATTACHMENT 2

Boring Logs - VER-35 and VER-70
Soil Boring and Well Construction Logs - 35D and 70D

Geosyntec consultants

engineers | scientists | innovators

Client:	Vistra
Project:	Vermilion Power Plant New East Ash Pond
Address:	10188 East 2150 North Road, Oakwood, IL

BORING LOG

Boring No. VER-35

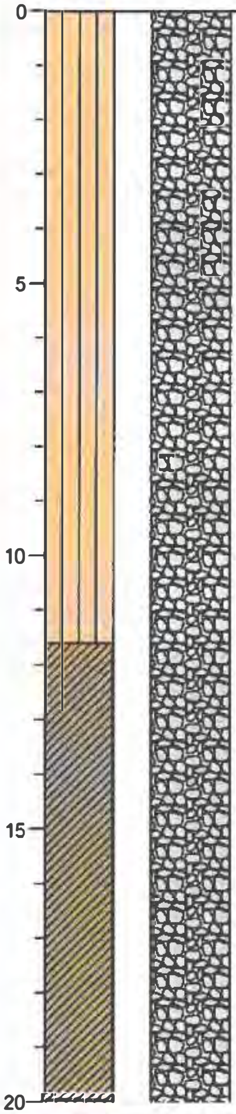
Page: 1 of 4

Drilling Start Date:	06/24/2023
Drilling End Date:	06/24/2023
Drilling Company:	Cascade Drilling
Drilling Method:	Sonic
Drilling Equipment:	Geoprobe
Driller:	Jeff Jehn
Logged By:	Andrew Kelley

Boring Depth (ft):	63
Boring Diameter (in):	6
Ground Surface Elev. (ft):	Not surveyed

Boring was advanced adjacent to well 35D.
Samples collected from 55-60 ft bgs and 60-63 ft bgs

DEPTH (ft) | LITHOLOGY | WATER LEVEL | BORING COMPLETION



Sample Type	Date & Time	Blow Counts	Recovery (ft)	SOIL/ROCK VISUAL DESCRIPTION
	10:35	NA	5.1/ 10	(0') GRAVELLY SILT (ML); light gray to brown (darkens downward), dry, loose, little sand, minor concretions.
				(3') CLAYEY SILT (ML); dark reddish brown, moist, firm, some black organics staining, few gravel, minor iron oxide stains.
	10:45		2.5/ 10	(10') As above.
				(10.6') GRAVELLY SILT (ML); light gray to brown, moist, loose, fine to coarse gravel, little sand.
				(11.6') SILTY CLAY (CL); dark grayish brown, moist, stiff, medium plasticity.

NOTES:

Geosyntec consultants

Client: Vistra
Project: Vermilion Power Plant New East Ash Pond
Address: 10188 East 2150 North Road, Oakwood, IL

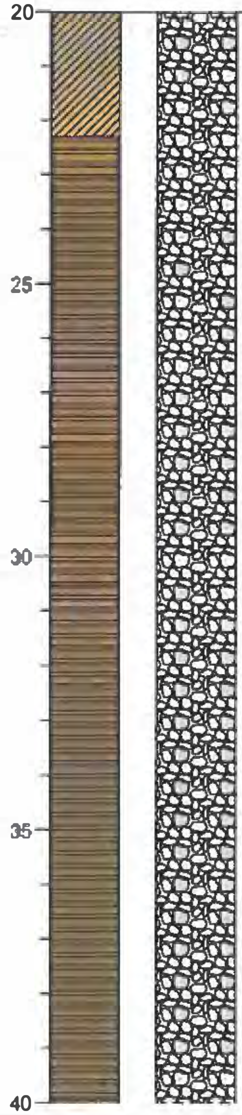
BORING LOG

Boring No. VER-35
Page: 2 of 4

Drilling Start Date:	06/24/2023
Drilling End Date:	06/24/2023
Drilling Company:	Cascade Drilling
Drilling Method:	Sonic
Drilling Equipment:	Geoprobe
Driller:	Jeff Jehn
Logged By:	Andrew Kelley

Boring Depth (ft):	63
Boring Diameter (in):	6
Ground Surface Elev. (ft):	Not surveyed

Boring was advanced adjacent to well 35D.
Samples collected from 55-60 ft bgs and 60-63 ft bgs



Sample Type	Date & Time	Blow Counts	Recovery (ft)	SOIL/ROCK VISUAL DESCRIPTION
	10:55	NA	8/8	(20') CLAY (CL); gray to light brown, moist, very soft, trace coarse gravel, high plasticity.
				(22.3') WEATHERED SHALE, gray, moist, highly decomposed, moderately disintegrated.
			2/2	(28') As above.
	11:55		8/10	(30') SHALE, gray, wet, highly decomposed, slightly disintegrated.
				(35.3') WEATHERED SHALE, gray, moist, highly decomposed, highly disintegrated.

NOTES:

Geosyntec consultants
engineers | scientists | innovators

Client: Vistra
Project: Vermilion Power Plant New East Ash Pond
Address: 10188 East 2150 North Road, Oakwood, IL

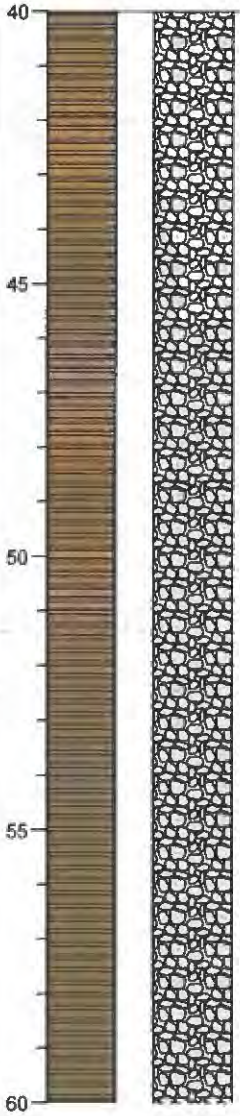
BORING LOG

Boring No. VER-35
Page: 3 of 4

Drilling Start Date:	06/24/2023
Drilling End Date:	06/24/2023
Drilling Company:	Cascade Drilling
Drilling Method:	Sonic
Drilling Equipment:	Geoprobe
Driller:	Jeff Jehn
Logged By:	Andrew Kelley

Boring Depth (ft):	63
Boring Diameter (in):	6
Ground Surface Elev. (ft):	Not surveyed

Boring was advanced adjacent to well 35D.
Samples collected from 55-60 ft bgs and 60-63 ft bgs



	COLLECT			
Sample Type	Date & Time	Blow Counts	Recovery (ft)	SOIL/ROCK VISUAL DESCRIPTION
	12:10	NA	2/2	(40') As above.
	13:20		4/5	(42') WEATHERED SHALE, gray, moist, highly decomposed, highly disintegrated.
	13:40		3.3/4	(47') As above.
	14:05		3/4	(51') As above: slightly decomposed, competent at 1.5-1.6 ft.
	14:20		4/5	(55') As above: slightly less weathered.

NOTES:

Geosyntec consultants
engineers | scientists | innovators

Client:	Vistra
Project:	Vermilion Power Plant New East Ash Pond
Address:	10188 East 2150 North Road, Oakwood, IL

BORING LOG

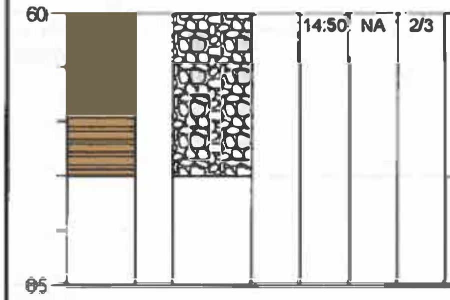
Boring No. VER-35

Page: 4 of 4

Drilling Start Date:	06/24/2023
Drilling End Date:	06/24/2023
Drilling Company:	Cascade Drilling
Drilling Method:	Sonic
Drilling Equipment:	Geoprobe
Driller:	Jeff Jehn
Logged By:	Andrew Kelley

Boring Depth (ft):	63
Boring Diameter (in):	6
Ground Surface Elev. (ft):	Not surveyed

Boring was advanced adjacent to well 35D.
Samples collected from 55-60 ft bgs and 60-63 ft bgs



DEPTH (ft)	LITHOLOGY	WATER LEVEL	BORING COMPLETION	COLLECT: Sample Type	COLLECT: Date & Time	COLLECT: Blow Counts	COLLECT: Recovery (ft)	SOIL/ROCK VISUAL DESCRIPTION
60					14:50	NA	2/3	(60') As above: gray, moist, highly decomposed, highly disintegrated, few fragments are slightly more competent.
								(63') End of Boring.
65								

NOTES:

SOIL BORING LOG INFORMATION

NATURAL
RESOURCE
TECHNOLOGY

Page 1 of 3

Facility/Project Name Vermilion Power Station	License/Permit/Monitoring Number	Boring Number MW35D	
Boring Drilled By: Name of crew chief (first, last) and Firm Bruno Williamson Ramsey Geotechnical Engineering	Date Drilling Started 3/1/2017	Date Drilling Completed 3/3/2017	Drilling Method rotary/auger
Common Well Name MW35D	Final Static Water Level Feet (NAVD88)	Surface Elevation 581.25 Feet (NAVD88)	Borehole Diameter 7.3 inches
Local Grid Origin ☐ (estimated: ☐) or Boring Location ☒ State Plane 1,279,955.58 N, 1,151,276.17 E [✓ E]/W 1/4 of 1/4 of Section , T N, R	Lat 40° 10' 47.14212" Long 87° 44' 8.06652"	Local Grid Location Feet ☐ N ☐ S Feet ☐ E ☐ W	
Facility ID	County Vermilion	State IL	Civil Town/City/ or Village Danville

Sample Number and Type	Sample Length Att. & Recovered (in)	Blow Counts	Depth In Feet	Soil/Rock Description And Geologic Origin For Each Major Unit	U S C S	Graphic Log	Well Diagram	Soil Properties: Compressive Strength (tsf)	Moisture Content	Liquid Limit	Plasticity Index	P 200	RQD/ Comments
1 SS	24 16.5	2 2 3 3		0 - 2.5' **FILL, SILT**: ML, very dark grayish brown (10YR 3/2), 15-30% silt, trace wood and roots, cohesive, low plasticity, moist.	(FILL) ML								
2 SS	24 19	1 3 3 3		2.5 - 4.3' **SANDY LEAN CLAY**: s(CL), weak red (2.5YR 4/2), 5-15% fine sand, sand content increasing with depth, low plasticity, moist.	s(CL)								
3 SS	24 21	2 3 4 3		4.3 - 8' **POORLY-GRADED SAND**: SP, yellowish brown (10YR 5/6), fine sand, 15-30% clay, moist. 5.1' trace clay.									
4 SS	24 18	3 3 3 3		7.5' trace gravel and cobbles.	SP								Auger bringing up cobbles on flights.
5 SS	24 10	3 4 4 22		8 - 8.5' **FAT CLAY**: CH, very dark grayish brown (10YR 3/2), trace silt, high plasticity, moist.	CH			0.5					
				8.5 - 10' **Weathered SHALE Bedrock** BDX (SH), very dark grayish brown (10YR 3/2) to very dark greenish gray (GLEY 1 3/10Y), highly weathered, red (7.5YR 4/6) discoloration, fissile, moist.	BDX (SH)								
6 SS	15 15	20 34 50 for 3"		10 - 15.6' **Weathered SHALE Bedrock** to **SHALE**: BDX (SH), gray (GLEY 1 6/N), weak, fissile, intensely fractured, red (7.5YR 4/6) discoloration, dry.	BDX (SH)								

Depth In Feet: 1 2 3 4 5 6 7 8 9 10 11 12

I hereby certify that the information on this form is true and correct to the best of my knowledge.

Signature	Firm Natural Resource Technology 234 W. Florida St., Fifth Floor, Milwaukee, WI 53204	Tel: (414) 837-3607 Fax: (414) 837-3608

SOIL BORING LOG INFORMATION SUPPLEMENT

NATURAL
RESOURCE
TECHNOLOGY

Boring Number MW35D

Page 2 of 3

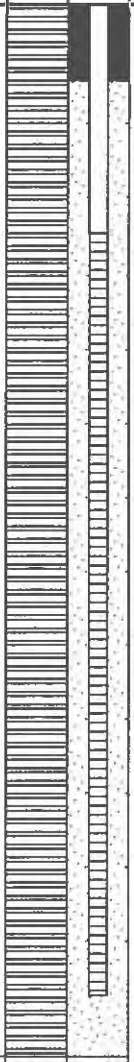
Sample		Blow Counts	Depth In Feet	Soil/Rock Description And Geologic Origin For Each Major Unit	U S C S	Graphic Log	Well Diagram		Soil Properties					RQD/ Comments
Number and Type	Length Att. & Recovered (in)								Compressive Strength (tsf)	Moisture Content	Liquid Limit	Plasticity Index	P 200	
7 SS	8 9	45 50 for 2"		10 - 15.6' **Weathered SHALE Bedrock** to SHALE: BDX (SH), gray (GLEY 1 6/N), weak, fissile, intensely fractured, red (7.5YR 4/6) discoloration, dry. *(continued)*										
			13											
8 SS	9 7	31 50 for 3"	14		BDX (SH)									
			15											
9 CORE	120 120		16	15.6 - 45.8' SHALE: BDX (SH), dark reddish gray (10YR 4/1) to gray (2.5Y 5/1), microcrystalline, thinly bedded to laminated, weak, slightly decomposed (very dark gray (10YR 3/1) to black (10YR 2/1) discoloration in partly healed fractures), competent, dry to moist in fractures.										Core 9, RQD = 89%. Light brown gray return water. 4" diameter outer casing set from 0-16 ft bgs.
			17											
			18											
			19											
			20											
			21											
			22											
			23											
			24		BDX (SH)									
			25											
10 CORE	131.3 120		26	25.6' partly to totally healed fractures.										Core 10, RQD = 89%. Light gray return water.
			27											
			28											
			29											
			30											
			31											
			32											

SOIL BORING LOG INFORMATION SUPPLEMENT

NATURAL
RESOURCE
TECHNOLOGY

Boring Number MW35D

Page 3 of 3

Sample									Soil Properties					
Number and Type	Length Att. & Recovered (in)	Blow Counts	Depth In Feet	Soil/Rock Description And Geologic Origin For Each Major Unit	U S C S	Graphic Log	Well Diagram		Compressive Strength (tsf)	Moisture Content	Liquid Limit	Plasticity Index	P 200	RQD/ Comments
11 CORE	111.1 120		33 34 35 36 37 38 39 40 41	15.6 - 45.8' **SHALE:** BDX (SH), dark reddish gray (10YR 4/1) to gray (2.5Y 5/1), microcrystalline, thinly bedded to laminated, weak, slightly decomposed (very dark gray (10YR 3/1) to black (10YR 2/1) discoloration in partly healed fractures), competent, dry to moist in fractures. *(continued)*	BDX (SH)									Core 11, RQD = 93%. Gray return water.
			42 43 44 45	41.9' - 43' crossbedding.										
				45.8' End of Boring.										

NATURAL RESOURCE TECHNOLOGY

MONITORING WELL CONSTRUCTION

Facility/Project Name: Vermilion Power Station

Facility License, Permit or Monitoring No.:

Facility ID:

Type of Well: mw

Distance from Waste/Source: ft.

State: IL

Local Grid Location of Well: ____ ft. ☐ N. ☐ S. ____ ft. ☐ E. ☐ W.

Local Grid Origin ☐ (estimated: ☐) or Well Location ☒

Lat. 40° 10' 47.142" Long. 87° 44' 8.067" or

St. Plane 1,279,955.58 ft. N, 1,151,276.17 ft. E. [✓ E]/W

Section Location of Waste/Source: ____ 1/4 of ____ 1/4 of Sec. ____, T. ____ N, R. ____ ☐ E ☐ W

Location of Well Relative to Waste/Source: u ☐ Upgradient s ☐ Sidegradient d ☐ Downgradient n ☐ Not Known

Gov. Lot Number:

Well Name: MW35D

Date Well Installed: 03/03/2017

Well Installed By: (Person's Name and Firm) Bruno Williamson, Ramsey Geotechnical Engineering

A. Protective pipe, top elevation ____ ft. MSL

B. Well casing, top elevation 584.15 ft. MSL

C. Land surface elevation 581.25 ft. MSL

D. Surface seal, bottom 579.3 ft. MSL or 2.0 ft.

12. USCS classification of soil near screen:
GP ☐ GM ☐ GC ☐ GW ☐ SW ☐ SP ☐
SM ☐ SC ☐ ML ☐ MH ☐ CL ☐ CH ☐
Bedrock ☒

13. Sieve analysis attached? ☐ Yes ☒ No

14. Drilling method used: Rotary ☐ Hollow Stem Auger ☐ HSA / Rotary Other ☒

15. Drilling fluid used: Water ☒ 0 2 Air ☐ Drilling Mud ☐ 0 3 None ☐

16. Drilling additives used? ☐ Yes ☒ No

Describe

17. Source of water (attach analysis, if required): City of Champaign

E. Bentonite seal, top 551.3 ft. MSL or 30.0 ft.

F. Fine sand, top ____ ft. MSL or ____ ft.

G. Filter pack, top 548.3 ft. MSL or 33.0 ft.

H. Screen joint, top 546.3 ft. MSL or 35.0 ft.

I. Well bottom 536.3 ft. MSL or 45.0 ft.

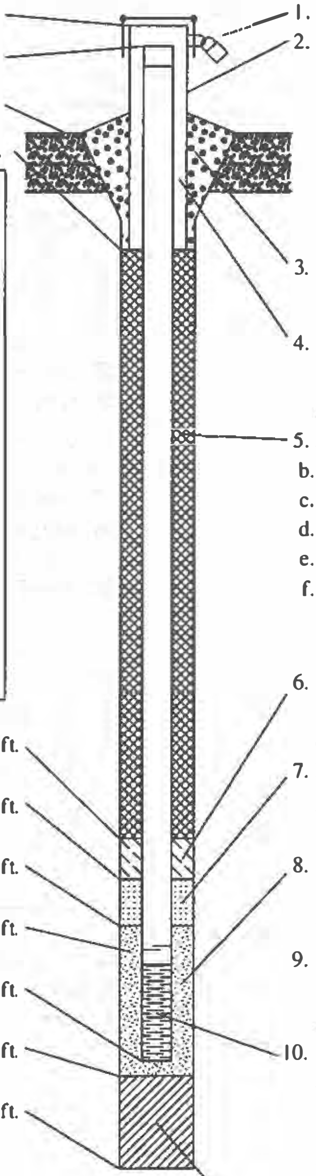
J. Filter pack, bottom 535.5 ft. MSL or 45.8 ft.

K. Borehole, bottom 535.5 ft. MSL or 45.8 ft.

L. Borehole, diameter 7.3 in.

M. O.D. well casing 2.38 in.

N. I.D. well casing 1.99 in.



1. Cap and lock? ☒ Yes ☐ No

2. Protective cover pipe:
   - a. Inside diameter: 6.0 in.
   - b. Length: 6.0 ft.
   - c. Material: Steel ☒ Other ☐
   - d. Additional protection? ☒ Yes ☐ No If yes, describe: 4" diameter protective PVC casing

3. Surface seal: Bentonite ☐ Concrete ☒ Other ☐

4. Material between well casing and protective pipe: Bentonite ☒ Sand Other ☒

5. Annular space seal: a. Granular/Chipped Bentonite ☐
   - b. ____ Lbs/gal mud weight . . . Bentonite-sand slurry ☐
   - c. ____ Lbs/gal mud weight . . . Bentonite slurry ☐
   - d. 30 % Bentonite . . . Bentonite-cement grout ☒
   - e. ____ Ft³ volume added for any of the above
   - f. How installed: Tremie ☒ Tremie pumped ☐ Gravity ☐

6. Bentonite seal: a. Bentonite granules ☐
   - b. ☐ 1/4 in. ☒ 3/8 in. ☐ 1/2 in. Bentonite chips ☒
   - c. ____ Other ☐

7. Fine sand material: Manufacturer, product name & mesh size
   - a. ____
   - b. Volume added ____ ft³

8. Filter pack material: Manufacturer, product name & mesh size
   - a. NSF Quartz Sand #10-20
   - b. Volume added ____ ft³

9. Well casing: Flush threaded PVC schedule 40 ☒ Flush threaded PVC schedule 80 ☐ Other ☐

10. Screen material: Schedule 40 PVC
   - a. Screen Type: Factory cut ☒ Continuous slot ☐ Other ☐
   - b. Manufacturer ____
   - c. Slot size: 0.100 in.
   - d. Slotted length: 10.0 ft.

11. Backfill material (below filter pack): None ☒ Other ☐

I hereby certify that the information on this form is true and correct to the best of my knowledge.

Date Modified: 4/6/2017

Signature:

Firm: Natural Resource Technology
234 W. Florida Street, Floor 5, Milwaukee, WI 53204
Tel: (414) 837-3607
Fax: (414) 837-3608

Geosyntec consultants

engineers | scientists | innovators

Client:	Vistra
Project:	Vermilion Power Plant New East Ash Pond
Address:	10188 East 2150 North Road, Oakwood, IL

BORING LOG

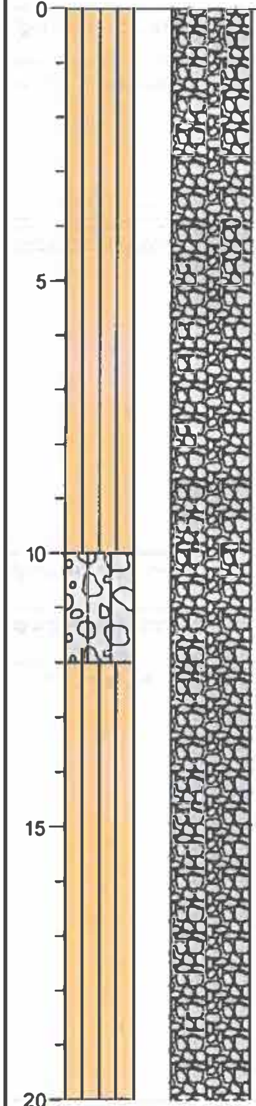
Boring No. **VER-70**

Page: **1 of 4**

Drilling Start Date:	06/23/2023
Drilling End Date:	06/23/2023
Drilling Company:	Cascade Drilling
Drilling Method:	Sonic
Drilling Equipment:	Geoprobe
Driller:	Jeff Jehn
Logged By:	Andrew Kelley

Boring Depth (ft):	80
Boring Diameter (in):	6
Ground Surface Elev. (ft):	Not surveyed

Boring was advanced adjacent to well 70D. Samples collected from 30-40 ft bgs, 41-42 ft bgs and 75-80 ft bgs



DEPTH (ft)	Sample Type	Date & Time	Blow Counts	Recovery (ft)	SOIL/ROCK VISUAL DESCRIPTION
0		10:40	NA	6/10	(0') SILT WITH GRAVEL (ML); light brown, dry, loose, fine to coarse gravel.
					(1') SILT (ML); brown to tan, dry, firm, moderate concretions, little gravel, few clay.
					(3.6') SILT (ML); gray to dark gray with little brown, dry, firm, few fine sand, few fine gravel, coarsens downwards, moderate concretions.
10		10:55		4/10	(10') SILTY GRAVEL (GM); gray to dark gray, moist, loose, some fine to coarse sand.
					(10.5') SILTY GRAVEL (GM); light gray, moist, loose, fines downward.
					(12') SANDY SILT (ML); brown, moist, medium dense, firm, little clay, little fine gravel.

NOTES:

Geosyntec consultants
engineers | scientists | innovators

Client:	Vistra
Project:	Vermilion Power Plant New East Ash Pond
Address:	10188 East 2150 North Road, Oakwood, IL

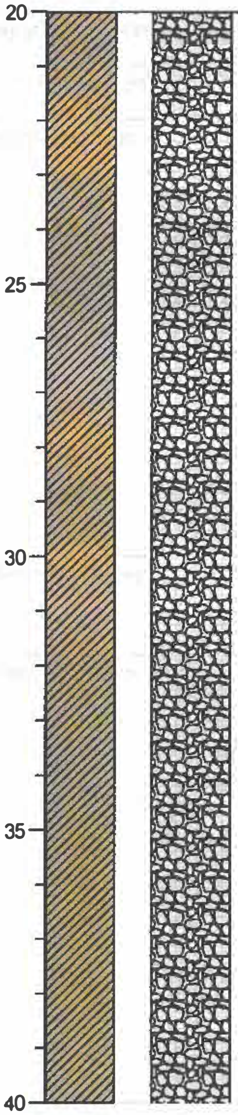
BORING LOG

Boring No. VER-70
Page: 2 of 4

Drilling Start Date:	06/23/2023
Drilling End Date:	06/23/2023
Drilling Company:	Cascade Drilling
Drilling Method:	Sonic
Drilling Equipment:	Geoprobe
Driller:	Jeff Jehn
Logged By:	Andrew Kelley

Boring Depth (ft):	80
Boring Diameter (in):	6
Ground Surface Elev. (ft):	Not surveyed

Boring was advanced adjacent to well 70D.
Samples collected from 30-40 ft bgs, 41-42 ft bgs and 75-80 ft bgs



DEPTH (ft)	LITHOLOGY	WATER LEVEL	BORING COMPLETION	COLLECT Sample Type	Date & Time	Blow Counts	Recovery (ft)	SOIL/ROCK VISUAL DESCRIPTION
20					13:00	NA	3/10	(20') CLAY WITH SILT (CL); grayish brown, wet, stiff, little sand, little fine to coarse gravel.
								(21') SILTY CLAY (CL); grayish brown, wet, soft, little fine gravel, few sand.
								(21.3') SANDY CLAY (CL); grayish brown, wet, very stiff, some gravel.
25								
30							3/10	(30') GRAVELLY CLAY WITH SAND (CL); grayish brown, wet, firm, sand coarsens downward.
								(31.8') CLAY (CL); dark gray to black, wet, firm, little gravel, few roots observed, dark organics.
35								
40								

NOTES:

Geosyntec consultants

Client:	**Vistra**
Project:	**Vermillon Power Plant New East Ash Pond**
Address:	**10188 East 2150 North Road, Oakwood, IL**

BORING LOG

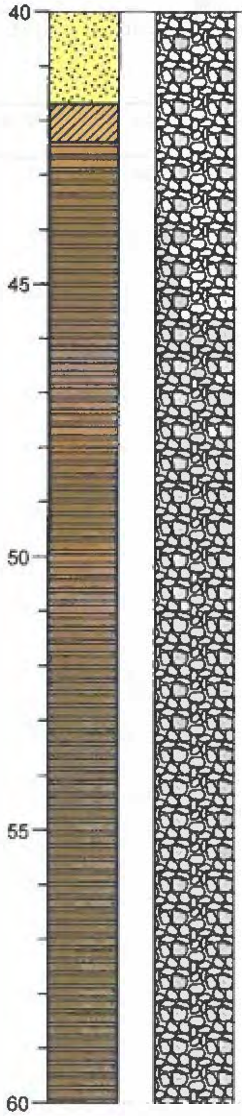
Boring No. **VER-70**

Page: **3 of 4**

Drilling Start Date:	**06/23/2023**
Drilling End Date:	**06/23/2023**
Drilling Company:	**Cascade Drilling**
Drilling Method:	**Sonic**
Drilling Equipment:	**Geoprobe**
Driller:	**Jeff Jehn**
Logged By:	**Andrew Kelley**

Boring Depth (ft):	**80**
Boring Diameter (in):	**6**
Ground Surface Elev. (ft):	**Not surveyed**

Boring was advanced adjacent to well 70D.
Samples collected from 30-40 ft bgs, 41-42 ft bgs and 75-80 ft bgs

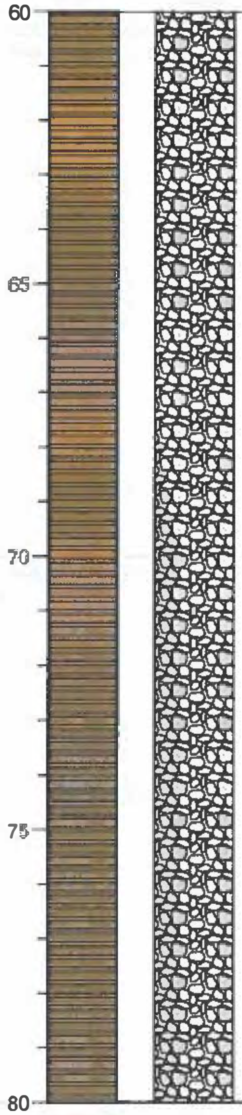


DEPTH (ft)	LITHOLOGY	WATER LEVEL	BORING COMPLETION	COLLECT: Sample Type	COLLECT: Date & Time	COLLECT: Blow Counts	COLLECT: Recovery (ft)	SOIL/ROCK VISUAL DESCRIPTION
40					13:50	NA	8/10	(40') POORLY GRADED SAND (SP): brown with hint of gray, wet, medium dense, fine grained.
								(41.7') CLAY (CL); brownish gray, moist, very stiff, few coarse gravel, some sand.
								(42.4') SHALE, gray, moist, laminated, highly decomposed, moderately disintegrated.
50					14:30		5/10	(50') As above.
60								

NOTES:

Geosyntec consultants	**Client:** Vistra **Project:** Vermilion Power Plant New East Ash Pond **Address:** 10188 East 2150 North Road, Oakwood, IL	**BORING LOG** **Boring No.** VER-70 **Page:** 4 of 4

Drilling Start Date:	06/23/2023	Boring Depth (ft):	80
Drilling End Date:	06/23/2023	Boring Diameter (in):	6
Drilling Company:	Cascade Drilling	Ground Surface Elev. (ft):	Not surveyed
Drilling Method:	Sonic	Boring was advanced adjacent to well 70D. Samples collected from 30-40 ft bgs, 41-42 ft bgs and 75-80 ft bgs	
Drilling Equipment:	Geoprobe		
Driller:	Jeff Jehn		
Logged By:	Andrew Kelley		



DEPTH (ft)	LITHOLOGY	WATER LEVEL	BORING COMPLETION	COLLECT Sample Type	Date & Time	Blow Counts	Recovery (ft)	SOIL/ROCK VISUAL DESCRIPTION
60					15:15	NA	1/10	(60') SHALE, gray to dark gray, wet (driller water), foliated, highly decomposed, slightly disintegrated, weaker and more highly disintegrated shale likely washed out by driller fluids.
70					17:00		10/10	(70') SHALE, gray to dark gray, wet, highly decomposed, moderately disintegrated, coated in wet clay (likely slough).
75								(75') SHALE, gray to dark gray, moist, highly decomposed, slightly disintegrated.
80								(80') End of Boring.

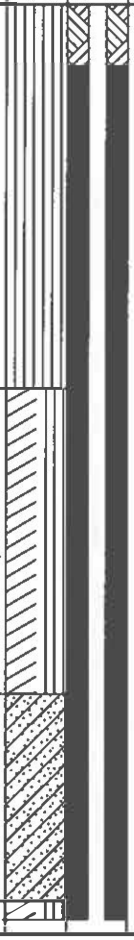
NOTES:

RAMBOLL

SOIL BORING LOG INFORMATION

Page 1 of 3

Facility/Project Name Vermilion Power Station		License/Permit/Monitoring Number	Boring Number 70D
Boring Drilled By: Name of crew chief (first, last) and Firm Jason Greer Cascade Drilling	Date Drilling Started 3/4/2021	Date Drilling Completed 3/4/2021	Drilling Method Mini Sonic
Common Well Name 70D	Final Static Water Level Feet (NAVD88)	Surface Elevation 591.90 Feet (NAVD88)	Borehole Diameter 6.0 inches
Local Grid Origin ☐ (estimated: ☐) or Boring Location ☐ State Plane 1,278,929.46 N, 1,150,617.15 E [✓ E]/W 1/4 of 1/4 of Section , T N, R	Lat ° ' " Long ° ' "	Local Grid Location Feet ☐ N ☐ S Feet ☐ E ☐ W	
Facility ID	County Vermilion	State Illinois	Civil Town/City/ or Village Oakwood



Sample Number and Type	Sample Length Att. & Recovered (in)	Blow Counts	Depth In Feet	Soil/Rock Description And Geologic Origin For Each Major Unit	U S C S	Graphic Log	Well Diagram	PID 10.6 eV Lamp	Soil Properties: Compressive Strength (tsf)	Moisture Content	Liquid Limit	Plasticity Index	P 200	RQD/ Comments
1 CS	60 47		0	0 - 6.3' **SILT:** ML, dark brown (10YR 3/3) to brown (10YR 4/3), clay (15-25%), sand, (0-5%), roots (0-5%), stiff, slow dilatancy, low toughness, low plasticity, moist.	ML				1.5					CS= Core Sample
			3						1.5					
2 CS	60 60		5						1.5					
			6.3	6.3 - 11.3' **SILTY CLAY:** CL/ML, brown (10YR 4/3), sand (0-10%), gravel (0-5%), firm, slow dilatancy, low toughness, medium plasticity, moist.	CL/ML				0.75					
			9						0.75					
			9.4	9.4' color change to yellowish brown (10YR 5/4).										
3 CS	120 120		10											
			11.3	11.3 - 14.7' **CLAYEY SAND:** SC, yellowish brown (10YR 5/6), rounded fine sand, silt (5-10%), gravel (0-5%), loose, wet.	SC									
			15											

I hereby certify that the information on this form is true and correct to the best of my knowledge.

Signature	Firm Ramboll 234 W. Florida Street, Milwaukee, WI 53204	Tel: (414) 837-3607 Fax: (414) 837-3608

Template: RAMBOLL_IL_BORING LOG - Project: 845_VERMILION_2021 (2).GPJ

SOIL BORING LOG INFORMATION SUPPLEMENT

Boring Number 70D

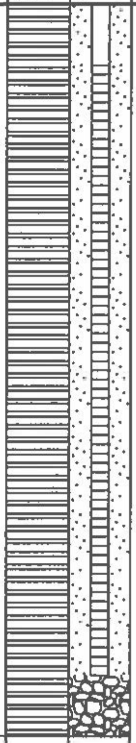
Page 2 of 3

Sample: Number and Type	Sample: Length Att & Recovered (in)	Blow Counts	Depth In Feet	Soil/Rock Description And Geologic Origin For Each Major Unit	U S C S	Graphic Log	Well Diagram	PID 10.6 eV Lamp	Soil Properties: Compressive Strength (tsf)	Soil Properties: Moisture Content	Soil Properties: Liquid Limit	Soil Properties: Plasticity Index	Soil Properties: P 200	RQD/ Comments
				14.7 - 15' **SILTY CLAY**: CL/ML, yellowish brown (10YR 5/6), soft, slow dilatancy, low toughness, medium plasticity.	CL/ML									
			16	15 - 16.2' **CLAYEY SAND**: SC, yellowish brown (10YR 5/6), rounded fine sand, silt (5-10%), gravel (0-5%), loose, wet.	SC									
			17 18	16.2 - 18.8' **POORLY-GRADED SAND WITH CLAY**: SP-SC, ???, subrounded to rounded, fine to medium sand, loose, wet.	SP-SC									
			19	18.8 - 19.6' **LEAN CLAY**: CL, dark gray (10YR 4/1), gravel, (0-5%), sand (0-5%), stiff, no dilatancy, low toughness, medium plasticity, moist.	CL				2.5					
4 CS	120 97		20	19.6 - 20.3' **Weathered SHALE Bedrock** BDX (SH), gray (10YR 5/1), dry.	BDX (SH)									
			21 22 23 24 25 26 27 28 29	20.3 - 52' **SHALE**: BDX (SH), gray (10YR 5/1).										
5 CS	132 132		30 31 32 33 34 35 36 37 38 39 40		BDX (SH)									

SOIL BORING LOG INFORMATION SUPPLEMENT

Boring Number 70D

Page 3 of 3



Sample									Soil Properties					
Number and Type	Length Att. & Recovered (in)	Blow Counts	Depth In Feet	Soil/Rock Description And Geologic Origin For Each Major Unit	U S C S	Graphic Log	Well Diagram	PID 10.6 eV Lamp	Compressive Strength (tsf)	Moisture Content	Liquid Limit	Plasticity Index	P 200	RQD/ Comments
6 CS	132 132		41 42 43 44 45 46 47 48 49 50 51 52	20.3 - 52' **SHALE:** BDX (SH), gray (10YR 5/1). *(continued)*	BDX (SH)									
				52' End of Boring.										

MONITORING WELL CONSTRUCTION

Facility/Project Name: Vermilion Power Station

Facility License, Permit or Monitoring No.:

Facility ID:

Type of Well: Well Code 12/pz

Distance from Waste/Source: ft.

State: Illinois

Local Grid Location of Well: ft. ☐ N. ☐ S. ft. ☐ E. ☐ W.

Local Grid Origin ☐ (estimated: ☐) or Well Location ☐

Lat. ° ' " Long. ° ' " or

St. Plane 1,278,929 ft. N, 1,150,617 ft. E. [✓ E]/W

Section Location of Waste/Source: 1/4 of 1/4 of Sec T. N, R. ☐ E ☐ W

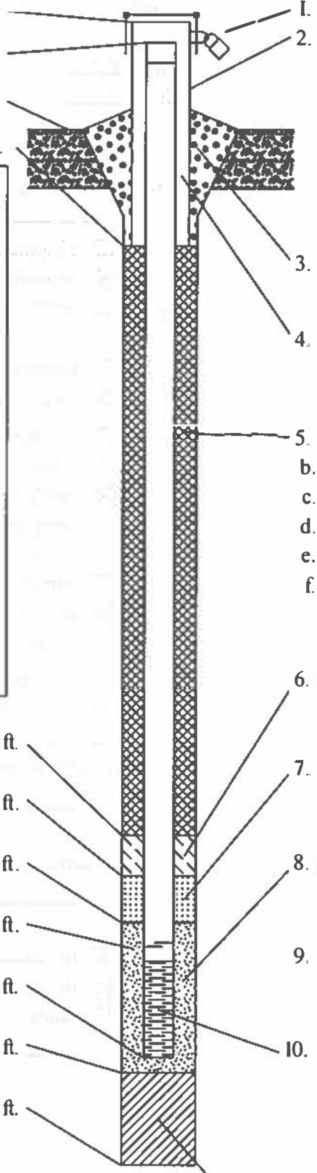
Location of Well Relative to Waste/Source: u ☐ Upgradient s ☐ Sidegradient d ☒ Downgradient n ☐ Not Known

Gov. Lot Number:

Well Name: 70D

Date Well Installed: 03/04/2021

Well Installed By: (Person's Name and Firm) Jason Greer, Cascade Drilling



A. Protective pipe, top elevation 595.10 ft. MSL

B. Well casing, top elevation 594.52 ft. MSL

C. Land surface elevation 591.9 ft. MSL

D. Surface seal, bottom 590.9 ft. MSL or 1.0 ft.

12. USCS classification of soil near screen:
GP ☐ GM ☐ GC ☐ GW ☐ SW ☐ SP ☐
SM ☐ SC ☐ ML ☐ MH ☐ CL ☐ CH ☐
Bedrock ☒

13. Sieve analysis attached? ☐ Yes ☒ No

14. Drilling method used: Rotary ☐ Hollow Stem Auger ☐ Sonic Other ☒

15. Drilling fluid used: Water ☒ 0 2 Air ☐ Drilling Mud ☐ 0 3 None ☐

16. Drilling additives used? ☐ Yes ☒ No

Describe

17. Source of water (attach analysis, if required): Potable City Water

E. Bentonite seal, top 557.9 ft. MSL or 34.0 ft.

F. Fine sand, top ft. MSL or ft.

G. Filter pack, top 552.9 ft. MSL or 39.0 ft.

H. Screen joint, top 550.9 ft. MSL or 41.0 ft.

I. Well bottom 540.9 ft. MSL or 51.0 ft.

J. Filter pack, bottom 540.9 ft. MSL or 51.0 ft.

K. Borehole, bottom 539.9 ft. MSL or 52.0 ft.

L. Borehole, diameter 6.0 in.

M. O.D. well casing 2.38 in.

N. I.D. well casing 2.07 in.

1. Cap and lock? ☒ Yes ☐ No

2. Protective cover pipe:
   a. Inside diameter: 4.0 in.
   b. Length: 5.0 ft.
   c. Material: Steel ☒ Other ☐
   d. Additional protection? ☒ Yes ☐ No
   If yes, describe: 4 Steel Bollards

3. Surface seal: Bentonite ☐ Concrete ☒ Other ☐

4. Material between well casing and protective pipe: Bentonite ☐ Sand Other ☒

5. Annular space seal: a. Granular/Chipped Bentonite ☐
   b. Lbs/gal mud weight . . . Bentonite-sand slurry ☐
   c. 9.2 Lbs/gal mud weight . . . Bentonite slurry ☒
   d. % Bentonite . . . Bentonite-cement grout ☐
   e. Ft^3 volume added for any of the above
   f. How installed: Tremie ☐ Tremie pumped ☒ Gravity ☐

6. Bentonite seal: a. Bentonite granules ☐
   b. ☐ 1/4 in. ☒ 3/8 in. ☐ 1/2 in. Bentonite chips ☒
   c. Other ☐

7. Fine sand material: Manufacturer, product name & mesh size
   a. NA
   b. Volume added 0 ft^3

8. Filter pack material: Manufacturer, product name & mesh size
   a. FILTERSIL 0.85
   b. Volume added ft^3

9. Well casing: Flush threaded PVC schedule 40 ☒ Flush threaded PVC schedule 80 ☐ Other ☐

10. Screen material: Schedule 40 PVC
   a. Screen Type: Factory cut ☒ Continuous slot ☐ Other ☐
   b. Manufacturer Johnson Screens
   c. Slot size: 0.010 in.
   d. Slotted length: 10.0 ft

11. Backfill material (below filter pack): None ☐ Formation Materials Other ☒

I hereby certify that the information on this form is true and correct to the best of my knowledge

Date Modified 3/31/2021

Signature

Firm: Ramboll
234 W. Florida Street, Milwaukee, WI 53204
Tel: (414) 837-3607
Fax: (414) 837-3608

ATTACHMENT 3

Sequential Extraction Procedure Laboratory Analytical Reports

eurofins | Environment Testing

ANALYTICAL REPORT

PREPARED FOR

JOB DESCRIPTION

Vermilion SEP

JOB NUMBER

ANALYTICAL REPORT

PREPARED FOR

Attn: Allison Kreinberg
Geosyntec Consultants Inc
941 Chatham Lane
Suite 103
Columbus, Ohio 43221
Generated 8/3/2023 11:56:48 AM

JOB DESCRIPTION

Vermilion SEP

JOB NUMBER

140-32513-1

Eurofins Knoxville
5815 Middlebrook Pike
Knoxville TN 37921

See page two for job notes and contact information.

my EOL

Eurofins Knoxville

Job Notes

This report may not be reproduced except in full, and with written approval from the laboratory. The results relate only to the samples tested. For questions please contact the Project Manager at the e-mail address or telephone number listed on this page.

The test results in this report relate only to the samples as received by the laboratory and will meet all requirements of the methodology, with any exceptions noted. This report shall not be reproduced except in full, without the express written approval of the laboratory. All questions should be directed to the Eurofins TestAmerica Project Manager.

Authorization

Ryan Henry

Authorized for release by
Ryan Henry, Project Manager I
WilliamR.Henry@et.eurofinsus.com
(865)291-3006

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8/3/2023 11:56:48 AM

Table of Contents

Definitions/Glossary

Client: Geosyntec Consultants Inc
Project/Site: Vermilion SEP

Job ID: 140-32513-1

Qualifiers

Metals

Qualifier	Qualifier Description
B	Compound was found in the blank and sample.
J	Result is less than the RL but greater than or equal to the MDL and the concentration is an approximate value.

Glossary

Abbreviation	These commonly used abbreviations may or may not be present in this report.
¤	Listed under the "D" column to designate that the result is reported on a dry weight basis
%R	Percent Recovery
CFL	Contains Free Liquid
CFU	Colony Forming Unit
CNF	Contains No Free Liquid
DER	Duplicate Error Ratio (normalized absolute difference)
Dil Fac	Dilution Factor
DL	Detection Limit (DoD/DOE)
DL, RA, RE, IN	Indicates a Dilution, Re-analysis, Re-extraction, or additional Initial metals/anion analysis of the sample
DLC	Decision Level Concentration (Radiochemistry)
EDL	Estimated Detection Limit (Dioxin)
LOD	Limit of Detection (DoD/DOE)
LOQ	Limit of Quantitation (DoD/DOE)
MCL	EPA recommended "Maximum Contaminant Level"
MDA	Minimum Detectable Activity (Radiochemistry)
MDC	Minimum Detectable Concentration (Radiochemistry)
MDL	Method Detection Limit
ML	Minimum Level (Dioxin)
MPN	Most Probable Number
MQL	Method Quantitation Limit
NC	Not Calculated
ND	Not Detected at the reporting limit (or MDL or EDL if shown)
NEG	Negative / Absent
POS	Positive / Present
PQL	Practical Quantitation Limit
PRES	Presumptive
QC	Quality Control
RER	Relative Error Ratio (Radiochemistry)
RL	Reporting Limit or Requested Limit (Radiochemistry)
RPD	Relative Percent Difference, a measure of the relative difference between two points
TEF	Toxicity Equivalent Factor (Dioxin)
TEQ	Toxicity Equivalent Quotient (Dioxin)
TNTC	Too Numerous To Count

Job ID: 140-32513-1

Laboratory: Eurofins Knoxville

Narrative

Job Narrative
140-32513-1

Receipt
The samples were received on 7/3/2023 at 11:15am and arrived in good condition, and where required, properly preserved and on ice. The temperature of the cooler at receipt was 20.3° C.

Receipt Exceptions
The Field Sampler was not listed on the Chain of Custody.

Metals
7 Step Sequential Extraction Procedure

These soil samples were prepared and analyzed using Eurofins TestAmerica Knoxville standard operating procedure KNOX-MT-0008, "7 Step Sequential Extraction Procedure". SW-846 Method 6010B as incorporated in Eurofins TestAmerica Knoxville standard operating procedure KNOX-MT-0007 was used to perform the final instrument analyses.

An aliquot of each sample was sequentially extracted using the steps listed below:

- Step 1 - Exchangeable Fraction: A 5 gram aliquot of sample was extracted with 25 mL of 1M magnesium sulfate (MgSO4), centrifuged and filtered. 5 mL of the resulting leachate was digested using method 3010A and analyzed by method 6010B. Results are reported in mg/kg on a dry weight basis.
- Step 2 - Carbonate Fraction: The sample residue from step 1 was extracted with 25 mL of 1M sodium acetate/acetic acid (NaOAc/HOAc) at pH 5, centrifuged and filtered. 5 mL of the resulting leachate was digested using method 3010A and analyzed by method 6010B. Results are reported in mg/kg on a dry weight basis.
- Step 3 - Non-crystalline Materials Fraction: The sample residue from step 2 was extracted with 25 mL of 0.2M ammonium oxalate (pH 3), centrifuged and filtered. 5 mL of the resulting leachate was digested using method 3010A and analyzed by method 6010B. Results are reported in mg/kg on a dry weight basis.
- Step 4 - Metal Hydroxide Fraction: The sample residue from step 3 was extracted with 25 mL of 1M hydroxylamine hydrochloride solution in 25% v/v acetic acid, centrifuged and filtered. 5 mL of the resulting leachate was digested using method 3010A and analyzed by method 6010B. Results are reported in mg/kg on a dry weight basis.
- Step 5 - Organic-bound Fraction: The sample residue from step 4 was extracted three times with 25 mL of 5% sodium hypochlorite (NaClO) at pH 9.5, centrifuged and filtered. The resulting leachates were combined and 5 mL were digested using method 3010A and analyzed by method 6010B. Results are reported in mg/kg on a dry weight basis.
- Step 6 - Acid/Sulfide Fraction: The sample residue from step 5 was extracted with 25 mL of a 3:1:2 v/v solution of HCl-HNO3-H2O, centrifuged and filtered. 5 mL of the resulting leachate was diluted to 50 mL with reagent water and analyzed by method 6010B. Results are reported in mg/kg on a dry weight basis.
- Step 7 - Residual Fraction: A 1.0 g aliquot of the sample residue from step 6 was digested using HF, HNO3, HCl and H3BO3. The digestate was analyzed by ICP using method 6010B. Results are reported in mg/kg on a dry weight basis.

In addition, a 1.0 g aliquot of the original sample was digested using HF, HNO3, HCl and H3BO3. The digestate was analyzed by ICP using method 6010B. Total metal results are reported in mg/kg on a dry weight basis.

Results were calculated using the following equation:

$$\text{Result, µg/g or mg/Kg, dry weight} = (C \times V \times V1 \times D) / (W \times S \times V2)$$

Where:
C = Concentration from instrument readout, µg/mL
V = Final volume of digestate, mL
D = Instrument dilution factor
V1 = Total volume of leachate, mL
V2 = Volume of leachate digested, mL
W = Wet weight of sample, g

Case Narrative

Job ID: 140-32513-1 (Continued)

Laboratory: Eurofins Knoxville (Continued)

S = Percent solids/100

A method blank, laboratory control sample and laboratory control sample duplicate were prepared and analyzed with each SEP step in order to provide information about both the presence of elements of interest in the extraction solutions, and the recovery of elements of interest from the extraction solutions. Results outside of laboratory QC limits do not reflect out of control performance, but rather the effect of the extraction solution upon the analyte.

A laboratory sample duplicate was prepared and analyzed with each batch of samples in order to provide information regarding the reproducibility of the procedure.

SEP Report Notes:

The final report lists the results for each step, the result for the total digestion of the sample, and a sum of the results of steps 1 through 7 by element.

Magnesium was not reported for step 1 because the extraction solution for this step (magnesium sulfate) contains high levels of magnesium.

Sodium was not reported for steps 2 and 5 since the extraction solution for these steps contain high levels of sodium.

The sum of steps 1 through 7 is much higher than the total result for sodium and magnesium due to the magnesium and sodium introduced by the extraction solutions.

The digestates for steps 1, 2 and 5 were analyzed at a dilution due to instrument problems caused by the high solids content of the digestates. The reporting limits were adjusted accordingly.

The serial diilution is analyzed at an additional 5 fold dilution using the dilution factors applied to the duplicate and the associated original sample. Due to a limitation of the expanded deliverable forms, the dilutions of the duplicate and serial dilution in the expanded deliverable are not expressed on a per analyte basis.

Please refer to the summary section of the report for the duplicate information as it contains the dilution factors at which the sample was analyzed.

Method 6010B: The serial dilution performed for the following samples associated with batch 140-75976 were outside control limits: VER-35 55-60 20230624 (140-32513-1), (140-32513-A-1-C SD ^10) and (140-32513-A-1-C SD ^5)

Method 6010B: The following samples were diluted to bring the concentration of target analyte, Iron, within the calibration range: VER-35 55-60 20230624 (140-32513-1), VER-35 60-63 20230624 (140-32513-2) and VER-70 75-80 20230623 (140-32513-3). Elevated reporting limits (RLs) are provided.

Method 6010B SEP: The serial dilution performed for the following samples associated with batch 140-75894 was outside control limits: VER-35 55-60 20230624 (140-32513-1), (140-32513-A-1-S SD ^5) and (140-32513-A-1-W SD ^5)

No additional analytical or quality issues were noted, other than those described above or in the Definitions/Glossary page.

General Chemistry

% Moisture: The samples were analyzed for percent moisture using SOP number KNOX-WC-0012 (based on Modified MCAWW 160.3 and SM2540B and on the percent moisture determinations described in methods 3540C and 3550B).

No additional analytical or quality issues were noted, other than those described above or in the Definitions/Glossary page.

Sample Summary

Client: Geosyntec Consultants Inc
Project/Site: Vermilion SEP

Job ID: 140-32513-1

Lab Sample ID	Client Sample ID	Matrix	Collected	Received
140-32513-1	VER-35 55-60 20230624	Solid	06/24/23 14:20	07/03/23 11:15
140-32513-2	VER-35 60-63 20230624	Solid	06/24/23 14:50	07/03/23 11:15
140-32513-3	VER-70 75-80 20230623	Solid	06/23/23 17:00	07/03/23 11:15

Client Sample Results

Client: Geosyntec Consultants Inc
Project/Site: Vermilion SEP

Job ID: 140-32513-1

Client Sample ID: VER-35 55-60 20230624

Date Collected: 06/24/23 14:20
Date Received: 07/03/23 11:15

Lab Sample ID: 140-32513-1

Matrix: Solid
Percent Solids: 95.4

Method: SW846 6010B SEP - SEP Metals (ICP) - Step 1

Analyte	Result	Qualifier	RL	MDL	Unit	D	Prepared	Analyzed	Dil Fac
Iron	ND		21	12	mg/Kg	☼	07/11/23 08:00	07/27/23 13:01	4
Lithium	ND		10	0.63	mg/Kg	☼	07/11/23 08:00	07/27/23 13:01	4
Manganese	7.6		3.1	0.13	mg/Kg	☼	07/11/23 08:00	07/27/23 13:01	4

Method: SW846 6010B SEP - SEP Metals (ICP) - Step 2

Analyte	Result	Qualifier	RL	MDL	Unit	D	Prepared	Analyzed	Dil Fac
Iron	560		16	9.1	mg/Kg	☼	07/12/23 08:00	07/27/23 13:51	3
Lithium	0.56	J	7.9	0.47	mg/Kg	☼	07/12/23 08:00	07/27/23 13:51	3
Manganese	29		2.4	0.88	mg/Kg	☼	07/12/23 08:00	07/27/23 13:51	3

Method: SW846 6010B SEP - SEP Metals (ICP) - Step 3

Analyte	Result	Qualifier	RL	MDL	Unit	D	Prepared	Analyzed	Dil Fac
Iron	4300		5.2	3.0	mg/Kg	☼	07/13/23 08:00	07/27/23 14:40	1
Lithium	0.52	J	2.6	0.16	mg/Kg	☼	07/13/23 08:00	07/27/23 14:40	1
Manganese	110	B	0.79	0.028	mg/Kg	☼	07/13/23 08:00	07/27/23 14:40	1

Method: SW846 6010B SEP - SEP Metals (ICP) - Step 4

Analyte	Result	Qualifier	RL	MDL	Unit	D	Prepared	Analyzed	Dil Fac
Iron	20000		5.2	3.0	mg/Kg	☼	07/17/23 08:00	07/28/23 12:49	1
Lithium	13		2.6	0.16	mg/Kg	☼	07/17/23 08:00	07/28/23 12:49	1
Manganese	430		0.79	0.14	mg/Kg	☼	07/17/23 08:00	07/28/23 12:49	1

Method: SW846 6010B SEP - SEP Metals (ICP) - Step 5

Analyte	Result	Qualifier	RL	MDL	Unit	D	Prepared	Analyzed	Dil Fac
Iron	ND		79	46	mg/Kg	☼	07/19/23 08:00	07/28/23 13:39	5
Lithium	4.1	J	39	2.3	mg/Kg	☼	07/19/23 08:00	07/28/23 13:39	5
Manganese	46		12	1.9	mg/Kg	☼	07/19/23 08:00	07/28/23 13:39	5

Method: SW846 6010B SEP - SEP Metals (ICP) - Step 6

Analyte	Result	Qualifier	RL	MDL	Unit	D	Prepared	Analyzed	Dil Fac
Iron	11000		5.2	3.0	mg/Kg	☼	07/19/23 08:00	07/28/23 14:29	1
Lithium	13		2.6	0.16	mg/Kg	☼	07/19/23 08:00	07/28/23 14:29	1
Manganese	130		0.79	0.26	mg/Kg	☼	07/19/23 08:00	07/28/23 14:29	1

Method: SW846 6010B SEP - SEP Metals (ICP) - Step 7

Analyte	Result	Qualifier	RL	MDL	Unit	D	Prepared	Analyzed	Dil Fac
Iron	4300		5.2	4.3	mg/Kg	☼	07/20/23 08:00	07/31/23 12:46	1
Lithium	15		2.6	0.16	mg/Kg	☼	07/20/23 08:00	07/31/23 12:46	1
Manganese	31		0.79	0.32	mg/Kg	☼	07/20/23 08:00	07/31/23 12:46	1

Method: SW846 6010B SEP - SEP Metals (ICP) - Sum of Steps 1-7

Analyte	Result	Qualifier	RL	MDL	Unit	D	Prepared	Analyzed	Dil Fac
Iron	41000		5.0	4.1	mg/Kg			08/02/23 14:24	1
Lithium	46		2.5	0.15	mg/Kg			08/02/23 14:24	1
Manganese	780		0.75	0.052	mg/Kg			08/02/23 14:24	1

Method: SW846 6010B - SEP Metals (ICP) - Total

Analyte	Result	Qualifier	RL	MDL	Unit	D	Prepared	Analyzed	Dil Fac
Iron	38000		10	8.6	mg/Kg	☼	07/21/23 08:00	07/31/23 14:12	2
Lithium	42		2.6	0.16	mg/Kg	☼	07/21/23 08:00	07/31/23 13:22	1
Manganese	610		0.79	0.32	mg/Kg	☼	07/21/23 08:00	07/31/23 13:22	1

Client Sample Results

Client: Geosyntec Consultants Inc
Project/Site: Vermilion SEP

Job ID: 140-32513-1

Client Sample ID: VER-35 60-63 20230624
Date Collected: 06/24/23 14:50
Date Received: 07/03/23 11:15

Lab Sample ID: 140-32513-2
Matrix: Solid
Percent Solids: 95.4

Method: SW846 6010B SEP - SEP Metals (ICP) - Step 1

Analyte	Result	Qualifier	RL	MDL	Unit	D	Prepared	Analyzed	Dil Fac
Iron	ND		21	12	mg/Kg	☼	07/11/23 08:00	07/27/23 13:11	4
Lithium	ND		10	0.63	mg/Kg	☼	07/11/23 08:00	07/27/23 13:11	4
Manganese	7.9		3.1	0.13	mg/Kg	☼	07/11/23 08:00	07/27/23 13:11	4

Method: SW846 6010B SEP - SEP Metals (ICP) - Step 2

Analyte	Result	Qualifier	RL	MDL	Unit	D	Prepared	Analyzed	Dil Fac
Iron	570		16	9.1	mg/Kg	☼	07/12/23 08:00	07/27/23 14:01	3
Lithium	0.62	J	7.9	0.47	mg/Kg	☼	07/12/23 08:00	07/27/23 14:01	3
Manganese	29		2.4	0.88	mg/Kg	☼	07/12/23 08:00	07/27/23 14:01	3

Method: SW846 6010B SEP - SEP Metals (ICP) - Step 3

Analyte	Result	Qualifier	RL	MDL	Unit	D	Prepared	Analyzed	Dil Fac
Iron	4200		5.2	3.0	mg/Kg	☼	07/13/23 08:00	07/27/23 14:50	1
Lithium	0.74	J	2.6	0.16	mg/Kg	☼	07/13/23 08:00	07/27/23 14:50	1
Manganese	110	B	0.79	0.028	mg/Kg	☼	07/13/23 08:00	07/27/23 14:50	1

Method: SW846 6010B SEP - SEP Metals (ICP) - Step 4

Analyte	Result	Qualifier	RL	MDL	Unit	D	Prepared	Analyzed	Dil Fac
Iron	18000		5.2	3.0	mg/Kg	☼	07/17/23 08:00	07/28/23 12:59	1
Lithium	12		2.6	0.16	mg/Kg	☼	07/17/23 08:00	07/28/23 12:59	1
Manganese	380		0.79	0.14	mg/Kg	☼	07/17/23 08:00	07/28/23 12:59	1

Method: SW846 6010B SEP - SEP Metals (ICP) - Step 5

Analyte	Result	Qualifier	RL	MDL	Unit	D	Prepared	Analyzed	Dil Fac
Iron	ND		79	46	mg/Kg	☼	07/19/23 08:00	07/28/23 13:49	5
Lithium	3.9	J	39	2.3	mg/Kg	☼	07/19/23 08:00	07/28/23 13:49	5
Manganese	35		12	1.9	mg/Kg	☼	07/19/23 08:00	07/28/23 13:49	5

Method: SW846 6010B SEP - SEP Metals (ICP) - Step 6

Analyte	Result	Qualifier	RL	MDL	Unit	D	Prepared	Analyzed	Dil Fac
Iron	11000		5.2	3.0	mg/Kg	☼	07/19/23 08:00	07/28/23 14:39	1
Lithium	14		2.6	0.16	mg/Kg	☼	07/19/23 08:00	07/28/23 14:39	1
Manganese	140		0.79	0.26	mg/Kg	☼	07/19/23 08:00	07/28/23 14:39	1

Method: SW846 6010B SEP - SEP Metals (ICP) - Step 7

Analyte	Result	Qualifier	RL	MDL	Unit	D	Prepared	Analyzed	Dil Fac
Iron	4200		5.2	4.3	mg/Kg	☼	07/20/23 08:00	07/31/23 12:57	1
Lithium	14		2.6	0.16	mg/Kg	☼	07/20/23 08:00	07/31/23 12:57	1
Manganese	30		0.79	0.33	mg/Kg	☼	07/20/23 08:00	07/31/23 12:57	1

Method: SW846 6010B SEP - SEP Metals (ICP) - Sum of Steps 1-7

Analyte	Result	Qualifier	RL	MDL	Unit	D	Prepared	Analyzed	Dil Fac
Iron	38000		5.0	4.1	mg/Kg			08/02/23 14:24	1
Lithium	45		2.5	0.15	mg/Kg			08/02/23 14:24	1
Manganese	730		0.75	0.052	mg/Kg			08/02/23 14:24	1

Method: SW846 6010B - SEP Metals (ICP) - Total

Analyte	Result	Qualifier	RL	MDL	Unit	D	Prepared	Analyzed	Dil Fac
Iron	37000		10	8.6	mg/Kg	☼	07/21/23 08:00	07/31/23 14:22	2
Lithium	39		2.6	0.16	mg/Kg	☼	07/21/23 08:00	07/31/23 13:33	1
Manganese	520		0.79	0.33	mg/Kg	☼	07/21/23 08:00	07/31/23 13:33	1

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Client Sample Results

Client: Geosyntec Consultants Inc
Project/Site: Vermilion SEP

Job ID: 140-32513-1

Client Sample ID: VER-70 75-80 20230623
Date Collected: 06/23/23 17:00
Date Received: 07/03/23 11:15

Lab Sample ID: 140-32513-3
Matrix: Solid
Percent Solids: 90.0

Method: SW846 6010B SEP - SEP Metals (ICP) - Step 1

Analyte	Result	Qualifier	RL	MDL	Unit	D	Prepared	Analyzed	Dil Fac
Iron	ND		22	13	mg/Kg	☼	07/11/23 08:00	07/27/23 13:16	4
Lithium	ND		11	0.67	mg/Kg	☼	07/11/23 08:00	07/27/23 13:16	4
Manganese	7.6		3.3	0.14	mg/Kg	☼	07/11/23 08:00	07/27/23 13:16	4

Method: SW846 6010B SEP - SEP Metals (ICP) - Step 2

Analyte	Result	Qualifier	RL	MDL	Unit	D	Prepared	Analyzed	Dil Fac
Iron	730		17	9.7	mg/Kg	☼	07/12/23 08:00	07/27/23 14:06	3
Lithium	ND		8.3	0.50	mg/Kg	☼	07/12/23 08:00	07/27/23 14:06	3
Manganese	36		2.5	0.93	mg/Kg	☼	07/12/23 08:00	07/27/23 14:06	3

Method: SW846 6010B SEP - SEP Metals (ICP) - Step 3

Analyte	Result	Qualifier	RL	MDL	Unit	D	Prepared	Analyzed	Dil Fac
Iron	5500		5.6	3.2	mg/Kg	☼	07/13/23 08:00	07/27/23 14:55	1
Lithium	0.41	J	2.8	0.17	mg/Kg	☼	07/13/23 08:00	07/27/23 14:55	1
Manganese	130	B	0.83	0.030	mg/Kg	☼	07/13/23 08:00	07/27/23 14:55	1

Method: SW846 6010B SEP - SEP Metals (ICP) - Step 4

Analyte	Result	Qualifier	RL	MDL	Unit	D	Prepared	Analyzed	Dil Fac
Iron	31000		11	6.4	mg/Kg	☼	07/17/23 08:00	07/28/23 14:55	2
Lithium	12		2.8	0.17	mg/Kg	☼	07/17/23 08:00	07/28/23 13:04	1
Manganese	510		0.83	0.14	mg/Kg	☼	07/17/23 08:00	07/28/23 13:04	1

Method: SW846 6010B SEP - SEP Metals (ICP) - Step 5

Analyte	Result	Qualifier	RL	MDL	Unit	D	Prepared	Analyzed	Dil Fac
Iron	61	J	83	49	mg/Kg	☼	07/19/23 08:00	07/28/23 13:54	5
Lithium	4.4	J	42	2.4	mg/Kg	☼	07/19/23 08:00	07/28/23 13:54	5
Manganese	54		12	2.1	mg/Kg	☼	07/19/23 08:00	07/28/23 13:54	5

Method: SW846 6010B SEP - SEP Metals (ICP) - Step 6

Analyte	Result	Qualifier	RL	MDL	Unit	D	Prepared	Analyzed	Dil Fac
Iron	14000		5.6	3.2	mg/Kg	☼	07/19/23 08:00	07/28/23 14:44	1
Lithium	15		2.8	0.17	mg/Kg	☼	07/19/23 08:00	07/28/23 14:44	1
Manganese	160		0.83	0.28	mg/Kg	☼	07/19/23 08:00	07/28/23 14:44	1

Method: SW846 6010B SEP - SEP Metals (ICP) - Step 7

Analyte	Result	Qualifier	RL	MDL	Unit	D	Prepared	Analyzed	Dil Fac
Iron	5500		5.6	4.6	mg/Kg	☼	07/20/23 08:00	07/31/23 13:17	1
Lithium	19		2.8	0.17	mg/Kg	☼	07/20/23 08:00	07/31/23 13:17	1
Manganese	39		0.83	0.34	mg/Kg	☼	07/20/23 08:00	07/31/23 13:17	1

Method: SW846 6010B SEP - SEP Metals (ICP) - Sum of Steps 1-7

Analyte	Result	Qualifier	RL	MDL	Unit	D	Prepared	Analyzed	Dil Fac
Iron	57000		5.0	4.1	mg/Kg			08/02/23 14:24	1
Lithium	51		2.5	0.15	mg/Kg			08/02/23 14:24	1
Manganese	940		0.75	0.052	mg/Kg			08/02/23 14:24	1

Method: SW846 6010B - SEP Metals (ICP) - Total

Analyte	Result	Qualifier	RL	MDL	Unit	D	Prepared	Analyzed	Dil Fac
Iron	66000		28	23	mg/Kg	☼	07/21/23 08:00	07/31/23 15:08	5
Lithium	42		2.8	0.17	mg/Kg	☼	07/21/23 08:00	07/31/23 13:39	1
Manganese	720		0.83	0.34	mg/Kg	☼	07/21/23 08:00	07/31/23 13:39	1

Default Detection Limits

Method: 6010B SEP - SEP Metals (ICP) - Step 1

Prep: 3010A

SEP: Exchangeable

Analyte	RL	MDL	Units
Iron	5.0	2.9	mg/Kg
Lithium	2.5	0.15	mg/Kg
Manganese	0.75	0.031	mg/Kg

Method: 6010B SEP - SEP Metals (ICP) - Step 2

Prep: 3010A

SEP: Carbonate

Analyte	RL	MDL	Units
Iron	5.0	2.9	mg/Kg
Lithium	2.5	0.15	mg/Kg
Manganese	0.75	0.28	mg/Kg

Method: 6010B SEP - SEP Metals (ICP) - Step 3

Prep: 3010A

SEP: Non-Crystalline

Analyte	RL	MDL	Units
Iron	5.0	2.9	mg/Kg
Lithium	2.5	0.15	mg/Kg
Manganese	0.75	0.027	mg/Kg

Method: 6010B SEP - SEP Metals (ICP) - Step 4

Prep: 3010A

SEP: Metal Hydroxide

Analyte	RL	MDL	Units
Iron	5.0	2.9	mg/Kg
Lithium	2.5	0.15	mg/Kg
Manganese	0.75	0.13	mg/Kg

Method: 6010B SEP - SEP Metals (ICP) - Step 5

Prep: 3010A

SEP: Organic-Bound

Analyte	RL	MDL	Units
Iron	15	8.8	mg/Kg
Lithium	7.5	0.44	mg/Kg
Manganese	2.3	0.37	mg/Kg

Method: 6010B SEP - SEP Metals (ICP) - Step 6

SEP: Acid/Sulfide

Analyte	RL	MDL	Units
Iron	5.0	2.9	mg/Kg
Lithium	2.5	0.15	mg/Kg
Manganese	0.75	0.25	mg/Kg

Method: 6010B SEP - SEP Metals (ICP) - Step 7

Prep: Residual

Analyte	RL	MDL	Units
Iron	5.0	4.1	mg/Kg
Lithium	2.5	0.15	mg/Kg
Manganese	0.75	0.31	mg/Kg

Default Detection Limits

Client: Geosyntec Consultants Inc
Project/Site: Vermilion SEP

Job ID: 140-32513-1

Method: 6010B SEP - SEP Metals (ICP) - Sum of Steps 1-7

Analyte	RL	MDL	Units
Iron	5.0	4.1	mg/Kg
Lithium	2.5	0.15	mg/Kg
Manganese	0.75	0.052	mg/Kg

Method: 6010B - SEP Metals (ICP) - Total

Prep: Total

Analyte	RL	MDL	Units
Iron	5.0	4.1	mg/Kg
Lithium	2.5	0.15	mg/Kg
Manganese	0.75	0.31	mg/Kg

QC Sample Results

Client: Geosyntec Consultants Inc
Project/Site: Vermilion SEP

Job ID: 140-32513-1

Method: 6010B - SEP Metals (ICP) - Total

Lab Sample ID: MB 140-75187/5-A
Matrix: Solid
Analysis Batch: 75976

Client Sample ID: Method Blank
Prep Type: Total/NA
Prep Batch: 75187

Analyte	MB Result	MB Qualifier	RL	MDL	Unit	D	Prepared	Analyzed	Dil Fac
Iron	ND		5.0	4.1	mg/Kg		07/21/23 08:00	07/31/23 12:31	1
Lithium	ND		2.5	0.15	mg/Kg		07/21/23 08:00	07/31/23 12:31	1
Manganese	ND		0.75	0.31	mg/Kg		07/21/23 08:00	07/31/23 12:31	1

Lab Sample ID: LCS 140-75187/6-A
Matrix: Solid
Analysis Batch: 75976

Client Sample ID: Lab Control Sample
Prep Type: Total/NA
Prep Batch: 75187

Analyte	Spike Added	LCS Result	LCS Qualifier	Unit	D	%Rec	%Rec Limits
Iron	50.0	53.2		mg/Kg		106	80 - 120
Lithium	5.00	5.23		mg/Kg		105	80 - 120
Manganese	5.00	5.21		mg/Kg		104	80 - 120

Lab Sample ID: LCSD 140-75187/7-A
Matrix: Solid
Analysis Batch: 75976

Client Sample ID: Lab Control Sample Dup
Prep Type: Total/NA
Prep Batch: 75187

Analyte	Spike Added	LCSD Result	LCSD Qualifier	Unit	D	%Rec	%Rec Limits	RPD	RPD Limit
Iron	50.0	54.5		mg/Kg		109	80 - 120	2	30
Lithium	5.00	5.14		mg/Kg		103	80 - 120	2	30
Manganese	5.00	5.27		mg/Kg		105	80 - 120	1	30

Lab Sample ID: 140-32513-1 DU
Matrix: Solid
Analysis Batch: 75976

Client Sample ID: VER-35 55-60 20230624
Prep Type: Total/NA
Prep Batch: 75187

Analyte	Sample Result	Sample Qualifier	DU Result	DU Qualifier	Unit	D	RPD	RPD Limit
Lithium	42		42.1		mg/Kg	☼	0	30
Manganese	610		613		mg/Kg	☼	0.8	30

Lab Sample ID: 140-32513-1 DU
Matrix: Solid
Analysis Batch: 75976

Client Sample ID: VER-35 55-60 20230624
Prep Type: Total/NA
Prep Batch: 75187

Analyte	Sample Result	Sample Qualifier	DU Result	DU Qualifier	Unit	D	RPD	RPD Limit
Iron	38000		39200		mg/Kg	☼	2	30

Method: 6010B SEP - SEP Metals (ICP)

Lab Sample ID: MB 140-75184/5-B ^4
Matrix: Solid
Analysis Batch: 75871

Client Sample ID: Method Blank
Prep Type: Step 1
Prep Batch: 75207

Analyte	MB Result	MB Qualifier	RL	MDL	Unit	D	Prepared	Analyzed	Dil Fac
Iron	ND		20	12	mg/Kg		07/11/23 08:00	07/27/23 12:47	4
Lithium	ND		10	0.60	mg/Kg		07/11/23 08:00	07/27/23 12:47	4
Manganese	ND		3.0	0.12	mg/Kg		07/11/23 08:00	07/27/23 12:47	4

QC Sample Results

Client: Geosyntec Consultants Inc
Project/Site: Vermilion SEP

Job ID: 140-32513-1

Method: 6010B SEP - SEP Metals (ICP) (Continued)

Lab Sample ID: LCS 140-75184/6-B ^5
Matrix: Solid
Analysis Batch: 75871

Client Sample ID: Lab Control Sample
Prep Type: Step 1
Prep Batch: 75207

Analyte	Spike Added	LCS Result	LCS Qualifier	Unit	D	%Rec	%Rec Limits
Iron	50.0	54.4		mg/Kg		109	80 - 120
Lithium	5.00	5.66	J	mg/Kg		113	80 - 120
Manganese	5.00	5.54		mg/Kg		111	80 - 120

Lab Sample ID: LCSD 140-75184/7-B ^5
Matrix: Solid
Analysis Batch: 75871

Client Sample ID: Lab Control Sample Dup
Prep Type: Step 1
Prep Batch: 75207

Analyte	Spike Added	LCSD Result	LCSD Qualifier	Unit	D	%Rec	%Rec Limits	RPD	RPD Limit
Iron	50.0	54.2		mg/Kg		108	80 - 120	0	30
Lithium	5.00	5.44	J	mg/Kg		109	80 - 120	4	30
Manganese	5.00	5.51		mg/Kg		110	80 - 120	1	30

Lab Sample ID: 140-32513-1 DU
Matrix: Solid
Analysis Batch: 75871

Client Sample ID: VER-35 55-60 20230624
Prep Type: Step 1
Prep Batch: 75207

Analyte	Sample Result	Sample Qualifier	DU Result	DU Qualifier	Unit	D	RPD	RPD Limit
Iron	ND		ND		mg/Kg	☼	NC	30
Lithium	ND		ND		mg/Kg	☼	NC	30
Manganese	7.6		7.29		mg/Kg	☼	4	30

Lab Sample ID: MB 140-75227/5-B ^3
Matrix: Solid
Analysis Batch: 75871

Client Sample ID: Method Blank
Prep Type: Step 2
Prep Batch: 75260

Analyte	MB Result	MB Qualifier	RL	MDL	Unit	D	Prepared	Analyzed	Dil Fac
Iron	ND		15	8.7	mg/Kg		07/12/23 08:00	07/27/23 13:36	3
Lithium	ND		7.5	0.45	mg/Kg		07/12/23 08:00	07/27/23 13:36	3
Manganese	ND		2.3	0.84	mg/Kg		07/12/23 08:00	07/27/23 13:36	3

Lab Sample ID: LCS 140-75227/6-B ^5
Matrix: Solid
Analysis Batch: 75871

Client Sample ID: Lab Control Sample
Prep Type: Step 2
Prep Batch: 75260

Analyte	Spike Added	LCS Result	LCS Qualifier	Unit	D	%Rec	%Rec Limits
Iron	50.0	ND		mg/Kg		3	
Lithium	5.00	5.13	J	mg/Kg		103	80 - 120
Manganese	5.00	5.01		mg/Kg		100	80 - 120

Lab Sample ID: LCSD 140-75227/7-B ^5
Matrix: Solid
Analysis Batch: 75871

Client Sample ID: Lab Control Sample Dup
Prep Type: Step 2
Prep Batch: 75260

Analyte	Spike Added	LCSD Result	LCSD Qualifier	Unit	D	%Rec	%Rec Limits	RPD	RPD Limit
Iron	50.0	ND		mg/Kg		3		28	
Lithium	5.00	4.95	J	mg/Kg		99	80 - 120	4	30
Manganese	5.00	4.96		mg/Kg		99	80 - 120	1	30

QC Sample Results

Client: Geosyntec Consultants Inc
Project/Site: Vermilion SEP

Job ID: 140-32513-1

Method: 6010B SEP - SEP Metals (ICP) (Continued)

Lab Sample ID: 140-32513-1 DU
Matrix: Solid
Analysis Batch: 75871

Client Sample ID: VER-35 55-60 20230624
Prep Type: Step 2
Prep Batch: 75260

Analyte	Sample Result	Sample Qualifier	DU Result	DU Qualifier	Unit	D	RPD	RPD Limit
Iron	560		531		mg/Kg	☼	5	
Lithium	0.56	J	ND		mg/Kg	☼	NC	30
Manganese	29		27.9		mg/Kg	☼	4	30

Lab Sample ID: MB 140-75274/5-B
Matrix: Solid
Analysis Batch: 75871

Client Sample ID: Method Blank
Prep Type: Step 3
Prep Batch: 75294

Analyte	MB Result	MB Qualifier	RL	MDL	Unit	D	Prepared	Analyzed	Dil Fac
Iron	ND		5.0	2.9	mg/Kg		07/13/23 08:00	07/27/23 14:26	1
Lithium	ND		2.5	0.15	mg/Kg		07/13/23 08:00	07/27/23 14:26	1
Manganese	0.0935	J	0.75	0.027	mg/Kg		07/13/23 08:00	07/27/23 14:26	1

Lab Sample ID: LCS 140-75274/6-B
Matrix: Solid
Analysis Batch: 75871

Client Sample ID: Lab Control Sample
Prep Type: Step 3
Prep Batch: 75294

Analyte	Spike Added	LCS Result	LCS Qualifier	Unit	D	%Rec	%Rec Limits
Iron	50.0	51.9		mg/Kg		104	80 - 120
Lithium	5.00	4.98		mg/Kg		100	80 - 120
Manganese	5.00	5.04		mg/Kg		101	80 - 120

Lab Sample ID: LCSD 140-75274/7-B
Matrix: Solid
Analysis Batch: 75871

Client Sample ID: Lab Control Sample Dup
Prep Type: Step 3
Prep Batch: 75294

Analyte	Spike Added	LCSD Result	LCSD Qualifier	Unit	D	%Rec	%Rec Limits	RPD	RPD Limit
Iron	50.0	49.5		mg/Kg		99	80 - 120	5	30
Lithium	5.00	4.82		mg/Kg		96	80 - 120	3	30
Manganese	5.00	4.89		mg/Kg		98	80 - 120	3	30

Lab Sample ID: 140-32513-1 DU
Matrix: Solid
Analysis Batch: 75871

Client Sample ID: VER-35 55-60 20230624
Prep Type: Step 3
Prep Batch: 75294

Analyte	Sample Result	Sample Qualifier	DU Result	DU Qualifier	Unit	D	RPD	RPD Limit
Iron	4300		4280		mg/Kg	☼	1	30
Lithium	0.52	J	0.516	J	mg/Kg	☼	1	30
Manganese	110	B	114		mg/Kg	☼	2	30

Lab Sample ID: MB 140-75320/5-B
Matrix: Solid
Analysis Batch: 75894

Client Sample ID: Method Blank
Prep Type: Step 4
Prep Batch: 75407

Analyte	MB Result	MB Qualifier	RL	MDL	Unit	D	Prepared	Analyzed	Dil Fac
Iron	ND		5.0	2.9	mg/Kg		07/17/23 08:00	07/28/23 12:35	1
Lithium	ND		2.5	0.15	mg/Kg		07/17/23 08:00	07/28/23 12:35	1
Manganese	ND		0.75	0.13	mg/Kg		07/17/23 08:00	07/28/23 12:35	1

QC Sample Results

Method: 6010B SEP - SEP Metals (ICP) (Continued)

Lab Sample ID: LCS 140-75320/6-B
Matrix: Solid
Analysis Batch: 75894

Client Sample ID: Lab Control Sample
Prep Type: Step 4
Prep Batch: 75407

Analyte	Spike Added	LCS Result	LCS Qualifier	Unit	D	%Rec	%Rec Limits
Iron	50.0	55.0		mg/Kg		110	80 - 120
Lithium	5.00	5.38		mg/Kg		108	80 - 120
Manganese	5.00	5.49		mg/Kg		110	80 - 120

Lab Sample ID: LCSD 140-75320/7-B
Matrix: Solid
Analysis Batch: 75894

Client Sample ID: Lab Control Sample Dup
Prep Type: Step 4
Prep Batch: 75407

Analyte	Spike Added	LCSD Result	LCSD Qualifier	Unit	D	%Rec	%Rec Limits	RPD	RPD Limit
Iron	50.0	54.6		mg/Kg		109	80 - 120	1	30
Lithium	5.00	5.41		mg/Kg		108	80 - 120	0	30
Manganese	5.00	5.45		mg/Kg		109	80 - 120	1	30

Lab Sample ID: 140-32513-1 DU
Matrix: Solid
Analysis Batch: 75894

Client Sample ID: VER-35 55-60 20230624
Prep Type: Step 4
Prep Batch: 75407

Analyte	Sample Result	Sample Qualifier	DU Result	DU Qualifier	Unit	D	RPD	RPD Limit
Iron	20000		19600		mg/Kg	☼	4	30
Lithium	13		12.6		mg/Kg	☼	3	30
Manganese	430		406		mg/Kg	☼	5	30

Lab Sample ID: MB 140-75406/5-B ^5
Matrix: Solid
Analysis Batch: 75894

Client Sample ID: Method Blank
Prep Type: Step 5
Prep Batch: 75487

Analyte	MB Result	MB Qualifier	RL	MDL	Unit	D	Prepared	Analyzed	Dil Fac
Iron	ND		75	44	mg/Kg		07/19/23 08:00	07/28/23 13:24	5
Lithium	ND		38	2.2	mg/Kg		07/19/23 08:00	07/28/23 13:24	5
Manganese	ND		11	1.9	mg/Kg		07/19/23 08:00	07/28/23 13:24	5

Lab Sample ID: LCS 140-75406/6-B ^5
Matrix: Solid
Analysis Batch: 75894

Client Sample ID: Lab Control Sample
Prep Type: Step 5
Prep Batch: 75487

Analyte	Spike Added	LCS Result	LCS Qualifier	Unit	D	%Rec	%Rec Limits
Iron	150	ND		mg/Kg		-0.07	
Lithium	15.0	16.9	J	mg/Kg		112	80 - 150
Manganese	15.0	3.96	J	mg/Kg		26	1 - 60

Lab Sample ID: LCSD 140-75406/7-B ^5
Matrix: Solid
Analysis Batch: 75894

Client Sample ID: Lab Control Sample Dup
Prep Type: Step 5
Prep Batch: 75487

Analyte	Spike Added	LCSD Result	LCSD Qualifier	Unit	D	%Rec	%Rec Limits	RPD	RPD Limit
Iron	150	ND		mg/Kg		-0.5		156	
Lithium	15.0	16.7	J	mg/Kg		111	80 - 150	1	30
Manganese	15.0	4.01	J	mg/Kg		27	1 - 60	1	30

Method: 6010B SEP - SEP Metals (ICP) (Continued)

Lab Sample ID: 140-32513-1 DU
Matrix: Solid
Analysis Batch: 75894

Client Sample ID: VER-35 55-60 20230624
Prep Type: Step 5
Prep Batch: 75487

Analyte	Sample Result	Sample Qualifier	DU Result	DU Qualifier	Unit	D	RPD	RPD Limit
Iron	ND		ND		mg/Kg	☼	NC	
Lithium	4.1	J	4.21	J	mg/Kg	☼	2	30
Manganese	46		40.0		mg/Kg	☼	14	30

Lab Sample ID: MB 140-75511/5-A
Matrix: Solid
Analysis Batch: 75894

Client Sample ID: Method Blank
Prep Type: Step 6
Prep Batch: 75511

Analyte	MB Result	MB Qualifier	RL	MDL	Unit	D	Prepared	Analyzed	Dil Fac
Iron	ND		5.0	2.9	mg/Kg		07/19/23 08:00	07/28/23 14:14	1
Lithium	ND		2.5	0.15	mg/Kg		07/19/23 08:00	07/28/23 14:14	1
Manganese	ND		0.75	0.25	mg/Kg		07/19/23 08:00	07/28/23 14:14	1

Lab Sample ID: LCS 140-75511/6-A
Matrix: Solid
Analysis Batch: 75894

Client Sample ID: Lab Control Sample
Prep Type: Step 6
Prep Batch: 75511

Analyte	Spike Added	LCS Result	LCS Qualifier	Unit	D	%Rec	%Rec Limits
Iron	50.0	54.8		mg/Kg		110	80 - 120
Lithium	5.00	5.27		mg/Kg		105	80 - 120
Manganese	5.00	5.47		mg/Kg		109	80 - 120

Lab Sample ID: LCSD 140-75511/7-A
Matrix: Solid
Analysis Batch: 75894

Client Sample ID: Lab Control Sample Dup
Prep Type: Step 6
Prep Batch: 75511

Analyte	Spike Added	LCSD Result	LCSD Qualifier	Unit	D	%Rec	%Rec Limits	RPD	RPD Limit
Iron	50.0	50.7		mg/Kg		101	80 - 120	8	30
Lithium	5.00	4.89		mg/Kg		98	80 - 120	7	30
Manganese	5.00	5.06		mg/Kg		101	80 - 120	8	30

Lab Sample ID: 140-32513-1 DU
Matrix: Solid
Analysis Batch: 75894

Client Sample ID: VER-35 55-60 20230624
Prep Type: Step 6
Prep Batch: 75511

Analyte	Sample Result	Sample Qualifier	DU Result	DU Qualifier	Unit	D	RPD	RPD Limit
Iron	11000		10600		mg/Kg	☼	4	30
Lithium	13		12.7		mg/Kg	☼	4	30
Manganese	130		127		mg/Kg	☼	2	30

Lab Sample ID: MB 140-75565/5-A
Matrix: Solid
Analysis Batch: 75976

Client Sample ID: Method Blank
Prep Type: Step 7
Prep Batch: 75565

Analyte	MB Result	MB Qualifier	RL	MDL	Unit	D	Prepared	Analyzed	Dil Fac
Iron	ND		5.0	4.1	mg/Kg		07/20/23 08:00	07/31/23 12:16	1
Lithium	ND		2.5	0.15	mg/Kg		07/20/23 08:00	07/31/23 12:16	1
Manganese	ND		0.75	0.31	mg/Kg		07/20/23 08:00	07/31/23 12:16	1

QC Sample Results

Client: Geosyntec Consultants Inc
Project/Site: Vermilion SEP

Job ID: 140-32513-1

Method: 6010B SEP - SEP Metals (ICP) (Continued)

Lab Sample ID: LCS 140-75565/6-A
Matrix: Solid
Analysis Batch: 75976

Client Sample ID: Lab Control Sample
Prep Type: Step 7
Prep Batch: 75565

Analyte	Spike Added	LCS Result	LCS Qualifier	Unit	D	%Rec	%Rec Limits
Iron	50.0	54.2		mg/Kg		108	80 - 120
Lithium	5.00	5.37		mg/Kg		107	80 - 120
Manganese	5.00	5.35		mg/Kg		107	80 - 120

Lab Sample ID: LCSD 140-75565/7-A
Matrix: Solid
Analysis Batch: 75976

Client Sample ID: Lab Control Sample Dup
Prep Type: Step 7
Prep Batch: 75565

Analyte	Spike Added	LCSD Result	LCSD Qualifier	Unit	D	%Rec	%Rec Limits	RPD	RPD Limit
Iron	50.0	54.0		mg/Kg		108	80 - 120	0	30
Lithium	5.00	5.29		mg/Kg		106	80 - 120	2	30
Manganese	5.00	5.30		mg/Kg		106	80 - 120	1	30

Lab Sample ID: 140-32513-1 DU
Matrix: Solid
Analysis Batch: 75976

Client Sample ID: VER-35 55-60 20230624
Prep Type: Step 7
Prep Batch: 75565

Analyte	Sample Result	Sample Qualifier	DU Result	DU Qualifier	Unit	D	RPD	RPD Limit
Iron	4300		4610		mg/Kg	☼	6	30
Lithium	15		16.0		mg/Kg	☼	9	30
Manganese	31		32.3		mg/Kg	☼	3	30

QC Association Summary

Client: Geosyntec Consultants Inc
Project/Site: Vermilion SEP

Job ID: 140-32513-1

Metals

SEP Batch: 75184

Lab Sample ID	Client Sample ID	Prep Type	Matrix	Method	Prep Batch
140-32513-1	VER-35 55-60 20230624	Step 1	Solid	Exchangeable	
140-32513-2	VER-35 60-63 20230624	Step 1	Solid	Exchangeable	
140-32513-3	VER-70 75-80 20230623	Step 1	Solid	Exchangeable	
MB 140-75184/5-B ^4	Method Blank	Step 1	Solid	Exchangeable	
LCS 140-75184/6-B ^5	Lab Control Sample	Step 1	Solid	Exchangeable	
LCSD 140-75184/7-B ^5	Lab Control Sample Dup	Step 1	Solid	Exchangeable	
140-32513-1 DU	VER-35 55-60 20230624	Step 1	Solid	Exchangeable	

Prep Batch: 75187

Lab Sample ID	Client Sample ID	Prep Type	Matrix	Method	Prep Batch
140-32513-1	VER-35 55-60 20230624	Total/NA	Solid	Total	
140-32513-2	VER-35 60-63 20230624	Total/NA	Solid	Total	
140-32513-3	VER-70 75-80 20230623	Total/NA	Solid	Total	
MB 140-75187/5-A	Method Blank	Total/NA	Solid	Total	
LCS 140-75187/6-A	Lab Control Sample	Total/NA	Solid	Total	
LCSD 140-75187/7-A	Lab Control Sample Dup	Total/NA	Solid	Total	
140-32513-1 DU	VER-35 55-60 20230624	Total/NA	Solid	Total	

Prep Batch: 75207

Lab Sample ID	Client Sample ID	Prep Type	Matrix	Method	Prep Batch
140-32513-1	VER-35 55-60 20230624	Step 1	Solid	3010A	75184
140-32513-2	VER-35 60-63 20230624	Step 1	Solid	3010A	75184
140-32513-3	VER-70 75-80 20230623	Step 1	Solid	3010A	75184
MB 140-75184/5-B ^4	Method Blank	Step 1	Solid	3010A	75184
LCS 140-75184/6-B ^5	Lab Control Sample	Step 1	Solid	3010A	75184
LCSD 140-75184/7-B ^5	Lab Control Sample Dup	Step 1	Solid	3010A	75184
140-32513-1 DU	VER-35 55-60 20230624	Step 1	Solid	3010A	75184

SEP Batch: 75227

Lab Sample ID	Client Sample ID	Prep Type	Matrix	Method	Prep Batch
140-32513-1	VER-35 55-60 20230624	Step 2	Solid	Carbonate	
140-32513-2	VER-35 60-63 20230624	Step 2	Solid	Carbonate	
140-32513-3	VER-70 75-80 20230623	Step 2	Solid	Carbonate	
MB 140-75227/5-B ^3	Method Blank	Step 2	Solid	Carbonate	
LCS 140-75227/6-B ^5	Lab Control Sample	Step 2	Solid	Carbonate	
LCSD 140-75227/7-B ^5	Lab Control Sample Dup	Step 2	Solid	Carbonate	
140-32513-1 DU	VER-35 55-60 20230624	Step 2	Solid	Carbonate	

Prep Batch: 75260

Lab Sample ID	Client Sample ID	Prep Type	Matrix	Method	Prep Batch
140-32513-1	VER-35 55-60 20230624	Step 2	Solid	3010A	75227
140-32513-2	VER-35 60-63 20230624	Step 2	Solid	3010A	75227
140-32513-3	VER-70 75-80 20230623	Step 2	Solid	3010A	75227
MB 140-75227/5-B ^3	Method Blank	Step 2	Solid	3010A	75227
LCS 140-75227/6-B ^5	Lab Control Sample	Step 2	Solid	3010A	75227
LCSD 140-75227/7-B ^5	Lab Control Sample Dup	Step 2	Solid	3010A	75227
140-32513-1 DU	VER-35 55-60 20230624	Step 2	Solid	3010A	75227

SEP Batch: 75274

Lab Sample ID	Client Sample ID	Prep Type	Matrix	Method	Prep Batch
140-32513-1	VER-35 55-60 20230624	Step 3	Solid	Non-Crystalline	

QC Association Summary

Metals (Continued)

SEP Batch: 75274 (Continued)

Lab Sample ID	Client Sample ID	Prep Type	Matrix	Method	Prep Batch
140-32513-2	VER-35 60-63 20230624	Step 3	Solid	Non-Crystalline	
140-32513-3	VER-70 75-80 20230623	Step 3	Solid	Non-Crystalline	
MB 140-75274/5-B	Method Blank	Step 3	Solid	Non-Crystalline	
LCS 140-75274/6-B	Lab Control Sample	Step 3	Solid	Non-Crystalline	
LCSD 140-75274/7-B	Lab Control Sample Dup	Step 3	Solid	Non-Crystalline	
140-32513-1 DU	VER-35 55-60 20230624	Step 3	Solid	Non-Crystalline	

Prep Batch: 75294

Lab Sample ID	Client Sample ID	Prep Type	Matrix	Method	Prep Batch
140-32513-1	VER-35 55-60 20230624	Step 3	Solid	3010A	75274
140-32513-2	VER-35 60-63 20230624	Step 3	Solid	3010A	75274
140-32513-3	VER-70 75-80 20230623	Step 3	Solid	3010A	75274
MB 140-75274/5-B	Method Blank	Step 3	Solid	3010A	75274
LCS 140-75274/6-B	Lab Control Sample	Step 3	Solid	3010A	75274
LCSD 140-75274/7-B	Lab Control Sample Dup	Step 3	Solid	3010A	75274
140-32513-1 DU	VER-35 55-60 20230624	Step 3	Solid	3010A	75274

SEP Batch: 75320

Lab Sample ID	Client Sample ID	Prep Type	Matrix	Method	Prep Batch
140-32513-1	VER-35 55-60 20230624	Step 4	Solid	Metal Hydroxide	
140-32513-2	VER-35 60-63 20230624	Step 4	Solid	Metal Hydroxide	
140-32513-3	VER-70 75-80 20230623	Step 4	Solid	Metal Hydroxide	
MB 140-75320/5-B	Method Blank	Step 4	Solid	Metal Hydroxide	
LCS 140-75320/6-B	Lab Control Sample	Step 4	Solid	Metal Hydroxide	
LCSD 140-75320/7-B	Lab Control Sample Dup	Step 4	Solid	Metal Hydroxide	
140-32513-1 DU	VER-35 55-60 20230624	Step 4	Solid	Metal Hydroxide	

SEP Batch: 75406

Lab Sample ID	Client Sample ID	Prep Type	Matrix	Method	Prep Batch
140-32513-1	VER-35 55-60 20230624	Step 5	Solid	Organic-Bound	
140-32513-2	VER-35 60-63 20230624	Step 5	Solid	Organic-Bound	
140-32513-3	VER-70 75-80 20230623	Step 5	Solid	Organic-Bound	
MB 140-75406/5-B ^5	Method Blank	Step 5	Solid	Organic-Bound	
LCS 140-75406/6-B ^5	Lab Control Sample	Step 5	Solid	Organic-Bound	
LCSD 140-75406/7-B ^5	Lab Control Sample Dup	Step 5	Solid	Organic-Bound	
140-32513-1 DU	VER-35 55-60 20230624	Step 5	Solid	Organic-Bound	

Prep Batch: 75407

Lab Sample ID	Client Sample ID	Prep Type	Matrix	Method	Prep Batch
140-32513-1	VER-35 55-60 20230624	Step 4	Solid	3010A	75320
140-32513-2	VER-35 60-63 20230624	Step 4	Solid	3010A	75320
140-32513-3	VER-70 75-80 20230623	Step 4	Solid	3010A	75320
MB 140-75320/5-B	Method Blank	Step 4	Solid	3010A	75320
LCS 140-75320/6-B	Lab Control Sample	Step 4	Solid	3010A	75320
LCSD 140-75320/7-B	Lab Control Sample Dup	Step 4	Solid	3010A	75320
140-32513-1 DU	VER-35 55-60 20230624	Step 4	Solid	3010A	75320

Prep Batch: 75487

Lab Sample ID	Client Sample ID	Prep Type	Matrix	Method	Prep Batch
140-32513-1	VER-35 55-60 20230624	Step 5	Solid	3010A	75406
140-32513-2	VER-35 60-63 20230624	Step 5	Solid	3010A	75406

QC Association Summary

Client: Geosyntec Consultants Inc
Project/Site: Vermilion SEP

Job ID: 140-32513-1

Metals (Continued)

Prep Batch: 75487 (Continued)

Lab Sample ID	Client Sample ID	Prep Type	Matrix	Method	Prep Batch
140-32513-3	VER-70 75-80 20230623	Step 5	Solid	3010A	75406
MB 140-75406/5-B ^5	Method Blank	Step 5	Solid	3010A	75406
LCS 140-75406/6-B ^5	Lab Control Sample	Step 5	Solid	3010A	75406
LCSD 140-75406/7-B ^5	Lab Control Sample Dup	Step 5	Solid	3010A	75406
140-32513-1 DU	VER-35 55-60 20230624	Step 5	Solid	3010A	75406

SEP Batch: 75511

Lab Sample ID	Client Sample ID	Prep Type	Matrix	Method	Prep Batch
140-32513-1	VER-35 55-60 20230624	Step 6	Solid	Acid/Sulfide	
140-32513-2	VER-35 60-63 20230624	Step 6	Solid	Acid/Sulfide	
140-32513-3	VER-70 75-80 20230623	Step 6	Solid	Acid/Sulfide	
MB 140-75511/5-A	Method Blank	Step 6	Solid	Acid/Sulfide	
LCS 140-75511/6-A	Lab Control Sample	Step 6	Solid	Acid/Sulfide	
LCSD 140-75511/7-A	Lab Control Sample Dup	Step 6	Solid	Acid/Sulfide	
140-32513-1 DU	VER-35 55-60 20230624	Step 6	Solid	Acid/Sulfide	

Prep Batch: 75565

Lab Sample ID	Client Sample ID	Prep Type	Matrix	Method	Prep Batch
140-32513-1	VER-35 55-60 20230624	Step 7	Solid	Residual	
140-32513-2	VER-35 60-63 20230624	Step 7	Solid	Residual	
140-32513-3	VER-70 75-80 20230623	Step 7	Solid	Residual	
MB 140-75565/5-A	Method Blank	Step 7	Solid	Residual	
LCS 140-75565/6-A	Lab Control Sample	Step 7	Solid	Residual	
LCSD 140-75565/7-A	Lab Control Sample Dup	Step 7	Solid	Residual	
140-32513-1 DU	VER-35 55-60 20230624	Step 7	Solid	Residual	

Analysis Batch: 75871

Lab Sample ID	Client Sample ID	Prep Type	Matrix	Method	Prep Batch
140-32513-1	VER-35 55-60 20230624	Step 1	Solid	6010B SEP	75207
140-32513-1	VER-35 55-60 20230624	Step 2	Solid	6010B SEP	75260
140-32513-1	VER-35 55-60 20230624	Step 3	Solid	6010B SEP	75294
140-32513-2	VER-35 60-63 20230624	Step 1	Solid	6010B SEP	75207
140-32513-2	VER-35 60-63 20230624	Step 2	Solid	6010B SEP	75260
140-32513-2	VER-35 60-63 20230624	Step 3	Solid	6010B SEP	75294
140-32513-3	VER-70 75-80 20230623	Step 1	Solid	6010B SEP	75207
140-32513-3	VER-70 75-80 20230623	Step 2	Solid	6010B SEP	75260
140-32513-3	VER-70 75-80 20230623	Step 3	Solid	6010B SEP	75294
MB 140-75184/5-B ^4	Method Blank	Step 1	Solid	6010B SEP	75207
MB 140-75227/5-B ^3	Method Blank	Step 2	Solid	6010B SEP	75260
MB 140-75274/5-B	Method Blank	Step 3	Solid	6010B SEP	75294
LCS 140-75184/6-B ^5	Lab Control Sample	Step 1	Solid	6010B SEP	75207
LCS 140-75227/6-B ^5	Lab Control Sample	Step 2	Solid	6010B SEP	75260
LCS 140-75274/6-B	Lab Control Sample	Step 3	Solid	6010B SEP	75294
LCSD 140-75184/7-B ^5	Lab Control Sample Dup	Step 1	Solid	6010B SEP	75207
LCSD 140-75227/7-B ^5	Lab Control Sample Dup	Step 2	Solid	6010B SEP	75260
LCSD 140-75274/7-B	Lab Control Sample Dup	Step 3	Solid	6010B SEP	75294
140-32513-1 DU	VER-35 55-60 20230624	Step 1	Solid	6010B SEP	75207
140-32513-1 DU	VER-35 55-60 20230624	Step 2	Solid	6010B SEP	75260
140-32513-1 DU	VER-35 55-60 20230624	Step 3	Solid	6010B SEP	75294

QC Association Summary

Metals

Analysis Batch: 75894

Lab Sample ID	Client Sample ID	Prep Type	Matrix	Method	Prep Batch
140-32513-1	VER-35 55-60 20230624	Step 4	Solid	6010B SEP	75407
140-32513-1	VER-35 55-60 20230624	Step 5	Solid	6010B SEP	75487
140-32513-1	VER-35 55-60 20230624	Step 6	Solid	6010B SEP	75511
140-32513-2	VER-35 60-63 20230624	Step 4	Solid	6010B SEP	75407
140-32513-2	VER-35 60-63 20230624	Step 5	Solid	6010B SEP	75487
140-32513-2	VER-35 60-63 20230624	Step 6	Solid	6010B SEP	75511
140-32513-3	VER-70 75-80 20230623	Step 4	Solid	6010B SEP	75407
140-32513-3	VER-70 75-80 20230623	Step 4	Solid	6010B SEP	75407
140-32513-3	VER-70 75-80 20230623	Step 5	Solid	6010B SEP	75487
140-32513-3	VER-70 75-80 20230623	Step 6	Solid	6010B SEP	75511
MB 140-75320/5-B	Method Blank	Step 4	Solid	6010B SEP	75407
MB 140-75406/5-B ^5	Method Blank	Step 5	Solid	6010B SEP	75487
MB 140-75511/5-A	Method Blank	Step 6	Solid	6010B SEP	75511
LCS 140-75320/6-B	Lab Control Sample	Step 4	Solid	6010B SEP	75407
LCS 140-75406/6-B ^5	Lab Control Sample	Step 5	Solid	6010B SEP	75487
LCS 140-75511/6-A	Lab Control Sample	Step 6	Solid	6010B SEP	75511
LCSD 140-75320/7-B	Lab Control Sample Dup	Step 4	Solid	6010B SEP	75407
LCSD 140-75406/7-B ^5	Lab Control Sample Dup	Step 5	Solid	6010B SEP	75487
LCSD 140-75511/7-A	Lab Control Sample Dup	Step 6	Solid	6010B SEP	75511
140-32513-1 DU	VER-35 55-60 20230624	Step 4	Solid	6010B SEP	75407
140-32513-1 DU	VER-35 55-60 20230624	Step 5	Solid	6010B SEP	75487
140-32513-1 DU	VER-35 55-60 20230624	Step 6	Solid	6010B SEP	75511

Analysis Batch: 75976

Lab Sample ID	Client Sample ID	Prep Type	Matrix	Method	Prep Batch
140-32513-1	VER-35 55-60 20230624	Step 7	Solid	6010B SEP	75565
140-32513-1	VER-35 55-60 20230624	Total/NA	Solid	6010B	75187
140-32513-1	VER-35 55-60 20230624	Total/NA	Solid	6010B	75187
140-32513-2	VER-35 60-63 20230624	Step 7	Solid	6010B SEP	75565
140-32513-2	VER-35 60-63 20230624	Total/NA	Solid	6010B	75187
140-32513-2	VER-35 60-63 20230624	Total/NA	Solid	6010B	75187
140-32513-3	VER-70 75-80 20230623	Step 7	Solid	6010B SEP	75565
140-32513-3	VER-70 75-80 20230623	Total/NA	Solid	6010B	75187
140-32513-3	VER-70 75-80 20230623	Total/NA	Solid	6010B	75187
MB 140-75187/5-A	Method Blank	Total/NA	Solid	6010B	75187
MB 140-75565/5-A	Method Blank	Step 7	Solid	6010B SEP	75565
LCS 140-75187/6-A	Lab Control Sample	Total/NA	Solid	6010B	75187
LCS 140-75565/6-A	Lab Control Sample	Step 7	Solid	6010B SEP	75565
LCSD 140-75187/7-A	Lab Control Sample Dup	Total/NA	Solid	6010B	75187
LCSD 140-75565/7-A	Lab Control Sample Dup	Step 7	Solid	6010B SEP	75565
140-32513-1 DU	VER-35 55-60 20230624	Step 7	Solid	6010B SEP	75565
140-32513-1 DU	VER-35 55-60 20230624	Total/NA	Solid	6010B	75187
140-32513-1 DU	VER-35 55-60 20230624	Total/NA	Solid	6010B	75187

Analysis Batch: 76083

Lab Sample ID	Client Sample ID	Prep Type	Matrix	Method	Prep Batch
140-32513-1	VER-35 55-60 20230624	Sum of Steps 1-7	Solid	6010B SEP	
140-32513-2	VER-35 60-63 20230624	Sum of Steps 1-7	Solid	6010B SEP	
140-32513-3	VER-70 75-80 20230623	Sum of Steps 1-7	Solid	6010B SEP	

QC Association Summary

General Chemistry

Analysis Batch: 75814

Lab Sample ID	Client Sample ID	Prep Type	Matrix	Method	Prep Batch
140-32513-1	VER-35 55-60 20230624	Total/NA	Solid	Moisture	
140-32513-2	VER-35 60-63 20230624	Total/NA	Solid	Moisture	
140-32513-3	VER-70 75-80 20230623	Total/NA	Solid	Moisture	
140-32513-1 DU	VER-35 55-60 20230624	Total/NA	Solid	Moisture	

Lab Chronicle

Client: Geosyntec Consultants Inc
Project/Site: Vermilion SEP

Job ID: 140-32513-1

Client Sample ID: VER-35 55-60 20230624

Lab Sample ID: 140-32513-1

Date Collected: 06/24/23 14:20
Date Received: 07/03/23 11:15

Matrix: Solid

Prep Type	Batch Type	Batch Method	Run	Dil Factor	Initial Amount	Final Amount	Batch Number	Prepared or Analyzed	Analyst	Lab
Sum of Steps 1-7	Analysis	6010B SEP		1			76083	08/02/23 14:24	KNC	EET KNX
	Instrument ID:	NOEQUIP								
Total/NA	Analysis	Moisture		1			75814	07/26/23 15:29	ACW	EETKNX
	Instrument ID:	NOEQUIP								

Client Sample ID: VER-35 55-60 20230624

Lab Sample ID: 140-32513-1

Date Collected: 06/24/23 14:20
Date Received: 07/03/23 11:15

Matrix: Solid
Percent Solids: 95.4

Prep Type	Batch Type	Batch Method	Run	Dil Factor	Initial Amount	Final Amount	Batch Number	Prepared or Analyzed	Analyst	Lab
Total/NA	Prep	Total			1.00 g	50mL	75187	07/21/23 08:00	LAH	EETKNX
Total/NA	Analysis	6010B		1			75976	07/31/23 13:22	KNC	EETKNX
	Instrument ID:	DUO								
Total/NA	Prep	Total			1.00 g	50mL	75187	07/21/23 08:00	LAH	EET KNX
Total/NA	Analysis	6010B		2			75976	07/31/23 14:12	KNC	EET KNX
	Instrument ID:	DUO								
Step 1	SEP	Exchangeable			5.00 g	25 mL	75184	07/10/23 12:30	LAH	EET KNX
Step 1	Prep	3010A			5 mL	50mL	75207	07/11/23 08:00	LAH	EET KNX
Step 1	Analysis	6010B SEP		4			75871	07/27/23 13:01	KNC	EET KNX
	Instrument ID:	DUO								
Step 2	SEP	Carbonate			5.00 g	25 mL	75227	07/11/23 08:00	LAH	EET KNX
Step 2	Prep	3010A			5 mL	50 mL	75260	07/12/23 08:00	LAH	EETKNX
Step 2	Analysis	6010B SEP		3			75871	07/27/23 13:51	KNC	EETKNX
	Instrument ID:	DUO								
Step 3	SEP	Non-Crystalline			5.00 g	25mL	75274	07/12/23 08:00	LAH	EET KNX
Step 3	Prep	3010A			5 mL	50mL	75294	07/13/23 08:00	LAH	EET KNX
Step 3	Analysis	6010B SEP		1			75871	07/27/23 14:40	KNC	EET KNX
	Instrument ID:	DUO								
Step 4	SEP	Metal Hydroxide			5.00g	25 mL	75320	07/13/23 08:00	LAH	EET KNX
Step 4	Prep	3010A			5 mL	50mL	75407	07/17/23 08:00	LAH	EET KNX
Step 4	Analysis	6010B SEP		1			75894	07/28/23 12:49	KNC	EET KNX
	Instrument ID:	DUO								
Step 5	SEP	Organic-Bound			5.00 g	75mL	75406	07/17/23 08:00	LAH	EET KNX
Step 5	Prep	3010A			5 mL	50 mL	75487	07/19/23 08:00	LAH	EET KNX
Step 5	Analysis	6010B SEP		5			75894	07/28/23 13:39	KNC	EET KNX
	Instrument ID:	DUO								
Step 6	SEP	Acid/Sulfide			5.00 g	250 mL	75511	07/19/23 08:00	LAH	EET KNX
Step 6	Analysis	6010B SEP		1			75894	07/28/23 14:29	KNC	EETKNX
	Instrument ID:	DUO								
Step 7	Prep	Residual			1.00 g	50mL	75565	07/20/23 08:00	LAH	EETKNX
Step 7	Analysis	6010B SEP		1			75976	07/31/23 12:46	KNC	EETKNX
	Instrument ID:	DUO								

Lab Chronicle

Client: Geosyntec Consultants Inc
Project/Site: Vermilion SEP

Job ID: 140-32513-1

Client Sample ID: VER-35 60-63 20230624

Lab Sample ID: 140-32513-2

Date Collected: 06/24/23 14:50
Date Received: 07/03/23 11:15

Matrix: Solid

Prep Type	Batch Type	Batch Method	Run	Dil Factor	Initial Amount	Final Amount	Batch Number	Prepared or Analyzed	Analyst	Lab
Sum of Steps 1-7	Analysis	6010B SEP		1			76083	08/02/23 14:24	KNC	EETKNX
	Instrument ID: NOEQUIP									
Total/NA	Analysis	Moisture		1			75814	07/26/23 15:29	ACW	EET KNX
	Instrument ID: NOEQUIP									

Client Sample ID: VER-35 60-63 20230624

Lab Sample ID: 140-32513-2

Date Collected: 06/24/23 14:50
Date Received: 07/03/23 11:15

Matrix: Solid
Percent Solids: 95.4

Prep Type	Batch Type	Batch Method	Run	Dil Factor	Initial Amount	Final Amount	Batch Number	Prepared or Analyzed	Analyst	Lab
Total/NA	Prep	Total			1.00 g	50mL	75187	07/21/23 08:00	LAH	EET KNX
Total/NA	Analysis	6010B		1			75976	07/31/23 13:33	KNC	EET KNX
	Instrument ID: DUO									
Total/NA	Prep	Total			1.00 g	50 mL	75187	07/21/23 08:00	LAH	EET KNX
Total/NA	Analysis	6010B		2			75976	07/31/23 14:22	KNC	EET KNX
	Instrument ID: DUO									
Step 1	SEP	Exchangeable			5.00 g	25 mL	75184	07/10/23 12:30	LAH	EET KNX
Step 1	Prep	3010A			5 mL	50mL	75207	07/11/23 08:00	LAH	EET KNX
Step 1	Analysis	6010B SEP		4			75871	07/27/23 13:11	KNC	EET KNX
	Instrument ID: DUO									
Step 2	SEP	Carbonate			5.00 g	25mL	75227	07/11/23 08:00	LAH	EET KNX
Step 2	Prep	3010A			5 mL	50mL	75260	07/12/23 08:00	LAH	EETKNX
Step 2	Analysis	6010B SEP		3			75871	07/27/23 14:01	KNC	EETKNX
	Instrument ID: DUO									
Step 3	SEP	Non-Crystalline			5.00 g	25mL	75274	07/12/23 08:00	LAH	EET KNX
Step 3	Prep	3010A			5 mL	50mL	75294	07/13/23 08:00	LAH	EET KNX
Step 3	Analysis	6010B SEP		1			75871	07/27/23 14:50	KNC	EET KNX
	Instrument ID: DUO									
Step 4	SEP	Metal Hydroxide			5.00 g	25mL	75320	07/13/23 08:00	LAH	EET KNX
Step 4	Prep	3010A			5 mL	50 mL	75407	07/17/23 08:00	LAH	EET KNX
Step 4	Analysis	6010B SEP		1			75894	07/28/23 12:59	KNC	EET KNX
	Instrument ID: DUO									
Step 5	SEP	Organic-Bound			5.00 g	75mL	75406	07/17/23 08:00	LAH	EET KNX
Step 5	Prep	3010A			5 mL	50 mL	75487	07/19/23 08:00	LAH	EET KNX
Step 5	Analysis	6010B SEP		5			75894	07/28/23 13:49	KNC	EET KNX
	Instrument ID: DUO									
Step 6	SEP	Acid/Sulfide			5.00 g	250 mL	75511	07/19/23 08:00	LAH	EET KNX
Step 6	Analysis	6010B SEP		1			75894	07/28/23 14:39	KNC	EET KNX
	Instrument ID: DUO									
Step 7	Prep	Residual			1.00 g	50 mL	75565	07/20/23 08:00	LAH	EETKNX
Step 7	Analysis	6010B SEP		1			75976	07/31/23 12:57	KNC	EET KNX
	Instrument ID: DUO									

Lab Chronicle

Client: Geosyntec Consultants Inc
Project/Site: Vermilion SEP

Job ID: 140-32513-1

Client Sample ID: VER-70 75-80 20230623
Date Collected: 06/23/23 17:00
Date Received: 07/03/23 11:15

Lab Sample ID: 140-32513-3
Matrix: Solid

Prep Type	Batch Type	Batch Method	Run	Dil Factor	Initial Amount	Final Amount	Batch Number	Prepared or Analyzed	Analyst	Lab
Sum of Steps 1-7	Analysis	6010B SEP		1			76083	08/02/23 14:24	KNC	EETKNX
	Instrument ID: NOEQUIP									
Total/NA	Analysis	Moisture		1			75814	07/26/23 15:29	ACW	EET KNX
	Instrument ID: NOEQUIP									

Client Sample ID: VER-70 75-80 20230623
Date Collected: 06/23/23 17:00
Date Received: 07/03/23 11:15

Lab Sample ID: 140-32513-3
Matrix: Solid
Percent Solids: 90.0

Prep Type	Batch Type	Batch Method	Run	Dil Factor	Initial Amount	Final Amount	Batch Number	Prepared or Analyzed	Analyst	Lab
Total/NA	Prep	Total			1.00 g	50mL	75187	07/21/23 08:00	LAH	EET KNX
Total/NA	Analysis	6010B		1			75976	07/31/23 13:39	KNC	EET KNX
	Instrument ID: DUO									
Total/NA	Prep	Total			1.00 g	50mL	75187	07/21/23 08:00	LAH	EETKNX
Total/NA	Analysis	6010B		5			75976	07/31/23 15:08	KNC	EET KNX
	Instrument ID: DUO									
Step 1	SEP	Exchangeable			5.00 g	25 mL	75184	07/10/23 12:30	LAH	EET KNX
Step 1	Prep	3010A			5 mL	50 mL	75207	07/11/23 08:00	LAH	EET KNX
Step 1	Analysis	6010B SEP		4			75871	07/27/23 13:16	KNC	EET KNX
	Instrument ID: DUO									
Step 2	SEP	Carbonate			5.00 g	25 mL	75227	07/11/23 08:00	LAH	EET KNX
Step 2	Prep	3010A			5 mL	50 mL	75260	07/12/23 08:00	LAH	EET KNX
Step 2	Analysis	6010B SEP		3			75871	07/27/23 14:06	KNC	EET KNX
	Instrument ID: DUO									
Step 3	SEP	Non-Crystalline			5.00 g	25 mL	75274	07/12/23 08:00	LAH	EET KNX
Step 3	Prep	3010A			5 mL	50 mL	75294	07/13/23 08:00	LAH	EET KNX
Step 3	Analysis	6010B SEP		1			75871	07/27/23 14:55	KNC	EET KNX
	Instrument ID: DUO									
Step 4	SEP	Metal Hydroxide			5.00 g	25 mL	75320	07/13/23 08:00	LAH	EET KNX
Step 4	Prep	3010A			5 mL	50 mL	75407	07/17/23 08:00	LAH	EET KNX
Step 4	Analysis	6010B SEP		1			75894	07/28/23 13:04	KNC	EET KNX
	Instrument ID: DUO									
Step 4	SEP	Metal Hydroxide			5.00 g	25 mL	75320	07/13/23 08:00	LAH	EET KNX
Step 4	Prep	3010A			5 mL	50 mL	75407	07/17/23 08:00	LAH	EET KNX
Step 4	Analysis	6010B SEP		2			75894	07/28/23 14:55	KNC	EET KNX
	Instrument ID: DUO									
Step 5	SEP	Organic-Bound			5.00 g	75 mL	75406	07/17/23 08:00	LAH	EET KNX
Step 5	Prep	3010A			5 mL	50 mL	75487	07/19/23 08:00	LAH	EET KNX
Step 5	Analysis	6010B SEP		5			75894	07/28/23 13:54	KNC	EET KNX
	Instrument ID: DUO									
Step 6	SEP	Acid/Sulfide			5.00 g	250 mL	75511	07/19/23 08:00	LAH	EET KNX
Step 6	Analysis	6010B SEP		1			75894	07/28/23 14:44	KNC	EET KNX
	Instrument ID: DUO									
Step 7	Prep	Residual			1.00 g	50mL	75565	07/20/23 08:00	LAH	EET KNX
Step 7	Analysis	6010B SEP		1			75976	07/31/23 13:17	KNC	EET KNX
	Instrument ID: DUO									

Lab Chronicle

Client: Geosyntec Consultants Inc
Project/Site: Vermilion SEP

Job ID: 140-32513-1

Client Sample ID: Method Blank

Lab Sample ID: MB 140-75184/5-B ^4

Date Collected: N/A
Date Received: N/A

Matrix: Solid

Prep Type	Batch Type	Batch Method	Run	Dil Factor	Initial Amount	Final Amount	Batch Number	Prepared or Analyzed	Analyst	Lab
Step 1	SEP	Exchangeable			5.00 g	25 mL	75184	07/10/23 12:30	LAH	EET KNX
Step 1	Prep	3010A			5 mL	50 mL	75207	07/11/23 08:00	LAH	EET KNX
Step 1	Analysis	6010B SEP		4			75871	07/27/23 12:47	KNC	EET KNX

Instrument ID: DUO

Client Sample ID: Method Blank

Lab Sample ID: MB 140-75187/5-A

Date Collected: N/A
Date Received: N/A

Matrix: Solid

Prep Type	Batch Type	Batch Method	Run	Dil Factor	Initial Amount	Final Amount	Batch Number	Prepared or Analyzed	Analyst	Lab
Total/NA	Prep	Total			1.00 g	50 mL	75187	07/21/23 08:00	LAH	EET KNX
Total/NA	Analysis	6010B		1			75976	07/31/23 12:31	KNC	EET KNX

Instrument ID: DUO

Client Sample ID: Method Blank

Lab Sample ID: MB 140-75227/5-B ^3

Date Collected: N/A
Date Received: N/A

Matrix: Solid

Prep Type	Batch Type	Batch Method	Run	Dil Factor	Initial Amount	Final Amount	Batch Number	Prepared or Analyzed	Analyst	Lab
Step 2	SEP	Carbonate			5.00 g	25 mL	75227	07/11/23 08:00	LAH	EET KNX
Step 2	Prep	3010A			5 mL	50 mL	75260	07/12/23 08:00	LAH	EET KNX
Step 2	Analysis	6010B SEP		3			75871	07/27/23 13:36	KNC	EET KNX

Instrument ID: DUO

Client Sample ID: Method Blank

Lab Sample ID: MB 140-75274/5-B

Date Collected: N/A
Date Received: N/A

Matrix: Solid

Prep Type	Batch Type	Batch Method	Run	Dil Factor	Initial Amount	Final Amount	Batch Number	Prepared or Analyzed	Analyst	Lab
Step 3	SEP	Non-Crystalline			5.00 g	25 mL	75274	07/12/23 08:00	LAH	EETKNX
Step 3	Prep	3010A			5 mL	50 mL	75294	07/13/23 08:00	LAH	EET KNX
Step 3	Analysis	6010B SEP		1			75871	07/27/23 14:26	KNC	EET KNX

Instrument ID: DUO

Client Sample ID: Method Blank

Lab Sample ID: MB 140-75320/5-B

Date Collected: N/A
Date Received: N/A

Matrix: Solid

Prep Type	Batch Type	Batch Method	Run	Dil Factor	Initial Amount	Final Amount	Batch Number	Prepared or Analyzed	Analyst	Lab
Step 4	SEP	Metal Hydroxide			5.00 g	25 mL	75320	07/13/23 08:00	LAH	EET KNX
Step 4	Prep	3010A			5 mL	50 mL	75407	07/17/23 08:00	LAH	EET KNX
Step 4	Analysis	6010B SEP		1			75894	07/28/23 12:35	KNC	EET KNX

Instrument ID: DUO

Lab Chronicle

Client Sample ID: Method Blank

Lab Sample ID: MB 140-75406/5-B ^5

Date Collected: N/A
Date Received: N/A

Matrix: Solid

Prep Type	Batch Type	Batch Method	Run	Dil Factor	Initial Amount	Final Amount	Batch Number	Prepared or Analyzed	Analyst	Lab
Step 5	SEP	Organic-Bound			5.00 g	75 mL	75406	07/17/23 08:00	LAH	EET KNX
Step 5	Prep	3010A			5 mL	50 mL	75487	07/19/23 08:00	LAH	EET KNX
Step 5	Analysis	6010B SEP		5			75894	07/28/23 13:24	KNC	EET KNX

Instrument ID: DUO

Client Sample ID: Method Blank

Lab Sample ID: MB 140-75511/5-A

Date Collected: N/A
Date Received: N/A

Matrix: Solid

Prep Type	Batch Type	Batch Method	Run	Dil Factor	Initial Amount	Final Amount	Batch Number	Prepared or Analyzed	Analyst	Lab
Step 6	SEP	Acid/Sulfide			5.00 g	250 mL	75511	07/19/23 08:00	LAH	EET KNX
Step 6	Analysis	6010B SEP		1			75894	07/28/23 14:14	KNC	EET KNX

Instrument ID: DUO

Client Sample ID: Method Blank

Lab Sample ID: MB 140-75565/5-A

Date Collected: N/A
Date Received: N/A

Matrix: Solid

Prep Type	Batch Type	Batch Method	Run	Dil Factor	Initial Amount	Final Amount	Batch Number	Prepared or Analyzed	Analyst	Lab
Step 7	Prep	Residual			1.00 g	50 mL	75565	07/20/23 08:00	LAH	EET KNX
Step 7	Analysis	6010B SEP		1			75976	07/31/23 12:16	KNC	EET KNX

Instrument ID: DUO

Client Sample ID: Lab Control Sample

Lab Sample ID: LCS 140-75184/6-B ^5

Date Collected: N/A
Date Received: N/A

Matrix: Solid

Prep Type	Batch Type	Batch Method	Run	Dil Factor	Initial Amount	Final Amount	Batch Number	Prepared or Analyzed	Analyst	Lab
Step 1	SEP	Exchangeable			5.00 g	25 mL	75184	07/10/23 12:30	LAH	EET KNX
Step 1	Prep	3010A			5 mL	50 mL	75207	07/11/23 08:00	LAH	EET KNX
Step 1	Analysis	6010B SEP		5			75871	07/27/23 12:52	KNC	EET KNX

Instrument ID: DUO

Client Sample ID: Lab Control Sample

Lab Sample ID: LCS 140-75187/6-A

Date Collected: N/A
Date Received: N/A

Matrix: Solid

Prep Type	Batch Type	Batch Method	Run	Dil Factor	Initial Amount	Final Amount	Batch Number	Prepared or Analyzed	Analyst	Lab
Total/NA	Prep	Total			1.00 g	50 mL	75187	07/21/23 08:00	LAH	EET KNX
Total/NA	Analysis	6010B		1			75976	07/31/23 12:36	KNC	EET KNX

Instrument ID: DUO

Lab Chronicle

Client: Geosyntec Consultants Inc
Project/Site: Vermilion SEP

Job ID: 140-32513-1

Client Sample ID: Lab Control Sample

Lab Sample ID: LCS 140-75227/6-B ^5

Date Collected: N/A
Date Received: N/A
Matrix: Solid

Prep Type	Batch Type	Batch Method	Run	Dil Factor	Initial Amount	Final Amount	Batch Number	Prepared or Analyzed	Analyst	Lab
Step 2	SEP	Carbonate			5.00 g	25 mL	75227	07/11/23 08:00	LAH	EETKNX
Step 2	Prep	3010A			5 mL	50 mL	75260	07/12/23 08:00	LAH	EETKNX
Step 2	Analysis	6010B SEP		5			75871	07/27/23 13:41	KNC	EETKNX
	Instrument ID: DUO									

Client Sample ID: Lab Control Sample

Lab Sample ID: LCS 140-75274/6-B

Date Collected: N/A
Date Received: N/A
Matrix: Solid

Prep Type	Batch Type	Batch Method	Run	Dil Factor	Initial Amount	Final Amount	Batch Number	Prepared or Analyzed	Analyst	Lab
Step 3	SEP	Non-Crystalline			5.00 g	25 mL	75274	07/12/23 08:00	LAH	EETKNX
Step 3	Prep	3010A			5 mL	50 mL	75294	07/13/23 08:00	LAH	EET KNX
Step 3	Analysis	6010B SEP		1			75871	07/27/23 14:31	KNC	EET KNX
	Instrument ID: DUO									

Client Sample ID: Lab Control Sample

Lab Sample ID: LCS 140-75320/6-B

Date Collected: N/A
Date Received: N/A
Matrix: Solid

Prep Type	Batch Type	Batch Method	Run	Dil Factor	Initial Amount	Final Amount	Batch Number	Prepared or Analyzed	Analyst	Lab
Step 4	SEP	Metal Hydroxide			5.00 g	25 mL	75320	07/13/23 08:00	LAH	EETKNX
Step 4	Prep	3010A			5 mL	50 mL	75407	07/17/23 08:00	LAH	EETKNX
Step 4	Analysis	6010B SEP		1			75894	07/28/23 12:40	KNC	EET KNX
	Instrument ID: DUO									

Client Sample ID: Lab Control Sample

Lab Sample ID: LCS 140-75406/6-B ^5

Date Collected: N/A
Date Received: N/A
Matrix: Solid

Prep Type	Batch Type	Batch Method	Run	Dil Factor	Initial Amount	Final Amount	Batch Number	Prepared or Analyzed	Analyst	Lab
Step 5	SEP	Organic-Bound			5.00 g	75 mL	75406	07/17/23 08:00	LAH	EETKNX
Step 5	Prep	3010A			5 mL	50mL	75487	07/19/23 08:00	LAH	EETKNX
Step 5	Analysis	6010B SEP		5			75894	07/28/23 13:29	KNC	EETKNX
	Instrument ID: DUO									

Client Sample ID: Lab Control Sample

Lab Sample ID: LCS 140-75511/6-A

Date Collected: N/A
Date Received: N/A
Matrix: Solid

Prep Type	Batch Type	Batch Method	Run	Dil Factor	Initial Amount	Final Amount	Batch Number	Prepared or Analyzed	Analyst	Lab
Step 6	SEP	Acid/Sulfide			5.00 g	250mL	75511	07/19/23 08:00	LAH	EETKNX
Step 6	Analysis	6010B SEP		1			75894	07/28/23 14:19	KNC	EETKNX
	Instrument ID: DUO									

Lab Chronicle

Client Sample ID: Lab Control Sample

Lab Sample ID: LCS 140-75565/6-A

Date Collected: N/A
Date Received: N/A
Matrix: Solid

Prep Type	Batch Type	Batch Method	Run	Dil Factor	Initial Amount	Final Amount	Batch Number	Prepared or Analyzed	Analyst	Lab
Step 7	Prep	Residual			1.00 g	50mL	75565	07/20/23 08:00	LAH	EET KNX
Step 7	Analysis	6010B SEP		1			75976	07/31/23 12:21	KNC	EET KNX
	Instrument ID: DUO									

Client Sample ID: Lab Control Sample Dup

Lab Sample ID: LCSD 140-75184/7-B ^5

Date Collected: N/A
Date Received: N/A
Matrix: Solid

Prep Type	Batch Type	Batch Method	Run	Dil Factor	Initial Amount	Final Amount	Batch Number	Prepared or Analyzed	Analyst	Lab
Step 1	SEP	Exchangeable			5.00 g	25 mL	75184	07/10/23 12:30	LAH	EET KNX
Step 1	Prep	3010A			5 mL	50 mL	75207	07/11/23 08:00	LAH	EET KNX
Step 1	Analysis	6010B SEP		5			75871	07/27/23 12:57	KNC	EET KNX
	Instrument ID: DUO									

Client Sample ID: Lab Control Sample Dup

Lab Sample ID: LCSD 140-75187/7-A

Date Collected: N/A
Date Received: N/A
Matrix: Solid

Prep Type	Batch Type	Batch Method	Run	Dil Factor	Initial Amount	Final Amount	Batch Number	Prepared or Analyzed	Analyst	Lab
Total/NA	Prep	Total			1.00 g	50mL	75187	07/21/23 08:00	LAH	EET KNX
Total/NA	Analysis	6010B		1			75976	07/31/23 12:41	KNC	EET KNX
	Instrument ID: DUO									

Client Sample ID: Lab Control Sample Dup

Lab Sample ID: LCSD 140-75227/7-B ^5

Date Collected: N/A
Date Received: N/A
Matrix: Solid

Prep Type	Batch Type	Batch Method	Run	Dil Factor	Initial Amount	Final Amount	Batch Number	Prepared or Analyzed	Analyst	Lab
Step 2	SEP	Carbonate			5.00 g	25mL	75227	07/11/23 08:00	LAH	EET KNX
Step 2	Prep	3010A			5 mL	50 mL	75260	07/12/23 08:00	LAH	EET KNX
Step 2	Analysis	6010B SEP		5			75871	07/27/23 13:46	KNC	EET KNX
	Instrument ID: DUO									

Client Sample ID: Lab Control Sample Dup

Lab Sample ID: LCSD 140-75274/7-B

Date Collected: N/A
Date Received: N/A
Matrix: Solid

Prep Type	Batch Type	Batch Method	Run	Dil Factor	Initial Amount	Final Amount	Batch Number	Prepared or Analyzed	Analyst	Lab
Step 3	SEP	Non-Crystalline			5.00 g	25mL	75274	07/12/23 08:00	LAH	EET KNX
Step 3	Prep	3010A			5 mL	50 mL	75294	07/13/23 08:00	LAH	EET KNX
Step 3	Analysis	6010B SEP		1			75871	07/27/23 14:36	KNC	EET KNX
	Instrument ID: DUO									

Lab Chronicle

Client: Geosyntec Consultants Inc

Project/Site: Vermilion SEP

Job ID: 140-32513-1

Client Sample ID: Lab Control Sample Dup

Lab Sample ID: LCSD 140-75320/7-B

Date Collected: N/A

Matrix: Solid

Date Received: N/A

Prep Type	Batch Type	Batch Method	Run	Dil Factor	Initial Amount	Final Amount	Batch Number	Prepared or Analyzed	Analyst	Lab
Step 4	SEP	Metal Hydroxide			5.00 g	25 mL	75320	07/13/23 08:00	LAH	EETKNX
Step 4	Prep	3010A			5 mL	50 mL	75407	07/17/23 08:00	LAH	EET KNX
Step 4	Analysis	6010B SEP		1			75894	07/28/23 12:44	KNC	EET KNX
	Instrument ID: DUO									

Client Sample ID: Lab Control Sample Dup

Lab Sample ID: LCSD 140-75406/7-B ^5

Date Collected: N/A

Matrix: Solid

Date Received: N/A

Prep Type	Batch Type	Batch Method	Run	Dil Factor	Initial Amount	Final Amount	Batch Number	Prepared or Analyzed	Analyst	Lab
Step 5	SEP	Organic-Bound			5.00 g	75 mL	75406	07/17/23 08:00	LAH	EET KNX
Step 5	Prep	3010A			5 mL	50mL	75487	07/19/23 08:00	LAH	EET KNX
Step 5	Analysis	6010B SEP		5			75894	07/28/23 13:34	KNC	EET KNX
	Instrument ID: DUO									

Client Sample ID: Lab Control Sample Dup

Lab Sample ID: LCSD 140-75511/7-A

Date Collected: N/A

Matrix: Solid

Date Received: N/A

Prep Type	Batch Type	Batch Method	Run	Dil Factor	Initial Amount	Final Amount	Batch Number	Prepared or Analyzed	Analyst	Lab
Step 6	SEP	Acid/Sulfide			5.00 g	250 mL	75511	07/19/23 08:00	LAH	EET KNX
Step 6	Analysis	6010B SEP		1			75894	07/28/23 14:24	KNC	EET KNX
	Instrument ID: DUO									

Client Sample ID: Lab Control Sample Dup

Lab Sample ID: LCSD 140-75565/7-A

Date Collected: N/A

Matrix: Solid

Date Received: N/A

Prep Type	Batch Type	Batch Method	Run	Dil Factor	Initial Amount	Final Amount	Batch Number	Prepared or Analyzed	Analyst	Lab
Step 7	Prep	Residual			1.00 g	50mL	75565	07/20/23 08:00	LAH	EET KNX
Step 7	Analysis	6010B SEP		1			75976	07/31/23 12:26	KNC	EET KNX
	Instrument ID: DUO									

Client Sample ID: VER-35 55-60 20230624

Lab Sample ID: 140-32513-1 DU

Date Collected: 06/24/23 14:20

Matrix: Solid

Date Received: 07/03/23 11:15

Prep Type	Batch Type	Batch Method	Run	Dil Factor	Initial Amount	Final Amount	Batch Number	Prepared or Analyzed	Analyst	Lab
Total/NA	Analysis	Moisture		1			75814	07/26/23 15:29	ACW	EET KNX
	Instrument ID: NOEQUIP									

Lab Chronicle

Client: Geosyntec Consultants Inc
Project/Site: Vermilion SEP

Job ID: 140-32513-1

Client Sample ID: VER-35 55-60 20230624
Date Collected: 06/24/23 14:20
Date Received: 07/03/23 11:15

Lab Sample ID: 140-32513-1 DU
Matrix: Solid
Percent Solids: 95.4

Prep Type	Batch Type	Batch Method	Run	Dil Factor	Initial Amount	Final Amount	Batch Number	Prepared or Analyzed	Analyst	Lab
Total/NA	Prep	Total			1.00 g	50mL	75187	07/21/23 08:00	LAH	EETKNX
Total/NA	Analysis	6010B		1			75976	07/31/23 13:28	KNC	EET KNX
	Instrument ID: DUO									
Total/NA	Prep	Total			1.00 g	50mL	75187	07/21/23 08:00	LAH	EETKNX
Total/NA	Analysis	6010B		2			75976	07/31/23 14:17	KNC	EETKNX
	Instrument ID: DUO									
Step 1	SEP	Exchangeable			5.00 g	25 mL	75184	07/10/23 12:30	LAH	EET KNX
Step 1	Prep	3010A			5 mL	50 mL	75207	07/11/23 08:00	LAH	EET KNX
Step 1	Analysis	6010B SEP		4			75871	07/27/23 13:06	KNC	EET KNX
	Instrument ID: DUO									
Step 2	SEP	Carbonate			5.00 g	25mL	75227	07/11/23 08:00	LAH	EET KNX
Step 2	Prep	3010A			5 mL	50mL	75260	07/12/23 08:00	LAH	EET KNX
Step 2	Analysis	6010B SEP		3			75871	07/27/23 13:56	KNC	EET KNX
	Instrument ID: DUO									
Step 3	SEP	Non-Crystalline			5.00 g	25 mL	75274	07/12/23 08:00	LAH	EETKNX
Step 3	Prep	3010A			5 mL	50mL	75294	07/13/23 08:00	LAH	EET KNX
Step 3	Analysis	6010B SEP		1			75871	07/27/23 14:45	KNC	EET KNX
	Instrument ID: DUO									
Step 4	SEP	Metal Hydroxide			5.00 g	25mL	75320	07/13/23 08:00	LAH	EET KNX
Step 4	Prep	3010A			5 mL	50mL	75407	07/17/23 08:00	LAH	EET KNX
Step 4	Analysis	6010B SEP		1			75894	07/28/23 12:54	KNC	EET KNX
	Instrument ID: DUO									
Step 5	SEP	Organic-Bound			5.00 g	75mL	75406	07/17/23 08:00	LAH	EET KNX
Step 5	Prep	3010A			5 mL	50mL	75487	07/19/23 08:00	LAH	EET KNX
Step 5	Analysis	6010B SEP		5			75894	07/28/23 13:44	KNC	EET KNX
	Instrument ID: DUO									
Step 6	SEP	Acid/Sulfide			5.00 g	250 mL	75511	07/19/23 08:00	LAH	EET KNX
Step 6	Analysis	6010B SEP		1			75894	07/28/23 14:34	KNC	EET KNX
	Instrument ID: DUO									
Step 7	Prep	Residual			1.00 g	50mL	75565	07/20/23 08:00	LAH	EET KNX
Step 7	Analysis	6010B SEP		1			75976	07/31/23 12:51	KNC	EET KNX
	Instrument ID: DUO									

Laboratory References:

EET KNX = Eurofins Knoxville, 5815 Middlebrook Pike, Knoxville, TN 37921, TEL (865)291-3000

Accreditation/Certification Summary

Client: Geosyntec Consultants Inc
Project/Site: Vermilion SEP

Job ID: 140-32513-1

Laboratory: Eurofins Knoxville

All accreditations/certifications held by this laboratory are listed. Not all accreditations/certifications are applicable to this report.

Authority	Program	Identification Number	Expiration Date
	AFCEE	N/A	
ANAB	Dept. of Defense ELAP	L2311	02-13-25
ANAB	Dept. of Energy	L2311.01	02-13-25
ANAB	ISO/IEC 17025	L2311	02-13-25
Arkansas DEQ	State	88-0688	06-16-24
Colorado	State	TN00009	02-29-24
Connecticut	State	PH-0223	09-30-23
Florida	NELAP	E87177	06-30-24
Georgia (DW)	State	906	07-27-25
Hawaii	State	NA	07-27-23 *
Kansas	NELAP	E-10349	10-31-23
Kentucky (DW)	State	90101	12-31-23
Louisiana (All)	NELAP	83979	06-30-24
Louisiana (DW)	State	LA019	12-31-23
Maryland	State	277	03-31-24
Michigan	State	9933	07-27-25
Nevada	State	TN00009	07-31-23 *
New Hampshire	NELAP	2999	01-17-24
New Jersey	NELAP	TN001	07-01-24
New York	NELAP	10781	03-31-24
North Carolina (DW)	State	21705	07-31-24
North Carolina (WW/SW)	State	64	12-31-23
Oklahoma	State	9415	08-31-23
Oregon	NELAP	TNI0189	01-01-24
Pennsylvania	NELAP	68-00576	12-01-23
Tennessee	State	02014	07-27-25
Texas	NELAP	T104704380-22-17	08-31-23
US Fish & Wildlife	US Federal Programs	058448	07-31-24
USDA	US Federal Programs	525-22-279-18762	10-06-25
Utah	NELAP	TN00009	07-31-24
Virginia	NELAP	460176	09-14-23
Washington	State	C593	01-19-24
West Virginia (DW)	State	9955C	12-31-23
West Virginia DEP	State	345	04-30-24
Wisconsin	State	998044300	08-31-23

* Accreditation/Certification renewal pending - accreditation/certification considered valid.

Method Summary

Client: Geosyntec Consultants Inc
Project/Site: Vermilion SEP

Job ID: 140-32513-1

Method	Method Description	Protocol	Laboratory
6010B	SEP Metals (ICP) - Total	SW846	EETKNX
6010B SEP	SEP Metals (ICP)	SW846	EET KNX
Moisture	Percent Moisture	EPA	EET KNX
3010A	Preparation, Total Metals	SW846	EET KNX
Acid/Sulfide	Sequential Extraction Procedure, Acid/Sulfide Fraction	TAL-KNOX	EET KNX
Carbonate	Sequential Extraction Procedure, Carbonate Fraction	TAL-KNOX	EETKNX
Exchangeable	Sequential Extraction Procedure, Exchangeable Fraction	TAL-KNOX	EETKNX
Metal Hydroxide	Sequential Extraction Procedure, Metal Hydroxide Fraction	TAL-KNOX	EET KNX
Non-Crystalline	Sequential Extraction Procedure, Non-crystalline Materials	TAL-KNOX	EET KNX
Organic-Bound	Sequential Extraction Procedure, Organic Bound Fraction	TAL-KNOX	EETKNX
Residual	Sequential Extraction Procedure, Residual Fraction	TAL-KNOX	EET KNX
Total	Preparation, Total Material	TAL-KNOX	EET KNX

Protocol References:

EPA = US Environmental Protection Agency
SW846 = "Test Methods For Evaluating Solid Waste, Physical/Chemical Methods", Third Edition, November 1986 And Its Updates.
TAL-KNOX = TestAmerica Laboratories, Knoxville, Facility Standard Operating Procedure.

Laboratory References:

EET KNX = Eurofins Knoxville, 5815 Middlebrook Pike, Knoxville, TN 37921. TEL (865)291-3000

Eurofins TestAmerica, Knoxville
5815 Middlebrook Pike
Knoxville, TN 37921-5947
phone 865.291.3000 fax 865.584.4315

Chain of Custody Record

eurofins Environment Testing TestAmerica

Regulatory Program: ☐ DW ☐ NPDES ☐ RCRA ☑ Other:

TestAmerica Laboratories, Inc. d/b/a Eurofins TestAmerica

Client Contact	Project Manager: Allison Kreinberg	Site Contact: NA	Date:	COC No:
Geosyntec Consultants, Inc.	Tel/Fax:	Lab Contact: Ryan Henry	Carrier:	1 of 1 COCs
941 Chatham Lane, Suite 103	Analysis Turnaround Time			Sampler:
Columbus, OH 43221	☐ CALENDAR DAYS ☐ WORKING DAYS			For Lab Use Only:
(614) 468-0421 Phone	TAT if different from Below			Walk-in Client:
	☒ 2 weeks			Lab Sampling:
Project Name: Vistra	☐ 1 week			
Site: Vermilion	☐ 2 days			Job / SDG No.:
P O #	☐ 1 day			

Sample Identification	Sample Date	Sample Time	Sample Type (C=Comp. G=Grab)	Matrix	# of Cont.	Filtered Sample (Y / N)	Perform MS / MSD (Y / N)	6010B SEP (Li, Fe, Mn)	Sample Specific Notes:
VER-35 55-60 20230624	6/24/2023	1420	G	Solid	1	N	N	X	
VER-35 60-63 20230624	6/24/2023	1450	G	Solid	1	N	N	X	
VER-70 75-80 20230623	6/23/2023	1700	G	Solid	1	N	N	X	

No Custody Seal
Received Ambient RT: 20.0/CT: 20.3
DH 7/3/23
1 Box FedEx 7804 7929 1869 G

140-32513 Chain of Custody

Preservation Used: 1= Ice, 2= HCl; 3= H2SO4; 4=HNO3; 5=NaOH; 6= Other

Possible Hazard Identification:
Are any samples from a listed EPA Hazardous Waste? Please List any EPA Waste Codes for the sample in the Comments Section if the lab is to dispose of the sample.

☑ Non-Hazard ☐ Flammable ☐ Skin Irritant ☐ Poison B ☐ Unknown

Sample Disposal (A fee may be assessed if samples are retained longer than 1 month)

☐ Return to Client ☐ Disposal by Lab ☑ Archive for ______ Months

Special Instructions/QC Requirements & Comments:

Custody Seals Intact: ☐ Yes ☐ No	Custody Seal No.:		Cooler Temp. (°C): Obs'd: ______ Corr'd: ______ Therm ID No.: ______		
Relinquished by: Indu Keller	Company: GEOSYNTEC	Date/Time: 6/28/23	Received by: Dean Hill	Company: ETA Knx	Date/Time: 7/3/23 ~~9:00~~ 11:15
Relinquished by:	Company:	Date/Time:	Received by:	Company:	Date/Time:
Relinquished by:	Company:	Date/Time:	Received in Laboratory by:	Company:	Date/Time:

Form No. CA-C-WI-002, Rev. 4.21, dated 4/4/2019

Loc: 140
32513

EUROFINS/TESTAMERICA KNOXVILLE SAMPLE RECEIPT/CONDITION UPON RECEIPT ANOMALY CHECKLIST **Log In Number:**

Review Items	Yes	No	NA	If No, what was the problem?	Comments/Actions Taken
1. Are the shipping containers intact?	✓			☐ Containers, Broken	
2. Were ambient air containers received intact?			✓	☐ Checked in lab	ID,
3. The coolers/containers custody seal if present, is it intact?			✓	☐ Yes ☐ NA	
4. Is the cooler temperature within limits? (> freezing temp. of water to 6 °C, VOST: 10°C) Thermometer ID : SC73 Correction factor: +0.3°C			✓	☐ Cooler Out of Temp, Client Contacted, Proceed/Cancel ☐ Cooler Out of Temp, Same Day Receipt	
5. Were all of the sample containers received intact?	✓			☐ Containers, Broken	
6. Were samples received in appropriate containers?			✓	☐ Containers, Improper; Client Contacted; Proceed/Cancel	
7. Do sample container labels match COC? (IDs, Dates, Times)	✓			☐ COC & Samples Do Not Match ☐ COC Incorrect/Incomplete ☐ COC Not Received	
8. Were all of the samples listed on the COC received?	✓			☐ Sample Received, Not on COC ☐ Sample on COC, Not Received	
9. Is the date/time of sample collection noted?	✓			☐ COC; No Date/Time; Client Contacted	**Labeling Verified by:** **Date:**
10. Was the sampler identified on the COC?		✓		☐ Sampler Not Listed on COC	
11. Is the client and project name/# identified?	✓			☐ COC Incorrect/Incomplete	**pH test strip lot number:**
12. Are tests/parameters listed for each sample?	✓			☐ COC No tests on COC	
13. Is the matrix of the samples noted?	✓			☐ COC Incorrect/Incomplete	
14. Was COC relinquished? (Signed/Dated/Timed)	✓			☐ COC Incorrect/Incomplete	
15. Were samples received within holding time?	✓			☐ Holding Time - Receipt	
16. Were samples received with correct chemical preservative (excluding Encore)?			✓	☐ pH Adjusted, pH Included (See box 16A) ☐ Incorrect Preservative	
17. Were VOA samples received without headspace?			✓	☐ Headspace (VOA only)	
18. Did you check for residual chlorine, if necessary? (e.g. 1613B, 1668) Chlorine test strip lot number:			✓	☐ Residual Chlorine	
19. For 1613B water samples is pH<9?			✓	☐ If no, notify lab to adjust	
20. For rad samples was sample activity info. Provided?			✓	☐ Project missing info	

	Box 16A: pH Preservation	Box 18A: Residual Chlorine
Preservative:		
Lot Number:		
Exp Date:		
Analyst:		
Date:		
Time:		

Project #: 14016199 PM Instructions:

Sample Receiving Associate: Date: 7/3/23

13 12 11 10 9 8 7 6 5 4 3 2 1

ATTACHMENT 4
X-Ray Diffraction
Laboratory Analytical Report

SGS

Quantitative X-Ray Diffraction by Rietveld Refinement

Report Prepared for:	*Environmental Services*
Project Number/ LIMS No.	*Custom XRD/MI4526-AUG23*
Sample Receipt:	*August 10, 2023*
Sample Analysis:	*August 31, 2023*
Reporting Date:	*September 13, 2023*

Instrument:	BRUKER AXS D8 Advance Diffractometer
Test Conditions:	Co radiation, 35 kV, 40 mA; Detector: LYNXEYE Regular Scanning: Step: 0.02°, Step time: 0.75s, 2θ range: 6-80° Clay Section Scanning: Step: 0.01°, Step time:0.2s, 2θ range: 3-40°
Interpretations:	PDF2/PDF4 powder diffraction databases issued by the International Center for Diffraction Data (ICDD). DiffracPlus Eva and Topas software.
Detection Limit:	0.5-2%. Strongly dependent on crystallinity.

Contents:

1) Method Summary
2) Quantitative XRD Results
3) XRD Pattern(s)

Kim Gibbs

Zhihai (Adrian) Zhang, Ph.D
Mineralogist

Kim Gibbs, H.B.Sc., P.Geo.
Senior Mineralogist

ACCREDITATION: SGS Natural Resources Lakefield is accredited to the requirements of ISO/IEC 17025 for specific tests as listed on our scope of accreditation, including geochemical, mineralogical and trade mineral tests. To view a list of the accredited methods, please visit the following website and search SGS Canada Inc. - Minerals: https://www.scc.ca/en/search/palcan.

SGS Natural Resources
a division of SGS Canada Inc.

P.O. Box 4300, 185 Concession Street, Lakefield, Ontario, Canada K0L 2H0
Tel: (705) 652-2000 Fax: (705) 652-6365 www.sgs.com www.sgs.com/met
Member of the SGS Group (SGS SA)

SGS

Method Summary

The Rietveld Method of Mineral Identification by XRD (ME-LR-MIN-MET-MN-D05) method used by SGS Natural Resources is accredited to the requirements of ISO/IEC 17025.

Mineral Identification and Interpretation:

Mineral identification and interpretation involves matching the diffraction pattern of an unknown material to patterns of single-phase reference materials. The reference patterns are compiled by the Joint Committee on Powder Diffraction Standards - International Center for Diffraction Data (JCPDS-ICDD) database and released on software as Powder Diffraction Files (PDF).

Interpretations do not reflect the presence of non-crystalline and/or amorphous compounds, except when internal standards have been added by request. Mineral proportions may be strongly influenced by crystallinity, crystal structure and preferred orientations. Mineral or compound identification and quantitative analysis results should be accompanied by supporting chemical assay data or other additional tests.

Clay Mineral Separation and Identification:

Clay minerals are typically fine-grained (<2 μm) phyllosilicates in sedimentary rock. Due to the poor crystallinity and fine size of clay minerals, separation of the clay fraction from bulk samples by centrifuge is required. A slide of the oriented clay fraction is prepared and scanned followed by a series of procedures (the addition of ethylene glycol and high temperature heating). Clay minerals are identified by their individual diffraction patterns and changes in their diffraction pattern after different treatments. Clay speciation and mineral identification of the bulk sample are performed using DIFFRACplus EVA (Bruker AXS).

Quantitative Rietveld Analysis:

Quantitative Rietveld Analysis is performed by using Topas 4.2 (Bruker AXS), a graphics based profile analysis program built around a non-linear least squares fitting system, to determine the amount of different phases present in a multicomponent sample. Whole pattern analyses are predicated by the fact that the X-ray diffraction pattern is a total sum of both instrumental and specimen factors. Unlike other peak intensity-based methods, the Rietveld method uses a least squares approach to refine a theoretical line profile until it matches the obtained experimental patterns.

Rietveld refinement is completed with a set of minerals specifically identified for the sample. Zero values indicate that the mineral was included in the refinement calculations, but the calculated concentration was less than 0.05wt%. Minerals not identified by the analyst are not included in refinement calculations for specific samples and are indicated with a dash.

Environmental Services
Custom XRD/MI4526-AUG23
13-Sep-23

Summary of Rietveld Quantitative Analysis X-Ray Diffraction Results

Mineral/Compound	VER-35 55-60 20230624 AUG4526-01 (wt %)	VER-35 60-63 20230624 AUG4526-02 (wt %)	VER-70 30-40 20230623 AUG4526-03 (wt %)	VER-70 41-42 20230623 AUG4526-04 (wt %)	VER-70 75-80 20230623 AUG4526-05 (wt %)
Quartz	38.5	38.1	48.6	48.2	35.0
Chlorite	6.9	6.8	1.2	3.6	7.7
Muscovite	23.4	23.0	13.5	15.2	27.0
Albite	12.6	12.6	10.6	10.8	11.5
Microcline	1.0	1.1	1.3	1.1	0.7
Siderite	4.9	5.0	0.9	0.1	5.4
Actinolite	-	-	0.8	-	-
Dolomite	-	-	11.7	11.7	-
Clays					
Illite	7.1	8.0	7.4	5.6	5.2
Kaolinite	5.6	5.4	3.2	3.7	7.5
Montmorillonite	-	-	0.8	-	-
TOTAL	100	100	100	100	100

Zero values indicate that the mineral was included in the refinement, but the calculated concentration is below a measurable value.

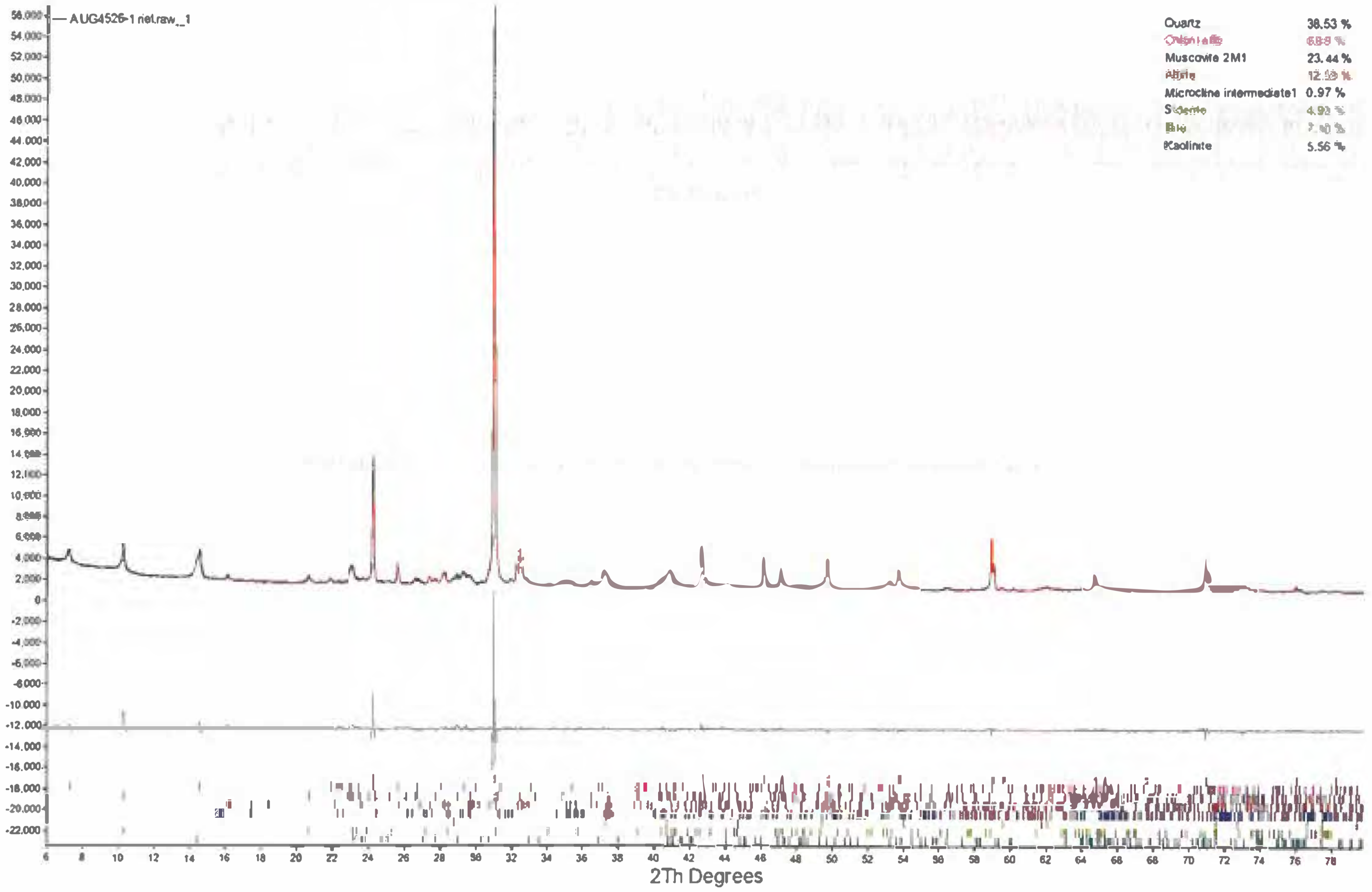
Dashes indicate that the mineral was not identified by the analyst and not included in the refinement calculation for the sample.

The weight percent quantities indicated have been normalized to a sum of 100%. The quantity of amorphous material has not been determined.

Mineral/Compound	Formula
Quartz	SiO_2
Chlorite	$(Fe,(Mg,Mn)_5,Al)(Si_3Al)O_{10}(OH)_8$
Muscovite	$KAl_2(AlSi_3O_{10})(OH)_2$
Albite	$NaAlSi_3O_8$
Microcline	$KAlSi_3O_8$
Siderite	$FeCO_3$
Illite	$(K,H_3O)(Al,Mg,Fe)_2(Si,Al)_4O_{10}[(OH)_2,(H_2O)]$
Kaolinite	$Al_2Si_2O_5(OH)_4$
Actinolite	$Ca_2(Mg,Fe)_5Si_8O_{22}(OH)_2$
Dolomite	$CaMg(CO_3)_2$
Montmorillonite	$(Na,Ca)_{0.3}(Al,Mg)_2Si_4O_{10}(OH)_2 \cdot 10H_2O$

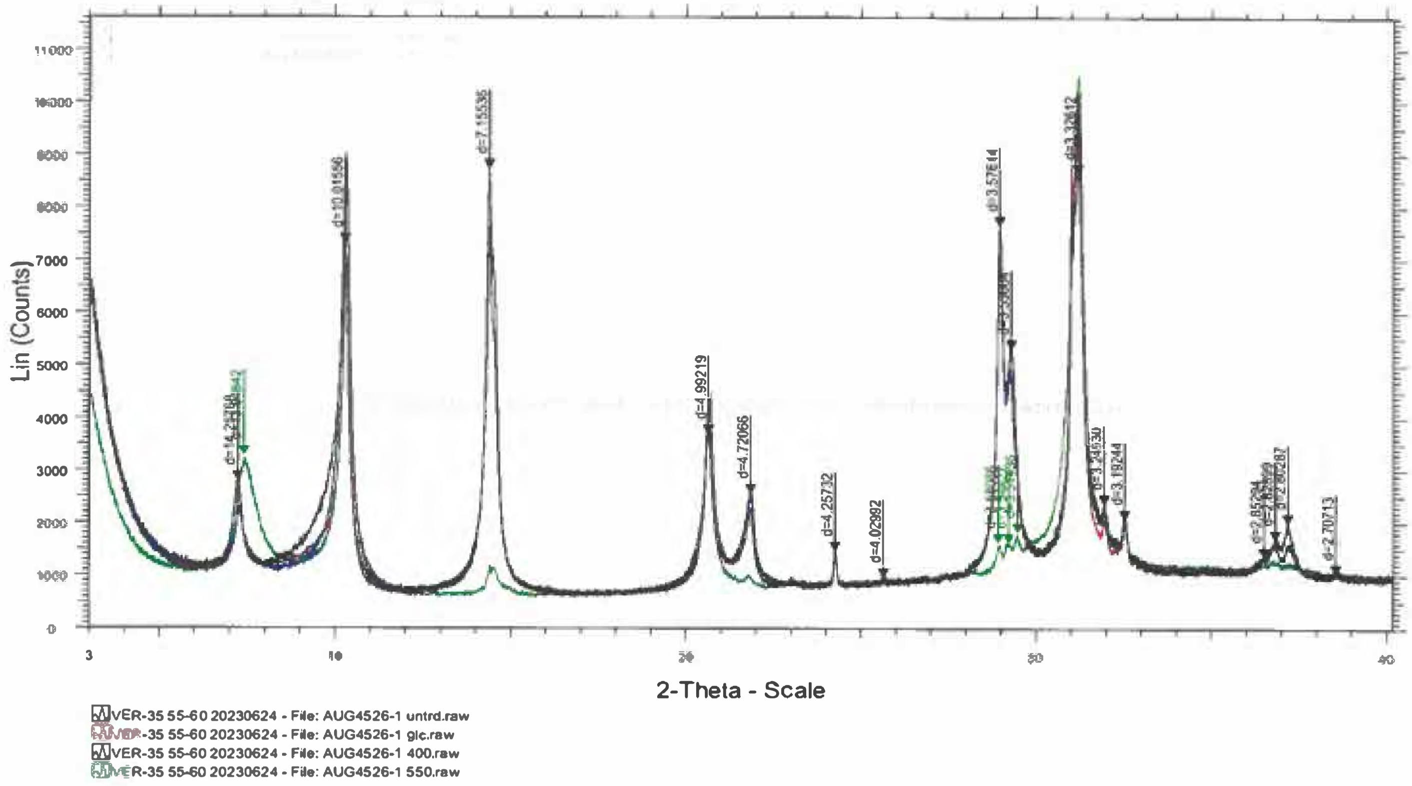
Environmental Services
Custom XRD/MI4526-AUG23
13-Sep-23

VER-35 55-60 20230624



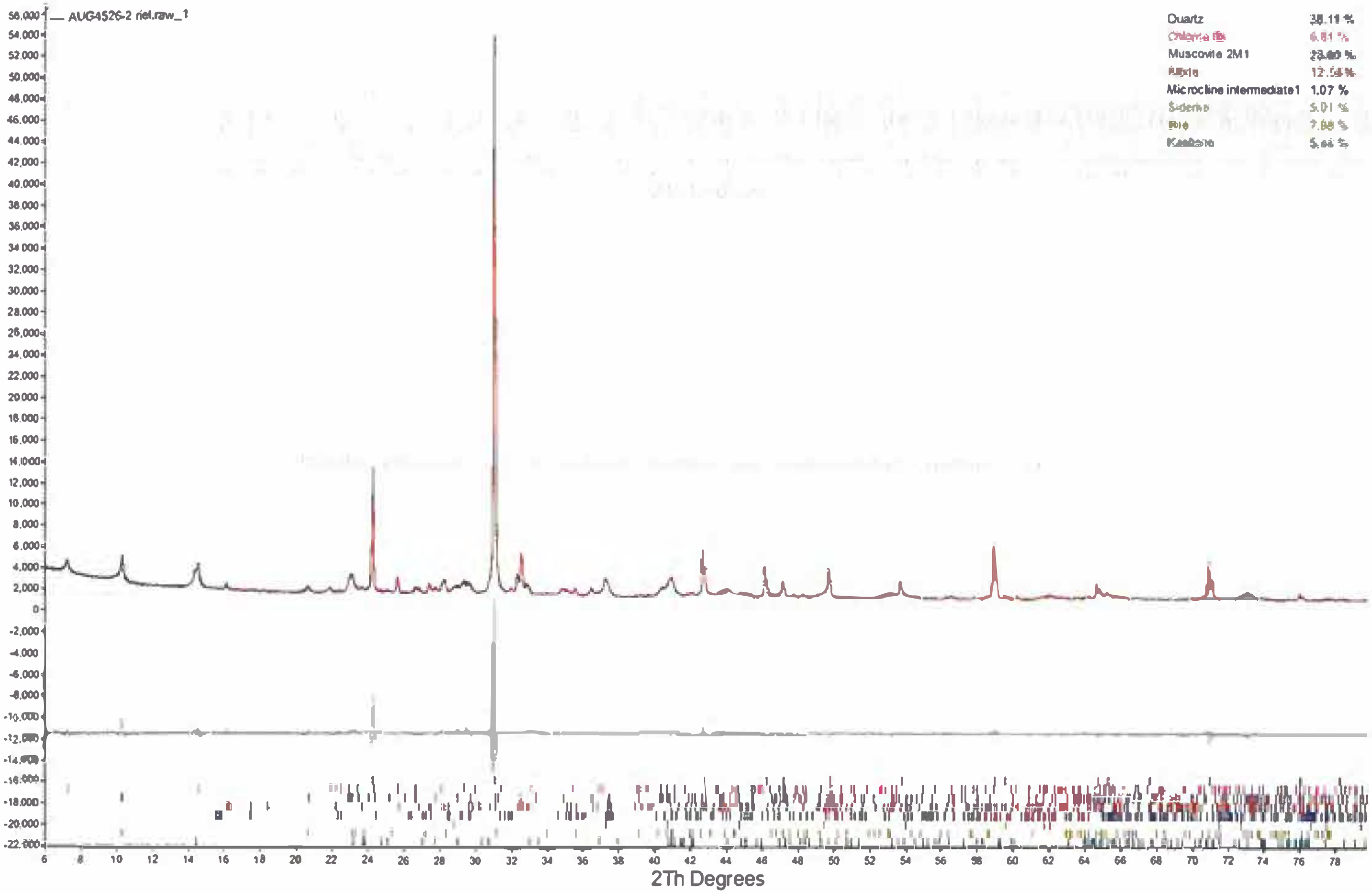
Environmental Services
Custom XRD/MI4526-AUG23
13-Sep-23

VER-35 55-60 20230624



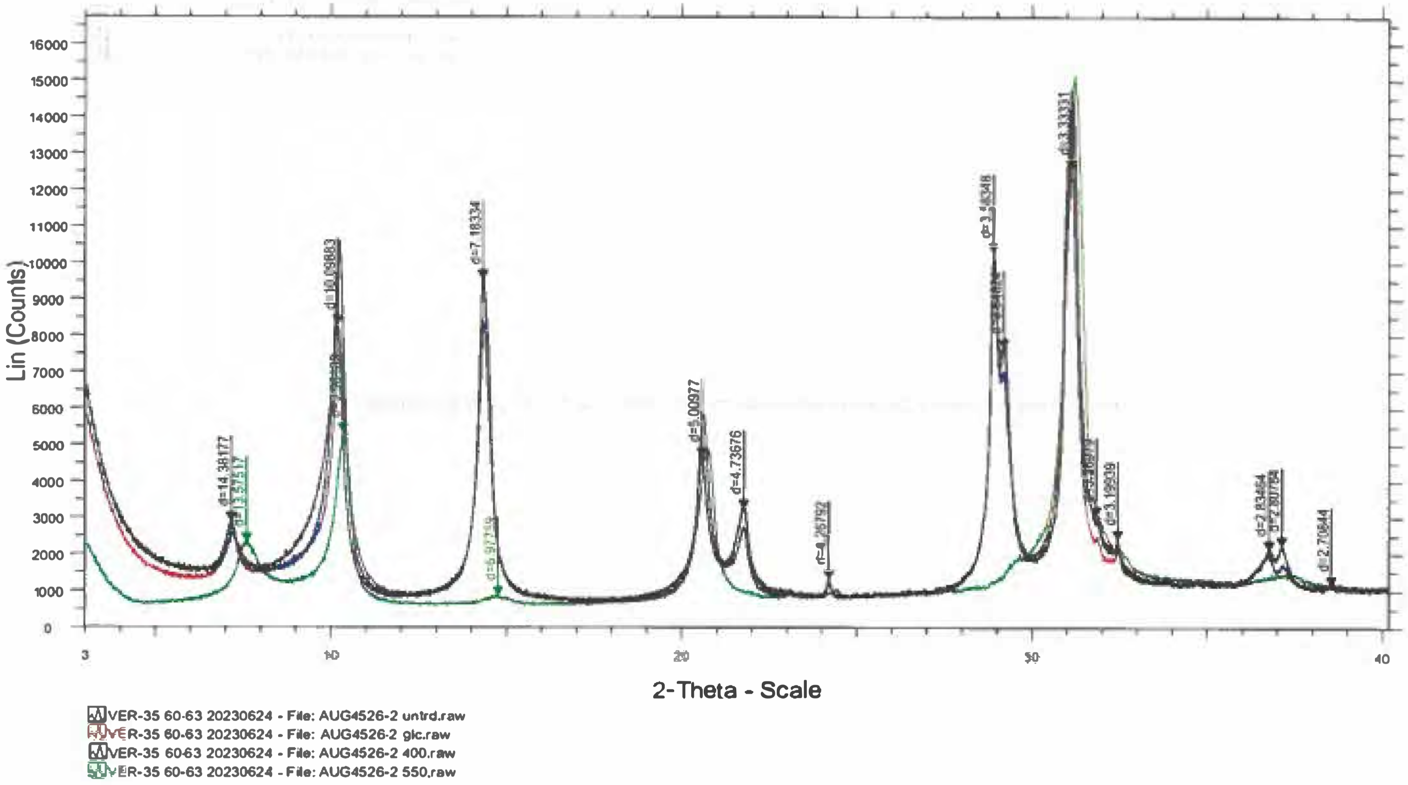
Environmental Services
Custom XRD/MI4526-AUG23
13-Sep-23

VER-35 60-63 20230624



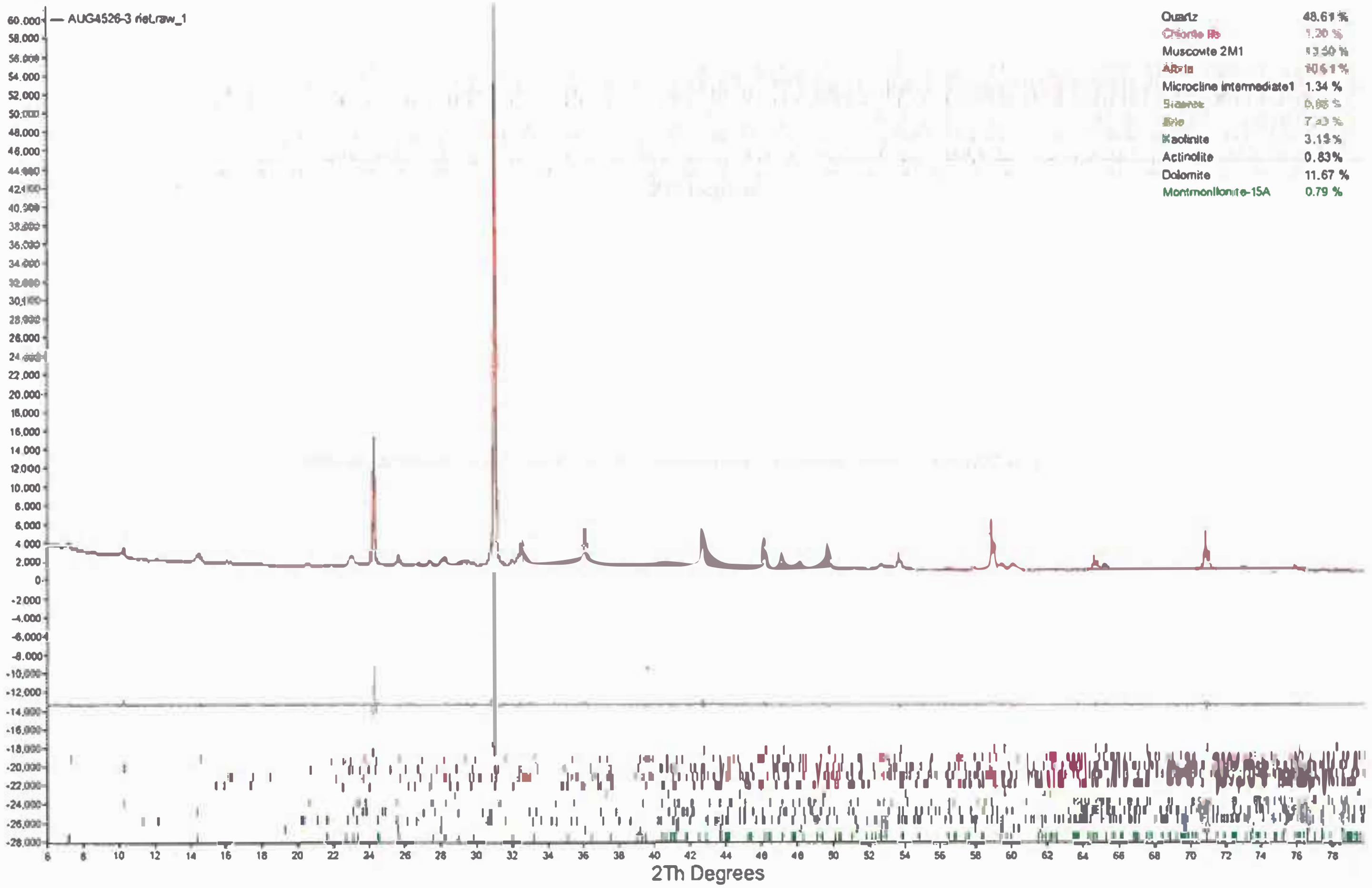
Environmental Services
Custom XRD/MI4526-AUG23
13-Sep-23

VER-35 60-63 20230624



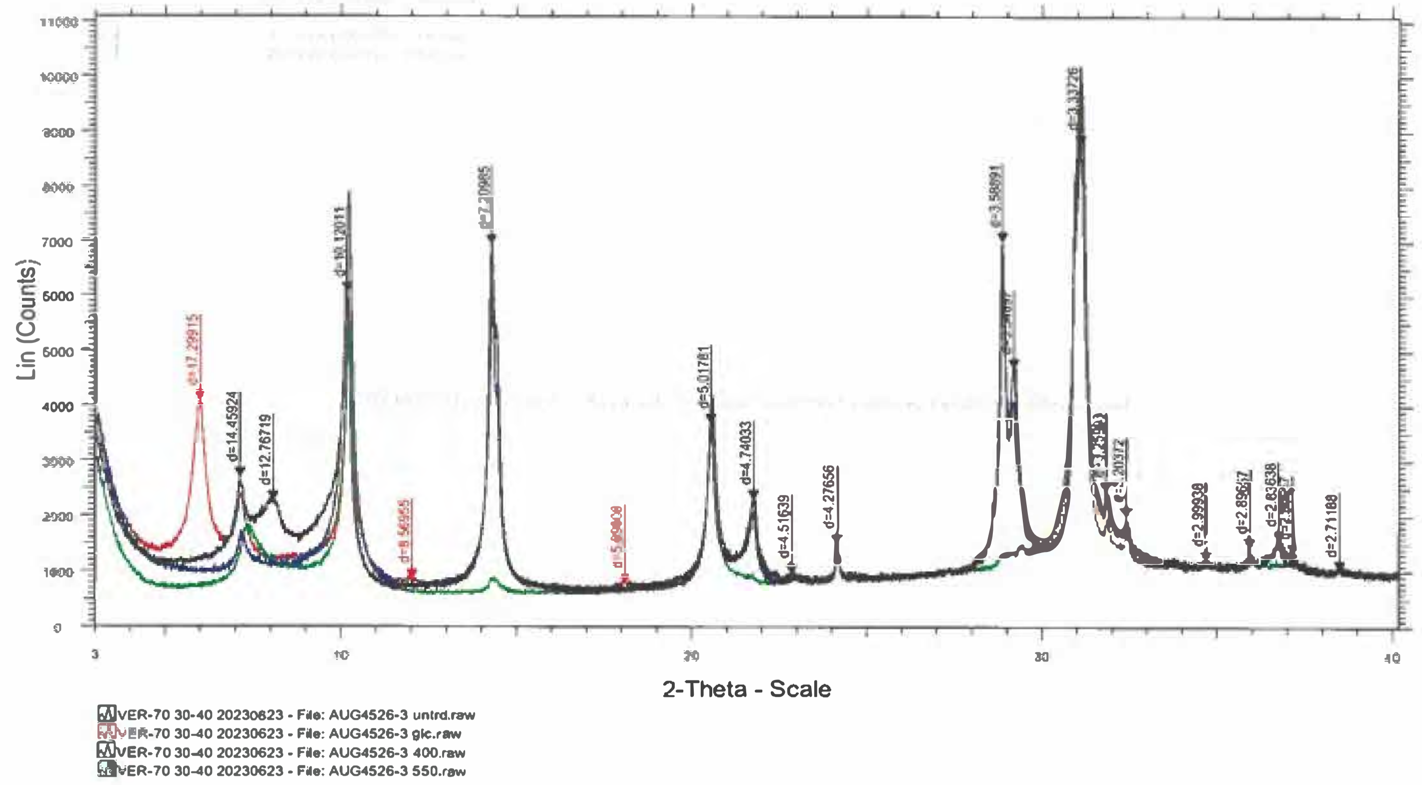
Environmental Services
Custom XRD/MI4526-AUG23
13-Sep-23

VER-70 30-40 20230623



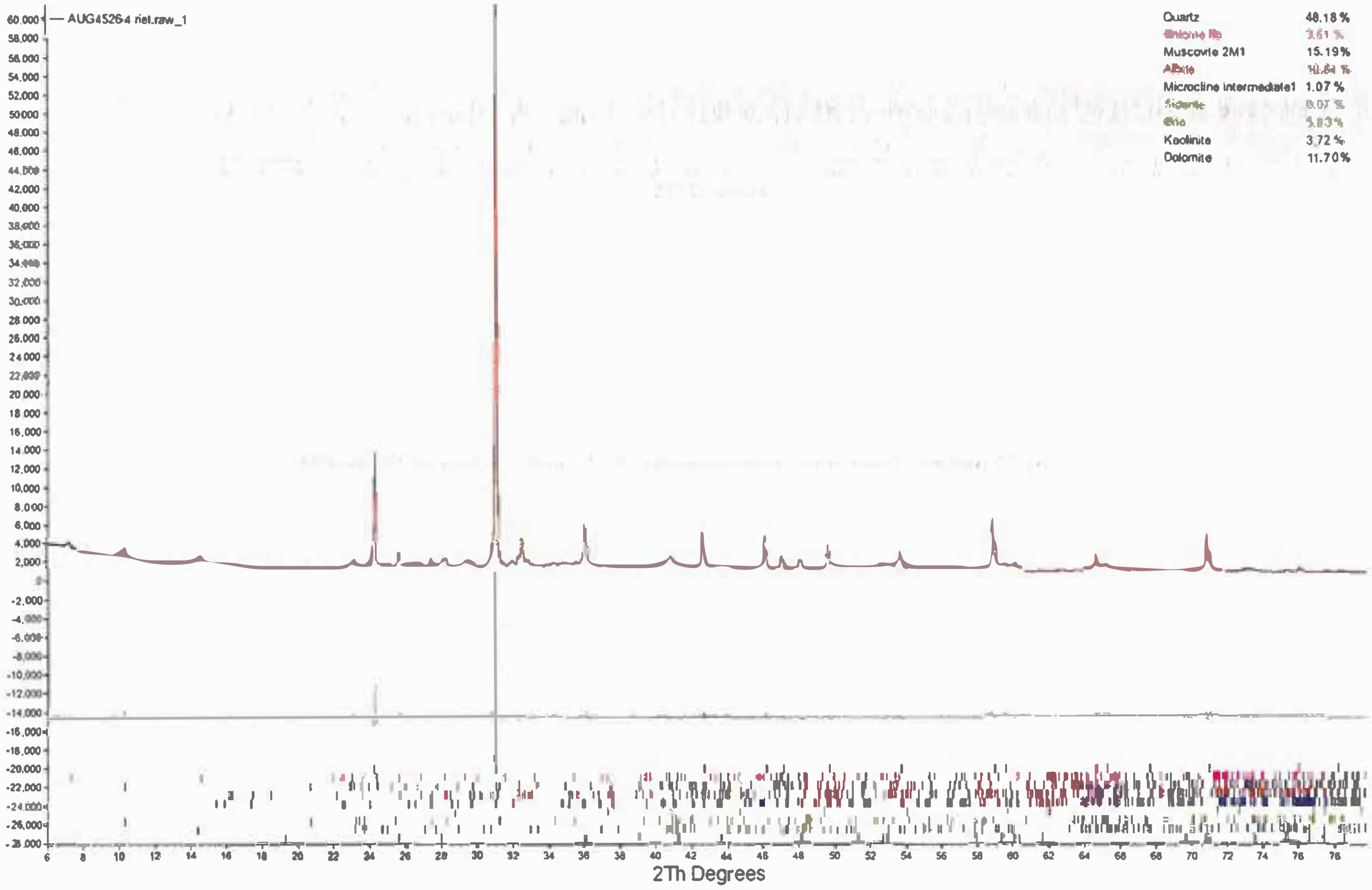
Environmental Services
Custom XRD/MI4526-AUG23
13-Sep-23

VER-70 30-40 20230623



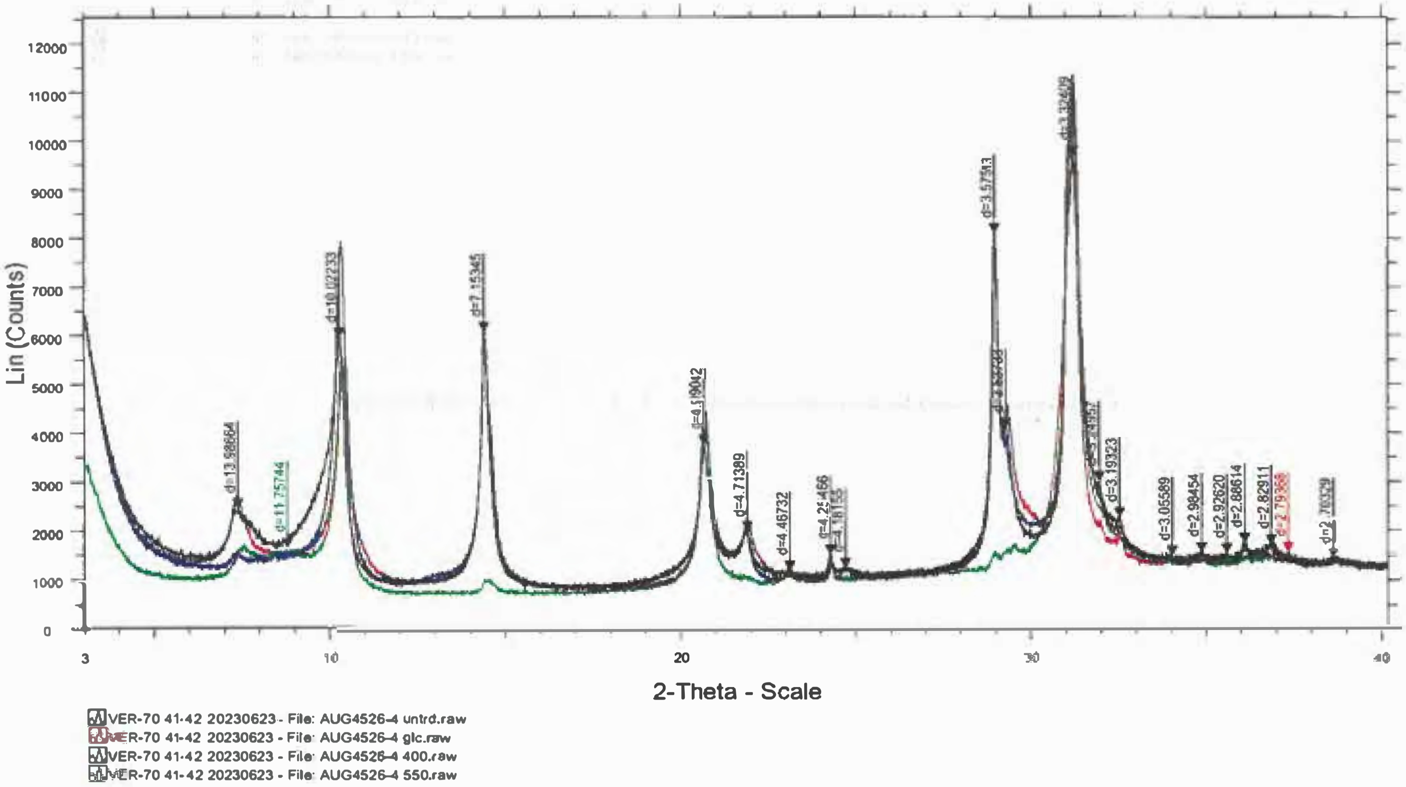
Environmental Services
Custom XRD/MI4526-AUG23
13-Sep-23

VER-70 41-42 20230623

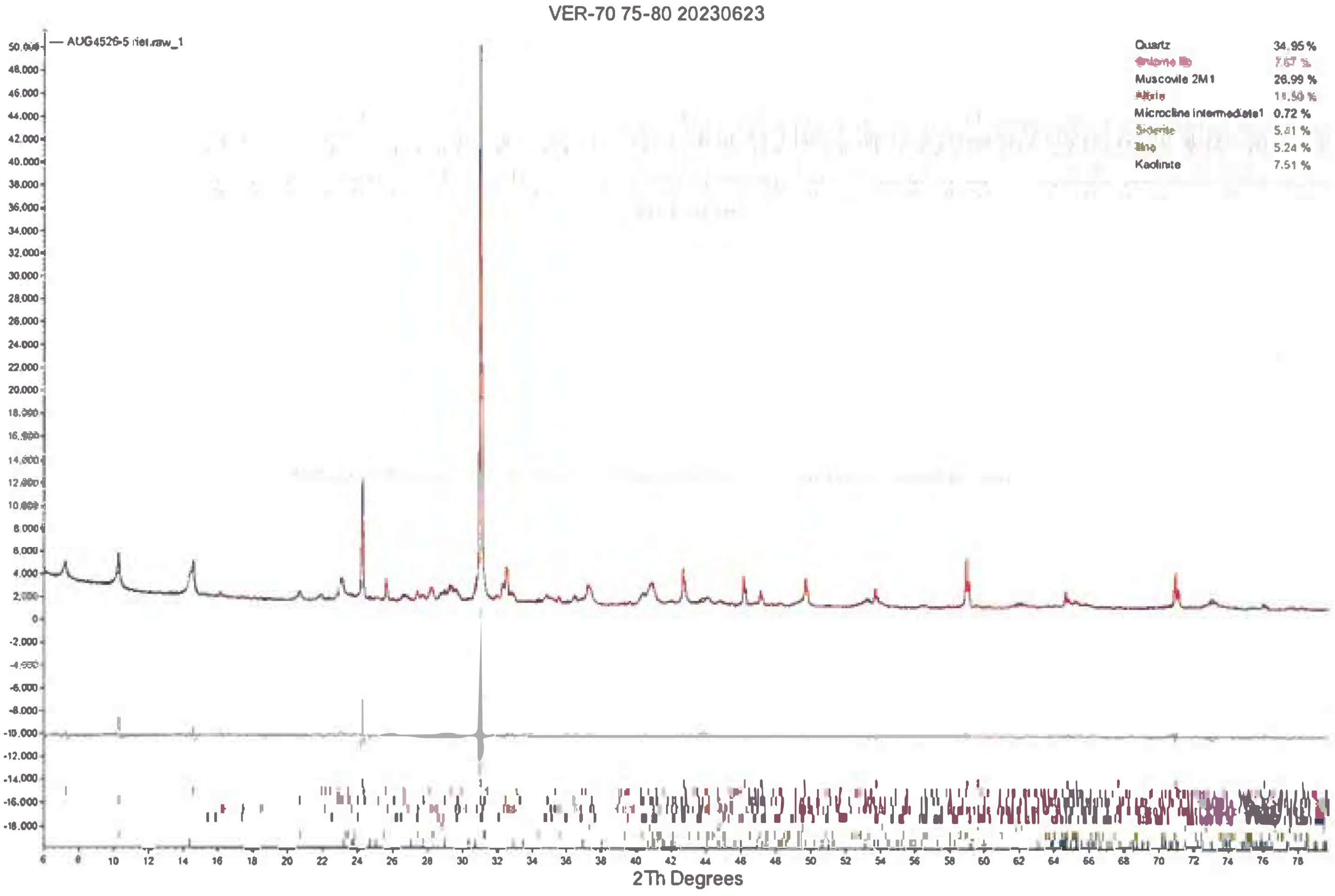


Environmental Services
Custom XRD/MI4526-AUG23
13-Sep-23

VER-70 41-42 20230623



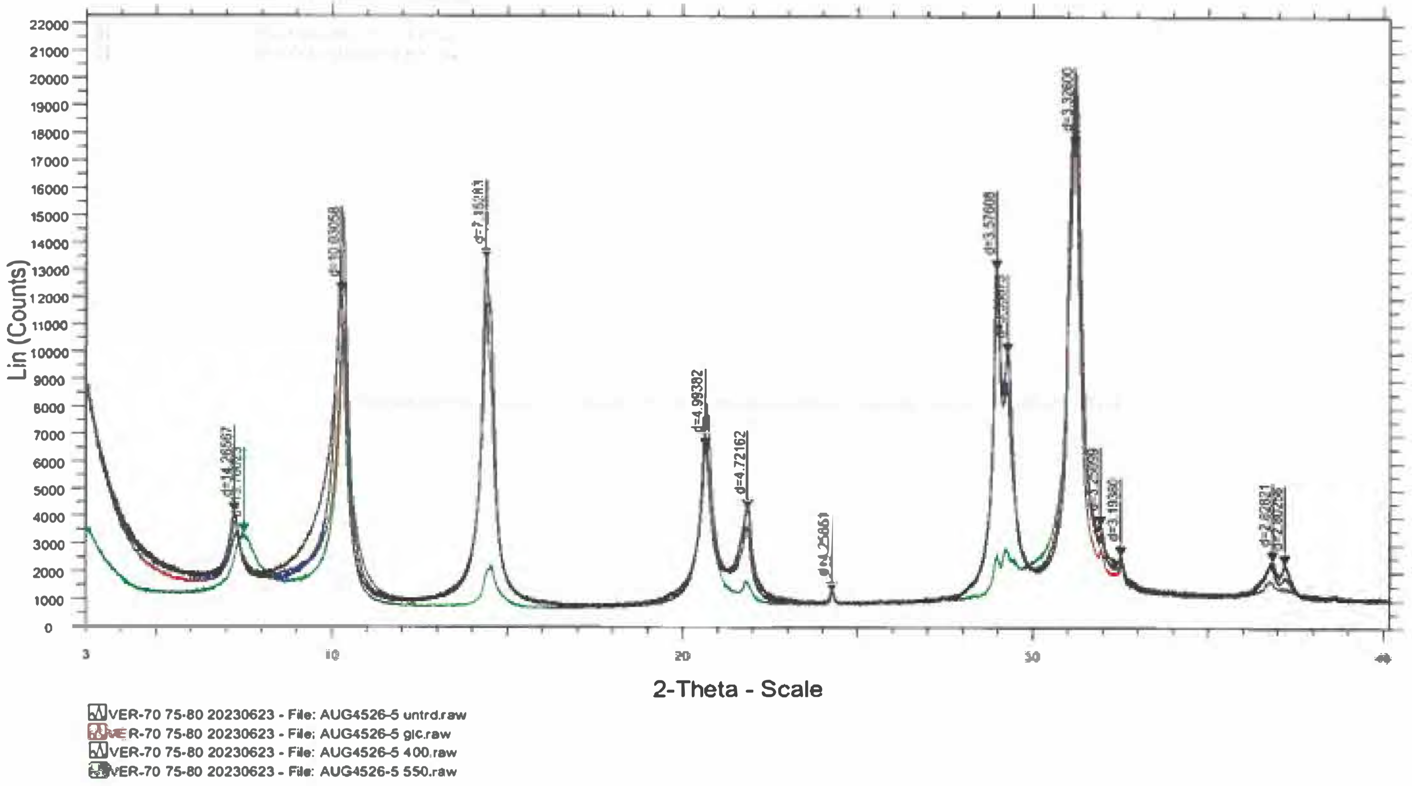
Environmental Services
Custom XRD/MI4526-AUG23
13-Sep-23



VER-70 75-80 20230623

Environmental Services
Custom XRD/MI4526-AUG23
13-Sep-23

VER-70 75-80 20230623



ATTACHMENT 5

Principal Component Analysis Input Data

ELECTRONIC PCA DATA FOR ATTACHMENT 5
35 I.A.C. § 845 ALTERNATIVE SOURCE DEMONSTRATION
VERMILION POWER PLANT
NEW EAST ASH POND
OAKWOOD, IL

Well	HSU	Date	Well Type	pH (SU)	Alkalinity, bicarbonate (mg/L)	Alkalinity, carbonate (mg/L)	Barium (mg/L)	Boron (mg/L)	Calcium (mg/L)	Chloride (mg/L)	Fluoride (mg/L)
16A	BCU	4/1/2021	Downgradient	7.50	390	1.5	0.261	0.675	40.8	131	0.77
16A	BCU	4/21/2021	Downgradient	7.20	407	1.5	0.335	0.613	71.10	106	0.64
16A	BCU	5/11/2021	Downgradient	7.40	361	1.5	0.245	0.807	36.6	139	0.78
16A	BCU	6/3/2021	Downgradient	7.26	405	1.5	0.272	0.716	51.60	128	0.68
16A	BCU	6/17/2021	Downgradient	7.40	406	1.5	0.251	0.746	42.20	144	0.78
16A	BCU	7/8/2021	Downgradient	7.31	404	1.5	0.249	0.768	38.00	151	0.77
16A	BCU	7/27/2021	Downgradient	7.45	390	1.5	0.248	0.794	35.30	163	0.84
16A	BCU	8/17/2021	Downgradient	7.50	393	1.5	0.261	0.755	33.30	176	0.84
35D	BCU	4/1/2021	Downgradient	8.20	707	1.5	0. .11	2.01	112.0	529	0.76
35D	BCU	4/21/2021	Downgradient	7.76	533	1.5	0.0294	1.8	93.60	281	0.65
35D	BCU	6/3/2021	Downgradient	7.25	637	1.5	0.0546	2.5	98.10	461	0.75
35D	BCU	6/17/2021	Downgradient	7.25	603	1.5	0.14	1.8	99.40	393	0.75
35D	BCU	7/8/2021	Downgradient	7.22	582	1.5	0.0297	1.9	86.00	372	0.74
35D	BCU	7/27/2021	Downgradient	7.37	507	1.5	0.0263	1.5	70.40	234	0.79
350	BCU	8/17/2021	Downgradient	7.30	491	1.5	0.0269	1.4	65.7	199	0.76
70D	BCU	4/1/2021	Downgradient	7.60	262	1.5	0.3360	0.712	39.6	317	0.76
70D	BCU	4/21/2021	Downgradient	7.28	334	1.5	0.521	1.01	48.1	517	0.57
70D	BCU	6/3/2021	Downgradient	7.03	416	1.5	0.687	1.56	68.6	665	0.47
70D	BCU	6/17/2021	Downgradient	7.14	443	1.5	0.7260	1.33	73.1	680	0.5
70D	BCU	7/8/2021	Downgradient	6.85	527	1.5	0.954	1.58	82.5	735	0.41
70D	BCU	7/27/2021	Downgradient	6.96	540	1.5	0.734	1.54	78.1	745	0.44
70D	BCU	8/17/2021	Downgradient	6.84	610	1.5	0.761	1.54	91.5	716	0.36
71D	BCU	4/1/2021	Downgradient	7.60	258	1.5	0.299	0.58	37.7	172	0.92
71D	BCU	6/17/2021	Downgradient	7.15	475	1.5	0.4	1.1	28.7	563	0.73
71D	BCU	8/17/2021	Downgradient	6.95	628	1.5	0.677	1.3	34.9	674	0.56
22	BCU	4/1/2021	Upgradient	7.40	390	1.5	0.0723	0.41	41.5	23	0.43
22	BCU	4/20/2021	Upgradient	7.58	407	1.5	0.0798	0.4	37.5	11	0.4000
22	BCU	5/10/2021	Upgradient	7.29	395	1.5	0.0795	0.433	45.7	11	0.4200
22	BCU	6/3/2021	Upgradient	7.26	390	1.5	0.0787	0.361	48.3	7	0.3800
22	BCU	6/17/2021	Upgradient	7.23	406	1.5	0.0791	0.377	50.3	7	0.3900
22	BCU	7/8/2021	Upgradient	7.20	412	1.5	0.082	0.348	47.7	7	0.37
22	BCU	7/27/2021	Upgradient	7.34	401	1.5	0.0795	0.311	48.2	7	0.39
22	BCU	8/17/2021	Upgradient	7.26	402	1.5	0.0785	0.34	47.1	7	0.38
NED1	CCR	4/1/2021	CCR	9.20	1.5	81	0.032	18.6	497.0	44	0.3200
NED1	CCR	4/21/2021	CCR	8.86	4	62	0.029	19.3	472.0	32	0.3800
NED1	CCR	5/11/2021	CCR	7.88	132	1.5	0.0289	14	674.0	18	0.2
NED1	CCR	6/4/2021	CCR	7.55	117	1.5	0.0319	13.5	532.0	18	0.24
NED1	CCR	8/17/2021	CCR	8.73	18	41	0.0314	18.3	531.0	25	0.29
10	UCU	4/1/2021	Upgradient	6.80	550	1.5	0.079	0.0587	182.0	6	0.13
10	UCU	4/21/2021	Upgradient	6.80	546	1.5	0.047	0.0587	193.0	6	0.14
10	UCU	5/10/2021	Upgradient	6.76	476	1.5	0.068	0.053	160.0	4	0.14
10	UCU	6/3/2021	Upgradient	6.74	579	1.5	0.0795	0.0835	186.0	5	0.14
10	UCU	6/17/2021	Upgradient	6.76	550	1.5	0.0625	0.111	186.0	6	0.14
10	UCU	7/8/2021	Upgradient	6.69	561	1.5	0.068	0.0499	166.0	5	0.13
10	UCU	7/27/2021	Upgradient	6.80	550	1.5	0.0712	0.237	182.0	4	0.14
10	UCU	8/17/2021	Upgradient	6.69	582	1.5	0.0772	0.0695	192.0	5	0.13
70S	UU	4/1/2021	Downgradient	7.00	310	1.5	0.018	0.457	253.0	19	0.14
70S	UU	4/21/2021	Downgradient	6.94	270	1.5	0.0205	0.403	281.0	17	0.14
70S	UU	5/10/2021	Downgradient	6.99	262	1.5	0.0185	0.382	270.0	16	0.14
70S	UU	6/3/2021	Downgradient	6.91	272	1.5	0.0165	0.424	245.0	15	0.14
70S	UU	6/17/2021	Downgradient	6.85	278	1.5	0.0187	0.363	250.0	15	0.15
70S	UU	7/8/2021	Downgradient	6.80	305	1.5	0.0172	0.253	220.0	14	0.16
70S	UU	7/27/2021	Downgradient	7.01	287	1.5	0.01	0.556	229.0	11	0.17
70S	UU	8/17/2021	Downgradient	6.87	272	1.5	0.02	0.538	232.0	15	0.16
71S	UU	4/1/2021	Downgradient	6.90	422	1.5	0.0476	0.179	115.0	2	0.18
71S	UU	4/21/2021	Downgradient	6.73	419	1.5	0.0534	0.215	116.0	3	0.17
71S	UU	5/12/2021	Downgradient	6.84	403	1.5	0.0487	0.227	124.0	3	0.18
71S	UU	6/3/2021	Downgradient	6.71	419	1.5	0.0446	0.229	116.0	2	0.18
71S	UU	6/17/2021	Downgradient	6.76	422	1.5	0.0421	0.219	117.0	2	0.19
71S	UU	7/8/2021	Downgradient	6.60	462	1.5	0.0493	0.173	128.0	2	0.19
71S	UU	7/27/2021	Downgradient	6.83	421	1.5	0.0462	0.251	132.0	2	0.2
71S	UU	8/17/2021	Downgradient	6.73	442	1.5	0.0672	0.272	122.0	3	0.19

Notes:
mg/L = milligrams per liter
SU= standard units
HSU = hydrostratigraphic unit
CCR = coal combustion residual
BCU = Bedrock Confining Unit
UCU = Upper Confining Unit
UU = Upper Unit
Non-detect values were replaced with half of detection limit.

DOCUMENT
17

Rees, Jeromy

From: Fuller, Rhys <Rhys.Fuller@vistracorp.com>
Sent: Tuesday, December 5, 2023 12:15 PM
To: MacDonna, Keegan
Subject: [External] RE: Groundwater Monitoring at Vermilion Power Plant – NPDES Permit IL0004057

Keegan,

Can they set the data to be reported +2 months after the quarter ends given the 60 day language in SC12? If DMR is programmed as you suggest then it basically forces us to sample during the first two months of each quarter given the lab turn around times and I don't read that as being the intent behind SC12 (we juggle a lot of groundwater sampling and Vermilion is typically later on our quarterly schedule).

Also, can you confirm that we are not required to submit hard copies (as we've historically done) given we'll be entering the data into nDMR (something that has not previously been required)? Or is the intent for us to do both?

Thanks,

Rhys
618-975-1799

From: MacDonna, Keegan <Keegan.MacDonna@Illinois.gov>
Sent: Tuesday, December 5, 2023 11:31 AM
To: Fuller, Rhys <Rhys.Fuller@vistracorp.com>
Subject: Groundwater Monitoring at Vermilion Power Plant – NPDES Permit IL0004057

EXTERNAL EMAIL

Good Morning Rhys,

I wanted to let you know that our Compliance Assurance Section is working on coding the parameters of the NPDES Permit for Vermilion Power Plant into the federal DMR tracking system. The quarterly DMR submission months for the groundwater monitoring required by Special Condition 12 have been set as January, April, July, and October. I wanted to make you aware of this, since that means that sample data for the groundwater monitoring wells will need to be submitted by next month. If you have any questions or concerns, please let me know.

Sincerely,

Illinois EPA

Keegan MacDonna | Environmental Protection Engineer
Bureau of Water, Division of Water Pollution Control
Permit Section – Industrial Unit
1021 N. Grand Ave. East, Springfield, IL 62794-9276
☎ (217) 524-3336 ✉ keegan.macdonna@illinois.gov
www.epa.illinois.gov

DOCUMENT
18

Rees, Jeromy

From:	Fuller, Rhys <Rhys.Fuller@vistracorp.com>
Sent:	Tuesday, December 5, 2023 3:01 PM
To:	MacDonna, Keegan
Subject:	[External] RE: Groundwater Monitoring at Vermilion Power Plant – NPDES Permit IL0004057

Thanks, that makes sense.

From: MacDonna, Keegan <Keegan.MacDonna@Illinois.gov>
Sent: Tuesday, December 5, 2023 2:33 PM
To: Fuller, Rhys <Rhys.Fuller@vistracorp.com>
Subject: RE: Groundwater Monitoring at Vermilion Power Plant – NPDES Permit IL0004057

EXTERNAL EMAIL

I followed up with Compliance, and it sounds like they have modified it to match the 60 day language in SC12. When a sample is taken in January, the due date would be 3/31/2024. The April sample would be due 6/30, the July sample would be due 9/30, and the October sample would be due 12/31/24.

They also noted that the groundwater monitoring data would not be entered into the DMR system, since DMRs are not intended to capture groundwater data. You can either submit hard copies as you have done in the past, or submit them via email to EPA.PrmtSpecCondtns@Illinois.gov.

Illinois EPA

Keegan MacDonna | Environmental Protection Engineer
Bureau of Water, Division of Water Pollution Control
Permit Section – Industrial Unit
1021 N. Grand Ave. East, Springfield, IL 62794-9276
☎ (217) 524-3336 ✉ keegan.macdonna@illinois.gov
www.epa.illinois.gov

From: Fuller, Rhys <Rhys.Fuller@vistracorp.com>
Sent: Tuesday, December 5, 2023 12:15 PM
To: MacDonna, Keegan <Keegan.MacDonna@Illinois.gov>
Subject: [External] RE: Groundwater Monitoring at Vermilion Power Plant – NPDES Permit IL0004057

Keegan,

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Thanks,

Rhys
618-975-1799

From: MacDonna, Keegan <Keegan.MacDonna@Illinois.gov>
Sent: Tuesday, December 5, 2023 11:31 AM
To: Fuller, Rhys <Rhys.Fuller@vistracorp.com>
Subject: Groundwater Monitoring at Vermilion Power Plant – NPDES Permit IL0004057

EXTERNAL EMAIL

Good Morning Rhys,

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Sincerely,

Illinois EPA

Keegan MacDonna | Environmental Protection Engineer
Bureau of Water, Division of Water Pollution Control
Permit Section – Industrial Unit
1021 N. Grand Ave. East, Springfield, IL 62794-9276
(217) 524-3336 keegan.macdonna@illinois.gov
www.epa.illinois.gov

DOCUMENT
19

Rees, Jeromy

From: Hunt, Lauren <Lauren.Hunt@Illinois.gov>
Sent: Tuesday, December 5, 2023 11:44 AM
To: Seif, Josiah
Subject: RE: Vermilion Power Plant New East Ash Pond received on December 1st 2023.

We didn't get the notification in the GWS BOW email box. That was what I was requesting.

Lauren I. Hunt, M.S.
(she/they/he)
Environmental Protection Geologist III
Illinois Environmental Protection Agency
Bureau of Water
Groundwater Section
1021 N. Grand Avenue
PO Box 13
Springfield, IL 62702
D: 217-524-9048
C: 309-361-0037
Lauren.hunt@illinois.gov
Hours: 8:30 am to 5:30 pm Tuesday through Friday
8:30 am to 4 pm Mondays and alternating Mondays off
Working remotely Mondays and Fridays.

From: Seif, Josiah <Josiah.Seif@Illinois.gov>
Sent: Tuesday, December 5, 2023 11:08 AM
To: Hunt, Lauren <Lauren.Hunt@Illinois.gov>
Subject: RE: Vermilion Power Plant New East Ash Pond received on December 1st 2023.

Yes, will do. I thought everyone was checking for the emails on the generic GWS file too? Just so I understand…I still need to notify everyone, if it is mail for their site?

From: EPA.BOW.GWS.CCR <EPA.BOW.GWS.CCR@Illinois.gov>
Sent: Tuesday, December 5, 2023 11:05 AM
To: Seif, Josiah <Josiah.Seif@Illinois.gov>
Subject: RE: Vermilion Power Plant New East Ash Pond received on December 1st 2023.

Hi. Can you forward the listserve email? it was Justin's site. thanks. Lauren

Lauren I. Hunt, M.S.
(she/they/he)
Environmental Protection Geologist III
Illinois Environmental Protection Agency
Bureau of Water
Groundwater Section
1021 N. Grand Avenue
PO Box 13
Springfield, IL 62702
D: 217-524-9048
C: 309-361-0037
Lauren.hunt@illinois.gov
Hours: 8:30 am to 5:30 pm Tuesday through Friday
8:30 am to 4 pm Mondays and alternating Mondays off

Working remotely Mondays and Fridays.

From: Seif, Josiah <Josiah.Seif@Illinois.gov>
Sent: Tuesday, December 5, 2023 9:17 AM
To: EPA.BOW.GWS.CCR <EPA.BOW.GWS.CCR@Illinois.gov>; Hunt, Lauren <Lauren.Hunt@Illinois.gov>; MacDonna, Keegan <Keegan.MacDonna@Illinois.gov>
Cc: Summers, Michael <Michael.Summers@Illinois.gov>; Dunaway, Lynn <LYNN.DUNAWAY@Illinois.gov>; Rompot, Derek <Derek.Rompot@Illinois.gov>
Subject: Vermilion Power Plant New East Ash Pond received on December 1st 2023.

ASD For the **Vermilion Power Plant New East Ash Pond** was received on December 1st 2023. It was misplaced and just arrived today, 12/5 to permits. The document has been scanned to the N:Drive, Listserve has been notified and hard copy has been placed in the Impoundment. If you have any questions, please feel free to ask.

Thank you,

Josiah M. Seif

Josiah M. Seif
CCR Office Coordinator
Bureau of Water
Illinois Environmental Protection Agency
217-782-0610
Josiah.Seif@illinois.gov

DOCUMENT
20

Rees, Jeromy

From:	Jenny Cassel <jcassel@earthjustice.org>
Sent:	Tuesday, December 19, 2023 12:00 PM
To:	Bierwagen, Justin; EPA.BOW.GWS.CCR
Cc:	Thomas Cmar; Mychal Ozaeta; Melissa Legge; arehn
Subject:	[External] Prairie Rivers Network comments on ASD for Vermilion NEAP
Attachments:	12.19.23 PRN comments on ASD for Vermilion.pdf

Mr. Bierwagen and others it may concern in the Illinois EPA Groundwater Section,

Please see attached comments, submitted on behalf of Prairie Rivers Network, on Dynegy's "alternate source demonstration" for the Vermilion New East Ash Pond. We appreciate your consideration of these comments, pursuant to 35 IAC 845.650(e)(3), and strongly urge you not to concur with the ASD.

Sincerely,
Jenny Cassel

Jenny Cassel
Senior Attorney, Clean Energy Program
Earthjustice
311 S. Wacker Drive, Suite 1400
Chicago, IL 60606
T: 312-500-2198 (direct)
jcassel@earthjustice.org

December 19, 2023

Groundwater Section staff
Illinois Environmental Protection Agency
EPA.BOW.GWS.CCR@illinois.gov

RE: Public Comments on Alternative Source Demonstration for Vermilion NEAP

Dear Illinois EPA Groundwater Section staff,

Pursuant to 35 I.A.C. § 845.650(e)(3), on behalf of Prairie Rivers Network, Earthjustice respectfully submits these public comments concerning the alternative source demonstration ("ASD") submitted for the New East Ash Pond ("NEAP") at the former Vermilion plant. We urge IEPA not to concur because Dynegy failed to demonstrate that the NEAP did not contribute to the contamination found in groundwater monitoring wells.

Under the Part 845 rules, an alternative source demonstration ("ASD") is a:

> demonstration . . . that a source other than the CCR surface impoundment caused the contamination and the CCR surface impoundment *did not contribute* to the contamination, or that the exceedance . . . resulted from error in sampling, analysis, statistical evaluation, natural variation in groundwater quality, or a change in potentiometric surface and groundwater flow direction.

35 I.A.C. § 845.650(e) (emphasis added).

Dynegy has not met this high bar for avoiding corrective action. First, it inappropriately relies on a geochemical analysis called a "Piper plot" as evidence that the NEAP is not contributing to the pollution at issue. Second, Dynegy has not provided adequate information to substantiate its assertion that comparisons of groundwater concentrations with porewater concentrations demonstrate that the NEAP is not contributing to groundwater exceedances. Third, Dynegy has not shown that shallow groundwater cannot be contributing to high concentrations of CCR pollutants in deeper groundwater. Fourth and finally, Dynegy has not conclusively shown that the NEAP did not contribute to chloride, lithium, sulfate and total dissolved solids ("TDS") contamination in monitoring wells ("MW") 35D and 70D because it lacks a groundwater monitoring program approved by the Agency following public review and comment. Without an approved groundwater monitoring program, the Agency cannot make a supported decision that the purported "demonstration" establishes that the NEAP has not contributed to exceedances.

1. Comparisons of porewater to groundwater, including those based on the "ionic composition" of the waters, do not suffice to demonstrate that the NEAP did not contribute to contamination in MWs 35D and 70D.

One "line of evidence" that Dynegy offers in support of its purported demonstration that NEAP did not contribute to the chloride, lithium, sulfate and TDS pollution found in MWs 35D and 70D involves comparing the chemistry of CCR porewater to that of groundwater.[1] Dynegy relies on a "Piper plot" in claiming that geochemistry at the site shows that CCR leachate from the NEAP is not contributing to the pollution. However, the U.S. Environmental Protection Agency ("USEPA") has *rejected* the use of such "Piper plots" in ASDs. As USEPA explained in its final Part A decision for the Gavin power plant,[2] a Piper plot "does not consider hydrogeology" and reliance on such plots "seeks to set aside the information about site geology and hydrology that has been used to characterize the direction of groundwater flow, and instead to determine where groundwater sampled from compliance wells came from based solely on chemistry." [3] Because relying on a Piper plot analysis would disregard site-specific hydrogeology, USEPA determined that, "in the context of the CCR regulations, it is inappropriate as part of the ASD to use Piper plots to determine from where groundwater at compliance wells is coming."[4]

The Illinois legislature provided that Part 845 is to be "at least as protective and comprehensive" as the federal CCR rule.[5] Accordingly, Illinois EPA should reject "Piper plots" as evidence, both in this instance and where offered as support for other ASDs, that a CCR surface impoundment is not contributing to groundwater pollution.

A second "line of evidence" that Dynegy offers in support of its ASD is the argument that concentrations of chloride in NEAP porewater are less than chloride concentrations in groundwater.[6] IEPA should also reject this line of evidence. Dynegy does not provide adequate information about exactly where in the NEAP the porewater sample was taken, whether more than one sample was taken, the pH of the sampled porewater, or other geochemical information that potentially could allow the Agency to determine that the NEAP is not contributing to chloride exceedances. This same lack of information casts doubt on Dynegy's third "line of evidence," since it also relies, in part, on a distinction between groundwater and porewater.[7]

Given Dynegy's admission that sulfate and TDS exceedances at wells 70S are attributable to the NEAP,[8] claims that the NEAP does not contribute to exceedances of those and other pollutants in a deeper well in the same location (70D) or MW 35D are suspect and must be closely scrutinized. Dynegy has not met its burden with this ASD.

---

[1] Dynegy ASD for Vermilion at 9-10 of 17.

[2] USEPA, Hazardous and Solid Waste Management System: Disposal of Coal Combustion Residuals From Electric Utilities; A Holistic Approach to Closure Part A: Final Decision on Request For Extension of Closure Date Submitted by Gavin Power, LLC ("Final Gavin Part A Decision"), Notice of availability of final decision, 87 Fed. Reg. 72,989 (Nov. 28, 2022); Final Gavin Part A Decision, available at https://www.regulations.gov/document/EPA-HQ-OLEM-2021-0590-0100.

[3] Final Gavin Part A Decision at 67-68.

[4] *Id*.

[5] 415 ILCS 5/22.59(g)(1).

[6] Dynegy ASD for Vermilion at 10-11 of 17.

[7] *See* Dynegy ASD for Vermilion at 12 of 17 ("Principal component analysis (PCA) shows that BCU groundwater is distinct from CCR porewater.")

[8] *See id*. at 5 of 17 ("Sulfate and TDS GWPS exceedances at well 70S will be addressed in accordance with 35 I.A.C. § 845.660"); 35 I.A.C. § 845.660 (requiring initiation of an assessment of corrective measures).

2. Dynegy has not shown that there is no connection between deeper groundwater and groundwater potentially affected by the NEAP.

As noted above, Dynegy's obligation is to demonstrate that the NEAP is not contributing to exceedances in groundwater. Dynegy undercuts its own arguments: while claiming that deeper groundwater is separate from shallow groundwater, it acknowledges that analysis has "indicated…that the wells that 'draw water from the bedrock are *either only slightly connected to* or completely isolated from the local groundwater flow system…."[9] If indeed the bedrock groundwater is "slightly connected to" groundwater closer to the surface, then CCR pollutants in the shallower groundwater may be contributing to exceedances in deeper monitoring wells. Dynegy has not met its burden.

3. IEPA has not yet approved a groundwater monitoring program under Part 845 for the NEAP.

IEPA should also reject Dynegy's ASD because Vermilion lacks an approved groundwater monitoring program under Part 845. An approved groundwater monitoring program – which includes appropriate locations, depths, and number of background and downgradient monitoring wells, as well as satisfactory sampling procedures and determinations of which wells accurately represent "background" groundwater quality – is an *essential prerequisite for any ASD.* Without an approved program, owners/operators may be engaging in a variety of erroneous monitoring practices that result in contamination from the CCR surface impoundment not being fully detected or characterized.

Among other flaws, owners or operators may have set up a groundwater monitoring system that is missing contaminant pathways; treating CCR-contaminated wells as "background" wells, resulting in pollution associated with the CCR surface impoundment improperly not being classified as an exceedance; or failing to account for "mounding" or other hydrogeological characteristics that affect groundwater flow direction. In short, without an IEPA-approved program properly revealing what contamination is coming from a CCR surface impoundment, *there is insufficient information for IEPA to determine—or for owners/operators to demonstrate—that pollution is NOT coming from the impoundment.*

Our concerns about serious flaws in groundwater monitoring performed by industry, absent review and approval (after public comment) from the Agency, are far from hypothetical. USEPA has reviewed the groundwater monitoring systems of multiple CCR surface impoundments – including one here in Illinois[10] – and found, or proposed to find, numerous grave errors in how that monitoring is being carried out.

Many of these evaluations have come in the form of USEPA's review of owners/operators' "Part A" applications. To obtain an extension of the deadline to cease receipt of CCR in a CCR surface impoundment that is required to close, owners/operators were required to demonstrate,

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[9] Dynegy ASD for Vermilion at 13 of 17 (emphasis added).

[10] *See* https://www.epa.gov/coalash/coal-combustion-residuals-ccr-part-implementation (noting proposed denial of Waukegan "Part A" application, with link to proposed denial).

among other things, full compliance with the CCR rule at the entire facility where the CCR surface impoundment is located.[11] As of this writing, USEPA has issued thirteen proposed decisions on Part A applications, one of which it finalized.[12] It evaluated compliance with the groundwater monitoring mandates of the CCR rule at eight of those facilities.[13]

At *every* site that USEPA reviewed as part of its Part A evaluations, including one in Illinois (Waukegan), it identified serious problems with facilities' groundwater monitoring systems:

- At the Gavin coal-fired power plant, USEPA found that the owner/operator failed to thoroughly characterize groundwater flow direction, failed to properly establish background wells, and lacked adequate downgradient wells, among other flaws.[14]

- At the Waukegan plant, USEPA proposed to find that Midwest Generation did not properly characterize groundwater flow direction, lacked sufficient wells to fully monitor potential contamination, improperly used "intrawell" statistical analysis of monitoring results, and used improper "background" wells that were dug through CCR.[15]

- At the Ottumwa, Clifty Creek, and Spurlock plants, USEPA proposed to find that, among other deficiencies, the groundwater monitoring wells were too far apart or not properly sited, leaving potential contaminant pathways unmonitored.[16]

- At A.B. Brown, USEPA proposed to find, among other concerns, that the groundwater monitoring wells were not placed in sufficient locations to detect all potential contaminant pathways, that groundwater flow characterization was inadequate, and samples were improperly evaluated using "intrawell" statistical analysis.[17]

- At Mountaineer, USEPA proposed to find, among other flaws, that the company did not appropriately locate either background or downgradient wells, and improperly analyzed groundwater monitoring data, including by excluding so-called "outlier" data and by using intrawell analysis.[18]

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[11] USEPA, Hazardous and Solid Waste Management System: Disposal of Coal Combustion Residuals From Electric Utilities; A Holistic Approach to Closure, 85 Fed. Reg. 53,516 (Aug. 28, 2020).
[12] *See* https://www.epa.gov/coalash/coal-combustion-residuals-ccr-part-implementation (listing CCR surface impoundments for which USEPA has issued proposed and final decisions).
[13] *See id*. (noting proposed decisions, including complete and incomplete or ineligible applications).
[14] *See* final Gavin Part A decision at 45-54 and 70-76, available at https://www.regulations.gov/document/EPA-HQ-OLEM-2021-0590-0100.
[15] *See* proposed Waukegan Part A decision at 31-47, available at https://www.regulations.gov/document/EPA-HQ-OLEM-2023-0209-0001.
[16] *See* proposed Ottumwa Part A decision at 43-46, available at https://www.regulations.gov/document/EPA-HQ-OLEM-2021-0593-0002; proposed Clifty Creek Part A decision at 44-45, available at https://www.regulations.gov/document/EPA-HQ-OLEM-2021-0587-0023; and proposed Spurlock Part A decision at 55-56, available at https://www.regulations.gov/document/EPA-HQ-OLEM-2021-0595-0002;
[17] *See* proposed A.B. Brown Part A decision at 31-47, available at https://www.regulations.gov/document/EPA-HQ-OLEM-2022-0335-0001.
[18] *See* proposed Mountaineer Part A decision at 33-48, available at https://www.regulations.gov/document/EPA-HQ-OLEM-2021-0842-0001.

- At the Calaveras plant, USEPA proposed to find, among other flaws, that groundwater monitoring wells are improperly spaced, inadequate in number, and not located at the waste boundary, and the company did not appropriately identify background wells.[19]

USEPA has likewise identified severe deficiencies in the groundwater monitoring programs at multiple CCR facilities in Alabama[20] and at one facility in Kansas to which it sent a letter summarizing conversations regarding compliance concerns.[21]

In effect, *every time* USEPA has taken a close look at the groundwater monitoring program for a CCR surface impoundment or landfill, it has identified deficiencies that could lead to contamination from those CCR units being released undetected. There is no reason to believe those deficiencies are limited to sites outside of Illinois; indeed, as noted, one facility where USEPA found those deficiencies is the Waukegan plant. Until IEPA fulfills the critical oversight role assigned to it by the Coal Ash Pollution Prevention Act and Part 845, namely, it has reviewed and approved the groundwater monitoring program for Vermilion, *all ASDs for the site should be denied.*

4. Conclusion

Dynegy admits that the NEAP is leaking, and its Vermilion ash ponds continue to pose a grave threat to Illinois' only National Scenic River, the Middle Fork of the Vermilion River. Though PRN believes that Dynegy and IEPA have made the proper choice, in a separate proceeding, to excavate the impoundments and move the ash to an onsite landfill, IEPA must move expeditiously to issue a construction permit for closure by removal so that the coal ash can be moved, further contamination halted, and the Middle Fork restored.

Commenters reserve the right to provide additional comment on this or any other ASDs for Vermilion once an approved groundwater monitoring system, set out in IEPA-approved operating permit, is in place.

Thank you for taking these comments into consideration.

Best,

Jennifer Cassel
Thom Cmar
Mychal Ozaeta
Melissa Legge
Earthjustice

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[19] *See* proposed Calaveras Part A decision at 47-55, available at https://www.regulations.gov/document/EPA-HQ-OLEM-2022-0333-0001.

[20] Alabama: Denial of State Coal Combustion Residuals Permit Program, 88 Fed. Reg. 55,220, 55,239 - 55,241, 55,249 - 55,253, 55,260 - 55,267, and 55,271 - 55,272 (Aug. 14, 2023).

[21] USEPA, Letter re: Notice of Potential Violations/Opportunity to Confer, Tecumseh Energy Center, Tecumseh, Kansas, Enclosure 1 at 1-4 (Jan. 2021), attached hereto.

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Counsel for Prairie Rivers Network

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Mr. Jared Morrison
Director, Water and Waste Programs
Evergy Kansas Central, Inc.
818 S. Kansas Avenue
P.O. Box 889
Topeka, Kansas 66601

Re: Notice of Potential Violations/Opportunity to Confer
Tecumseh Energy Center, Tecumseh, Kansas

Dear Mr. Morrison:

Thank you for taking the time on January 25, 2021, and March 9, 2021, to discuss disposal of coal combustion residuals (CCR) at the Evergy Tecumseh Energy Center (TEC) located near Tecumseh, Kansas, and the requirements of 40 C.F.R. Part 257, Subpart D (the CCR Rule). After further review of the information posted on your publicly accessible CCR compliance web site (TEC CCR web site), the U.S. Environmental Protection Agency (the EPA or the Agency) continues to be concerned about compliance with the CCR Rule at TEC.

According to the TEC CCR web site, two units at the facility are subject to requirements in the CCR Rule: one surface impoundment (Bottom Ash Settling Area or BASA) and one landfill (322 Landfill). The Agency has reviewed the following documents posted for these units:

- Annual Groundwater Monitoring and Corrective Action (GWMCA) Reports (2017, 2018, 2019 and 2020, revised March 6, 2021)
- Groundwater Monitoring Systems Certification (2017, revised March 9, 2021)
- Statistical Method Certifications (2017, 2018, 2019)
- Closure Plan TEC Industrial Landfill 322 (2016, revised Mar 4, 2021)
- Post-Closure Plan TEC Industrial Landfill 322 (2016, revised March 4, 2021)

This review identified several missing, erroneous, or incomplete elements, which represent potential violations, described in Enclosure 1. The EPA's priority is to ensure Evergy is operating in compliance with the CCR Rule. While we appreciate Evergy's efforts to date to comply with the CCR Rule, and offers to perform additional work, the EPA has continuing concerns as to whether some requirements are being met. Based on the issues highlighted in the May 13, 2021, letter from Mr. Mark Anstoetter, and the results of the January and March meetings, we believe that further discussions are warranted. The EPA is interested in discussing the issues identified in Mr. Anstoetter's letter and developing an agreed-upon compliance schedule to address areas of noncompliance if possible. A proposed compliance schedule is set forth in Enclosure 2.

The EPA also believes that these potential violations are likely significant enough to warrant the assessment of a civil penalty. The terms of any agreed-upon resolution of areas of noncompliance, a compliance schedule and penalty would be incorporated into a Consent Agreement and Final Order issued pursuant to Section 3008(a) of RCRA, 42 U.S.C. § 6928(a).

Any submittal that TEC prepares to comply with the CCR Rule must be maintained, placed in the operating record, and posted by TEC in accordance with the recordkeeping, notification and publicly accessible CCR web site requirements, pursuant to 40 C.F.R. §§ 257.105, 257.106 and 257.107. Please note that original versions of documents must remain on the CCR web site for 5 years, in accordance with 40 C.F.R. § 257.107(c).

To schedule a call to discuss these issues, please contact Kelley Catlin in the Office of Regional Counsel within 10 calendar days of receipt of this letter at (913) 551-7110 or Bob Aston, at (913) 551-7392. Thank you for your prompt attention to this important matter.

Sincerely,

Wendy Lubbe
Acting Director
Enforcement and Compliance Assurance Division

cc: Mark Anstoetter, Esq.
Shook, Hardy and Bacon
manstoetter@shb.com

Julie Coleman, Director (e-copy)
Bureau of Waste Management
Kansas Department of Health and Environment

ENCLOSURE 1
Potential Violations
Tecumseh Energy Center

1) Reporting monitoring data

- 40 C.F.R. § 257.90(e)(3) – The Annual Groundwater Monitoring and Corrective Action (GWMCA) Reports must include all monitoring data obtained under 40 C.F.R. §§ 257.90 through 257.98. This includes results of laboratory analysis of groundwater or other environmental media samples for the presence of constituents in Appendices III and IV to 40 C.F.R. part 257 (or of other constituents, such as those supporting characterization of site conditions that may ultimately affect a remedy), any required statistical analyses performed on those results, measured groundwater elevations, and calculated groundwater flow rate and direction. The posted Annual GWMCA Reports do not include all the required information.

2) Groundwater monitoring system

- 40 C.F.R. § 257.91 – The performance standards require that a groundwater monitoring system consist of a sufficient number of wells, installed at appropriate locations and depths, to accurately characterize the quality of groundwater upgradient and passing the downgradient boundary of the unit. The following issues with the groundwater monitoring system have been identified:

    - 40 C.F.R. § 257.91(c) – Each groundwater monitoring system is required to have a sufficient number of wells to accurately characterize groundwater quality, including at least three downgradient wells[1]. In December 2019 at the BASA, MW-9 was not monitored due to lack of water in the well. This resulted in failure of the BASA groundwater monitoring system to meet the requirement to have a minimum of 3 downgradient wells in the BASA groundwater monitoring system during this semi-annual period.

    - 40 C.F.R. § 257.91(f) – The certification by a professional engineer (P.E.) that the groundwater monitoring systems have been designed and constructed to meet the requirements of 40 C.F.R. § 257.91 must document the basis supporting the determination for monitoring systems using only one upgradient and three downgradient wells. The groundwater monitoring systems for both the BASA and the 322 Landfill each consist of only one upgradient and three downgradient wells. The P.E. certification for the systems does not include the basis for the certification. This basis must include the criteria specified in 40 C.F.R. § 257.91(b), which is required to

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[1] As the EPA explained in the preamble to the CCR Rule (see 80 FR 21400), "As a practical matter, the EPA expects that there will be few cases, if any, where four wells will be sufficient, given that this requirement was originally developed for hazardous waste management units that are typically much smaller than CCR units. As mentioned above, a small unit with simple geology, a flat and constant hydraulic gradient, uniform hydraulic conductivity, low seepage velocity, and high dispersivity potential would be the type of unit for which the minimum number of wells could be sufficient to meet the overall performance standard. Although the EPA is finalizing a requirement for one upgradient and three downgradient wells as a regulatory minimum, the Agency expects large CCR units to have many more wells because most CCR sites have hydrologic settings that are too complex for the regulatory minimum to be adequate."

be considered when determining the appropriate number, spacing and depths of groundwater monitoring wells.

TEC has not provided any of the information required to support the design of the groundwater monitoring systems in the system certifications, except potentiometric maps included in the Annual GWMCA Reports. Some of the potentiometric maps appear to be based on an insufficient number of groundwater elevation data points to support the contours drawn. Moreover, there is evidence that both the BASA and the 322 Landfill groundwater monitoring systems do not meet the performance standard in 40 C.F.R. § 257.91.

With regard to the BASA, the analysis and data included in the BASA Alternate Source Demonstrations (ASDs) indicate background groundwater quality may not be properly characterized. Potentiometric maps included in the revised 2018 Annual GWMCA Report indicate at least a 90-degree shift in groundwater flow direction. This shift in flow direction results in monitoring well MW-11, which is designated as a side gradient well, being downgradient during 2018. This shift in flow direction similarly affects upgradient well MW-7. During 2018, MW-7 is depicted as either side gradient and potentially downgradient of the BASA unit and may not represent true background conditions. This shift in groundwater flow direction is not noted in the revised 2018 GWMCA Report. Additionally, the BASA is located next to a water feature that appears to exert seasonal or temporal influence on groundwater flow direction.

With regard to the 322 Landfill, this unit is too large for one upgradient and three downgradient wells to be spatially adequate to represent groundwater quality. The unit is approximately 56 acres, and its western and eastern boundaries are each approximately 2500 feet long. However, there are no groundwater monitoring wells along the western boundary of the unit and only one downgradient well on the eastern boundary of the unit, approximately 300 feet south of the northeast corner of the unit (see Figure 1 in the 2020 Annual GWMCA Report). Potentiometric flow maps depict groundwater flow toward the north/northeast, and groundwater is depicted as migrating toward the unit in this direction along the entire length of the western boundary and away from it along the entire length of the eastern boundary. 40 C.F.R. § 257.91(a)(2) requires that the downgradient monitoring system be “installed at the waste boundary that ensures detection of groundwater contamination,” such that “all potential contaminant pathways must be monitored.” Thus, the existence of over 2,000 feet of unmonitored, downgradient waste boundary along the eastern side of the landfill does not ensure detection of groundwater contamination.

The number, spacing, and depths of groundwater monitoring wells needed to sufficiently monitor upgradient groundwater quality and at the downgradient boundary must be determined using site-specific information as required by 40 C.F.R. § 257.91(b), which is currently missing from the reports and certifications available for review. However, simply based on size and available information it appears that neither background groundwater quality nor groundwater quality at the downgradient unit boundary are accurately characterized at either the BASA or the 322 Landfill.

3) Groundwater sampling and analysis requirements

- 40 C.F.R. § 257.93(d) – Background groundwater quality must be established for each constituent in a hydraulically upgradient well, or a background well that meets the requirements of 40 C.F.R. § 257.91(a)(1). 40 C.F.R. § 257.91(a)(1) allows background groundwater quality to be established in a well that has not been affected by leakage from a CCR unit and is not hydraulically upgradient if either of two criteria is met:

  - inability to determine a groundwater flow gradient; or
  - samples from other wells are as representative or more representative of background groundwater quality than samples from a hydraulically upgradient well.

  Intrawell comparisons conducted at the BASA do not appear to meet these requirements, as discussed below.

- 40 C.F.R. § 257.93(c) – The rate and direction of groundwater flow must be determined each time groundwater is sampled. The determination of the rate of groundwater flow has not been included in the Annual GWMCA Reports.

When conducting "intrawell" data comparison, samples taken at different times from the same well are used to characterize both background groundwater quality and downgradient groundwater quality. When conducting "interwell" data comparison, samples from one or more upgradient or side-gradient wells characterize background groundwater quality and samples from one or more down-gradient wells characterize groundwater quality down-gradient from the unit.

TEC has utilized intrawell comparisons at certain wells for certain constituents in Appendix IV to 40 C.F.R. part 257, for which interwell comparisons would have yielded a statistically significant level (SSL) (e.g., see Table II in the 2019 Annual GWMCA Report for the BASA for MW-9 for arsenic and cobalt and MW-10 for arsenic). This approach was implemented for the October 2019 sampling event, after TEC prepared an ASD in which TEC claimed there was natural variation in groundwater quality occurring below the BASA, for particular Appendix IV constituents only.

TEC has not provided data that indicate a groundwater flow gradient is not present at the BASA. Accordingly, the first criterion set forth at 40 C.F.R. § 257.91(a)(1)(i), that would allow background to be established in a non-upgradient well, is not met. With respect to the second criterion set forth at 40 C.F.R. § 257.91(a)(1)(ii), TEC has provided no information that indicates that the samples taken from the downgradient wells at the BASA are as or more representative of background groundwater quality than could be obtained from an up-gradient well.

If background groundwater quality samples are obtained from either an upgradient or a side-gradient well, interwell data comparisons would necessarily be used to identify SSIs or SSLs, because samples to characterize groundwater quality at the downgradient unit boundary would necessarily come from different wells than background samples. Additionally, samples that characterize background groundwater quality must always be taken from a well unimpacted by releases from a CCR unit.

If it can be demonstrated that samples obtained from wells located at the downgradient boundary of the CCR unit characterize background groundwater quality as accurately or more accurately than samples from an upgradient well, then all data analyzed for SSIs or SSLs would come from the same wells, and intrawell data comparisons would be used. As noted above, samples that characterize background groundwater quality must always be taken from a well unimpacted by releases from the CCR unit. Like many other CCR units, the BASA operated for decades (since construction in 1968) prior to becoming regulated by the CCR Rule. The 2019 Annual GWMCA Report indicates in a footnote to Table II that data collected through June 2019 were used to characterize background in the intrawell statistical analysis of the October 2019 groundwater data. Samples would need to have been obtained from these wells long before that time in order for them to be known to be unimpacted by the CCR unit. Therefore, intrawell data comparisons are inappropriate to demonstrate compliance with the requirements of the CCR Rule at the BASA.

4) Assessment Monitoring program

Whenever there is an SSI over background levels for one or more of the constituents in Appendix III to 40 C.F.R. part 257 at any monitoring well at the waste boundary, an assessment monitoring program must be established. The following issues with the assessment monitoring program at the BASA have been identified:

- 40 C.F.R. § 257.95(b) – The assessment monitoring program requires annual sampling for all constituents in Appendix IV to 40 C.F.R. part 257. This sampling was last conducted at the BASA on June 25, 2019. No sampling was conducted in 2020 to meet this requirement, as reported in Section 2.3.3 of the 2020 Annual GWMCA Report (amended March 6, 2021).

- 40 C.F.R. § 257.95(d)(1) – The assessment monitoring program requires semi-annual monitoring at all wells for all constituents in Appendix III to 40 C.F.R. part 257 and for those constituents in Appendix IV to 40 C.F.R. part 257 that were detected in the sampling event conducted in accordance with 40 C.F.R. § 257.93(b). This sampling was last conducted timely on March 20-21, 2019. The next sampling event occurred on October 10, 2019, beyond the semi-annual timeframe. No sampling was conducted in 2020 to meet this requirement, as reported in Section 2.3.3 of the 2020 Annual GWMCA Report (amended March 6, 2021).

5) The Alternate Source Demonstrations (ASD)

In order to rebut the site-specific monitoring data and analysis that resulted in an SSI or SSL, an ASD must be supported by site-specific facts and analytical data. Merely speculative or theoretical bases for the conclusions are insufficient. An ASD should be conclusive, rather than probable or possible.

At the BASA, constituents in Appendix IV to 40 C.F.R. part 257 were detected at SSLs in September 2018 and March 2019. The 2019 Annual GWMCA Report included ASDs for these sampling events. These ASDs do not support a determination that the SSLs detected (arsenic in MW-9 and MW-10 and cobalt in MW-9) in both September 2018 and March 2019 are due to an alternate source rather than the BASA, in accordance with requirements in 40 C.F.R. § 257.95(g)(3)(ii). Specific concerns regarding the validity of the ASDs include:

- No alternative source was credibly identified that would have contributed to the SSIs/SSLs detected. The EPA has previously outlined the expectations for a valid ASD in the Solid Waste Disposal Facility Criteria, Technical Manual[2] for the Municipal Solid Waste Landfill regulatory program at 40 C.F.R. part 258. In Chapter 5, beginning on page 286, and further explained on page 280, a facility seeking an ASD must document that "*an* alternative source exists" and that a hydraulic connection exists between *the* alternative source and the well with the significant increase. Furthermore, the facility must document that "constituents (or precursor constituents) are present at *the alternative source* or along the flow path *from the alternative source* prior to possible release from the regulated unit." The ASD regulatory

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[2] Solid Waste Disposal Facility Criteria, Technical Manual (November 1993), EPA530-93-017 https://archive.epa.gov/epawaste/nonhaz/municipal/web/pdf/subparte.pdf

language at 40 C.F.R. part 258 tracks the ASD regulatory language at 40 C.F.R. part 257. Just as this approach makes sense and has been appropriate for ASDs under Part 258 for over 25 years, the Agency believes the same approach is appropriate for Part 257.

- Claims that variation in groundwater quality between upgradient and downgradient wells is occurring naturally are unsupported by data in the ASD. While the ASD highlights average decreasing concentrations of some constituents (e.g., boron, chloride and sulfate) from upgradient to downgradient wells as evidence of the BASA not impacting groundwater, the ASD neglects to address that higher calcium concentrations exist downgradient, and fluoride concentration patterns are mixed; the Appendix III sampling data are inconclusive in proving natural groundwater variation. Some Appendix IV sampling data show similar uneven concentration patterns, but some are more clearly at elevated levels downgradient for key constituents like arsenic. Sampling results do not indicate the presence of Appendix IV constituents at unexpected high concentrations in the aquifer matrix downgradient of the background wells. Other possible reasons for such variations include improper characterization of background groundwater quality (see prior discussion on the 2018 groundwater potentiometric maps), or changes in groundwater chemistry below the unit caused by releases from the BASA to the aquifer. Sampling from additional wells or other environmental media could better substantiate a claim of groundwater natural variability as the cause of constituent concentration patterns.

- The leachate tests are of limited value for the following reasons:

    - Not enough information is provided about the sampling collection protocols (e.g., depth, volume, location of samples), the typical residence time of ash in the unit, or how the composition of ash being disposed may have changed over time.

    - Ash collected from the impoundment may have already leached a substantial fraction of the contaminant mass and provide an incomplete estimate of total release potential.

    - Not enough information is provided to determine whether the selected leachate test accurately reflects field conditions. This is in part due to the lack of field parameter results in Annual GWMCA Reports. These tests are not useful in an ASD if they are not similar to conditions in the unit (e.g., pH of liquid or the liquid to solid ratio).

    - The leaching test results do not provide evidence to refute that elevated arsenic and cobalt at MW-9 and MW-10 are being at least partially caused by the unit.

- The evidence presented, primarily leachability testing, does not outweigh the significant amount of field data indicating the detections are the result of a leak in the BASA. This evidence includes the following:

    - The BASA does not have a liner to inhibit infiltration of releases into the underlying, uppermost aquifer.

    - Approximately 20 feet of hydraulic head was present within the BASA during operation to drive the sluiced ash water into the underlying, uppermost aquifer throughout the 35 years of operational history.

  - Following dewatering of the BASA in September 2019, the groundwater elevations dropped approximately nine feet in MW-8, MW-9 and MW-10, confirming a direct hydraulic connection between sluiced ash in BASA and groundwater at these downgradient wells.

  - Multiple SSIs above background occurred at all three downgradient wells (MW-8, MW-9, MW-10) in each of the four monitoring events in 2018 and 2019.

Because an ASD meeting the requirements of 40 C.F.R. § 257.95(g)(3)(ii) was not completed within 90 days of finding that an SSL was detected, TEC became subject to the requirements of 40 C.F.R. § 257.95(g) and was also required to initiate an Assessment of Corrective Measures within 90 days after detecting the SSL in accordance with 40 C.F.R. § 257.96.

While the EPA is not foreclosing TEC from continuing its efforts to identify an alternative source, TEC must, in parallel, work through the assessment monitoring and corrective action program.

6) Closure and post-closure requirements

For the reasons stated above, the EPA believes the BASA is subject to corrective action requirements. Accordingly, the Closure Plan must be amended, and a Post-closure Care Plan must be developed to reflect that the unit has triggered corrective action requirements. The Post-closure Care Plan must incorporate changes necessary to reflect that closure will be complete when constituent concentrations throughout the unit and any areas affected by releases from the CCR unit have been removed and groundwater monitoring concentrations do not exceed the groundwater protection standards, in accordance with 40 C.F.R. § 257.102(c).

Regarding the 322 Landfill, the EPA identified issues associated with the Post-closure Care Plan. In general, the plan should document actions to be taken to comply with the performance standards for post-closure care in 40 C.F.R. § 257.104. The Post-closure Care Plan lacked specificity regarding actions to be taken, frequency or timing of activities discussed, and criteria for implementing described contingencies. By failing to provide specific measures or any guiding procedures or principles, it fails to serve as a plan. As such, the Landfill Post-closure Care Plan does not meet the requirements at 40 C.F.R. § 257.104(d):

- 40 C.F.R. § 257.104(d)(1)(i) requires that the plan contain a description of monitoring and maintenance activities required in 40 C.F.R. § 257.104(b)(1), to maintain the integrity and effectiveness of the final cover system. Section 5.1 of the Landfill Post-closure Plan states that inspections will initially occur weekly, then quarterly or semi-annually, and that “Inspection frequency will be reduced as final cover conditions are found to be stable and depending on the need for periodic maintenance.” The Plan does not provide any criteria for evaluating stability or any method for conducting inspections. It does not specify what level of periodic maintenance might warrant more or less frequent inspections.

- Additionally, potential damage to the final cover, due to the lack of planned actions to restrict public access to the cover, necessitates the need for more frequent inspections than semi-annual.

- Section 5.2 of the Landfill Post-closure Plan provides a list of possible measures that could be used to control public access to the landfill (e.g., site security, fencing, lockable gates, and/or site surface water features) to prevent cover damage. This list simply represents a broad range of options, all or none of which may be implemented. If any of these measures were to be implemented, there is no information about their design (e.g., fence height) or requirements for maintenance or inspection.

ENCLOSURE 2
Proposed Compliance Schedule
Tecumseh Energy Center

#	CCR Rule	Summary of Issues Discussed	Projected Time Frame for Correction
1	40 C.F.R. § 257.90(e)	Incomplete Reports	30 days
2	40 C.F.R. § 257.91(c)	BASA groundwater monitoring system lacked sufficient number of wells	30 days
3	40 C.F.R. § 257.91(f)	Incomplete groundwater monitoring system certification	30 days
4	40 C.F.R. § 257.93(c)	Failure to report groundwater flow rate	30 days
5	40 C.F.R. § 257.95(b)	Conduct annual assessment monitoring for all constituents in Appendix III and IV	30 days
6	40 C.F.R. § 257.95(d)	Conduct semi-annual assessment monitoring for all constituents in Appendix III and for Appendix IV identified in sampling required by item 5	90 days
7	40 C.F.R. § 257.91	Submit a plan to install additional wells at 322 Landfill	45 days
8	40 C.F.R. § 257.95(g) and 40 C.F.R. § 257.96	Submit a plan to conduct initial fieldwork to characterize nature and extent of release from BASA and initiate an assessment of corrective measures (ACM)	45 days
9	40 C.F.R. § 257.93(d) and § 257.91(a)(1)	Establish background levels in wells as required and re-analyze groundwater monitoring data to identify SSLs for inclusion in ACM	45 days
10	40 C.F.R. § 257.104 and §§ 257.102(b), (c)	Develop a BASA Post-closure Care Plan and amend the Closure Plan to reflect the fact that corrective actions requirements apply	45 days
11	40 C.F.R. §257.104	Amend 322 Landfill Post-closure Plan to identify planned land use and to include a plan for actions in accordance with requirements to prevent damage to cap.	45 days
12	40 C.F.R. § 257.105-257.107	Notification and reporting requirements	Ongoing

DOCUMENT 21

Rees, Jeromy

From: Bierwagen, Justin
Sent: Wednesday, December 20, 2023 11:28 AM
To: Dunaway, Lynn
Cc: Hunt, Lauren
Subject: Vermilion Asd Draft Review
Attachments: Draft ASD Vermilion Letter.docx

Hey Lynn,

I wanted to send over my ASD Review for Vermilion for your review. The issue I had was under LOE #5 they claim that the Bedrock groundwater is isolated from the groundwater in the Quaternary deposit, but then later say it may slightly be connected. So hopefully you can give some insight on this and give it a final determination!

Thanks,

Justin M. Bierwagen B.S.
Environmental Protection Geologist 1
Illinois Environmental Protection Agency
Bureau of Water
Division of Public Water Supplies
Groundwater Section
1021 N. Grand Avenue
Springfield, IL 62702
D: 217-785-1871
Justin.Bierwagen@Illinois.gov
Hours: 7:30 am to 5:30 pm Tuesday through Thursday & 7:30 am to 5:00 pm Friday

ILLINOIS ENVIRONMENTAL PROTECTION AGENCY
1021 NORTH GRAND AVENUE EAST, P.O. BOX 19276, SPRINGFIELD, ILLINOIS 62794-9276 • (217) 782-3397
JB PRITZKER, GOVERNOR
JOHN J. KIM, DIRECTOR

217-782-1020

July 8, 2024

Dianna Tickner
Dynegy Midwest Generation, LLC
1500 Eastport Plaza Drive
Collinsville, Illinois 62234

Re: Vermilion Power Plant East Power Plant New East Ash Pond; W1838000002-4
Alternative Source Demonstration (ASD) Submittal

Dear Mrs. Tickner:

The purpose of this correspondence is to notify you that the Illinois Environmental Protection Agency (Illinois EPA) does not concur with the Vermilion New East Ash Pond System Alternative Source Demonstration (ASD) dated December 1, 2023. The Illinois EPA does not concur due to the following data gaps:

- Characterization that the draw water from the bedrock is completely isolated from local groundwater flow system.

If you have any questions, please contact: **Justin Bierwagen** Illinois EPA, Bureau of Water, Groundwater Section DPWS #13, P.O. Box 19276, Springfield, Illinois 62794-9276. If you have any questions concerning the investigation described above, please call 217-782-1020.

Sincerely,

Michael Summers, P.G.
Manager, Groundwater Section
Division of Public Water Supplies
Bureau of Water

cc: Justin Bierwagen
Lynn Dunaway
Keegan MacDonna
Records 06M

2125 S. First Street, Champaign, IL 61820 (217) 278-5800
1101 Eastport Plaza Dr., Suite 100, Collinsville, IL 62234 (618) 346-5120
9511 Harrison Street, Des Plaines, IL 60016 (847) 294-4000
595 S. State Street, Elgin, IL 60123 (847) 608-3131
2309 W. Main Street, Suite 116, Marion, IL 62959 (618) 993-7200
412 SW Washington Street, Suite D, Peoria, IL 61602 (309) 671-3022
4302 N. Main Street, Rockford, IL 61103 (815) 987-7760

CC2: Jenny Cassel via email
Andrew Rehn via email
Faith Bugel via email
Mychal Ozaeta via email
Lauren Piette via email

DOCUMENT
22

Rees, Jeromy

From: Bierwagen, Justin
Sent: Thursday, December 28, 2023 8:18 AM
To: Dunaway, Lynn
Subject: RE: Vermilion Asd Draft Review
Attachments: Draft ASD Vermilion Letter.docx

Lynn,
Added your comments!

Thanks,

Justin

From: Dunaway, Lynn <LYNN.DUNAWAY@Illinois.gov>
Sent: Thursday, December 21, 2023 2:15 PM
To: Bierwagen, Justin <Justin.Bierwagen@Illinois.gov>
Cc: Hunt, Lauren <Lauren.Hunt@Illinois.gov>
Subject: RE: Vermilion Asd Draft Review

Justin,
I would add that there was no assessment of the interaction between shallow bedrock groundwater and the old east pond, which is up gradient of the NEAP, based on Fig.1. Also they provided no analysis of the leachable metals from the CCR in the NEAP.

Lynn

From: Bierwagen, Justin <Justin.Bierwagen@Illinois.gov>
Sent: Wednesday, December 20, 2023 11:28 AM
To: Dunaway, Lynn <LYNN.DUNAWAY@Illinois.gov>
Cc: Hunt, Lauren <Lauren.Hunt@Illinois.gov>
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- Characterization that the draw water from the bedrock is completely isolated from local groundwater flow system.
- No assessment of the interaction between bedrock groundwater and the old east pond. Based on Fig.1 shows to be upgradient of the New East Ash Pond.
- Lack of analysis of the leachable metals from the CCR in the New East Ash Pond.

If you have any questions, please contact: **Justin Bierwagen** Illinois EPA, Bureau of Water, Groundwater Section DPWS #13, P.O. Box 19276, Springfield, Illinois 62794-9276. If you have any questions concerning the investigation described above, please call 217-782-1020.

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Michael Summers, P.G.
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