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UNITED STATES ENVIRONMENTAL PROTECTION AGENCY
WASHINGTON, D.C. 20460

OCT 15 1993

OFFICE OF WATER

Dear Environmental Advocate:

On October 1, 1993, I signed a memorandum regarding the Office of Water's Policy and Technical Guidance on Interpretation and Implementation of Aquatic Life Metals Criteria. This memorandum covers a number of areas including the expression of aquatic life criteria, total maximum daily loads, National Pollution Discharge Elimination System permits and enforcement, effluent monitoring, and ambient monitoring. The policy and guidance in this document considers comments received from the U.S. Environmental Protection Agency (EPA) Regional Offices, recommendations made to EPA by the participants in a meeting held in January 1993 in Annapolis, Maryland, and public comments in the June 8, 1993, Federal Register notice requesting general public comments on the Annapolis meeting recommendations. As stated in the enclosed memorandum, we will continue to issue guidance as more information becomes available.

Sincerely yours,

Martha G. Prothro
Acting Assistant Administrator

Enclosure

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UNITED STATES ENVIRONMENTAL PROTECTION AGENCY
WASHINGTON, D.C. 20460

OCT 1 1993

OFFICE OF WATER

MEMORANDUM

SUBJECT: Office of Water Policy and Technical Guidance on Interpretation and Implementation of Aquatic Life Metals Criteria

FROM: Martha G. Prothro
Acting Assistant Administrator for Water

TO: Water Management Division Directors
Environmental Services Division Directors
Regions I-X

Introduction

The implementation of metals criteria is complex due to the site-specific nature of metals toxicity. We have undertaken a number of activities to develop guidance in this area, notably the Interim Metals Guidance, published May 1992, and a public meeting of experts held in Annapolis, MD, in January 1993. This memorandum transmits Office of Water (OW) policy and guidance on the interpretation and implementation of aquatic life criteria for the management of metals and supplements my April 1, 1993, memorandum on the same subject. The issue covers a number of areas including the expression of aquatic life criteria; total maximum daily loads (TMDLs), permits, effluent monitoring, and compliance; and ambient monitoring. The memorandum covers each in turn. Attached to this policy memorandum are three guidance documents with additional technical details. They are: Guidance Document on Expression of Aquatic Life Criteria as Dissolved Criteria (Attachment #2), Guidance Document on Dynamic Modeling and Translators (Attachment #3), and Guidance Document on Monitoring (Attachment #4). These will be supplemented as additional data become available. (See the schedule in Attachment #1.)

Since metals toxicity is significantly affected by site-specific factors, it presents a number of programmatic challenges. Factors that must be considered in the management of metals in the aquatic environment include: toxicity specific to effluent chemistry; toxicity specific to ambient water chemistry; different patterns of toxicity for different metals; evolution of the state of the science of metals toxicity, fate, and transport; resource limitations for monitoring, analysis, implementation, and research functions; concerns regarding some of the analytical data currently on record due to possible sampling and analytical contamination; and lack of standardized protocols for clean and ultraclean metals analysis. The States have the key role in the risk management process of balancing these factors in the management of water programs. The site-specific nature of this issue could be perceived as requiring a permit-by-permit approach to implementation. However, we believe

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that this guidance can be effectively implemented on a broader level, across any waters with roughly the same physical and chemical characteristics, and recommend that we work with the States with that perspective in mind.

Expression of Aquatic Life Criteria

o Dissolved vs. Total Recoverable Metal

A major issue is whether, and how, to use dissolved metal concentrations ("dissolved metal") or total recoverable metal concentrations ("total recoverable metal") in setting State water quality standards. In the past, States have used both approaches when applying the same Environmental Protection Agency (EPA) criteria numbers. Some older criteria documents may have facilitated these different approaches to interpretation of the criteria because the documents were somewhat equivocal with regards to analytical methods. The May 1992 interim guidance continued the policy that either approach was acceptable.

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. This conclusion regarding metals bioavailability is supported by a majority of the scientific community within and outside the Agency. One reason is that a primary mechanism for water column toxicity is adsorption at the gill surface which requires metals to be in the dissolved form.

The position that the dissolved metals approach is more accurate has been questioned because it neglects the possible toxicity of particulate metal. It is true that some studies have indicated that particulate metals appear to contribute to the toxicity of metals, perhaps because of factors such as desorption of metals at the gill surface, but these same studies indicate the toxicity of particulate metal is substantially less than that of dissolved metal.

Furthermore, any error incurred from excluding the contribution of particulate metal will generally be compensated by other factors which make criteria conservative. For example, metals in toxicity tests are added as simple salts to relatively clean water. Due to the likely presence of a significant concentration of metals binding agents in many discharges and ambient waters, metals in toxicity tests would generally be expected to be more bioavailabile than metals in discharges or in ambient waters.

If total recoverable metal is used for the purpose of water quality standards, compounding of factors due to the lower bioavailability of particulate metal and lower bioavailability of metals as they are discharged may result in a conservative water quality standard. The use of dissolved metal in water quality standards gives a more accurate result. However, the majority of the participants at the Annapolis meeting felt that total recoverable measurements in ambient water had some value, and that exceedences of criteria on a total recoverable basis were an indication that metal loadings could be a stress to the ecosystem, particularly in locations other than the water column.

The reasons for the potential consideration of total recoverable measurements include risk management considerations not covered by evaluation of water column toxicity. The ambient water quality criteria are neither designed nor intended to protect sediments, or to prevent effects due to food webs containing sediment dwelling organisms. A risk manager, however, may consider sediments and food chain effects and may decide to take a conservative approach for metals, considering that metals are very persistent chemicals. This conservative approach could include the use of total recoverable metal in water quality standards. However, since consideration of sediment impacts is not incorporated into the criteria methodology, the degree of conservatism inherent in the total recoverable approach is unknown. The uncertainty of metal impacts in sediments stem from the lack of sediment criteria and an imprecise understanding of the fate and transport of metals. EPA will continue to pursue research and other activities to close these knowledge gaps.

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. (See the paragraph below and the attached guidance for technical details on developing dissolved criteria.) EPA will also approve a State risk management decision to adopt standards based on total recoverable metal, if those standards are otherwise approvable as a matter of law.

o Dissolved Criteria

In the toxicity tests used to develop EPA metals criteria for aquatic life, some fraction of the metal is dissolved while some fraction is bound to particulate matter. The present criteria were developed using total recoverable metal measurements or measures expected to give equivalent results in toxicity tests, and are articulated as total recoverable. Therefore, in order to express the EPA criteria as dissolved, a total recoverable to dissolved correction factor must be used. Attachment #2 provides guidance for calculating EPA dissolved criteria from the published total recoverable criteria. The data expressed as percentage metal dissolved are presented as recommended values and ranges. However, the choice within ranges is a State risk management decision. We have recently supplemented the data for copper and are proceeding to further supplement the data for copper and other metals. As testing is completed, we will make this information available and this is expected to reduce the magnitude of the ranges for some of the conversion factors provided. We also strongly encourage the application of dissolved criteria across a watershed or waterbody, as technically sound and the best use of resources.

o Site-Specific Criteria Modifications

While the above methods will correct some site-specific factors affecting metals toxicity, further refinements are possible. EPA has issued guidance (Water Quality Standards Handbook, 1983; Guidelines for Deriving Numerical Aquatic Site-Specific Water Quality Criteria by Modifying National Criteria, EPA-600/3-H4-099, October 1984) for three site-specific criteria development methodologies: recalculation procedure, indicator species procedure (also known as the water-effect ratio (WER)) and resident species procedure. Only the first two of these have been widely used.

In the National Toxics Rule (57 FR 60848, December 22, 1992), EPA identified the WER as an optional method for site-specific criteria development for certain metals. EPA committed in the NTR preamble to provide guidance on determining the WER. A draft of this guidance has been circulated to the States and Regions for review and comment. 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 will issue the guidance as "interim." EPA will accept WERs developed using this guidance, as well as by using other scientifically defensible protocols. OW expects the interim WER guidance will be issued in the next two months.

Total Maximum Daily Loads (TMDLs) and National Pollutant Discharge Elimination System (NPDES) Permits

o Dynamic Water Quality Modeling

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 for those criteria protecting aquatic life. These models provide another way to incorporate site-specific data. The 1991 Technical Support Document for Water Quality-based Toxics Control (TSD) (EPA/505/2-90-001) describes dynamic, as well as static (steady-state) models. 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 exceedence 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.

Dynamic models have received increased attention over the last few years as a result of the widespread belief that steady-state modeling is over-conservative due to environmentally conservative dilution assumptions. This belief has led to the misconception that dynamic models will always lead to less stringent regulatory controls (e.g., NPDES effluent limits) than steady-state models, which is not true in every application of dynamic models. EPA considers dynamic models to be a more accurate approach to implementing water quality criteria and continues to recommend their use. Dynamic modeling does require commitment of resources to develop appropriate data. (See Attachment #3 and the TSD for details on the use of dynamic models.)

o Dissolved-Total Metal Translators

Expressing water quality criteria as the dissolved form of a metal poses a need to be able to translate from dissolved metal to total recoverable metal for TMDLs and NPDES permits. 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.

EPA's NPDES regulations require that limits of metals in permits be stated as total recoverable in most cases (see 40 CFR §122.45(c)) except when an effluent guideline specifies the limitation in another form of the metal, the approved analytical methods measure only dissolved metal, or the permit writer expresses a metals limit in another form (e.g., dissolved, valent, or total) when required to carry out provisions of the Clean Water Act. This is because the chemical conditions in ambient waters frequently differ substantially from those in the effluent, and there is no assurance that effluent particulate metal would not dissolve after discharge. The NPDES rule does not require that State water quality standards be expressed as total recoverable; rather, the rule requires permit writers to translate between different metal forms in the calculation of the permit limit so that a total recoverable limit can be established. Both the TMDL and NPDES uses of water quality criteria require the ability to translate between dissolved metal and total recoverable metal. Attachment #3 provides methods for this translation.

Guidance on Monitoring

o Use of Clean Sampling and Analytical Techniques

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 (including effluent variability), assess permit compliance, and conduct research. The quality of trace level metal data, especially below 1 ppb, may be compromised due to contamination of samples during collection, preparation, storage, and analysis. Depending on the level of metal present, the use of "clean" and "ultraclean" techniques for sampling and analysis may be critical to accurate data for implementation of aquatic life criteria for metals.

The magnitude of the contamination problem increases as the ambient and effluent metal concentration decreases and, therefore, problems are more likely in ambient measurements. "Clean" techniques refer to those requirements (or practices for sample collection and handling) necessary to produce reliable analytical data in the part per billion (ppb) range. "Ultraclean" techniques refer to those requirements or practices necessary to produce reliable analytical data in the part per trillion (ppt) range. Because typical concentrations of metals in surface waters and effluents vary from one metal to another, the effect of contamination on the quality of metals monitoring data varies appreciably.

We plan to develop protocols on the use of clean and ultra-clean techniques and are coordinating with the United States Geological Survey (USGS) on this project, because USGS has been doing work on these techniques for some time, especially the sampling procedures. We anticipate that our draft protocols for clean techniques will be available in late calendar year 1993. The development of comparable protocols for ultra-clean techniques is underway and will be available in 1995. In developing these protocols, we will consider the costs of these techniques and will give guidance as to the situations where their use is necessary. Appendix B to the WER guidance document provides some general guidance on the use of

clean analytical techniques. (See Attachment #4.) We recommend that this guidance be used by States and Regions as an interim step, while the clean and ultra-clean protocols are being developed.

o Use of Historical Data

The concerns about metals sampling and analysis discussed above raise corresponding concerns about the validity of historical data. Data on effluent and ambient metal concentrations are collected by a variety of organizations including Federal agencies (e.g., EPA, USGS), State pollution control agencies and health departments, local government agencies, municipalities, industrial dischargers, researchers, and others. The data are collected for a variety of purposes as discussed above.

Concern about the reliability of the sample collection and analysis procedures is greatest where they have been used to monitor very low level metal concentrations. Specifically, studies have shown data sets with contamination problems during sample collection and laboratory analysis, that have resulted in inaccurate measurements. For example, in developing a TMDL for New York Harbor, some historical ambient data showed extensive metals problems in the harbor, while other historical ambient data showed only limited metals problems. Careful resampling and analysis in 1992/1993 showed the latter view was correct. The key to producing accurate data is appropriate quality assurance (QA) and quality control (QC) procedures. 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.

With respect to effluent monitoring reported by an NPDES permittee, the permittee is responsible for collecting and reporting quality data on a Discharge Monitoring Report (DMR). Permitting authorities should continue to consider the information reported to be true, accurate, and complete as certified by the permittee. Where the permittee becomes aware of new information specific to the effluent discharge that questions the quality of previously submitted DMR data, the permittee must promptly submit that information to the permitting authority. The permitting authority will consider all information submitted by the permittee in determining appropriate enforcement responses to monitoring/reporting and effluent violations. (See Attachment #4 for additional details.)

Summary

The management of metals in the aquatic environment is complex. The science supporting our technical and regulatory programs is continuing to evolve, here as in all areas. The policy and guidance outlined above represent the position of OW and should be incorporated into ongoing program operations. We do not expect that ongoing operations would be delayed or deferred because of this guidance.

If you have questions concerning this guidance, please contact Jim Hanlon, Acting Director, Office of Science and Technology, at 202-260-5400. If you have questions on specific details of the guidance, please contact the appropriate OW Branch Chief. The Branch Chiefs responsible for the various areas of the water quality program are: Bob April (202-260-6322, water quality criteria), Elizabeth Fellows (202-260-7046, monitoring and data issues), Russ Kinerson (202-260-1330, modeling and translators), Don Brady (202-260-7074, Total Maximum Daily Loads), Sheila Frace (202-260-9537, permits), Dave Sabock (202-260-1315, water quality standards), Bill Telliard (202-260-7134, analytical methods) and Dave Lyons (202-260-8310, enforcement).

Attachments

ATTACHMENT #1

TECHNICAL GUIDANCE FOR METALS

Schedule of Upcoming Guidance

Water-effect Ratio Guidance - September 1993

Draft "Clean" Analytical Methods - Spring 1994

Dissolved Criteria - currently being done; as testing is completed, we will release the updated percent dissolved data

Draft Sediment Criteria for Metals - 1994

Final Sediment Criteria for Metals - 1995

ATTACHMENT #2

GUIDANCE DOCUMENT ON DISSOLVED CRITERIA

Expression of Aquatic Life Criteria

October 1993

Percent Dissolved in Aquatic Toxicity Tests on Metals

The attached table contains all the data that were found concerning the percent of the total recoverable metal that was dissolved in aquatic toxicity tests. This table is intended to contain the available data that are relevant to the conversion of EPA's aquatic life criteria for metals from a total recoverable basis to a dissolved basis. (A factor of 1.0 is used to convert aquatic life criteria for metals that are expressed on the basis of the acid-soluble measurement to criteria expressed on the basis of the total recoverable measurement.) Reports by Grunwald (1992) and Brungs et al. (1992) provided references to many of the documents in which pertinent data were found. Each document was obtained and examined to determine whether it contained useful data.

"Dissolved" is defined as metal that passes through a 0.45-μm membrane filter. If otherwise acceptable, data that were obtained using 0.3-μm glass fiber filters and 0.1-μm membrane filters were used, and are identified in the table; these data did not seem to be outliers.

Data were used only if the metal was in a dissolved inorganic form when it was added to the dilution water. In addition, data were used only if they were generated in water that would have been acceptable for use as a dilution water in tests used in the derivation of water quality criteria for aquatic life; in particular, the pH had to be between 6.5 and 9.0, and the concentrations of total organic carbon (TOC) and total suspended solids (TSS) had to be below 5 mg/L. Thus most data generated using river water would not be used.

Some data were not used for other reasons. Data presented by Carroll et al. (1979) for cadmium were not used because 9 of the 36 values were above 150%. Data presented by Davies et al. (1976) for lead and Holcombe and Andrew (1978) for zinc were not used because "dissolved" was defined on the basis of polarography, rather than filtration.

Beyond this, the data were not reviewed for quality. Horowitz et al. (1992) reported that a number of aspects of the filtration procedure might affect the results. In addition, there might be concern about use of "clean techniques" and adequate QA/QC.

Each line in the table is intended to represent a separate piece of information. All of the data in the table were determined in fresh water, because no saltwater data were found. Data are becoming available for copper in salt water from the New York

Harbor study; based on the first set of tests, Hansen (1993) suggested that the average percent of the copper that is dissolved in sensitive saltwater tests is in the range of 76 to 82 percent.

A thorough investigation of the percent of total recoverable metal that is dissolved in toxicity tests might attempt to determine if the percentage is affected by test technique (static, renewal, flow-through), feeding (were the test animals fed and, if so, what food and how much), water quality characteristics (hardness, alkalinity, pH, salinity), test organisms (species, loading), etc.

The attached table also gives the freshwater criteria concentrations (CMC and CCC) because percentages for total recoverable concentrations much (e.g., more than a factor of 3) above or below the CMC and CCC are likely to be less relevant. When a criterion is expressed as a hardness equation, the range given extends from a hardness of 50 mg/L to a hardness of 200 mg/L.

The following is a summary of the available information for each metal:

Arsenic(III)

The data available indicate that the percent dissolved is about 100, but all the available data are for concentrations that are much higher than the CMC and CCC.

Cadmium

Schuytema et al. (1984) reported that "there were no real differences" between measurements of total and dissolved cadmium at concentrations of 10 to 80 ug/L (pH = 6.7 to 7.8, hardness = 25 mg/L, and alkalinity = 33 mg/L); total and dissolved concentrations were said to be "virtually equivalent".

The CMC and CCC are close together and only range from 0.66 to 8.6 ug/L. The only available data that are known to be in the range of the CMC and CCC were determined with a glass fiber filter. The percentages that are probably most relevant are 75, 92, 89, 78, and 80.

Chromium(III)

The percent dissolved decreased as the total recoverable concentration increased, even though the highest concentrations reduced the pH substantially. The percentages that are probably

most relevant to the CMC are 50-75, whereas the percentages that are probably most relevant to the CCC are 86 and 61.

Chromium(VI)

The data available indicate that the percent dissolved is about 100, but all the available data are for concentrations that are much higher than the CMC and CCC.

Copper

Howarth and Sprague (1978) reported that the total and dissolved concentrations of copper were "little different" except when the total copper concentration was above 500 ug/L at hardness = 360 mg/L and pH = 8 or 9. Chakoumakos et al. (1979) found that the percent dissolved depended more on alkalinity than on hardness, pH, or the total recoverable concentration of copper.

Chapman (1993) and Lazorchak (1987) both found that the addition of daphnid food affected the percent dissolved very little, even though Chapman used yeast-trout chow-alfalfa whereas Lazorchak used algae in most tests, but yeast-trout chow-alfalfa in some tests. Chapman (1993) found a low percent dissolved with and without food, whereas Lazorchak (1987) found a high percent dissolved with and without food. All of Lazorchak's values were in high hardness water; Chapman's one value in high hardness water was much higher than his other values.

Chapman (1993) and Lazorchak (1987) both compared the effect of food on the total recoverable LC50 with the effect of food on the dissolved LC50. Both authors found that food raised both the dissolved LC50 and the total recoverable LC50 in about the same proportion, indicating that food did not raise the total recoverable LC50 by sorbing metal onto food particles; possibly the food raised both LC50s by (a) decreasing the toxicity of dissolved metal, (b) forming nontoxic dissolved complexes with the metal, or (c) reducing uptake.

The CMC and CCC are close together and only range from 6.5 to 34 ug/L. The percentages that are probably most relevant are 74, 95, 95, 73, 57, 53, 52, 64, and 91.

Lead

The data presented in Spehar et al. (1978) were from Holcombe et al. (1976). Both Chapman (1993) and Holcombe et al. (1976) found that the percent dissolved increased as the total recoverable concentration increased. It would seem reasonable to expect more precipitate at higher total recoverable concentrations and

therefore a lower percent dissolved at higher concentrations. The increase in percent dissolved with increasing concentration might be due to a lowering of the pH as more metal is added if the stock solution was acidic.

The percentages that are probably most relevant to the CMC are 9, 18, 25, 10, 62, 68, 71, 75, 81, and 95, whereas the percentages that are probably most relevant to the CCC are 9 and 10.

Mercury

The only percentage that is available is 73, but it is for a concentration that is much higher than the CMC.

Nickel

The percentages that are probably most relevant to the CMC are 88, 93, 92, and 100, whereas the only percentage that is probably relevant to the CCC is 76.

Selenium

No data are available.

Silver

There is a CMC, but not a CCC. The percentage dissolved seems to be greatly reduced by the food used to feed daphnids, but not by the food used to feed fathead minnows. The percentages that are probably most relevant to the CMC are 41, 79, 79, 73, 91, 90, and 93.

Zinc

The CMC and CCC are close together and only range from 59 to 210 ug/L. The percentages that are probably most relevant are 31, 77, 77, 99, 94, 100, 103, and 96.

Recommended Values (%)[A] and Ranges of Measured Percent Dissolved Considered Most Relevant in Fresh Water

Metal	CMC		CCC	
	Recommended Value (%)	(Range %)	Recommended Value (%)	(Range %)
Arsenic(III)	95	100-104[B]	95	100-104[B]
Cadmium	85	75-92	85	75-92
Chromium(III)	85	50-75	85	61-86
Chromium(VI)	95	100[B]	95	100[B]
Copper	85	52-95	85	52-95
Lead	50	9-95	25	9-10
Mercury	85	73[B]	NA[E]	NA[E]
Nickel	85	88-100	85	76
Selenium	NA[E]	NA[C]	NA[E]	NA[C]
Silver	85	41-93	YY[D]	YY[D]
Zinc	85	31-103	85	31-103

[A] The recommended values are based on current knowledge and are subject to change as more data becomes available.

[B] All available data are for concentrations that are much higher than the CMC.

[C] NA = No data are available.

[D] YY = A CCC is not available, and therefore cannot be adjusted.

[E] NA = Bioaccumulative chemical and not appropriate to adjust to percent dissolved.

Concn.[A] (ug/L)	Percent Diss.[B]	n[C]	Species[D]	SRF[E]	Food	Hard.	Alk.	pH	Ref.
ARSENIC(III) (Freshwater: CCC = 190 ug/L; CMC = 360 ug/L)									
600-15000	104	5	?	?	?	48	41	7.6	Lima et al. 1984
12600	100	3	FM	F	No	44	43	7.4	Spehar and Fiandt 1986
CADMIUM (Freshwater: CCC = 0.66 to 2.0 ug/L; CMC = 1.8 to 8.6 ug/L)[F]									
0.16	41	?	DM	R	Yes	53	46	7.6	Chapman 1993
0.28	75	?	DM	R	Yes	103	83	7.9	Chapman 1993
0.4-4.0	92[G]	?	CS	F	No	21	19	7.1	Finlayson and Verrue 1982
13	89	3	FM	F	No	44	43	7.4	Spehar and Fiandt 1986
15-21	96	8	FM	S	No	42	31	7.5	Spehar and Carlson 1984
42	84	4	FM	S	No	45	41	7.4	Spehar and Carlson 1984
10	78	?	DM	S	No	51	38	7.5	Chapman 1993
35	77	?	DM	S	No	105	88	8.0	Chapman 1993
51	59	?	DM	S	No	209	167	8.4	Chapman 1993
6-80	80	8	?	S	No	47	44	7.5	Call et al. 1982
3-232	90[H]	5	?	F	?	46	42	7.4	Spehar et al. 1978
450-6400	70	5	FM	F	No	202	157	7.7	Pickering and Gast 1972

CHROMIUM(III) (Freshwater: CCC = 120 to 370 ug/L; CMC = 980 to 3100 ug/L)[F]

5-13	94	?	SG	F	?	25	24	7.3	Stevens and Chapman 1984
19-495	86	?	SG	F	?	25	24	7.2	Stevens and Chapman 1984
>1100	50-75	?	SG	F	No	25	24	7.0	Stevens and Chapman 1984
42	54	?	DM	R	Yes	206	166	8.2	Chapman 1993
114	61	?	DM	R	Yes	52	45	7.4	Chapman 1993
16840	26	?	DM	S	No	<51	9	6.3[I]	Chapman 1993
26267	32	?	DM	S	No	110	9	6.7	Chapman 1993
27416	27	?	DM	S	No	96	10	6.0[I]	Chapman 1993
58665	23	?	DM	S	No	190	25	6.2[I]	Chapman 1993

CHROMIUM(VI) (Freshwater: CCC = 11 ug/L; CMC = 16 ug/L)

>25,000	100	1	FM,GF	F	Yes	220	214	7.6	Adelman and Smith 1976
43,300	99.5	4	FM	F	No	44	43	7.4	Spehar and Fiandt 1986

COPPER (Freshwater: CCC = 6.5 to 21 ug/L; CMC = 9.2 to 34 ug/L)[F]

10-30	74	?	CT	F	No	27	20	7.0	Chakoumakos et al. 1979
40-200	78	?	CT	F	No	154	20	6.8	Chakoumakos et al. 1979
30-100	79	?	CT	F	No	74	23	7.6	Chakoumakos et al. 1979
100-200	82	?	CT	F	No	192	72	7.0	Chakoumakos et al. 1979
20-200	86	?	CT	F	No	31	78	8.3	Chakoumakos et al. 1979
40-300	87	?	CT	F	No	83	70	7.4	Chakoumakos et al. 1979
10-80	89	?	CT	F	No	25	169	8.5	Chakoumakos et al. 1979

300-1300	92	?	CT	F	No	195	160	7.0	Chakoumakos et al. 1979
100-400	94	?	CT	F	No	70	174	8.5	Chakoumakos et al. 1979
3-4[J]	125-167	2	CD	R	Yes	31	38	7.2	Carlson et al. 1986a,b
12-91[J]	79-84	3	CD	R	Yes	31	38	7.2	Carlson et al. 1986a,b
18-19	95	2	DA	S	No	52	55	7.7	Carlson et al. 1986b
20[J]	95	1	DA	R	No	31	38	7.2	Carlson et al. 1986b
50	96	2	FM	S	No	52	55	7.7	Carlson et al. 1986b
175[J]	91	2	FM	R	No	31	38	7.2	Carlson et al. 1986b
5-52	>82[K]	?	FM	F	Yes[L]	47	43	8.0	Lind et al. 1978
6-80	83[O]	?	CS	F	No	21	19	7.1	Finlayson and Verrue 1982
6.7	57	?	DM	S	No	49	37	7.7	Chapman 1993
35	43	?	DM	S	Yes	48	39	7.4	Chapman 1993
13	73	?	DM	R	Yes	211	169	8.1	Chapman 1993
16	57	?	DM	R	Yes	51	44	7.6	Chapman 1993
51	39	?	DM	R	Yes	104	83	7.8	Chapman 1993
32	53	?	DM	S	No	52	45	7.8	Chapman 1993
33	52	?	DM	S	No	105	79	7.9	Chapman 1993
39	64	?	DM	S	No	106	82	8.1	Chapman 1993
25-84	96	14	FM,GM	S	No	50	40	7.0	Hammermeister et al. 1983
17	91	6	DM	S	No	52	43	7.3	Hammermeister et al. 1983
120	88	14	SG	S	No	48	47	7.3	Hammermeister et al. 1983
15-90	74	19	?	S	No	48	47	7.7	Call et al. 1982
12-162	80[M]	?	BG	F	Yes[L]	45	43	7-8	Benoit 1975
28-58	85	6	DM	R	No	168	117	8.0	Lazorchak 1987
26-59	79	7	DM	R	Yes[M]	168	117	8.0	Lazorchak 1987
56,101	86	2	DM	R	Yes[N]	168	117	8.0	Lazorchak 1987

96	86	4	FM	F	No	44	43	7.4	Spehar and Fiandt 1986
160	94	1	FM	S	No	203	171	8.2	Geckler et al. 1976
230-3000	>69->79	?	CR	F	No	17	13	7.6	Rice and Harrison 1983

LEAD (Freshwater: CCC = 1.3 to 7.7 ug/L; CMC = 34 to 200 ug/L)[F]

17	9	?	DM	R	Yes	52	47	7.6	Chapman 1993
181	18	?	DM	R	Yes	102	86	7.8	Chapman 1993
193	25	?	DM	R	Yes	151	126	8.1	Chapman 1993
612	29	?	DM	S	No	50	--	---	Chapman 1993
952	33	?	DM	S	No	100	--	---	Chapman 1993
1907	~38	?	DM	S	No	150	--	---	Chapman 1993
7-29	10	?	EZ	R	No	22	--	---	JRB Associates 1983
34	62[H]	?	BT	F	Yes	44	43	7.2	Holcombe et al. 1976
58	68[H]	?	BT	F	Yes	44	43	7.2	Holcombe et al. 1976
119	71[H]	?	BT	F	Yes	44	43	7.2	Holcombe et al. 1976
235	75[H]	?	BT	F	Yes	44	43	7.2	Holcombe et al. 1976
474	81[H]	?	BT	F	Yes	44	43	7.2	Holcombe et al. 1976
4100	82[H]	?	BT	F	No	44	43	7.2	Holcombe et al. 1976
2100	79	7	FM	F	No	44	43	7.4	Spehar and Fiandt 1986
220-2700	96	14	FM,GM,DM	S	No	49	44	7.2	Hammermeister et al. 1983
580	95	14	SG	S	No	51	48	7.2	Hammermeister et al. 1983

MERCURY(II) (Freshwater: CMC = 2.4 ug/L)

172	73	1	FM	F	No	44	43	7.4	Spehar and Fiandt 1986

NICKEL (Freshwater: CCC = 88 to 280 ug/L; CMC = 790 to 2500 ug/L)[F]

21	81	?	DM	R	Yes	51	49	7.4	Chapman 1993
150	76	?	DM	R	Yes	107	87	7.8	Chapman 1993
578	87	?	DM	R	Yes	205	161	8.1	Chapman 1993
645	88	?	DM	S	No	54	43	7.7	Chapman 1993
1809	93	?	DM	S	No	51	44	7.7	Chapman 1993
1940	92	?	DM	S	No	104	84	8.2	Chapman 1993
2344	100	?	DM	S	No	100	84	7.9	Chapman 1993
4000	90	?	PK	R	No	21	--	---	JRB Associates 1983

SELENIUM (FRESHWATER: CCC = 5 ug/L; CMC = 20 ug/L)

No data are available.

SILVER (Freshwater: CMC = 1.2 to 13 ug/L; a CCC is not available)

0.19	74	?	DM	S	No	47	37	7.6	Chapman 1993
9.98	13	?	DM	S	Yes	47	37	7.5	Chapman 1993
4.0	41	?	DM	S	No	36	25	7.0	Nebeker et al. 1983
4.0	11	?	DM	S	Yes	36	25	7.0	Nebeker et al. 1983
3	79	?	FM	S	No	51	49	8.1	UWS 1993
2-54	79	?	FM	S	Yes[O]	49	49	7.9	UWS 1993
2-32	73	?	FM	S	No	50	49	8.1	UWS 1993
4-32	91	?	FM	S	No	48	49	8.1	UWS 1993
5-89	90	?	FM	S	No	120	49	8.2	UWS 1993
6-401	93	?	FM	S	No	249	49	8.1	UWS 1993

ZINC (Freshwater: CCC = 59 to 190 ug/L; CMC 65 to 210 ug/L)[F]

52	31	?	DM	R	Yes	211	169	8.2	Chapman 1993
62	77	?	DM	R	Yes	104	83	7.8	Chapman 1993
191	77	?	DM	R	Yes	52	47	7.5	Chapman 1993
356	74	?	DM	S	No	54	47	7.6	Chapman 1993
551	78	?	DM	S	No	105	85	8.1	Chapman 1993
741	76	?	DM	S	No	196	153	8.2	Chapman 1993
7[I]	71-129	2	CD	R	Yes	31	38	7.2	Carlson et al. 1986b
18-273[I]	81-107	2	CD	R	Yes	31	38	7.2	Carlson et al. 1986b
167[I]	99	2	CD	R	No	31	38	7.2	Carlson et al. 1986b
180	94	1	CD	S	No	52	55	7.7	Carlson et al. 1986b
188-393[I]	100	2	FM	R	No	31	38	7.2	Carlson et al. 1986b
551	100	1	FM	S	No	52	55	7.7	Carlson et al. 1986b
40-500	95[G]	?	CS	F	No	21	19	7.1	Finlayson and Verrue 1982
1940	100	?	AS	F	No	20	12	7.1	Sprague 1964
5520	83	?	AS	F	No	20	12	7.9	Sprague 1964
<4000	90	?	FM	F	No	204	162	7.7	Mount 1966
>4000	70	?	FM	F	No	204	162	7.7	Mount 1966
160-400	103	13	FM,GM,DM	S	No	52	43	7.5	Hammermeister et al. 1983
240	96	13	SG	S	No	49	46	7.2	Hammermeister et al. 1983

[A] Total recoverable concentration.

[B] Except as noted, a 0.45-μm membrane filter was used.

[C] Number of paired comparisons.

[D] The abbreviations used are:

AS = Atlantic salmon
BT = Brook trout
CD = *Ceriodaphnia dubia*
CR = Crayfish
CS = Chinook salmon
CT = Cutthroat trout
DA = Daphnids
DM = *Daphnia magna*
EZ = *Elassoma zonatum*
FM = Fathead minnow
GF = Goldfish
GM = Gammarid
PK = *Palaemonetes kadiakensis*
SG = *Salmo gairdneri*

[E] The abbreviations used are:

S = static
R = renewal
F = flow-through

[F] The two numbers are for hardnesses of 50 and 200 mg/L, respectively.

[G] A 0.3-μm *glass fiber* filter was used.

[H] A 0.10-μm membrane filter was used.

[I] The pH was below 6.5.

[J] The dilution water was a clean river water with TSS and TOC below 5 mg/L.

[K] Only limited information is available concerning this value.

[L] It is assumed that the solution that was filtered was from the test chambers that contained fish and food.

[M] The food was algae.

[N] The food was yeast-trout chow-alfalfa.

[O] The food was frozen adult brine shrimp.

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ATTACHMENT #3

GUIDANCE DOCUMENT
ON DYNAMIC MODELING AND TRANSLATORS
August 1993

Total Maximum Daily Loads (TMDLs) and Permits

o Dynamic Water Quality Modeling

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. Dynamic models make best use of the specified magnitude, duration, and frequency of water quality criteria and thereby provide a more accurate calculation of discharge impacts on ambient water quality. In contrast, steady-state modeling is based on various simplifying assumptions which makes it less complex and less accurate than dynamic modeling. Building on accepted practices in water resource engineering, ten years ago OW devised methods allowing the use of probability distributions in place of worst-case conditions. The description of these models and their advantages and disadvantages is found in the 1991 Technical Support Document for Water Quality-based Toxic Control (TSD).

Dynamic models have received increased attention in the last few years as a result of the perception that static modeling is over-conservative due to environmentally conservative dilution assumptions. This has led to the misconception that dynamic models will always justify less stringent regulatory controls (e.g. NPDES effluent limits) than static models. In effluent dominated waters where the upstream concentrations are relatively constant, however, a dynamic model will calculate a more stringent wasteload allocation than will a steady state model. The reason is that the critical low flow required by many State water quality standards in effluent dominated streams occurs more frequently than once every three years. When other environmental factors (e.g. upstream pollutant concentrations) do not vary appreciably, then the overall return frequency of the steady state model may be greater than once in three years. A dynamic modeling approach, on the other hand, would be more stringent, allowing only a once in three year return frequency. As a result, EPA considers dynamic models to be a more accurate rather than a less stringent approach to implementing water quality criteria.

The 1991 TSD provides recommendations on the use of steady state and dynamic water quality models. The reliability of any modeling technique greatly depends on the accuracy of the data used in the analysis. Therefore, the selection of a model also depends upon the data. EPA recommends that steady state wasteload allocation analyses generally be used where few or no whole effluent toxicity or specific chemical measurements are available, or where daily receiving water flow records are not available. Also, if staff resources are insufficient to use and defend the use of dynamic models, then steady state

models may be necessary. If adequate receiving water flow and effluent concentration data are available to estimate frequency distributions, EPA recommends that one of the dynamic wasteload allocation modeling techniques be used to derive wasteload allocations which will more exactly maintain water quality standards. The minimum data required for input into dynamic models include at least 30 years of river flow data and one year of effluent and ambient pollutant concentrations.

o Dissolved-Total Metal Translators

When water quality criteria are expressed as the dissolved form of a metal, there is a need to translate TMDLs and NPDES permits to and from the dissolved form of a metal to the total recoverable form. TMDLs for toxic metals must be able to calculate 1) the dissolved metal concentration in order to ascertain attainment of water quality standards and 2) the total recoverable metal concentration in order to achieve mass balance. In meeting these requirements, TMDLs consider metals to be conservative pollutants and quantified as total recoverable to preserve conservation of mass. The TMDL calculates the dissolved or ionic species of the metals based on factors such as total suspended solids (TSS) and ambient pH. (These assumptions ignore the complicating factors of metals interactions with other metals.) In addition, this approach assumes that ambient factors influencing metal partitioning remain constant with distance down the river. This assumption probably is valid under the low flow conditions typically used as design flows for permitting of metals (e.g., 7Q10, 4B3, etc) because erosion, resuspension, and wet weather loadings are unlikely to be significant and river chemistry is generally stable. In steady-state dilution modeling, metals releases may be assumed to remain fairly constant (concentrations exhibit low variability) with time.

EPA's NPDES regulations require that metals limits in permits be stated as total recoverable in most cases (see 40 CFR §122.45(c)). Exceptions occur when an effluent guideline specifies the limitation in another form of the metal or the approved analytical methods measure only the dissolved form. Also, the permit writer may express a metals limit in another form (e.g., dissolved, valent, or total) when required, in highly unusual cases, to carry out the provisions of the CWA.

The preamble to the September 1984 National Pollutant Discharge Elimination System Permit Regulations states that the total recoverable method measures dissolved metals plus that portion of solid metals that can easily dissolve under ambient conditions (see 49 Federal Register 38028, September 26, 1984). This method is intended to measure metals in the effluent that are or may easily become environmentally active, while not measuring metals that are expected to settle out and remain inert.

The preamble cites, as an example, effluent from an electroplating facility that adds lime and uses clarifiers. This effluent will be a combination of solids not removed by the clarifiers and residual dissolved metals. When the effluent from the clarifiers, usually with a

high pH level, mixes with receiving water having significantly lower pH level, these solids instantly dissolve. Measuring dissolved metals in the effluent, in this case, would underestimate the impact on the receiving water. Measuring with the total metals method, on the other hand, would measure metals that would be expected to disperse or settle out and remain inert or be covered over. Thus, measuring total recoverable metals in the effluent best approximates the amount of metal likely to produce water quality impacts.

However, the NPDES rule does not require in any way that State water quality standards be in the total recoverable form; rather, the rule requires permit writers to consider the translation between differing metal forms in the calculation of the permit limit so that a total recoverable limit can be established. Therefore, both the TMDL and NPDES uses of water quality criteria require the ability to translate from the dissolved form and the total recoverable form.

Many toxic substances, including metals, have a tendency to leave the dissolved phase and attach to suspended solids. The partitioning of toxics between solid and dissolved phases can be determined as a function of a pollutant-specific partition coefficient and the concentration of solids. This function is expressed by a linear partitioning equation:

$$C = \frac{C_{Tr}}{1 + K_d \cdot TSS \cdot 10^{-6}}$$

where,

C = dissolved phase metal concentration,
C_{Tr} = total metal concentration,
TSS = total suspended solids concentration, and
K_d = partition coefficient.

A key assumption of the linear partitioning equation is that the sorption reaction reaches dynamic equilibrium at the point of application of the criteria; that is, after allowing for initial mixing the partitioning of the pollutant between the adsorbed and dissolved forms can be used at any location to predict the fraction of pollutant in each respective phase.

Successful application of the linear partitioning equation relies on the selection of the partition coefficient. The use of a partition coefficient to represent the degree to which toxics adsorb to solids is most readily applied to organic pollutants; partition coefficients for metals are more difficult to define. Metals typically exhibit more complex speciation and complexation reactions than organics and the degree of partitioning can vary greatly depending upon site-specific water chemistry. Estimated partition coefficients can be determined for a number of metals, but waterbody or site-specific observations of dissolved and adsorbed concentrations are preferred.

EPA suggests three approaches for instances where a water quality criterion for a metal is expressed in the dissolved form in a State's water quality standards:

1. Using clean analytical techniques and field sampling procedures with appropriate QA/QC, collect receiving water samples and determine site specific values of K_d for each metal. Use these K_d values to "translate" between total recoverable and dissolved metals in receiving water. This approach is more difficult to apply because it relies upon the availability of good quality measurements of ambient metal concentrations. This approach provides an accurate assessment of the dissolved metal fraction providing sufficient samples are collected. EPA's initial recommendation is that at least four pairs of total recoverable and dissolved ambient metal measurements be made during low flow conditions or 20 pairs over all flow conditions. EPA suggests that the average of data collected during low flow or the 95th percentile highest dissolved fraction for all flows be used. The low flow average provides a representative picture of conditions during the rare low flow events. The 95th percentile highest dissolved fraction for all flows provides a critical condition approach analogous to the approach used to identify low flows and other critical environmental conditions.

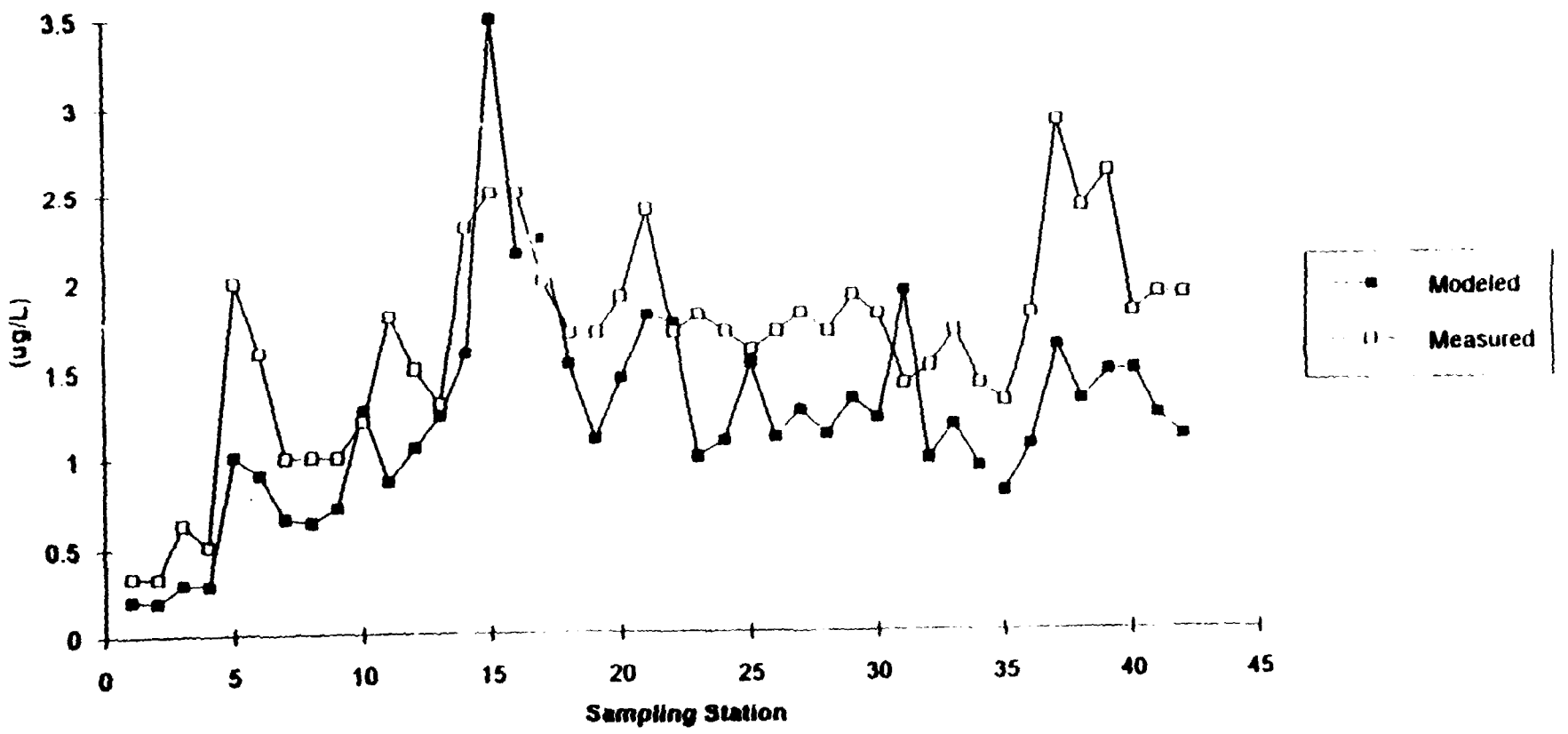
2. Calculate the total recoverable concentration for the purpose of setting the permit limit. Use a value of 1 unless the permittee has collected data (see #1 above) to show that a different ratio should be used. The value of 1 is conservative and will not err on the side of violating standards. This approach is very simple to apply because it places the entire burden of data collection and analysis solely upon permitted facilities. In terms of technical merit, it has the same characteristics of the previous approach. However, permitting authorities may be faced with difficulties in negotiating with facilities on the amount of data necessary to determine the ratio and the necessary quality control methods to assure that the ambient data are reliable.

3. Use the historical data on total suspended solids (TSS) in receiving waterbodies at appropriate design flows and K_d values presented in the Technical Guidance Manual for Performing Waste Load Allocations. Book II. Streams and Rivers. EPA-440/4-84-020 (1984) to "translate" between (total recoverable) permits limits and dissolved metals in receiving water. This approach is fairly simple to apply. However, these K_d values are suspect due to possible quality assurance problems with the data used to develop the values. EPA's initial analysis of this approach and these values in one site indicates that these K_d values generally over-estimate the dissolved fraction of metals in ambient waters (see Figures following). Therefore, although this approach may not provide an accurate estimate of the dissolved fraction, the bias in the estimate is likely to be a conservative one.

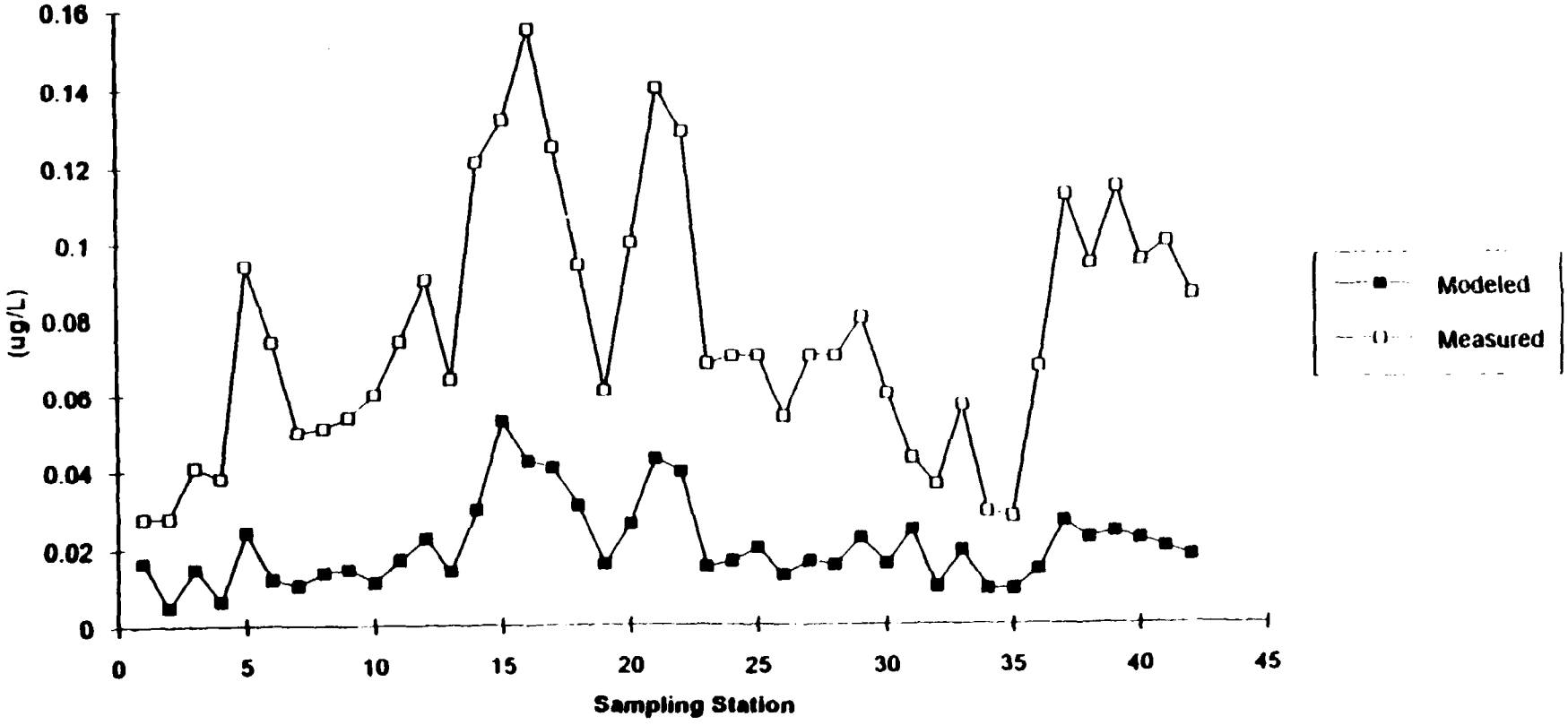
EPA suggests that regulatory authorities use approaches #1 and #2 where States express their water quality standards in the dissolved form. In those States where the standards are in the total recoverable or acid soluble form, EPA recommends that no

translation be used until the time that the State changes the standards to the dissolved form. Approach #3 may be used as an interim measure until the data are collected to implement approach #1.

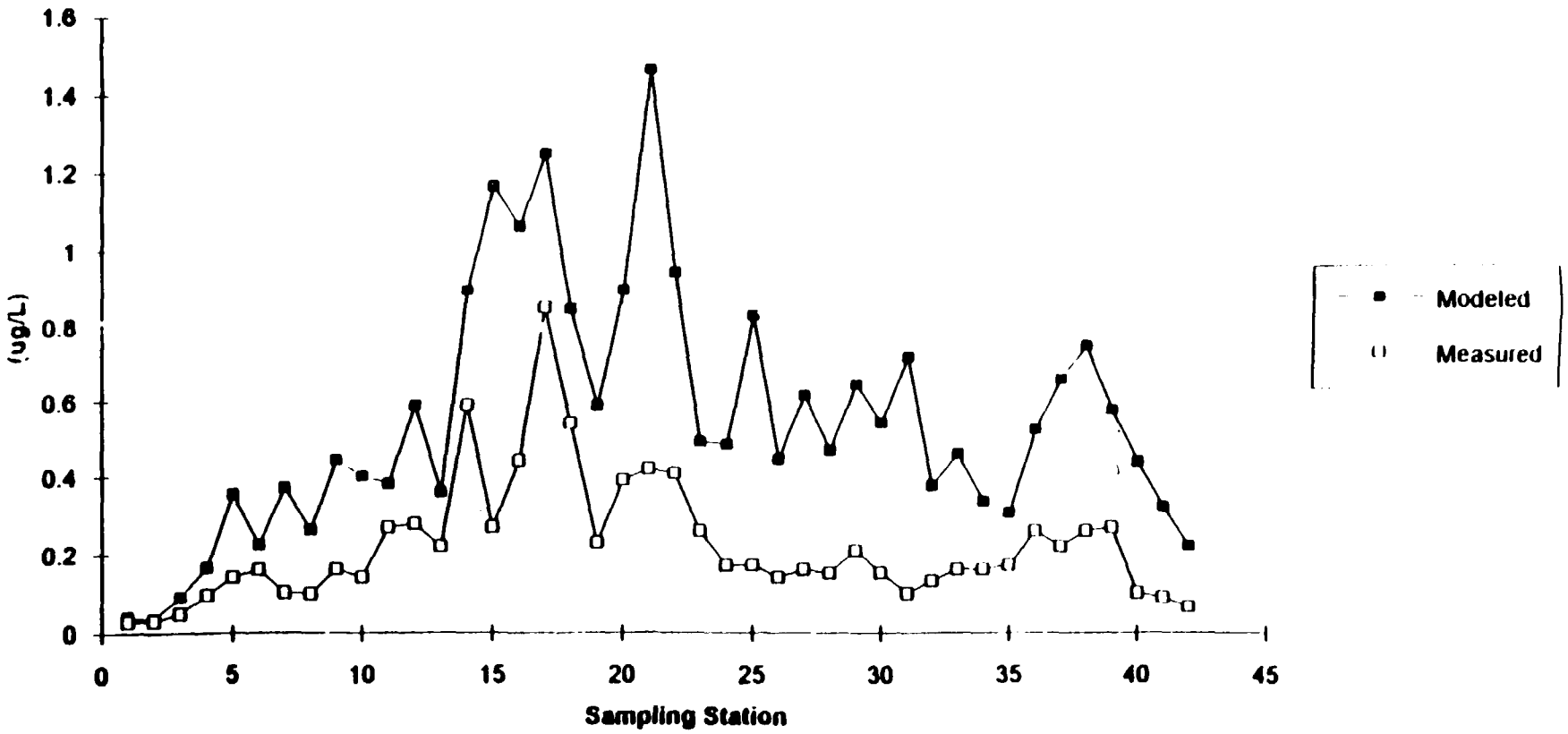
Measured vs. Modeled Dissolved Copper Concentrations

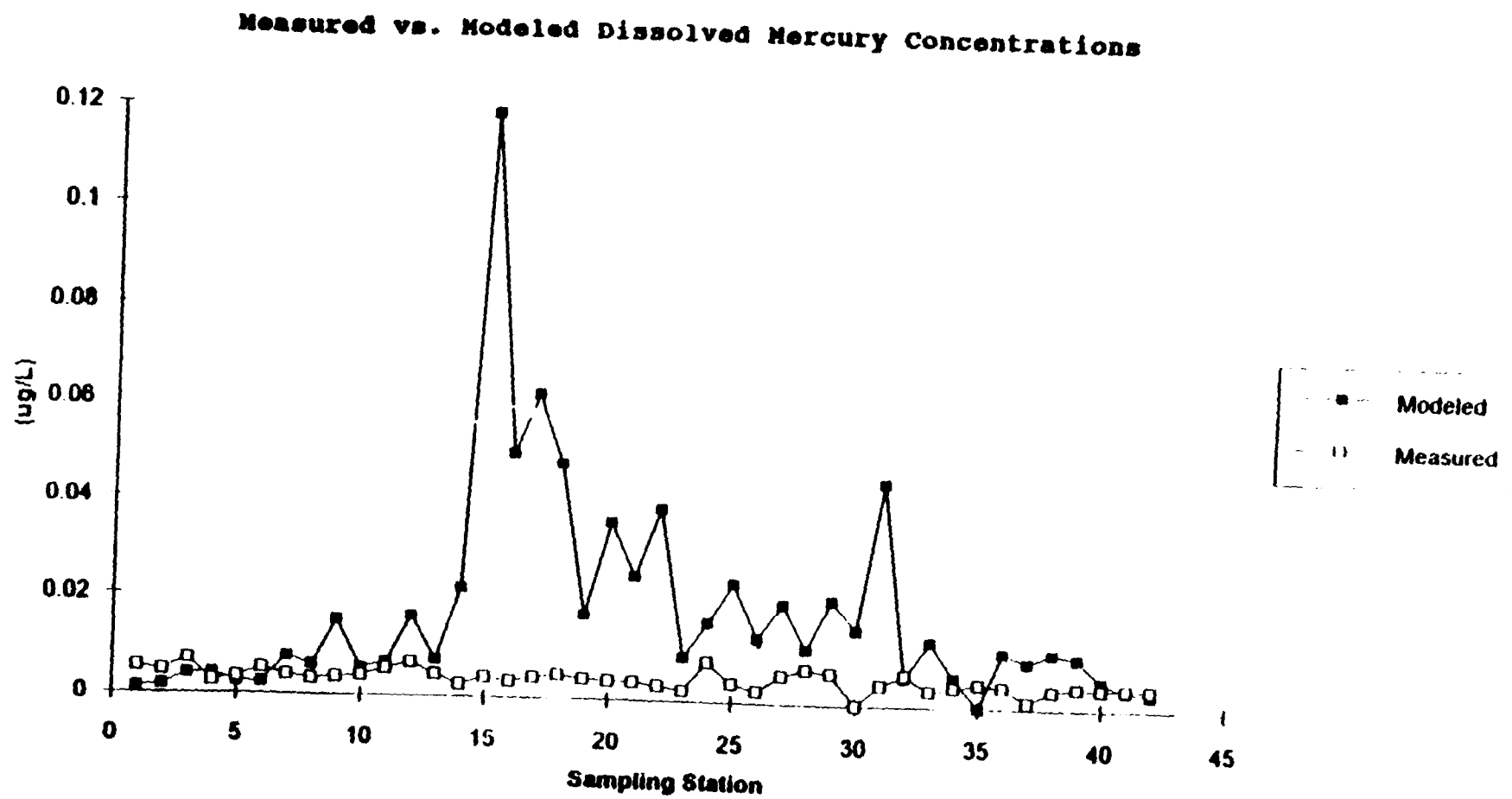


Measured vs. Modeled Dissolved Cadmium Concentrations

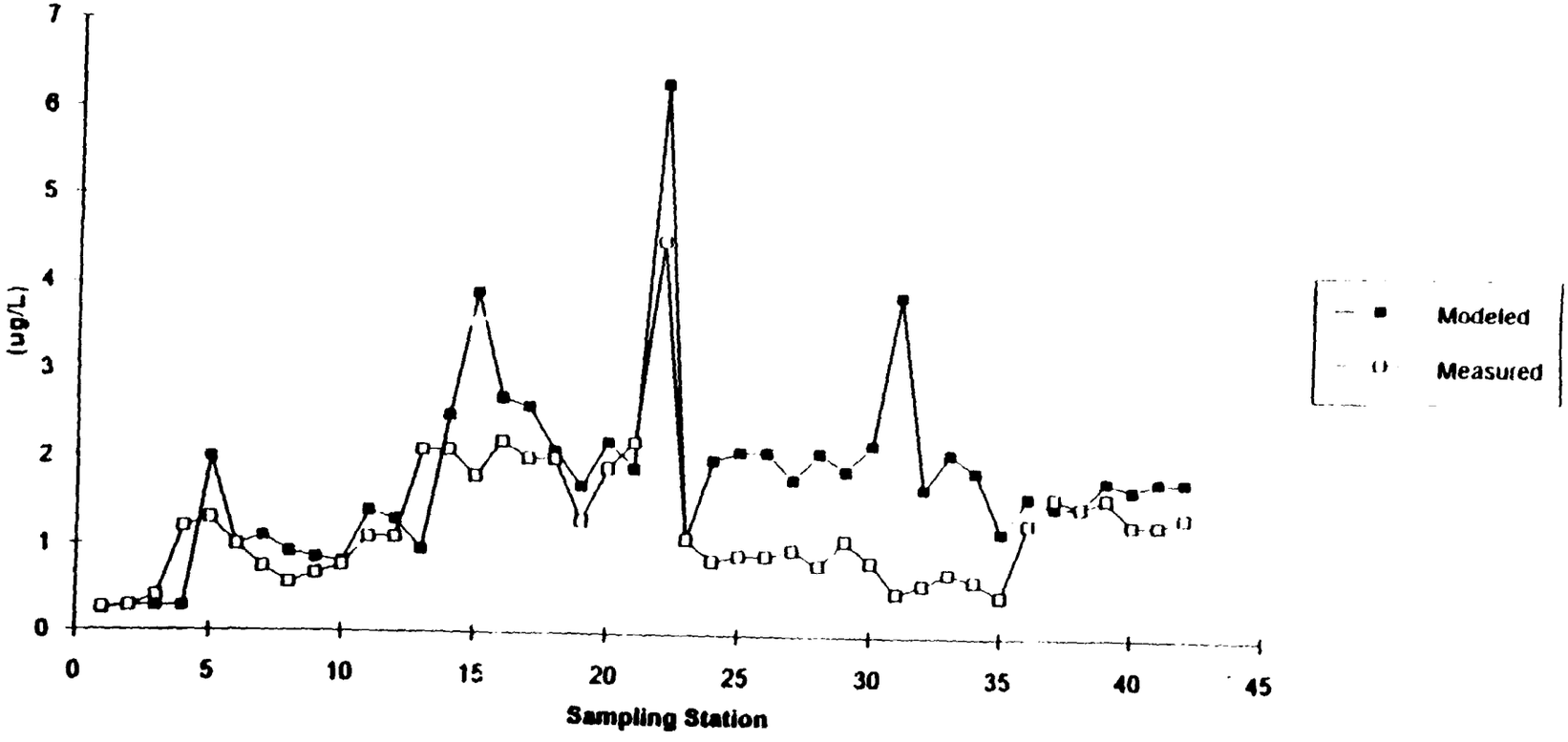


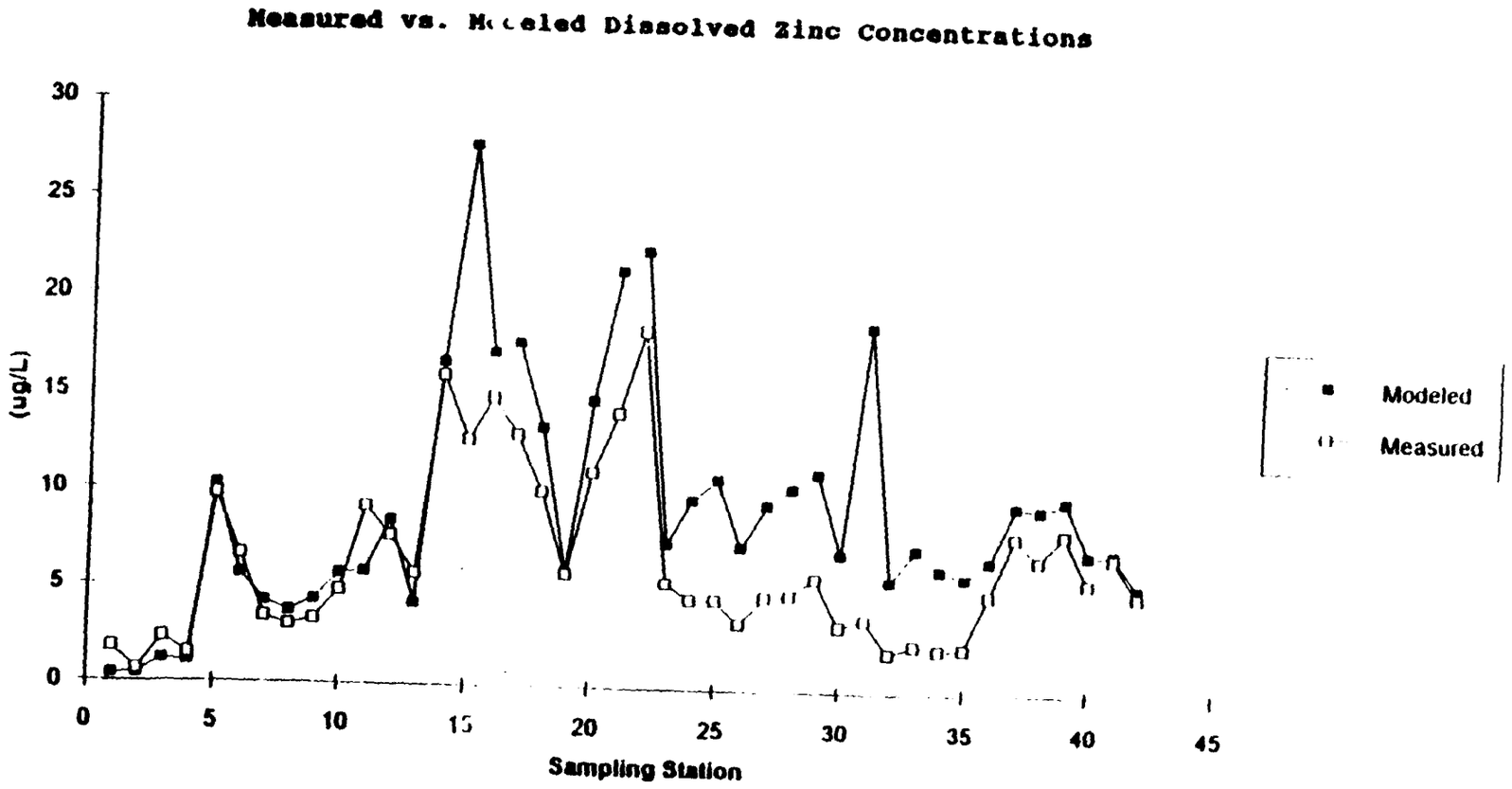
Measured vs. Modeled Dissolved Lead Concentrations



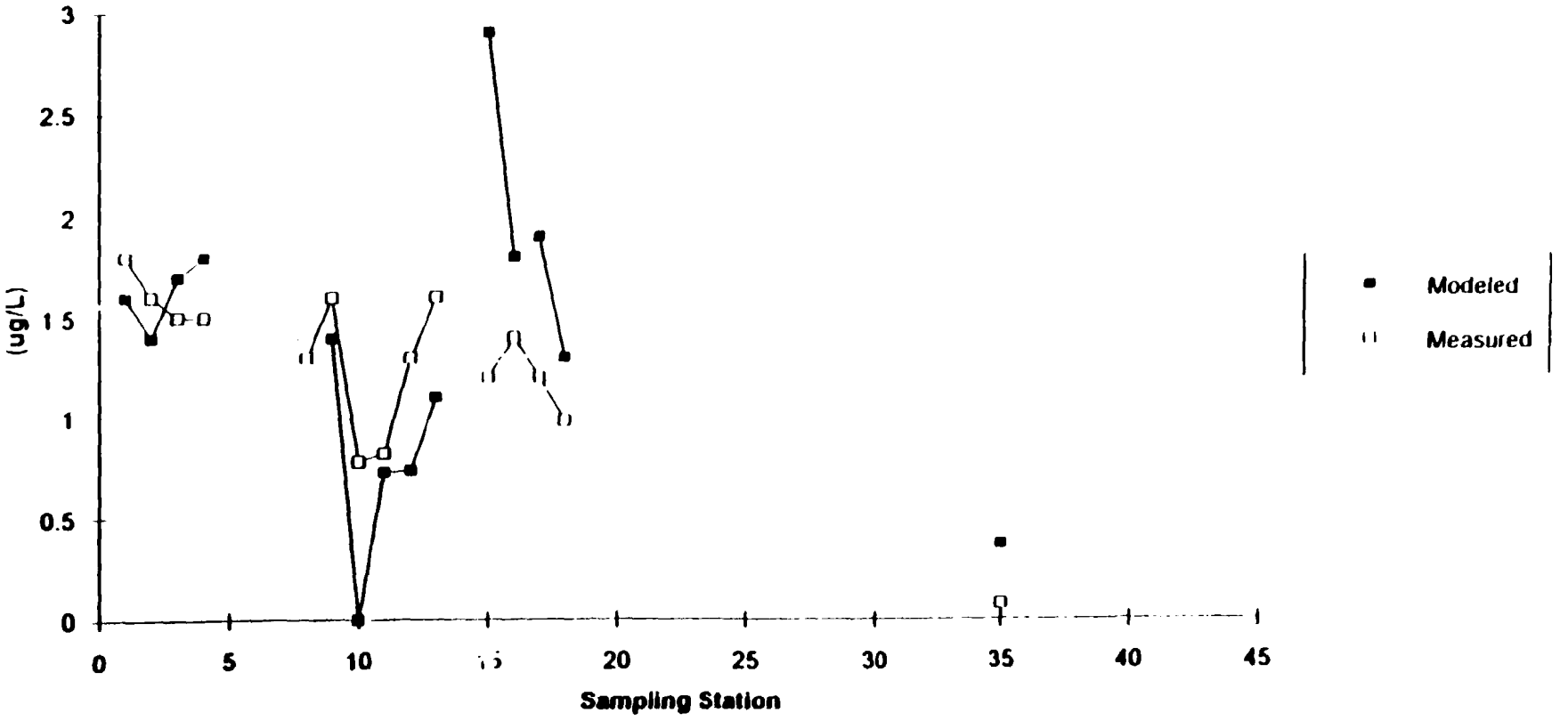

Measured vs. Modeled Dissolved Mercury Concentrations
0.12
0.1
0.08
0.06
0.04
0.02
0
(ug/L)
0
5
10
15
20
25
30
35
40
45
Sampling Station
Modeled
Measured

Measured vs. Modeled Dissolved Nickel Concentrations




Measured vs. Modeled Dissolved Zinc Concentrations
30
25
20
15
10
5
0
(ug/L)
0
5
10
15
20
25
30
35
40
45
Sampling Station
Modeled
Measured

Measured vs. Modeled Dissolved Arsenic Concentrations



ATTACHMENT #4

GUIDANCE DOCUMENT
ON CLEAN ANALYTICAL TECHNIQUES AND MONITORING
October 1993

Guidance on Monitoring

o Use of Clean Sampling and Analytical Techniques

Appendix B to the WER guidance document (attached) provides some general guidance on the use of clean techniques. The Office of Water recommends that this guidance be used by States and Regions as an interim step while the Office of Water prepares more detailed guidance.

o Use of Historical DMR Data

With respect to effluent or ambient monitoring data reported by an NPDES permittee on a Discharge Monitoring Report (DMR), the certification requirements place the burden on the permittee for collecting and reporting quality data. The certification regulation at 40 CFR 122.22(d) requires permittees, when submitting information, to state: "I certify under penalty of law that this document and all attachments were prepared under my direction or supervision in accordance with a system designed to assure that qualified personnel properly gather and evaluate the information submitted. Based on my inquiry of the person or persons who manage the system, or those persons directly responsible for gathering the information, the information submitted is, to the best of my knowledge and belief, true, accurate, and complete. I am aware that there are significant penalties for submitting false information, including the possibility of fine and imprisonment for knowing violations."

Permitting authorities should continue to consider the information reported in DMRs to be true, accurate, and complete as certified by the permittee. Under 40 CFR 122.41(l)(8), however, as soon as the permittee becomes aware of new information specific to the effluent discharge that calls into question the accuracy of the DMR data, the permittee must submit such information to the permitting authority. Examples of such information include a new finding that the reagents used in the laboratory analysis are contaminated with trace levels of metals, or a new study that the sampling equipment imparts trace metal contamination. This information must be specific to the discharge and based on actual measurements rather than extrapolations from reports from other facilities. Where a permittee submits information

In addition to submitting the information described above, the permittee also must develop procedures to assure the collection and analysis of quality data that are true, accurate, and complete. For example, the permittee may submit a revised quality assurance plan that describes the specific procedures to be undertaken to reduce or eliminate trace metal contamination.

Appendix B. Guidance Concerning the Use of "Clean Techniques" and QA/QC in the Measurement of Trace Metals

Recent information (Shiller and Boyle 1987; Windom et al. 1991) has raised questions concerning the quality of reported concentrations of trace metals in both fresh and salt (estuarine and marine) surface waters. A lack of awareness of true ambient concentrations of metals in saltwater and freshwater systems can be both a cause and a result of the problem. The ranges of dissolved metals that are typical in surface waters of the United States away from the immediate influence of discharges (Bruland 1983; Shiller and Boyle 1985,1987; Trefry et al. 1986; Windom et al. 1991) are:

Metal	Salt water (ug/L)	Fresh water (ug/L)
Cadmium	0.01 to 0.2	0.002 to 0.08
Copper	0.1 to 3.	0.4 to 4.
Lead	0.01 to 1.	0.01 to 0.19
Nickel	0.3 to 5.	1. to 2.
Silver	0.005 to 0.2	----------
Zinc	0.1 to 15.	0.03 to 5.

The U.S. EPA (1983,1991) has published analytical methods for monitoring metals in waters and wastewaters, but these methods are inadequate for determination of ambient concentrations of some metals in some surface waters. Accurate and precise measurement of these low concentrations requires appropriate attention to seven areas:

1. Use of "clean techniques" during collecting, handling, storing, preparing, and analyzing samples to avoid contamination.
2. Use of analytical methods that have sufficiently low detection limits.
3. Avoidance of interference in the quantification (instrumental analysis) step.
4. Use of blanks to assess contamination.
5. Use of matrix spikes (sample spikes) and certified reference materials (CRMs) to assess interference and contamination.
6. Use of replicates to assess precision.
7. Use of certified standards.

In a strict sense, the term "clean techniques" refers to techniques that reduce contamination and enable the accurate and precise measurement of trace metals in fresh and salt surface waters. In a broader sense, the term also refers to related issues concerning detection limits, quality control, and quality assurance. Documenting data quality demonstrates the amount of confidence that can be placed in the data, whereas increasing the sensitivity of methods reduce the problem of deciding how to

interpret results that are reported to be below detection limits.

This appendix is written for those analytical laboratories that want guidance concerning ways to lower detection limits, increase precision, and/or increase accuracy. The ways to achieve these goals are to increase the sensitivity of the analytical methods, decrease contamination, and decrease interference. Ideally, validation of a procedure for measuring concentrations of metals in surface water requires demonstration that agreement can be obtained using completely different procedures beginning with the sampling step and continuing through the quantification step (Bruland et al. 1979), but few laboratories have the resources to compare two different procedures. Laboratories can, however, (a) use techniques that others have found useful for improving detection limits, accuracy, and precision, and (b) document data quality through use of blanks, spikes, CRMs, replicates, and standards.

In general, in order to achieve accurate and precise measurement of a particular concentration, both the detection limit and the blanks should be less than one-tenth of that concentration. Therefore, the term "metal-free" can be interpreted to mean that the total amount of contamination that occurs during sample collection and processing (e.g., from gloves, sample containers, labware, sampling apparatus, cleaning solutions, air, reagents, etc.) is sufficiently low that blanks are less than one-tenth of the lowest concentration that needs to be measured.

Atmospheric particulates can be a major source of contamination (Moody 1982; Adeloju and Bond 1985). The term "class-100" refers to a specification concerning the amount of particulates in air (Moody 1982); although the specification says nothing about the composition of the particulates, generic control of particulates can greatly reduce trace-metal blanks. Except during collection of samples and initial cleaning of equipment, all handling of samples, sample containers, labware, and sampling apparatus should be performed in a class-100 bench, room, or glove box.

Nothing contained or not contained in this appendix adds to or subtracts from any regulatory requirements set forth in other EPA documents concerning metal analyses. The word "must" is used in this appendix merely to indicate items that are considered very important by analytical chemists who have worked to increase accuracy and precision and lower detection limits in trace-metal analysis. Some items are considered important because they have been found to have received inadequate attention in some laboratories performing trace-metal analyses.

Two topics that are not addressed in this appendix are:

1. The "ultraclean techniques" that are likely to be necessary when trace analyses of mercury are performed.
2. Safety in analytical laboratories.

Other documents should be consulted if these topics are of concern.

Avoiding contamination by use of "clean techniques"

Measurement of trace metals in receiving waters must take into account the potential for contamination during each step in the process. Regardless of the specific procedures used for collection, handling, storage, preparation (digestion, filtration, and/or extraction), and quantification (instrumental analysis), the general principles of contamination control must be applied. Some specific recommendations are:

a. Non-talc latex or class-100 polyethylene gloves must be worn during all steps from sample collection to analysis. (Talc seems to be a particular problem with zinc; gloves made with talc cannot be decontaminated sufficiently.) Gloves should only contact surfaces that are metal-free; gloves should be changed if even suspected of contamination.
b. The acid used to acidify samples for preservation and digestion and to acidify water for final cleaning of labware, sampling apparatus, and sample containers must be metal-free. The quality of the acid used should be better than reagent-grade. Each lot of acid must be analyzed for the metal(s) of interest before use.
c. The water used to prepare acidic cleaning solutions and to rinse labware, sample containers, and sampling apparatus may be prepared by distillation, deionization, or reverse osmosis, and must be demonstrated to be metal-free.
d. The work area, including bench tops and hoods, should be cleaned (e.g., washed and wiped dry with lint-free, class-100 wipes) frequently to remove contamination.
e. All handling of samples in the laboratory, including filtering and analysis, must be performed in a class-100 clean bench or a glove box fed by particle-free air or nitrogen; ideally the clean bench or glove box should be located within a class-100 clean room.
f. Labware, reagents, sampling apparatus, and sample containers must never be left open to the atmosphere; they should be stored in a class-100 bench, covered with plastic wrap, stored in a plastic box, or turned upside down on a clean surface. Minimizing the time between cleaning and using will help minimize contamination.
g. Separate sets of sample containers, labware, and sampling apparatus should be dedicated for different kinds of samples, e.g., receiving water samples, effluent samples, etc.
h. To avoid contamination of clean rooms, samples that contain very high concentrations of metals and do not require use of "clean techniques" should not be brought into clean rooms.
i. Acid-cleaned plastic, such as high-density polyethylene (HDPE), low-density polyethylene (LDPE), or a fluoroplastic, must be the only material that ever contacts a sample, except possibly during digestion for the total recoverable

measurement. (Total recoverable samples can be digested in some plastic containers.) Even HDPE and LDPE might not be acceptable for mercury, however.

j. All labware, sample containers, and sampling apparatus must be acid-cleaned before use or reuse.
   1. Sample containers, sampling apparatus, tubing, membrane filters, filter assemblies, and other labware must be soaked in acid until metal-free. The amount of cleaning necessary might depend on the amount of contamination and the length of time the item will be in contact with samples. For example, if an acidified sample will be stored in a sample container for three weeks, ideally the container should have been soaked in an acidified metal-free solution for at least three weeks.
   2. It might be desirable to perform initial cleaning, for which reagent-grade acid may be used, before the items are allowed into a clean room. For most metals, items should be either (a) soaked in 10 percent concentrated nitric acid at 50°C for at least one hour, or (b) soaked in 50 percent concentrated nitric acid at room temperature for at least two days; for arsenic and mercury, soaking for up to two weeks at 50°C in 10 percent concentrated nitric acid might be required. For plastics that might be damaged by strong nitric acid, such as polycarbonate and possibly HDPE and LDPE, soaking in 10 percent concentrated hydrochloric acid, either in place of or before soaking in a nitric acid solution, might be desirable.
   3. Chromic acid must not be used to clean items that will be used in analysis of metals.
   4. Final soaking and cleaning of sample containers, labware, and sampling apparatus must be performed in a class-100 clean room using metal-free acid and water. The solution in an acid bath must be analyzed periodically to demonstrate that it is metal-free.
   5. After labware and sampling apparatus are cleaned, they may be stored in a clean room in a weak acid bath prepared using metal-free acid and water. Before use, the items should be rinsed at least three times with metal-free water. After the final rinse, the items should be moved immediately, with the open end pointed down, to a class-100 clean bench. Items may be dried on a class-100 clean bench; items must not be dried in an oven or with laboratory towels. The sampling apparatus should be assembled in a class-100 clean room or bench and double-bagged in metal-free polyethylene zip-type bags for transport to the field; new bags are usually metal-free.
   6. After sample containers are cleaned, they should be filled with metal-free water that has been acidified to a pH of 2 with metal-free nitric acid (about 0.5 mL per liter) for storage until use. At the time of sample collection, the sample containers should be emptied and rinsed at least twice with the solution being sampled before the actual

sample is placed in the sample container.

k. Field samples must be collected in a manner that eliminates the potential for contamination from the sampling platform, probes, etc. Exhaust from boats and the direction of wind and water currents should be taken into account. The people who collect the samples must be specifically trained on how to collect field samples. After collection, all handling of samples in the field that will expose the sample to air must be performed in a portable class-100 clean bench or glove box.

l. Samples must be acidified (after filtration if dissolved metal is to be measured) to a pH of less than 2, except that the pH must be less than 1 for mercury. Acidification should be done in a clean room or bench, and so it might be desirable to wait and acidify samples in a laboratory rather than in the field. If samples are acidified in the field, metal-free acid can be transported in plastic bottles and poured into a plastic container from which acid can be removed and added to samples using plastic pipettes. Alternatively, plastic automatic dispensers can be used.

m. Such things as probes and thermometers must not be put in samples that are to be analyzed for metals. In particular, pH electrodes and mercury-in-glass thermometers must not be used if mercury is to be measured. If pH is measured, it must be done on a separate aliquot.

n. Sample handling should be minimized. For example, instead of pouring a sample into a graduated cylinder to measure the volume, the sample can be weighed after being poured into a tared container; alternatively, the container from which the sample is poured can be weighed. (For saltwater samples, the salinity or density should be taken into account when weight is converted to volume.)

o. Each reagent used must be verified to be metal-free. If metal-free reagents are not commercially available, removal of metals will probably be necessary.

p. For the total recoverable measurement, samples should be digested in a class-100 bench, not in a metallic hood. If feasible, digestion should be done in the sample container by acidification and heating.

q. The longer the time between collection and analysis of samples, the greater the chance of contamination, loss, etc.

r. Samples must be stored in the dark, preferably between 0 and 4°C with no air space in the sample container.

Achieving low detection limits

a. Extraction of the metal from the sample can be extremely useful if it simultaneously concentrates the metal and eliminates potential matrix interferences. For example, ammonium 1-pyrrolidinedithiocarbamate and/or diethylammonium diethyldithiocarbamate can extract cadmium, copper, lead,

nickel, and zinc (Bruland et al. 1979; Nriagu et al. 1993).

b. The detection limit should be less than ten percent of the lowest concentration that is to be measured.

Avoiding interferences

a. Potential interferences must be assessed for the specific instrumental analysis technique used and each metal to be measured.
b. If direct analysis is used, the salt present in high-salinity saltwater samples is likely to cause interference in most instrumental techniques.
c. As stated above, extraction of the metal from the sample is particularly useful because it simultaneously concentrates the metal and eliminates potential matrix interferences.

Using blanks to assess contamination

a. A laboratory (procedural, method) blank consists of filling a sample container with analyzed metal-free water and processing (filtering, acidifying, etc.) the water through the laboratory procedure in exactly the same way as a sample. A laboratory blank must be included in each set of ten or fewer samples to check for contamination in the laboratory, and must contain less than ten percent of the lowest concentration that is to be measured. Separate laboratory blanks must be processed for the total recoverable and dissolved measurements, if both measurements are performed.
b. A field (trip) blank consists of filling a sample container with analyzed metal-free water in the laboratory, taking the container to the site, processing the water through tubing, filter, etc., collecting the water in a sample container, and acidifying the water the same as a field sample. A field blank must be processed for each sampling trip. Separate field blanks must be processed for the total recoverable measurement and for the dissolved measurement, if filtrations are performed at the site. Field blanks must be processed in the laboratory the same as laboratory blanks.

Assessing accuracy

a. A calibration curve must be determined for each analytical run and the calibration should be checked about every tenth sample. Calibration solutions must be traceable back to a certified standard from the U.S. EPA or the National Institute of Science and Technology (NIST).
b. A blind standard or a blind calibration solution must be included in each group of about twenty samples.

c. At least one of the following must be included in each group of about twenty samples:
   1. A matrix spike (spiked sample; the method of known additions).
   2. A CRM, if one is available in a matrix that closely approximates that of the samples. Values obtained for the CRM must be within the published values.

The concentrations in blind standards and solutions, spikes, and CRMs must not be more than 5 times the median concentration expected to be present in the samples.

Assessing precision

a. A sampling replicate must be included with each set of samples collected at each sampling location.
b. If the volume of the sample is large enough, replicate analysis of at least one sample must be performed along with each group of about ten samples.

Special considerations concerning the dissolved measurement

Whereas the total recoverable measurement is especially subject to contamination during the digestion step, the dissolved measurement is subject to both loss and contamination during the filtration step.

a. Filtrations must be performed using acid-cleaned plastic filter holders and acid-cleaned membrane filters. Samples must not be filtered through glass fiber filters, even if the filters have been cleaned with acid. If positive-pressure filtration is used, the air or gas must be passed through a 0.2-um in-line filter; if vacuum filtration is used, it must be performed on a class-100 bench.
b. Plastic filter holders must be rinsed and/or dipped between filtrations, but they do not have to be soaked between filtrations if all the samples contain about the same concentrations of metal. It is best to filter samples from low to high concentrations. A membrane filter must not be used for more than one filtration. After each filtration, the membrane filter must be removed and discarded, and the filter holder must be either rinsed with metal-free water or dilute acid and dipped in a metal-free acid bath or rinsed at least twice with metal-free dilute acid; finally, the filter holder must be rinsed at least twice with metal-free water.
c. For each sample to be filtered, the filter holder and membrane filter must be conditioned with the sample, i.e., an initial portion of the sample must be filtered and discarded.

The accuracy and precision of the dissolved measurement should be

assessed periodically. A large volume of a buffered solution (such as aerated 0.05 N sodium bicarbonate) should be spiked so that the concentration of the metal of interest is in the range of the low concentrations that are to be measured. The total recoverable concentration and the dissolved concentration of the metal in the spiked buffered solution should be measured alternately until each measurement has been performed at least ten times. The means and standard deviations for the two measurements should be the same. All values deleted as outliers must be acknowledged.

Reporting results

To indicate the quality of the data, reports of results of measurements of the concentrations of metals must include a description of the blanks, spikes, CRMs, replicates, and standards that were run, the number run, and the results obtained. All values deleted as outliers must be acknowledged.

Additional information

The items presented above are some of the important aspects of "clean techniques"; some aspects of quality assurance and quality control are also presented. This is not a definitive treatment of these topics; additional information that might be useful is available in such publications as Patterson and Settle (1976), Zief and Mitchell (1976), Bruland et al. (1979), Moody and Beary (1982), Moody (1982), Bruland (1983), Adeloju and Bond (1985), Berman and Yeats (1985), Byrd and Andreae (1986), Taylor (1987), Sakamoto-Arnold (1987), Tramontano et al. (1987), Puls and Barcelona (1989), Windom et al. (1991), U.S. EPA (1992), Horowitz et al. (1992), and Nriagu et al. (1993).

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