Water Quality-Based Permitting for Trace Metals
Fact Sheet
April 1996

Background

Under the Federal Water Pollution Control Act Amendments of 1972, commonly known as the Clean Water Act (CWA), pollutant discharges into the nations waters are controlled through the National Pollutant Discharge Elimination System (NPDES). Under this system, individual facilities are issued NPDES permits that provide limitations on the type, concentration, and volume of pollutants that may be legally discharged. Typically, these pollutant controls are based on technology-based standards. If, however, these technology-based controls are not adequate to protect the water quality standard designated for the facility's receiving water, stricter controls are warranted. In such cases, NPDES permits contain water quality-based controls.

Water quality-based controls reflect water quality standards established by States or by EPA when a state has not adopted water quality standards approved by EPA pursuant to the Clean Water Act. Water quality standards consist of: a designated use or uses of a waterbody or a segment of a waterbody; water quality criteria that are necessary to protect the designated use or uses; and an antidegradation policy. These water quality standards serve two purposes: (1) they establish water quality goals for a specific waterbody, and (2) they are the basis for establishing water quality-based treatment controls and strategies beyond the technology-based controls required by CWA Sections 301(b) and 306.

In the 1987 amendments to the Clean Water Act, Congress strengthened the emphasis on water quality-based permitting by mandating under Section 303(c)(2)(B) that States adopt specific numeric criteria for all toxic pollutants that could be expected to interfere with the designated uses of a water body. Under Section 304(l), Congress also required States to implement water quality-based control strategies necessary to ensure that the water quality standard would be attained. In 1988, EPA responded to the new requirements by issuing *Guidance for State Implementation of Water Quality Standards for CWA Section 303(c)(2)(B)* and *Final Guidance for Implementation of Requirements under Section 304(l) of the Clean Water Act as Amended*. In early 1990, EPA completed a "preliminary assessment" of compliance with these requirements; the results of this assessment indicated that only seven states were in compliance. In November 1991, EPA proposed numeric criteria and standards for the 35 states and territories that still had failed to meet the requirements. After proposing this "National Toxics Rule" (57 *FR* 60848), eight additional states submitted water quality standards and water quality-based control strategies necessary to meet the requirements of CWA Sections 303(c)(2)(B) and 304(l), bringing the number of states and territories in compliance to a total of 43. On December 22, 1992 the National Toxics Rule was promulgated for the fourteen remaining states and territories.

Following initial proposal and promulgation of the National Toxics Rule, the EPA Office of Water initiated a number of activities intended to support the implementation of numeric criteria for metals in State water quality standards. In May 1992, EPA released *Interim Guidance on Interpretation and Implementation of Aquatic Life Criteria for Metals*. As a follow-up to the May 1992 interim guidance, EPA held an open meeting in January 1993 to discuss metals criteria and permit issues, particularly concerns about the most

appropriate form of metals in ambient waters and effluents. The meeting, which was held in Annapolis, MD, included participants from the academic, consultant, and regulated communities, as well as those from States, EPA laboratories, EPA Regions, and EPA Headquarters. Their recommendations for short-term actions can be summarized as follows: (1) prepare guidance on clean analytical techniques, (2) write permits in terms of total recoverable metal, (3) apply criteria as dissolved metal, (4) use the water-effect ratio to better account for bioavailability, (5) evaluate under- and over-protective factors in the standards-to-permits process, and (6) consider stable organometallic compounds to be a separate class of chemicals. The agency solicited comments on these recommendations in a July 9, 1993 *FR* notice.

Based upon the recommendations offered by the Annapolis meeting participants and by others following the meeting, the Office of Water (OW) issued an October 1993 policy memorandum concerning the implementation of metals criteria. Although most states have subsequently adopted their own plans for meeting the requirements of the 1987 amendments, others have not. In addition, the plans adopted by many of the states include the use of numeric criteria published by EPA. The Office of Water, therefore, has issued a number of interim guidance documents or initiated other activities related to the recommendations from the Annapolis meeting and the subsequent policy memorandum. On May 4, 1995 EPA published an Interim Final Rule (60 *FR* 22228) that stayed the aquatic life metals criteria that were published in the December 1992 National Toxics Rule (57 *FR* 60848) and simultaneously promulgated (as interim final) for these same metals, criteria expressed as dissolved metal. The May 1995 rule also described existing OW policies and guidance documents. These policies and guidance are summarized below.

Expression of Aquatic Life Criteria

The October 1993 policy memorandum issued by OW 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 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 0.4 µm 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 adsorbed to or complexed with organic colloids and ligands. Some or all of this may be unavailable biologically. The Office of Water is currently evaluating alternate definitions of dissolved metals, and is relying in part, on studies being performed by the U.S. Geological Survey. Given these issues, the October 1993 metals policy further states:

> *Until the scientific uncertainties are better 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 metals, if those*

standards are otherwise approvable as a matter of law.

The adoption of the October 1993 policy did not change the Agency's position that the existing total recoverable criteria published under CWA Section 304(a) continue to be scientifically defensible. EPA developed the total recoverable criteria using high-quality analytical data, and these criteria are still scientifically defensible.

Conversion of Total Recoverable Metal Criteria to Dissolved Metals 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. EPA has subsequently reproduced the test conditions, for the purpose of estimating the percentage dissolved during the tests. This information is the basis for factors to convert total recoverable metal criteria to dissolved criteria. Working from the premise that the dissolved fraction more closely approximates the biologically available fraction than does the total recoverable fraction, these conversion factors have the effect of reducing the water quality criteria concentrations. Conversion factors that resulted from these studies are found in an Interim Final Rule published on May 4, 1995 (60 *FR* 22228).

Site Specific Criteria Modifications

EPA has issued guidance for three methods for developing site-specific criteria: the recalculation procedure, the indicator species procedure (also known as the water-effect ratio), and the resident species procedure. Current guidance on the recalculation and water-effect procedures is found in the *Interim Guidance on Determination and Use of Water-Effect Ratios for Metals* (February 1994; EPA-823-B-94-001). Guidance on the resident species procedure is in the *Guidelines for Deriving Numerical Aquatic Site-Specific Water Quality Criteria by Modifying National Criteria* (EPA-600/3-84-099, October 1984).

The water-effect ratio (WER) compares a pollutant's toxicity in site water with its toxicity in typical lab water in order to adjust the criterion for local bioavailability. With respect to the use of water-effect ratios, the October 1993 policy states:

> *As justified by water characteristics and as recommended by the WER guidance, we strongly encourage the application of the WER across a watershed or waterbody as opposed to application on a discharger by discharger basis, as technically sound and an efficient use of resources.*

In order to meet current needs, but allow for changes suggested by protocol users, EPA has issued the WER guidance as "interim". EPA will accept WERs developed using this guidance or by other scientifically defensible protocols.

TMDLs and NPDES Permits

Although not specifically part of the reassessment of water quality criteria for metals, dynamic or probabilistic models are another useful tool for implementing water quality criteria, especially those for protecting aquatic

life. These models provide another way to incorporate site-specific criteria. The October 1993 policy states:

> *Dynamic models make the best use of the specified magnitude, duration, and frequency of water quality criteria and, therefore, provide a more accurate representation of the probability that a water quality standard exeedance will occur. In contrast steady-state models make a number of simplifying, worst case assumptions which makes them less complex and less accurate than dynamic models...EPA considers dynamic models to be a more accurate approach to implementing water quality criteria and continues to recommend their use.*

Guidance on the use of dynamic models can be found in the attachments to the October 1993 policy statement and in the 1991 *Technical Support Document for Water Quality-based Toxics Control* (EPA/505/2-90-001).

Translating from a Dissolved Ambient Water Quality Criterion to a Total Recoverable Concentration in Effluent

Although EPA recommends that water quality standards be defined in terms of dissolved metal concentrations, NPDES regulations require that, in most cases, effluent discharges be defined in terms of total recoverable metal concentrations. This is because the chemical conditions in ambient waters frequently differ substantially from those in effluent, and there is no assurance that effluent particulate metals would not dissolve after discharge. Similarly, total maximum daily loads (TMDLs) for metals must be able to calculate (1) dissolved metal in order to ascertain attainment of water quality standards, and (2) total recoverable metal in order to achieve mass balance necessary for permitting purposes.

Many different properties influence this dissolved to total recoverable ratio. Important factors include water temperature, pH, hardness ($CaCO_3$ concentration), concentrations of metal binding sites such as concentrations of total suspended solids (TSS), particulate organic carbon (POC), dissolved organic carbon (DOC), and acid volatile sulfides (AVS) 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 most straightforward approach is to analyze the mixture to determine the ratio of dissolved and total recoverable metals fractions. This ratio 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 concentration in the effluent that will not exceed the dissolved concentration in the water column.

Specific guidance for the translation of dissolved water quality criteria to total recoverable concentrations in effluent can be found in a February 16, 1996 draft document titled *The Metals Translator: A Guidance for Calculating a Total Recoverable Permit Limit from a Dissolved Criterion*.

Sampling and Analysis of Trace Metals

In assessing waterbodies to determine the potential for toxicity problems due to metals, the quality of the data used is an important issue. Metals data are used to determine attainment status for water quality standards, discern trends in water quality, estimate background loads for TMDLs, calibrate fate and transport models,

estimate effluent concentrations, assess permit compliance and conduct research. When the May 1992 interim guidance and the October 1993 policy statement were issued by EPA, two obstacles to the ability to gather metals data of acceptable quality were identified.

First, existing EPA methods for the analysis of many metals were not capable of yielding detection and quantitation levels necessary to reliably measure metals at the water quality criteria levels. Second, recent research by EPA, USGS, and others suggested that, unless specific measures are taken to preclude contamination during sample collection and analysis, the quality of metals data gathered at ambient water quality criteria levels may be compromised. Specifically, recent studies have shown that metals concentrations reported in EPA and USGS databases and in effluent discharges may be largely due to sample contamination rather than actual sample concentration.

To ensure that metals data accurately reflect the concentrations of the waterbody sampled, the Office of Water has recently released a draft sampling method, seven draft analytical methods, and guidance on establishing cost-effective clean rooms in existing facilities. The new methods are capable of measuring metals at water quality criteria levels and include the procedures necessary to preclude contamination at these levels. A list of the draft guidance and methods is as follows:

- *Method 1631: Mercury in Water by Oxidation, Purge and Trap, and Cold Vapor atomic Fluorescence Spectrometry*. EPA 821-R-96-001.
- *Method 1632: Determination of Inorganic Arsenic in Water by Hydride Generation Flame Atomic Absorption*. EPA 821-R-96-002.
- *Method 1636: Determination of Hexavalent Chromium by Ion Chromatography*. EPA 821-R-96-003.
- *Method 1637: Determination of Trace Elements in Ambient Waters by Chelation Preconcentration with Graphite Furnace Atomic Absorption*. EPA 821-R-96-004.
- *Method 1638: Determination of Trace Elements in Ambient Waters by Inductively Coupled Plasma-Mass Spectrometry*. EPA 821-R-96-005.
- *Method 1639: Determination of Trace Elements in Ambient Waters by Stabilized Temperature Graphite Furnace Atomic Absorption*. EPA 821-R-96-006.
- *Method 1640: Determination of Trace Elements in Ambient Waters by On-Line Chelation Preconcentration and Inductively Coupled Plasma-Mass Spectrometry*. EPA 821-R-96-007.
- *Method 1669: Sampling Ambient Water for Trace Metals at EPA Water Quality Criteria Levels*. EPA 821-R-96-008.
- *Guidance on Establishing Trace Metal Clean Rooms in Existing Facilities*. EPA 821-B-96-001.

EPA is now aware of several studies in which the techniques employed in the above guidance have been applied and have been of great benefit in determining that either an environmental problem does not exist or that the magnitude of the problem is considerably less than initially envisioned. Therefore, the added costs associated with the sample handling and quality control protocols contained in the draft guidance are often trivial when compared to the cost saved by avoiding unnecessary pollution controls that might otherwise have been required.

Because CWA Section 304(h) requires the Administrator to promulgate test procedures for the analysis of pollutants regulated under the act, the analytical guidance documents are written in the form of analytical

methods. The Office of Water has completed preliminary validation studies for many of these draft methods; when validations studies are completed, OW intends to propose the revised versions at 40 *CFR* Part 136 for use in compliance monitoring. These methods would *not* replace those already approved for use. Rather, they are intended to complement the existing EPA metals methods, thereby providing permitting authorities, permittees, and other interested parties with the analytical capabilities to measure metals at technology-based or at water quality-based levels as their needs dictate.

Use of Trace Metals Data

As noted above, the quality of data used to support CWA programs is an important issue, and in particular, the quality of trace level metals data may be compromised due to contamination during sampling and analysis. Appropriate quality assurance and quality control procedures are key to producing precise and accurate data unbiased by contamination. In April 1995, OW released *Guidance on the Documentation and Evaluation of Trace Metals Data Collected for Clean Water Act Compliance Monitoring* (EPA 821-B-96-002). This document contains guidance that is applicable to the review of trace metals data submitted for compliance monitoring purposes under the NPDES system when these data are collected using the sampling and analysis protocols cited above. The guidance is applicable to the examination of recently gathered trace metals data and to historical data in existing EPA databases.

With respect to such data, the October 1993 policy memorandum states:

> *We believe that most historical data for metals, collected and analyzed with appropriate QA and QC, at levels of 1 ppb or higher, are reliable. The data used in development of EPA criteria are also considered reliable, both because they meet the above test and because the toxicity test solutions are created by adding known amounts of metals.*

Additional guidance regarding the use of historical data may be found in the April 1995 document.

Summary

This fact sheet summarizes EPA Office of Water policy regarding the implementation of metals criteria in NPDES permits and other CWA programs. None of the documents cited in this fact sheet are intended to serve as requirements for States or permittees. Rather, these documents are intended to serve as guidance to be used at the discretion of State permitting authorities and consistent with their approved NPDES permit programs.