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# **The Metals Translator: Guidance For Calculating A Total Recoverable Permit Limit From A Dissolved Criterion**

## FORWARD

This document is the result of a successful collaborative effort between the United States Environmental Protection Agency (USEPA), Electric Power Research Institute (EPRI), and Utility Water Act Group (UWAG). Methods and procedures suggested in this guidance are for the specific purpose of developing the metals translator in support of the dissolved metals criteria and should not be interpreted to constitute a change in EPA regulatory policy as to how metals should be measured for such regulatory purposes as compliance monitoring.

This document provides guidance to EPA, States, and Tribes on how best to implement the Clean Water Act and EPA's regulations to use dissolved metal concentrations for the application of metals aquatic life criteria and to calculate a total recoverable permit limit from a dissolved criterion. It also provides guidance to the public and to the regulated community on appropriate protocols that may be used in implementing EPA's regulations. The document does not, however, substitute for EPA's regulations, nor is it a regulation itself. Thus, it cannot impose legally-binding requirements on EPA, States, or the regulated community, and may not apply to a particular situation based upon the circumstances. EPA may change this guidance in the future, as appropriate.

This document will be revised to reflect ongoing peer reviews and technical advances and to reflect the results of planned as well as ongoing studies in this technically challenging area. Comments from users will be welcomed. Send comments to USEPA, Office of Science and Technology, Standards and Applied Science Division (4305), 401 M Street SW, Washington, DC 20460.

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## ABSTRACT

On October 1, 1993, in recognition that the dissolved fraction is a better representation of the biologically active portion of the metal than is the total or total recoverable fraction, the Office of Water recommended that dissolved metal concentrations be used for the application of metals aquatic life criteria and that State water quality standards for the protection of aquatic life (with the exception of chronic mercury criterion) be based on dissolved metals. Consequently, with few exceptions, each metal's total recoverable-based criterion must be multiplied by a *conversion factor* to obtain a dissolved criterion that should not be exceeded in the water column. The Wasteload Allocations (WLA) or Total Maximum Daily Loads (TMDLs) must then be translated into a total recoverable metals permit limit.

By regulation (40 CFR 122.45(c)), the permit limit, in most instances, must be expressed as total recoverable metal. This regulation exists because chemical differences between the effluent discharge and the receiving water body are expected to result in changes in the partitioning between dissolved and adsorbed forms of metal. As we go from total recoverable to dissolved criteria, an additional calculation called a *translator* is required to answer the question "What fraction of metal in the effluent will be dissolved in the receiving water?" Translators are not designed to consider bioaccumulation of metals.

This technical guidance examines what is needed in order to develop a metals translator. *The translator is the fraction of total recoverable metal in the downstream water that is dissolved*; that is, the dissolved metal concentration divided by the total recoverable metal concentration. The translator may take one of three forms. (1) It may be assumed to be equivalent to the criteria conversion factors. (2) It may be developed directly as the ratio of dissolved to total recoverable metal. (3) Or it may be developed through the use of a partition coefficient that is functionally related to the number of metal binding sites on the adsorbent in the water column (i.e., concentrations of TSS, TOC, or humic substances).

Appendix A illustrates how the translator is applied in deriving permit limits for metals for single sites and as part of a TMDL for multiple sources. Appendix B presents some indications of site specificity in translator values. Appendix C illustrates the process of calculating the translator. Appendix D provides some detail of a statistical procedure to estimate sample size. Appendices E and F present information on clean sampling and analytical techniques which the reader *may elect* to follow. This material (E and F) is presented *only* to assist the reader by providing more detailed discussion rather than only providing literature citations; these procedures are *not* prescriptive.

## ACKNOWLEDGMENT

Many people have contributed long hours reviewing and editing the many drafts of this document. The success of technical guidance documents, such as this one, depends directly on the quality of such reviews and the quality of the reviewers suggestions. As such, we thank the many reviewers for their contributions. We wish to express our gratitude to the Coors Brewing Company for making available a large and very complete data set for our use in developing this technical guidance document; and to the City of Palo Alto, Dept. of Public Works for permitting us to use the data they are collecting as part of a NPDES Permit Application. The Cadmus Group, Inc. and EA Engineering, Science and Technology, Inc also contributed to the success of this document.

Development of this document has been a collaborative effort between industry and the USEPA; it has been authored by Russell S. Kinerson, Ph.D. (USEPA), Jack S. Mattice, Ph.D. (EPRI), and James F. Stine (UWAG).

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## Executive Summary

This guidance presents procedures that may be used to determine translator values that more accurately reflect site specific conditions. In this Executive Summary, steps to implement the dissolved metals policy through development and use of the translator are presented.

Before beginning a translator study one should make a *determination of reasonable potential* with a translator of 1 (all the metal in the effluent becomes dissolved in the receiving water). If the releases of metal from a discharge do not pose a reasonable potential of exceeding water quality criteria levels with the largest possible translator, then a permit limit does not have to be written for their release. However, if a discharge has a water quality based permit limit for a metal, and the State is adopting standards based on dissolved metals, then a translator study is needed.

In the toxicity tests to derive metal criteria, some fraction of the metal was dissolved and some fraction was bound to particulate matter. Assuming that the dissolved fraction more closely approximates the biologically available fraction than does total recoverable, conversion factors have been calculated. The conversion factors are predictions of how different the criteria would be if they had been based on measurements of the dissolved concentrations.

The translator is the fraction of total recoverable metal in the downstream water that is dissolved;  $f_D = C_D/C_T$ . It may be determined directly by measurements of dissolved and total recoverable metal concentrations in water samples taken from the well mixed effluent and receiving water (i.e., at or below the edge of the mixing zone). *EPA encourages that site specific data be generated to develop site*

*specific translators.*

If the translator is being developed to show a functional relationship to environmental properties such as TSS, pH, and salinity, samples should be collected under an appropriate range of conditions in order to develop a statistically robust translator. If the translator is not to be functionally related to adsorbent concentrations, or other environmental parameters, the study would normally be designed to collect samples under low flow conditions where TSS concentrations are relatively constant. Either the directly determined translator (the ratio of  $C_D/C_T$ ) or a translator calculated by using a partition coefficient ( $K_p$ ) may be used.

The most direct procedure for determining a site-specific metal translator is simply to determine  $f_D$  by measuring  $C_T$  and  $C_D$  and to develop the dissolved fraction as the ratio  $C_D/C_T$ . The translator is calculated as the geometric mean of the dissolved fractions.

A partition coefficient may be derived as a function of TSS and other factors such as pH, salinity, etc. The partition coefficient is the ratio of the particulate-sorbed and dissolved metal species multiplied by the adsorbent concentration. Use of the partition coefficient may provide advantages over the dissolved fraction when using dynamic simulation for Waste Load Allocation (WLA) or the Total Maximum Daily Load (TMDL) calculations and permit limit determinations because  $K_p$  allows for greater mechanistic representation of the effects that changing environmental variables have on  $f_D$ .

## 1. INTRODUCTION

The U.S. Environmental Protection Agency (EPA) issued a policy memorandum on October 1, 1993, entitled *Office of Water Policy and Technical Guidance on Interpretation and Implementation of Aquatic Life Metals Criteria* ("Metals Policy").<sup>1</sup> The Metals Policy states:

*It is now the policy of the Office of Water that the use of dissolved metal to set and measure compliance with water quality standards is the recommended approach, because dissolved metal more closely approximates the bioavailable fraction of metal in the water column than does total recoverable metal.*

The primary mechanism for toxicity to organisms that live in the water column is by adsorption to or uptake across the gills; this physiological process requires metal to be in a dissolved form. This is not to say that particulate metal is nontoxic, only that particulate metal appears to exhibit substantially less toxicity than does dissolved metal. Dissolved metal is *operationally defined* as that which passes through a 0.45  $\mu\text{m}$  or a 0.40  $\mu\text{m}$  filter and particulate metal is *operationally defined* as total recoverable metal minus dissolved metal. Even at that, a part of what is measured as dissolved is particulate metal that is small enough to pass through the filter, or that is adsorbed to or complexed with organic colloids and ligands. Some or all of this may be unavailable biologically.

The Metals Policy further states:

*Until the scientific uncertainties are better*

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<sup>1</sup> The complete October 1, 1993 memorandum can be obtained from EPA's Office of Water Resource Center (202) 260-7786 or the Office of Water Docket.

*resolved, a range of different risk management decisions can be justified. EPA recommends that State water quality standards be based on dissolved metal. EPA will also approve a State risk management decision to adopt standards based on total recoverable metal, if those standards are otherwise approvable as a matter of law.*<sup>2</sup>

The adoption of the Metals Policy did not change the Agency's position that the existing total recoverable criteria published under Section 304(a) of the Clean Water Act continue to be scientifically defensible. When developing and adopting its own standards, a State, in making its risk management decision, may wish to consider sediment, food chain effects and other fate-related issues and decide to adopt total recoverable or dissolved metals criteria.

Because EPA's Section 304(a) criteria are expressed as total recoverable metal, to express the criteria as dissolved, application of a conversion factor is necessary to account for the particulate metal present in the laboratory toxicity tests used to develop the total recoverable criteria.

By regulation (40 CFR 122.45(c)), the permit limit, in most instances, must be expressed as total recoverable metal.<sup>3</sup> Because chemical differences between the discharged effluent and the receiving water are expected to result in changes in the partitioning between

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<sup>2</sup> See Section 510, Federal Water Pollution Control Act, Public Law 100-4, 33 U.S.C. 466 et seq.

<sup>3</sup> For example, metals in the effluent of an electroplating facility that adds lime and uses clarifiers will be a combination of solids not removed by the clarifiers and residual dissolved metals. When the effluent from the clarifiers, usually with a high pH level, mixes with receiving water with a significantly lower pH level, these solids instantly dissolve. Measuring dissolved metals in the effluent, in this case, would underestimate the impact on the receiving water.

dissolved and adsorbed forms of metal, an additional calculation using what is called a *translator* is required. This *translator* calculation answers the question "What fraction of metal in the effluent will be dissolved in the receiving water body?" Translators are not designed to consider bioaccumulation of metals.

### 1.1 Considerations of Reasonable Potential

Water quality-based permit limitations are imposed when a discharge presents a reasonable potential to cause or contribute to a violation of the applicable water quality standard. . If the releases of metal from a facility are sufficiently low so as to pose no reasonable potential of exceeding water quality criteria levels, then a permit limit does not have to be written for their release. If a facility has a water quality based permit limit for a metal, and the State is adopting standards based on dissolved metals, then a translator is needed to produce a permit limit expressed as total recoverable metal. Of course, if the facility has a technology based permit limit for the metal and the limit is more stringent than a limitation necessary to meet water quality standards, then no translator is required or appropriate.

### 1.2. Margin of Safety

TMDLs must ensure attainment of applicable water quality standards, including all numeric and narrative criteria. TMDLs include waste load allocations (WLAs) for point sources and load allocations (LAs) for nonpoint sources, including natural background, such that the sum of these allocations is not greater than the loading capacity of the water for the pollutant(s) addressed by the TMDL, minus the sum of a specified margin of safety (MOS) and any capacity reserved for future growth. The MOS shall be sufficient to account for technical

uncertainties in establishing the TMDL and shall describe the manner in which the MOS is determined and incorporated into the TMDL. The MOS may be provided by leaving a portion of the loading capacity unallocated or by using conservative modeling assumptions to establish WLAs and LAs. If a portion of the loading capacity is left unallocated to provide a MOS, the amount left unallocated shall be described. If conservative modeling assumptions are relied on to provide a MOS, the specific assumptions providing the MOS shall be identified. For example, a State may recommend using the 90<sup>th</sup> percentile translator value to address MOS needs and account for variability of data and to use the critical 10<sup>th</sup> and 90<sup>th</sup> percentiles for other variables such as hardness and TSS when conducting steady-state modeling.

### 1.3. Converting from Total Recoverable to Dissolved Criteria

In the toxicity tests used to develop metals criteria for aquatic life, some fraction of the metal is dissolved and some fraction is bound to particulate matter. When the toxicity tests were originally conducted, metal concentrations were expressed as total. Some of the tests were repeated and some test conditions were simulated, for the purpose of determining the percent of total recoverable metal that is dissolved. Working from the premise that the dissolved fraction more closely approximates the biologically available fraction than does total recoverable, these *conversion factors* have the effect of reducing the water quality criteria concentrations. The conversion factors are predictions of how different the criteria would be if they had been based on measurements of the dissolved concentrations in all of the toxicity tests that were most important in the derivation of the criteria.

Consequently each metal's total recoverable criterion must be multiplied by a *conversion factor* to obtain a dissolved criterion

that should not be exceeded in the water column. For example, the silver acute conversion factor of 0.85 is a weighted average and is used as a prediction of how much the final acute value would change if dissolved had been measured. At a hardness of 100 mg/L as calcium carbonate (CaCO<sub>3</sub>), the acute total recoverable criterion is 4.06 µg/L while the dissolved silver criterion is 3.45 µg/L.

For additional details on aquatic life criteria for metals, the reader is referred to FR 60(86): 22229-22237.

Both freshwater (acute and chronic) and saltwater (acute) conversion factors<sup>4</sup> are presented (Tables 1 and 2); conversion factors for saltwater chronic criteria are not currently available. Where possible, these conversion factors are given to three decimal places as they are intermediate values in the calculation of dissolved criteria. Most freshwater aquatic life criteria are hardness-dependent<sup>5</sup> as are the conversion factors for Cd and Pb. The values shown in these tables are with a hardness of 100 mg/L. Conversion factors (CF) for any hardness can be calculated using the following equations:

#### Cadmium

Acute:

$$CF = 1.136672 - [\ln(\text{hardness}) (0.041838)]$$

Chronic:

$$CF = 1.101672 - [\ln(\text{hardness}) (0.041838)]$$

#### Lead

Acute and Chronic:

$$CF = 1.46203 - [\ln(\text{hardness}) (0.145712)]$$

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<sup>4</sup> Federal Register / Vol. 60, No.86 / 22229-22237 / Thursday, May 4, 1995 / Rules and Regulations. Water Quality Standards: Establishment of Numeric Criteria for Priority Toxic Pollutants; States' Compliance--Revision of Metals Criteria.

<sup>5</sup> Although most of the freshwater aquatic life criteria for metals are hardness dependent, those for trivalent arsenic, trivalent chromium, mercury, aluminum, iron, and selenium are not.

Table 1. Freshwater Criteria Conversion Factors for Dissolved Metals

Metal	Conversion Factors	
	Acute	Chronic
Arsenic	1.000	1.000
Cadmium *	0.944	0.909
Chromium (III)	0.316	0.860
Chromium (VI)	0.982	0.962
Copper	0.960	0.960
Lead *	0.791	0.791
Mercury	0.85	N/A
Nickel	0.998	0.997
Silver	0.85	N/A
Zinc	0.978	0.986

\* Conversion factors for Cd and Pb are hardness dependent. The values shown are with a hardness of 100 mg/L as calcium carbonate (CaCO<sub>3</sub>).

Table 2. Saltwater Criteria Conversion Factors for Dissolved Metals

Metal	Conversion Factors (Acute)
Arsenic	1.000
Cadmium	0.994
Chromium (III)	N/A
Chromium (IV)	0.993
Copper	0.83
Lead	0.951
Mercury	0.85
Nickel	0.990
Selenium	0.998
Silver	0.85
Zinc	0.946

The fractions of metals in dissolved and particulate phases are very dependent on water

chemistry. Because of the (typically) great differences between chemical properties of effluents, the chemical properties of receiving waters, and the chemical properties of the waters used in the toxicity tests, there is no reason to expect that the conversion factors can be used to estimate either the fraction of metal that would be in the dissolved phase in the receiving waters or the total recoverable metal concentration in the effluent that would result in a receiving water concentration not exceeding a criterion concentration. Thus, a translator is required to derive a total recoverable permit limit from a dissolved criterion<sup>6</sup>.

#### 1.4. Translating from a Dissolved Metal Ambient Water Quality Criterion to a Total Recoverable Concentration in the Effluent

As the effluent mixes with the receiving water, the chemical properties of the mixture will determine the fraction of the metal that is dissolved and the fraction of the metal that is in particulate form (typically adsorbed to surfaces of other compounds). Many different properties influence this dissolved to total recoverable metal ratio. Important factors include water temperature, pH, hardness, concentrations of metal binding sites such as concentrations of total suspended solids (TSS), particulate organic carbon (POC), and dissolved organic carbon (DOC), as well as concentrations of other metals and organic compounds that compete with the metal ions for the binding sites. It is difficult to predict the result of such complex chemistry. The

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<sup>6</sup>As a reasonable worst case, however, it may be assumed that metal in the receiving environment would be biologically available to the same extent as during toxicity testing; and the conversion factors may be used as translators if a site-specific translator is not developed. In that case, the water quality criterion that already has been multiplied by the conversion factor would be divided by the conversion factor.

most straightforward approach is to analyze the mixture to determine the dissolved and total recoverable metal fractions. This ratio of dissolved to total recoverable metal concentrations can then be used to translate from a dissolved concentration in the water column downstream of the effluent discharge (the criterion concentration) to the total recoverable metal concentration in the effluent that will not exceed that dissolved concentration in the water column.

Appendix A presents an example that summarizes the steps involved in applying the dissolved metals policy, using the translator, to develop a permit limit.

#### 1.5. Developing Translators

*The purpose of this technical guidance document is to present additional details regarding development and application of the metals translator to go from a dissolved metal criterion to a total recoverable permit limit.* This chapter identifies different approaches that may be used in developing site specific translators. In the following chapters, we will focus on designing and conducting field studies, analytical chemistry procedures, data analysis, and application of the metals translator to meet mass balance requirements.

There is always a translator in going from a dissolved criterion to a total recoverable permit limit. The rebuttable presumption is that the metal is dissolved to the same extent as it was during criteria development. The default translator value should be that the translator equals the conversion factor. This represents a reasonable worst case.

*EPA encourages that site specific data be generated to develop site specific partition coefficients (translators), and use of translators based on EPA's old data (as published in USEPA, 1984 and presented in Table 3 below)*

be phased out unless other data as suggested below, have been generated that establish their validity for the sites in question. The guidance released on October 1, 1993 identified three methods of estimating the metals translator. One of these was the use of the relationships developed from the STORET data (USEPA, 1984). In the years between 1984 and 1993 there was general recognition that the relationships had some inaccuracies due to contaminated metals data and other factors. However, limited comparisons of predictions from these relationships with data generated and analyzed with good QA/QC indicated generally good agreement and some tendency to be conservative. The stream data for lead were reanalyzed and a better relationship was developed. The parameters for these default partition coefficient estimation equations are presented in Table 3 where  $K_p$  has units of L/kg with TSS expressed as mg/L.

Table 3. Calculation of Default Partition Coefficients [ $K_p = K_{pO} \cdot TSS^\alpha$ ]

Metal	Lakes		Streams	
	$K_{pO}$	$\alpha$	$K_{pO}$	$\alpha$
Cu	2.85E+06	-0.9000	1.04E+06	-0.7436
Zn	3.34E+06	-0.6788	1.25E+06	-0.7038
Pb	2.0E+06	-0.5337	2.80E+06	-0.8
Cr(III)	2.17E+06	-0.2662	3.36E+06	-0.9304
Cd	3.52E+06	-0.9246	4.00E+06	-1.1307
Ni	2.21E+06	-0.7578	4.90E+05	-0.5719

Site specific conditions may render these default partition coefficients overly or underly protective. Data presented in Appendix B illustrate the variability that exists between different sites in some values of the dissolved metal fractions. Recent work by Sung (1995) demonstrates that reliance on the relationships in Table 3 does not always provide for

conservative estimates of the translator. Similar conclusions have been arrived at with data from rivers and streams in Washington.<sup>7</sup> Therefore, it may be appropriate to develop a dissolved to total recoverable ratio based on a single sample to confirm that the partition coefficient produces an estimate of the translator that is either reasonably accurate or conservative.

This guidance document presents procedures that may be used to determine translator values that accurately reflect site specific conditions.

The procedures in this document do not cover all possible approaches. Greater precision can be achieved by means of more elaborate procedures which, at the current time, are generally used only in research situations. Although, the use of such procedures is acceptable, they will not be discussed in this document.

### 1.5.1. Direct Measurement of the Translator

As mentioned in Section 1.4, the most straightforward approach for translating from a dissolved water quality criterion to a total recoverable effluent concentration is to analyze directly the dissolved and total recoverable fractions. The translator is the fraction of total recoverable metal that is dissolved and may be determined directly by measurements of dissolved and total recoverable metal concentrations in water samples.

### 1.5.2. Calculating the Translator Using the Partition Coefficient

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<sup>7</sup>Personal communication with Gregory Pelletier, Department of Ecology, Olympia, WA (206)-407-6485.

The partition coefficient ( $K_p$ ) may be derived as a function of the number of metal binding sites associated with the adsorbent. USEPA (1984) and the technical support accompanying EPA's Dissolved Policy Memorandum expressed the translator according to Eqn 2.7. The role of TSS is evident from this equation; as TSS increases, the dissolved fraction decreases because of the increased number of binding sites.

There is a general tendency to assume that the partition coefficient will increase with increasing TSS. It is important to recognize that in both the laboratory and in the field,  $K_p$  has been observed to be constant or to decrease with increasing particulate concentrations (Di Toro, 1985).

The fraction of the total metal in the downstream water that is dissolved (the translator) may be determined indirectly by means of a partition coefficient. The partition coefficient, in turn, may be either a function of varying adsorbent concentrations or be related to a constant adsorbent concentration associated with critical flow conditions. See Section 3.1.1 for considerations of factors affecting the appropriate design flow for metals.

### 1.5.3. The Translator as a Rebuttable Presumption

In the Technical Support Document for Water Quality-based Toxics Control (EPA, 1991a) commonly called the TSD, as well as in other documents, EPA has discussed the options one has for translators. These options include using a translator which assumes no difference between dissolved and total recoverable metal concentrations. The TSD identifies this as the most stringent approach and suggests it would be appropriate in waters with low solids concentrations, situations where the discharged form of the metal was mostly in the dissolved phase, or where data to use other

options are unavailable. There are some advantages to its use including the fact that it is already being used by some States, it is easy to explain and implement, and it effectively implements the statutory requirement found in §303(d) of the Clean Water Act calling for a margin of safety (MOS) in developing TMDLs. The disadvantage is that, as demonstrated by the conversion factors used to convert total recoverable water quality criteria into the dissolved form, it is highly unlikely that metals will remain totally in the dissolved form, even in high quality water. Furthermore, when the assumption that all of the metal is dissolved is applied in combination with dissolved criteria conversion factors, the resulting permit limit is more restrictive than that which existed when metal criteria were expressed as total recoverable. *Therefore, as a rebuttable presumption, conversion factors can be used as the translator where no site-specific translator is developed; this is the reasonable worst case*<sup>8</sup>.

### 1.6. Applying Metals Translators

If the translator is to be a function of adsorbent concentrations (e.g., TSS) it is critical that samples be collected under a broad range of TSS conditions to develop a statistically robust translator. If the translator is not to be functionally related to adsorbent concentrations the study would normally be designed to collect samples under low flow conditions where TSS concentrations are relatively constant. Either the directly determined ratio ( $C_D/C_T$ ) or a translator calculated using a partition coefficient ( $K_p$ ) may be used.

In actuality, metal partitioning in receiving water bodies is more complicated

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<sup>8</sup>Using the conversion factors as a translator will produce the same result as assuming no difference between dissolved and total recoverable metal concentrations.

than can be explained by TSS alone. Consequently, it is possible and permissible to develop the translator on some basis other than TSS, such as humic substances or POC.<sup>9</sup> The materials presented in Appendix C guide the reader through a possible evaluation of other factors that might be warranted in some studies.

Basically, the translator is applied by dividing a dissolved WLA or permit limitation by the translator to produce a total recoverable permit limitation. Appendix A contains a detailed explanation of how permit limits can be derived.

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<sup>9</sup>If the adsorbent is POC, then  $K_p (L/mg) = C_p (\mu g/L) / (C_D (\mu g/L) \cdot POC (mg/L))$

## 2. UNDERSTANDING THE METALS TRANSLATOR

**T**he translator is the fraction of the total recoverable metal in the downstream water that is dissolved. The reason for using a metal translator is to allow calculation of a total recoverable permit limit from a dissolved criterion.

A translator is used to estimate the concentration of total recoverable metal in the effluent discharge that equates to (or results in) the criterion concentration in the receiving water body. In this chapter we will explore some of the possible approaches to developing site specific metals translators. The purpose of this document is to help implement EPA's dissolved metals policy; therefore, every attempt has been made to keep the following discussion as technically simple as possible. As you read this discussion, keep in mind that the metals partition between dissolved and adsorbed forms. The partition coefficient expresses this equilibrium relationship and may be used to calculate the dissolved fraction. The following discussion presents only the essential equations needed to develop the translator. For a comprehensive discussion of partition coefficients, see Thomann and Mueller (1987).

### 2.1. Sorption-Desorption Theory

In effluents and receiving waters, metals can exist in either of two basic phases; adsorbed to particulates or dissolved in water. More precisely, these "particulates" are sorbents including clays and related minerals, humic substances, organic and inorganic ligands, and iron and sulfur compounds. The total concentration of a metal in the water column can be expressed as

$$C_T = C_p + C_D \quad [\text{Eqn 2.1}]$$

where  $C_T$  = total metal,  
 $C_p$  = particulate sorbed metal, and  
 $C_D$  = dissolved metal.

The metal concentrations are typically expressed as mass per volume (i.e.,  $C_D$  (mass/vol water),  $C_p$  (mass/vol solids plus water, the bulk volume)).

For a given adsorbent concentration (e.g., TSS)  $C_p$  can be expressed as

$$C_p = x \cdot m \quad [\text{Eqn 2.2}]$$

where  $x$  is the metal concentration of the particulate phase expressed on a dry weight solids basis (e.g.,  $\mu\text{g}/\text{mg}$ ) and  $m$  is the adsorbent concentration (mass of solids/vol of solids and water; e.g.,  $\text{mg}/\text{L}$ ). With these dimensions,  $C_p$  has units of  $\mu\text{g}/\text{L}$ .

### 2.2. The Partition Coefficient and the Dissolved Fraction

The distribution of metal at equilibrium between the particulate and dissolved forms is the partition coefficient  $K_p$  ( $\text{L}/\text{mg}$ ). The partition coefficient is the slope of the data of particulate metal ( $\mu\text{g}/\text{mg}$ ) against dissolved metal ( $\mu\text{g}/\text{L}$ )

$$K_p = x / C_D \quad [\text{Eqn. 2.3}]$$

Combining Eqn. 2.3 with Eqn 2.2 provides other useful relationships between dissolved and particulate metals concentrations

$$C_p = C_D \cdot K_p \cdot m \quad [\text{Eqn 2.4}]$$

Substituting Eqn 2.4 into Eqn. 2.1 gives

$$\begin{aligned} C_T &= C_p + C_D \\ C_T &= (C_D \cdot K_p \cdot m) + C_D \end{aligned}$$

$$C_T = C_D (K_p \cdot m + 1) \quad [\text{Eqn 2.5}]$$

The translator, or dissolved metal fraction,  $f_D$ , is defined as

$$f_D = C_D / C_T \quad [\text{Eqn. 2.6}]$$

Substituting Eqn 2.6 into Eqn 2.5 and solving for  $f_D$  gives

$$f_D = (1 + K_p \cdot m)^{-1} \quad [\text{Eqn. 2.7}]$$

The distribution of metal between dissolved and adsorbed phases therefore depends on the partition coefficient and the adsorbent concentration. This is the basis of the metals translator.

### 2.2.1. Developing Site Specific Partition Coefficients

As we saw in Eqn. 2.3, the partition coefficient is not measured directly, rather it is calculated from measured values (at equilibrium) of adsorbed metal per unit adsorbent<sup>10</sup> ( $x$ ) divided by the concentration of

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<sup>10</sup> TSS is used throughout this document as the measure of metal binding sites. It is possible to use other measures of the binding sites such as total organic carbon (TOC), particulate organic carbon (POC), dissolved organic carbon (DOC), or some combination of TSS, TOC, DOC, etc.

dissolved metal ( $C_D$ ).

$$K_p = x / C_D$$

We also saw in Eqn. 2.2 that  $C_p = x \cdot m$ . If we let  $m = \text{TSS}$ , then  $x = C_p / \text{TSS}$ .

Substituting into Eqn 2.3 gives

$$K_p = (C_p / \text{TSS}) / C_D \quad [\text{Eqn. 2.8}]$$

which rearranges<sup>11</sup> to

$$K_p = C_p / (C_D \cdot \text{TSS}) \quad [\text{Eqn. 2.9}]$$

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<sup>11</sup> If  $K_p$  is desired with units of L/kg, Eqn 2.9 is modified by the conversion factor of  $10^6$  kg/mg:  

$$K_p (\text{L/kg}) = C_p (\mu\text{g/L}) / (C_D (\mu\text{g/L}) \cdot \text{TSS} (\text{mg/L}) \cdot 10^6 (\text{kg/mg}))$$

### 3. FIELD STUDY DESIGN

**C**onsideration should be given to use of clean sampling and analytical techniques. These are recommended but not necessarily required; however, it is essential that appropriate procedures be used to detect metals at the concentrations present in the effluent and receiving waters. Clean sampling and analytical methods are useful ways of obtaining good data when traditional methods may provide data with significantly high or low bias. Sufficient quality control data must accompany environmental data to allow its validation.<sup>12</sup>

A statistically valid field study design, with attendant QA/QC, (e.g., adequate number of samples, field blanks, spiked samples, etc.) is essential for the successful development of a metals translator. Recognizing that a key factor in metals availability to biota in the water column is the partitioning of metals between the solid phase material and water, TSS (which contains humic materials, clay minerals, other organic matter both living and dead) emerges as the obvious environmental variable of interest. However, the composition of TSS is highly variable both in terms of the constituents (e.g., sand, silt, clay, planktonic organisms, and decomposing organic materials) and their size distributions. Highly variable relationships between TSS and metals partitioning must be anticipated because of the temporal (e.g., season of year, type and magnitude of storm) and the spatial variability (e.g., such as may be associated with changes in hydrology, geochemistry, or presence, number, and type of effluent dischargers) of the receiving water

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<sup>12</sup>Measurements made below the quantitation levels (QL) will suffer from significant analytical variability, which may directly affect the ratio (especially if the ratio is near 1.0). Test measurements capable of achieving extremely low detection levels and QLs should be sought to avoid the excessive analytical variability. The choice of laboratories and analytical methods can be critical to the success of a translator study.

bodies. For example, pH may vary over several units as a result of acidic precipitation in the watershed, photosynthetic activity in the water body (lowest pH at dawn and highest pH in early afternoon coincident with peak photosynthetic activity of phytoplankton and other aquatic vegetation), or effluent discharge to the water body. Changes in pH over a specific range may have a marked effect on metal solubility. Consequently, it may be important to consider the normal range of pH when designing the study and to collect samples under pH conditions that would render the metal or metals of interest most soluble, or over a narrow range of pH conditions to reduce scatter in the resulting data set. The pH effect is of concern in geographic areas that have little buffering capacity and on "acid sensitive" streams.

Industrial and municipal waste waters and receiving waters vary greatly in chemical constituents and characteristics. This chapter presents general guidelines and considerations to assist in establishing effective sampling programs for varied situations.

#### 3.1. Sampling Schedule

The sampling design should be adequate to evaluate spatial and/or temporal variability and to properly characterize the environmental condition. The choice of when and where to conduct the study, how long to study, and how frequently to sample may be influenced by the type of translator being developed.

For instance, the translator may be developed specifically for use under conditions that are most likely to be representative of "critical flow" or "design" conditions. (The critical flow may or may not be the same as the 7Q10 or 4B3 design low flow; this is discussed in Section 3.1.1 below.) To meet this application, samples should be collected under

conditions that approximate the critical flow.

On the other hand, the translator may be developed for use over a broad range of flow and associated TSS concentrations. If this is desired, then the samples should be collected to produce a data set representative of a broad range of conditions.

### 3.1.1. Considerations of Appropriate Design Flow Conditions for Metals

*In the absence of data to the contrary, the normal assumption will be that low flow (limited dilution capacity) is the critical flow for metals.*<sup>13</sup> However, determining the period of critical flow is more complicated for metals than for many other pollutants because one cannot necessarily ascertain the appropriate design conditions without a field study to generate data on flow, pH, and adsorbent concentrations. If one were to collect samples of TSS, POC, water flow, hardness pH, ambient metals, etc. over a prolonged period (i.e., several years) then one could examine the data set to determine which combination of conditions would result in the highest dissolved metal concentration for a "unit load" of metal in the effluent stream. The flow regime associated with this critical condition would constitute the design flow. Because the dissolved metals concentration in the receiving water depends on metals partitioning to solids as well as dilution of dissolved metals in the water, and because the lowest TSS (or other adsorbent) concentrations do not always correspond with low stream flow conditions, there will be some combination of TSS, flow, hardness and pH that will result in the greatest dissolved concentration.

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<sup>13</sup>It is important to recognize that worst-case acute dilution (highest concentration of effluent) may not occur during periods of low flow and TSS, especially in estuarine waters. Under such circumstances, the data to develop the translator should be collected to represent the critical conditions.

For instance, consider a facility that has high solids releases and contributes a sizeable fraction of the receiving water flow. It may be that TSS concentrations in the mixing zone show a bimodal distribution with stream flow (high under low flow conditions because of the effluent dominance, low under higher stream flow conditions because of greater dilution, and high under high flow conditions because of upstream nonpoint source solids loadings). It is conceivable that the low TSS may be more important than low flow in achieving water quality standards in this stream segment. Additionally, pH may vary throughout the day, may vary seasonally, or may be somehow correlated with flow. Information of this nature should also be used in selecting the most appropriate conditions and most appropriate time to conduct the study. *To reduce variability in the data caused by factors other than adsorbent concentration, it will be helpful to measure pH and, to the extent possible, collect samples under similar pH conditions.* As suggested above, samples should be collected under pH conditions that would render the metal(s) of interest most soluble.

### 3.1.2. Frequency and Duration of Sampling

A field study to develop a metals translator is expected to extend over several months. A long sampling schedule has many advantages, chief among them is the ability to generate data that are representative of the many conditions that characterize receiving water bodies. Ideally, prior to collecting data to develop a metals translator, the receiving water body would have been studied sufficiently to characterize temporally, if not spatially, distributions of flow, TSS, hardness, and pH. To the extent that such data exist, the sampling can be stratified to reduce variability. If such data are available to characterize the system, statistical methods may be used to determine the frequency of sampling. *In the absence of such data, EPA suggests weekly or*

*biweekly sampling during specified receiving water flow conditions when developing the translator for use under "design flow" conditions and biweekly or monthly sampling when developing the translator for use over a range of flow conditions.*

In addition to receiving water conditions, it is equally important to consider variable plant operations when determining sampling frequency. In addition to continuous and uniform releases, the range of conditions may include:

- (1) Seasonal operation,
- (2) Less than 24 hour per day operation,
- (3) Special times during the day, week or month, or
- (4) Any combination of the above.

When monitoring these types of operations, it is necessary to sample during normal working shifts in the season of productive operations.

### **3.2. Sampling Locations**

Depending on state guidance or regulatory negotiations, samples may be collected from the effluent, the receiving water before mixing with the effluent, the receiving water at the edge of the mixing zone, and/or the receiving water in the far field (beyond the mixing zone). Results obtained from these different locations may differ substantially.

The magnitude of the translator may depend on the concentration of effluent in the downstream water. The concentration of effluent in the downstream water will depend on where the sample is taken, which will not be the same for acute and chronic mixing zones. The criteria maximum concentration (CMC) applies at all points except those inside a CMC mixing zone; thus if there is no CMC mixing

zone, the CMC applies at the end of the pipe. The criteria chronic concentration (CCC) applies at all points outside the CCC mixing zone.

There are some practical difficulties involved in selecting the sampling location in the receiving environment. In the absence of a mixing zone study it is very difficult to define with any certainty the shape and extent of a mixing zone, or the dilution and dispersion that occur within the mixing zone. Many states have separate boundaries for compliance with acute and chronic criteria. Dilution and dispersion processes are influenced not only by volume, velocity, and other characteristics of the discharge, but also by convection, currents, and wind effects in the receiving water. As a result, extensive sampling and computer modeling are typically required to estimate the nature and extent of mixing.

The following approaches are acceptable for the purpose of developing the translator. When deciding where to locate sampling stations, consideration should be given to sampling at the point of complete mixing (rather than at the edge of the mixing zone) if existing environmental factors constitute a basis for concern that downstream conditions may result in nontoxic metal becoming toxic.

#### **3.2.1. Collect Samples at or Beyond the Edge of the Mixing Zone**

It is recommended that samples be collected at or beyond the edge of the mixing zone. Appropriate field sampling techniques and appropriate QA/QC are discussed in Appendix E. It is important to recognize that if samples are not also collected from the ambient water (background), then the subsequent analysis (for permit limit determination) implicitly assumes that *all* of the metal in the receiving water comes from the discharger.

The translator should result in a permit limit that is protective of the receiving water. In order to ensure this, *under some conditions*, it may be important that samples be collected from a point where complete mixing has occurred. It may be advisable within a given river segment to take the samples well below the edge of the mixing zone in order to ensure good mixing and to reduce variability in the data set. Environmental processes that might cause nontoxic metal to become toxic include fate processes such as oxidation of organic matter or sulfides or an effluent or tributary that lowers the pH of the downstream water. The approach of collecting samples beyond the edge of the mixing zone may be especially valuable in estuarine and coastal ocean locations where the ebb and flow of tidal cycles complicate the hydrodynamics.<sup>14</sup> In areas where cumulative discharge effects can be anticipated, the individual contributions and combined effects of the multiple discharges must be considered in developing the translator, as well as in the TMDL allocation and development of the permit limit.

### 3.2.2. Collect Samples from the Far Field

There are times when concerns for far field effects will require evaluation of the ratios of dissolved and total recoverable metals and metal partitioning beyond the mixing zone. Far field sampling is appropriate in circumstances where changes in geology, land use/land cover, or low pH effluent discharges from other facilities may alter the water body chemistry. Far field studies also may be required where spatial changes in water chemistry and hydrology affect sorption-desorption rates and settling rates respectively with the potential adverse effects on the biological integrity of benthic communities. The potential for increased dilution resulting in lower metal

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<sup>14</sup>This document does not discuss hydrologic differences that are specific to marine and estuarine discharges.

concentrations and increased analytical difficulties must also be considered when contemplating these studies. If, however, the samples are collected within the same reach, there should not be any appreciable increase in dilution.

If samples for translators are collected from far-field locations a translator will result whose value is established based on the characteristics of the receiving water, not on the characteristics at the edge of the mixing zone or on the characteristics of the effluent before it is fully mixed. Recent investigations of discharges from a Waste Water Treatment Plant (WWTP) to a lowflow stream in Florida have demonstrated an apparent increase in the dissolved fraction of silver at a distance (travel time) of four hours downstream of the discharge.<sup>15</sup>

### 3.2.3. Collect Samples from Effluent and Ambient Water and Combine in the Laboratory

Samples are collected from the effluent (i.e., end of pipe) and the ambient receiving water (i.e., upstream of the outfall in rivers and streams; outside of the influence of the discharge in lakes, reservoirs, estuaries, and oceans). Appropriate QA/QC and field sampling techniques are discussed in Appendix E. Mixing and filtration must be done as soon as possible to minimize risk of changes to the dissolved/total metals ratio due to adsorption onto the container and partitioning effects. The Agency is soliciting data that will allow recommendations to be developed regarding maximum delays in combining the samples and how long the combined sample should be allowed to equilibrate before filtering an aliquot for the dissolved portion.

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<sup>15</sup>Personal communication with Tim Fitzpatrick, Florida Department of Environmental Protection, Tallahassee, FL.

Samples are collected from the effluent and the receiving water before it mixes with the discharge and are mixed in accordance with the dilution factor to create a simulated downstream water in proportion to the dilution that the mixing zone is designed to achieve. The mixed waters are analyzed for dissolved and total recoverable metal. The translator is calculated from the dissolved fractions.

For rivers and streams, the receiving water samples would be collected upstream of the discharge. For lakes, reservoirs, estuaries, and oceans, the samples would be collected at a point beyond the influence of the discharge, yet representative of water that will mix with the discharge. In tidal situations, where the effluent plume may move in different directions over the tidal cycle, some knowledge of the hydrodynamics of the receiving water will be necessary to select the appropriate point as well as the appropriate sampling time within the tidal cycle. In estuaries that are dominated by either river flow or tidal flushing, the sampling location should reflect the dominant source of dilution water.

*In cases of multiple discharges to the same river segment, for example, the translator should be developed as  $f_D$  at the downstream end of the river segment and applied to all dischargers to that segment*

### 3.3. Number of Samples

Most statistics textbooks (e.g., Sriedecor, 1956; Steel and Torrie, 1980; Zar, 1984; Gilbert, 1987)) present discussions of sample size (i.e., number of samples). Generally, sample size is affected by the variance of the data, the allowable error in the estimation of the mean, and the desired confidence level. If data have been collected previously, they can be used to provide a good estimate of the expected variance.

From a statistical basis we can specify a theoretical minimum number of samples. Beyond this consideration, it is necessary to be cognizant of such factors as spatial and temporal variability in physical and chemical conditions that may affect the value of the translator and to design the study to appropriately account for these differences. Seasonality of receiving water flow and associated chemical properties need to be considered. The value of the translator must be appropriate to provide protection to the water body during the low flow or otherwise critical condition associated with a particular critical time of the year.

In the metals guidance memorandum (Prothro, 1993), EPA recommended the development of site-specific chemical translators based on the determination of dissolved-to-total ratios: EPA's initial recommendation was that at least four pairs of total recoverable and dissolved ambient metal measurements be made during low flow conditions or 20 pairs over all flow conditions. EPA suggested that the average of data collected during low flow or the 95th percentile highest dissolved fraction for all flows be used. The low flow average provides a representative picture of conditions during the rare low flow events. The 95th percentile highest dissolved fraction for all flows provides a critical condition approach roughly analogous to the approach used to identify low flows and other critical environmental conditions.

The collection of dissolved and total concentrations at low flows is still the recommended approach, but the collection of at least 10 samples, rather than 4, is recommended to achieve higher confidence in the data. The 95<sup>th</sup> percentile or other extreme percentile of  $f_D$  (e.g., 90<sup>th</sup> percentile) may be used as an alternative method of including a MOS in TMLDs or WLAs. Additional details of determining the required sample size are presented in Appendix D.

### 3.4 Parameters to Measure

Ideally the field study is designed to generate data on total recoverable ( $C_T$ ), dissolved ( $C_D$ ), and particulate metal fractions ( $C_P$ ) as well as TSS, POC, pH, hardness, and stream (volume) flow. A complete data set allows for more complete understanding of the environmental fate and transport processes and may result in a more accurate permit limit because of reduced variability and uncertainties.

Depending on the means by which the translator is being developed, some of these data elements may not need to be generated. For instance, it may be desirable to estimate  $C_P = C_T - C_D$  rather than to measure  $C_P$ . Of course, if  $C_P$  is the parameter of greatest interest, calculating  $C_P$  from the dissolved and total recoverable concentrations incorporates the uncertainty associated with the latter two measurements. A direct measurement of the particulate fraction may reduce this uncertainty. Of course, the measurement of the particulate fraction then increases the total uncertainty because of the uncertainty associated with its measurement. It is likely that if the three fractions (total, dissolved, and particulate) are measured, the sum of these three fractions will not equal  $C_T$ . *It is possible to develop the translator from a study that only generates data on total recoverable and dissolved concentrations in the downstream water.*

### 3.5. The Need for Caution in Sampling

The sampling procedures for metals that have been used routinely over the years have recently come into question in the academic and regulatory communities because the concentrations of metals that have been entered in some databases have been shown to be the result of contamination. At EPA's Annapolis Metals Conference in January of 1993, the consensus of opinion was (1) that

many of the historical low-concentration ambient metals data are unreliable because of contamination during sampling and/or analysis, and (2) that new guidance is needed for sampling and analysis that will produce reliable results for trace metals determinations.

EPA has released guidance for sampling in the form of Method 1669 "Sampling Ambient Water for Determination of Trace Metals at EPA Water Quality Criteria Levels" (USEPA, 1995a). This sampling method describes the apparatus, techniques, and quality control necessary to assure reliable sampling. Method 1669 was developed based on information from the U.S. Geological Survey and researchers in academia, marine laboratories, and the commercial laboratory community. A summary of salient points are presented in Appendix E. Interested readers may also wish to refer to the 1600 series of methods, CFR 40, Part 136, July 1, 1995.

Note that recent studies conducted by the USGS (Horowitz, 1996) indicate that great bias can be introduced into dissolved metals determinations by filtration artifacts. The use of the Gelman #12175 capsule filter, which has an effective filtration area of  $600 \text{ cm}^2$ , and the practice of limiting the volume of sample passed through the filter to 1000 ml are necessary to ensure unbiased collection of dissolved metals. Variations from these recommendations must be demonstrated to produce equivalent quality data.

#### 4. DATA GENERATION AND ANALYSIS

**D**etermination of metals' concentrations at ambient criteria levels is not presently routine in many commercial and industrial laboratories. To familiarize laboratories with the equipment and techniques that will allow determination of metals at trace levels, the Agency has supplemented existing analytical methods for determination of metals at these levels, and published this information in the "Quality Control Supplement for Determination of Trace Metals at EPA Water Quality Criteria Levels Using EPA Metals Methods" (QC Supplement; USEPA, 1994a). The QC Supplement is based on the procedures and techniques used by researchers in marine research laboratories who have been at the forefront of trace metals determinations.

An overview of the QC Supplement is presented in Appendix E for the reader's convenience. Persons actually developing a metal translator should read the QC Supplement

##### 4.1. Analytical Data Verification and Validation

In addition to Method 1669 for sampling (USEPA, 1995a) and analytical methods for determination of trace metals (USEPA, 1994b), the Agency has produced guidance for verification and validation of analytical data received (USEPA, 1995b). This guidance was produced in response to the Agency's need to prevent unreliable trace metals data from entering Agency databases and other databases in the environmental community and relies on established techniques from the Agency's data gathering in its Water and Superfund analytical programs to rigorously assess and document the quality of analytical data. General issues covered in the

guidance include:

- The data elements that must be reported by laboratories and permittees so that Agency reviewers can validate the data.
- The review of data collected and reported in accordance with data elements reported.
- A *Data Inspection Checklist* that can be used to standardize procedures for documenting the findings of each data inspection.

##### 4.2. Evaluation of Censored Data Sets

Frequently data sets are generated that contain values that are lower than limits deemed reliable enough to report as numerical values (i.e., quantitation levels [QL]). These data points are often reported as nondetected and are referred to as censored. The level of censoring is based on the confidence with which the analytical signal can be discerned from the noise. While the concentration may be highly uncertain for substances below the reporting limit, it does not necessarily mean that the concentration is zero (USEPA, 1992).

Measurements made below the quantitation levels will suffer from analytical variability, which may directly effect the ratio, especially if  $C_D/C_T$  is near 1.0. Extremely low detection levels and quantitation levels should be sought to avoid excessive analytical variability.

This guidance does not address whether or not it is appropriate to use test measurements below quantitation or detection levels in any context other than chemical translator studies conducted by the discharger. For translator studies, measurements at or above a detection level that is reliably achievable by the

particular laboratory performing the analyses can be used. If concentrations are near the detection level, some of the samples may be reported as below the detection level (i.e., nondetects). If both total recoverable and dissolved concentrations are nondetects, the data pair should be discarded. If only the dissolved concentration is nondetect, it could be assumed to equal one-half the detection level. Some studies have collected enough data so that incomplete records, including records where dissolved concentrations were nondetects, were discarded prior to analysis. If, for example, the translator is a function of TSS, the TSS concentration that accompanies each total recoverable and dissolved data pair must also be at or above the detection level. Alternatively, assuming that an adequate number of samples have been collected, incomplete records may be eliminated from analysis.

#### 4.3 Calculating the Translator Value

The most direct procedure for determining a site-specific metal translator is simply to determine  $f_D$  by measuring  $C_T$  and  $C_D$  and to develop the dissolved fraction as the ratio  $C_D/C_T$ . The first step (Box 1) is to calculate the dissolved fraction in the receiving water. The translator is calculated as the geometric mean of the dissolved fractions.

#### Box 1. The Translator is the Dissolved Fraction: $f_D = C_D/C_T$

- Step 1 - For each field sample determine  $f_D = C_D/C_T$
- Step 2 - If the translator is not dependent on TSS, determine the geometric mean  
 $GM_{f_D} = \exp(\sum_i^n \ln(f_D) / n)$   
 and upper percentile values of the dissolved fraction. If the data are found not to be log-normal, then alternative transformations should be considered to normalize the data and determine the transformed mean and percentiles. Also, alternative upper percentiles may be adopted as a state's policy to address MOS (e.g., 90<sup>th</sup> or 95<sup>th</sup> percentiles may be appropriate.)
- Step 3 - If the translator is found to be dependent on TSS, regression equations relating  $f_D$  to TSS should be developed. Appropriate transformations should be used to meet the normality assumptions for regression analysis (for example log-transformation of  $f_D$  and TSS may be appropriate). The regression equation or an upper prediction interval may be considered for estimation of  $f_D$  from TSS depending on the strategy for addressing MOS.

As a general comment on the proposed use of the geometric mean, the geometric mean is only an appropriate estimate of the central tendency if the data are log-normal. Alternative measures of central tendency or transformations should be considered if the distribution of  $f_D$  is found not to be log-normal. For example, the arcsine square root transformation is often used to normalize populations of percentages or proportions

(square root of each value is transformed to its arcsine).

A partition coefficient may be derived as a function of TSS and other factors such as pH, salinity, etc. (Box 2). The partition coefficient is the ratio of the particulate-sorbed and dissolved metal species multiplied by the adsorbent concentration. The dissolved fraction and the partition coefficient are related as shown in step 3.

have on  $f_D$ .

Examples of these analyses to determine appropriate translator values are presented in Appendix C.

**Box 2. The Translator is the Dissolved Fraction ( $f_D$ ) Calculated via Site Specific Partition Coefficients**

Step 1 - For each field sample determine

$$C_p = C_T - C_D,$$
$$K_p = C_p / (C_D \cdot TSS)$$

Step 2 - Fit least squares regressions to data (transformed, stratified by pH, etc.) as appropriate to solve for  $K_p$ .

Step 3 - Substitute the regression derived value of  $K_p$  in Eqn 2.7,  
 $f_D = (1 + K_p \cdot TSS)^{-1}$

Step 4 Determine  $f_D$  for a TSS value representative of critical conditions.

The partition coefficient may provide advantages over the dissolved fraction when using dynamic simulation for Waste Load Allocation (WLA) or the Total Maximum Daily Load (TMDL) calculations and permit limit determinations because  $K_p$  allows for greater mechanistic representation of the effects that changing environmental variables

## 5. SITE-SPECIFIC STUDY PLAN

**C**hapter 3 discusses the considerations involved in designing a field study for a site-specific chemical translator for metals. Chapter 4 and Appendix D discuss analytical chemistry considerations. This Chapter provides guidance on preparing a basic study plan for implementing a translator study, with specific considerations for each of four types of receiving waters: rivers or streams, lakes or reservoirs, estuaries, and oceans. It can be used for all of the options discussed in this guidance. This generic plan is based on the determination of dissolved-to-total ratios in a series of 10 or more samples. With this guidance, the discharger should be able to prepare a study plan that its environmental staff could implement or one that could be used to solicit bids from outside consultants to conduct the studies. *In most cases, the study plan should be submitted to the state for review and approval before implementation.*

The format of this chapter is to present sequentially the essential sections of a study plan: objective, approach, parameters, sampling stations, sampling schedule, preparation, sampling procedure, field protocol, and data analysis. Within each section a three-tiered format is used to provide instructions for the study plan preparer. The basic directions for preparing the section are presented left-justified on the page. Under each direction is a checklist of decisions or selections, designated with the symbol □, that the preparer must make to complete that direction. Under each of these decision points is a list of important considerations, noted by the symbol ●. References to more detailed discussions are provided where appropriate. If any state guidance for translator studies exists, it would supersede any of the considerations discussed below unless the state and the discharger agree to an alternative plan.

Much of the basic study plan is presented in a generic context that is applicable to any type of receiving water. Where differences in the study plan would occur for different receiving waters, the considerations are highlighted with a ♦. Dischargers on run-of-river reservoirs, or on lakes or reservoirs dominated by riverain discharges during runoff events, should generally follow the considerations listed for rivers/streams.

### 5.1. Objective

State the objective of the project. For example,

"To determine the acute [or chronic or acute and chronic] metals translator for [list metals] in the discharge from Outfall 00X."

### 5.2. Approach

Describe briefly the approach adopted in the study plan to achieve the objective. For example,

"Samples of effluent and upstream receiving water will be collected and mixed in proportions appropriate to the dilution at the edge of the [acute/chronic] mixing zone[s]. These mixed samples will be analyzed for total recoverable and dissolved [list metals]. The translator will be calculated as the geometric mean of the ratios of dissolved metal to total recoverable metal for all sample pairs."

Equipment blanks and field blanks are critical to document sample quality.

especially at low concentrations which can be significantly biased by even small amounts of contaminants. Field duplicate samples are also very important to establish precision in sampling and final sample preparation.

### 5.3. Parameters

Prepare a table listing parameters, analytical methods, and required detection levels.

- Select parameters—see Section 3.4.
- Select analytical methods and detection levels—see Section 4.
- Detection level will be the primary determinant of the analytical methods to be used. Metals potentially requiring GFAA and perhaps ultralow analyses are those with very low aquatic life criteria and concentrations below 10  $\mu\text{g/L}$ . Prime candidates are cadmium (fresh water), copper (salt water), mercury, and silver.
- Ideally, the detection level should be 5-10 times lower than the concentration of dissolved metal. An ultralow detection level should be considered if dissolved concentrations are less than 1-2 times higher than the standard detection level.
- Detection levels and methods should be reviewed with the analytical laboratory expected to perform the analyses before finalizing the study plan. One or more test samples may be advisable if detection levels or concentrations are unknown in any particular matrix.
- ◆ **Estuary/Ocean** Chloride interference may affect detection levels, particularly for GFAA methods. Special steps may

be necessary to achieve detection levels low enough to produce a valid translator. Such alternatives include matrix modifiers, background-correction instrumentation, and extraction or preconcentration. If uncertain, check with a local laboratory experienced in saltwater matrix analyses. Preliminary testing and detection level studies may be necessary to determine if a problem exists.

As an option for justifying the selected methods and detection levels to the regulatory agency, prepare a narrative of the rationale for the selections made.

Identify the laboratory that will be analyzing the samples and provide evidence of state certification, if required.

Describe laboratory protocols and QA requirements.

- Select standard or clean (class-100) practices—see Section 3.1, 4.3.
- Select QA requirements
  - Trip blank
  - Duplicate analysis of all samples and blanks
  - Laboratory method blank for each batch of samples
  - MS/MSD on each batch of samples

### 5.4. Sampling Stations

Prepare a map and/or a narrative description of the sampling stations.

- Select a sample location option—see Sections 3.2, 3.2.1, 3.2.2, 3.2.3.
- Conceptually, collecting samples at the

edge of the mixing zone is the most direct way to determine the translator. However, the edge of the mixing zone may be difficult to define, especially if stream flow and discharge rate (e.g., number of units operating) will be variable over the course of the study. Even if the mixing zone's dimensions are prescribed exactly, the samples may have to be collected at some critical hydrologic condition to represent the critical toxicological conditions. An alternative option may be to collect effluent and upstream receiving water samples, and mix them in the appropriate proportions before analysis. In addition, far-field sampling may be required to establish that dissolved metal concentrations do not increase after the effluent is well-mixed with the receiving water.

- Definition of the "upstream" sampling point will vary with the receiving water type:
- ◆ **River/Stream** Immediately upstream of the influence of the discharge, or any point further upstream with no contributing source between it and the outfall
- ◆ **Lake/Reservoir** Beyond the influence of the discharge (dilution > 100:1), generally in a direction toward the headwaters of the lake/reservoir if possible
- ◆ **Estuary/Ocean** Beyond the influence of the discharge (dilution > 100:1), generally in a direction away from the movement of the discharge plume at the time of sampling

- Determine whether grab or composite samples will be used—see Appendix E.
- Wastewater treatment plant effluent—24-hour composite
- Noncontact cooling water—same as receiving water
- ◆ **River/Stream**—Grab, under low-flow conditions
- ◆ **Lake/reservoir**—Grab
- ◆ **Estuary/Ocean**—Grab (slack tide) for acute; tidal composite for chronic

### 5.5. Sampling Schedule

Specify the number of samples, frequency of sampling, study period, and any other conditions (e.g., season, stream flow) affecting the sampling schedule.

- Select the number of samples—see Section 3.3.
- The recommended minimum number of samples for a low-flow sampling program is 10; 12 would be appropriate if monthly sampling for a year is desired to incorporate seasonality.
- If sampling occurs over a wide range of flows or the translator is developed through regression analyses, 20 or more samples may be appropriate.
- Select the frequency of sampling—see Section 3.1.2.
- Weekly sampling is recommended; monthly sampling may be appropriate if seasonality is expected to be an issue.
- ◆ **River/Stream** The interval between samples will have to be somewhat flexible because samples should be collected under low-flow conditions: e.g., if a sample is to be collected on Wednesday and the river flow is high

on that day, sampling should be postponed until the first day when flow returns to base-flow levels, or it will have to be postponed until the next planned weekly event.

- ◆ **Estuary/Ocean** Monthly or biweekly sampling may be required if state regulations reference critical monthly tidal periods, such as biweekly neap tides.
- Determine the study period—see Section 3.1.
- ◆ **River/Stream** Generally, the low-flow period of the year (e.g., July through October in the East and Midwest) is preferred, unless the time constraints of the permitting process or the local hydrologic regimen dictate otherwise.
- ◆ **Lake/Reservoir** Unless there are seasonal discharges or reservoir operating procedures that significantly affect water quality, study period generally is not critical to study plan. Algal bloom conditions should be avoided.
- ◆ **Estuary** May need to split sampling between low- and high-salinity seasons, because large changes in salinity between seasons indicates the dominance of different water sources (fresh water at low salinity and salt water at high salinity) with potentially different particulate matter concentrations or binding capacities.
- ◆ **Ocean** Unless seasonal currents significantly affect water quality, study period generally is not critical to study plan.
- Determine other important considerations
- Plant operating conditions should be considered. Samples should be

collected during periods of typical operation, particularly with respect to operations that affect the TSS concentration or the concentration or the total:dissolved ratio of the metal(s) being studied.

- If copper is being studied by an electric utility, and the plant has copper and non-copper condenser tubes, sampling should occur when the units with copper tubing are operating.
- ◆ **River/stream** Sampling should be conducted under base-flow conditions, which could be defined in terms of measured stream flow (e.g., less than the 25th percentile low flow), stream stage (e.g., stream height less than 1.5 feet at gaging station XYZ), turbidity (e.g., less than 5 NTU), TSS concentration (e.g., less than 10 mg/L), visual appearance (e.g., no visible turbidity), or days since last significant rainfall (e.g., more than 3 days since rainfall of 0.2 inches or more).
- ◆ **Lake/Reservoir** As long as the sampling location is unaffected by runoff, hydrologic considerations are not significant.
- ◆ **Estuary/Ocean** Since acute criteria are generally considered to have an exposure duration of 1 hour, samples for acute translators should be collected under worst-case tidal conditions—generally low slack when dilution is typically at its lowest. Chronic criteria are usually expressed with a 4-day average exposure duration, so sampling over a tidal cycle is appropriate for chronic translators. If the discharger is willing to accept the conservatism of sampling for a chronic translator under worst-case conditions—slack tide—then sampling costs could be reduced substantially.

## 5.6. Preparation

Prepare a list of equipment and supplies that need to be assembled before each sampling event; for example.

Sample bottles, labeled, with preservative (for total recoverable)

Samples bottles, labeled, without preservative (for dissolved

Sample bottle carrier, e.g., clean plastic cooler

Waterproof marker for filling in bottle labels

Chain-of-custody form

Sampling gear—e.g., sampling bottle, sampling pole (plastic or aluminum if aluminum is not being studied), high-speed peristaltic pump and teflon tubing

Field portable glove box (for on-site filtering and compositing)  
Plastic gloves (non-talc)

Filtering apparatus, if required for field crew

Field notebook or log sheet

Safety equipment

Describe cleaning requirements for sample bottles and sampling equipment that will come in contact with samples.

- Select standard or clean sampling/analysis.

Prepare a list of actions to be completed before the sampling event, such as contacts to be made (discharger, consultant, laboratory, regulatory agency).

Prepare a list of contacts and phone numbers.

## 5.7 Sampling Procedure

Prepare detailed instructions on the correct procedure for collecting a sample at any station.

Start with guidance on the careful sampling techniques necessary to avoid sample contamination. For example,

1. Given the low metals concentrations expected, extreme care needs to be taken to ensure that samples are not contaminated during sample collection. *Smoking or eating is not permitted while on station, at any time when sample bottles are being handled, or during filtration.*
2. Each person on the field crew should wear clean clothing, i.e., free of dirt, grease, etc. that could contaminate sampling apparatus or sample bottles.
3. An equipment blank should be done with the actual equipment used for the environmental samples. The field blank described in this section should be performed with the sampling equipment BEFORE the environmental samples are collected. This blank will serve to verify equipment and sampling protocol cleanliness.
4. Each person handling sampling apparatus or sample bottles should wear the sampling gloves provided. One person only should handle sample bottles, and that person should touch nothing else while collecting or transferring samples.

Then provide step-by-step instructions

for the sampling crew to follow. The specific steps will vary depending on what type of water/wastewater is being sampled and what type of sampling device is being used. For grab samples collected by hand using a sampling pole to which the sample bottles are attached, the guidance might continue:

5. Attach unpreserved bottle to sample collecting pole. Plunge pole 2 to 3 feet under water surface quickly. Pull sample bottle up and fill preserved bottle from unpreserved sample bottle, leaving ½ to 1 inch of air space at the top. Swirl to mix acid, close cap tightly, and return bottle to carrier.
6. Collect duplicate sample by plunging unpreserved sample bottle back under water, retrieving, and capping bottle tightly for dissolved sample, again leaving ½ to 1 inch of air space in the bottle. Return bottle to carrier.

Other sampling procedures may be chosen to produce acceptable quality data, e.g. a closed sampling system with immediate sample processing. Equipment for in-line sample collection used for filtering with the (essentially mandatory) Gelman capsule filter can be used for sample collection. See Method 1669 § 8.2.8 for a description of sampling steps and Method 1669 § 8.3 for on-site composting and filtration in a glove box. See also Appendix E.2.

### 5.8. Field Protocol

Provide a list of criteria which the field crew leader should review before starting sampling to ensure that proper conditions exist.

- Is there a discharge? Are operating conditions at the facility appropriate for measuring the metals of concern in the effluent?

- Are hydrologic conditions (e.g., base flow, slack tide) acceptable?

Describe *in clear, simple instructions* the sequence of actions that the field crew will follow from the beginning to end of a sampling event. This sequence will vary from project to project. Typical steps might include:

1. Before embarking, confirm number and type (preserved/unpreserved) of sample bottles, and read off checklist of equipment/supplies.
2. Before beginning sampling, fill in chain-of-custody forms and bottle labels with all information except time of sampling.
  - Each bottle should have a unique sample number, and it should be labeled "Total" or "Dissolved." If preservative has been added to the bottles before sampling, the label should note that fact.
  - Chain-of-custody forms pre-prepared with everything but the sampling date and time are recommended.
  - Provide sample chain-of-custody form and bottle label as attachments to study plan.
3. At Station 1, fill in sampling time on label of two samples bottles, one preserved and one unpreserved. Collect samples following the procedure outline above. Return bottles to carrier immediately after collection. Fill in field notebook or log form—weather, hydrologic conditions, plant operating status (if known), sample bottle numbers and collection time (total and dissolved), and unusual observations or circumstances.
4. At Station 2, fill in sampling time on labels of two sample bottles, one

preserved and one unpreserved. Collect samples following the procedure outline above. Return bottles to carrier immediately after collection. Fill in field notebook or log form—weather, hydrologic conditions, plant operating status (if known), sample bottle numbers and collection time (total and dissolved), and unusual observations or circumstances.

5. After finishing at Station 2, collect the field blanks—one preserved and one unpreserved. Fill in sampling time on label, open sample bottle, and pour in laboratory water. Cap bottles tightly and place in carrier. Note bottle numbers and collection time in field notebook or log sheet.
  - If additional sampling gear is used in collecting the samples, the field blanks should be collected by rinsing that gear three times with the laboratory water, and then filling the gear with enough water to transfer to the 2 field blank bottles. If a pump or an automatic sampler is used, several sample bottle volumes of laboratory water should be pumped through the sampler tubing before the field blank bottles are filled.
6. Complete chain-of-custody. Check bottle carrier to ensure bottles are upright and well packed.
7. Deliver samples to laboratory. Have sample custodian sign chain-of-custody for receipt of samples, and obtain a copy of the chain-of-custody.

Depending on the project, additional instructions may be needed for setting up

automatic samplers, field filtering, and overnight shipping of samples. Because data quality is directly dependent on quality control, the Quality Control Supplement (EPA, 1994a) should be reviewed.

## 5.9. Data Analysis

Describe the method for calculating the chemical translator.

- Select a calculation procedure—see Sections 1.5.
- Specify the treatment for values below the detection level—see Section 4.2.

## 5.10. Schedule

Provide a schedule for the entire study, from selection of consultant or mobilization of field effort through completion of final study report.

- Link schedule to receipt of approval from state, if required
- Emphasize impact of delays on study if sampling must occur within a certain calendar timeframe
- Incorporate contingencies for sampling events postponed because of unacceptable conditions

## 5.11. State Approval

Provide a signoff line for state regulatory agency. This is recommended, but not mandatory.

## 6. BUILDING A SPREADSHEET MODEL

**A**s discussed in earlier chapters, a series of steps must be taken to implement the dissolved metals policy, including converting the water quality criteria from the total recoverable to the dissolved form, translation from the dissolved CCC or CMC to the total recoverable metal concentration in the discharger's waste stream, calculating the WLA or TMDL, and developing the permit limit. These steps or calculations are easily handled using a simple spreadsheet model. Use of these equations, whether in a spreadsheet or not, can avoid many common mistakes.

The following equations may be used to translate dissolved criteria to total recoverable permit limits with translators developed through studies such as those described in Chapter 5. This model may be used as a static model with design flow conditions, it may be used in a continuous mode (i.e., using daily flow and other data), or it may be used (with programs such as @RISK or Crystal Ball) to perform Monte Carlo analyses. These calculations do not provide concentration estimates between the point of discharge and the point of complete mixing.

The in-stream total recoverable concentration is estimated by solving the following equation:

$$C_t = (\theta \cdot Q_u \cdot C_u + Q_e \cdot C_e) / (\theta \cdot Q_u + Q_e)$$

[Eqn 6.1]

where  $C_t$  = pollutant concentration at the edge of the mixing zone,

- $Q_u$  = upstream flow,
- $C_u$  = upstream pollutant concentration (background),
- $Q_e$  = effluent flow,
- $C_e$  = effluent pollutant concentration, and

$\theta$  = fraction of flow available for mixing.

For example, with Eqn 6.1, the downstream TSS concentration is estimated from mass balance calculations of upstream and effluent loadings:

$$TSS = (\theta \cdot Q_u \cdot TSS_u + Q_e \cdot TSS_e) / (\theta \cdot Q_u + Q_e)$$

[Eqn 6.2]

For translators developed from partitioning equations<sup>16</sup>, (Eqn 2.7), the dissolved in-stream concentration can be expressed as:

$$C_d = C_t / (1 + K_p \cdot TSS)$$

[Eqn 6.3]

By setting the dissolved in-stream concentration ( $C_d$ ) equal to the dissolved criterion concentration ( $C_d = CC_d$ ) and rearranging the equation, we can solve for the in-stream total recoverable concentration ( $C_t'$ ) that equates to a dissolved in-stream concentration equal to the dissolved criterion. Note that this corresponds to Eqn 2.5.

$$C_t' = CC_d (1 + K_p \cdot TSS)$$

[Eqn 6.4]

The total recoverable concentration in the effluent ( $C_e'$ ) that equates to a dissolved in-stream concentration which equals the dissolved criterion in the mixed receiving waters is calculated by Eqn 6.5. This represents the maximum release that will still allow attainment of water quality standards,

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<sup>16</sup>If the translator has been determined directly from measurements of dissolved and total recoverable metal in the downstream water, Eqns 6.3 and 6.4 are not be used. Instead, the dissolved criterion concentration is divided by  $f_o$  to calculate  $C_t'$  which in turn is used in Eqn 6.5.

If the partition coefficient has units of L/kg, then both Eqns 6.3 and 6.4 contain the term 1E-6.

that is the maximum WLA or the maximum TMDL.

$$C_e' = (C_u' (\theta \cdot Q_u + Q_e) - \theta \cdot Q_u \cdot C_u) / Q_e$$

[Eqn 6.5]

Table 4 presents a simple spreadsheet that utilizes these relationships. Note that the second equation in the spreadsheet calculates  $K_p$  and the third equation calculates the associated  $f_D$ . In studies where the translator is developed directly as  $f_D$ , the  $K_p$  equation in the spreadsheet is deleted and  $f_D$  is changed from an equation to an input parameter.

Streamix, an EPA developed spreadsheet application for mixing zone analyses, has been enhanced to consider metal partitioning between dissolved and particulate-sorbed forms. This version, developed for EXCEL, is called METALMIX and provides details of mixing between the point of discharge and the point of complete mix.

Beyond these approaches, EPA's DYNTOX model (USEPA, 1995c) has been modified to properly account for the distribution of metals between dissolved and particulate-sorbed forms. DYNTOX supports Continuous Simulation, Monte Carlo, and Lognormal Probabilistic Analyses

Table 4. Spreadsheet to Calculate Total Recoverable Waste Load Allocation based on Dissolved Criterion

Variables:	Input Values:
Q_u	104
TSS_u	325
C_u	19
Q_e	8.75
TSS_e	1845
Hardness_u	100
Hardness_e	50
mixing fraction (theta)	0.25
	<b>Equations:</b>
CC_d	=EXP(a*LN(Hardness_mix)+b)*conv_fact <dissolved criterion concentration>
Kp	=2.8*TSS_mix^-0.8 <example only>
fD	=1/(1 + Kp*TSS_mix)
Hardness_mix	=(theta * Q_u * Hardness_u + Q_e * Hardness_e) / (theta * Q_u + Q_e)
TSS_mix	=(theta * Q_u * TSS_u + Q_e * TSS_e) / (theta * Q_u + Q_e)
C_t_prime	=CC_d*(1 / fD) <instream total recov conc that equates to dissolved criterion>
C_e_prime	=(C_t_prime * (theta * Q_u + Q_e) - theta * Q_u * C_u) / Q_e <effluent total recov conc resulting in the dissolved criterion in receiving water>

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## APPENDIX A

### Deriving Permit Limits for Metals

**T**his Appendix summarizes the steps involved in applying the dissolved metals policy and illustrates how the translator is used in developing a permit limit.

#### A.1 The Setting for the Example

Our example site is a river which has been identified as being water quality-limited because of high copper concentrations with potential adverse impacts on aquatic life. Copper loading to the impaired reach comes from naturally occurring and anthropogenic sources in the watershed (background) and permitted point source discharges, including two metal plating facilities and a publicly owned treatment works (POTW). For the sake of simplicity, steady-state modeling is used. Episodic, precipitation-driven runoff loadings from urban and industrial areas adjacent to the river could be accounted for using continuous simulation.

Design low flows are typically used for calculating steady-state wasteload allocations (WLAs), including the 1-day average low flow with a ten year recurrence period (1Q10) for acute criteria and the 7-day average low flow with a ten-year recurrence period (7Q10) for chronic criteria. Analysis of 30 years of records from the USGS gage above the sources indicates a 1Q10 flow of 111.77 cfs and a 7Q10 flow of 140.09 cfs.

The two metal plating facilities in our example have multiport diffusers, which have been shown to quickly achieve complete mixing across the width of the river. The POTW effluent enters the same reach as the

facility discharges and is released to a bend in the river where mixing also occurs rapidly. The State's water quality regulations require that water quality criteria are met at the edge of the mixing zone.

#### A.2 Water Quality Standards and Criteria

Water quality standards consist of criteria, designated uses, and an anti-degradation statement. The river, in this example, is classified as having designated uses for aquatic habitat and primary contact recreation (i.e., "fishable, swimmable"), and the State has adopted the federal water quality criteria into its water quality standards to protect aquatic life and human health. The numeric water quality criteria for acute toxicity (criterion maximum concentration, or CMC) and chronic toxicity (criterion continuous concentration, or CCC) to aquatic life are part of the water quality standards and are based on the dissolved fraction of metals. The CMC and CCC depend on ambient hardness concentrations as expressed by the following equation form (as total recoverable metal):

$$WQC_{Metal} = \exp [a \cdot \ln(H) + b] \quad (1)$$

where  $a$  and  $b$  are metal-specific constants defined as part of the water quality criterion. For copper in freshwater systems, these constants are:

Copper	$a$	$b$
Chronic Criteria ( $\mu\text{g/L}$ )	0.8545	-1.465
Acute Criteria ( $\mu\text{g/L}$ )	0.9422	-1.464

At 100 mg/L hardness, these lead to a CCC of 11.8 µg/L and a CMC of 17.7 µg/L. These criteria concentrations are expressed on the basis of total recoverable metal (Box A-1).

### A.3 Change from Total Recoverable to Dissolved Criteria

As illustrated in Box A-1, each metal's total recoverable criterion must be multiplied by a *conversion factor* to obtain a dissolved criterion that should not be exceeded in the water column. The criteria are based on a total recoverable concentration. For example, the copper acute (and chronic) conversion factor of 0.960 is a weighted average and is used as a prediction of how much the final value would change if dissolved had been measured. Where possible, these conversion factors are given to three decimal places as they are intermediate values in the calculation of dissolved criteria. At a hardness of 100 mg/L, the acute dissolved criterion is 17.0 µg/L. Most of the freshwater aquatic life criteria and their conversion factors are hardness-dependent. Box A-1 shows an example calculation of dissolved and total recoverable copper criteria concentrations.

### A.4 Translating from a Dissolved Metal Ambient Criterion to a Total Recoverable Concentration in the Effluent

As the effluent mixes with the receiving water, the chemical properties of the mixture will determine the fraction of the metal that is dissolved and the fraction of the metal that is in particulate form (typically adsorbed to surfaces of other compounds). The most direct approach to determining the fraction of the total recoverable metal in the downstream water that is dissolved ( $f_p$ ) is to analyze the downstream water (the mixing zone of effluent and receiving water) to determine the dissolved and total recoverable metal fractions. This ratio

#### Box A-1. Calculation of Acute (CMC) and Chronic (CCC) WQC for Copper

Hardness (mg/L)	100
Conversion Factor	0.96

CMC <sub>(total recoverable)</sub> (µg/L) =	
exp[.9422 x ln(100) - 1.464] =	17.7
CMC <sub>(dissolved)</sub> (µg/L) = 17.7 x .96 =	17.0

CCC <sub>(total recoverable)</sub> (µg/L) =	
exp[.8545 x ln(100) - 1.465] =	11.8
CCC <sub>(dissolved)</sub> (µg/L) = 11.8 x .96 =	11.4

can then be used to *translate* from a dissolved concentration in the water column (the criterion concentration or some fraction thereof) to the total recoverable metal concentration in the effluent that will equate to that dissolved concentration in the water column.

### A.5 Calculation of WLAs for a Point Source

For this example, it is assumed that the site-specific data have been collected and analyzed to determine that  $f_p = 0.4$ .

From analysis of existing data, the average background concentration of total recoverable copper in the river at low flow (upstream of the effluent discharge) is 4 µg/L and varies within a relatively small range, from less than 2 to 9.5 µg/L, with the average declining to about 3 µg/L above median flows. For this analysis the mean background concentration is used.

The (instream) total recoverable concentration [ $C_{instream}$ ] that equates to the dissolved criterion concentration is expressed as:

$$[C_{instream}] = WQC_{(dissolved)} \cdot \frac{1}{f_D} \quad (2)$$

Given the information on the design flows and background concentrations (Box A-2), WLAs, expressed as total recoverable metal, are calculated to meet the dissolved CCC and dissolved CMC at the edge of the mixing zone assuming that the effluent is mixed rapidly and that a simple, mass-balance equation is appropriate.

Chronic and acute WLAs (for any single source, without consideration of other sources) can be calculated at the 7Q10 and 1Q10 flows, respectively, for total recoverable copper concentration, using Equation 3.

$$WLA_{(total\ metal)} = \frac{[C_{instream}] \cdot (Q_e + Q_s) - Q_s C_s}{Q_e} \quad (3)$$

where  $[C_{instream}]$  is calculated from Equation 2,  
 $Q_e$  is the effluent flow,  
 $Q_s$  is the receiving water flow, and  
 $C_s$  is the background (upstream) concentration.

$$\begin{aligned} WLA_u &= \frac{42.5 \cdot (50 + 111.77) - 111.77 \cdot 4}{50} \\ &= 128.6 \mu\text{g/L total recoverable Cu} \end{aligned} \quad (4)$$

#### A.6 Calculating the TMDL for Multiple Point Sources

The previous section shows the calculation of wasteload allocations for a

single point source. Concentrations in the receiving water, however, are influenced by all three point sources simultaneously. In other words, the full assimilative capacity of the water body is not available to each source; instead, this capacity must be apportioned between all three sources via the TMDL procedure.

The three permitted point sources in our example all operate within the effluent limits specified in their current NPDES permits. They do not, however, address cumulative impacts of all three sources. Permits for the two metal finishing facilities specify a maximum daily limit (MDL) of 3380  $\mu\text{g/L}$  and an average monthly limit (AML) of 2070  $\mu\text{g/L}$ .

In addition to potential impairment under current permit limits, the POTW is undergoing a significant (60%) capacity expansion, and its increased effluent flow will also increase copper loading at current effluent concentrations. At an average concentration of 81  $\mu\text{g/L}$  of total recoverable copper and an increased effluent flow of 80 cfs, the load from the POTW (see Box A-3) would be 35 lbs/day. The increased flow from the plant also has a significant impact on low flow volumes in the receiving water, requiring recalculation of the WLAs.

The TMDL analysis is straightforward when multiple, steady-state sources are considered using hydrologically based design conditions. The strategy is to:

#### Box A-2. Data for Calculation of WLAs and Existing Permit Limits for the POTW

Effluent Flow (cfs)	50
Average Effluent Concentration, as Total Recoverable Copper ( $\mu\text{g/L}$ )	81
Coefficient of Variation of Load	0.12

**Box A-3. Conversion Factors for Concentration and Load**

Concentration to load rate:

$$(\mu\text{g/L}) \times (\text{cfs}) \times 0.005394 = (\text{lbs/day})$$

Load rate to concentration:

$$(\text{lbs/day}) / (\text{cfs}) \times 185.4 = (\mu\text{g/L})$$

- (1) calculate the acute and chronic dissolved (for metals) criteria concentrations [Eqn 1],
- (2) calculate the instream concentration [ $C_{\text{instream}}$ ] (in terms of total recoverable metal) that equates to the dissolved criterion concentration [Eqn 2],
- (3) calculate the total loading capacity (TMDL) of the waterbody (in terms of total recoverable metal) [Eqn 6],
- (4) calculate the background load,
- (5) calculate the allocatable portion of the loading capacity (i.e., the difference between the loading capacity and background) [Eqn 7],
- (6) calculate the current loadings from the sources and their fractional contributions to the total current load,
- (7) compare the current total loadings to the waterbody with the required TMDL (if either the acute or chronic total loadings exceed the TMDL then the loads must be reduced), and
- (8) reduce loadings from the point sources, equitably allocating waste loads to the discharging facilities.

The steady-state TMDL for a given location or reach of the river is calculated (in units of cfs -  $\mu\text{g/L}$ ) as:

$$TMDL = WQC \cdot (\Sigma Q_e + Q_s) \quad (5)$$

where

$\Sigma Q_e$  is the total flow of effluents discharging to the reach (cfs),  
 $Q_s$  is the appropriate flow (e.g., 7Q10) of the river upstream of all the discharges (cfs), and  
WQC is the water quality criterion expressed in  $\mu\text{g/L}$ .

*TMDLs for metals are developed on the basis of the instream total recoverable metal concentrations that equate to the dissolved criteria concentrations. Consequently, the term WQC in Equation 5 is replaced with the term [ $C_{\text{instream}}$ ] as calculated by Equation 2.*

$$TMDL = [C_{\text{instream}}] \cdot (\Sigma Q_e + Q_s) \quad (6)$$

The calculated TMDL is then divided among WLAs for point sources; LAs, for nonpoint sources and background loads; and a margin of safety (MOS). The TMDL and the portion of the TMDL taken up by background load (at 4  $\mu\text{g/L}$ ) can be calculated in terms of total copper mass, as shown in Table A-1.

Because the current loading for the chronic TMDL exceeds the allocatable portion, loadings from all of the NPDES permitted sources must be reduced. Many different mechanisms or schemes for apportioning the necessary reductions in allocations are possible. Assume for the purpose of this example that the State has determined that necessary reductions will be applied equally to all point sources. Reduced TMDL-based WLAs can then be calculated based on the current proportion of load attributable to a given source:

$$WLA_i = [TMDL - Background] \times f_i \quad (7)$$

where  $WLA_i$  is the WLA for *source I*, and  $f_i$  is the proportion of the existing load attributable to a given source.

The allocation fraction,  $f_i$ , is simply a proportionality constant that is arrived at by dividing the current load from *source<sub>i</sub>* by the sum of all the loads (e.g.,  $f_i = PS1 / (PS1 + PS2 + POTW + MOS)$ ). The allocation fraction is then multiplied by the Allocatable Portion to yield the Allowed Load as in Table A-2. In the calculations summarized in Table A-2 and A-3, a MOS of 10 percent of the allowable TMDL has been applied.

**Table A-1. Calculation of TMDL (Total Recoverable Copper)**

	Acute TMDL	Chronic TMDL
TMDL <small>(total recoverable copper)</small> (lbs/day) [Eqn 6]	44.11	33.76
Background <small>(total recoverable copper)</small> at design flow (lbs/day) [Background = $Q_s * C_s$ ]	2.41	3.02
Allocatable Portion (lbs/day) [Allocatable Portion = TMDL - Background]	41.69	30.73
Current Loading (lbs/day) [Loading = PS1 + PS2 + POTW + Background]	42.38	42.99

**Table A-2. Allocation of Loads to Achieve the (Chronic) TMDL**

Source	Current Load (lbs/day)	Allocation Fraction ( $f_i$ )	Allocatable Portion (TMDL - Background)	Allowed Load (lbs/day)
PS1	1.67	0.04	30.73	1.16
PS2	3.35	0.08	30.73	2.32
POTW	34.95	0.79	30.73	24.18
MOS	4.44	0.10	30.73	3.07
SUM	44.41	1		30.73

Table A-3. Allocation of Loads to Achieve the (Acute) TMDL

Source	Current Load (lbs/day)	Allocation Fraction $(f_i)$	Allocatable Portion (TMDL - Background)	Allowed Load (lbs/day)
PS1	1.67	0.04	41.69	1.57
PS2	3.35	0.08	41.69	3.14
POTW	34.95	0.79	41.69	32.81
MOS	4.44	0.10	41.69	4.17
SUM	44.41	1		41.69

## A.7 Calculating the Permit Limits for a Point Source

Permit limits for the POTW are developed in accordance with USEPA (1991a) guidance on establishing WLAs and permit limits for single sources. In accordance with NPDES regulations, effluent

### Box A-4. Calculation of LTA Multipliers

#### LTA<sub>c</sub>

$$CV = 0.12$$

$$z_{99} = 2.326$$

$$\sigma^2_{.4} = \ln [CV^2/4+1] = 0.00359$$

$$\exp [0.5 \sigma^2_{.4} - z_{99} \sigma_{.4}] = 0.87$$

#### LTA<sub>a</sub>

$$CV = 0.12$$

$$z_{99} = 2.326$$

$$\sigma^2 = \ln [CV^2+1] = 0.014297$$

$$\exp [0.5 \sigma^2 - z_{99} \sigma] = 0.76$$

limits for the POTW are expressed in the permit as mass units (pounds per day total recoverable copper), using the conversion factors shown in Box A-3. The WLA<sub>c</sub> for total recoverable copper (Table A-2) is equivalent to 24.18 lbs/day and is more restrictive than the WLA<sub>a</sub> 32.81 lbs/day (Table A-3). Converting the WLA to a permit limit involves two additional considerations: (1) there is variability in the effluent concentration, and concentrations on any given day may be greater or less than the average value used to calculate the WLA; and (2) permit compliance will be assessed from limited sampling (e.g., weekly), which means

there will be uncertainty in the estimation of actual load from the facility. These issues are addressed by (1) calculating a **long-term average** (LTA) which accounts for the variability in actual load, and (2) using the LTA to calculate a **maximum daily limit** (MDL) and **average monthly limit** (AML) which serve as trigger values for compliance monitoring.

The permit limits are developed using a steady-state, two-value WLA model, as described in Chapter 5 of USEPA (1991a). First, variability in effluent load, expressed through the coefficient of variation (CV), is incorporated into the calculation of appropriate long-term averages (LTAs). The chronic long-term average (LTA<sub>c</sub>) for copper was calculated from

$$\begin{aligned} LTA_c &= WLA \cdot \exp [0.5 \sigma^2_{.4} - z_{99} \sigma_{.4}] \\ &= 24.18 \text{ lbs/day} \cdot 0.87 \\ &= 21.0 \text{ lbs/day} \end{aligned} \quad (9)$$

where the value for the factor  $\exp [0.5 \sigma^2_{.4} - z_{99} \sigma_{.4}]$  was calculated from the coefficient of variation of effluent concentrations (CV, defined as standard deviation divided by the mean, and assumed to be 0.12) by the methods of USEPA (1991a, Table 5-1), using the 99th percentile occurrence probability (Box A-4).

The acute LTA<sub>a</sub> was calculated in a similar manner, again using a 99th occurrence probability as a multiplier:

$$\begin{aligned} LTA_a &= 32.81 \text{ lbs/day} \cdot 0.76 \\ &= 24.9 \text{ lbs/day} \end{aligned} \quad (10)$$

The limiting LTA for copper discharges from the facility is the smaller of the  $LTA_a$  and  $LTA_c$ , or 21.0 lbs/day. This is well below the current average load from the facility of 43.95 lbs/day.

The permit for the POTW is written to ensure an LTA load not to exceed 21.0 lbs/day total recoverable copper through the specification of an MDL and AML for compliance monitoring. The MDL for copper is calculated using the expression

$$\begin{aligned} MDL &= LTA \cdot \exp [z_{99} \sigma - 0.5 \sigma^2] \\ &= 21.0 \text{ lbs/day} \cdot 1.37 \\ &= 28.8 \text{ lbs/day} \end{aligned} \quad (11)$$

where the value for  $\exp [z_{99} \sigma - 0.5 \sigma^2]$  is taken from Table 5-2 in USEPA (1991a), using a CV value of 0.12 and the column for the 99th percentile basis. The AML for copper is calculated from

$$\begin{aligned} AML &= LTA \cdot \exp [z_{99} \sigma_n - 0.5 \sigma_n^2] \\ &= 21.0 \text{ lbs/day} \cdot 1.15 \\ &= 24.2 \text{ lbs/day} \end{aligned} \quad (12)$$

where the value for  $\exp [z_{99} \sigma_n - 0.5 \sigma_n^2]$  is taken from Table 5-2 in USEPA (1991a), in which  $n$  equals 4 samples per month for total recoverable copper, using the 99th percentile basis.

APPENDIX B

Table B-1. Comparison of average  $f_d$  data from three locations in the U.S. Three different calculation methods are used with the Pima County data.

	NY/NJ Harbor	Boulder, CO	Pima County, AZ		
			Cd/Ct	Cd/(Cd+Cp)	by regression from logKp
Copper	0.56	0.23	0.37	0.43	0.42
Cadmium	1.00	0.51	0.71	0.51	0.69
Lead	0.18	0.29	0.20	0.28	0.26
Nickel	0.86	~ 1.0	---	---	---
Zinc	0.90	0.44	0.61	0.63	0.65

These data illustrate two points. First, notice the similarity in the values of the translators for each of the metals in the Pima County study. The differences between column 1 and column 2 of the Pima County data arise from limits in the analytical precision of measurements of dissolved and particulate sorbed fractions. Second, notice the differences in the values of the translators between the three sites represented in this table. These differences reflect the site specificity of the translator, further strengthening the case for development of site specific translator values in contrast to the use of nation wide values.

Preliminary data collected for the City of Palo Alto Regional Water Quality Control Plant permit renewal process (Table B-2) suggest a translator value of 0.62 for copper (62% of the copper in the downstream water is dissolved). This differs from all of the translator values in Table B-1.

**Table B-2. Data Collected in Palo Alto, CA for Cu Permit Limit from a Waste Water Treatment Plant.**

Station#	Date	Cd	Ct	Cp	TSS	fD
Station 1	9/7/89	2.6	3.4	0.8	89	0.76
Station 1	10/2/89	3.3	4.5	1.2	290	0.73
Station 1	10/25/89	3	4	1	52	0.75
Station 1	1/10/90	2.9	4.1	1.2	49	0.71
Station 1	2/7/90	1.4	8	6.6	228	0.18
Station 1	3/7/90	3	5	2	77	0.60
Station 1	7/9/90	4.2	9.6	5.4	180	0.44
Station 1	8/7/90	6.3	7	0.7	83	0.90
Station 1	9/19/90	3.6	5.7	2.1	125	0.63
Station 1	12/12/90	2.9	5.9	3	57	0.49
Station 1	1/10/91	3.5	4.3	0.8	46	0.81
Station 1	2/13/91	4	4.7	0.7	55	0.85
Station 1	10/10/91	4.3	4.6	0.3	78	0.93
Station 1	2/19/92	2	9.9	7.9	250	0.20
Station 2	9/7/89	3	5	2	110	0.60
Station 2	10/2/89	2.2	4.5	2.3	160	0.49
Station 2	10/25/89	6	11	5	132	0.55
Station 2	1/10/90	2.9	4.1	1.2	46	0.71
Station 2	2/7/90	1.7	6.1	4.4	110	0.28
Station 2	3/7/90	4.3	5	0.7	60	0.86
Station 2	7/9/90	6.8	7.2	0.4	100	0.94
Station 2	8/7/90	6.5	8.2	1.7	48	0.79
Station 2	9/19/90	3.9	5.6	1.7	65	0.70
Station 2	12/12/90	2.8	4.6	1.8	51	0.61
Station 2	1/10/91	4.2	4.8	0.6	61	0.88
Station 2	2/13/91	4.5	4.8	0.3	47	0.94
Station 2	10/10/91	4.5	4.7	0.2	77	0.96
Station 2	2/19/92	2	4.9	2.9	120	0.41
Mean		3.7	5.8	2.1	101.6	0.67
Stdev		1.4	2.0	2.0	65.5	0.22
95%		6.4	9.8	6.2	243.4	0.94
25%		2.9	4.6	0.7	54.3	0.53
Geomean		3.4	5.5	1.4	86.6	0.62

## APPENDIX C

### C. Developing the Metals Translator

**A**s may be concluded from the discussion in Chapter 2, there are several ways of developing the metals translator. This Appendix presents two suggested possibilities and illustrates their application.

#### C.1. Minimum Data Requirements

*Samples should be collected to characterize completely mixed effluent plus receiving water downstream of the discharge (such as should occur at, or below, the edge of the mixing zone). These represent the absolute minimum in data requirements. Ideally, samples should be collected from the effluent and the upstream receiving water (before mixing with the effluent) to quantify metal loading and background concentrations. An alternative to collecting the downstream samples on site is to combine upstream and effluent waters to meet the desired dilution fraction in the mixing zone. In addition, there may be occasions when it is desirable to collect samples to characterize the far-field conditions, particularly when encountering deposits containing metals, mine tailings, drainage waters of high acidity, or different geologic substrates.*

To keep this simple and to avoid having to develop data on the kinetics of metal adsorption and desorption, the translator should be developed to describe equilibrium partitioning. Equilibrium partitioning also reduces the frequency for which far field effects need to be investigated. It also lets us apply the same translator for evaluation of both acute and chronic mixing zones.

#### C.2. The Translator is the Ratio of $C_D/C_T$

*The translator is the fraction of the total recoverable metal in the downstream water that is dissolved ( $f_D = C_D/C_T$ ). It is calculated from data collected over some period of time and some range of flow conditions. For example, samples may be collected weekly for three months under conditions of "relatively low flow" (which may or may not include design low flow conditions) or samples may be collected monthly for a period of one or more years under a broad range of flow conditions. Under this latter sampling scheme we may expect to have a broad range of TSS conditions. The dissolved fraction may be determined (directly) from measurements of dissolved and total recoverable metal concentrations collected from waters downstream of the effluent discharge. The dissolved fraction may be related to a constant adsorbent concentration associated with low flow conditions or a function of varying adsorbent concentrations.*

Note that this ratio ( $C_D/C_T$ ), as exemplified by Eqn 2.6 and 2.7, is not a partition coefficient but it does embody a partition coefficient. As shown by Eqn 2.3 and Eqn 2.8, the partition coefficient is the ratio of the particulate-sorbed and the dissolved metal species. The dissolved fraction and the partition coefficient are related according to  $f_D = (1 + K_p \cdot m)^{-1}$ . It is important to distinguish between the dissolved fraction ( $f_D$ ) and the partition coefficient ( $K_p$ ) because what we're interested is the dissolved fraction. We're only using the partition coefficient because it is one way of getting to the dissolved fraction.

This guidance uses TSS as a default parameter to represent all of the ion adsorption sites. It is generally recognized, however, that humic substances play a major

role in the environmental fate and availability of metal ions in the environment. The humic and fulvic acids are mixtures of naturally occurring polyelectrolytes that have different types of functional groups to which ions can bind. Benedetti, et. al. (1995) write that metal binding in natural systems will be affected by humic acids whose chemical heterogeneity and polyelectric properties will affect metal binding. Multivalent cations will compete for the same sites, along with other ions and protons in the aquatic systems, and hence influence the binding of each other.

The following step-by-step examples are designed to guide the reader through possible sequences of data analyses leading to the development of the metals translator. One set of data was collected during the New York/New Jersey Harbor study. The data presented here are a subset of the total and do not include samples that are incomplete (i.e., records lacking pH or POC values) to simplify this presentation. The data set reflects spatial differences. The data are not a time series at a single location. However, there would not be a great difference in the following analyses if the data did represent a time series.

The second data set was provided by the Coors Brewing Company. Again, the data presented here are a subset of the total. The original data set contains time series data for several variables at several locations. To simplify this example, however, the data for only one metal and one site are presented.

### C.2.1. Spatial Example Using the Ratio of $C_D/C_T$

The most direct procedure for determining a site-specific metal translator is simply to determine  $f_D$  by measuring  $C_T$  and  $C_D$  and to develop the dissolved fraction as the ratio  $C_D/C_T$ . This is illustrated, using data

from Table 1 and following the sequence as outlined in Box C-1. The metal concentrations in Table 1 are for lead. The data records, numbers 1 through 27, represent spatially separate sampling stations in the estuary. The first step (Step 1 in Box C-1) is to calculate the dissolved fraction in the receiving water. The result of this calculation is shown in Column 8 of Table 1.

#### Box C-1. The Translator is the Dissolved Fraction: $f_D = C_D/C_T$

Step 1 - For each field sample determine  $f_D = C_D/C_T$

Step 2 - If the translator is not dependent on TSS, determine the geometric mean  $GM_{f_D} = \exp(\sum_{i=1}^n \ln(f_{D_i}) / n)$  and upper percentile values of the dissolved fraction. If the data are found not to be log-normal, then alternative transformations should be considered to normalize the data and determine the transformed mean and percentiles. Also, alternative upper percentiles may be adopted as a state's policy to address MOS (e.g., 90<sup>th</sup> or 95<sup>th</sup> percentiles may be appropriate.)

Step 3 - If the translator is found to be dependent on TSS, regression equations relating  $f_D$  to TSS should be developed. Appropriate transformations should be used to meet the normality assumptions for regression analysis (for example log-transformation of  $f_D$  and TSS may be appropriate). The regression equation or an upper prediction interval may be considered for estimation of  $f_D$  from TSS depending on the strategy for addressing MOS.

Step 2 indicates that there is a lot of variation in the values of  $f_D$ ; the mean is 0.21 with a standard deviation is 0.17. The variability in this dataset indicates that it is unwise to attempt to spatially average  $f_D$  values in this situation. To do so would be to ignore spatially critical conditions. Because, it does not provide a good representation of the waterbody, one cannot accept the mean  $f_D$  (0.21) as the translator.

The translator should be calculated as a geometric mean or other estimate of central tendency (see Section 4.3). Use of the arithmetic mean is appropriate when the values can range from minus infinity to plus infinity. The geometric mean is equivalent to using the arithmetic mean of the logarithms of the values. The dissolved fraction cannot be negative, but the logarithms of the dissolved fraction can be. The distribution of the

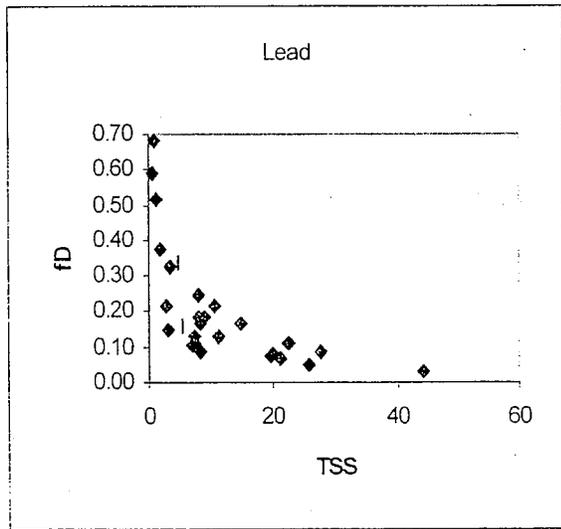


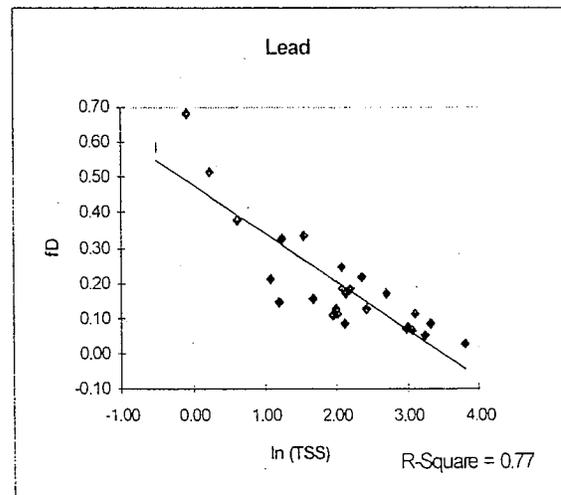
Figure 1. Dissolved fraction (lead) vs TSS.

logarithms of the translator is therefore more likely to be normally distributed. Figure 1 displays the arithmetic distributions of the dissolved fractions with TSS. Note that the skewed distributions suggest that logarithmic

transformations would be appropriate. Examination of Figure 2 further supports the logarithmic transformation of values and the choice of the geometric mean. Even at that, the geometric mean value of the dissolved fraction (0.16 does not provide a good representation of the waterbody in which TSS is spatially correlated. *The translator needs to account for the spatial and/or temporal variability evidenced in the waterbody.*

In order to account for the spatial variability of this waterbody, we need a translator that can be tied functionally to important physical or chemical variables. TSS concentrations vary spatially throughout the estuary. Spatial variability in TSS concentrations requires the use of a translator that includes the relationship between TSS and  $f_D$ . This empirically derived relationship is valid for this estuary.

Figure 2. Dissolved fraction (lead) vs log transformation of TSS.



The regression of the natural logarithm of  $f_D$  against the natural logarithm of TSS (Figure 2) provides a reasonably good fit as evidenced by the R Square of 0.77. The

dissolved fraction is highly correlated with TSS; therefore the translator (Figure 2) takes the form of:

$$\ln(f_D) = -0.6017 - 0.6296 \cdot \ln(\text{TSS}).$$

*The translator is the dissolved fraction, not the regression equation. The way to use the regression equation is to select TSS concentrations that are representative of specific locations in the estuary and calculate  $f_D$  values that serve as the translators for the discharges in these respective locations.*

Sung, et.al. (1995) have demonstrated a relationship between  $K_p$  and salinity for Cd, Cu, and Zn in the Savannah River Estuary. It may well be that by considering salinity as well as TSS, more variability could have been accounted for in the relationship portrayed in Figure 2.

**Table C-1. Example Data Used to Calculate Translator for Lead**  
(Source: NY/NJ Harbor Study)

No.	pH	POC	TSS	Cr	Cd	Cp	fd	Kp	(Cr/Cd)-1
1	8.8	0.132	0.61	0.046	0.027	0.019	0.59	1.15	0.704
2	8.6	0.104	0.92	0.044	0.03	0.014	0.68	0.51	0.467
3	8.6	0.159	1.88	0.25	0.094	0.156	0.38	0.88	1.660
4	8.4	0.280	1.28	0.31	0.16	0.15	0.52	0.73	0.938
5	8.4	0.376	3.32	0.68	0.10	0.58	0.15	1.75	5.800
6	8.4	0.190	2.94	0.46	0.098	0.362	0.21	1.26	3.694
7	8.2	0.183	5.36	0.89	0.14	0.75	0.16	1.00	5.357
8	8.3	0.351	4.71	0.80	0.27	0.53	0.34	0.42	1.963
9	8.4	0.266	3.50	0.67	0.22	0.45	0.33	0.58	2.045
10	8.1	0.416	7.98	2.40	0.59	1.81	0.25	0.38	3.068
11	8.1	1.060	44.42	9.10	0.27	8.83	0.03	0.74	32.704
12	8.1	0.538	11.08	3.40	0.44	2.96	0.13	0.61	6.727
13	8.1	0.596	10.60	3.90	0.85	3.05	0.22	0.34	3.588
14	8.2	0.785	14.77	3.20	0.54	2.66	0.17	0.33	4.926
15	8.4	0.626	8.95	1.40	0.26	1.14	0.19	0.49	4.385
16	8.4	0.602	19.94	2.20	0.17	2.03	0.08	0.60	11.941
17	8.3	0.540	21.10	2.10	0.14	1.96	0.07	0.66	14.000
18	8.3	0.676	19.45	2.10	0.15	1.95	0.07	0.67	13.000
19	8.2	0.629	25.70	2.90	0.15	2.75	0.05	0.71	18.333
20	8.4	0.726	27.75	1.90	0.16	1.74	0.08	0.39	10.875
21	8.4	0.494	22.30	1.50	0.17	1.33	0.11	0.35	7.824
22	8.4	2.360	7.89	1.40	0.26	1.14	0.19	0.56	4.385
23	8.4	0.427	7.32	1.70	0.22	1.48	0.13	0.92	6.727
24	8.4	0.414	8.48	1.60	0.27	1.33	0.17	0.58	4.926
25	8.5	1.470	8.22	1.20	0.10	1.10	0.08	1.34	11.000
26	8.5	0.407	7.09	0.82	0.088	0.732	0.11	1.17	8.318
27	8.6	0.381	7.52	0.58	0.065	0.515	0.11	1.05	7.923
Mean		0.56	11.30	1.76	0.22	1.54	0.21	0.75	7.31
Stdev		0.46	10.23	1.80	0.19	1.72	0.17	0.36	6.77
95%		1.35	27.14	3.75	0.58	3.02	0.57	1.31	17.03
25%		0.32	4.11	0.68	0.10	0.52	0.10	0.50	3.33
Geomean		0.44	7.26	1.06	0.17	0.82	0.16	0.67	4.90

**Table C-2. Time Series Example Calculating the Translator for Zinc.**  
(Source: Coors Brewing Company Study)

DATE	pH	TSS	CT	CD	(CT/CD)-1	fD
10/16/91	7.5	3	0.47	0.24	0.96	0.51
11/13/91	7.3	32	0.72	0.27	1.67	0.38
12/11/91	8.1	5	0.47	0.20	1.35	0.43
01/16/92	8.2	8	0.43	0.38	0.13	0.88
02/18/92	8.2	7	0.55	0.19	1.86	0.35
03/18/92	8.1	7	0.49	0.24	1.07	0.48
04/14/92	7.2	14	0.84	0.44	0.92	0.52
05/12/92	7.7	15	0.34	0.18	0.87	0.54
06/17/92	7.5	8	0.25	0.15	0.64	0.61
07/15/92	7.5	5	0.18	0.13	0.43	0.70
08/18/92	7.2	23	0.26	0.08	2.12	0.32
09/09/92	7.2	4	0.22	0.03	5.72	0.15
10/14/92	8.0	7	0.25	0.11	1.27	0.44
11/16/92	8.2	13	0.44	0.22	1.00	0.50
12/15/92	7.9	1	0.47	0.24	0.97	0.51
01/12/93	8.8	6	0.67	0.32	1.08	0.48
02/18/93	7.9	12	0.71	0.38	0.87	0.54
03/16/93	8.1	10	0.57	0.22	1.58	0.39
04/13/93	8.0	18	0.48	0.16	2.04	0.33
05/12/93	7.5	20	0.42	0.08	4.10	0.20
06/15/93	8.1	64.6	0.54	0.10	4.67	0.18
07/15/93	7.5	10	0.14	0.06	1.25	0.44
08/12/93	7.8	6	0.17	0.09	0.94	0.52
09/16/93	8.1	4	0.24	0.12	1.09	0.48
10/13/93	8.1	5	0.26	0.12	1.11	0.47
11/10/93	8.4	1.7	0.30	0.15	1.03	0.49
12/13/93	7.9	4.6	0.45	0.23	1.00	0.50
01/13/94	7.5	1.8	0.33	0.17	0.97	0.51
02/11/94	7.9	5.5	0.49	0.24	1.01	0.50
03/09/94	8.4	5	0.34	0.09	2.57	0.28
04/07/94	8.3	16	0.48	0.14	2.54	0.28
05/12/94	7.6	47.7	0.72	0.09	7.35	0.12
07/13/94	7.8	6	0.13	0.05	1.43	0.41
08/23/94	8.0	13	0.14	0.05	2.20	0.31
09/20/94	8.1	6	0.15	0.06	1.30	0.44
10/18/94	8.0	5.5	0.28	0.14	1.06	0.49
Mean		11.68	0.40	0.17	1.73	0.43
Stdev		12.90	0.19	0.10	1.50	0.15
95%		0.71	0.71	0.33	0.71	0.71
25%		5.00	0.25	0.09	0.97	0.34
Geomean		7.90	0.35	0.14	1.33	0.40

### C.2.2. Time Series Example Using the Ratio of $C_D/C_T$

Using a data set developed over a three year time span on Clear Creek in Colorado and the same analytical procedure as described in Box 1,  $f_D$  is calculated as the ratio of  $C_D/C_T$ . A subset of the collected data, Table C-2, illustrate the approach.

This subset includes the following variables: total recoverable Zn, dissolved Zn, TSS, and pH that were measured at one sampling location. Additionally, presented in Table 2 are  $f_D$  values (Box C-1 - Step 1). *This data set was censored in the following manner. When calculating  $f_D$ , if the dissolved concentration was found to exceed the total recoverable concentration,  $C_D$ , was set equal to  $C_T$  and  $f_D$  calculated as 1 (100% dissolved metal).*

At the pH levels encountered in Clear Creek during the three year sampling period, no relationship was obtained between pH and  $f_D$ . This is not an unexpected result because pH is in the 7 to 9 range; the major effect of pH on the dissolved fraction is normally observed at low pH levels. Relationships based on POC (not shown) provide no improvement over the TSS based relationships.

The translator value selected for Zn on Clear Creek is the geometric mean of the  $f_D$  values (0.40).

### C.3. The Translator Calculated Using Site Specific Partition Coefficients

It is important to remember with this method, as with the previous method, that the translator is the dissolved fraction in the downstream water.

Box C-2 provides a procedure for developing the translator via partition coefficients. In Step 1 calculate the particulate fraction, the partition coefficient, and the dissolved metal

#### Box C-2. The Translator is the Dissolved Fraction ( $f_D$ ) Calculated via Site Specific Partition Coefficients

Step 1 - For each field sample determine

$$C_p = C_T - C_D,$$
$$K_p = C_p / (C_D \cdot \text{TSS})$$

Step 2 - Fit least squares regressions to data (transformed, stratified by pH, etc.) as appropriate to solve for  $K_p$ .

Step 3 - Substitute the regression derived value of  $K_p$  in Eqn 2.7,  $f_D = (1 + K_p \cdot \text{TSS})^{-1}$

Step 4 Determine  $f_D$  for a TSS value representative of the critical conditions.

fraction.  $C_p$  is calculated as the difference<sup>17</sup> between total recoverable and dissolved metal concentrations. The partition coefficient the ratio of the particulate-sorbed and the dissolved metal species times the adsorbent concentration (Eqn 2.9). The

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<sup>17</sup>The particulate fraction can also be measured in the laboratory by filtering the solids, scraping the solids from the filter, drying, weighing, and subjecting to appropriate chemical analyses. The increased number of steps may provide opportunities for additional sources of error, accompanied by increased uncertainty. See Eqn 2.2, 2.3, and 2.4.

dissolved fraction and the partition coefficient are related according to Eqn 2.7.

### C.3.1. Spatial Example Using Partition Coefficients

Using the same NY/NJ Harbor data as used above (Table C-1), this example

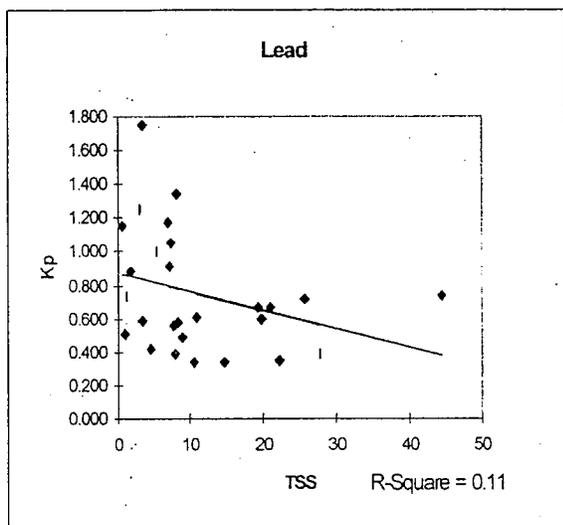


Figure 3.  $K_p$  as a function of TSS.

demonstrates the calculation of  $K_p$  and how it may be used to arrive at site-specific values of  $f_D$ .

The partition coefficient - TSS data are not as well behaved (Figure 3) as are the  $f_D$  - TSS data. However, Shi, et. al. (1996) show that after algebraic rearrangement of Eqn 2.7 to

$$(Ct/Cd)-1 = K_p \cdot TSS,$$

$K_p$  can be obtained by linear regression. The slope of the curve is the partition coefficient (Figure 4).

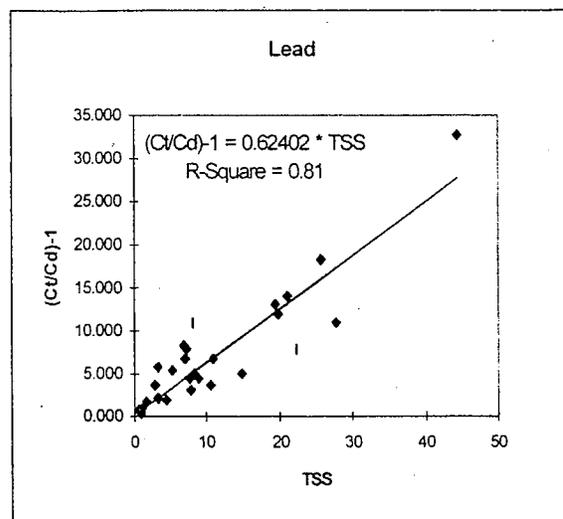


Figure 4. The fraction  $[(Ct/Cd)-1]$  as a function of TSS.

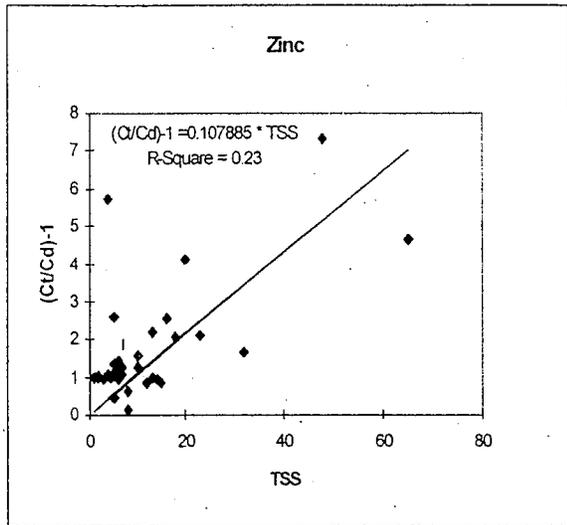
By regression analysis,  $K_p = 0.624$  L/mg. This value is used in Eqn 2.7 along with an appropriate value of TSS to calculate the translator.

### C.3.2. Time Series Example Using Partition Coefficients

Continuing the analysis of data collected from Clear Creek, this section demonstrates estimating the dissolved fraction by using a site-specific partition coefficient. The particulate sorbed fraction is operationally defined as  $C_T - C_D$  and the partition coefficient is calculated as a function of TSS according to Equation 2.8 following the procedure given in Box 2 - Step 1. Table C-2 presents the data generated by the field study as well as the calculated values.

Substitute the regression derived value of  $K_p$  in Eqn 2.7, as suggested in Box 2 - Step 3. As in the previous example, the way to use this equation is to select TSS concentrations that are representative of

critical conditions in the receiving waterbody and calculate the dissolved fractions



(translator values) .

Figure 5. The fraction [(Ct/Cd)-1] as a function of TSS.

APPENDIX D

3.0 5  
4.0 4

D.1. Sample Size

Statistically, the most important objective for a metal translator study is to determine the mean concentrations of total and dissolved metal within an acceptable confidence interval of the true mean such that the estimated dissolved fraction is a good representation of the true dissolved fraction.

The null hypothesis ( $H_0$ ) is: mean total concentration ( $\mu_t$ ) = mean dissolved concentration ( $\mu_d$ ).

To determine sample size, three factors must be selected:

1. Type I error ( $\alpha$ ) is the probability of rejecting a true hypothesis.
2. Type II error ( $\beta$ ) is the probability of accepting a false hypothesis.
3. The expected difference between the means ( $\Delta$ ), expressed as a multiple of the standard deviation ( $\sigma$ ), which is assumed to be equal for the two populations ( $\sigma = \sigma_t = \sigma_d$ ):

$$\Delta = (\mu_t - \mu_d) / \sigma$$

For a translator study, the null hypothesis is assumed to be false, i.e., there is a difference between total and dissolved concentrations. Therefore,  $\beta$  must be small to ensure that a translator is not rejected (no difference detected between the means) when a difference does exist. For  $\alpha$  and  $\beta$  levels of 0.05, the following shows the relationship between  $\Delta$  and  $n$ , assuming a  $t$  distribution:

$\alpha$	$\beta$	$\Delta$	$n$
0.05	0.05	1.0	27
		2.0	8

A sample size of 4, therefore, would determine that a difference exists only if the difference between the means is  $4\sigma$  or more. At very low concentrations typical of many metals—for example, if the dissolved copper concentration is  $3 \mu\text{g/L}$  and the total concentration is  $6 \mu\text{g/L}$  and  $\sigma$  is  $1 \mu\text{g/L}$ —this sample size would not be adequate to demonstrate that a difference exists. The translator would be rejected, therefore, even though it is actually valid. A sample size of 8, on the other hand, would be large enough to show a difference between the two means and support the use of a translator other than 1.

A sample size of 10 (or greater) is recommended because it would allow demonstration of a significant difference for  $\Delta$  somewhat less than 2.0, while still keeping  $\alpha = \beta = 0.05$ . Furthermore, if 1 or 2 samples have to be discarded because of undetectable concentrations, outlier concentrations, or other sampling or analytical problems, there would still be an adequate number of samples to meet the assumed statistical criteria. The only really reliable method of estimating how many samples are going to be needed is to collect some data, examine the statistical variability, and project from that basis.

## APPENDIX E

### E.1. Topics covered in Method 1669 include:

**C**ontamination control, including: minimizing exposure of the sample, the wearing of gloves, use of metal-free apparatus, and avoiding sources of contamination.

- Safety, including: use of material safety data sheets and descriptions of the risks of sampling in and around water and in hot and cold weather.
- Apparatus and materials for sampling, including: descriptions and part numbers for sample bottles, surface sampling devices such as poles and bottles, a subsurface jar sampling device, continuous flow samplers including peristaltic and submersible pumps, glove bag for processing samples, gloves, storage bags, a boat for collection of samples on open waters, filtration apparatus consistent with the apparatus studied and used by USGS, and apparatus for field preservation of samples.
- Reagents and standards for sample preservation, blanks, and for processing samples for determination of trivalent chromium.
- Site selection
- Sample collection procedures, including: "clean hands/dirty hands" techniques, precautions concerning wind direction and currents, manual collection of surface and sub-surface samples, depth sampling using a jar sampler, and continuous flow sampling using a pump.

- Field filtration and preservation procedures using an inflatable glove bag, and instructions for packaging and shipment to the laboratory.
- Quality assurance/quality control procedures, including: collection of an equipment blank, field blank, and field duplicate.
- Re-cleaning procedures for cleaning the equipment and apparatus between sites.
- Suggestions for pollution prevention and waste management.
- Twenty references to the technical literature on which the Method is based and a glossary of unique terms used in the Method.

Table E-1 details some of the differences between standard sampling for metals and sampling for trace metals using the procedures outlined below and detailed in Method 1669.

**Table E-1. Standard vs. Trace Metals Sampling**

Component	Standard Sampling Technique (USEPA, 1983, 1991b)	Trace Metals Sampling Technique (USEPA, 1995a)
Bottles	Borosilicate glass, polyethylene, polypropylene, or Teflon®	Fluoropolymer, polyethylene, or polycarbonate, filled and stored with 0.1% ultrapure HCl solution
Cleaning	Wash with detergent; rinse successively with tap water, 1:1 HNO <sub>3</sub> , tap water, 1:1 HCl, tap water, deionized distilled water (GFAA methods; EPA, 1983). Soak overnight; wash with detergent; rinse with water; soak in HNO <sub>3</sub> :HCl:water (1:2:9); rinse with water; oven dry (ICP Method 200.7; USEPA, 1991b)	Detergent wash, DI water rinse, soak for 2 h minimum in hot, concentrated HNO <sub>3</sub> , DI water rinse, soak for 48 h minimum in hot, dilute ultrapure HCl solution, drain, fill with 0.1% ultrapure HCl solution, double bag, and store until use.
Gloves	No specification.	Powder-free (non-talc, class-100) latex, polyethylene, or polyvinyl chloride.
Filter	0.45 µm membrane; glass or plastic filter holder	Gelman #12175 capsule filter or equivalent capacity 0.45 µm filter with a minimum 600 cm <sup>2</sup> filtration area. Rinsing the #12175 filter with 1000 ml ultrapure water is adequate cleaning for current ambient level determinations.
Preservative	Conc. redistilled HNO <sub>3</sub> , 5 ml/L (GFAA methods; USEPA, 1983). 1:1 HNO <sub>3</sub> to pH <2 (3ml/L) (ICP Method 200.7; USEPA, 1991b)	Ultrapure HNO <sub>3</sub> to pH <2 or lab preserve and soak for 2 days. Lab preserve samples for mercury to preclude atmospheric contamination.

## **E.2. Method of Sampling**

Sampling Method 1669 (USEPA, 1995a) provides detailed guidance on steps that can be followed to collect a reliable sample and preclude contamination. Choose manual or continuous sampling depending upon which method is best for the specific sampling program. Only trained personnel should be entrusted the task of sample collection.

### **E.2.1. Manual Sampling of Surface Water or Effluent**

In the manual sampling procedure, the sampling team puts on gloves and orients themselves with respect to the wind and current to minimize contamination. "Dirty hands" opens the sample bag. "Clean hands" removes the sample bottle from the bag, removes the cap from the bottle, and discards the dilute acid solution in the bottle into a carboy for wastes. "Clean hands" submerges the bottle, collects a partial sample, replaces the cap, rinses the bottle and cap with sample, and discards the sample away from the site. After two more rinses, "clean hands" fills the bottle, replaces the cap, and returns the sample to the sample bag. "Dirty hands" reseals the bag for further processing (filtration and/or preservation) or for shipment to the laboratory.

### **E.2.2. Grab Sampling of Subsurface Water or Effluent Using a Pole Sampler**

In sampling with the pole (grab) sampling device, "dirty hands" removes the pole and sampling device from storage and opens the bag. "Clean hands" removes the sampling device from the bag. "Dirty hands" opens the sample bag. "Clean hands" removes the sample bottle, empties the dilute acid shipping solution into the carboy for

wastes, and installs the bottle in the sampling device. Using the pole, "dirty hands" submerges the sampling device to the desired depth and pulls the cord to fill the sample bottle. After filling, rinsing, and retrieval, "clean hands" removes the sample bottle from the sampling device, caps the bottle, and places it in the sample bag. "Dirty hands" reseals the bag for further processing or shipment.

### **E.2.3. Grab Sampling of Subsurface Water or Effluent Using a Jar Sampler**

In sampling with the jar sampling device, "dirty hands" removes the device from its storage container and opens the outer bag. "Clean hands" opens the inner bag, removes the jar sampler, and attaches the pump to the flush line. "Dirty hands" lowers the weighted sampler to the desired depth and turns on the pump, allowing a large volume of water to pass through the system. After stopping the pump, "dirty hands" pulls up the sampler and places it in the field-portable glove bag. "Clean hands" aliquots the sample into various sample bottles contained within the glove bag. If field filtration and/or preservation are required, these operations are performed at this point. After filtration/preservation, "clean hands" caps each bottle and returns it to its bag. "Dirty hands" seals the bag for shipment to the laboratory.

### **E.2.4. Continuous Sampling of Surface Water, Subsurface Water, or Effluent Using a Submersible Pump**

In the continuous-flow sampling technique using a submersible pump, the sampling team prepares for sampling by setup of the pump, tubing, batteries, and, if

required, the filtration apparatus. "Clean hands" removes the submersible pump from its storage bag and installs the lengths of tubing required to achieve the desired depth. "Dirty hands" connects the battery leads and cable to the pump, lowers it to the desired depth, and turns on the pump. The pump is allowed to run for 5 - 10 minutes to pump 50 - 100 liters through the system. If required, "clean hands" attaches the filter to the outlet tube. "Dirty hands" unseals the bag containing the sample bottle. "Clean hands" removes the bottle, discards the dilute acid shipping solution into the waste carboy, rinses the bottle and cap three times with sample, collects the sample, caps the bottle, and places the bottle back in the bag. "Dirty hands" seals the bag for further processing or shipment.

### E.3. Preservation

Samples to be analyzed for total recoverable metals are preserved with concentrated nitric acid ( $\text{HNO}_3$ ) to a pH less than 2. In normal natural waters, 3-5 ml of acid per liter of sample is recommended (EPA, 1983, 1991b) to achieve the required pH. The nitric acid must be known to be free of the metal(s) of interest. Method 1669 provides specifications for the acid. Samples for total recoverable metals should be preserved immediately after sample collection. It is common for laboratories to recommend sample acidification in a controlled uncontaminating environment for both total recoverable and dissolved metal fractions.

Field preservation is necessary for trivalent and hexavalent chromium. Field preservation is advised for hexavalent chromium in order to provide sample stability for up to 30 days.

To preclude contamination from atmospheric sources, mercury samples should be shipped unfiltered and unpreserved via overnight courier and filtered and/or preserved upon receipt at the laboratory.

### E.4. Filtration

Because the operational definition of "dissolved" is so greatly affected by filtration artifacts, the Gelman #12175 capsule filter or equivalent capacity filter must be used, regardless of how the samples are collected. (The next largest capacity filter is approximately  $80 \text{ cm}^2$  surface area.) The minimization of filtration artifacts can be assured with high capacity tortuous path filters and limited sample volume ( $\leq 1000 \text{ ml}$ ). The Gelman #12175 capsule filter has equivalent filtration area of  $600 \text{ cm}^2$ .

The filtration procedure given in Method 1669 is used for samples collected using the manual, grab, or jar collection systems. In-line filtration using the continuous-flow approach was described above. The filtration procedure used in Method 1669 is based on procedures used by USGS, and the capsule filter is the filter evaluated and used by USGS.

The filtration system is set up inside a glove bag, and a peristaltic pump is placed immediately outside of the glove bag. Tubing from the pump is passed through small holes in the glove bag to assure that all metallic parts of the pump are isolated from the sample. The capsule filter is also placed inside the glove bag.

Using "clean hands/dirty hands" techniques, blank water and sample are pumped through the system and collected. The sample is acidified, placed back inside the sample bag, and shipped to the laboratory.

## E.5. Field Quality Assurance

The study plan should describe the sampling location(s), sampling schedule, and collection methodology, including explicit information on the sampling protocol. Detailed requirements and procedures for field quality control and quality assurance are given in USEPA Method 1669. If Method 1669 is not used, deviations from that Method should be described and the Method should be supplemented by standard operating procedures (SOPs) where appropriate. It is desirable to include blind QC samples as part of the project.

- Equipment blank - Prior to the use of any sampling equipment at a given site, the laboratory or equipment cleaning contractor is required to generate equipment blanks to demonstrate that the equipment is free from contamination. Two types of equipment blanks are required: bottle blanks and sampling equipment blanks.

Equipment blanks must be run on all equipment that will be used in the field. If, for example, samples are to be collected using both a grab sampling device and the jar sampling device, then an equipment blank must be run on both pieces of equipment.

The equipment blank must be analyzed using the same analytical procedures used for analysis of samples so that contamination at the same level is detected. If any metal(s) of interest or any potentially interfering substance is detected in the equipment blank, the source of contamination/interference must be

identified and removed. The equipment must be demonstrated to be free from the metal(s) of interest before the equipment may be used in the field.

- Field blank - In order to demonstrate that sample contamination has not occurred during field sampling and sample processing, at least one (1) field blank must be generated for every ten (10) samples that are collected at a given site. The field blank is collected prior to sample collection and should be collected for each trip to a given site if fewer than 10 samples are collected per sampling trip.

Field blanks are generated by filling a large, pre-cleaned carboy or other appropriate container with reagent water (water shown to be free from metals at the level required) in the laboratory, transporting the filled container to the sampling site, processing the water through each of the sample processing steps and equipment (e.g., tubing, sampling devices, filters, etc.) that will be used in the field, collecting the field blank in one of the sample bottles, and shipping the bottle to the laboratory for analysis.

If it is necessary to clean the sampling equipment between samples, a field blank should be collected after the cleaning procedures but before the next sample is collected.

- Field duplicate - A field duplicate is used to assess the precision of the field sampling and analytical processes. It is recommended that at least one (1) field duplicate sample

be collected for every ten (10) samples that are collected at a given site or for each sampling trip if fewer than 10 samples are collected per sampling trip.

The field duplicate is collected either by splitting a larger volume into two aliquots in the glove bag, by using a sampler with dual inlets that allows simultaneous collection of two samples, or by collecting two samples in rapid succession.

## APPENDIX F

### F.1. Laboratory Facility, Equipment, and Reagents

**M**any of the laboratories presently performing metals determinations are incapable of making measurements at or near ambient criteria levels because of limitations in facilities, equipment, or reagents. The QC Supplement suggests the facilities modifications necessary to assure reliable determinations at these levels. The modifications required can be extensive or minimal, depending on the existing capabilities of the laboratory. The ideal facility is a class-100 clean room with walls constructed of plastic sheeting attached without metals fasteners, down-flow ventilation, air-lock entrances, pass-through doors, and adhesive mats for use at entry points to control dust and dirt from entering via foot traffic. If painted, paints that do not contain the metal(s) of interest must be used.

Class-100 clean benches, one installed in the clean room; the other adjacent to the analytical instrument(s) for preparation of samples and standards, are recommended to preclude airborne dirt from contaminating the labware and samples.

All labware must be metal free. Suitable construction materials are fluoropolymer (FEP, PTFE), conventional or linear polyethylene, polycarbonate, or polypropylene. Only fluoropolymer should be used when mercury is a target analyte. The QC supplement suggests cleaning procedures for labware. Gloves, plastic wrap, storage bags, and filters may all be used new without additional cleaning unless results of the equipment blank pinpoint any of these materials as a source of contamination. In this case, either an

alternate supplier should be found or the materials will need to be cleaned.

Each reagent lot should be tested for the metals of interest by diluting and analyzing an aliquot from the lot using the techniques and instrumentation to be used for analysis of samples. The lot will be acceptable if the concentration of the metal of interest is below the detection limit of the method being used. Ultrapure acids are available and should be used to preclude contamination from this source, although technical grades of acid may be pure enough to be used for the first steps in the cleaning processes.

Reagent water--water demonstrated to be free from the metal(s) of interest and potentially interfering substances at the method detection limit (MDL) for that metal in the analytical method being used--is critical to reliable determination of metals at trace levels. Reagent water may be prepared by distillation, deionization, reverse osmosis, anodic/cathodic stripping voltammetry, or other techniques that remove the metal(s) and potential interferant(s).

### F.2. Analytical Methods

The test methods currently in 40 CFR Part 136 may not be sufficiently sensitive for trace metals determinations. The Agency believes dischargers may use more sensitive methods, such as stabilized temperature graphite furnace atomic absorption spectroscopy (STGF AA) and inductively coupled plasma/ mass spectrometry (ICP/MS) (USEPA, 1994c) even though those methods have not yet been approved in 40 CFR Part 136 for general use in Clean Water Act applications. In some instances, STGF AA and ICP/MS may be preceded by hydride generation or on-line or off-line preconcentration to achieve these levels. The

Agency is developing methods for those metals that cannot as yet be measured at ambient criteria levels. The methods being developed use the apparatus and techniques described in the open technical literature. This guidance does not address the use on non-Part 136 methods in any context other than metal translator studies performed by the discharger.

Although analyses by STGFAA are generally cheaper than those by ICP/MS, the cost differences are usually not a limiting consideration given the implications of obtaining a precise and accurate translator value. Achieving low detection levels can add appreciably to the cost, but those costs may be justified if a translator means the difference between permit compliance and noncompliance.

### F.3. Laboratory Quality Control

The QC Supplement provides detailed quality control procedures that should assure reliable results. The QC Supplement requires each laboratory that performs trace metals determinations to operate a formal quality assurance program. The minimum requirements of this program consist of an initial demonstration of laboratory capability, analysis of samples spiked with metals of interest to evaluate and document data quality, and analysis of standards and blanks as tests of continued performance. Laboratory performance is compared to established performance criteria to determine if the results of analyses meet the performance characteristics of the method. This formal QA program has the following required elements:

- The analyst must make an initial demonstration of the ability to generate acceptable accuracy and precision with the method used for

analysis of samples. This demonstration is comprised of tests to prove that the laboratory can achieve the MDL in the EPA method and the precision and accuracy specified in the QC Supplement.

- Analyses of blanks are required initially and with each batch of samples started through the analytical process at the same time to demonstrate freedom from contamination.
- The laboratory must spike at least 10% of the samples with the metal(s) of interest to monitor method performance. When results of these spikes indicate atypical method performance for samples, an alternative extraction or cleanup technique must be used to bring method performance within acceptable limits.
- The laboratory must, on an ongoing basis, demonstrate through calibration verification and through analysis of a laboratory control sample that the analytical system is in control.
- The laboratory must maintain records to define the quality of data that are generated.

In recognition of advances that are occurring in analytical technology, the analyst is permitted to exercise certain options to eliminate interferences or lower the costs of measurements. These options include alternate digestion, concentration, and cleanup procedures and changes in instrumentation. Alternate determinative techniques, such as the substitution of a colorimetric technique or changes that degrade method performance, are not

allowed. If an analytical technique other than the technique specified in the EPA method is used, then that technique must have a specificity equal to or better than the specificity of the techniques in EPA method for the analytes of interest.

