Ambient Water Quality Criteria - Saltwater Copper Addendum

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Saltwater Copper Criteria Addendum (Dissolved)

New acceptable acute data for copper are given in Table A1. These new data were used with those given in Table 1 of the current copper criteria document (U.S. EPA, 1985) to obtain the values given in Table A3. There are no new chronic values. All of the concentrations listed in Table A3 represent dissolved values. Table A1 list whether the new data is based on nominal, measured total, or measured dissolved concentrations. All data for which measured dissolved values were not available were adjusted to dissolved using dissolved-to-nominal (0.90) or dissolved-to-total (0.83) ratios to provide the dissolved values used in Table A3. These dissolved-to-nominal and dissolved-to-total ratios are based on the geometric mean of such ratios calculated from laboratory water (sand-filtered, Narragansett Bay seawater) used in the Hudson site-specific copper criteria study (SAIC 1993).

Criterion Maximum Concentration (CMC)

There are now 26 saltwater Genus Mean Acute Values (GMAV), an increase of six over the current copper document (Table A3). The six new genera are *Mulinia, Tigriopus, Arbacia, Cyprinodon, Fundulus,* and *Atherinops* (Table A1).

Three of the original four most sensitive genera remain so (*Crassostrea, Paralichthys,* and *Mytilus*). *Mytilus edulis* also remains the most sensitive saltwater species. However, the existing acute value for *Mytilus edulis* is based on unmeasured copper concentrations. The Guidelines (Stephan, et al., 1985) state that measured concentrations take precedence over unmeasured. Since there are now measured values for *M. edulis* (ToxScan, 1991a,b,c; SAIC, 1993), the acute value in the current copper document has been eliminated from the Species Mean Acute Value for this species. Summer flounder, *Paralichthys dentatus,* remains the second most sensitive species. There are no new data for this species. The original data for this species are from a flow-through measured test. The acute value was adjusted to dissolved using the 0.83 ratio from the Hudson study. Data for *Mulinia lateralis* (the third most sensitive species) was not available from the original copper document. The "laboratory water" data from the Hudson site-specific study (SAIC, 1993) were used to calculate the SMAV. There are six IC50 values based on measured dissolved copper for this species, ranging from 14.9 to 21.0 µg/L. The geometric mean of these six values is 17.70 µg/L.

There were two GMAVs that tied for the fourth most sensitive, sea urchin and oysters. *Crassostrea* was selected as the fourth most sensitive because one of the species, *C. gigas,* was slightly more sensitive than *Arbacia.* As with *Mytilus edulis,* the original values for *C. gigas,* were based on unmeasured copper concentrations. There are now two sources of measured data. There are five IC50s based on measured dissolved copper for this species from a copper site-specific study in San Francisco Bay (S.R. Hansen & Associates, 1992), and one based on measured total copper (Knezovich, et al., 1981; Harrison, et al., 1981). The IC50 from the latter was adjusted to dissolved using the 0.83 dissolved to total ratio from the Hudson study. The other oyster species, *C. virginica,* is the only unmeasured value among the four most sensitive genera. There are no new data for this species, therefore the values in the current document are retained. However, they have been adjusted to dissolved using the dissolved to nominal ratio of 0.90 from the Hudson study.

The Genus Mean Acute Values (GMAV) for the four most sensitive species differ by a factor of only 2.2. Using the method of calculation outlined in the Guidelines, the saltwater dissolved copper Final Acute Value (FAV) is 10.39 µg/L. The FAV, however, is lowered to 9.625 µg/L to protect the commercially important blue mussel. The Criterion Maximum Concentration (CMC) is the FAV divided by two, and rounded to two significant figures. Therefore the new saltwater dissolved copper CMC is 4.8 µg/L.

Criterion Continuous Concentration (CCC)

There are no new saltwater chronic data for copper. However, there is new information since the current copper criteria document was published that changes how the Final Chronic Value (FCV) should be calculated. The FCV was calculated by dividing the FAV by a Final Acute-Chronic Ratio (FACR). The current copper document assumed an FACR of 2.0 since the acute tests used to derive the FAV were from embryo-larval tests with molluscs, and a limited number of other taxa. More recent information, summarized in Appendix D) suggests that the FACR should be calculated from the existing Acute-Chronic Ratios in the current document. However, all of the ACRs should not be used.

When the species mean ACR seems to increase (or decrease) as the species mean acute value (SMAV) increases, the FACR can be calculated as the geometric mean of ACRs for species whose SMAVs are close to the FAV. The FACR used here is the geometric mean of the four species mean ACRs for *Daphnia, Gammarus, Physa* and *Mysidopsis*. These taxa included two freshwater species with SMAVs within a factor of two of the freshwater FAV, a sensitive freshwater mollusc, and the only saltwater ACR. This and some other valid options for obtaining the FACR are described in Appendix D.

The FACR is 3.127, the geometric mean of the above four species ACRs. The Final Chronic Value (FCV), calculated by dividing the FAV by this ratio, is 3.078 µg/L. The criterion continuous concentration (CCC) is equal to the FCV rounded to two significant figures. The CCC is 3.1 µg/L dissolved copper. In Appendix D, the best options for calculating the FACR yielded a narrow range of values for the CCC, 3.1-3.5 µg/L.

National Criteria

The procedures described in the "Guidelines for Deriving Numerical National Water Quality Criteria for the Protection of Organisms and Their Uses" indicates that, except where a locally important species is very sensitive, saltwater aquatic organisms and their uses should not be affected unacceptably if the four-day average concentration of dissolved copper does not exceed 3.1 µg/L more than once every three years on the average and if the 24-hour average concentration does not exceed 4.8 µg/L more than once every three years on the average.

References

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Dorfman, D. 1977. Tolerance of *Fundulus heteroclitus* to different metals in salt waters. Bull. N.J. Acad. Sci. 22:21-23.

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SAIC. 1993. Toxicity testing to support the New York/New Jersey Harbor site-specific copper criteria study. Science Applications International Corporation. Final Report EPA Contract No. 68-C8-0066. Work Assignment C-4-94.

S.R. Hansen & Associates. 1992. Development of a site-specific criterion for copper for San Francisco Bay--Final Report. Prepared for California Regional Water Quality Control Board, Oakland, CA. October.

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ToxScan. 1991a. Results of provision E5F spiked metals toxicity testing--14 to 21 February 1991. Prepared for Kinnetic Laboratories, Inc. for "Site-Specific Water Quality

Objectives for South San Francisco Bay" report by Larry Walker Associates and Kinnetic Laboratories under subcontract to CH2M Hill. April.

ToxScan. 1991b Results of provision E5F spiked metals toxicity testing--27 February to 6 March 1991. Prepared for Kinnetic Laboratories, Inc. for "Site-Specific Water Quality Objectives for South San Francisco Bay" report by Larry Walker Associates and Kinnetic Laboratories under subcontract to CH2M Hill. Revised July.

ToxScan. 1991c Results of provision E5F spiked metals toxicity testing--2 to 9 April 1991. Prepared for Kinnetic Laboratories, Inc. for "Site-Specific Water Quality Objectives for South San Francisco Bay" report by Larry Walker Associates and Kinnetic Laboratories under subcontract to CH2M Hill. Revised July.

U.S. EPA. 1985. Ambient water quality criteria for copper - 1984. EPA 440/5-84-031. National Technical Information Service. PB85-227023.

Table A1. New Acute Values for Saltwater Copper Criteria Addendum.

Species	Duration (hr)	Chemical	Method[a]	Salinity/ Temp.[b]	LC_{50}, EC_{50} IC_{50} (μg/L)	Nominal, Total or Dissolved	Reference
Polychaete, *Nereis virens*	96	Copper citrate	SM	–/14.4 to 20	>249	Total	Raymont & Shields, 1963
Blue mussel, *Mytilus edulis*	48	Copper chloride	SM	30/16	12.5	Dissolved	SAIC, 1993
Blue mussel, *Mytilus edulis*	48	Copper chloride	SM	30/16	14.1	Dissolved	SAIC, 1993
Blue mussel, *Mytilus edulis*	48	Copper chloride	SM	30/16	11.3	Dissolved	SAIC, 1993
Blue mussel, *Mytilus edulis*	48	Copper chloride	SM	30/16	11.9	Dissolved	SAIC, 1993
Blue mussel, *Mytilus edulis*	48	Copper sulfate	SM	27/--	5.787[c]	Dissolved	ToxScan, 1991a
Blue mussel, *Mytilus edulis*	48	Copper sulfate	SM	28/--	8.889[c]	Dissolved	ToxScan, 1991b
Blue mussel, *Mytilus edulis*	48	Copper sulfate	SM	26/--	6.278[c]	Dissolved	ToxScan, 1991c
Blue mussel, *Mytilus edulis*	48	Copper sulfate	SU	33/--	7.21[d]	Nominal	ToxScan, 1991a
Blue mussel, *Mytilus edulis*	48	Copper sulfate	SU	32/--	6.40[d]	Nominal	ToxScan, 1991b
Blue mussel, *Mytilus edulis*	48	Copper sulfate	SU	32/--	5.84[d]	Nominal	ToxScan, 1991c
Pacific oyster, *Crassostrea gigas*	48	Copper chloride	SM	30/20	12.06	Total	Knezovich, et al., 1981; Harrison, et al., 1981
Pacific oyster, *Crassostrea gigas*	48	not stated	SM	33/16	15.78[e]	Dissolved	S.R. Hansen & Associates, 1992
Pacific oyster, *Crassostrea gigas*	48	not stated	SM	33/16	26.66[e]	Dissolved	S.R. Hansen & Associates, 1992

Species	Duration (hr)	Chemical	Method[a]	Salinity/ Temp.[b]	LC_{50}, EC_{50} IC_{50} (µg/L)	Nominal, Total or Dissolved	Reference
Pacific oyster, *Crassostrea gigas*	48	not stated	SM	33/16	16.17[e]	Dissolved	S.R. Hansen & Associates, 1992
Pacific oyster, *Crassostrea gigas*	48	not stated	SM	33/16	27.02[e]	Dissolved	S.R. Hansen & Associates, 1992
Pacific oyster, *Crassostrea gigas*	48	not stated	SM	34/16	17.54[e]	Dissolved	S.R. Hansen & Associates, 1992
Coot clam, *Mulinia lateralis*	48	Copper chloride	SM	30/20	21.0	Dissolved	SAIC, 1993
Coot clam, *Mulinia lateralis*	48	Copper chloride	SM	30/20	19.3	Dissolved	SAIC, 1993
Coot clam, *Mulinia lateralis*	48	Copper chloride	SM	30/20	14.9	Dissolved	SAIC, 1993
Coot clam, *Mulinia lateralis*	48	Copper chloride	SM	30/20	17.3	Dissolved	SAIC, 1993
Coot clam, *Mulinia lateralis*	48	Copper chloride	SM	30/20	16.9	Dissolved	SAIC, 1993
Coot clam, *Mulinia lateralis*	48	Copper chloride	SM	30/20	17.4	Dissolved	SAIC, 1993
Copepod, *Tigriopus californica*	96	Copper nitrate	SU	35/16	229	Nominal	O'Brien, et al., 1988
Copepod, *Tigriopus californica*	96	Copper nitrate	SU	35/16	76.2	Nominal	O'Brien, et al., 1988
Copepod, *Tigriopus californica*	96	Copper nitrate	SU	35/16	19.1	Nominal	O'Brien, et al., 1988
Copepod, *Tigriopus californica*	96	Copper nitrate	SU	35/16	159	Nominal	O'Brien, et al., 1988
Copepod, *Tigriopus californica*	96	Copper nitrate	SU	35/16	184	Nominal	O'Brien, et al., 1988

Species	Duration (hr)	Chemical	Method[a]	Salinity/ Temp.[b]	LC_{50}, EC_{50} IC_{50} (μg/L)	Nominal, Total or Dissolved	Reference
Copepod, *Tigriopus californica*	96	Copper nitrate	SU	35/16	261	Nominal	O'Brien, et al., 1988
Copepod, *Tigriopus californica*	96	Copper nitrate	SU	35/16	305	Nominal	O'Brien, et al., 1988
Copepod, *Tigriopus californica*	96	Copper nitrate	SU	35/16	375	Nominal	O'Brien, et al., 1988
Copepod, *Tigriopus californica*	96	Copper nitrate	SU	35/16	496	Nominal	O'Brien, et al., 1988
Copepod, *Tigriopus californica*	96	Copper nitrate	SU	35/16	413	Nominal	O'Brien, et al., 1988
Copepod, *Tigriopus californica*	96	Copper nitrate	SU	35/16	394	Nominal	O'Brien, et al., 1988
Copepod, *Tigriopus californica*	96	Copper nitrate	SU	35/16	394	Nominal	O'Brien, et al., 1988
Copepod, *Tigriopus californica*	96	Copper nitrate	SU	35/16	762	Nominal	O'Brien, et al., 1988
Mysid shrimp, *Mysidopsis bahia*	96	Copper chloride	RM	30/20	164	Dissolved	SAIC, 1993
Sea urchin, *Arbacia punctulata*	48	Copper chloride	SM	30/20	21.4	Dissolved	SAIC, 1993
Sheepshead minnow, *Cyprinodon variegatus*	96	Copper chloride	RM	30/25	368	Total	Hughes, et al.,1989
Mummichog, *Fundulus heteroclitus*	96	Copper sulfate	SU	5.5/20	3,100	Nominal	Dorfman, 1977
Mummichog, *Fundulus heteroclitus*	96	Copper sulfate	SU	23.6/20	2,000	Nominal	Dorfman, 1977
Mummichog, *Fundulus heteroclitus*	96	Copper chloride	SU	6.1/20	2,300	Nominal	Dorfman, 1977

Species	Duration (hr)	Chemical	Method[a]	Salinity/ Temp.[b]	LC_{50}, EC_{50} IC_{50} (µg/L)	Nominal, Total or Dissolved	Reference
Mummichog, *Fundulus heteroclitus*	96	Copper chloride	SU	24/20	400	Nominal	Dorfman, 1977
Inland silverside, *Menidia beryllina*	96	Copper sulfate	SM	--/--	115.4	Dissolved	ToxScan, 1991a
Inland silverside, *Menidia beryllina*	96	Copper sulfate	SM	--/--	96.5	Dissolved	ToxScan, 1991b
Inland silverside, *Menidia beryllina*	96	Copper sulfate	SM	--/--	123.0	Dissolved	ToxScan, 1991c
Topsmelt, *Atherinops affinis*	96	Copper chloride	SU	33/21	288	Nominal	Anderson, et al., 1991
Topsmelt, *Atherinops affinis*	96	Copper chloride	SU	33/21	212	Nominal	Anderson, et al., 1991
Topsmelt, *Atherinops affinis*	96	Copper chloride	SU	33/21	235	Nominal	Anderson, et al., 1991

[a] S=static; R=renewal; F=flow-through; U=unmeasured; M=measured

[b] Salinity expressed as g/L; temperature as °C

[c] IC_{50} recalculated from author's data based on # normal larvae/ml. Measured concentrations in two unmeasured treatments were determined from dissolved-to-nominal ratios from the measured treatments.

[d] Nominal data not used in the calculation of the SMAV for *Mytilus* because other measured data are available for this species.

[e] Dissolved IC_{50} values recalculated from author's data using measured copper concentrations in controls. Measured concentrations in several unmeasured treatments were determined from dissolved-to-nominal ratios from the available measured treatments.

Table A2. New Chronic Values for Saltwater copper Criteria Addendum

There are no new marine chronic values.

Table A3. Ranked Genus Mean Acute Values for saltwater copper criteria addendum. All copper concentrations are dissolved. If measured dissolved concentrations were not available from the original data, then nominal or measured total concentrations were converted to dissolved using the 0.90 or 0.83 ratios, respectively, from the Hudson site-specific study (SAIC, 1993).

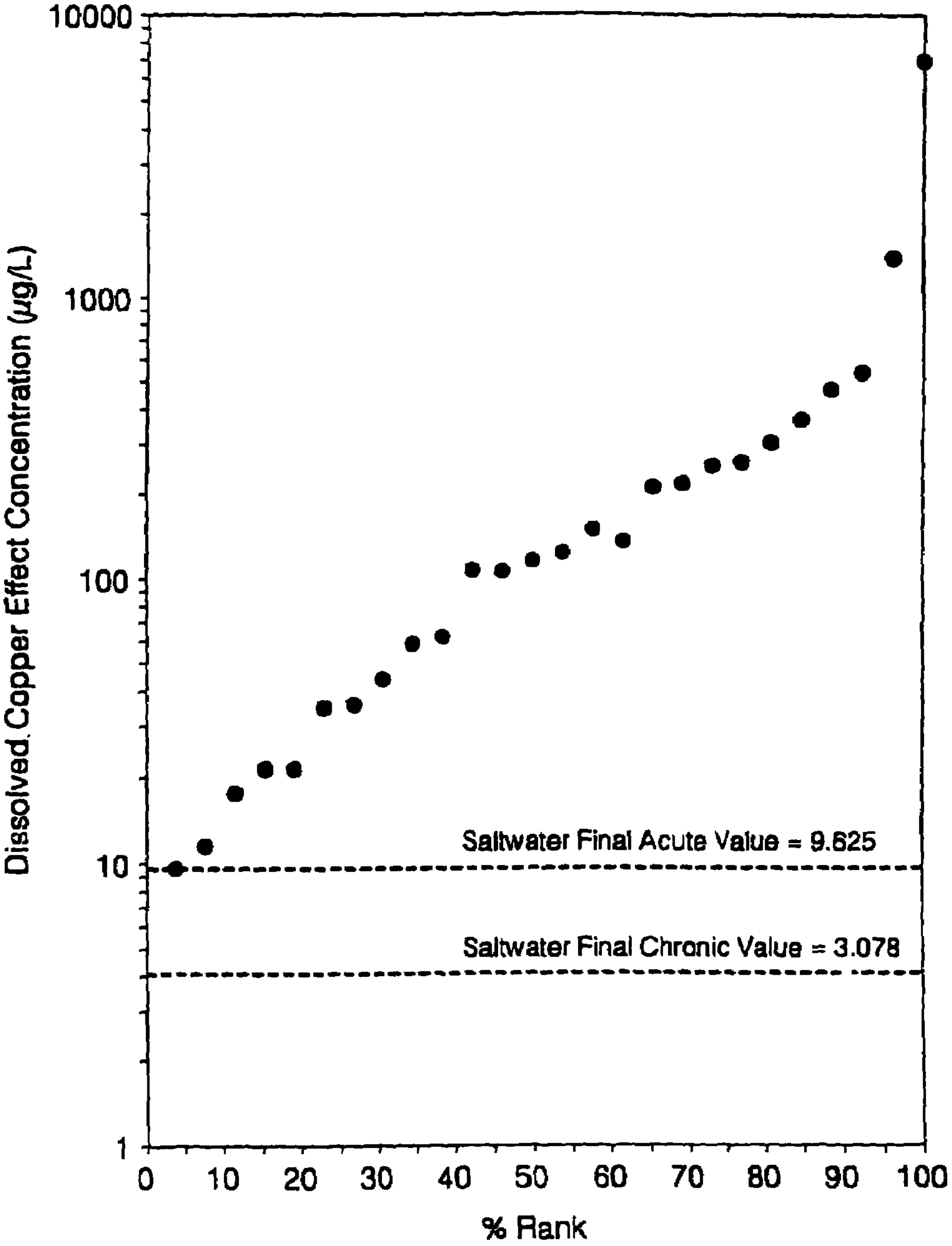
	Genus Mean Acute Value		Species Mean Acute Value	Species Mean Acute-Chronic
26	6925	Common rangia, *Rangia cuneata*	6925	
25	1391	Mummichog, *Fundulus heteroclitus*	1391	
24	540	Green crab, *Carcinus maenus*	540	
23	473.4	Copepod, *Eurytemora affinis*	473.4	
22	370.5	Florida pompano, *Trachinotus carolinus*	370.5	
21	305.4	Sheepshead, *Cyprinodon variegatus*	305.4	
20	>260.1	Polychaete worm, *Nereis diversicolor*	327.4	
		Polychaete worm, *Nereis virens*	>206.7	
19	252	Spot, *Leiostomus xanthurus*	252	
18	218.7	Topsmelt, *Atherinops affinis*	218.7	
17	212.4	Copepod, *Tigriopus californica*	212.4	
16	135.5	Mysid, *Mysidopsis bahia*	157.0	3.346
		Mysid, *Mysidopsis bigelowi*	117.0	
15	150.6	Polychaete worm, *Neanthes arenaceodentata*	150.6	
14	124.2	Copepod, *Pseudolaptomus coronatus*	124.2	
13	116.3	Atlantic silverside, *Menidia menidia*	112.5	

Table 3 for Saltwater Copper Criteria Addendum, Continued

	Genus Mean Acute Value		Species Mean Acute Value	Species Mean Acute-Chronic
		Tidewater silverside, *Menidia peninusulae*	126	
		Inland silverside, *Menidia beryllina*	111.1	
12	107.0	Winter flounder, *Pseudopleuronectes americanus*	107.0	
11	108	Polychaete worm, *Phyllodoce maculata*	108	
10	62.35	American lobster, *Homarus americanus*	62.35	
9	59.04	Black abalone, *Haliotis cracherodil*	45	
		Red abalone, *Haliotis rutescens*	77.47	
8	44.1	Dungeness crab, *Cancer magister*	44.1	
7	35.97	Copepod, *Acartia clausi*	46.8	
		Copepod, *Acartia tonsa*	27.65	
6	35.1	Soft-shell clam, *Mya arenaria*	35.1	
5	21.4	Sea urchin, *Arbacia punctulata*	21.4	
4	21.4	Pacific oyster, *Crassostrea gigas*	17.84	
		Eastern oyster, *Crassostrea virginica*	25.67	
3	17.70	Coot clam, *Mulinia lateralis*	17.70	
2	11.56	Summer flounder, *Paralichthys dentatus*	11.56	
1	9.625	Blue mussel, *Mytilus edulis*	9.625	

APPENDIX A.

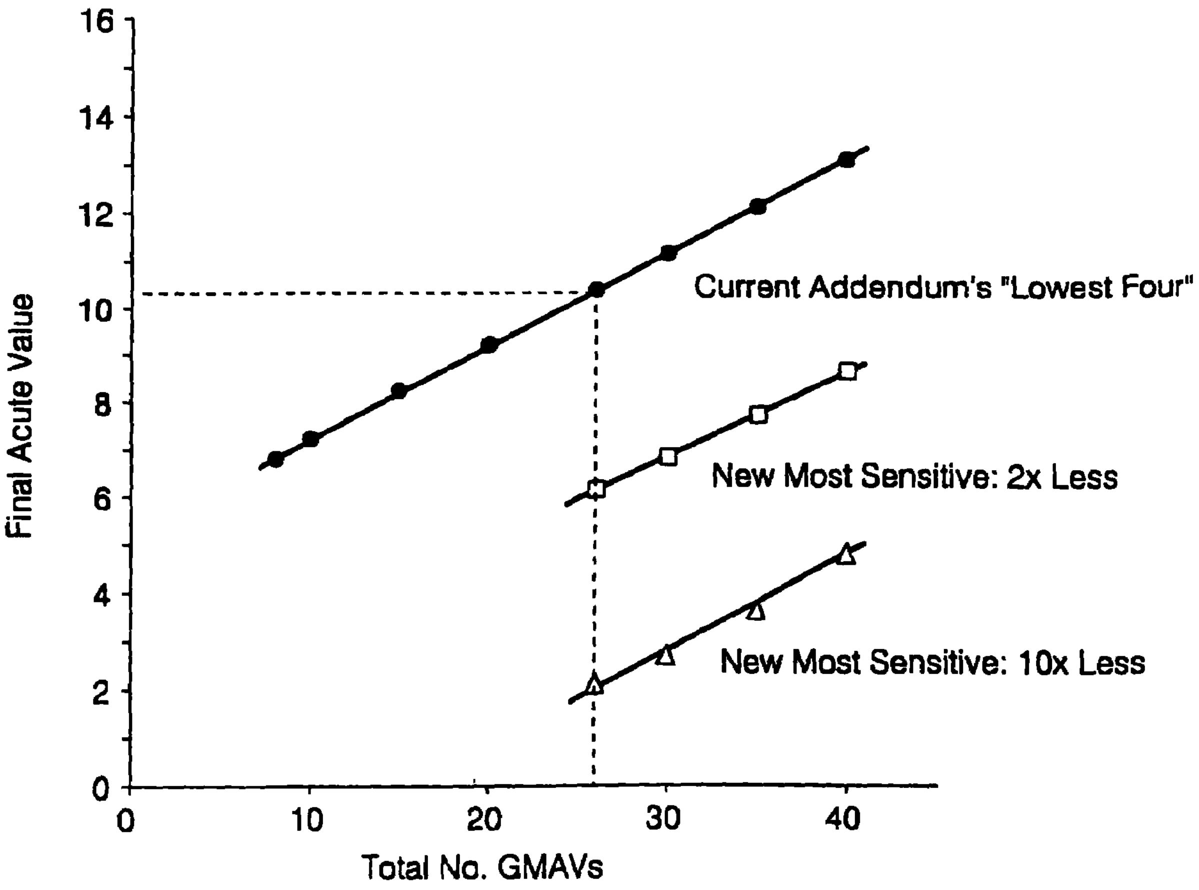
Plot of Dissolved Copper Effect Verses Percentage Rank for Genus Mean Acute Values from Table A3.



Ranked Summary of Dissolved Copper GMAVs

APPENDIX B.

Plot of Final Acute Value verses the total number of GMAVs. The solid circles represent how the FAV would change if additional GMAVs were found, but none of them were more sensitive than the most sensitive four GMAVs. The open squares represent how the FAV would change if additional data were found and a new most sensitive GMAV was found that was one half the value of the current most sensitive GMAV. The open triangles are the same thing, except the new most sensitive value is one tenth of the current most sensitive GMAV.



16
14
12
10
8
6
4
2
0
Final Acute Value
0
10
20
30
40
Total No. GMAVs
Current Addendum's "Lowest Four"
New Most Sensitive: 2x Less
New Most Sensitive: 10x Less

APPENDIX C.

List of References Not Cited in the 1985 Copper Criteria Document that Contained Unused Data

References for Data Not Used in the Saltwater Copper Criteria Addendum

Brown, B. and M. Ahsanullah. 1971. Effect of heavy metals on mortality and growth. Mar. Poll. bull. 2:182-187.

(Non-resident species)

Eisler, R. and G.R. Gardner. 1973. Acute toxicology to an estuarine teleost of mixtures of cadmium, copper and zinc salts. J. Fish. Biol. 5:131-142.

(The copper values are nominal and the authors indicate that an insoluble precipitate formed in the test medium. Thus, the nominal concentrations are unreliable.)

Lang, W.H., D.C. Miller, P.J. Ritacco and M. Marcy. 1981. The effect of copper and cadmium on the behavior and development of barnacle larvae. In: F.J. Vernberg, A. Calabrese, F.P. Thurberg and W.B. Vernberg. *Biological Monitoring of Marine Pollutants.* pp. 165-203.

(Larvae were fed during the test. In addition, the food was an algal diet that contained the chelator EDTA in the medium.)

Saliba, L.G. and M. Ahsanullah. 1973. Acclimation and tolerance of *Artemia salina* and *Ophryotrocha labronica* to copper sulfate. Marine Biology. 23:297-302.

(Insufficient data to determine a 96-hr LC50 and non-resident species [*O. labronica*])

Shackley, S.E., P.E. King and S.M. Gordon. 1981. Vitellogenesis and trace metals in marine teleosts. J. Fish Biol. 18:349-352.

(No survival data.)

Wisely, B. and R.A.P. Blick. 1967. Mortality of marine invertebrate larvae in mercury, copper and zinc solutions. Aust. J. Mar. Freshwat. Res. 18:63-72.

(Exposure durations were only a few hours.)

APPENDIX D.

Options for Deriving the Final Chronic Value for the Saltwater Copper Criterion

Background

This appendix provides an explanation of options that were considered for deriving the chronic, saltwater criterion for copper. It examines: (1) the approach used to derive the 1985 national copper criterion; (2) developments since 1985 regarding the use of 2.0 as the acute-chronic ratio for embryo-larval tests with molluscs; (3) alternative approaches to deriving a chronic criterion for copper.

Aquatic Life Criteria Guidelines Approach for Deriving the Final Chronic Value

For deriving a final chronic value (FCV), the aquatic life criteria guidelines (hereafter referred to as "the Guidelines"; Stephan et al., 1985) require a minimum database of three chronic tests with a fish and an invertebrate using both freshwater and saltwater organisms. Full life cycle chronic tests are required, except for fish were partial life cycle and early life stage tests are acceptable as surrogates. The Guidelines recommend at least eight methods (p. 36-47) as acceptable for obtaining a final chronic value, which is intended to provide protection from the chronic effects of a substance on aquatic life. These methods include deriving a final acute-chronic ratio (FACR) to be used to adjust the final acute value (FAV) to obtain a FCV, or other methods to derive a FCV. The methods are intended to be selected with judgement to estimate the FCV directly from chronic toxicity data, or indirectly, using the most appropriate acute-chronic ratio (ACR) at the FAV concentration. A summary of the eight methods is provided below.

Method 1. A FCV can be obtained directly using the equation for deriving the FAV, providing that eight families have been tested chronically (e.g., as performed for the freshwater FCV for cadmium). All other methods first require derivation of a final cute-chronic ratio (FACR) and division of this value into the FAV.

Method 2. When the species mean ACR seems to increase or decrease as the species mean acute value (SMAV) increases, the FACR should be calculated as the geometric mean of the ACRs for species whose SMAVs are close to the FAV.

Method 3. Similarly, the FACR is calculated as the geometric mean of all ACRs if no major trend is apparent for a number of species whose ACRs are within a factor of ten. Methods 2 and 3 have been used most often for deriving the FCV. Examples include the derivation of criteria for arsenic III, cadmium (SW), chlorine, chlorpyrifos, chromium VI, cyanide (FW), endosulfan, hexachlorocyclohexane (FW), lead (SW), nickel (SW), parathion (FW), pentachlorophenol (SW), selenium (SW), and zinc (SW).

Method 4. When acute tests used to derive the FAV are from embryo larval tests with molluscs, and a limited number of other taxa, it has been considered appropriate to assume that the ACR is 2.0; thus the CMC equals the CCC [e.g., copper (SW), cyanide (SW)].

Method 5. When a species mean chronic value from a test with measured concentrations for a commercially or recreationally-important species is less than the FCV derived using other methods, the FCV is lowered to protect that species [e g., ammonia (FW)].

Method 6. When ACRs are the same across a water quality characteristic and the CMC is water quality dependant, or if water quality relationship is unique for chronic toxicity and similar across species, develop a water quality-dependant final chronic equation. Examples include: ammonia (FW), chromium III (FW), copper (FW), nickel (FW), pentachlorophenol (FW), and zinc (FW).

Method 7. Method 7 recommends the use of appropriate field data for setting the FCV [e.g., selenium (FW)].

Method 8. The final method recommended by the Guidelines is the use of sound scientific evidence over the Guidelines rules to develop criteria.

The preceding demonstrates that many procedures are acceptable and, with judgement, have been used to derive final chronic values. It might also be noted that for some substances, considerations of bioaccumulation, plant, and other data have been used to derive a CCC that is lower than the FCV.

Derivation of the 1985 Saltwater Copper Criterion

The 1985 saltwater chronic criterion utilized Method 4 because mollusc embryo larval tests were represented in three of the four most sensitive genus mean acute values (GMAVs) used to calculate the FAV. The copper criterion was not lowered to protect commercially important molluscs because test concentrations were not measured. Setting the FACR to 2.0, per Method 4, assumed that the mollusc embryo larval tests, in absence of a chronic database from mollusc life cycle tests, was a surrogate for a life cycle test. The Guidelines' authors believed the basis for this was the comparisons between early life stage tests with fishes (where embryos and newly hatched larvae are exposed) and entire life cycle tests with fishes. Macek and Sleight, III (1977), McKim (1977) and Hansen (1984) observed a general one-to-one relationship between these two tests. Just prior to publication of the copper criterion, the first life cycle toxicity tests with a mollusc (*Crepidula fornicata*) was developed (Nelson et al., 1983) and results with silver confirmed that mollusc larvae were uniquely sensitive. Unfortunately, an ACR could not be obtained because an embryo larval acute test was not conducted.

Developments Since 1985 Regarding an ACR of 2.0 for Copper

Concern in the late 1980s about the observed effects of tributyltin (TBT) on bivalve and gastropod molluscs in the field, at concentrations acceptable in standard laboratory studies, stimulated development of costly, labor-intensive, high risk, long-term exposures of molluscs. The TBT water quality criteria document (U.S. EPA 1993) contains results from long-term (14 to 49-day duration) tests with hard clams, Pacific oysters and European oysters that began with larvae or spat (as shown in Table D-1). Acute values from the TBT water quality criteria document for embryo larval tests with hard clams (1.36 μg/L - mean of two values, 1.13 μg/L and 1.65 μg/L) and with Pacific oysters (1.56 μg/L) are listed in Table D-1. Because species within a genus generally have acute values within a factor of two, it may be reasonable to assume that the acute value for European oysters would also be about 1 μg/L.

If Method 4 using the ACR of 2.0 were generically appropriate to derive chronically acceptable concentrations for molluscs, no chronic effects would be expected at concentrations less than about 0.5 μg/L. However, this is not what actual data show. Growth of hard clams was reduced at concentrations between 0.01 and 0.5 μg TBT/L, for Pacific oysters at 0.02 to 0.2 μg/L, and for European oysters at 0.02 to 2.0 μg/L. Shell thickening, a TBT-specific response, was observed at 0.02-2.0 μg/L and 0.01 to 0.05 μg/L in two laboratory studies and about 0.018 to 0.60 μg/L in the field. Mortality of Pacific oysters occurred at 0.24 μg/L. From these data, it is concluded that an across-chemical, generic ACR of 2.0 does not apply to embryo larval tests with molluscs and that ACRs for molluscs, like those for the invertebrates and fishes, are likely to be chemical specific. Although a search for comparable data for other pollutants might be of interest, the available data indicate that other methods for deriving the FCV (as described previously) should now be chosen for derivation of the copper criterion.

Alternative Approaches to Deriving Copper Criterion

In lieu of using an assumed mollusc ACR of 2.0, two general approaches were considered. These approaches are described below as "Approach A" and "Approach B".

Approach A (Geometric Mean)

This approach involves calculating a geometric mean FACR using Methods 2 and 3 described previously. For this approach, several options are available for deriving the FACR. Each approach has strengths and weaknesses. None is wrong.

Two freshwater species have acute values within a factor of two of the FAV and their ACRs differ by only a factor of 1.4 (Daphnia magna, ACR = 2.418 and Gammarus pseudolimnaeus, ACR = 3.297). The 1985 freshwater water quality criterion for copper used a geometric mean FACR of 2.823 from the acutely most sensitive daphnid and amphipod. This value, if used to derive the FACR for saltwater, has merit because it uses values closest to the freshwater copper FAV and was used to derive the freshwater FCV. Consequently, the New York Harbor site-specific criteria development used this approach.

The inclusion of a third ACR, 3.585 for the snail, Physa, in the calculation of the FACR has merit because this is the only datum for a sensitive mollusc from the database of species mean ACRs for copper. Inclusion of this ACR may be desirable because molluscs are among the most acutely sensitive saltwater species, thus, acute-to-chronic extrapolation is important for molluscs. Further, test-to-test variability of acute and chronic toxicity values is commonly a factor of two. Therefore, these three species could be viewed as having similar sensitivities and thus not subject to concerns about acute sensitivity-dependant ACRs.

An additional option in this general approach is to include the ACR for the mysid (Mysidopsis bahia) with the above freshwater species ACRs. Mysids are not among those saltwater species most sensitive to copper. The saltwater copper FAV in the 1985 criteria document is 5.8 µg/L and the mysid acute value is 181 µg/L; with mysids being ranked 14 out of 20 saltwater genera tested against copper. As a general rule, regardless of acute sensitivity rank, acute-chronic ratios for mysids are low, being similar to those of the most acutely sensitive freshwater and saltwater species whose ACRs have been used to derive the FACR (Table D-2). Regardless of sensitivity of mysids, for metals the average ratio of the mysid ACR to saltwater FACR is less than 1.0 (mean = 0.84, range 0.59 to 1.74); for all chemicals, the mean ratio is 0.73 (range 0.18 to 1.74). These data support the use of ACRs for mysids to calculate FACRs even when mysids are not particularly acutely sensitive.

Why does this appear to be true? It is possible that while some substances may have true species acute sensitivity-dependant ACRs, many are a function of the insolubility of substances in acute toxicity tests raising the acute values for insensitive species, a problem not occurring in chronic tests. Also, large individuals of juvenile life stages of some species commonly provide large acute values that result in large ACRs. Large acute values occur because incipient acute values were not achieved in 48 or 96-hour tests. Both conditions will increase ACRs for insensitive species. However, if small, early life stages had been tested, it is possible that ACRs, and the sensitivity-dependant ACRs, would be lower. In contrast, acute tests with mysids typically begin with small, newly released juveniles that are relatively sensitive. Therefore, ACRs for mysids are typically small, as if they were among the most acutely sensitive species.

For copper, the ACR for mysids of 3.346 is between those of the three most sensitive freshwater species (2.418 to 3.585). If all four ACRs (3 freshwater and 1 saltwater) are used, then the FACR is 3.127 as shown in Table D-3.

Approach B (Regression)

For this approach, the FACR would be derived using regression analyses of the log of species mean acute values and log of species mean ACRs from Table 3 of the copper water quality criteria document. While this method is not part of the National Guidelines, it is somewhat related to Method 1 (which uses FAV equations applied to species mean chronic values) and is allowed by Method 8.

Regression analyses used the log SMAVs and log ACRs because r^2 values were greatest and plots were linear. Mysid data were excluded as inappropriate to the observed freshwater slopes. Databases used include: (1) all freshwater data from table 3 in the copper water quality criteria document, (2) data from table 3 where SMAVs were less than 180 μg/L, and (3) data from table 3 where SMAVs were within a factor of two of the FAV. Relevant data used for these analyses (including: figures showing regression plots and lines of best fit; a table showing r^2, "F" probability, ACRs at the FAV of 18.6 μg/L and confidence limits on the calculated ACR) are provided in Table D-3. The ACR at the freshwater FAV of 18.6 μg/L, not at the recalculated saltwater

FAV or the 1985 saltwater FAV, is appropriate for adjusting the fifth percentile acute value to a chronically acceptable concentration.

The calculated ACRs from the regressions are similar (2.56 to 2.72) regardless of the data set used (Table D-3). Regressions based on fewer data points had less statistical significance and more uncertainty than the regression based on all the data.

The tabulated uncertainties in the FACR estimates appear to be less for the geometric mean-based estimates (Approach A) than for the regression-based estimates (Approach B). However, the uncertainty bands for the Approach A and Approach B are not directly comparable, because the Approach A simply assumes that the geometric mean ACR is the same as the ACR for the 5th percentile genus, while Approach B makes a statistical projection of what the ACR for the 5th percentile genus might be.

There are some differences in the assumptions underlying Approaches A and B. Approach B (regression) assumes that a relationship exists between the SMAV and ACR throughout the range of SMAVs, as illustrated in the Figure D-1 graphs. Consequently, the relationship can be extrapolated to obtain the ACR at the FAV. In contrast, Approach A (geometric mean) assumes that a relationship exists between the SMAV and ACR only at the higher SMAVs, thereby justifying excluding ACRs for insensitive species. Approach A, however, might assume that the slopes shown in Figure D-1 would level off at low SMAVs, such that the ACRs corresponding to SMAVs slightly above the FAV would be unbiased indicators of the ACR at the FAV.

TABLE D-1. Compilation of Laboratory and Field Data on the Effects of Tributyltin on Saltwater Organisms at Concentrations Less Than the Final Chronic Value of 0.0485 µg/L

Species	Experimental Design$^{(a)}$	Acute Value (µg/L)$^{(b)}$	Concentration (µg/L)	Response	Reference
Hard clam, Mercenaria mercenaria (4 hr, larvae-metamorphosis)	R,M, 14-d duration, < 150 larvae/replicate, 3 reps. measured = 80-100% of nominal at 0-4 hr, 20-30% at t=24 hr	1.36 (EC_{50})	Nominal:		Laughlin et al., 1987; 1988
			Control	100% growth (valve length)	
			0.01-0.5:	~75%-22% growth (valve length)$^{(c)}$	
Pacific oyster, Crassostrea gigas (spat)	R,N, 48-d duration, 20 spat/treatment	1.56 (EC_{50})	Nominal:		Lawler and Aldrich, 1987
			Control		
			0.01-0.05	shell thickening	
			control	100% growth (valve length)	
			0.01-0.2	101% growth (valve length)	
			0.02-0.2	0-72% growth (valve length)$^{(c)}$	
Pacific oyster, Crassostrea gigas (spat)	R,N, 49-d duration, 0.7 to 0.9 g/spat	1.56 (EC_{50})	Nominal:		Thain et al., 1987
			Control - 0.002	no shell thickening	
			0.02-2.0	shell thickening proportional to concentration increase	
Pacific oyster, Crassostrea gigas (spat)	Field	1.56 (EC_{50})	Measured		Thain et al., 1987
			0.011-0.015	no shell thickening	
			~0.018-0.060	shell thickening & decreased meat weight	

TABLE D-1. Compilation of Laboratory and Field Data on the Effects of Tributyltin on Saltwater Organisms at Concentrations Less Than the Final Chronic Value of 0.0485 μg/L

Species	Experimental Design[(a)]	Acute Value (μg/L)[(b)]	Concentration (μg/L)	Response	Reference
Pacific oyster, Crassostrea gigas (larvae & spat)	R,M/N, 21-d duration, 75,000 larvae/rep.	1.56 (EC_{50})	Measured: 0.24, 0.29, 0.69	100% mortality by day 11	Springborn Bionomics Inc. 1984
			Nominal: control, 0.025, 0.05-0.8	mortality 86% at 0.025 ug/L; 100% at all higher concentrations	
European oyster, Ostrea edulis (spat)	R,N, 20-d duration, 50 spat/treatment	----	control 0.02-2.0	100% length 76-81% length[(c)]	Thain and Waldock, 1985
			control 0.02-2.0	202% weight gain 151-50% weight gain	

(a) R = renewal; F = flow-through; N = nominal; M = measured.

(b) Acute values from Table 1 of the TBT criteria document.

(c) Response is significantly different from the control.

TABLE D-2. Summary of Acute-Chronic Ratios for Selected Chemicals.

COMPOUND	SPECIES	GMA PERCENT (#)	ACR	FW FACR	SW FACR	METHOD FOR SALTWATER
Arsenic (III)	Jordanella floridae	64% (9)	4.862	3.083	3.083	Method 3: Four total ACR's available
	Pimephalea promolas	43% (6)	4.66			from Table 3 and all were used
	Daphnia magna	29% (4)	4.748			
	Mysidopsis bahia	36% (4)	1.994			
Cadmium	Mysidopsis bigelowi	3% (1)	15.4		9.105	Method 3: Ten total ACR's available
	Mysidopsis bahia	3% (1)	5.384			from Table 3 and two SW ACR's used
Chromium (VI)	Ceriodaphnia reticulata	11% (3)	1.13 *	2.917	43.28	Method 3: Ten total ACR's available
	Simocephalus serrulatus	7% (2)	2.055 *			from Table 3 and two SW ACR's used
	Simocephalus vetulus	7% (2)	5.267 *			
	Daphnia pulex	0.3% (1)	5.92 *			
	Neanthes arenaceodentata	14% (3)	121.8			
	Mysidopsis bahia	10% (2)	15.38			
Copper	Daphnia magna	5% (2)	2.418 *	2.823	2	Method 4: Ten total ACR's available
	Physa integra	17% (7)	3.585			from Table 3. Mysid ACR is 1.4 X
	Gammarus pseudolimnaeus	10% (4)	3.297 *			the lowest; 2.0 was used.
	Mysidopsis bahia	70% (14)	3.346			
Lead	Salmo gairdneri	40% (4)	61.97	51.29	51.29	Method 3: Four total ACR's available
	Salvelinus fontinalis	50% (5)	49.35			from Table 3 and all were used
	Daphnia magna	20%(2)	18.13			
	Mysidopsis bahia	73% (8)	124.8			
Mercury	Daphnia magna	4% (1)	4.498	3.731	3.731	Method 2: Three total ACR's available
	Mysidopsis bahia	3% (1)	3.095			from Table 3 and two were used
Nickel	Pimephales promelas	22% (4)	35.58	17.99	17.99	Method 3: Three total ACR's available
	Daphnia magna	6% (1)	29.86			from Table 3 and all were used
	Mysidopsis bahia	15% (3)	5.478			
Silver	Salmo gairdneri	61% (11)	33.29	15.7	15.7	Method 2: Four total ACR's available
	Pimephales promelas	50% (9)	13.66			from Table 3 and three were used
	Mysidopsis bahia	100% (9)	8.512			
Tributyltin	Daphnia magna	42% (5)	36.6	14.69	14.69	Method 3: Four total ACR's available
	Pimephales promelas	25% (3)	10.01			from Table 3 and all were used
	Eurytemora affinis	44% (11)	27.24			
	Acanthomysis sculpta	4% (1)	4.664			
Zinc	Salmo gairdneri	20% (7)	1.554	2.208	2.208	Method 2 :Seven total ACR's available
	Oncorhynchus tshawytscha	17% (6)	0.7027			from Table 3 and four were used
	Daphnia magna	11% (4)	7.26			
	Mysidopsis bahia	25% (7)	2.997			

TABLE D-2 (Continued).

COMPOUND	SPECIES	GMA PERCENT (#)	ACR	FW FACR	SW FACR	METHOD FOR SALTWATER
Chlorpyrifos	Menidia beryllina	58% (7)	3.614	4.064	4.064	Method 3: Eight total ACR's available
	Menidia menidia	58% (7)	3.352			from Table 3 and five SW ACR's used
	Menidia peninsulae	58% (7)	1.374			
	Leuresthes tenuis	50% (6)	5.212			
	Mysidopsis bahia	8% (1)	12.5			
Endosulfan	Daphnia magna	100% (10)	11	3.9	3.9	Method 3: Four total ACR's available
	Pimephale promelas	20% (2)	3			from Table 3 and all were used
	Cypriondon variegatus	58% (7)	2.4			
	Mysidopsis bahia	67% (8)	2.8			
Methyl Parathion	Mysidopsis bahia	10% (1)	3.818	5.113	5.113	Method 3: Three total ACR's available
	Ceriodaphnia dubia	8% (2)	2.243			from Table 3 and all were used
	Pimephales promelas	79% (19)	15.62			
Phananthrene	Mysidopsis bahia	9% (1)	3.334	4.739	4.739	Method 3: Three total ACR's available
	Oncorhynchus mykiss	25% (2)	7.905			from Table 3 and all were used
	Daphnia magna	63% (5)	4.038			
Phenol	Ceriodaphnia dubia	4% (1)	0.6498	2 **	2 **	Method 8: Two total ACR's available for
	Mysidopsis bahia	21% (3)	2.087			inverts from Table 3 and both used
Selenium (IV)	Mysidopsis bahia	33% (5)	7.085	8.314	8.314	Method 3: Nine total ACR's available
	Cyprinodon variegatus	67% (10)	10.96			from Table 3 and two SW ACR's used
	Pimephales promelas	14% (3)	6.881			
	Daphnia pulex	27% (6)	5.586			
	Daphnia magna	27% (6)	13.31			
Tetrachloroethylene	Pimephales promelas	60% (3)	16	19	19	Method 8: Two total ACR's available for
	Mysidopsis bahia	100% (1)	23			inverts from Table 3 and both used
Thallium	Mysidopsis bahia	45% (5)	17.76	6.557	6.557	Method 3: Three total ACR's available
	Ceriodaphnia dubia	20% (2)	2.421			from Table 3 and one SW ACR used
Toxaphene	Cyprinodon variegatus	27% (4)	1.54		2	Method 8: Five total ACR's available
	Mysidopsis bahia	47% (7)	1.132			from Table 3 and none were used
	Ictalurus punctatus	7% (2)	28			
	Pimephales promelas	46% (13)	196			
	Daphnia magna	57% (16)	109.1			

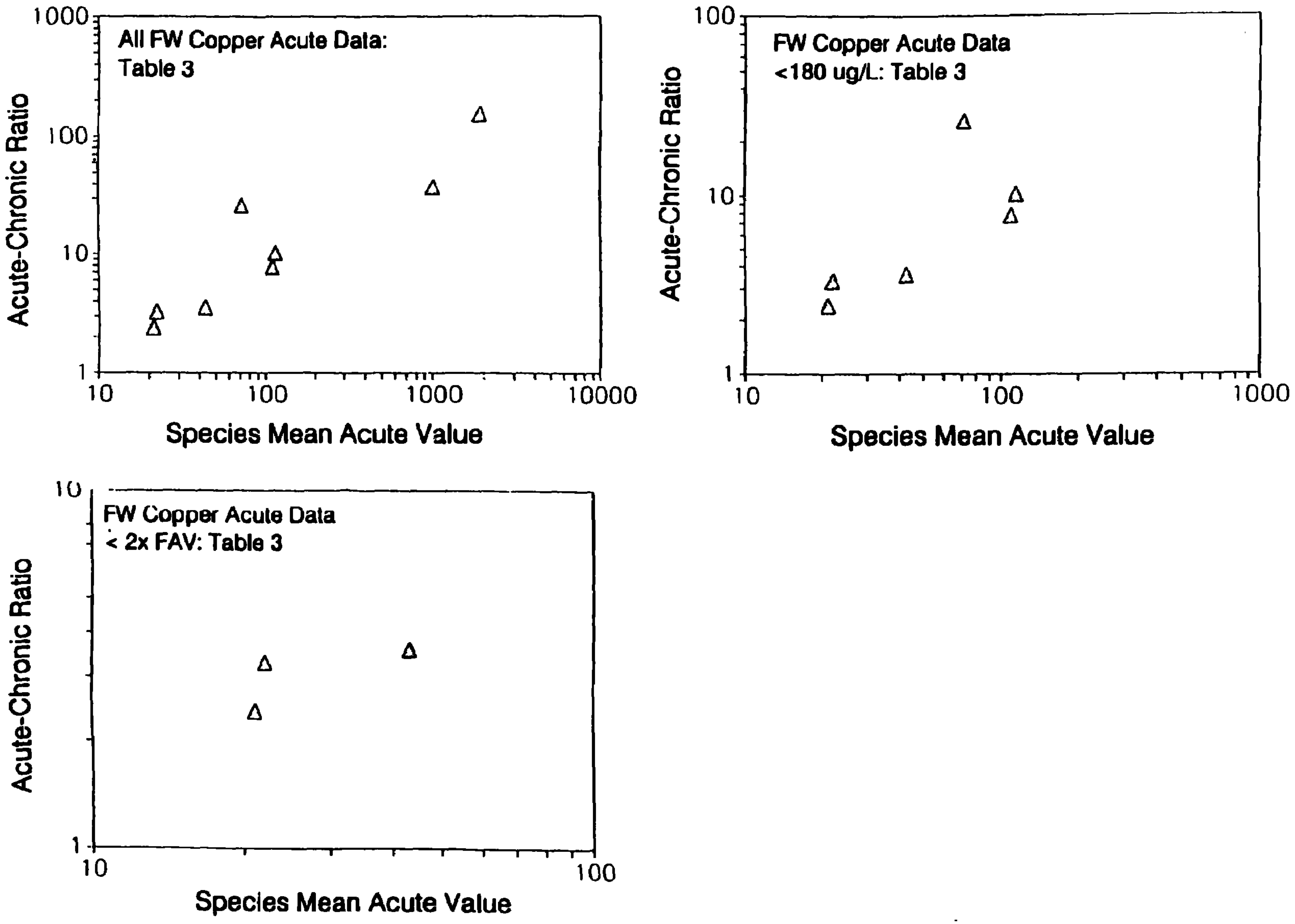
*Used only for FW FACR

** FACR for Invertebrates

Table D-3. Summary of Methods Considered For Deriving Acute-Chronic Ratios for Copper

Methods	r^2	F Probability	ACR at FAV of 18.6 μg/L	Lower 95% Confidence Interval	Upper 95% Confidence Interval	Range in 95% C.I.
Approach A (Geometric Mean Method)						
Gammarus, Daphnia, Physa & Mysidopsis	---	---	3.13	2.63	3.71	1.08
Gammarus, Daphnia & Mysidopsis	---	---	2.99	2.43	3.68	1.51
Gammarus, & Daphnia	---	---	2.82	2.08	3.83	1.75
Approach B (Regression Methods for Table 3 Freshwater Data)						
All ACRs	0.846	0.001	2.72	1.20	6.14	4.94
Acute values < 180 μg/L	0.561	0.087	2.56	0.46	7.58	6.72
Acute values within a factor or 2 of the FAV	0.495	0.503	2.66	1.02	6.95	5.93

Figure D-1. Regressions of Acute-Chronic Ratios with Freshwater Species Mean Acute Values for Copper



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