DEPARTMENT OF THE NAVY
OFFICE OF THE CHIEF OF NAVAL OPERATIONS
2000 NAVY PENTAGON
WASHINGTON, DC 20350-2000

IN REPLY REFER TO

5090
Ser N452/N4U732324
7 Apr 04

Water Docket
U.S. Environmental Protection Agency
Mail code: MC-4101T
1200 Pennsylvania Ave., NW
Washington, DC 20460
Attention: Docket ID No. OW-2003-0079

Dear Sir/Madam:

Subj: DRAFT AMBIENT WATER QUALITY CRITERIA FOR COPPER; NOTICE OF AVAILABILITY; 68 FR 75552; 31 DECEMBER 2003; DOCKET NUMBER OW-2003-0079

The Department of Defense (DoD) Clean Water Act Services Steering Committee, which represents the Departments of the Navy, Air Force, and Army, as well as several other Defense components and agencies, has reviewed and is providing comment on the Draft Ambient Water Quality Criteria for Copper, 68 FR 75552 (31 December 2003).

DoD recommends that EPA take into consideration the following enclosed comments regarding the scientific and technical merit of the proposed criteria: (1) develop copper bioavailability model (similar to biotic ligand model (BLM)) for seawater; (2) clarify the heavy use of South San Francisco Bay water-effect ratio (WER) study data in calculating the species mean acute value (SMAV); (3) include additional data on *Acartia tonsa* and *Crassostrea virginica*; (4) recalculate the SMAV for *Mytilus spp.*; (5) include data from additional dilution waters in genus mean acute value (GMAV) determination; (6) address issues associated with use of chronic tests for acute water quality criteria (WQC) development; (7) develop a broader data set for acute-to-chronic ratio (ACR) calculation; (8) provide a better description of the derivation of freshwater ambient water quality criteria using the BLM; (9) clarify the degree of lab analysis accuracy; and (10) explain the appropriate scenarios for applying the copper criteria.

In particular, DoD strongly encourages EPA to consider postponing the promulgation of a revised saltwater criterion

AVAILABILITY; 68 FR 75552; 31 DECEMBER 2003; DOCKET NUMBER OW-2003-0079

until the BLM or other bioavailability model for seawater is finalized and validated, as recommended in comment 1. Furthermore, DoD recognizes that water quality criteria are based solely on the factors listed in section 304(a) of the Clean Water Act, 33 U.S.C § 1314(a). Nevertheless, it is important that EPA recognize the economic and technical difficulties in achieving water quality standards. The promulgation of this low criterion (1.9 µg/L) would significantly increase the cost of implementation at many DoD facilities.

Thank you for providing an opportunity to comment on the draft criteria for copper. If you have any questions, our point of contact for this issue is Mr. Kent Avery at (202) 685-9322, or email at kent.avery@navy.mil.

Sincerely,

James G. Rudroff

for

LOUIS F. MAIURI
Afloat/Shore Environmental
Systems Integration Branch
Environmental Readiness Division

Enclosure (1): DoD CWASSC Comments on the Draft Ambient Water Quality Criteria for Copper

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Department of Defense (DoD) Clean Water Act Services Steering Committee (CWASSC)

Comments on the
Draft Ambient Water Quality Criteria for Copper; Notice of Availability
68 FR 75552 (31 December 2003)

1. Develop a copper bioavailability model (similar to biotic ligand model (BLM)) for seawater

Comment: For the development of copper criterion for the protection of aquatic life in freshwater, EPA has proposed to utilize the BLM (DiToro *et al.*, 2001; U.S. EPA, 2003) instead of the empirical relationships with water-hardness. This is done because it is now well known that complexing ligands in aquatic systems (both fresh and marine) reduce the toxicity of copper to the most sensitive organisms and life stages. The implementation of the BLM (a bioavailability model) to seawater could be accelerated by recent case studies and characterization of relevant environmental parameters in harbors and estuaries. (Blake *et al.*, 2004, Chadwick *et al.*, 2004, Rivera-Duarte *et al.*, 2004; Rosen *et al.*, 2004).

Discussion: In the BLM, the toxicity of copper is related to the metal bound to a biochemical site (biotic ligand) on the organism. This toxic fraction of copper is also related to the concentrations in the water of total dissolved copper, copper ion, and complexing ligands (Allen and Hansen, 1996). The complexing ligands compete with the biotic ligand for copper, other metals, and cations in the water. This competition generally keeps the concentration of bioavailable free copper ions below the toxic threshold except under heavy loading conditions. The use of the BLM, or any validated copper bioavailability model, improves the characterization and regulation of the toxic effects of copper. These methods provide a scientifically valid approach for the protection of aquatic life by incorporating environmental conditions more representative of each specific body of freshwater. Therefore, by measuring a fairly low number of environmental parameters (i.e., pH, hardness, alkalinity, dissolved organic carbon (DOC), total dissolved metal concentration, major cations (Ca2+, Mg2+, Na+, K+) and major anions (SO42-, Cl-)) in the freshwater, it is possible to estimate the specific critical concentration that will be toxic to the organism.

Seawater model. In comparison with their variability in freshwater, most of the parameters used for the calculation of the BLM are at near constant concentration in seawater. Major cations and anions in seawater are present at nearly constant ratios relative to the salinity of the water (Chester, 1990). This should make the implementation of the BLM to seawater relatively easy, as the concentrations of major cations and anions could be calculated from salinity and alkalinity measurements. In addition, the equilibrium between the biotic ligand and the organic ligands (DOC, total organic carbon (TOC)) will be affected in a relatively constant fashion by these major cations and anions. Therefore, the critical concentration of copper activity in seawater should be mainly affected by the concentration of organic ligands and by the total dissolved concentration of copper.

The only parameters that will be difficult to characterize are the binding strength and capacity of the biotic ligand. For freshwater, this was done by measuring the concentration of metal at the fish gill membrane and by calibrating the binding strength for each of the different competing fractions (i.e.,

metal, major cations and anions, hydrogen ion (pH), etc.). In seawater, as regulation is primarily driven by the response of larval stages of mussels, the binding strength and capacity should be measured in these larvae. A recent marine BLM case study has been conducted in San Francisco Bay using toxicity data from a water-effect ratio (WER) study with *Mytilus spp.* larval development (Santore, *et al.*, 2003). In this study, the BLM predicted WERs were compared to measured WERs in a transect from the Golden Gate Bridge to the south bay. The modeled values closely predicted the measured values with WERs varying from a ratio of about 2 to 4 based primarily on the changes in dissolved organic carbon. Also, the data to demonstrate the efficacy of the BLM in seawater is largely available, and a major effort in San Diego Bay has been conducted to characterize and model copper speciation, distribution, and toxicity in relationship to complexing ligands. This effort included the measurement of a series of environmental parameters that are needed for the implementation of the BLM, including total and total dissolved copper, DOC, pH, salinity, alkalinity, free copper ion, and toxicity. These data are in the process of being published (Blake *et al.*, 2004, Chadwick *et al.*, 2004, Rivera-Duarte *et al.*, 2004; Rosen *et al.*, 2004). These parameters will be provided with the information for additional case studies to further the BLM implementation for seawater, as they are made available to the personnel from HydroQual, the main developers of the BLM. The data to demonstrate the efficacy of the BLM in seawater is largely available. At this time, it would not be prudent for EPA to promulgate a highly conservative saltwater criterion.

Recommendation: It is recommended that EPA postpone promulgation of a revised saltwater criterion at this time and wait until the BLM for seawater is finalized and validated. With sustained effort by EPA and the water quality research community, we believe that a bioavailability model (BLM or similar) for copper in seawater could be available within approximately 2-3 years.

References:

a. Allen, H.E. and D.J. Hansen. 1996. The importance of trace metal speciation to water quality criteria. Water Environment Research, 68:42-54.
b. Blake, A.C., D.B. Chadwick, A. Zirino and I. Rivera-Duarte, 2004. Spatial and Temporal Variations in Copper Speciation in San Diego Bay. Estuaries (in press).
c. Chadwick, D.B., Zirino, A., Rivera-Duarte, I., Katz, C.N., and Blake, A.C., 2004. Modeling the mass balance and fate of copper in San Diego Bay. Limnology & Oceanography 2004, *49*: 355-366.
d. Chester, R. 1990. *Marine Geochemistry*. Unwin Hyman Ltd. 698 pp.
e. DiToro, D.M., H.E. Allen, H.L. Bergman, J.S. Meyer, P.R. Paquin and R.C. Santore. 2001. A Biotic Ligand Model of the acute toxicity of metals. I. Technical Basis. Environmental Toxicology and Chemistry, 20: 2383-2396.
f. Pagenkopf, G.K. 1983. Gill surface interaction model for trace-metal toxicity to fishes: Role of complexation, pH, and water hardness. Environmental Science & Technology, 17: 342-347.
g. Rivera-Duarte, I., G. Rosen, D. Lapota, D.B. Chadwick, L. Kear-Padilla, and A. Zirino, 2004. Control of Copper Toxicity to Larval Stages of Three Marine Invertebrates by Copper Complexation Capacity in San Diego Bay, California. Environmental Science & Technology, submitted for publication.
h. Rosen, G., I. Rivera-Duarte, L. Kear-Padilla, and D.B. Chadwick, 2004. Bioavailability of copper to bivalve and echinoderm embryos in San Diego Bay, California, USA. Environmental Toxicology & Chemistry, submitted for publication

i. Santore, R.C., M. Rooni, P.R. Paquin, K. Ben Wu, D. DiTorro. 2003. Developing site-specific water quality criteria for metals using the biotic ligand model. National TMDL Science and Policy 2003 Specialty Conference Proceedings (CD) Chicago, Nov 16-19, 2003.

2. Clarify the heavy use of South San Francisco Bay water-effect ratio (WER) study data in calculating the species mean acute value (SMAV)

Comment: The use of a large number of replicates from a single WER study as independent samples for averaging tends to overweigh and bias the data set towards a single study result.

Discussion: The proper calculation of the saltwater copper criteria is extremely important because it is based solely on the species mean acute value (SMAV) for *Mytilus spp.* A South San Francisco Bay WER study (City of San Jose, 1998) contributed 22 of the 29 EC50 values used to calculate the 6.188 µg/L SMAV (U.S. Environmental Protection Agency (EPA), 2003). The geometric mean of the other seven values is 9.6 µg/L. These seven values came from two other WER studies. The San Francisco Bay study, therefore, plays a significant role in driving down the SMAV. Although the result is a large dataset, most values are from the same study. These tests were conducted by the same laboratory, using the same test conditions (i.e. salinity), and with the same dilution water.

Recommendation: We suggest that it would be more appropriate to use the geometric mean of values from each study before taking a geometric mean of the studies as a whole to more evenly weigh the data.

References:

a. Section 10.0, Table 1b, page 37.
b. City of San Jose, 1998. Development of a site-specific water quality criterion for copper in South San Francisco Bay. Environmental Services Department, San Jose/Santa Clara Water Pollution Control Plant, San Jose, CA. 172 pp.
c. U.S. EPA, 2003. 2003 Draft Update of Ambient Water Quality Criteria for Copper. Environmental Protection Agency, November 2003. EPA/822/R-03/026

3. Include additional data on *Acartia tonsa* and *Crassostrea virginica*

Comment: Include additional data on *Acartia tonsa* and *Crassostrea virginica* from the Navy's Regional Water Effect Ratio (WER) Study for the Hampton Roads area of Virginia.

Discussion: In the Hampton Roads WER study, there were three test events using *Acartia tonsa* and one test event for *Crassostrea virginica.* The report has 17 data points for *Acartia tonsa* (six lab water tests per test event with one unacceptable value). This data may be found in table 16 of the report. The report has 6 data points for *Crassostrea virginica,* which are in Table 12 of the report. The *Crassostrea virginica* data points should be substituted in the database for the data generated by MacInnes and Calabrese (1978) since the data generated by the Navy is dissolved measured values while the older data were total recoverable values. The entire report is enclosed.

Recommendation: Include additional data for *Acartia tonsa* generated by the Navy in the Hampton Roads WER study. Substitute data generated by the Navy for *Crassostrea virginica* for the existing data generated by MacInnes and Calabrese.

References:

a. C2M HILL. *Regional Water Effect Ratio Study*. September 1999.
b. Section 10.0, Table 1b, page 38
c. MacInnes, J.R. and A. Calabrese. 1978. Response of embryos of the American oyster, *Crassostrea virginica*, to heavy metals at different temperatures. In: Physiology and behavior of marine organisms. McLusky, D.S. and A.J. Berry (Eds.). Pergamon Press, New York, NY. pp. 195-202.

4. Recalculate the species mean acute value (SMAV) for *Mytilus spp.*

Comment: It appears a calculation error was made for the *Mytilus spp.* SMAV.

Discussion: Our calculation of the geometric mean of the 29 individual values listed for *Mytilus spp.* SMAV was 6.386 µg/L. This is higher than the reported geomean value of 6.188 µg/L. This value needs to be accurate because it is used in calculating the criterion maximum concentration (CMC) and the criterion continuous concentration (CCC).

Recommendation: The SMAV value for *Mytilus spp.* should be rechecked and the discrepancy, if confirmed, corrected.

Reference: Section 10.0, Table 1b, page 36

5. Include data from additional dilution waters in genus mean acute value (GMAV) determination

Comment: Recent water-effect ratio (WER) studies have employed filtered, open coastal seawater which results in lower EC50s than might otherwise be observed with unfiltered, or more crudely filtered, seawater that still meets the minimum criteria.

Discussion: The guidelines for water quality criteria (WQC) derivation state that acute tests should be conducted in dilution water in which total organic carbon (TOC) and total suspended solids (TSS) do not exceed 5 mg/L (U.S. EPA, 1985). Much of the *Mytilus spp.* data that was added to the national dataset for copper in 2003 was from recent WER studies. However, the results included were only from the reference toxicant tests, or laboratory water tests. Some site water data could have been included in the results. For example, site water samples meeting the dilution water criteria in the South San Francisco Bay WER study resulted in EC50s as high as 17.5 µg/L of dissolved copper (City of San Jose, 1998). Although WQC are meant to be conservative, there is no apparent reason why other relevant data, which meets the guidelines, should not be incorporated into the calculation.

Recommendation: Recommend using all available toxicity data that meets the guidelines for deriving the species mean acute value (SMAV)/GMAV.

References:

a. Section 10.0, Table 1b, page 37
b. City of San Jose, 1998. Development of a site-specific water quality criterion for copper in South San Francisco Bay. Environmental Services Department, San Jose/Santa Clara Water Pollution Control Plant, San Jose, CA. 172 pp.
c. U.S. EPA, 1985. Guidelines for deriving numerical national water quality criteria for the protection of aquatic organisms and their uses. EPA/822/R-85/100.

6. Address issues associated with use of chronic tests for acute water quality criteria (WQC) development

Comment: Embryo-larval development tests are considered chronic tests by EPA for whole effluent toxicity testing (U.S.EPA, 1995). For WQC derivation, however, they have been used in acute tests (U.S.EPA, 1985).

Discussion: The final acute value (FAV) was lowered using embryo-larval development testing to protect the *Mytilus spp.* because of the sensitivity and economic importance of the species (Section 5.2, p. 17). The FAV was then divided by an acute-to-chronic ratio (ACR) to determine the chronic criterion (Section 5.3, p. 20). However, this step seems inappropriate for this particular case. Its application as a chronic toxicity test (U.S. EPA, 1995) suggests that an acute criterion, based solely on *Mytilus spp.* embryo-larvae development, is justifiably a chronic test. Furthermore, we believe that there are no chronic endpoints with sensitivities below that of the *Mytilus spp.* embryo test. Therefore, in this case, the acute criterion is effectively protective of chronic exposure and should not be lowered further than the criterion maximum concentration (CMC) for copper.

Recommendation: EPA should consider using embryo-larval development as a chronic test and adjust the species mean acute value (SMAV) and FAV accordingly.

References:

a. Section 5.2, page 17
b. Section 5.3, page 21
c. U.S.EPA, 1985. Guidelines for deriving numerical national water quality criteria for the protection of aquatic organisms and their uses. EPA/822/R-85/100.
d. U.S.EPA, 1995. Short-term methods for estimating the chronic toxicity of effluents and receiving waters to west coast marine and estuarine organisms. EPA/600/R-95/136.

7. Develop a broader data set for acute-to-chronic ratio (ACR) calculation

Comment: The saltwater ACR of 3.23 was derived using data from five freshwater species and only one saltwater species. The calculation of the ACR should take advantage of the wealth of chronic saltwater toxicity data available from routine reference toxicant tests conducted with copper by bioassay labs. This differs significantly from the ACR of 1.48 for the single saltwater species measured.

Discussion: Settling for only one saltwater data point (sheepshead minnow) for deriving the ACR is not necessary. Saltwater chronic toxicity tests using copper, as a reference toxicant, are conducted in bioassay labs on a regular basis (Chris Stransky, pers. comm.). Although the guidelines only require one saltwater test out of the three tests for ACR derivation, a more robust dataset can easily be generated using available data for several saltwater species. If the bioassay lab data does not meet EPA's requirements (i.e., by not having measured the concentrations in test solutions), appropriate data can be generated at a low cost. In addition, the ACR of 1.48 should not be used because this species is acutely insensitive to copper. The bias of using an acutely insensitive species is unknown, and further testing with more sensitive saltwater species would be a more appropriate action than the pooling of data for freshwater and saltwater species.

Recommendation: EPA should consider developing a broader set of chronic data for derivation of saltwater ACR. The ACR of 3.23 should not be used for the calculation of the saltwater chronic criterion, but a revision of the criterion should await additional data from the testing of sensitive saltwater species.

References:

a. Section 5.3, page 21
b. Chris Stransky, personal communication, AMEC Earth and Environmental, Inc., San Diego, CA.
c. U.S. EPA, 2003. 2003 Draft Update of Ambient Water Quality Criteria for Copper. Environmental Protection Agency. November 2003. EPA/822/R-03/026

8. Provide a better description of the derivation of freshwater ambient water quality criteria (AWQC) using the biotic ligand model (BLM)

Comment: The procedure for converting a BLM-derived site-water LC50 to a final acute value (FAV) is not adequately explained.

Discussion: According to the 1985 criteria derivation methodology document (Stephan et al., 1985) and the subject draft document (U.S. EPA, 2003), an FAV is an estimate of the fifth percentile of a sensitivity distribution represented by the average LC50s and EC50s. This is calculated using the genus mean acute value (GMAVs) of the tested genera. The current BLM only allows LC50 estimates for 4 species (2 in the same genus) for copper. The LC50 values are very different for different species in the same site water. How are any, or all, of these LC50s to be used to determine the FAV, since there is an insufficient number of species present to calculate an FAV by the method described in the 1985 criteria derivation methodology?

Recommendation: Recommend that EPA provide a clear and unambiguous description of the steps necessary to determine an ambient water quality criterion for site water when the appropriate chemical parameters have been measured. It would also be useful to have an example.

References:

a. Section 3.8, Page 10

b. Stephan, C.E., D.I. Mount, D.J. Hansen, J.H. Gentile, G.A. Chapman and W.A. Brungs. 1985. Guidelines for deriving numerical national water quality criteria for the protection of aquatic organisms and their uses. PB85- 227049. National Technical Information Service, Springfield, VA.
c. U.S. EPA, 2003. 2003 Draft Update of Ambient Water Quality Criteria for Copper. Environmental Protection Agency, November 2003. EPA/822/R-03/026

9. Clarify the degree of lab analysis accuracy

Comment: While the criterion maximum concentration (CMC) and the criterion continuous concentration (CCC) are very conservatively protective, discussion should be made to the degree of lab analysis accuracy that can be obtained for these low limits. A greater emphasis and discussion should be made in the document that any regulatory interpretation of this data must ensure that current laboratory methods can meet the toxicological levels that are discussed in this document.

Discussion: The genus mean acute value (GMAV) for the saltwater species ranged from 11.5 µg/l to 6,448 µg/l, which is magnitudes of order variable. The final acute value (FAV) of 12.3 µg/l represented the four most sensitive species of all 52 species evaluated and the bottom of the range. The FAV was then divided in half to protect commercially and recreationally important species and cut in half again to obtain the CMC. Lastly, the biotic ligand model (BLM) and the use of dissolved copper is more real world than the old standard, however, their model represents a hypothetical genus more sensitive than 95% of the tested genera. While no one can argue that the CMC and CCC are not protective, EPA's continued practice of deriving numbers that are protective but not measurable or obtainable has to be called into question.

Recommendation: Ensure that the CMC and CCC levels chosen are reproducible in the laboratory within reporting limits and not just detection limits. If they cannot be reproduced then heavy emphasis should be made in the document that these levels cannot be currently detected within laboratory reporting limits.

Reference: Section 1.1, Page 1.

10. Explain the appropriate scenarios for applying the copper criteria

Comment: Section 9.0 National Criteria Statement states that "saltwater aquatic organisms and their uses should not be affected unacceptably if the 4-day average concentration of dissolved copper does not exceed 1.9 µg/L more than once every 3 years on the average and if the 24 hour average concentration does not exceed 3.1 µg/L more than once every 3 years on the average." Based on this statement, it is assumed that the standards are developed for continuous flow exposure scenarios where it is possible to calculate a 4-day average concentration or a 24-hour average concentration. However, the document does not discuss the appropriateness (or inappropriateness) of applying such standards to intermittent discharges such as storm water discharge and furthermore does not provide recommendations for deriving criteria more applicable to storm water discharges.

Discussion: In some cases, (California Ocean Plan and San Diego Basin Plan) National Pollutant Discharge Elimination System storm water monitoring requirements are essentially derived based on aquatic life criteria. However, it is inappropriate to develop standards that are based on criteria developed under a continuous flow exposure scenario, especially when storm water monitoring is conducted in effluent prior to discharge to a water body.

Recommendation: The ambient water quality criteria document should emphasize the appropriate scenarios for applying the criteria and provide either criteria applicable to storm water discharge or methods for deriving such criteria.

Reference: Section 9.0, page 24