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September 26, 2012

CLERK'S OFFICE SEP 2 8 2012 STATE OF ILLINOIS Pollution Control Board

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Richard McGill Illinois Pollution Control Board 100 West Randolph, Suite 11-500 Chicago, Illinois 60601

Subject: Amendments to Title35.Subtitle G. Chapter I. Subchapter f. Part 742: - Tiered Approach to Corrective Action Objectives (TACO) – April 29, 2012

Dear Richard:

Illinois Petroleum Council appreciates the opportunity to comment on the proposed amendments to the TACO guidance related to vapor intrusion. Although the proposed updates to the guidance are an improvement for vapor inhalation risk assessment, it is important for the Board to consider some very recent field studies on petroleum vapor intrusion that are currently being used to support development of screening criteria. The Illinois Petroleum Council and our member companies are willing to discuss this information with the Illinois Pollution Control Board in greater detail, if the Board so desires. Please find attached our comments and recommendations for your consideration.

Sincerely,

Dan Eichholz Associate Director

Attachments

GENERAL COMMENTS:

Although several are still draft, it is important that the Agency consider recent field studies/data (see References) in the development of their proposed guidance. It is anticipated that two of the key studies involving analyses of soll-gas databases (Lahvis et al., 2012 and US EPA, 2012a)



will be in print later this year (hopefully, in the next few months). The Information contained In these studies is currently being used to support petroleum vapor intrusion guidance for the US EPA Office of Underground Storage Tanks (see attached),



CRC Care Australia (new effort) (see attached),



Initial Draft PVI Appendix B Guidance 7 July 2012Determination of Excl

and ITRC (<u>http://www.itrcweb.org/teampublic_PVI.asp</u>). The work of Lahvis et al. (2012) has also been used to underpin recently passed petroleum vapor intrusion guidance in California¹

(<u>http://www.waterboards.ca.gov/ust/lt_cls_plcy.shtml</u>) including adoption of a bioattenuation factor of 1,000x (see attached):



Screening criteria should not be based on models alone (i.e., the revised Johnson and Ettinger model) that are not well supported with field data for the development of site screening criteria for petroleum hydrocarbons.

I) ATTENUATION FACTORS

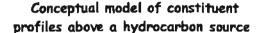
Use of Attenuation Factors for Petroleum Hydrocarbon Vapor Intrusion Screening:

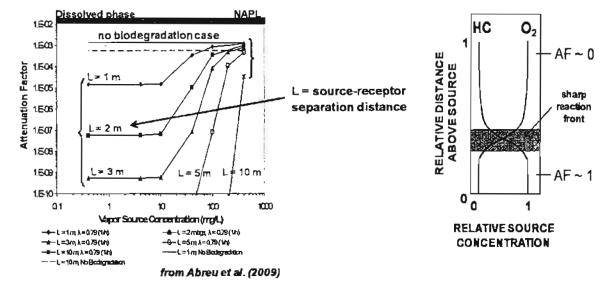
Attenuation factors, while perhaps appropriate for non-reactive VOCs, have been shown to have limited applicability for hydrocarbons (reactive VOCs). In particular, the attenuation factor has been shown in model and field studies to vary by orders of magnitude over short-vertical distances in the unsaturated zone (Abreu et al., 2009, Lahvis et al., 1999) at locations where hydrocarbon and oxygen (O_2) concentrations in soil gas are optimal for biodegradation (see

¹ It is important to note that the exclusion distance criteria defined in the California Low-Threat Closure Guidance were agreed a priori by a group of stakeholders in advance of supporting technical (model and field) data. The technical data were later used to justify the conservativeness of the proposed criteria.

attached figure - slightly modified for illustrative purposes from Abreu et al., 2009). Aerobic reaction fronts develop in the unsaturated zone because aerobic biodegradation rates are rapid (e.g., half-lives on the order of hours or days –

Abreu et al. (2009) (slightly modified)





DeVaull, 2007) and essentially instantaneous relative to the rates of physical transport (molecular diffusion, advection) generally associated with vapor intrusion (Davis et al., 2009). This phenomenon is also observed at field sites, where either the attenuation is limited or attenuation is complete depending on whether one measures below or above the reaction zone. This behavior is conceptually illustrated in the figure on the right.

The position of the aerobic reaction front above the hydrocarbon source will be dictated by the balance between metabolic (biologically driven) O_2 demand and O_2 availability in subsurface. The metabolic demand for O_2 is largely a function of the amount (source mass) and composition of hydrocarbons present in the unsaturated zone. These factors have the potential to vary depending on the source type (e.g., dissolved-phase versus LNAPL, gasoline versus diesel or crude oil), extent of weathering, and surface cover (e.g., building foundation, pavement) or presence of highly saturated or organic rich soils in the subsurface. In general, reaction fronts will tend to develop in close proximity (e.g., near the capillary zone) to dissolved phase hydrocarbon sources. The metabolic demand for O_2 is insufficient in such cases to drive conditions in the unsaturated zone sufficiently anaerobic. The reaction front is expected to occur close to the water table even when relatively impermeable surface covers (e.g., building foundations, pavement) are present at land surface (Abreu et al., 2009; McHugh et al., 2010). General experience supports this behavior. No cases of vapor intrusion are reported in the literature from dissolved-phase petroleum hydrocarbon sources separated vertically from building foundations (Davis, 2009; McHugh et al., 2010). The aerobic reaction front will tend to develop farther above or laterally from LNAPL sources (Roggemans et al., 2001; Abreu et al., 2009) as a result of higher rates of diffusion from the source and greater metabolic O_2 demand. The reaction from also tends to develop further from new, large volume gasoline sources than from weathered, small-volume diesel or crude sources. As demand for O2 increases, so too, do sensitivities to O2 availability. Consequently, the aerobic reaction front would tend to develop closer to LNAPL sources at sites where O₂ is readily available for biodegradation (e.g., sites where the land surface condition is open to the atmosphere) than sites where O_2 availability is limited by the presence of a building foundation or pavement. Lower threshold O_2 concentrations in soil gas sufficient to

support aerobic biodegradation are generally reported by DeVaull (2007) to be in the range of 1 to 4 % vol/vol. The aerobic reaction front may never develop between the source and building foundation at sites where O_2 demand exceeds O_2 availability. Based on documented occurrences of petroleum vapor intrusion, this condition would exist at sites where LNAPL is located in relatively close proximity (< 15 ft or ~5 m) to a building foundation, and at terminal, pipeline, and manufacturing sites with large-volume petroleum releases in the subsurface (McHugh et al., 2010).

Use of source-receptor separation distances in regulatory site screening is not new. The US Environmental Protection Agency (EPA), for example, has proposed a source-receptor separation distance of 100 ft (30 m) (US EPA, 2002). This distance is based on the fact that vapor intrusion could not be documented at residences displaced by > 100 ft (30 m) laterally from the interpolated edge of a chlorinated hydrocarbon ground-water plume. The 100-ft (30 m) screening distance was subsequently adopted by many US states for use at petroleum hydrocarbon vapor intrusion sites. More recently, some state (Connecticut DEP, 2003; Pennsylvania DEP, 2004; New Hampshire DES, 2006; Wisconsin DNR, 2010; California SWRBC, 2012; Michigan DEQ, 2012; New Jersey DEP, 2012) and federal agencies (Atlantic PIRI, 2006; ASTM, 2010) have proposed or adopted shorter screening distances for petroleum hydrocarbons ranging from 5 to 30 ft (3 to ~10 m) for dissolved-phase sources and from 30 to 100 ft (~10 to 30 m) for LNAPL sources. These distance criteria can only be applied if aerobic conditions in the unsaturated zone (e.g., O₂ concentrations in soil-gas must exceed 2% or 5% vol/vol) and the absence of preferential pathways for vapor migration can be documented. Of note, the federal and state screening distances cited here have been developed with limited consideration of field data.

IMPLICATION: The IEPA is cautioned on the use of attenuation factors to support the development of screening criteria for petroleum hydrocarbons given that they have limited applicability for reactive VOCs. In addition, the development of screening criteria should also consider field data and not simply a vapor transport model (i.e., the revised Johnson and Ettinger model) that is not well validated

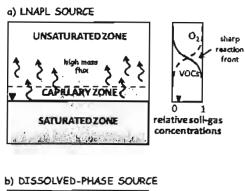
with field data.

II) CSM DISCUSSION:

The risk for vapor intrusion is fundamentally different for LNAPL (residual- or free-phase) and dissolved-phase sources (see Figure 1). It is important that strategies for site screening, site characterization, and remediation, bear this out. The differences in vapor intrusion potential for these 2 classes of sites have been well documented in modeling and field (Abreu et al., 2009; Davis, 2009; Lahvis et al., 2012; and Hers et al., 2012).

The potential for vapor intrusion is distinctly different for these 2 classes of sites because of significant differences in mass flux from the source related to:

 i) source strength: Source concentrations are typically much higher for LNAPL sources than for dissolved-phase sources. Higher source concentrations will generate higher rates of mass diffusion (flux). The higher mass flux will also be more sustained over time because LNAPL sources will contain approximately 500x more constituent mass (e.g., benzene) compared to dissolved-phase sources. O₂ demand and the potential for encountering limited (anaerobic) biodegradation



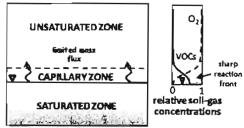


Figure 1. Differences in the conceptual model for vapor intrusion from a) LNAPL and b) dissolved-phase sources.

conditions are also unique with respect to LNAPL and dissolved-phase sources. These differences will affect the separation distance from the source at which hydrocarbon and O_2 concentrations are optimal for rapid biodegradation (i.e., the location where the reaction front develops above the source).

ii) source mass distribution: LNAPL sources will tend to distributed above the capillary zone as a result of smearing from water-table fluctuations. This phenomenon will tend to enhance mass flux to the unsaturated zone because of direct partitioning between LNAPL (residual) and vapor phases. Conversely, the mass flux will be more limited for dissolved-phase sources because the source is distributed below the capillary zone which serves as a barrier to vapor transport. Vapor diffusion from the source is limited by low effective air-phase porosity (i.e., high moisture saturation) and biodegradation in the capillary zone. The limitation of the capillary zone on hydrocarbon vapor transport is well recognized (McCarthy and Johnson, 1993).

IMPLICATION: The vapor intrusion risk posed by dissolved-phase and LNAPL hydrocarbon sources are uniquely different. These differences will greatly affect strategies for site screening and site characterization.

Source-Receptor Separation Distances: Dissolved vs. LNAPL sources

Bioattenuation is likely to be significant at all dissolved-phase sites (Lahvis et al., 2012; Davis, 2012; Hers et al, 2012; Peargin and Kohlhatkar, 2012; Wright, 2012), even for dissolved-phase benzene concentrations up to 15 mg/L (see Figure 2). Groundwater would essentially have to be in contact with the building foundation for there to be a potential for vapor intrusion. In such cases, it may be practical to establish a 1 m (3 ft) buffer distance to account for uncertainty in the source depth (water-table elevation). Of note, the maximum benzene

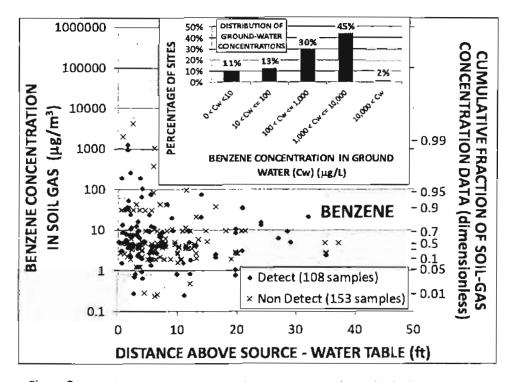
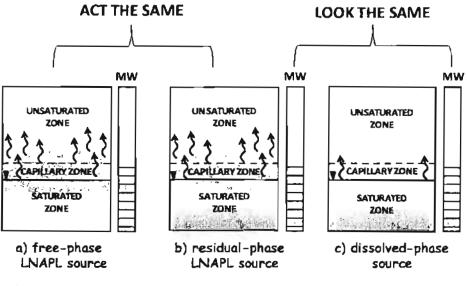


Figure 2. Plot of benzene concentrations in soll gas versus distance above a dissolved-phase hydrocarbon source. Non-detect values are plotted at the reporting limit. The plot includes 261 soil-gas measurements collected at 47 UST sites and 128 sample locations. The cumulative fraction of all (detect and non-detect) benzene soil-gas concentrations is noted on the right vertical axis. The histogram inset shows the corresponding distribution of measured benzene concentrations in ground water.

concentrations in soil gas observed above dissolved-phase hydrocarbon sources containing benzene < 15 mg/L are well less than the 370 μ g/m³ screening level proposed in the vapor intrusion guidance (Appendix B, Table H) (see attached figure from California State Water Resources Control Board, 2012).

The field studies show a larger source-separation distance (8 – 30 ft) is needed to attenuate vapors below levels of potential concern above LNAPL sources. The source-separation distance has also been shown to depend on source size (i.e., UST vs. non UST site). For example, Lahvis et al. (2012), Hers et al. (2012), Peargin and Kohlhatkar (2011) have noted a separation distance of around 15 ft for UST sites; Hers et al. (2012) have noted a separation distance of around 30 ft for non-UST sites. At non-UST sites, the surface boundary condition (e.g., pavement) may also have an effect on the source-separation distance (Hers et al., 2012).

It is important that the hydrocarbon source type and distribution be adequately characterized (in particular, differentiating residual-phase and dissolved phase sources) during the initial phases (e.g., monitoring well installation) of any site investigation. Source-type identification may not be possible from simple monitoring well observations (see Figure 3).



MW = Monitoring Well

Figure 3. Conceptual model illustrating the potential for vapor intrusion for a) free-phase LNAPL, b) residual-phase LNAPL, and c) dissolved-phase sources.

The identification of residual-phase LNAPL can be challenging. The agency may want to consider developing LNAPL indicator criteria similar to those shown in the attached table:

TYPE	INDICATOR	MEASURES AND SCREENING VALUES	
DIRECT	current or historic presence of LNAPL in ground water (including sheens) or soil	 laboratory and field/visual observations, including paint filter, shaker, and dye tests 	
INDIRECT	COC and TPH concentrations approaching (> 0.2) effective solubilities or effective soil saturation concentrations *	 ground water benzene > 3 mg/L gasoline (BTEX) > 20 mg/L diesel > 5 mg/L TPH-D soll gasoline > 500 mg/kg TPH-G diesel > 100 mg/kg TPH-D 	
INDIRECT	organic vapor analyzer (OVA) *	• > 500 ppmV	
INDIRECT	fluorescence response in LNAPL range	 UV, LIF, or UVIF fluorescence above background levels (visual observation) 	
INDIRECT	soil-gas profiles	 hydrocarbon and CO₂ concentrations in soil gas that show no decreas (or O₂ concentrations that show no increase) or remain relatively constant with distance from source 	

Table 2. Potential indicators of suspected LNAPL presence proximal to the observation.

* Garg and Beckett (2009, written communication) Note: Concentrations lower than the reference values can also be indicative of LNAPL sources.

IMPLICATION: It is important to try and distinguish between dissolved- and residual-phase hydrocarbon sources during initial phases of site investigation given the implications for site screening. The Agency should consider providing very clear guidance to assess source type during the initial stages of site investigation given the implications for site risk. The Agency may also want to think about separate screening criteria for UST and non-UST sites given that the unique risks (with respect to exclusion distance and sensitivity to surface boundary condition) these 2 classes of sites represent.

Groundwater

Hydrocarbon concentrations in ground water collected from monitoring wells screened across the water table (even as shallow as 5 ft) will be of little benefit in petroleum vapor intrusion risk assessment other than as indirect indicators of residual-phase LNAPL. As indicated in Lahvis et al. (2012) and Hers et al. (2012), hydrocarbon concentrations in soil gas are poorly correlated with concentrations in groundwater (see Figure 4). The poor correlation can be attributed to several factors including: a) the inability to accurately measure the water table concentrations from wells screened below the water table, b) biodegradation in the capillary zone, and c) the potential for encountering residual-phase LNAPL sources above the water table.

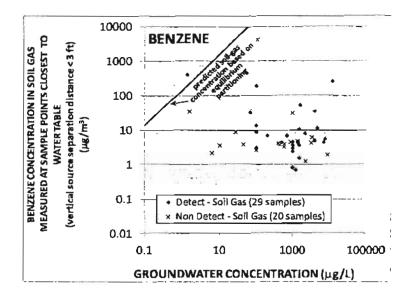


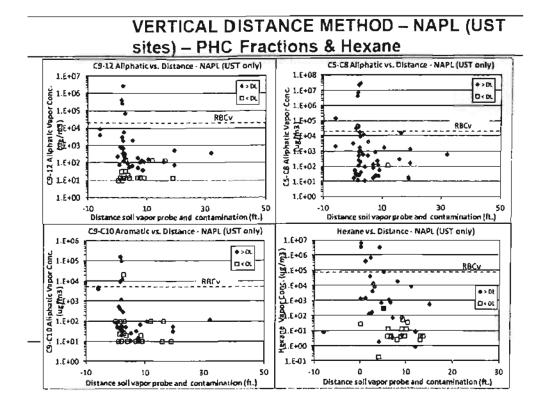
Figure 4. Plot of benzene concentrations in soil gas (from lowermost soil-gas sampling probe (ocations) versus benzene concentrations in ground water for the dissolved phase vapor source data set. The ground-water concentration measurements are from co-located or nearby ground-water monitoring wells. The plot includes 49 soil-gas / ground-water data pairs collected at 15 UST sites and 39 sample locations. Non-detect values are plotted at the reporting limit. The diagonal line indicates equilibrium partitioning of benzene between water and air according to Henry's law assuming a partition coefficient of 0.14 and a representative ground-water temperature of 15°C.

IMPLICATION: The Agency should be cautious about using groundwater concentration measurements (regardless of screen length) in site screening other than potentially as another line of evidence to help distinguish between dissolved and residual-phase hydrocarbon sources.

III) CONSTITUENTS OF POTENTIAL CONCERN

The soil-gas data indicate that benzene is the primary risk driver for vapour intrusion, especially at sites with dissolved-phase hydrocarbon sources composed primarily of soluble aromatic (BTEX) constituents (Lahvis et al., 2012; Hers et al. 2012). For example, TPH fractions and hexane are only observed in soil gas above risk-based threshold concentrations within 3 – 5 ft of an LNAPL source (see slides 21 and 22 below from Hers et al., 2012). In addition, the exclusion criteria derived for benzene are assumed to be conservative for naphthalene, which is 1) relatively less volatile than benzene, 2) similarly susceptible to biodegradation (Anderson et al., 2008), and 3) typically present in gasoline at lower molar fractions than benzene. Methyl tert-butyl ether (MTBE), which may be considered a potential constituent of concern for vapor intrusion in some regulatory jurisdictions, was also not considered in the statistical analysis. The exclusion of MTBE was justified on the basis that there are few, if any, confirmed reports of MTBE vapor intrusion in the literature, even though MTBE is a routine analyte in vapor intrusion investigations.

IMPLICATION: Benzene is likely to be the primary risk driver for vapor intrusion at petroleum hydrocarbon release sites.



VERTICAL DISTANCE METHOD - SUMMARY

	Dissolved Source	LNAPL Source- UST sites	LNAPL-non- USTsites
Oxygen	Most O ₂ conc. > 4%, and no O ₂ < 1%	O ₂ < 1% to 6 ft separation	O ₂ < 1% to 11 ft separation
Benzene (100 ug/m ³ threshold)	P _{KM} > 97% for Ds = 0 ft	Р _{км} ~ 100% for Ds = 15 ft	P > 93% @ 30 ft
Benzene (50 ug/m³ threshold)	P _{KM} > 94% to 95%, for Ds = 0-5 ft	Р _{км} ~ 100% for Ds = 15 ft	P > 93 @ 30 ft
Xylenes	Ds <= 3 ft	Ds <= 11 ft	Ds = 12 ft
Hexane	Ds = 0 ft	Ds <= 4 ft	N/A
C5-8 Ali	Ds 🗲 3 ft	Ds <≍ 3 ft	N/A
C9-12 Ali	Ds = 0 ft	Ds < = 2 ft	N/A
C9-10 Aro	Ds = 0 ft	Ds <= 2 ft	N/A

Ds = Separation distance where concentration < threshold



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IV) PREFERENTIAL PATHWAYS

The modeling work by Bozkurt et al. (In preparation) shows that "vapor intrusion risks are not substantially increased by preferential pathways unless they directly intersect areas where highly contaminated soil gas exists and building foundations" (reference available upon request. Experience has shown that preferential pathways of significance are not a common occurrence and are generally restricted to sites with sewer lines that intersect high concentration dissolved phase hydrocarbon/LNAPL plumes and building foundations (e.g., Pennsylvania DEP, 2001; Riis et al., 2010). In addition, preferential pathways have not been documented to play a significant role in enhancing preferential vapor migration at UST sites (from tank pits along piping line (coarse) backfill). Although I am not aware of any published studies, fractured rock is also often cited as a preferential pathway for sources located at depth.

IMPLICATION: Preferential pathways are likely to be restricted to sewers that intersect shallow groundwater plumes.

V) SURFACE BOUNDARY CONDITION

The type of surface boundary conditon (atmospheric, paved, building) is not likely to affect site screening at UST sites (Lahvis et al., 2012). Added sensitivity to the surface condition has, however, been observed at non-UST sites (Hers et al., 2012), potentially related to an additional demand for O_2 availability.

IMPLICATION: Surface covers can potentially limit O₂ availability and biodegradation at some non-UST sites with large LNAPL sources.

VI) FURTHER SITE ASSESSMENT

For dissolved-phase petroleum hydrocarbon sources (in the absence of residual-phase LNAPL), depth to groundwater is likely to be the critical control on petroleum vapor intrusion risk, not the hydrocarbon concentration in ground water. It may be prudent, therefore, to focus additional monitoring or data collection on the potential for ground water to contact a building foundation rather than ground-water sampling. For LNAPL sources, the key risk drivers are source (composition and distribution) and the vertical attenuation of the hydrocarbon in the unsaturated zone. Additional soil-gas sampling of hydrocarbons and signatures of hydrocarbon biodegradation (O_2 , CO_2 , CH_4) between the source and building foundation can be of benefit in such cases.

IMPLICATION: Strategies for additional site assessment may also differ depending on whether the source is dissolved-phase or LNAPL.