

GUIDANCE FOR ESTABLISHING A METALS TRANSLATOR

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FOREWORD

Methods and procedures suggested in this guidance are for the specific purpose of developing the metals translator in support of the dissolved metals permitting option in Rule 62-302.500(2)(d), Florida Administrative Code

The Department of Environmental Protection (DEP) may change this guidance in the future, as appropriate. Comments from users are welcomed. Send comments to FDEP, Nonpoint Source Management and Water Quality Standards Section, Mail Station 3570, 2600 Blair Stone Road, Tallahassee, FL 32399-2400

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ABSTRACT

The surface water quality criteria for metals in Chapter 62-302, F.A.C. are expressed as total recoverable metal. Rule 62-302.500(2)(d), F.A.C., allows permit limits for certain metals to be calculated based on the dissolved fraction. However, Federal regulation (40 CFR 122.45(c)), requires the permit limit, in most instances, 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. Therefore, 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?"

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 is developed directly as the ratio of dissolved to total recoverable metal. Appendix A provides some details of a statistical procedure to estimate sample size. Appendices B and C present information on clean sampling and analytical techniques which the reader *may elect* to follow. This material (B and C) is presented *only* to assist the reader by providing more detailed discussion rather than only providing literature citations; these procedures are *not* prescriptive.

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Executive Summary

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

Before beginning a translator study one should make a *determination of the need for a study by comparing the effluent total recoverable metal concentration to the total recoverable metal water quality criterion*. If the releases of metal from a discharge do not exceed water quality criteria levels then a translator study is not necessary.

In the toxicity tests to derive the total recoverable 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. To obtain the dissolved criterion to be used for establishing permit limits, multiply the total recoverable criterion by the conversion factor.

The translator (f_D) is the fraction of total recoverable metal in the downstream water that is dissolved; $f_D = C_D/C_T$. It is determined directly by measurements of dissolved and total recoverable metal concentrations in water samples taken at intervals from the point of discharge to the point of compliance with the total recoverable criteria. *Site specific data are required to develop site specific translators.*

The study should normally be designed to collect samples under critical flow conditions, that is under conditions that result in the greatest concentration of dissolved metal in the water column.

The procedure for determining a site-specific metal translator is 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 at a particular sampling site. A geometric mean is determined at each sampling location. Sample locations range from the point of discharge to the point of compliance with the total recoverable criteria. The highest geometric mean f_D is the f_D used for permit calculations.

Multiply the total recoverable metal criterion by the appropriate conversion factor and divide by the site-specific metal translator to determine the total recoverable concentration in the effluent that will not exceed the dissolved metal criteria in the receiving water.

1. INTRODUCTION

Dissolved metals criteria assume that 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 µm or a 0.40 µm filter.

Translators are not designed to consider bioaccumulation of metals.

1.1. 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 were based on measurements of the dissolved concentrations in all of the toxicity tests that were most important in the derivation of the criteria.

For this permitting option, each total recoverable criterion is multiplied by a conversion factor to obtain a dissolved criterion that should not be exceeded in the water column. The total recoverable criteria are listed in chapter 62-302, F.A.C. Both freshwater and saltwater conversion factors are presented in Tables 1 and 2. Most freshwater aquatic life criteria are hardness-dependent as are the conversion factors for Cd and Pb. The Conversion Factor values shown in these tables for Cadmium and Lead are valid for a hardness of 100 mg/L. Conversion factors (CF) for any hardness in the range of 25 to 400 mg/L can be calculated using the following equations:

Cadmium

Chronic:

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

Lead

Chronic:

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

Table 1. Freshwater Criteria Conversion Factors for Dissolved Metals

Metal	Conversion Factors
Cadmium*	0.909
Chromium (III)	0.860
Chromium (VI)	0.962
Copper	0.960
Lead*	0.791
Nickel	0.997
Silver	0.85
Zinc	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 (CaCO₃).

Table 2. Saltwater Criteria Conversion Factors for Dissolved Metals

Metal	Conversion Factors
Cadmium	0.994
Chromium (VI)	0.993
Copper	0.83
Lead	0.951
Nickel	0.990
Silver	0.85
Zinc	0.946

1.2. Translating from a Dissolved Metal Ambient Concentration to a Total Recoverable Permit Limit in the Effluent

As the effluent mixes with the receiving water, the chemical/physical 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.

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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 at critical flow conditions, that is under conditions that result in the greatest concentration of dissolved metal in the water column. Critical flow conditions would be the conditions under which the dissolved to total recoverable metal ratio is closest to 1.0. The dissolved fraction is determined (directly) from measurements of dissolved and total recoverable metal concentrations collected from waters downstream of the effluent discharge.

This ratio of dissolved to total recoverable metal concentrations can then be used to determine a total recoverable concentration in the effluent that will not exceed the dissolved metal criterion in the water column.

1.3. Developing Translators

The purpose of this technical guidance document is to present additional details regarding development of the metals translator. This chapter presents approaches that may be used in developing a site specific translator. The following chapters, will focus on designing and conducting field studies, analytical chemistry procedures, and data analysis. There is always a translator involved when going from a dissolved criterion to a total recoverable permit limit.

The procedures in this document do not cover all possible approaches. Greater precision can be achieved by means of more elaborate procedures such as developing site-specific partition coefficients. Although, the use of such procedures is acceptable, they will not be discussed in this document.

1.3.1. Direct Measurement of the Translator

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. Metal will adsorb onto TSS reducing the dissolved to total recoverable ratio, therefore, the study should normally be designed to collect samples under conditions where TSS concentrations are least to capture worst case conditions.

1.3.2 Option 1 – Determine the f_D for the effluent and background.

Samples are collected from the effluent and the receiving water upstream of the discharge. The geometric mean f_D is calculated separately for the effluent and the upstream location. The highest geometric mean f_D is used as the translator.¹

This approach assumes that the background and the effluent represent the range of f_D that will be encountered downstream of the discharge from the point of discharge to the point where the waterbody is in compliance with the total recoverable metal criteria. It assumes that at some point downstream, the metal concentration in the waterbody will return to equilibrium with the ratio of dissolved to total recoverable metal equal to the ratio measured upstream or out of the influence of the discharge. This assumption is only valid for free flowing non-tidal streams, with no tributaries or discharges that would alter the pH, DOC, POC, TSS in such a way that the dissolved fraction would increase over that anticipated by measuring the upstream or background dissolved/total recoverable ratio.

It is important to collect samples at critical flow; that is, under conditions that result in the greatest concentration of dissolved metal in the water column.

1.3.3. Option 2 - Measure dissolved to total recoverable ratio at multiple locations moving away from the point of discharge along the center line of the plume.

This option is applicable for all waterbodies not covered by Option 1.

Samples are collected from the effluent, a location near the point of discharge and at multiple locations moving away from the point of discharge along the center line of the plume until the total recoverable metal in the water column is equal to or less than the total recoverable metal criteria in Chapter 62-302, F.A.C.

The geometric mean of the dissolved to total recoverable ratios at each location are calculated separately and the highest geometric mean ratio is the f_D to be used for establishing permit limits.²

¹ Using the highest geometric mean f_D provides protection for aquatic life at all locations from the point of discharge outwards. Acceptable exceedence of the dissolved criterion at any point would require establishment of an approved mixing zone.

² The translator should be calculated as a geometric mean or other estimate of central tendency. 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 logarithms of the translator is therefore more likely to be normally distributed.

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1.3.4. Option 3 – Developing a translator for Open Ocean Domestic Waste Outfalls.

Collect samples from the effluent and the receiving water out of the influence of the discharge. At least 10 separate samples of receiving water and effluent should be taken for this translator option. The samples should be collected over at least a six month period and include what would be expected to be worst-case conditions.

Measure and report the TSS and total recoverable metals in the effluent.

If developing a translator for cadmium, copper, chromium, lead, nickel or zinc, the effluent and receiving water are mixed in a Teflon vessel at a ratio of 1 part effluent to 20 parts seawater. However, if the total recoverable metal concentration in the mixture will not meet the total recoverable water quality criterion at the 1:20 dilution, prepare an alternative test aliquot by adding sufficient seawater to effluent until the mixture meets the total recoverable metal criterion. This will be the mixture concentration to use to establish the translator.³

If developing a translator for silver, dilute the effluent with seawater in a Teflon vessel until the total recoverable silver concentration in the mixture meets the water quality criterion. This mixture concentration should be used to establish the translator.

The mixture should be mixed in the laboratory for 60 minutes. (Note the mixing time may be revised as more information becomes available). Prepare aliquots to measure dissolved metal and total recoverable metal.

For each dilution mixture, calculate the translator by dividing the dissolved metal concentration by the total recoverable metal concentration. Calculate the geometric mean and the 95th percentile. Use the 95th percentile high value as the dissolved metals translator for establishing total recoverable permit limits.

³ At the 1 part effluent to 20 parts seawater dilution, the mixture should meet the dissolved metal criterion. If the dissolved metal criterion is not met at this dilution, the discharge will be out of compliance with the dissolved metal criterion unless an additional mixing zone has been established. For silver, the dissolved metal criterion must not be exceeded at the end of pipe.

2. FIELD STUDY DESIGN

Consideration should be given to the use of clean sampling and analytical techniques. 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.

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 an 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 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.

2.1. Sampling Schedule

The sampling design should be adequate to evaluate spatial and/or temporal variability and to properly characterize the environmental condition.

For instance, the translator should 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 2.1.1 below.) To meet this application, samples should be collected under conditions that approximate the critical flow.

2.1.1. Consideration of Appropriate Design Flow Conditions for Metals

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.

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 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 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.

2.1.2. Frequency and Duration of Sampling

A field study to develop a metals translator is expected to extend over several months. 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, weekly or biweekly sampling during specified receiving water*

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flow conditions are recommended when developing the translator for use under "critical flow" or "design flow" conditions.

In addition to receiving water conditions, it is equally important to consider the plant operation schedules 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.

2.2. Sampling Locations

Samples are to be collected from the effluent, the receiving water before mixing with the effluent, the receiving water at intervals from the point of discharge to the point where the total recoverable metals concentration in the water column is less than the total recoverable criterion in Rule 62-302.530, F.A.C⁴. Results obtained from these different locations may differ substantially.

There are some practical difficulties involved in selecting sampling locations. 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. After one or more sampling events, it may be possible to narrow the sampling locations to two or three sites where the ratio of dissolved to total recoverable metal is the greatest. These sites can then be targeted for the full translator study.

Appropriate field sampling techniques and appropriate QA/QC are discussed in Appendix B. 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. 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. In areas where cumulative discharge effects can

⁴ The salt water total recoverable criterion for silver is found in 62-302.500, F.A.C.

be anticipated, the individual contributions and combined effects of the multiple discharges must be considered in developing the translator.

2.3. Number of Samples

Most statistics textbooks (e.g., Snedecor, 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 critical flow condition associated with a particular critical time of the year.

The collection of dissolved and total concentrations at critical flows is the recommended approach, the collection of at least 10 samples per sampling location is recommended to achieve higher confidence in the data. Additional details of determining the required sample size are presented in Appendix A.

2.4 Parameters to Measure

Ideally the field study is designed to generate data on total recoverable (C_T) and the dissolved (C_D) metal fraction 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.

It is possible to develop the translator from a study that only generates data on total recoverable and dissolved concentrations in the downstream water.

2.5. The Need for Caution in Sampling

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 is

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presented in Appendix B. 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 cm², 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.

3. DATA GENERATION AND ANALYSIS

Determination 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, EPA 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 C for the reader's convenience. Persons actually developing a metal translator should read the QC Supplement.

3.1. Analytical Data Verification and Validation

In addition to Method 1669 for sampling (USEPA, 1995a) and analytical methods for determination of trace metals (USEPA, 1994b), EPA 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.

3.2. Evaluation of Censored Data Sets

Frequently data sets are generated that contain values that are lower than the laboratory's Method Detection Level (MDL) or the Practical Quantitation Level (PQL). These data points are often reported with qualifier codes (i.e. U below MDL and I below PQL) 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 MDL, it does not necessarily mean that the concentration is zero (USEPA, 1992).

Measurements made below the PQL 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 document recommends selecting laboratories that are using test procedures such as those in EPA methods 1669, so that the majority of the analytical data will be generated above the laboratory's established PQL. For translator studies, extrapolating any testing measurements below the laboratory's MDL is strongly discouraged. If, after using the best available technologies there are concentrations below the MDL, it is acceptable to set those concentrations to a value equal to the MDL reported. If both total recoverable and dissolved concentrations are below the MDL, the data pair should be discarded.

3.3 Calculating the Translator Value

The 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. For each sampling location a translator is calculated as the geometric mean of the dissolved to total recoverable ratios measured at that location.

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 – Determine the geometric mean

$$GM_f_D = \exp(\sum_1^n \ln(f_D)/n)$$

at each sampling location.

Step 3 – The highest geometric mean will be used as the translator f_D .

Note: In some cases, the f_D for each field sample at a given location may vary substantially, or the samples may not have all been collected at critical flow conditions. In these cases, the geometric mean may ignore critical conditions and may not provide a good representation of the water body. Under these circumstances it may be appropriate to set the translator at the upper 95th percentile of the data set or to consider tying the translator to other physical or chemical variables through the use of a partition coefficient. Information on deriving a translator using the partition coefficient approach may be found in the document, "The Metals Translator: Guidance for Calculating a Total

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Recoverable Permit Limit from a Dissolved Criterion”, EPA 823-B-96-007. Refer to Appendix A for statistical analysis of data.

3.4 Establishing the Permit Limit

Multiply the total recoverable metal criterion by the appropriate conversion factor to determine the dissolved criterion to be met in the water column. Divide the dissolved criterion by the site-specific metal translator (f_D) to determine the total recoverable concentration in the effluent that will not exceed the dissolved metal criteria in the receiving water.

4. SITE-SPECIFIC STUDY PLAN

Chapter 2 discusses the considerations involved in designing a field study for a site-specific chemical translator for metals. Chapter 3 and Appendix C 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. This generic plan is based on the determination of dissolved-to-total recoverable ratios in a series of 10 or more samples at each sampling location. 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. *The study plan must be submitted to the Department 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.

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 riverine discharges during runoff events, should generally follow the considerations listed for rivers/streams.

4.1. Objective

State the objective of the project. For example,

"To determine the metals translator for [list metals] in the discharge from Outfall OOX."

4.2. Approach

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

Samples of effluent, upstream receiving water, and downstream receiving water will be collected and analyzed for total recoverable and dissolved [list metals]. At each sampling location a translator will be calculated as the geometric mean of

the ratios of dissolved metal to total recoverable metal for all sample pairs at that location.

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. Please refer to the latest version of the "DEP-SOP Manual for Field Operations for the frequency and number of equipment and field blanks needed to fully document sample quality. See also Chapter 62-160, F.A.C. for documentation and record-keeping requirements.

4.3. Parameters

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

- * Select parameters-see Section 2.
- * Select analytical methods and detection levels-see Section 3.

- ** Detection level and quantitation 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 µg/L. Prime candidates are cadmium (fresh water), copper (salt water), 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 MDLs low enough to produce a valid translator. Such alternatives include matrix modifiers, background- correction instrumentation, and extraction or pre-concentration. If uncertain, check with DEP Preliminary testing and MDL studies may be necessary to determine if a problem exists.

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

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

Describe laboratory protocols and required quality controls.

- * Select standard or clean (class-100) practices.
- * Select the appropriate QC requirements from “DEP SOP for laboratory operations and sample collection activities”.
 - ** Trip blank
 - ** Duplicate analysis of all samples and blanks
 - ** Laboratory method blank for each batch of samples
 - ** MS/MSD on each batch of samples

4.4. Sampling Stations

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

- * Select sampling locations -see Section 2.2.
- ** The samples may have to be collected at some critical hydrologic condition to represent the critical toxicological conditions.
- ** 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, generally in a direction toward the headwaters of the lake/reservoir if possible.
 - *** **Estuary/Ocean** Beyond the influence of the discharge, 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
 - ** Wastewater treatment plant effluent--24-hour composite
 - ** Noncontact cooling water--same as receiving water
 - *** **River/Stream**--Grab, under critical-flow conditions
 - *** **Lake/reservoir**--Grab
 - *** **Estuary/Ocean**--Grab low and high tides

4.5. 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 2.3.
- ** The recommended minimum number of samples for a critical-flow sampling program is 10.
- * Select the frequency of sampling--see Section 2.1.2.
- ** 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 the critical flow conditions
- *** **Estuary/Ocean** Monthly or biweekly sampling may be required to capture critical monthly tidal periods, such as biweekly neap tides.
- * Determine the study period--see Section 2.1.
- *** **River/Stream** The critical flow period of the year is preferred.
- *** **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** 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. Determine the critical salinity and collect samples under those conditions.
- *** **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 total to 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 critical-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 gauging station XYZ), turbidity (e.g., less than 5 NTU), TSS concentration (e.g., less than

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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** Samples should be collected under worst-case tidal conditions--generally low slack when dilution is typically at its lowest.

4.6 Preparation

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

Sample bottles, labeled (for total recoverable metals)

Sample bottles, labeled (for dissolved metals)

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), 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.

4.7 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.

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 cleaned sample collection container to sample collecting pole. Plunge pole 2 to 3 feet under water surface quickly. Pull container up and transfer to sample collection bottle for total recoverable metals. Add the appropriate amount of preservative to the sample bottle, leaving 1/2 to 1 inch of air space at the top. Swirl to mix acid, close cap tightly, and return bottle to carrier.

Alternatively, to reduce of contamination, add preservative when samples arrive at the testing laboratory.

6. Collect duplicate sample by plunging sample collection container back under water, retrieving, and capping bottle tightly for dissolved sample, again leaving 1/2 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

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sampling steps and Method 1669 § 8.3 for on-site composting and filtration in a glove box. See also Appendix E.2.

4.8. 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 sample bottles, one total recoverable and one dissolved. 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 total recoverable and one dissolved. 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.

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5. At subsequent stations, follow procedure for Station 2.
6. After finishing at the last Station , collect the field blanks--one total recoverable and one dissolved. 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.
7. Complete chain-of-custody. Check bottle carrier to ensure bottles are upright and well packed.
8. 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.

4.9. Data Analysis

Describe the method for calculating the chemical translator.

** See Section 3.3

4.10. 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
- ** 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

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4.11. State Approval

Provide a signoff line for state regulatory agency.

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APPENDIX A

A.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 (μ_t) = mean dissolved concentration (μ_d).

To determine sample size, three factors must be selected:

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

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

For a translator study, the null hypothesis is assumed to be false, i.e., there is a difference between total and dissolved concentrations. Therefore, β 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 β levels of 0.05, the following shows the relationship between Δ and n, assuming a t distribution:

α	β	Δ	n
0.05	0.05	1.0	27
		2.0	8
		3.0	5
		4.0	4

A sample size of 4, therefore, would determine that a difference exists only if the difference between the means is 4 σ 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 σ 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.

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A sample size of 10 (or greater) is recommended because it would allow demonstration of a significant difference for Δ 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 B

B.1. Topics covered in Method 1669 include:

Contamination 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 and blanks.
- 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 B- 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 B-1. Standard vs. Trace Metals Sampling

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Component	Standard Sampling Technique (USEPA, 1983, 1991b)	Trace Metals Sampling Techniques (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 ₃ , 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 ₃ :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 ₃ , 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 0.45µm filter with a minimum 600 cm ² filtration area. Rinsing the #12175 filter with 100 ml ultrapure water is adequate cleaning for current ambient level determinations.
Preservative	Conc. redistilled HNO ₃ , 5 ml/L (GFAA methods; USEPA, 1983). 1:1 HNO ₃ to pH < 2 (3ml/L) (ICP Method 200.7; USEPA, 1991b)	Ultrapure HNO ₃ to pH < 2 or lab preserve and soak for 2 days.

B.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.

B.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.

B.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.

B.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.

B.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.

B.3. Preservation

Samples to be analyzed for total recoverable metals are preserved with concentrated nitric acid (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.

B.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 cm^2 surface area.) The minimization of filtration artifacts can be assured with high capacity tortuous path filters and limited sample volume (≤ 1000 ml). The Gelman #12175 capsule filter has equivalent filtration area of 600 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.

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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.

B.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

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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 C

C.1. Laboratory Facility, Equipment, and Reagents

Many 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 Quality Control Supplement for Determination of Trace Metals at EPA Water Quality Criteria Levels Using EPA Metals Methods (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. 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 interferent(s).

C.2. Analytical Methods

The test methods currently in 40 CFR Part 136 may not be sufficiently sensitive for trace metals determinations. Dischargers may use more sensitive methods, such as stabilized temperature graphite furnace atomic absorption spectroscopy (STGFAA) 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, STGFAA and ICP/MS may be preceded by hydride generation or on-line or off-line preconcentration to achieve these levels. EPA 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.

C.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

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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.