

APPENDIX J

***Attachments to Office of Water Policy and
Technical Guidance on Interpretation and
Implementation of Aquatic Life Metals Criteria***

WATER QUALITY STANDARDS HANDBOOK

SECOND EDITION

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 4, 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

<u>Metal</u>	<u>CMC</u>		<u>CCC</u>	
	<u>Recommended Value (%)</u>	<u>(Range %)</u>	<u>Recommended Value (%)</u>	<u>(Range %)</u>
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	35	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.

<u>Concn.^A</u> <u>(ug/L)</u>	<u>Percent</u> <u>Diss.^B</u>	<u>n^C</u>	<u>Species^D</u>	<u>SRF^E</u>	<u>Food</u>	<u>Hard.</u>	<u>Alk.</u>	<u>pH</u>	<u>Ref.</u>
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 ^O	?	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	CaIl 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 ^l	Chapman 1993
26267	32	?	DM	S	No	110	9	6.7	Chapman 1993
27416	27	?	DM	S	No	96	10	6.0 ^l	Chapman 1993
58665	23	?	DM	S	No	190	25	6.2 ^l	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	?	CF	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 ^Q	?	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	7.6	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 ^H	?	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
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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 ⁰	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 ¹	71-129	2	CD	R	Yes	31	38	7.2	Carlson et al. 1986b
18-273 ¹	81-107	2	CD	R	Yes	31	38	7.2	Carlson et al. 1986b
167 ¹	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 ¹	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 ⁰	?	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- μ m 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- μ m glass fiber filter was used.

H A 0.10- μ m 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.

References

- Adelman, I.R., and L.L. Smith, Jr. 1976. Standard Test Fish Development. Part I. Fathead Minnows (*Pimephales promelas*) and Goldfish (*Carassius auratus*) as Standard Fish in Bioassays and Their Reaction to Potential Reference Toxicants. EPA-600/3-76-061a. National Technical Information Service, Springfield, VA. Page 24.
- Benoit, D.A. 1975. Chronic Effects of Copper on Survival, Growth, and Reproduction of the Bluegill (*Lepomis macrochirus*). Trans. Am. Fish. Soc. 104:353-358.
- Brungs, W.A., T.S. Holderman, and M.T. Southerland. 1992. Synopsis of Water-Effect Ratios for Heavy Metals as Derived for Site-Specific Water Quality Criteria.
- Call, D.J., L.T. Brooke, and D.D. Vaishnav. 1982. Aquatic Pollutant Hazard Assessments and Development of a Hazard Prediction Technology by Quantitative Structure-Activity Relationships. Fourth Quarterly Report. University of Wisconsin-Superior, Superior, WI.
- Carlson, A.R., H. Nelson, and D. Hammermeister. 1986a. Development and Validation of Site-Specific Water Quality Criteria for Copper. Environ. Toxicol. Chem. 5:997-1012.
- Carlson, A.R., H. Nelson, and D. Hammermeister. 1986b. Evaluation of Site-Specific Criteria for Copper and Zinc: An Integration of Metal Addition Toxicity, Effluent and Receiving Water Toxicity, and Ecological Survey Data. EPA/600/S3-86-026. National Technical Information Service, Springfield, VA.
- Carroll, J.J., S.J. Ellis, and W.S. Oliver. 1979. Influences of Hardness Constituents on the Acute Toxicity of Cadmium to Brook Trout (*Salvelinus fontinalis*).
- Chakoumakos, C., R.C. Russo, and R.V. Thurston. 1979. Toxicity of Copper to Cutthroat Trout (*Salmo clarki*) under Different Conditions of Alkalinity, pH, and Hardness. Environ. Sci. Technol. 13:213-219.
- Chapman, G.A. 1993. Memorandum to C. Stephan. June 4.
- Davies, P.H., J.P. Goettl, Jr., J.R. Sinley, and N.F. Smith. 1976. Acute and Chronic Toxicity of Lead to Rainbow Trout *Salmo gairdneri*, in Hard and Soft Water. Water Res. 10:199-206.
- Finlayson, B.J., and K.M. Verrue. 1982. Toxicities of Copper, Zinc, and Cadmium Mixtures to Juvenile Chinook Salmon. Trans. Am. Fish. Soc. 111:645-650.

Geckler, J.R., W.B. Horning, T.M. Neiheisel, Q.H. Pickering, E.L. Robinson, and C.E. Stephan. 1976. Validity of Laboratory Tests for Predicting Copper Toxicity in Streams. EPA-600/3-76-116. National Technical Information Service, Springfield, VA. Page 118.

Grunwald, D. 1992. Metal Toxicity Evaluation: Review, Results, and Data Base Documentation.

Hammermeister, D., C. Northcott, L. Brooke, and D. Call. 1983. Comparison of Copper, Lead and Zinc Toxicity to Four Animal Species in Laboratory and ST. Louis River Water. University of Wisconsin-Superior, Superior, WI.

Hansen, D.J. 1993. Memorandum to C.E. Stephan. April 15.

Holcombe, G.W., D.A. Benoit, E.N. Leonard, and J.M. McKim. 1976. Long-Term Effects of Lead Exposure on Three Generations of Brook Trout (*Salvelinus fontinalis*). J. Fish. Res. Bd. Canada 33:1731-1741.

Holcombe, G.W., and R.W. Andrew. 1978. The Acute Toxicity of Zinc to Rainbow and Brook Trout. EPA-600/3-78-094. National Technical Information Service, Springfield, VA.

Horowitz, A.J., K.A. Elrick, and M.R. Colberg. 1992. The Effect of Membrane Filtration Artifacts on Dissolved Trace Element Concentrations. Water Res. 26:753-763.

Howarth, R.S., and J.B. Sprague. 1978. Copper Lethality to Rainbow Trout in Waters on Various Hardness and pH. Water Res. 12:455-462.

JRB Associates. 1983. Demonstration of the Site-specific Criteria Modification Process: Selser's Creek, Ponchatoula, Louisiana.

Lazorchak, J.M. 1987. The Significance of Weight Loss of Daphnia magna Straus During Acute Toxicity Tests with Copper. Ph.D. Thesis.

Lima, A.R., C. Curtis, D.E. Hammermeister, T.P. Markee, C.E. Northcott, L.T. Brooke. 1984. Acute and Chronic Toxicities of Arsenic(III) to Fathead Minnows, Flagfish, Daphnids, and an Amphipod. Arch. Environ. Contam. Toxicol. 13:595-601.

Lind, D., K. Alto, and S. Chatterton. 1978. Regional Copper-Nickel Study. Draft.

Mount, D.I. 1966. The Effect of Total Hardness and pH on Acute Toxicity of Zinc to Fish. Air Water Pollut. Int. J. 10:49-56.

- Nebeker, A.V., C.K. McAuliffe, R. Mshar, and D.G. Stevens. 1983. Toxicity of Silver to Steelhead and Rainbow Trout, Fathead Minnows, and *Daphnia magna*. Environ. Toxicol. Chem. 2:95-104.
- Pickering, Q.P., and M.H. Gast. 1972. Acute and Chronic Toxicity of Cadmium to the Fathead Minnow (*Pimephales promelas*). J. Fish. Res. Bd. Canada 29:1099-1106.
- Rice, D.W., Jr., and F.L. Harrison. 1983. The Sensitivity of Adult, Embryonic, and Larval Crayfish *Procambarus clarkii* to Copper. NUREG/CR-3133 or UCRL-53048. National Technical Information Service, Springfield, VA.
- Schuytema, G.S., P.O. Nelson, K.W. Malueg, A.V. Nebeker, D.F. Krawczyk, A.K. Ratcliff, and J.H. Gakstatter. 1984. Toxicity of Cadmium in Water and Sediment Slurries to *Daphnia magna*. Environ. Toxicol. Chem. 3:293-308.
- Spehar, R.L., R.L. Anderson, and J.T. Fiandt. 1978. Toxicity and Bioaccumulation of Cadmium and Lead in Aquatic Invertebrates. Environ. Pollut. 15:195-208.
- Spehar, R.L., and A.R. Carlson. 1984. Derivation of Site-Specific Water Quality Criteria for Cadmium and the St. Louis River Basin, Duluth, Minnesota. Environ. Toxicol. Chem. 3:651-665.
- Spehar, R.L., and J.T. Fiandt. 1986. Acute and Chronic Effects of Water Quality Criteria-Based Metal Mixtures on Three Aquatic Species. Environ. Toxicol. Chem. 5:917-931.
- Sprague, J.B. 1964. Lethal Concentration of Copper and Zinc for Young Atlantic Salmon. J. Fish. Res. Bd. Canada 21:17-9926.
- Stevens, D.G., and G.A. Chapman. 1984. Toxicity of Trivalent Chromium to Early Life Stages of Steelhead Trout. Environ. Toxicol. Chem. 3:125-133.
- University of Wisconsin-Superior. 1993. Preliminary data from work assignment 1-10 for Contract No. 68-C1-0034.

**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:

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

where,

C = dissolved phase metal concentration,
 C_{Tf} = 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:

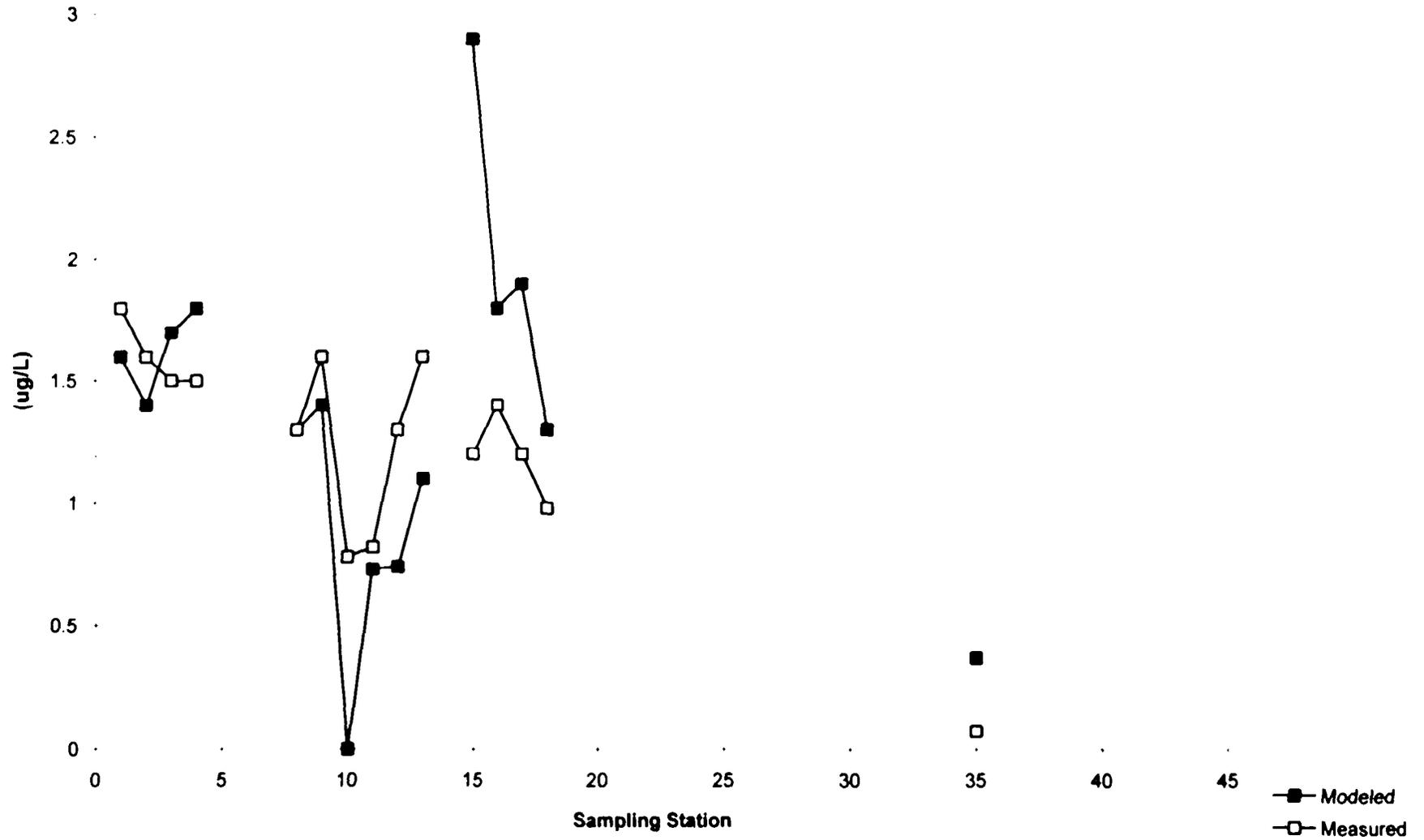
1. Using clean analytical techniques and field sampling procedures with appropriate QA/QC, collect receiving water samples and determine site specific values of K_d for each metal. Use these K_d values to "translate" between total recoverable and dissolved metals in receiving water. This approach is 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.

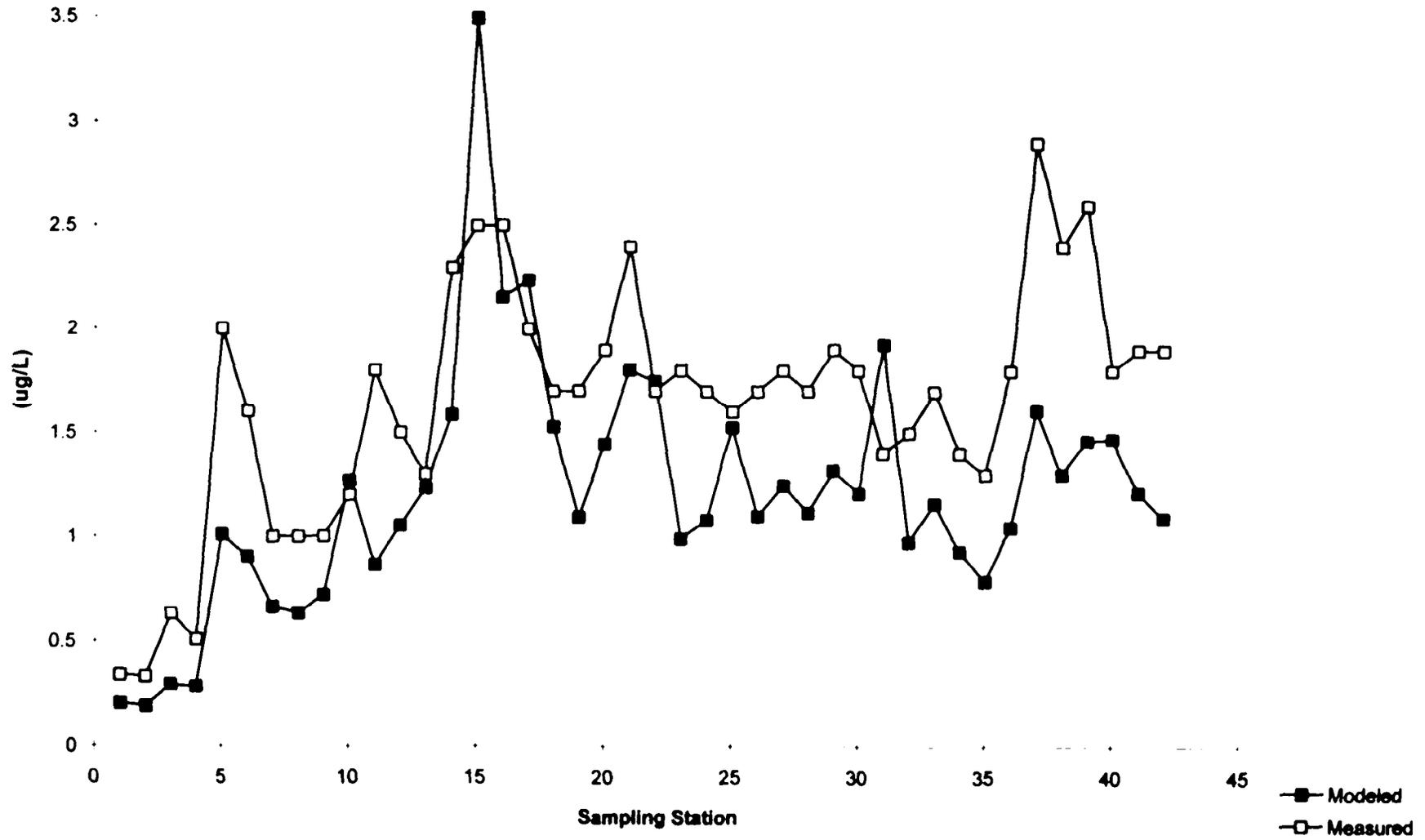
3. Use the historical data on total suspended solids (TSS) in receiving waterbodies at appropriate design flows and K_d values presented in the Technical Guidance Manual for Performing Waste Load Allocations. Book II. Streams and Rivers. EPA-440/4-84-020 (1984) to "translate" between (total recoverable) 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.

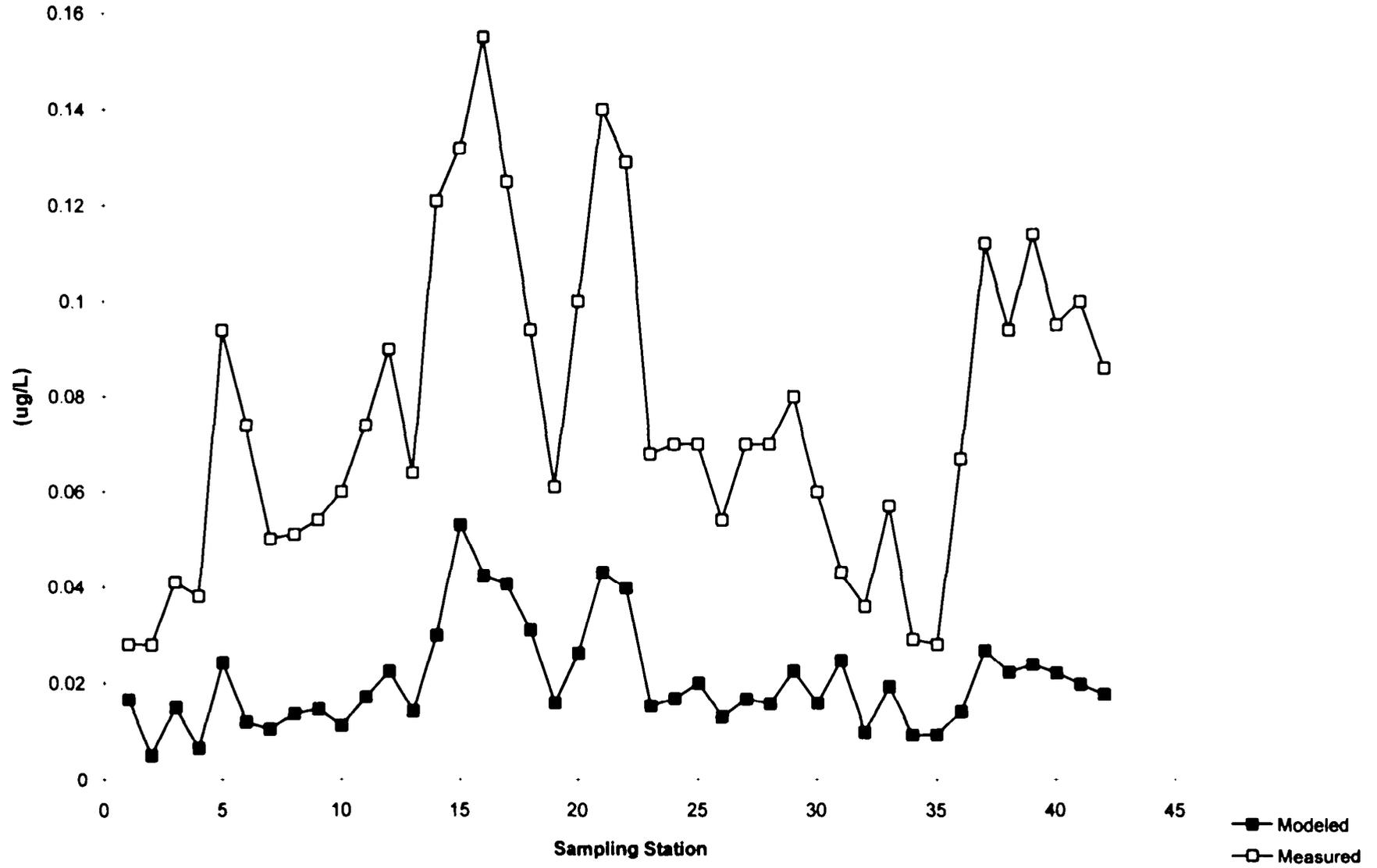
Measured vs. Modeled Dissolved Arsenic Concentrations



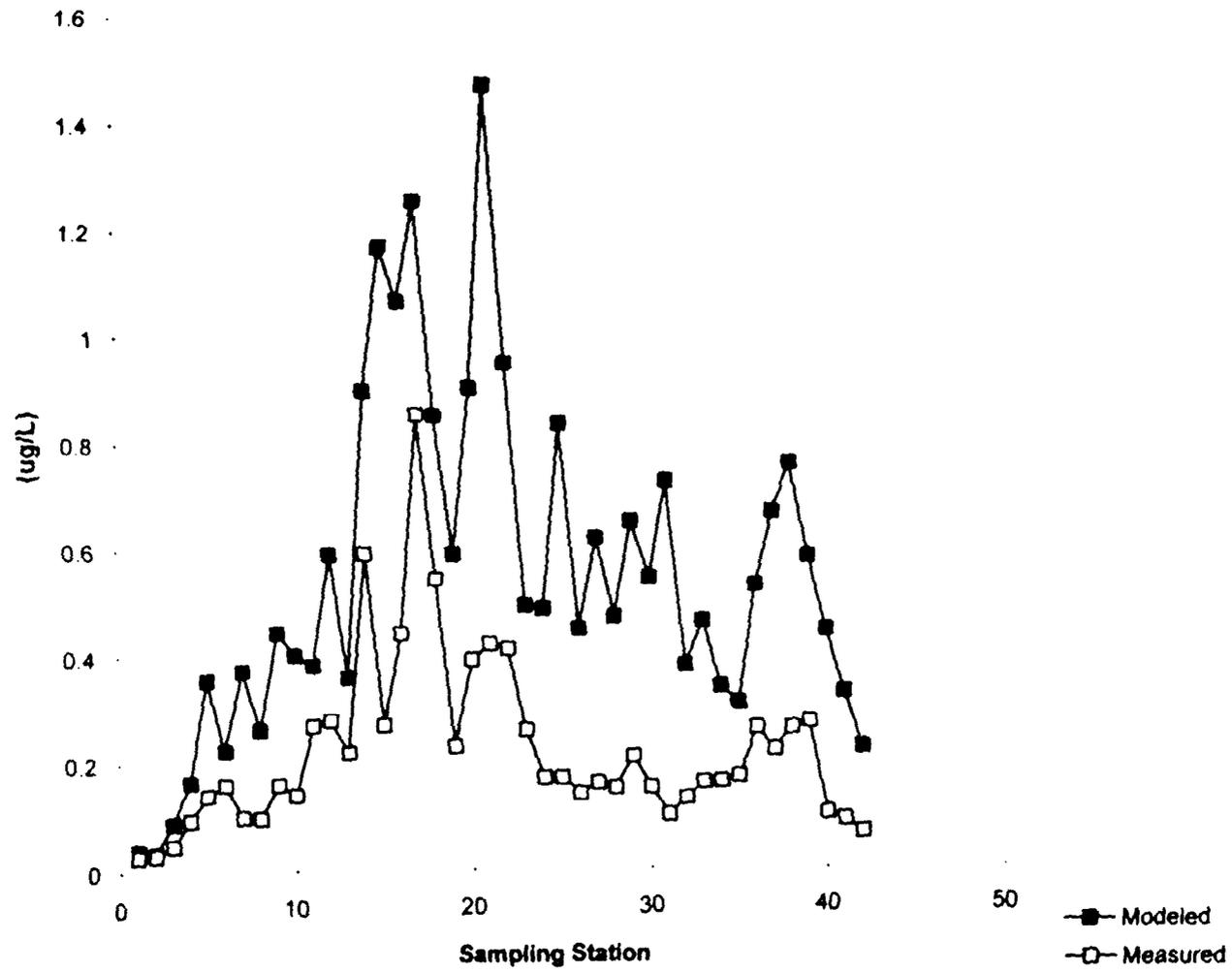
Measured vs. Modeled Dissolved Copper Concentrations



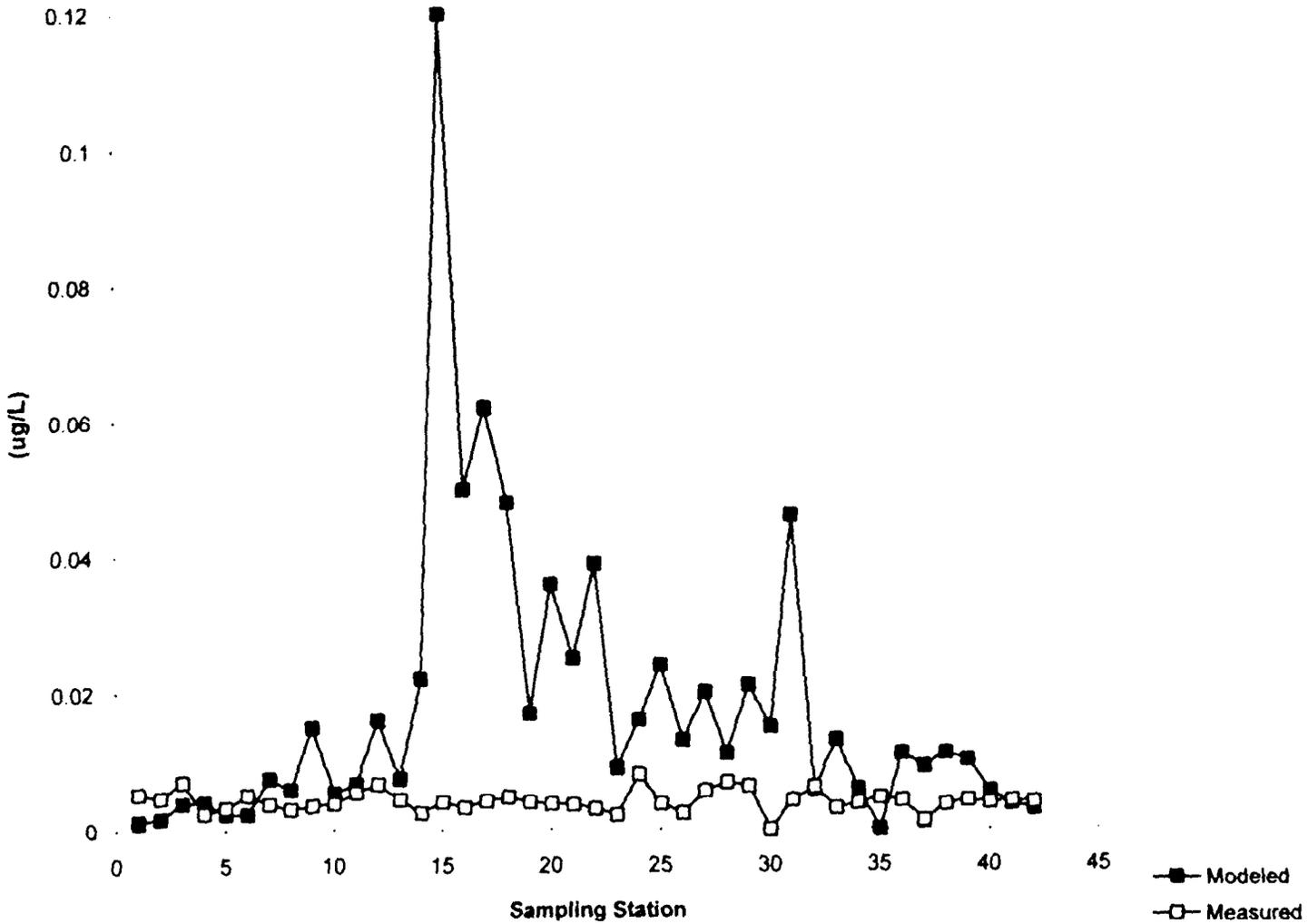
Measured vs. Modeled Dissolved Cadmium Concentrations



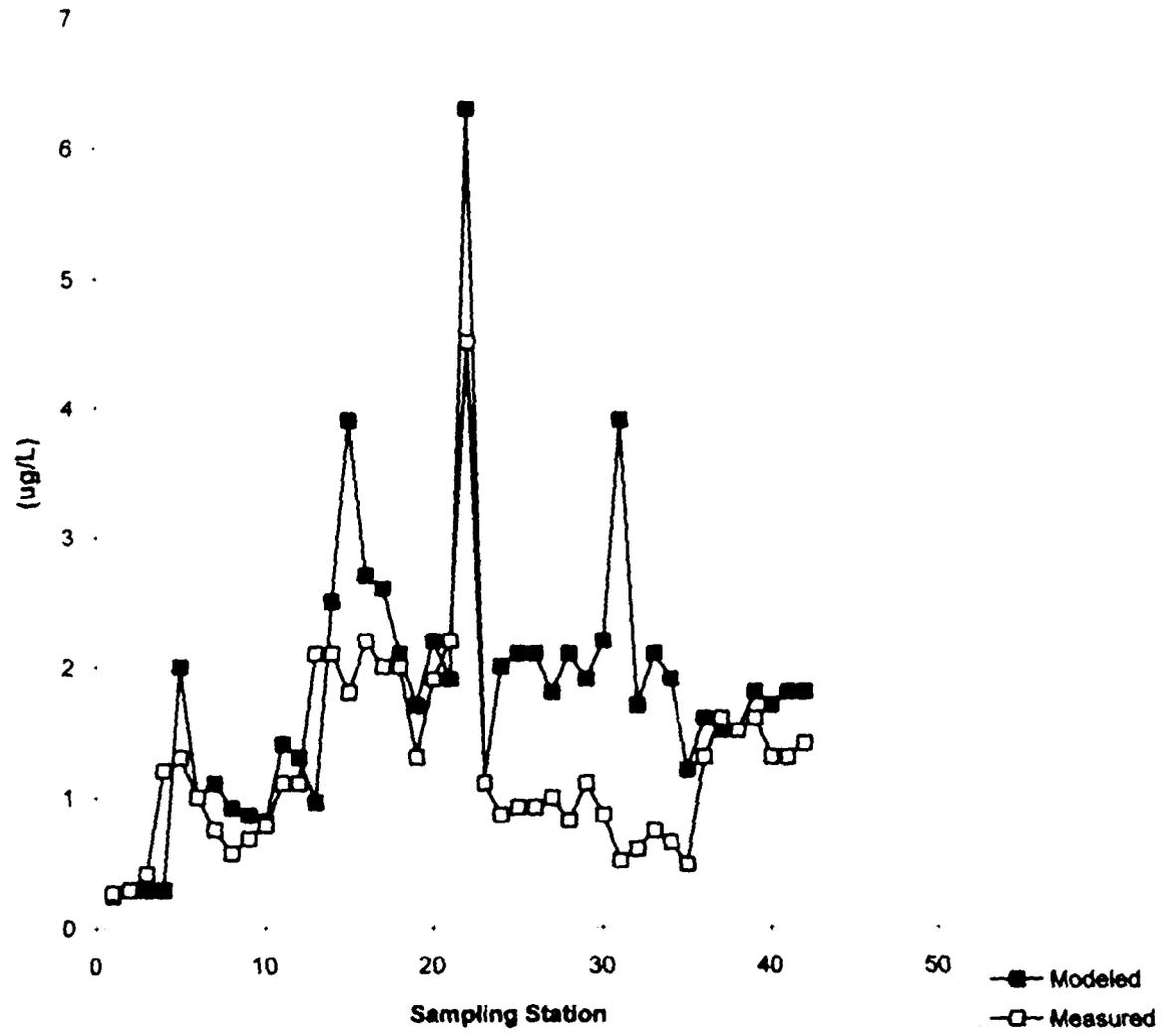
Measured vs. Modeled Dissolved Lead Concentrations



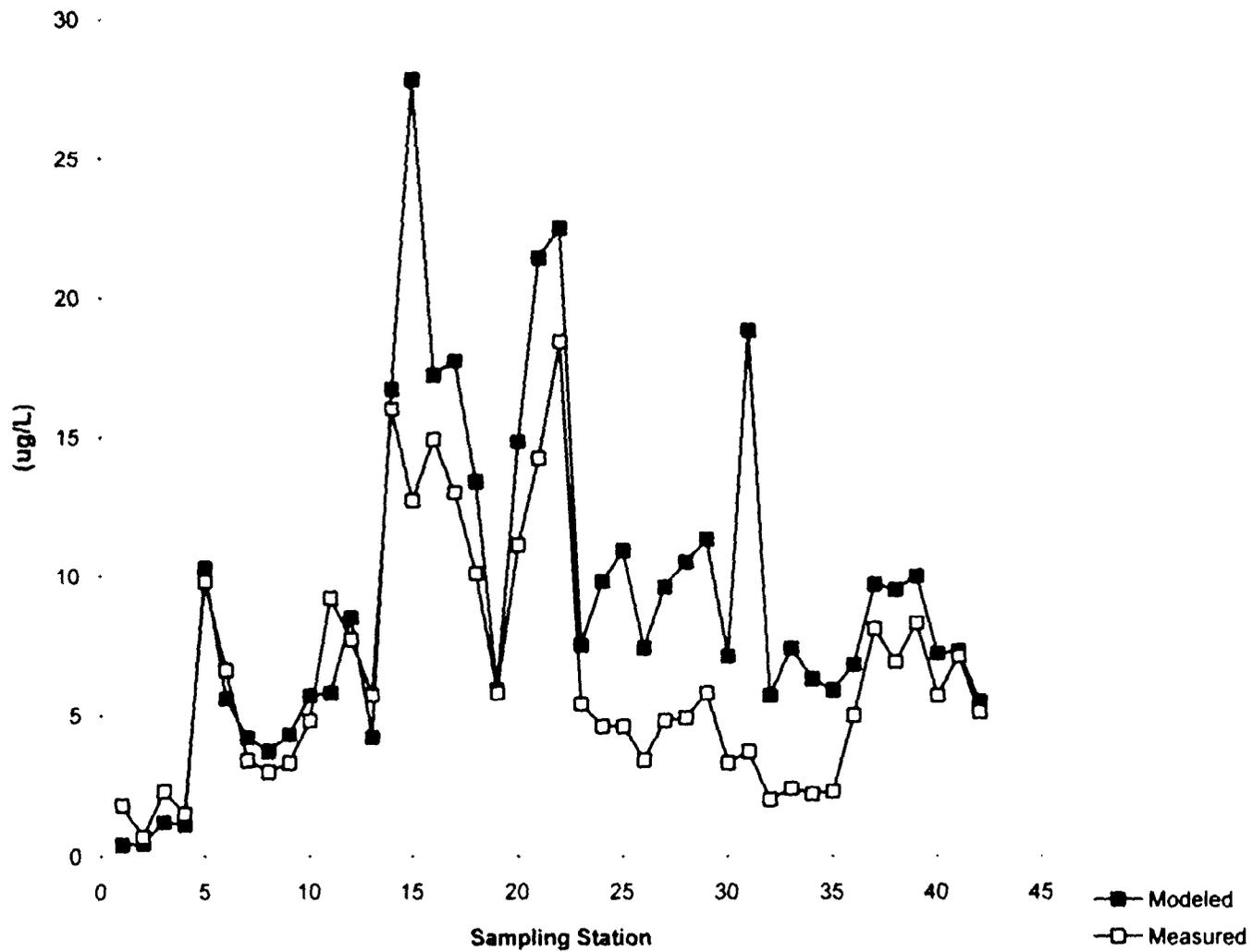
Measured vs. Modeled Dissolved Mercury Concentrations



Measured vs. Modeled Dissolved Nickel Concentrations



Measured vs. Modeled Dissolved Zinc Concentrations



**GUIDANCE DOCUMENT
ON CLEAN ANALYTICAL TECHNIQUES AND MONITORING**
October 1993

Guidance on Monitoring

o Use of Clean Sampling and Analytical Techniques

Pages 98-108 of the WER guidance document (Appendix L of the *Water Quality Standards Handbook-Second Edition*) 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(i)(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 supporting the contention that the previous data are questionable and the permitting authority agrees with the findings of the information, EPA expects that permitting authorities will consider such information in determining appropriate enforcement responses.

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.