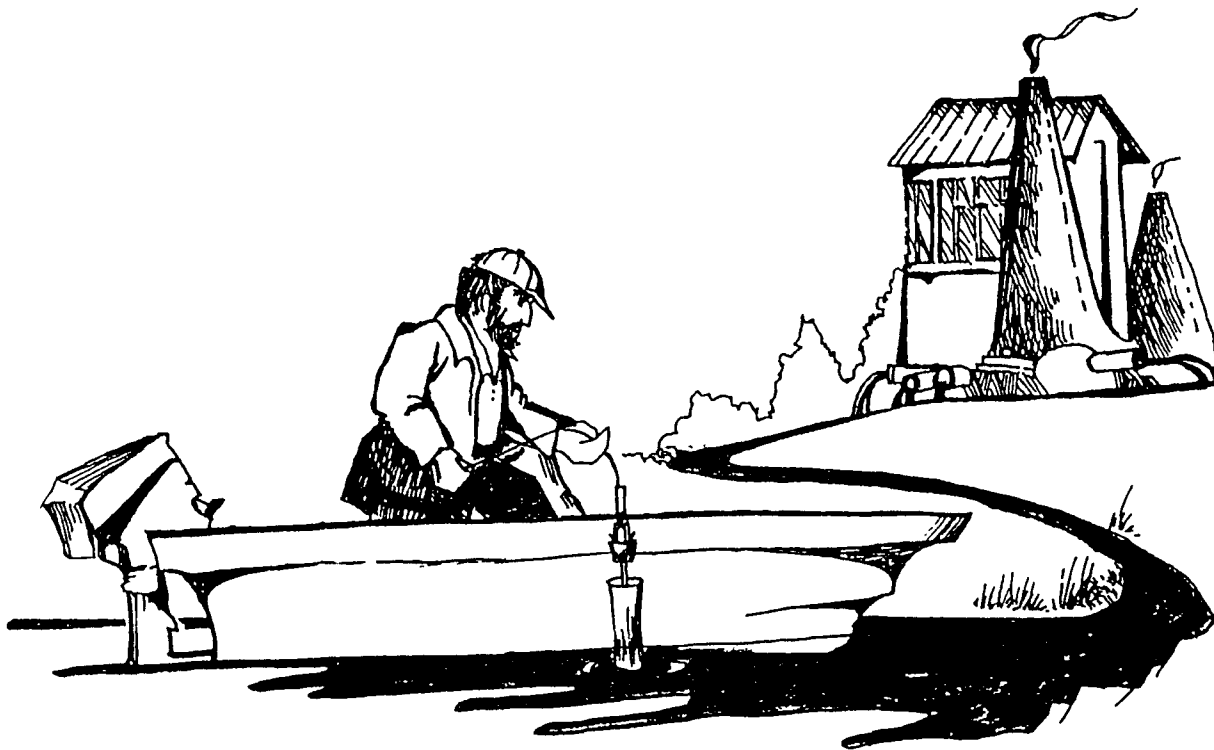




Interim Guidance on Interpretation and Implementation of Aquatic Life Criteria for Metals



Interim Guidance on Interpretation and Implementation of Aquatic Life Criteria for Metals

May 1992

**Health and Ecological Criteria Division
Office of Science and Technology
U.S. Environmental Protection Agency
Washington, DC 20460**

This document provides guidance for interpreting and implementing aquatic life criteria for metals in waters of the United States. It is issued in support of EPA regulations and initiatives involving the application of water quality criteria and standards. This document is agency guidance only. It does not establish or affect legal rights or obligations. It does not establish a binding norm, or prohibit alternatives not included in the document. It is not finally determinative of the issues addressed. Agency decisions in any particular case will be made by applying the law and regulations on the basis of specific facts when regulations are promulgated or permits are issued.

This document is expected to be revised periodically to reflect advances in this rapidly evolving area. Comments from readers are welcomed. Send comments to Health and Ecological Criteria Division (WH-586), U.S. EPA, 401 M Street SW, Washington, DC 20460.

Foreword

Synopsis

This guidance addresses the use of EPA (and corresponding State) metals criteria in water quality standards intended to protect aquatic life. This guidance also addresses the derivation of NPDES permit limits from such criteria. The main body of the document presents recommendations on the best current approaches for implementing aquatic life criteria for metals and measuring attainment of such criteria. This guidance supersedes past criteria document statements expressing criteria in terms of an acid soluble analytical method. Appendix A presents a case study illustrating derivation of site-specific criteria (item 3 below). Appendix B presents recommendations on the derivation of NPDES permit limits from ambient metals criteria. As described in Appendix B, it supersedes part of the Technical Support Document [1] discussion of metals.

The principal issue is the correlation between metals that are measured and metals that are biologically available. The bioavailability and toxicity of metals depend strongly on the exact physical and chemical form of the metal, and on the species affected. The form of the metal, in turn, can vary depending on the chemical characteristics of the surrounding water matrix. Because of differences between various effluents and site waters, and between laboratory toxicity test waters and many site waters, establishment and implementation of metals criteria are not straight forward. Consequently, this guidance presents three reasonable approaches that differ in their complexity.

- (1) The simplest approach is to measure total recoverable metals in ambient waters, and to compare such measurements to national or state-wide criteria.
- (2) A closer focus on biologically available metals can be obtained by measuring dissolved metals in ambient waters, and comparing such measurements to criteria appropriate for dissolved metal. Since effluent limits, for both technical and legal (40 CFR 122.45) reasons, are generally expressed in terms of total recoverable metal, it is necessary to translate between the total recoverable concentration in the effluent and the dissolved concentration in the ambient water.
- (3) Because of the complexity of metal chemistry, there is no one chemical analytical method that can accurately determine the metals that are bioavailable and toxic. For implementing metals criteria established from laboratory toxicity tests, an adjustment of the criteria value can address this constraint. It involves measur-

ing a pollutant's water-effect ratio in the receiving water covered by the standard. The water-effect ratio compares the toxicity of a pollutant in the actual site water to its toxicity in laboratory water, for two or more aquatic species. Because the metal's toxicity in laboratory water is the basis for the national criterion, the water-effect ratio is used in an adjustment to obtain a site-specific value. Implemented in conjunction with either of the first two alternatives, this adjustment may either increase or decrease the numeric value of the criterion.

Introduction

The principal problem in relating discharges of toxic metals to environmental impacts is the different toxicities of various metal species in ambient waters, and the varying fractions of such species with location and time. This results in the same metal concentration exerting different toxicity from place to place and from time to time. The chemical species involved include metals dissolved in a variety of forms, and metals sorbed to or within particulate matter. Metals may differ markedly from each other with respect to speciation and bioavailability.

Although metal toxicity may vary depending on the chemical characteristics of the water body, the national criteria have been designed to protect all or almost all bodies of water. However, this does not mean that the national criteria will always be overprotective. For example, some untested locally important species might be very sensitive to the material of concern, or the local aquatic organisms might have increased sensitivity due to diseases, parasites, other pollutants or water quality conditions, or extreme flow or temperature conditions [2].

Another problem involves metal speciation in effluents, and the potential transformations that may occur in moving from the chemical environment of the effluent to the chemical environment of the receiving water. Consequently, in contrast to an ambient measurement, which should respond predictably to metal that is actually bioavailable, an effluent measurement needs to respond also to metal that may not be bioavailable under effluent chemical conditions, but would possibly become bioavailable under ambient chemical conditions.

Because of the complexity of metal speciation and its effect on toxicity, the relationship between measured concentrations and toxicity is not precise. Consequently, any chemical analytical method that could be recommended would not guarantee precise comparability between concentrations measured in the field and concentrations employed in the toxicity tests underlying the criteria. However, the three approaches presented in this guidance should provide acceptable approximations.

EPA has recognized four methods of sample preparation for metals analysis. These lead to measurement of: (a) total metals, (b) total recoverable metals, (c) acid soluble metals, and (d) dissolved metals. Ordinarily, the four methods measure all of the dissolved metal present at the time of sampling. They differ in the amount of particulate metal that they measure.

The total metals procedure, the total recoverable metals procedure [3], and the acid soluble metals procedure [4, 5] measure metals that are dissolved in water or become dissolved when treated with acid. They differ in the concentration of acid and in the temperature used during the analytical procedure, both decreasing in the order cited above.

The dissolved procedure [3] measures metal that passes through a 0.45 μm filter at the time of sample collection. The results from this procedure are reported as "dissolved," although it may include metal that was bound to micro-particles ($<0.45 \mu\text{m}$) at the time of sample collection. More recent dissolved procedures recommend positive-pressure, in-line filtration through polycarbonate membrane filters having a uniform pore size selected from a range of 0.1-0.4 μm [6], and emphasize ultra-clean laboratories, labware, and reagents [7, 13]. Measurements using different filter sizes may, however, give different results.

Metals criteria documents issued in 1980 recommended the use of the total recoverable method. Beginning in 1984, although a final acid soluble method was not available, the criteria documents have stated that an acid soluble method would be a better way of measuring attainment of the criteria. Noting the unavailability of a final method, they recommended the continued use of the total recoverable method, which they acknowledge may be overly protective.

Because the acid soluble method uses a less rigorous digestion, it was expected that it would generally measure less of the particulate metal than the total recoverable method. It was therefore believed that the acid soluble method would more accurately measure bioavailable metal. Recently available ambient and effluent data suggest, however, that acid soluble results are ordinarily nearly identical to total recoverable results, while being somewhat different from dissolved results. Because an increased understanding of the complexity of metals bioavailability indicates that the acid soluble method will not significantly improve the correlation between measured metal and bioavailable metal, this guidance is not recommending the use of this method.

Bioavailability and toxicity vary with the form of the metal. Particulate metal is generally expected to have less bioavailability than dissolved metal. Nevertheless, the toxicity of ambient particulate metal is not necessarily zero. For example, some metal that is in the particulate phase in the ambient

Background on Analytical Methods

Bioavailability and Toxicity

Dissolved and Total Recoverable Approaches

water environment may become dissolved in the chemical environment associated with the gill or the gut.

In natural waters, some metals may exist in a variety of dissolved species that differ significantly in toxicity. For copper, the divalent free cation and some inorganic complexes have substantial toxicity, whereas dissolved organic complexes generally have significantly less toxicity. As a result, the same concentration of dissolved copper may exert different toxicity in different waters.

Toxicity tests that form the basis for the criteria are usually performed in an untreated or slightly treated natural water from an uncontaminated source, or in water that has been first purified and then reconstituted by the addition of appropriate mineral salts. Because such dilution water is generally lower in metal-binding particulate matter and dissolved organic matter than most ambient waters, these toxicity tests may overstate the ambient toxicity of non-biomagnified metals that interact with particulate matter or dissolved organic matter.

In most but not all toxicity tests underlying the criteria, the percentage of metal in the particulate phase is fairly low. For ambient waters, on the other hand, recent data suggest that typically 30-80 percent of the copper, nickel, and zinc, and 90-95 percent of the lead may be in a particulate phase measured by the total recoverable method but not by the dissolved method.

In freshwater laboratory tests, organic carbon concentrations of a few mg/L are typical, with chronic tests having higher concentrations than acute tests. In ambient waters, organic carbon concentrations are typically somewhat higher than this, and may be substantially higher at the edge of small mixing zones.

Because of the greater fraction of particulate metal in ambient waters, as well as the higher levels of dissolved organic binding agents in ambient waters, the fraction of metal that is biologically available may often be lower under ambient field conditions than under laboratory conditions, particularly for freshwaters.

Aquatic life criteria in ambient waters may be implemented either as total recoverable metal or as dissolved metal. Effluent limits must generally be expressed as total recoverable metal. For analyses of metals in the low $\mu\text{g/L}$ range or below, ultra-clean sample handling techniques [7, 13] should be used.

Ambient Waters

When used for expressing ambient water quality criteria, the total recoverable method provides greater safety than does the dissolved method. Nevertheless, when used for ambient waters,

total recoverable measurements may result in overestimating the toxicity. While toxicity testing has shown dissolved measurements to be better predictors of toxicity than total recoverable measurements, there are also some potential concerns with this approach, as discussed below.

First, EPA water quality criteria are generally based on the reported total recoverable concentrations in the toxicity tests. If used for dissolved standards, the criteria values need to be downwardly adjusted to account for the typical dissolved fraction in test dilution water. For copper, approximately 86 percent of the reported total concentration was dissolved during freshwater acute toxicity tests with the more sensitive species. Consequently, the copper freshwater acute criterion should be adjusted to 86 percent of its total recoverable criterion in order to serve as a dissolved criterion, particularly in waters having low concentrations of dissolved organic binding agents. While the adjustment may be small for most metals, a few metals, such as aluminum, may require much larger adjustments to account for the much lower percentage dissolved typically occurring during toxicity tests. Chronic criteria may require larger adjustments than acute criteria, due to the higher particulate concentrations caused by the addition of food during chronic tests.

Except for copper in freshwater, the factors are not yet available for converting EPA's published criteria into dissolved criteria. A re-examination of data underlying the metals criteria is now underway to compile the dissolved concentrations measured during toxicity tests. While preliminary analysis does not indicate that these dissolved adjustment factors are of sufficient magnitude to be of great concern, they should be considered in any adoption of dissolved metal standards subsequent to distribution of this information.

Second, by measuring comparatively little of the particulate fraction, it may be possible that the dissolved method could occasionally understate the toxicologically effective concentration. Although toxicity data suggest that this is not ordinarily a problem, it is more likely to be a concern if the dissolved concentration is only a very small percentage of the particulate concentration, such as may occur with aluminum.

In some situations the dissolved method may overstate the toxicologically effective concentration. When certain metals (such as copper) become complexed with elevated concentrations of dissolved organic matter, a reduction in toxicity may occur, compared to toxicity in laboratory water, which is low in organic matter. Where dissolved organic matter is likely to interact with the toxicant, the water-effect ratio approach is likely to be more accurate and is currently the recommended solution.

A review of the limited number of available site-specific studies found that the water-effect ratio (site water LC50 versus

Water-Effect Ratio Approach

lab water LC50) was generally significantly larger than the measured total recoverable versus dissolved ratio [10]. These limited freshwater data thus suggest that use of properly formulated dissolved criteria would be at least as protective as criteria derived from careful measurements of water-effect ratios.

Effluents

The dissolved method is generally not applied to effluents to determine achievement of effluent quality goals. Such use is generally barred by regulation (40 CFR 122.45). Because the chemical conditions in ambient surface waters may differ substantially from those in the effluent, there is no assurance that effluent particulate metal would not dissolve after discharge. A common method of removing metals from wastewaters is to chemically precipitate the metal and settle the resulting particles. Expressing a metals limitation in terms of dissolved metal would imply little concern about the effectiveness of the settling process or the fate of the discharged particulate metal.

Determining the total recoverable effluent limitation corresponding to a dissolved criterion would involve specifying the fraction of effluent total recoverable metal that would exist as dissolved metal under the chemical conditions of the receiving water. In the absence of site information, any values assumed for this fraction should be environmentally conservative.

Where greater accuracy is desired, the dissolved fraction of total recoverable metal could be evaluated by direct measurement of dissolved and total recoverable metal in the affected ambient waters, or possibly by geochemical model calculations (as discussed in Appendix B). All of the techniques involve approximations.

Due to the complexity of metals speciation, and due to the varying degrees of bioavailability and toxicity of the many forms and complexes, there is no chemical method that can assure that a unit of concentration measured in the field would always be toxicologically equivalent to a unit of concentration employed in the laboratory toxicity tests underlying the criteria.

For metals criteria derived from laboratory toxicity tests, one approach is to use a biological method to compare bioavailability and toxicity in receiving waters versus laboratory test waters. This involves running toxicity tests with at least two species, measuring acute (and possibly chronic) toxicity values for the pollutant using (a) the local receiving water, and (b) laboratory toxicity testing water, as the sources of toxicity test dilution water. A water-effect ratio is the acute (or chronic) value in site water

divided by the acute (or chronic) value in laboratory waters. An acute value is an LC50 or EC50 from a 48-96 hour test, as appropriate for the species. A chronic value is a concentration resulting from hypothesis testing or regression analysis of measurements of survival, growth, or reproduction in life cycle, partial life cycle, or early life stage tests with aquatic species.

Because the metal's toxicity in laboratory water is the basis for EPA's criterion, this water-effect ratio is used to adjust the national criterion (or corresponding State criterion) to a site-specific value. This adjustment may either increase or decrease the criterion. Because the water-effect ratio reflects differences in water chemistry, it is acceptable to assume that a ratio derived from acute LC50s or EC50s may be applied to both acute and chronic criteria, provided that the water-effect ratio is determined with an acutely sensitive species. Nevertheless, performing chronic tests is an option that could produce a different water-effect ratio, due to changes in water chemistry caused by the addition of food during chronic tests. While this may somewhat improve the accuracy of the resulting criteria, it will substantially increase the testing costs.

The principle of criteria adjustment using a water-effect ratio was set forth in previous guidance [8, 9]. The procedure applies to criteria derived from laboratory toxicity data. As such, it does not apply to the residue-based mercury chronic criteria, or the field-based selenium freshwater criterion. The basic features of the procedure as recommended herein are described below. Dischargers or private entities wishing to perform such testing should consult with the appropriate regulatory agency before proceeding.

- (1) At least two sensitive species, including at least one invertebrate, should be tested through standard toxicity testing protocols, using site dilution water and using laboratory dilution water. Test organisms should be drawn from the same population and tested under identical conditions (except for water source). Test species should ordinarily be selected from those species that were used for national criteria development in order to be able to ascertain whether the laboratory water results are comparable to the those in the criteria document.
- (2) Site water samples used for testing are to be representative of the receiving water to which the site-specific criteria value is to apply. For flowing waters, it is generally recommended that at least one sample correspond to a condition in which point or nonpoint pollutant contributions are reasonably well mixed with the flow of the receiving water. For other types of waters, it is generally recommended that a sample correspond to a dilution situation well outside any regulatory mixing zone. These recommendations are

intended to yield a water-effect ratio appropriate for the affected receiving water as a whole. These recommendations supersede those of the previous site-specific guidance [8, 9], which recommended that pristine waters always be used.

- (3) The laboratory dilution water should be comparable to what was used in tests underlying the national criteria. For any pollutant with a national or State criterion calculated from site-specific hardness, laboratory-water and site-water toxicity results should be computationally normalized to the same hardness, using the specified hardness slope.
- (4) The toxic metal should be added in the form of an inorganic salt having relatively high solubility. Nitrate salts are generally acceptable; chloride and sulfate salts of many metals are also acceptable. Results should be based on measured or nominal initial concentrations if static tests are performed, and on average measured concentrations if flow-through tests are performed.
- (5) Water quality characteristics affecting bioavailability and toxicity should be monitored. Measurements ordinarily should include both dissolved and total recoverable metal concentrations, hardness, pH, alkalinity, suspended solids, conductivity, dissolved solids or salinity, total organic carbon, dissolved organic carbon, temperature, and specific metal binding ligands (where known to be important).
- (6) The number of site water samples to be tested may vary with the size of the affected water body (or the size of the metal loading). Except in the smallest systems, a minimum of two site water samples should be collected in different seasons during times of relatively low flow or low dilution. In moderately sized and larger systems (e.g., multiple m^3/sec or double to triple digit cfs low flow), additional samples should be collected during other times in the year and possibly at additional locations appropriate for the segment under study.
- (7) In studies involving continuous discharges, samples ordinarily should not be taken from storm affected waters, which may contain particulate matter not present during design flow conditions. On the other hand, in effluent dominated situations, at least one sample should represent a higher dilution condition (less than 50 percent effluent) in order to portray ambient conditions. In all situations, it should be recog-

nized that the water-effect ratio may be affected by constituents contributed by point and nonpoint sources. Consequently, new measurements should be undertaken if newly implemented controls or other changes substantially affect ambient levels of suspended solids, organic carbon, or pH.

- (8) Additional testing should be performed before accepting unusually or inexplicably high values for the water-effect ratio, based on experience with the particular pollutant, and based on the chemical characteristics of the water. Retesting should also be performed for ratios having wide uncertainty ranges. EPA intends to compile additional information to assist in judging water-effect ratios in this manner. These recommendations, which focus concern on large and uncertain water-effect ratios, supersede the previous guidance [8, 9] recommendations that encourage retesting or rejection of small water-effect ratios.
- (9) Ordinarily, the acute and chronic criteria for the site are calculated by multiplying the national or State criteria by the geometric mean water-effect ratio for the two or more tested species. The previous site-specific guidance [8, 9] provides some additional suggestions for situations where the measured ratios differ significantly, and provides other alternatives for setting the chronic criterion.
- (10) As with other types of water quality-based control actions for toxic pollutants, it is recommended that the chemical-specific approach be implemented in conjunction with assessments of whole effluent toxicity and field ecology ("bioassessment") [1]. Nevertheless, in light of the stated limitations of these latter techniques with regard to identifying causative agents and predicting future changes [1], considerable caution is warranted in using such information (particularly ecological data) to make inferences about the adequacy of particular numeric criteria.

The water-effect ratio is affected not only by speciation among the various dissolved and particulate forms, but also by additive, synergistic, and antagonistic effects of other materials in the affected site waters. As such, the water-effect ratio is a much more comprehensive measure than a ratio of total recoverable metal to dissolved metal. Because the basic technique involves adding soluble metal salts to site water samples, it is most accurate where rapid sorption or complexation processes are involved.

Because effluent limits are generally expressed as total recoverable metal, simplicity would suggest deriving water-effect ratios in terms of total recoverable measurements. Derivation in

Relationship with Sediment Criteria

Current Technical Support and Future Research

terms of dissolved measurements is also acceptable, and may be preferred in situations involving highly variable suspended solids concentrations.

Data available from a limited number of site-specific studies performed in rather clean freshwater suggest that copper, lead, and cadmium often have substantial water-effect ratios, while zinc, in situations where it is preponderantly dissolved, often does not [10]. Much less information is available for such ratios in salt water.

For national or state-wide criteria expressed as dissolved or total recoverable metal, and for site-specific criteria derived from water-effect ratios, questions may be raised about the adequacy of water column criteria for protecting sediment. The issue is whether particulate metal settling from the water column could contribute to sediment quality problems, even where no toxicity is manifested in the water column.

Because sediment toxicity is considered to be determined primarily by the concentrations of pollutant dissolved in the sediment interstitial water, the question becomes whether the pollutant would have a greater propensity to become dissolved or bioavailable in the sediment than in the water column. While available information does not suggest that this is ordinarily the case, the ongoing development of sediment criteria should resolve this issue. Nevertheless, in those cases where the beneficial uses of a receiving water are known to be impaired by the toxicity of metals in sediments, water quality-based control requirements should be designed to abate any sources that would continue to cause sediment toxicity.

The Environmental Research Laboratories in Duluth and in Narragansett will continue to answer technical questions about the possible problems in applying the above methods to criteria for specific metals. The contact for freshwater is Charles Stephan (Duluth, Minnesota telephone (218) 720-5510). The contact for salt water is Gary Chapman (Newport, Oregon telephone (503) 867-4027).

EPA intends to undertake further work to facilitate the implementation of metals criteria in terms of dissolved measurements. For metals such as copper, silver, zinc, lead, and cadmium, the dependency of toxicity on factors other than hardness will be considered for inclusion. Where appropriate and feasible, EPA may develop equations relating dissolved metal criteria to hardness and organic matter concentration, and possibly pH and other water quality characteristics. EPA might also consider other biological or chemical techniques for ascertaining the effective concentration of bioavailable metals.

APPENDIX A

CASE STUDY: **Determination of the Water-Effect Ratio** **Using Indicator Species**

Norwalk River
Georgetown, Connecticut*

***Adapted from the 1983 Water Quality Standards Handbook [8] for purposes of illustrating an application.**

Connecticut's Upper Norwalk watershed, where this study was conducted, covers an area of 18.5 square miles and includes the region extending from the headwaters of the Norwalk River to its confluence with Comstock Brook.

Two secondary treatment plants discharge a total of 0.44 mgd of municipal wastewater to a reach 9-14 stream miles upstream of the study site. An area of failed septic systems in the same upstream vicinity also contributes to the pollutant loading of the river.

Although water quality is degraded somewhat in the immediate vicinity of these municipal pollutant sources, as the river flows southward towards Long Island Sound, it recovers to support a valuable recreational trout fishery. There are no industrial point source discharges of metals upstream of the study area.

Within the study area itself, the Gilbert and Bennett Manufacturing Company discharges treated process water to the Norwalk River at a point below Factory Pond in Georgetown, Connecticut. Gilbert and Bennett cleans, draws, and coats metal wire. Wastewater is primarily generated during the wire cleaning process. The wastewater treatment system of the facility consists of pH neutralization and equalization followed by precipitation and clarification of the effluent before discharge to the river. The treated wastewater is discharged intermittently to the river.

The Connecticut Department of Environmental Protection undertook the study of the Norwalk River site because the Gilbert and Bennett metal loadings were calculated to result in excursions of national water quality criteria for lead and zinc under design flow conditions. In order to evaluate the effect of site water on the toxicity of lead and zinc, EPA and the State used the indicator species (water-effect ratio) protocol.

By testing a sensitive invertebrate and a fish in both site and reconstituted laboratory dilution water, the water-effect ratio procedure accounts for differences in bioavailability and effective toxicity of a pollutant in the two waters. The procedure responds to the summation of all synergistic and antagonistic effects of site water quality characteristics (including pH, hardness, particulate matter, dissolved organic matter, and other contaminants). The procedure does not, however, elucidate factors causing the difference in toxicity.

A water-effect ratio is the ratio of a species LC50 in site water versus its LC50 in laboratory dilution water. The 1983 Water Quality Standards Handbook recommends that two relatively sensitive indicator species be tested, and that the geometric mean of the two results be used. The site-specific criterion would be calculated as the product of the national criterion and the water-effect ratio.

Introduction

Analyses Conducted

The results from the testing of metals toxicity in laboratory and site water forms the primary basis for the site-specific criteria. To provide additional information, the monitoring of ambient water chemistry, surveying of macroinvertebrates, and testing of whole effluent toxicity were also performed.

Chemical and Ecological Monitoring

Concentrations of several metals were measured in composite samples taken at each of four ambient stations and in grab samples of the Gilbert and Bennett main effluent. One ambient station was in the upstream control zone, two in the impact zone, and one in the recovery zone.

Benthic populations were sampled at five locations to assess the impact of the discharge on the stream community. One reference station was located in the upstream control zone. Three stations were in the Bennett and Gilbert impact zone, and one was in the recovery zone. Physical substrate, stream velocity, and water depth were similar at each location. Four Surber samples were collected at each of the five locations. Organisms were sorted in the field, preserved in 70 percent ethanol, and returned to the laboratory for identification and enumeration.

Toxicity Testing

Norwalk River water was withdrawn from a station upstream of Gilbert and Bennett and transported (along with the effluent samples) back to the laboratory. Toxicity tests were conducted in the sampled river water and in reconstituted water, with differing amounts of either lead or zinc added, in order to determine the LC50. Whole toxicity testing of one of the Gilbert and Bennett effluents was also performed, using both upstream Norwalk River water and reconstituted water for dilution.

Because the lead and zinc toxicity tests were run using upstream water, they do not indicate the effects of synergism, antagonism, or toxicant additivity with constituents of the Gilbert and Bennett effluent. Although this guidance recommends use of downstream water for at least one sample, the case study predates the guidance and does not follow this recommendation.

Ninety-six hour acute toxicity tests (static with measured concentrations of toxicant) were conducted with laboratory reared rainbow trout (*Oncorhynchus mykiss*, formerly *Salmo gairdneri*) and 48-hour acute toxicity tests (static with measured concentrations) were conducted with laboratory-reared *Daphnia magna*.

Water Chemistry and Ecological Quality

Mean instream concentrations of lead, zinc, and cadmium were higher in the impact and recovery zones than in the control zone. Levels of cadmium and copper appeared to exceed national acute criteria at all sampling locations both upstream and downstream of Gilbert and Bennett.

It should be noted that the metals data were generated using the sample handling and analytical protocols of the early 1980s, rather than more recent protocols emphasizing ultra-clean techniques. While the link between chemical quality and ecological quality is of great interest, it is not clear that these ambient metals data are sufficiently reliable to be used in such comparisons. If the ambient metals concentrations were reliably known, such information would be most useful for comparing concentrations in the control, impact, and recovery zones with the criteria derived from the water-effect ratio.

At the upstream reference location, 889 organisms from 44 taxa were collected. Most of the species collected could be classified as sensitive or facultative with respect to pollution tolerance. Species diversity was high (Shannon Diversity index of 3.4), indicating acceptable water quality and aquatic habitat.

At the three near downstream locations, the number of organisms, number of taxa, and diversity were reduced significantly. At some of the impact zone stations, the number of organisms was less than one-fourth, and number of taxa one-third that of the reference site. The Shannon index registered as low as 1.0.

At the recovery zone station (500 m downstream from the discharge), a larger number of organisms were found than at any of the other stations, including the upstream reference site. Diversity and numbers of taxa, however, remained at levels more characteristic of the impacted stations.

The ecological assessment demonstrated that the ecology of the Norwalk River was impaired, and strongly suggested that some type of pollutant release from Gilbert and Bennett was involved in the impairment. However, as noted in the Technical Support Document [1], ecological assessments cannot identify the causative agents, and generally do not predict the ecological quality as a function of chemical-specific concentrations. Consequently, these ecological data do not indicate the appropriateness of particular values for the water-effect ratio.

Toxicity Testing with Lead and Zinc

Table A-1 shows the results of static toxicity tests with daphnids and rainbow trout exposed to lead and zinc, in river water and in laboratory water.

Table A-1.—Toxicity of lead and zinc in Norwalk River and in laboratory water.

	DAPHNIA MAGNA		RAINBOW TROUT	
	48-hr LC50, µg/L (95% confid lim)	Water-Effect Ratio	96-hr LC50, µg/L (95% confid lim)	Water-Effect Ratio
<i>Lead</i>				
River water	1300 (950-1900)	4.1	9600 (7500-12000)	3.7
Lab water	320 (290-360)		2600 (1900-3600)	
<i>Zinc</i>				
River water	900 (740-1100)	2.3	1500 (1200-1800)	1.5
Lab water	400 (380-480)		1000 (850-1200)	

The toxicity of both lead and zinc was lower in Norwalk River water than in laboratory water. For both metals, the more sensitive species, *Daphnia magna*, had the higher water-effect ratio. This is consistent with general tendencies observed in other studies [10].

Whole Effluent Toxicity for One Effluent

In unspiked, static toxicity tests in which rainbow trout were exposed to one of the Gilbert and Bennett effluents, the effluent was rendered nontoxic by relatively little dilution of the effluent. As effluent constituted the bulk (60-68 percent) of the test water at dilutions toxic to half the organisms, it was not surprising that the whole effluent toxicity tests could not discern differences between toxicity in laboratory and river water. That is, toxicity was much reduced before enough laboratory or river water could be added to the effluent to discern differences between the added water.

The monitored effluent was not sufficiently toxic to daphnids to allow calculation of the dilution lethal to half the organisms. However, to eliminate toxicity to all the tested individuals, significantly more dilution was required with laboratory water than with river water. This suggests that this effluent may be less toxic in Norwalk River water than in laboratory water.

If the lead and zinc concentrations had been measured during the whole effluent toxicity tests, it would be possible to compare effect concentrations with the lead and zinc LC50 values shown in the previous section. In making such comparisons, however, it must be recognized that the cause of toxicity of the effluent is not known.

Finally, it should be noted that the tested effluent is only one of Gilbert and Bennett's releases to the Norwalk River. There is no disparity between the observed significant instream impacts and the relatively low toxicity of the one monitored effluent. The ecological assessment suggested that the unmonitored release was more toxic than the monitored one.

Calculation of the Site-Specific Criteria

The water-effect ratios for lead and zinc differed relatively little between species. If the overall water-effect ratio for each metal were calculated from the geometric mean of the species water-effect ratios, then the water-effect ratio for lead would be 3.9, and that for zinc would be 1.9.

It is assumed that the water-effect ratio would apply to both the acute and the chronic criteria. As the national criteria for lead and zinc are hardness dependent, for purposes of determining the value of the site-specific criteria during the survey period, it is appropriate to calculate the national criteria at the hardness of the laboratory reconstituted water, if different from the site water. The site-specific acute and chronic criteria for each metal would equal the national (or state-wide) criteria multiplied by the water-effect ratio for each metal.

Because all of the above toxicity tests and water-effect ratios were based on total recoverable metal, the resulting site-specific criteria would also be expressed as total recoverable metal.

When the site-specific criteria were used to calculate effluent limits, it was found that large reductions in current metals loadings would be required. This result is not surprising, considering the ecological effects observed downstream.

APPENDIX B

Derivation of Effluent Limits from Ambient Metals Criteria

The determination of the waste loads and effluent limits that allow attainment of water quality criteria is described in other EPA guidance [1, 11, 12]. The Waste Load Allocation Guidance Manuals [11, 12] are particularly suited to predicting far-field dissolved and total recoverable concentrations, such as would be necessary for evaluating watersheds with multiple dischargers. The Technical Support Document (TSD) [1] has additional guidance on the evaluation of mixing zones and the derivation of permit limits. Nevertheless, some additional discussion is provided below. This guidance supersedes the second paragraph of Section 5.7.3 "Metals" of the TSD [1].

Expressing state-wide or site-specific criteria as total recoverable metal has the advantage of providing a simple basis for calculating effluent limits. All of the effluent total recoverable metal would contribute to the ambient total recoverable concentration.

If criteria are expressed as dissolved metal, then it is necessary to establish what fraction of the effluent total recoverable metal contributes to the ambient dissolved metal.

Three alternatives may be considered for relating the ambient dissolved criterion for a specific metal to the effluent total recoverable limits: (a) directly measure dissolved and total recoverable metal in the receiving water, (b) assign environmentally conservative default values for the assumed ratio between dissolved and total recoverable metal, and (c) predict the percentage dissolved metal from a geochemical model such as MINTEQ.

Regardless of which alternative is used, it must be recognized that the goal is to set the effluent limit at a value such that the ambient water quality standard will be attained. In addition, compliance with regulatory requirements for technology-based limits, antidegradation, and antibacksliding is necessary.

Using Site-Specific Measurements

The concept is to measure the dissolved-total ratio for the particular metal in the receiving water affected by the discharger. Because the chemical properties of an effluent (particularly an industrial effluent) may be much different than the chemical properties of the receiving water below the discharger, it is appropriate to measure the ratio in the receiving water rather than in the effluent. As an approximation, it may be assumed that the measured dissolved-total metal ratio in the affected waters reflects the fraction of effluent total recoverable metal that remains or becomes dissolved in ambient water.

Total Recoverable Metal Criteria

Dissolved Metal Criteria

Samples on which measurements are made should be representative of the bulk of the receiving water. It is recommended that sampling be performed over a period of time, with samples representing the usual range of effluent and ambient quality, while emphasizing the season corresponding to the critical water quality conditions. Because the control strategy assumes that the dissolved concentration is related to the total recoverable concentration, it would be appropriate to verify that the dissolved and total recoverable concentrations are in fact correlated.

In freshwaters, an alternative approach to downstream sampling is to sample the effluent and the upstream waters and mix samples at an appropriate dilution. The dilution and the seasons for sampling should be related to the critical conditions, although it may be appropriate to reduce the dilution if necessary to detect and quantify the metal.

The most important constraint on the feasibility of carrying out site-specific measurements is the capability of analytical laboratories to detect and accurately quantify both the dissolved and total recoverable metal. Graphite furnace (flameless) atomic absorption AA techniques are usually needed. Furthermore, great care is needed to prevent external contamination of samples. The EPA- and USGS-recommended sample handling methods, commonly used, may produce inaccurate results when judged against newer techniques that emphasize highly purified reagents, Teflon and polyethylene labware, and clean laboratory environments [7, 13].

The high degree of imprecision of metals measurements tends to result in overstatement of the true variability of the dissolved-total ratio. As a result, unless a mean or median observed ratio is used, it may be necessary to compensate for the effect of measurement imprecision (by subtracting out the measurement imprecision variance).

In order to provide some sense of the general magnitude of typically observed dissolved-total metals ratios, data from several sources have been compiled in Table B-1. The ambient data underlying the tabulated values are considered to be reasonably reliable.

Using Environmentally Conservative Default Values

This option is best applied as the first tier of a tiered approach, where the second tier involves site-specific measurements. In this type of framework, the default (first-tier) percentage dissolved might be set at a reasonable worst-case value.

One possible worst-case assumption is that 100 percent of the effluent total recoverable metal will become dissolved in the receiving water. Such an assumption may be particularly appropriate for a metal, such as mercury, for which there are substantial uncertainties regarding long-term processes convert-

Table B-1.—Observed average fractions of dissolved metals in ambient waters.

METAL	FRESH WATER EAST COAST [7]	SALT WATER NY-NJ HARBOR AREA [13]		FRESH AND SALT WATER STORET ^a
		NEAR SURFACE	NEAR BOTTOM	
Aluminum				0.07 ^e
Cadmium	0.40	0.81 ^b	0.56 ^c	
Copper	0.62	0.50 ^c	0.23 ^d	0.4 ^f
Lead	0.10	0.08 ^c	0.03 ^d	
Nickel		0.73 ^c	0.41 ^d	0.6
Silver		0.11 ^c	0.08 ^c	
Zinc	0.20	0.60 ^d	0.29 ^d	

^aFor STORET data, means were estimated from cumulative distributions of concentrations, 1984-1990, in ambient streams, rivers, canals, lakes, reservoirs, and estuaries, for samples in which both dissolved and total recoverable metal were analyzed. The fraction dissolved for STORET data for cadmium, lead, silver, and zinc are not tabulated because most of these data are believed to be seriously compromised by external contamination of samples.

^bDissolved and total recoverable concentrations well correlated.

^cDissolved and total recoverable concentrations somewhat correlated.

^dDissolved and total recoverable concentrations not correlated.

^eFor any particular measurement of aluminum, the method of filtration may strongly affect the result.

^fFor much of the STORET copper data, external contamination of samples is likely to somewhat affect the absolute values of the measured concentrations, and may somewhat affect the dissolved-total ratio.

ing inorganic (including particulate) mercury into bioaccumulative methyl mercury. Where the background metal concentration is either negligible or entirely dissolved, and where the dissolved criterion is less than the corresponding total recoverable criterion, the assumption that all effluent total recoverable metal will become dissolved yields more restrictive limits than simply implementing a total recoverable criterion.

Other environmentally conservative default values may also be developed based on available information. Such values may differ in different parts of the country, due to variations in water quality characteristics.

Using a Geochemical Model

The equilibrium metal speciation model MINTEQ may offer assistance in understanding or predicting the fraction dissolved [14]. Using MINTEQ without obtaining site-specific input data may not be feasible, however. As the effort in obtaining the appropriate input data would likely be equivalent to simply measuring the site-specific fraction dissolved, the model may be more useful for providing insight into the controlling factors and predicting the effects of different environmental conditions. MINTEQ may be particularly useful for predicting whether the dissolved concentration will respond to reductions in the total concentration or whether it is controlled by factors such as solubility.