Development of Site-specific Copper Criteria for the NY/NJ Harbor Complex Using the Indicator Species Procedure

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Surface Water Quality Branch
U.S. Environmental Protection Agency
Region II

Summary

Historic effluent and ambient water quality data from the New York/New Jersey Harbor Complex indicated that copper and mercury were present at levels of concern. Therefore, pursuant to Section 304(l) of the Federal Clean Water Act (CWA), the waters of the New York/New Jersey Harbor Complex were listed by the States of New York and New Jersey as not meeting the applicable water quality standards (WQS) for copper and mercury due to point source discharges. In response to this, workgroups were formed under the New York/New Jersey Harbor Estuary Program (HEP) to oversee the development and application of appropriate WQS and discharge limits applicable to the Harbor Complex.

Since the copper criteria applicable to New York and New Jersey waters were not equivalent (NY criterion = 2.9 ug/l dissolved; NJ criterion = 2.9 ug/l total recoverable through a federal criteria promulgation) and because, on a national level, the U.S. Environmental Protection Agency (EPA) was leaning towards recommending the use of dissolved metals criteria, EPA recommended, and the HEP agreed, to develop a site-specific copper criterion for the waters of the Harbor Complex using the Indicator Species Procedure as presented in EPA's Water Quality Standards Handbook. This procedure produces a biologically-based adjustment to the applicable water quality criteria for copper. The adjustment is expressed as a Water Effect Ratio (WER). The WER represents a comparison of the toxicity of copper in site (Harbor) water vs. laboratory water typically used in the development of national criteria. The applicable criterion value is multiplied by the WER to calculate the site-specific criterion. The final WER (FWER) developed through this study is 1.5 based on the dissolved form of copper.

Independent from the development of the site-specific copper criterion, a literature search and toxicity data obtained through this study on species critical to the development of the national marine copper criterion has resulted in a recalculation of the national acute criterion value for use in NY/NJ Harbor, from 2.9 ug/l total recoverable copper to 5.29 ug/l dissolved copper. This recalculation results in an acute site-specific copper criterion for the New York/New Jersey Harbor complex of 7.9 ug/l dissolved copper (the recalculated national acute criterion of 5.29 ug/l dissolved copper x the FWER of 1.5 = 7.9 ug/l dissolved copper).

In addition, EPA and the States of New York and New Jersey have concluded that the 1985 national copper criteria document assumption that an acute criterion based on the endpoint of an embryo-larval mollusc test provides protection for chronic effects is no longer valid. Use of available data to calculate an acute to chronic ratio has resulted in a recalculated national chronic criterion for use in NY/NJ Harbor of 3.75 ug/l dissolved

copper. The chronic site-specific copper criterion for the NY/NJ Harbor is therefore 5.6 ug/l dissolved copper (the recalculated national chronic criterion of 3.75 ug/l dissolved copper x the FWER of 1.5 = 5.6 ug/l dissolved copper).

Background/Rationale for the Study

Historical ambient water quality data from the NY/NJ Harbor indicated relatively high concentrations of the following metals: copper, mercury, lead, nickel, arsenic, silver, cadmium and zinc. As summarized in Squibb et al. (1991), these data sets included those of the New York City Department of Environmental Protection (NYCDEP) Harbor Surveys (1974-87), New York State Department of Environmental Conservation (NYSDEC) monitoring (1982-86), Interstate Sanitation Commission monitoring (1987 and 1989), and EPA monitoring (1981-82).

Pursuant to Section 304(l) of the CWA, States were required to list waterbodies that were not attaining applicable WQS due entirely or substantially to discharges from point sources. The States of New York and New Jersey listed the Harbor on the 304(l) list on the basis of the previously discussed historical data, which indicated potential exceedances of the State WQS for copper and mercury due to point source discharges alone. Section 304(l) also mandated the development of appropriate water quality-based controls for these substances.

In response to Section 304(l) the WQS and Total Maximum Daily Load/Waste Load Allocation (TMDL/WLA) workgroups were formed under the HEP to oversee the development and application of appropriate WQS and discharge limits applicable to the Harbor Complex. The HEP is a partnership of Federal, State and local interests, including citizens and scientists, working to restore and maintain the natural resources of the Harbor complex. The WQS/TMDL/WLA workgroups included representatives of EPA, the States of New York and New Jersey, the New York City Department of Environmental Protection (NYCDEP), the Interstate Sanitation Commission, the Citizens Advisory Committee, and the Science and Technical Advisory Committee. Recently the New Jersey dischargers rejoined the workgroup.

The ensuing effort to oversee the application of appropriate metals criteria and discharge limits to the Harbor waters, including the development of a site-specific copper criterion, was dynamic in nature. This is due to the fact that concurrent with this process, knowledge on techniques involved with measuring metals levels and national guidance on implementing metals criteria and developing site-specific criteria were rapidly evolving. Decisions which were made regarding WQS applicable to the Harbor waters and on the site-specific copper study incorporated this evolving knowledge and are reflected throughout this report.

Ambient Data:

Two issues which arose early in the process were: the validity of the historic Harbor metals data used in the decision to list the Harbor waters under CWA Section 304(l), and the analytical techniques used for metals monitoring in general. It became generally accepted that all previous metals data not obtained using "clean techniques" in both the field and laboratory (which includes most historic metals data) yield artificially high results. Problems with the older sampling and analytical methods include sample contamination, salt matrix interference, high detection limits, and a lack of uniform EPA-approved methods for analysis of metals in estuarine and marine waters. In response to this finding, the HEP sponsored extensive metals monitoring in the Harbor from 1990 through 1992 (Battelle 1991, 1992a, 1992b). This monitoring employed the use of "clean techniques" to ensure the validity of the data obtained.

The "clean" metals data gathered through the HEP indicated that of the eight metals of concern, only four (copper, mercury, lead, and nickel) potentially exceeded WQS in all or part of the Harbor. The development of water quality-based limits for these substances is discussed in a technical support document entitled "Total Maximum Daily Loads (TMDLs) for Copper, Mercury, Nickel and Lead in NY-NJ Harbor" (EPA 1994). For mercury, nickel, and lead, the WQS/TMDL/WLA workgroup reached concurrence that the most stringent of the applicable, enforceable criteria would be used. Due to the issues discussed below regarding metals criteria in general, and copper in the Harbor specifically, the workgroup agreed to develop a site-specific copper criterion. The remainder of this document will address the development of the site-specific copper criterion.

Criteria:

It was recognized early in this process that controversy existed on a national scale regarding the appropriate form of the metal to be used in the interpretation and implementation of aquatic life criteria for metals. EPA's "Interim Guidance on Interpretation and Implementation of Aquatic Life Criteria for Metals" (1992) discusses this controversy. In summary, the forms which may currently be used are those which are measured by either the dissolved or total recoverable methods. The dissolved method measures metal that passes through a 0.45 um filter, while the total recoverable method measures dissolved metal plus metal which is bound to particles that cannot pass through a 0.45 um filter.

The principal issue regarding the technical validity of metals criteria is the correlation between metal that is measured and metal that is biologically available. The bioavailability and toxicity of metals depend strongly on the form of the metal, which can vary depending on the characteristics of the receiving water. Particle-bound metal is generally expected to be significantly less bioavailable and toxic than dissolved metal. Toxicity tests that form the basis for EPA's national criteria are usually performed in filtered water from an uncontaminated source, such as Narragansett Bay, Rhode Island for marine water quality criteria. Because such filtered water is lower in metal-binding particulate matter and dissolved organic matter than most ambient waters (particularly a waterbody such as the Harbor complex which exhibits relatively high levels of particulate matter), these toxicity tests may overestimate the ambient toxicity of non-biomagnifying metals that interact with particulate matter or dissolved organic matter. In theory, a lower proportion of metal added to ambient site waters would be present in a toxic form due to the binding capacity of particulate matter contained in the ambient receiving waters (the Harbor).

Copper exhibited Harbor-wide exceedances of the applicable New Jersey criterion (as promulgated by EPA) of 2.9 ug/l total recoverable copper. In addition to exceeding criteria throughout the Harbor complex, total recoverable copper levels also varied widely across the different areas of the Harbor in proportion with total suspended solids (TSS) levels. This indicated the linkage of total recoverable copper levels to particulate matter. Conversely, dissolved copper levels were observed to be below or near the New York State criterion of 2.9 ug/l dissolved copper and the variation in dissolved copper throughout different areas of the Harbor Complex was minimal and independent of TSS levels.

Preliminary water quality modeling analyses indicated that attainment of the copper criterion expressed as total recoverable may not be possible, even in the absence of point source discharges. The controversy regarding which analytical form of the metal would be appropriate to apply in interpreting aquatic life criteria for metals was therefore particularly important with regard to the Harbor complex, from both a technical and policy-making perspective.

Several EPA guidance documents (Water Quality Standards Handbook, 1983; Guidelines for Developing Numerical Aquatic Site-Specific Water Quality Criteria by Modifying National Criteria, 1984a; Interim Metals Guidance, 1992) present and describe the option of developing site-specific aquatic life criteria for metals using a procedure known as the Indicator Species Procedure. This procedure may be used where it is believed that physical and/or chemical characteristics of the ambient water at a particular site may influence biological availability and/or toxicity of a chemical. As previously noted, this is believed to occur for copper in the Harbor waters due to the relatively high levels of particulate matter observed in the Harbor waters as compared to dilution waters used in toxicity testing for criteria development. The Indicator Species Procedure allows for a biologically-based adjustment to EPA's national criteria. This adjustment is based on the toxicological determination of a WER used to account for any difference between the toxicity of a metal in "laboratory" dilution water and its toxicity in water from a particular site. A WER is calculated by dividing a value obtained for a toxicological endpoint in site water by the value obtained for the same endpoint in appropriate laboratory dilution water. A site-specific criterion can be calculated by multipyling a national or State criterion by the valid WER. The procedure therefore involves conducting toxicity tests (with at least two sensitive species) in both site water and laboratory dilution water which has been spiked with the substance of concern, and measuring the respective toxicological endpoints.

The site-specific copper study was co-funded by EPA and NYCDEP. Field sampling was conducted using NYCDEP's sampling vessel, the HSV Osprey. Science Applications International Corporation (SAIC) and Battelle Ocean Sciences were contracted to perform the toxicity testing and analytical work for this study, respectively.

__Study Design__

The previously mentioned EPA guidance on the Indicator Species Procedure was limited in terms of application of this procedure in an estuary, especially at a site as complex as the New York/New Jersey Harbor. Decisions needed to be made, therefore, concerning how to best represent the Harbor Complex for the field sampling necessary to support the WER toxicity testing. EPA Region II coordinated the design of the study and addressed these issues through the auspices of the HEP TMDL/WLA and WQS workgroups. Throughout this process, EPA Region II coordinated closely with EPA's experts on water quality criteria development in EPA's Environmental Research Laboratory - Narragansett (ERL-N) in the development of the study design, and later, with the interpretation of the results.

It was decided that the primary consideration was to ensure adequate representation of the entire distribution and range of observed TSS levels in the Harbor area. This was based on the belief that TSS was the key water quality parameter affecting the bioavailability of copper in the water column. The basis for this belief was the relation of TSS and total recoverable copper concentrations, and the issue regarding the bioavailability of particle-bound metal. The study was also designed to adequately represent the different geographical areas of the Harbor, as well as high and low flow conditions.

In order to satisfy these requirements, sampling was conducted in seven locations throughout the Harbor near existing HEP monitoring stations (see figure 1). These sampling areas are

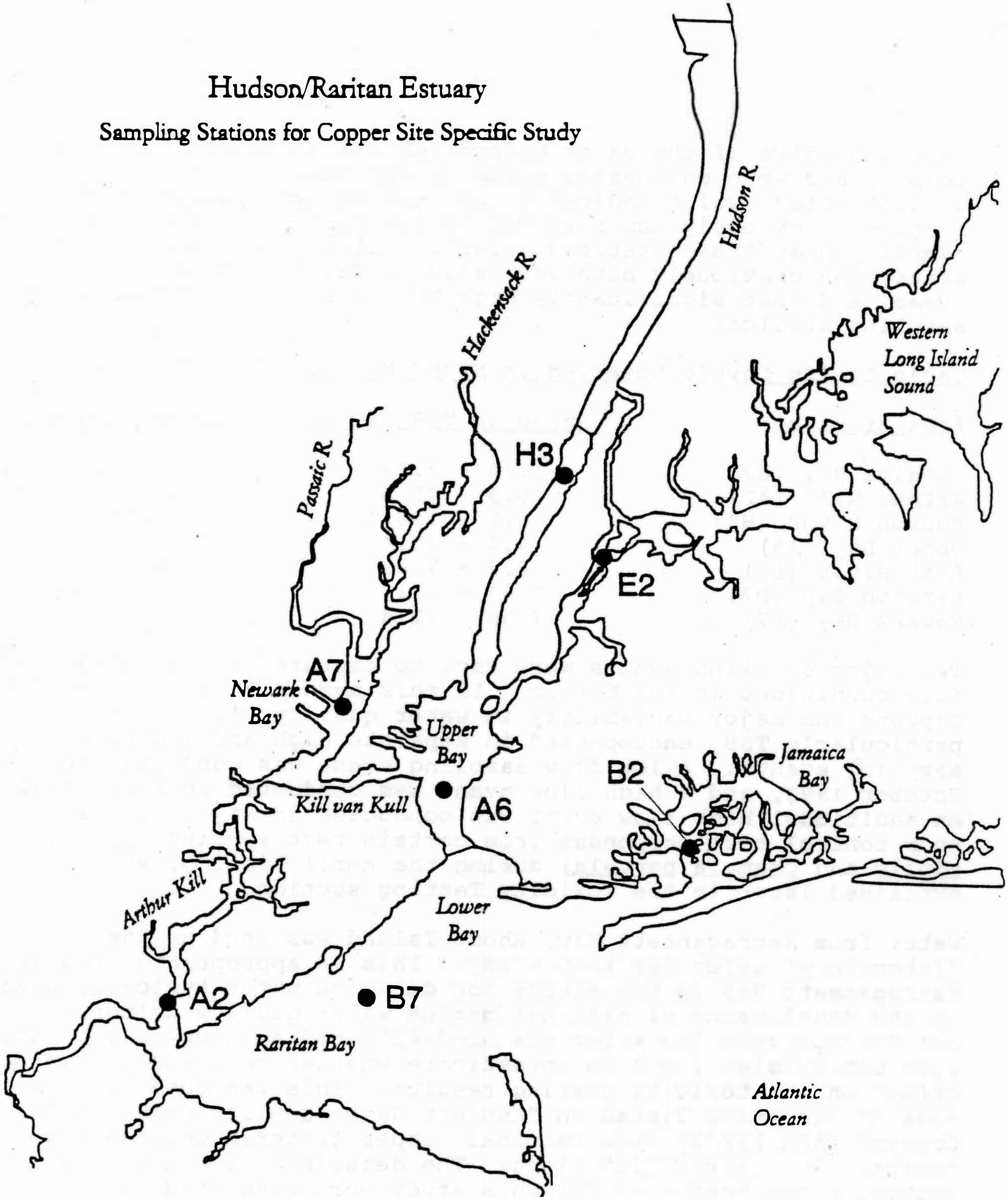

Figure 1. Map of Hudson/Raritan Estuary showing the seven sampling locations for the copper site specific study.

representative of the major hydrographical areas of the Harbor complex and were delineated based on HEP data on TSS concentrations which indicated that the entire distribution and range of previously observed TSS levels could be represented by sampling near these stations. Table 1 lists these sampling areas, the previously observed range of TSS levels in those areas, and some significantly high TSS values observed at certain sampling stations.

Table 1. TSS Levels Observed in NY/NJ Harbor

Area of Harbor	Range in TSS (mg/L)	Highest Levels
Jamaica Bay (B2)	1.28 - 3.32	-----------
Arthur Kill (A2)	6.9 - 25.5	44.42, 49.1
Hudson River (H3)	8.2 - 135.1	169, 409
Upper Bay (A6)	4.5 - 13.4	-----------
East River (E2)	6.2 - 7.89	-----------
Raritan Bay (B7)	2.94 - 8.13	-----------
Newark Bay (A7)	7.58 - 22.4	95.1

Two major sampling events were used to capture the high and low flow conditions in the Harbor. In this manner it was intended to capture the major variability in water quality parameters, particularly TSS, encompassed in separate high and low flow sampling events. A low flow sampling event was conducted in October 1992, and a high flow event was conducted in April 1993. An additional high flow event was conducted in May 1993 due to poor control test responses from certain test species (Mytilus edulis and Champia parvula) during the April testing, as explained later in the Toxicity Testing section.

Water from Narragansett Bay, Rhode Island was used as the "laboratory" water for this study. This is appropriate because Narragansett Bay is the source for dilution water typically used in the development of national marine water quality criteria. All Narragansett Bay water was sand-filtered and some was treated with ultraviolet light to investigate whether this would have any effect on the toxicity testing results. This was done because some of the tests listed in "Ambient Water Quality Criteria for Copper" (EPA 1984b) (the national copper criteria document) were treated with ultraviolet light. The details of the toxicity testing procedures used for this study were presented in SAIC's report (SAIC 1993a).

For each sampling event water samples were taken from the seven Harbor areas, and from Narragansett Bay. To increase the representation of TSS variability in the Harbor, the Hudson River sampling area was sampled three times over the course of a tidal cycle during each sampling event. Consequently, a series of ten side-by-side toxicity tests for each species used during each sampling event (species used are discussed in the following section of this report) were conducted with the following dilution water samples: three samples taken over the tidal cycle from the Hudson River sampling area, one sample each from the other six Harbor sampling areas, and one Narragansett Bay control water sample (the Narragansett Bay samples were separated into nonultraviolet light-treated samples and ultraviolet light-treated samples, and two replicates of Narragansett Bay samples were used for the second event).

As previously noted, a WER is generally calculated as the ratio of the value obtained for a toxicological endpoint (LC50, EC50, or IC50) in site water divided by the value for the same endpoint in the "laboratory" dilution water. To address potential variability in toxicity testing results between the different Harbor sampling areas and/or species used, the following plans were set forth based on the available guidance:

- <u>Variability in Harbor sampling areas</u>: Based on the assumption that the toxicity testing results for one species during one sampling event would not be statistically different across the different Harbor sampling areas, it was decided to use the geometric mean of the toxicity data for a single species during one sampling event as that species' WER for that particular sampling event. If the data were statistically different between different sampling areas, it is possible that different area-specific criteria would have been developed within the Harbor.

- <u>Variability in the different species' WERs</u>: Based on the assumption that the different species' WERs would not be statistically different, it was decided to use the geometric mean of the species WERs as the FWER.

<u>Duration and Frequency:</u>

This study was designed to develop an adjustment to the value of the applicable marine water quality criteria for copper. It was not designed to provide an adjustment to the allowable frequency and duration of criteria exceedances. As noted in the national copper criteria document (EPA 1984b), the suggested frequency of exceedance is once every three years. The suggested duration of exceedance is a one hour average concentration for an acute value and a four day average concentration for a chronic value. No new data has become available, through this study or otherwise, which would indicate that these national frequency and/or durations should be modified. Observation intervals from standard toxicity tests, including the tests conducted for this study, are not short enough to allow for any meaningful observation on whether the nationally recommended duration should be modified.

Species of Metal:

A WER and resultant site-specific criterion can be expressed as either dissolved or total recoverable metal. However, based in part on the results of a public meeting of experts held in Annapolis, Maryland in January 1993 (public noticed at 58 FR 32131, June 8, 1993), EPA guidance was revised (Prothro 1993) during the course of this study to include the recommendation that the best available option to approximate metals bioavailability would be to express metals criteria as dissolved (except for biomagnifying metals such as mercury and selenium). EPA and the States, therefore, decided that the WER and site-specific criterion would be expressed in terms of dissolved copper.

Species Used

Considerations regarding the selection of species for toxicity testing were as follows:

- Sensitivity: It is important to use species sensitive to copper with this procedure, because sensitive species yield more toxicologically meaningful results. More accurate estimates of site water effects can be obtained from test organisms that are relatively more sensitive to small changes in copper concentrations. If possible, it would be ideal to use species sensitive at the final acute value (FAV) from the national copper criteria document.

- Species should be selected for which standard test methods (either ASTM or EPA) exist.

- Species should be selected for which the required tests could be conducted in a qualified laboratory.

- At least one bivalve should be included because these organisms are among the most sensitive to copper. It was recognized as preferable if the bivalve included was Mytilus edulis (the blue mussel), because toxicity testing data on this organism drove the development of the national copper criterion recommendation (this is explained further in the following section on the recalculation of the national acute copper criterion).

Previously existing guidance on species selection recommended the use of two species, a fish and an invertebrate. However, it was decided that conducting toxicity tests with a fish species would not yield worthwhile data due to the relative insensitivity of fish to copper. It was also decided to use more than two species to help ensure that useful data would be obtained.

Toxicity Testing Results

The toxicity and analytical results were presented in detail in the respective reports of the two contractors (SAIC 1993a and Battelle 1993). These results are summarized throughout the remainder of this report. The following summaries of the results presented for each testing event, including the figures and tables, are mainly excerpts from SAIC's report (1993a). Raw physical and biological data from the toxicity testing were presented in SAIC's report (1993a).

First Event:

Water sampling for this event was conducted on October 20-21, 1992. This was a period of relatively low river flow and thus low TSS levels. At the time of the first sampling event, no supply of Mytilus was available. The following four species were therefore used for the first event:

Champia parvula - Red algae sexual reproduction test (although toxicity data on plant species are generally not used in national criteria development, this species was used as a replacement for Mytilus due to the fact that it is extremely sensitive to copper and that Mytilus was not available).

Mysidopsis bahia - Mysid shrimp acute survival test.

Arbacia punctulata - Sea urchin embryo-larval development test.

Mulinia lateralis - Bivalve embryo-larval development test.

- Summary of first event results:

WERs for the seven Harbor sampling areas were calculated from the data for the four species tested. Summary data for each species and station are presented in Table 2 and plotted in Figures 2 to 5, beginning on the following page. Although both total recoverable and dissolved data are presented, only the dissolved data are used in the development of the WER based on the decision to express the criteria as dissolved.

All of the performance controls for each species were judged to be acceptable, except that no judgement was made for the Arbacia tests. This is because no control test acceptability limits for embryo-larval tests with Arbacia have been established. Statistical comparisons between Narragansett Bay and the Harbor sites showed no difference between the two areas. However, the power to detect a difference with only data from the first event is limited because of the small number of Narragansett Bay results.

Table 2. First Event Results

Fifty percent effect concentrations for copper (µg/L) and calculated Water Effect Ratios (WER) for sampling event number one ("low flow"). Measured total and dissolved values are based on chemistry data received from Battelle. Chemistry data used to calculate effect concentrations are the mean of T-0 and T-48 chemistry values.

Measured Total Copper

	Champia		*Mulinia*		*Arbacia*		Mysids	
Station	IC50	WER	IC50	WER	IC50	WER	LC50	WER
NB-1	3.3		25.2		28.0		209	
NB-UV			18.9					
H3-low 1	13.8	4.18	b		b		b	
H3-high	a		36.1	1.43	63.0	2.25	341	1.63
H3-low 2	7.8	2.36	42.1	1.67	76.0	2.72	322	1.54
A2	a		40.2	1.60	41.5	1.48	265	1.26
A6	15.5	4.70	33.6	1.33	39.3	1.40	324	1.55
A7	7.7	2.33	33.6	1.33	42.5	1.52	310	1.48
B2	3.5	1.06	17.5	0.69	29.0	1.03	262	1.25
B7	18.8	5.70	36.8	1.46	56.6	2.03	383	1.83
E2	18.5	5.61	37.9[c]	1.50	65.0	2.33	277	1.32

Measured Dissolved Copper

	Champia		*Mulinia*		*Arbacia*		Mysids	
Station	IC50	WER	IC50	WER	IC50	WER	LC50	WER
NB-1	3.0		21.0		21.4	1.00	164	
NB-UV			19.3					
H3-low 1	8.1	2.70	b	b	b		b	
H3-high	a		17.7	0.88	36.2	1.72	220	1.34
H3-low 2	3.1	1.03	22.4	1.11	38.3	1.79	209	1.27
A2	a		28.6	1.42	26.0	1.22	189	1.15
A6	9.2	3.07	27.9	1.39	30.4	1.42	237	1.45
A7	5.9	1.97	27.6	1.37	28.3	1.32	218	1.33
B2	2.8	0.93	11.4	0.57	20.5	0.96	199	1.21
B7	11.8	3.93	22.8	1.13	34.5	1.61	284	1.73
E2	11.0	3.67	23.2[c]	1.15	38.4	1.79	204	1.24

a = poor reproduction in control, therefore IC50 could not be calculated.
b = spiking error, copper concentrations too high for several treatments.
c = poor control response, but essentially no effect at lowest two concentrations, therefore IC50 calculated without control.

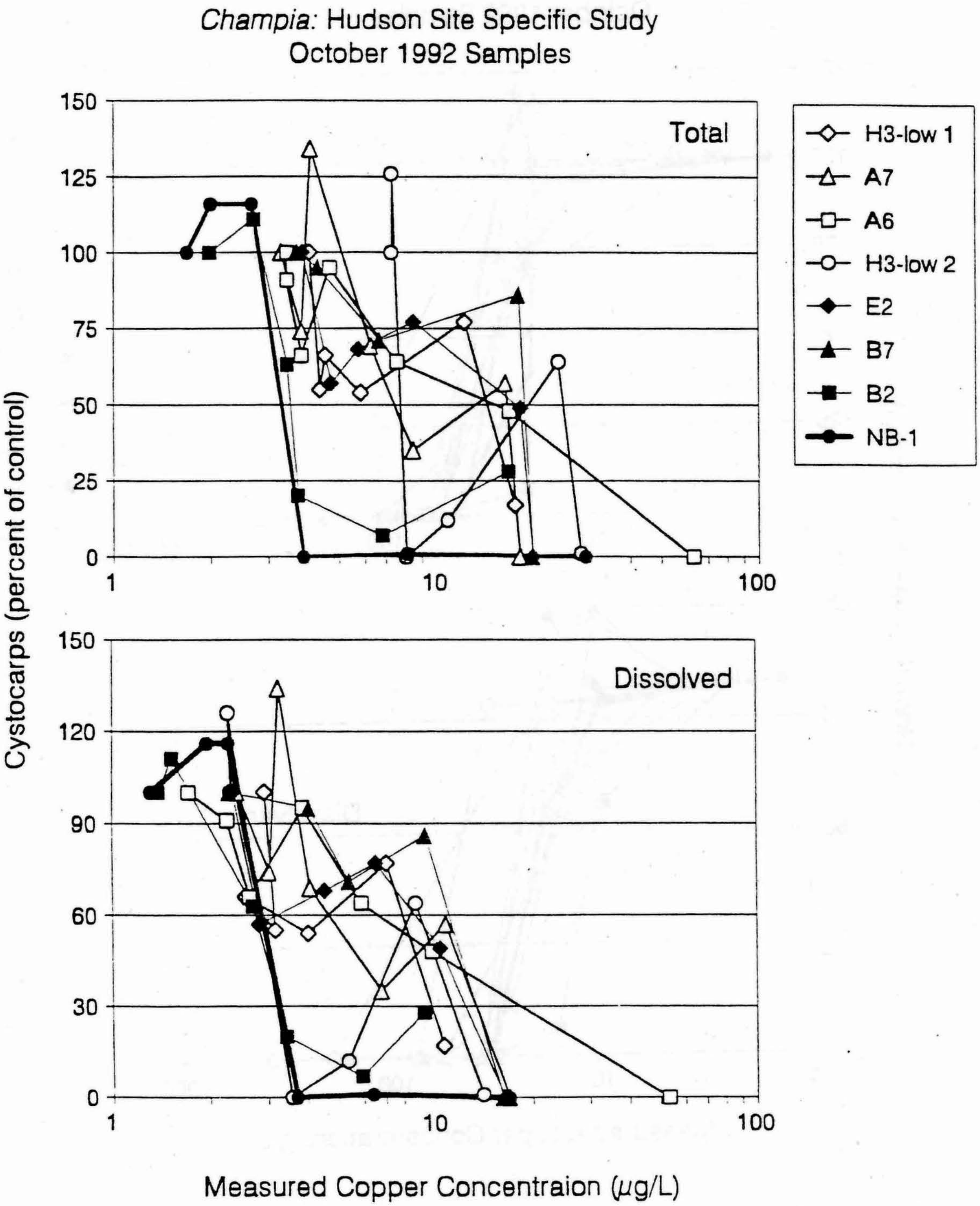

Figure 2.Mean number of cystocarps, expressed as percentage of control (this control is the zero-spiked treatment for each sample tested), produced by the marine red alga. *Champia parvula* exposed 48 hr to each copper concentration in Hudson/Raritan samples and the Narragansett Bay sample (NB-1) collected in October 1992. Copper data used for plots are the mean of T-0 and T-48 values.

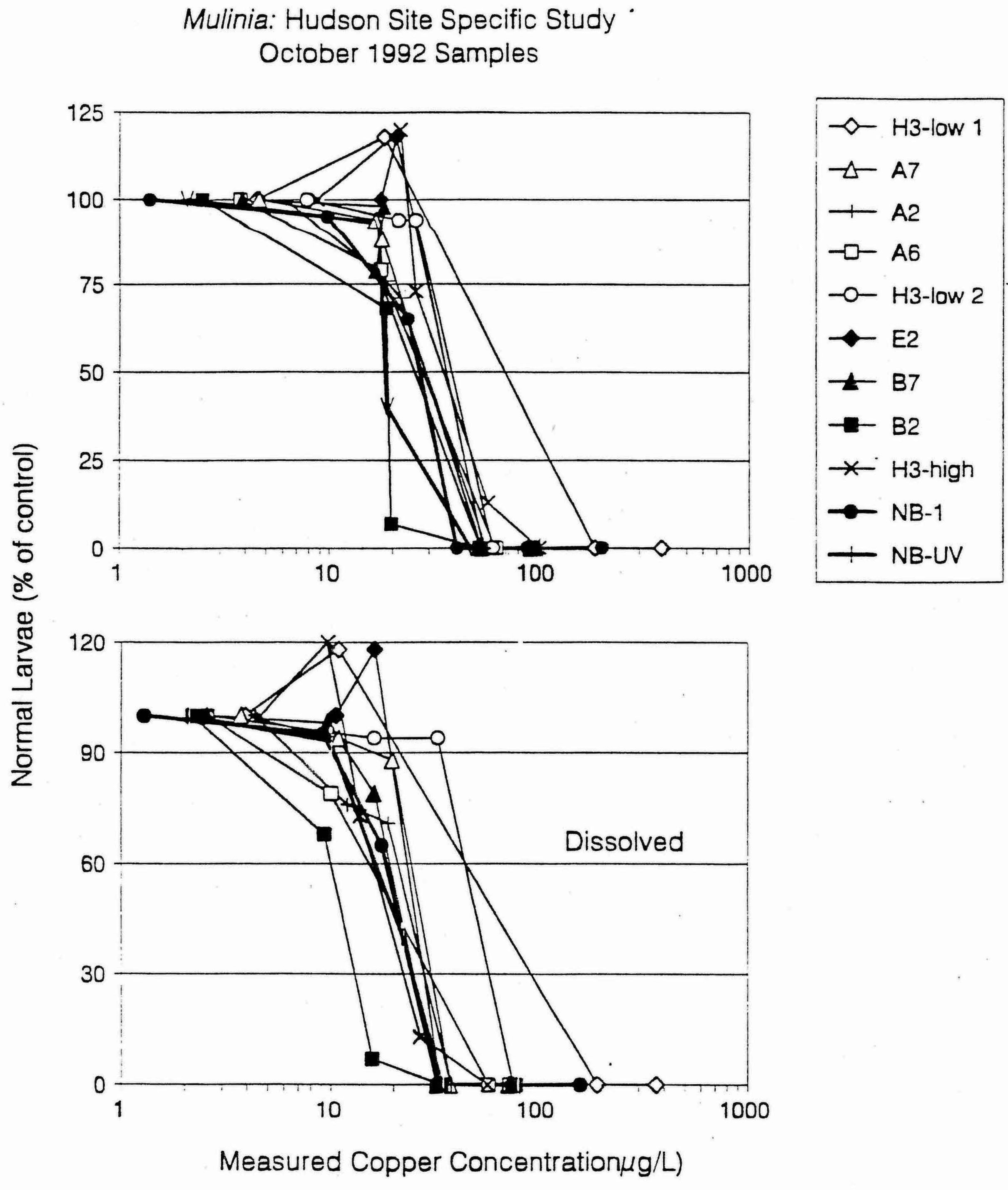

Figure 3. Mean number of normal *Mulinia lateralis* larvae, expressed as percentage of control (this control is the zero-spiked treatment for each sample tested), after 48 hr exposure to each copper concentration in Hudson/Raritan samples and the Narragansett Bay samples (NB-1 and NB-UV) collected in October 1992. The Narragansett Bay sample treated with ultra violet light is designated NB-UV. Copper data used for plots are the mean of T-0 and T-48 values.

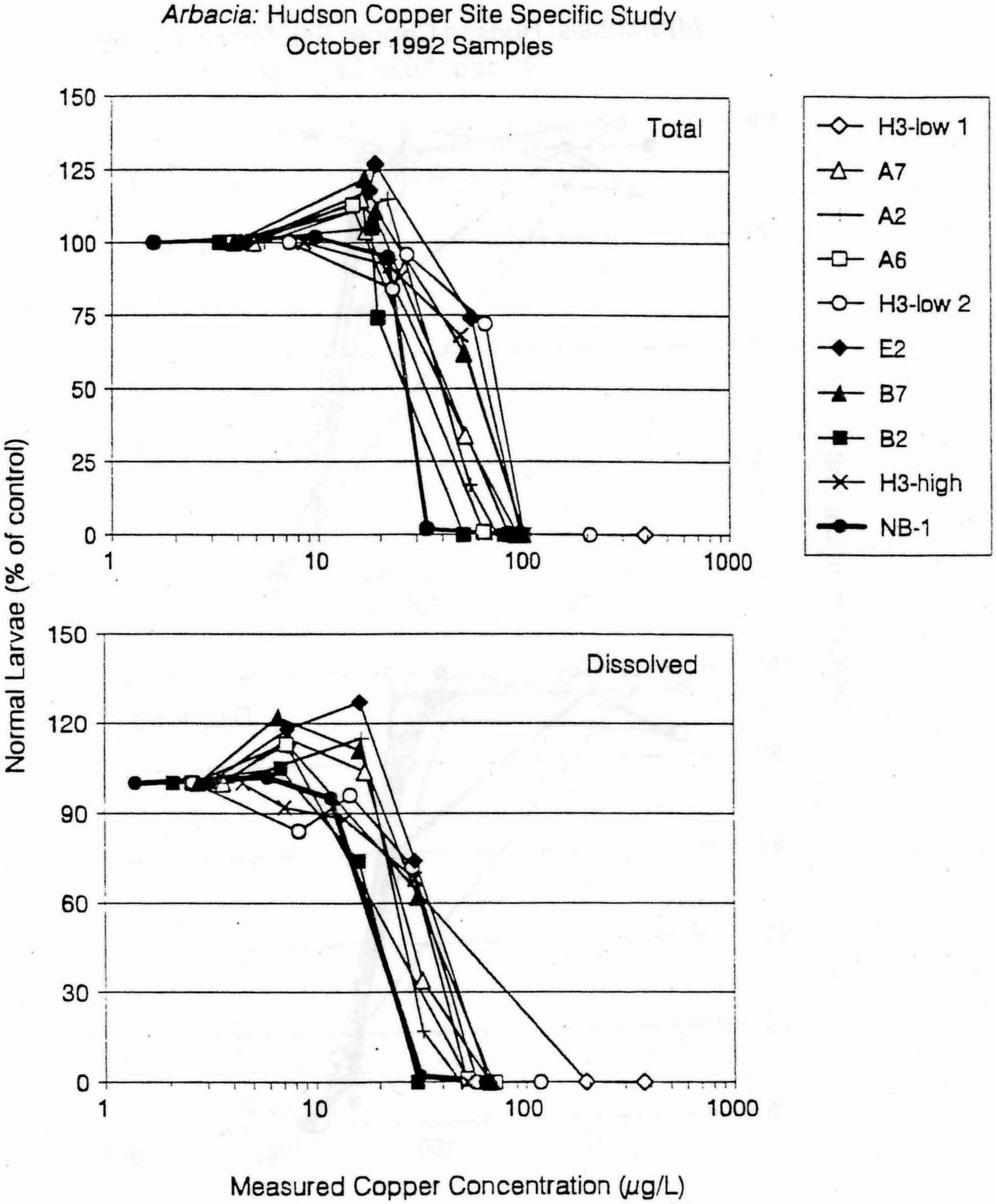

Figure 4. Mean number of normal *Arbacia punctulata* larvae, expressed as percentage of control (this control is the zero-spiked treatment for each sample tested), after 48 hr exposure to each copper concentration in Hudson/Raritan samples and the Narragansett Bay sample (NB-1) collected in October 1992. Copper data used for plots are the mean of T-0 and T-48 values.

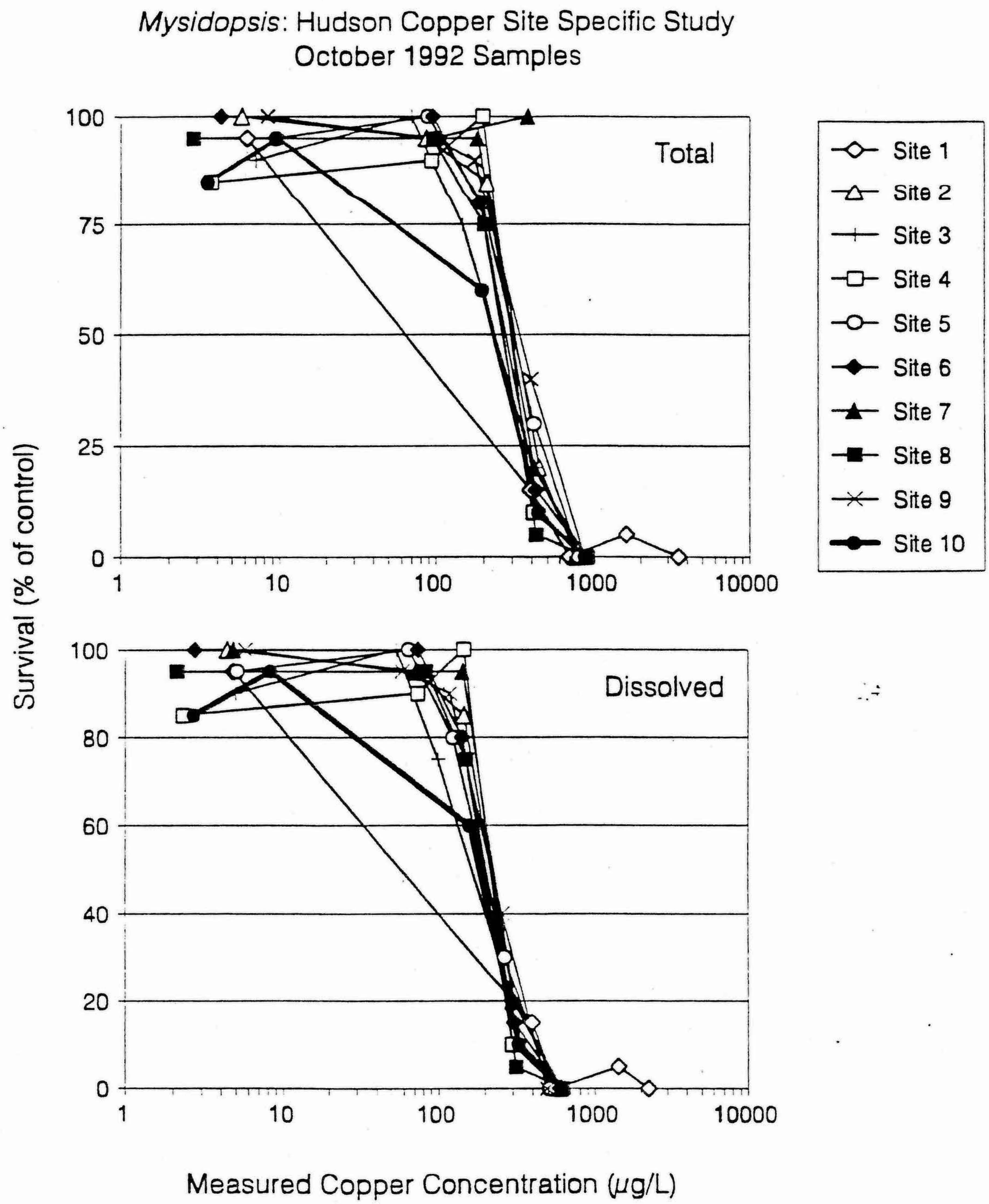

Figure 5. Mean survival of *Mysidopsis bahia* juveniles, expressed as percentage of control (this control is the zero-spiked treatment for each sample tested), after 96 hr exposure to each copper concentration in Hudson/Raritan samples and the Narragansett Bay sample (NB-1) collected in October 1992. Copper data used for plots are the mean of T-0 and T-48 values.

- Champia results: There is no clear distinction among the responses by Champia to copper exposures using the Harbor water samples (Figure 2). The Champia data are more variable than those for the other three species (Table 2). This can be explained in part by Champia's greater sensitivity to copper than the other species and Champia's steep dose response curve. Because of both these factors, a small change in water quality (thus a change in the bioavailability of copper) can cause a large change in Champia's response. Although there were no clear patterns, the response curve using Narragansett water shows a greater sensitivity to copper in laboratory water.

- Mulinia results: Unlike the results for Champia, the data from the Mulinia tests suggest that there is good agreement among the dose responses for the Harbor samples as well as the two Narragansett samples (Figure 3). This observation is consistent with the relatively narrow range in WERs for this species (Table 2). Treatment of Narragansett water with ultraviolet light had almost no effect on organism response. The WERs range from 0.57 to 1.42 for dissolved copper.

- Arbacia results: The results for Arbacia are similar to those for Mulinia in that there is no obvious distinction among the dose responses from the Harbor samples (Figure 4). The dose response data for the laboratory water (NB-1) is to the left of those for the Harbor samples, but this is not very defined for dissolved copper. This distinction, or lack thereof, is evident in the WERs for this species. The WERs range from 0.96 to 1.79 for dissolved copper. Overall the data for Arbacia are much more tightly grouped than those for Mulinia or Champia.

- Mysidopsis results: There are no obvious differences among the dose response data for Mysidopsis for all of the samples tested, including the laboratory water (Figure 5). This species is relatively insensitive to copper.

Based on the first event, WERs were developed for each species by taking the geometric mean of the Harbor sampling area WERs, as shown in Table 3.

Table 3. Geometric Mean Water Effect Ratios from the First Event

	WER
Champia	2.17
Mulinia	1.09
Arbacia	1.45
Mysidopsis	1.33

Second Event:

Water sampling for this event was conducted on April 14-15, 1993. This was a period of relatively high river flow (and higher TSS levels). Based on analysis of the data from the first event, amendments were made in regard to the species used for the second sampling event. Due to the relative insensitivity of Mysidopsis, it was decided to drop this species in favor of conducting additional replicate tests with the Narragansett Bay water. Also, supplies of Mytilus were available for the second event. Mytilus was substituted for Arbacia for this sampling event because of the bivalve's sensitivity and importance in development of the national criterion. The three species used for the second event were therefore:

Mytilus - Bivalve embryo-larval development test.

Mulinia - Bivalve embryo-larval development test.

Champia - Red algae sexual reproduction test.

- Summary of second event results:

Both the Champia and Mytilus tests were unacceptable due to poor organism response in the control tests (a third event was scheduled to attempt to test these two species again). The Mulinia performance controls were acceptable. As with the Mulinia results from the first event, all of the Harbor samples showed similar dose responses (Figure 6). For the second event there is an obvious (and statistically significant) distinction between the Narragansett samples and the Harbor samples. This is reflected in an increase in WERs for each of the stations except B7 (Raritan Bay), which remained unchanged (Table 4). It is notable that there was extremely good agreement among the dose-response curves for the Narragansett Bay samples.

A WER was developed for Mulinia for this sampling event by taking the geometric mean of the Harbor sampling area WERs. The WER for Mulinia for this event equals 1.72.

Third Event:

Water sampling for this event was conducted on May 10-11, 1993. As with the second event, this was a period of relatively high river flow and TSS levels). This event was conducted to retest Mytilus and Champia due to the fact that the performance controls from the second event were unacceptable for these species.

- Summary of third event results:

The Champia tests were again unacceptable due to poor control response. The Mytilus performance controls were acceptable. As

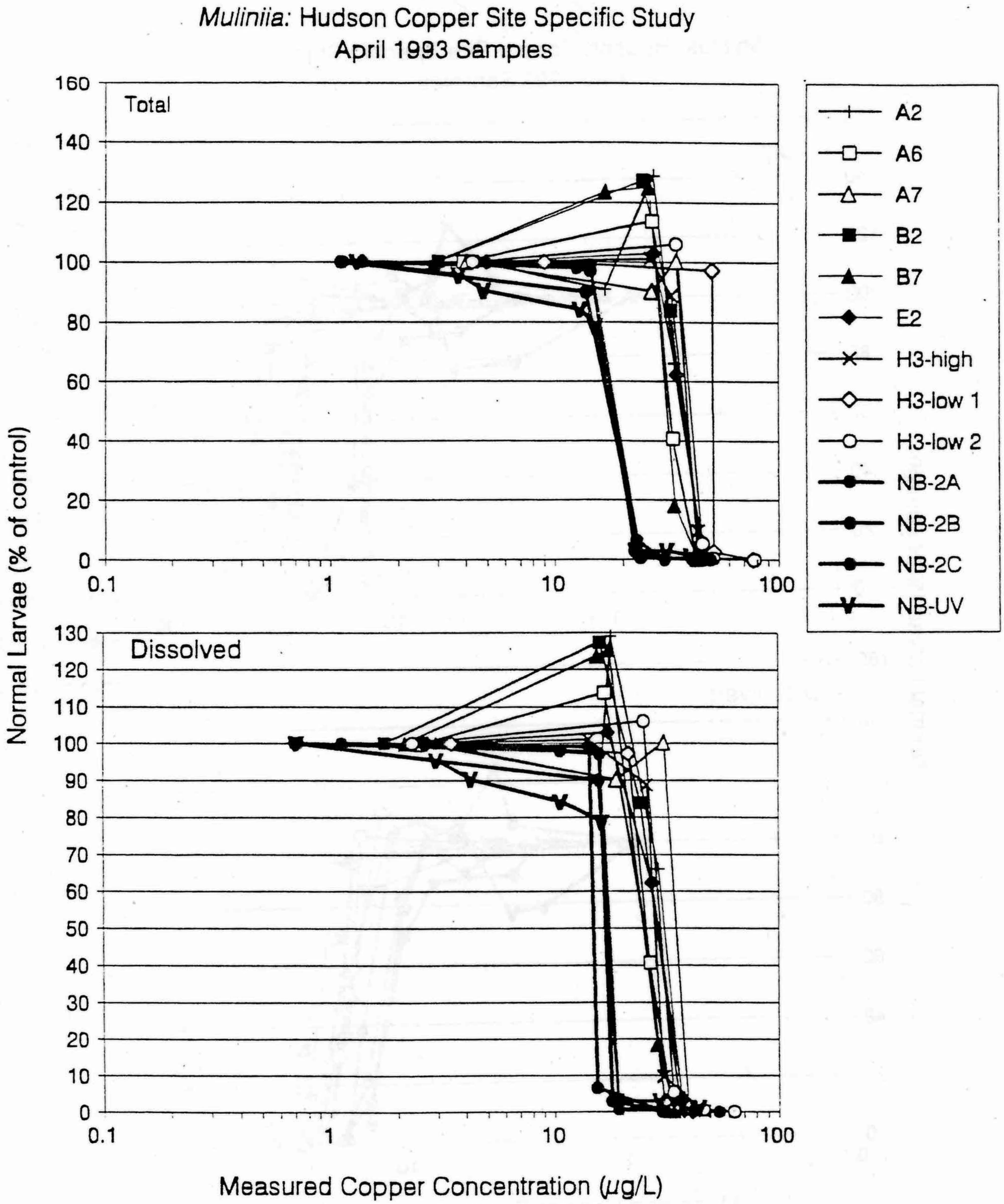

Figure 6. Mean number of normal *Mulinia lateralis* larvae, expressed as percentage of control (this control is the zero-spiked treatment for each sample tested), after 48 hr exposure to each copper concentration in Hudson/Raritan samples and the Narragansett Bay samples (NB-2A, -2B, -2C and -UV) collected in April 1993. The Narragansett Bay sample treated with ultra violet light is designated NB-UV. Copper data used for plots are the mean of T-0 and T-48 values.

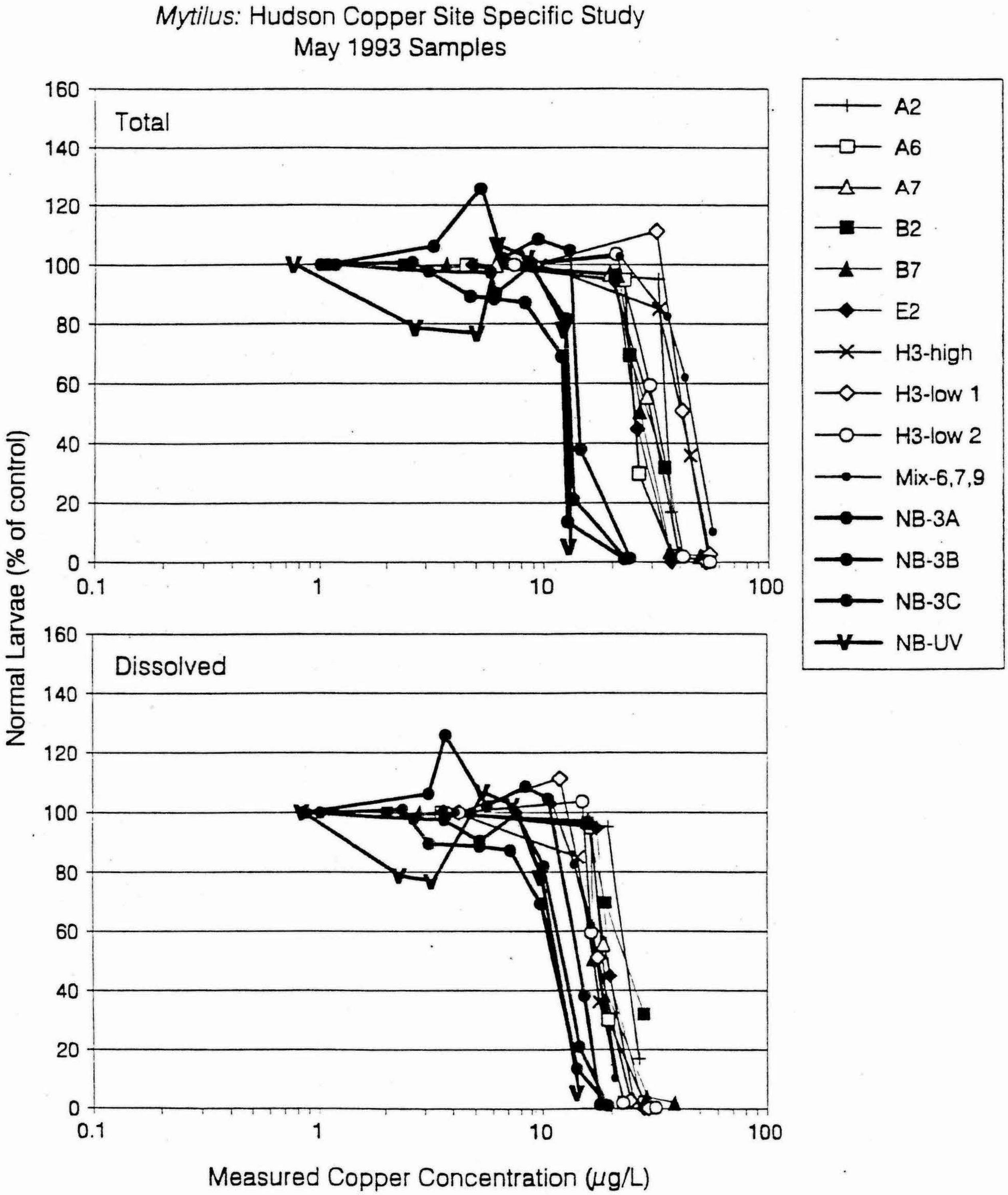

Figure 7. Mean number of normal *Mytilus edulis* larvae, expressed as percentage of control (this control is the zero-spiked treatment for each sample tested), after 48 hr exposure to each copper concentration in Hudson/Raritan samples and the Narragansett Bay samples (NB-3A, -3B, -3C and -UV) collected in April 1993. The Narragansett Bay sample treated with ultra violet light is designated NB-UV. Copper data used for plots are the mean of T-0 and T-48 values.

Table 4. Second and Third Event Results

IC50 values for high flow sampling events numbers 2 and 3 from April and May 1993 for embryo-larval tests with *Mulinia lateralis* and *Mytilus edulis*, respectively. Values are based on nominal total copper concentrations.

Station	*Mulinia*				*Mytilus*			
	IC50[a] (total)	WER[b] (total)	IC50 (dissolved)	WER (dissolved)	IC50 (total)	WER (total)	IC50 (dissolved)	WER (dissolved)
NB-A[c]	19.1		14.9		13.1		12.5	
NB-B	18.4		17.3		14.1		14.1	
NB-C	18.6		16.9		12.2		11.3	
NB-UV	18.4		17.4		12.8		11.9	
H3-low 1	51.4	2.76	26.0	1.57	41.2	3.16	17.5	1.41
H3-high	38.4	2.06	28.0	1.69	41.5	3.19	16.7	1.35
H3-low 2	48.7	2.62	32.8	1.98	31.5	2.42	17.3	1.39
A2	36.7	1.97	30.7	1.85	34.9	2.68	23.6	1.90
A6	32.5	1.75	24.7	1.49	25.2	1.94	18.4	1.48
A7	39.5	2.12	35.4	2.13	30.0	2.31	19.3	1.56
B2	37.0	1.99	28.1	1.69	29.4	2.26	23.6	1.90
B7	31.1	1.67	24.2	1.46	26.4	2.03	17.0	1.37
E2	37.4	2.01	29.1	1.75	25.6	1.97	19.5	1.57
Mix-6,7,9[d]	-				45.8	3.52	17.3	1.40

[a] 50% Inhibition Concentration calculated using ToxCalc from Tidepool Scientific Software.

[b] Water Effect Ratio, calculated by dividing the station IC50 value by the geometric value of the four Narragansett Bay values.

[c] NB = Narragansett Bay; A,B & C = replicate samples; and UV = ultra violet treated sample.

[d] Mixture of left over water samples from stations 6, 7 and 9. Used only with *Mytilus*.

with Mulinia for the second event, all of the Harbor samples showed similar dose responses (Figure 7). Again as with Mulinia for the second event, there is a statistically significant distinction between the Narragansett samples and the Harbor samples. There also was very good agreement among the dose response curves from the Narragansett Bay samples.

The WERs for Mytilus from this testing event are presented in Table 4. A WER was developed for Mytilus for this sampling event by taking the geometric mean of the Harbor sampling area WERs. The WER for Mytilus for this event is 1.54.

Table 5 summarizes the geometric mean of the Harbor sample 50% effect concentrations and WERs for all sampling events.

Table 5. Geometric Mean 50% Effect Concentrations and WERs from All Testing Events

	50% Effect Concentrations (IC50/LC50[a])	**WER[b]**
Test Series 1		
Champia	6.5	2.17
Mulinia	21.9	1.09
Arbacia	31.0	1.45
Mysidopsis	218	1.33
Test Series 2		
Mulinia	28.6	1.72
Test Series 3		
Mytilus	19.1	1.54

a = all values expressed in ug/l dissolved copper; IC50 = inhibition concentration affecting 50% of test organisms, LC50 = lethal concentration to 50% of test organisms. All test endpoints are IC50s except the Mysidopsis endpoints, which are LC50s.

b = all WERs presented are for dissolved copper

Data Used in Development of the FWER

Based on review of the data, several decisions were reached regarding the development of the FWER and subsequent site-specific criteria. One of these decisions involved a recalculation of the original national copper criteria, discussed later in the text. Another decision involved the data to be used in the development of the FWER. In the planning stages of this study, it was decided to test several species. Upon review of the results, technical agreement was reached not to include both the Mysidopsis data and the Champia data in the calculation of the site-specific criterion. For Mysidopsis, this decision is due to this organism's insensitivity to copper. In the development of a WER it is best to use data from test species that are sensitive near the marine water final acute value (FAV) for copper (5.8 ug/l) from the national criteria document (EPA 1984b), or as near as possible. Organisms that are insensitive to a substance may yield artificially low water effect ratios. The Narragansett Bay IC50 from this study for Mysidopsis was 164 ug/l dissolved copper, and the geometric mean of the Harbor IC50s was 218 ug/l dissolved copper. Also, it is not recommended to use toxicity data on insensitive species for WER development because the addition of high levels of the substance of concern to the test solutions may affect the chemistry of both the laboratory and the site test water. This may preclude the meaningful observation of any physical/chemical differences between the laboratory and site waters.

Champia was originally included because of its sensitivity and as a substitute for Mytilus, which was not available for the first event. However, EPA guidance recommends that data on organisms which are sensitive below the criterion level should not be included in FWER calculations. Such organisms generally yield relatively high WERs which may result in underprotection. The Champia data was therefore not included in the determination of the FWER.

Calculation of the FWER

Statistical analyses were conducted at EPA's ERL-N (Hansen, 1993 pers. comm.) to determine if there were significant differences in the toxicity of copper in laboratory vs. site water or between Harbor sampling areas. Changes in test organism response were evaluated as a function of increasing concentration, not point estimates of response such as toxicity test endpoint values. When an analysis of covariance is applied to the Mytilus data, the species whose sensitivity most closely approximated the national criterion concentration, it is demonstrated that the slopes and position of concentration response relationships for all tests conducted at the same time using Narragansett Bay ("laboratory") water were not different. In addition, comparisons between laboratory and Harbor water revealed highly significant differences supporting the conclusion of lesser availability of copper in the Harbor waters. The differences in the various test species' data detected between slopes of concentration-response relationships from the different Harbor sampling areas were small and within experimental error typically associated with these types of toxicity tests. Therefore, site water IC50 values and WERs were considered similar across sites and test species within the Harbor. These analyses support the appropriateness of the use of one WER throughout the Harbor complex.

The geometric mean of the IC50s across the Harbor sampling areas for a single species was used to calculate that species' WER for each of the three sampling events. For Mulinia, the one species tested during both major sampling events, the geometric mean of the pooled endpoints from both sampling events was used in the calculation of the species' WER. Where there was more than one Narragansett Bay test conducted on a species during one testing event, the geometric mean of these values was used in the WER calculation. The FWER was then derived as the geometric mean of the species-specific WERs. Tables 6 and 7 present respective summaries of the data not used, and the data which was used, in the development of the FWER. As shown in Table 7, the FWER for copper in NY/NJ Harbor is 1.5 for the dissolved form of copper.

Table 6. Data Not Used in Calculation of the FWER

	Geometric Mean IC50s (ug/l dissolved copper)		Species Water Effect Ratios
	Narr. Bay	Harbor	
Champia	3.0	6.5	2.17
Mysidopsis	164	218	1.33

Table 7. Data Used in Calculation of the FWER

	Geometric Mean IC50s (ug/l dissolved copper)		Species Water Effect Ratios
	Narr. Bay	Harbor	
Arbacia	21.4	31.0	1.45
Mulinia[a]	17.7	25.2	1.42
Mytilus	12.4	19.1	1.54
Final WER = Geo. Mean of Species WERs = 1.5			

a = For Mulinia, the one species tested during both sampling events, the geometric mean of the pooled endpoints from both sampling events was used in the calculation of the species' WER.

Recalculation of the National Acute Copper Criterion Value

Analysis of the toxicity data obtained through this study for Mytilus indicated that the national marine acute water quality criterion for copper of 2.9 ug/L expressed as the total recoverable form of the metal may be recalculated for application to this study. This procedure is independent from the development of the site-specific copper criterion. EPA Region II performed a literature search and worked with EPA ERL-N to recalculate the national criterion. SAIC produced a separate report (SAIC 1993b) which includes descriptions and references for the data used for each species. Corrections were made to this report in memoranda from David J. Hansen of EPA ERL-N (Hansen, 1994a and 1994b) to EPA Region II. The December 1993 SAIC report along with Hansen's memoranda (1994a and 1994b) include all data used in the recalculation procedure, which are described below (the recalculation procedure and the following discussion apply to the acute copper criterion; the chronic criterion, which until now was assumed to be equivalent to the acute criterion, is addressed in the next section of this report as well as in Hansen's memoranda (1994a and 1994b).

The original criterion was driven by toxicity data on the embryo-larval form of the bivalve Mytilus edulis (the blue mussel). The reason for this is that Mytilus is a commercially important species that is sensitive to copper at levels below the criterion which would be calculated using the statistical methodology contained in the "Guidelines for Deriving Numerical National Water Quality Criteria for the Protection of Aquatic Organisms and Their Uses" (EPA 1985)(EPA criteria development guidelines). The EPA aquatic life criteria development guidelines state that under these circumstances, the toxicity data for the commercially important species should be used to develop the criterion.

The original national copper toxicity dataset included only one toxicity test endpoint for Mytilus. The endpoint is 5.8 ug/L, and is a nominal copper concentration (a nominal concentration is unmeasured; it represents a calculation of the concentration of a substance added to the testing dilution water at the initiation of the test). The EPA aquatic life criteria development guidelines (1985) indicate that any valid toxicity data obtained using measured concentrations should supersede any nominal-based data for a particular species when developing criteria. Also, EPA recommends that the national criteria be recalculated if valid toxicity data is obtained at any time which would significantly affect the national dataset on which a national criterion is based.

The toxicity testing for WER development resulted in a series of four toxicity test endpoints for Mytilus based upon measured dissolved copper concentrations in the control tests using water from Narragansett Bay, Rhode Island. As previously noted, Narragansett Bay is the source for dilution water typically used in the development of national marine water quality criteria. These measured endpoints are significantly higher (12.5 ug/L, 14.1 ug/L, 11.3 ug/L, and 11.9 ug/L; geometric mean = 12.4 ug/L) than the one nominal endpoint used in the water quality criteria document (5.8 ug/L). In addition, a series of three toxicity test endpoints for Mytilus was obtained from a recent site-specific copper study conducted for San Francisco Bay through the San Francisco Bay Regional Water Quality Control Board (ToxScan, Inc. 1991). These measured endpoints are also higher (5.787 ug/L, 6.278 ug/L, and 8.889 ug/L; geometric mean = 7.24 ug/l) than the nominal endpoint used in the water quality criteria document.

Therefore, based upon the recommendations in the EPA aquatic life criteria development guidelines (1985), it was decided to undertake a recalculation of the national marine aquatic life copper criterion. However, as described below, because the development of the recalculated criteria used NY/NJ Harbor-specific data from this study, the recalculated criteria presented in this report are considered to be applicable only to NY/NJ Harbor waters.

The procedures for calculating acute aquatic life criteria are described in detail in the EPA aquatic life criteria development guidelines (1985). In summary, the statistical methodology uses the rank order of the acute sensitivity of genera, the acute values for the four most sensitive genera, and the total number of genera tested to calculate, by modified regression analysis, the FAV. This value represents that concentration above which 95 percent of the average acute values (LC50s or EC50s) occur. The acute criterion is then derived by dividing the FAV by 2, a factor that is the average ratio of LC50s to LC0s.

Procedures Used for the Recalculation: The EPA aquatic life criteria development guidelines (1985) state that in conducting a recalculation of a national criterion, it is necessary to add to the national dataset all relevant data on copper toxicity obtained since the original criteria document was published. As outlined below, the copper recalculation procedure therefore involved an extensive data search to update the national data set to include data from this study, as well as any other post-1984 data that may be relevant. The criteria for acceptable data are listed in the EPA aquatic life criteria development guidelines (1985). In summary, the criteria for acceptable data are as follows:

- Except for tests with saltwater annelids and mysids, results of acute tests during which the test organisms were fed should not be used, unless data indicate that the food did not affect the toxicity of the test material.

• Results of acute tests conducted in unusual dilution water should not be used.

• Only the following types of data on acute toxicity to aquatic animals should be used.

- Tests for embryos and larvae of barnacles, bivalve molluscs, sea urchins, lobsters, shrimp, and abalones should be reported as a 96-hr EC_{50} based on the percentage of organisms with incompletely developed shells plus the percentage of organisms killed. If such a 96-hr EC_{50} is not available, the lower of either the 96-hr EC_{50} based on the percentage of organisms with incompletely developed shells, or the 96-hr LC_{50}, should be used instead.

- Tests for all other fresh and saltwater animal species and older life stages of barnacles, bivalve molluscs, sea urchins, lobsters, shrimp, and abalones should be reported as a 96-hr EC_{50} based on the percentage of organisms exhibiting the loss of equilibrium, plus the percentage of organisms immobilized, plus the percentage of organisms killed. If such a 96-hr EC_{50} is not available, the 96-hr LC_{50} should be used instead.

- Tests with single-celled organisms are not considered acute tests, even if the duration was 96 hours or less.

- If the tests were conducted properly, acute values reported as "greater than" values and those which are above the solubility of the test material should be used, because rejection of such values would unnecessarily lower the FAV by eliminating values for resistant species.

- If the acute toxicity of the material has apparently been shown to be related to a water quality characteristic such as hardness or particulate matter for freshwater animals or salinity or particulate matter for saltwater animals, an FAV equation should be derived on that water quality characteristic.

- If data indicate that one or more life stages are at least a factor or two more resistant than one or more other life stages of the same species, the data for the more resistant life stages should not be used in calculating the SMAV.

- The agreement of the data within and between species in a genus should be considered, with questionable acute values not included in the calculation of the SMAV.

- For each species for which at least one acute value is available, the SMAV should be calculated as the geometric mean of the results of all flow-through tests in which the concentrations of the test material were measured. For a species for which no such result is available, the SMAV should be calculated as the geometric mean of all available acute values (i.e, nominal concentrations from flow-through tests, and/or results from static and renewal tests).

EPA undertook a comprehensive literature search in an effort to obtain all pertinent studies which have been conducted on the toxicity of copper to marine organisms since 1984 when the copper criteria document was last revised and published. All information found was evaluated and acceptable information was then used to update Tables 1 and 3 of the water quality criteria document. Table 1, in each of EPA's water quality criteria documents, is a listing of acute toxicity to aquatic organisms, while Table 3 is the ranked genus mean acute values (GMAV). Table 8 of this report is the updated Table 3 from the criteria document.

Table 8. Revised Ranked Genus Mean Acute Values (revised Table 3 of the national water quality criteria document for copper)

Rank	GMAV (ug/L.)	Species	SMAV (ug/L*)
27	30,000	Ophryotrocha labronica (polychaete worm)	30,000
26	7694	Rangia cuneata (Common rangia)	7694
25	1837	Fundulus heteroclitus (Mummichog)	1837
24	600	Carcinus maenus (Green crab)	600
23	526	Eurytemora affinis (Copepod)	526
22	411.7	Trachinotus carolinus (Florida pompano)	411.7
21	368	Cyprinodon variegatus (sheepshead minnow)	368
20	>301.0	Nereis diversicolor (Polychaete worm)	363.8
		Neries virens (polychaete worm)	>249
19	280	Leiostomus xanthurus (Spot)	280

Rank	GMAV (ug/L*)	Species	SMAV (ug/L*)
18	243	Atherinops affinis (topsmelt)	243
17	214	Tigriopus californica (copepod)	214
16	159.8	Mysidopsis bahia (Mysid)	181
		Mysidopsis bigelowi (Mysid)	141
15	150.6	Neanthes arenaceodentata (Polychaete worm)	150.6
14	138	Pseudodiaptomus coronatus	138
13	130	Menidia peninsulae (Tidewater silverside)	140
		Menidia menidia (Atlantic silverside)	135.6
		Menidia beryllina (Inland silverside)	115.7
12	128.9	Pseudopleuronectes americanus (Winter flounder)	128.9
11	120	Phyllodoce maculata (Polychaete worm)	120
10	69.28	Homarus americanus (American lobster)	69.28
9	65.6	Haliotis crahcerodil (Black abalone)	50
		Haliotis rufescens (Red abalone)	86.08
8	49	Cancer magister (Dungeness crab)	49
7	39.97	Acartia clausi (Copepod)	52
		Acartia tonsa (Copepod)	30.72
6	39	Mya arenaria (Soft-shell clam)	39
5	21.4	Arbacia punctulata (Sea urchin)	21.4
4	21.38	Crassostrea gigas (Pacific oyster)	17.80
		Crassostrea virginica (Eastern oyster)	25.67
3	17.70	Mulinia lateralis (Coot clam)	17.70
2	11.56	Paralichthys dentatus (Summer flounder)	11.56
1	9.625	Mytilus edulis (Blue mussel)	9.625
Final Acute Value (FAV) = 10.58 ug/L dissolved copper			

ug/l*: It should be noted that the final SMAVs for all species included in Table 3 have been corrected from the total recoverable form of copper to the dissolved form of copper, where necessary, by multiplying the total recoverable value by the dissolved to total metal ratio of 0.83, which was derived as the geometric mean of the dissolved to total recoverable copper ratios from the control tests conducted as part of the New York/Jersey Harbor Study.

The literature search consisted of the following:

- a search conducted through the EPA-Region II library, using numerous toxicity data bases available through the CD-ROM data base (including Toxline and Aqualine);

- a retrieval of aquatic toxics effects data through EPA's Aquatic Toxicity Information Retrieval (AQUIRE) data base; and,

- a survey of all of the other EPA coastal Regions (I, III, IV, VI, IX, and X) to ascertain if any applicable copper toxicity testing on marine organisms has been conducted by either the Region itself or one of its States.

All potentially applicable articles, including raw data, identified through the abstracts from the library literature search, the AQUIRE retrieval, and EPA Regional/State studies, were obtained to verify whether or not the data described was acceptable for inclusion in Tables 1 and 3.

Results: The majority of the data obtained through this literature search was found to be unacceptable for one or more of the following reasons:

- the organisms' exposure to copper was part of an overall, concurrent exposure to a number of different toxicants;

- the duration of the toxicity test was unacceptable;

- non-resident species to North America were used in the test;

- the tests were conducted on freshwater organisms; and/or

- the chelating agent EDTA (edetic acid) was used in the exposure medium.

Upon review, some of the data obtained was found to be acceptable for use in the recalculation procedure. A total of seven articles were found through the library search and the AQUIRE retrieval, which provided data on genera or species which were not currently included in Tables 1 and 3 of EPA's current water quality criteria document for copper. As a result of this literature search, the following genera or species and corresponding GMAVs presented in Table 9 of this report have been added to Tables 1 and 3 of the national copper dataset.

Table 9. Genera and Species Added to Tables 1 and 3 of National Copper Dataset

Genera/Species	GMAV (dissolved)
Fundulus heteroclitus (mummichog) (Gardner, et al., 1973, and Dorfman, et al., 1977)	1837 ug/L
Cyprinodon variegatus (sheepshead minnow) (Hughes, et al., 1989)	368 ug/L
Atherinops affinis (topsmelt) (Andersen, et al., 1991)	243 ug/L
Tigriopus californica (copepod) (O'Brien, et al., 1988)	214 ug/L
Ophryotrocha labronica (polychaete worm) (Brown, et al., 1971)	30,000 ug/L
Neries virens (polychaete worm) (Raymont, et al., 1963)	> 249 ug/L
Menidia beryllina (inland silverside) (Walker, et al., 1991)	130 ug/L

In addition to the above-referenced information, a significant amount of data was obtained from a recent site-specific copper study conducted for San Francisco Bay through the San Francisco Bay Regional Water Quality Control Board (ToxScan, Inc. 1991). Additional data was obtained from this study for two of the most sensitive species listed in Table 3 of the water quality criteria document as follows:

- Mytilus edulis (blue mussel), (San Franscico Bay-specific SMAV = 7.24 ug/L) which is the most sensitive organism to copper toxicity in the national dataset; and

- Crassostrea gigas (Pacific oyster), (San Franscico Bay-specific SMAV = 17.80 ug/L) one of the four most sensitive species, which in conjunction with Crassostrea virginica (eastern oyster) accounts for the GMAV for Crassostrea.

The toxicity testing data obtained from the New York/New Jersey Harbor and San Francisco Bay studies were used to recalculate Species Mean Acute Values (SMAVs) for Mytilus edulis and Crassostrea gigas by taking the geometric mean of all values obtained in both studies.

Summary of Revisions to the Four Most Sensitive Species/Genera:

Table 10. Comparison of the updated GMAVs with the 1984 Copper Criteria Document for the Four Most Sensitive Genera

Species	New York/New Jersey Harbor SMAVs (ug/L dissolved)	San Franscico Bay SMAVs (ug/L dissolved)	1984 Copper Criteria Document GMAVs (ug/L total recoverable)	Recalculated GMAVs (ug/L dissolved)
Mytilus edulis (blue mussel)	12.4	7.24	5.8	9.625
Paralichthys dentatus (summer flounder)	-	-	13.93	11.56
Mulinia lateralis (coot clam)	17.70	-	-	17.70
Crassostrea	-	-	14.92	21.38
Crassostrea gigas (Pacific oyster)	-	17.80	7.807	17.80
Crassostrea virginica (Eastern Oyster)	-	-	28.52	25.67

•Mytilus edulis: As previously mentioned, an SMAV was calculated for Mytilus edulis by replacing the 5.8 ug/L nominal based endpoint with the geometric mean of all lab control water values obtained in both the San Francisco Bay study and the New York/New Jersey Harbor study. The result is an SMAV of 9.625 ug/L dissolved copper.

•Paralichthys dentatus (summer flounder): No new data was obtained for Paralichthys dentatus. However, the SMAV for Paralichthys dentatus was adjusted from total recoverable to dissolved. The result is an SMAV of 11.56 ug/L.

•Mulinia lateralis (coot clam): Data from the lab control water values obtained in New York/New Jersey Harbor study were used to calculate an SMAV for Mulinia lateralis by taking the geometric mean of all values obtained. The result is an SMAV of 17.70 ug/L.

•Crassostrea (oyster): No new data was obtained for Crassostrea virginica. However, the SMAV for Crassostrea virginica was adjusted from total recoverable to dissolved. A geometric mean of the recalculated SMAV for Crassostrea gigas and the previous SMAV for Crassostrea virginica was taken to derive a GMAV for Crassostrea. The result is a GMAV of 21.38 ug/L.

The updated GMAVs for the four most sensitive species/genera are shown in the following table.

Table 11. Updated GMAVs for the Four Most Sensitive Genera

Genus/Species	GMAV (dissolved)
Mytilus edulis (blue mussel)	9.625 ug/L
Paralichthys dentatus (summer flounder)	11.56 ug/L
Mulinia lateralis (coot clam)	17.70 ug/L
Crassostrea (oyster)	21.38 ug/L

Final Recalculation:

Based upon all of the above-referenced information, a recalculation of the national marine aquatic life acute copper criterion was completed. The recalculation also took into consideration the following New York/New Jersey Harbor site-specific copper toxicity data presented in Table 11.

Table 12. Comparison of the Resultant IC50s from Copper Toxicity Tests for Mytlilus

San Franscico Bay Control Tests (ug/L dissolved)	New York/New Jersey Harbor Control Tests (ug/L dissolved)	New York/New Jersey Harbor Site Tests (ug/L dissolved)
5.787	12.5	17.5
6.278	14.1	16.7
8.889	11.3	17.3
	11.9	23.6
		18.4
		19.3
		23.6
		17.0
		19.5
Geometric Mean = 9.625 ug/L		Geometric Mean = 19.06 ug/L

The first two columns of the table present the individual IC50s from both the San Francisco Bay study and the New York/New Jersey Harbor water control tests. These values were used in calculating the revised SMAV of 9.625 ug/L for Mytilus edulis.

Once again the SMAV is based on the geometric mean of all of the values obtained from the lab control water tests of these studies.

The final column of the table outlines the individual IC50s obtained from using site water endpoints from each of the 10 sampling areas throughout New York/New Jersey Harbor Complex. A geometric mean of these values was also calculated, which resulted in a Harbor-wide SMAV of 19.06 ug/L.

The EPA aquatic life criteria development guidelines (1985) calls for the use of a variety of test species in calculating a final acute value (FAV) for any particular substance. However, in some cases, if the SMAV of a commercially or recreationally important species is lower than the calculated FAV, then the SMAV for that commercially or recreationally important species replaces the calculated FAV in order to provide protection for that important species.

Mytilus edulis is considered to be a commercially or recreationally important species, and is the most sensitive of the four most sensitive marine species to copper. As outlined above, the revised SMAV for Mytilus edulis has been calculated to be 9.625 ug/L dissolved copper. This value is lower than the calculated FAV of 10.58 ug/L dissolved copper, which was calculated based on the methodology specified in the EPA aquatic life criteria development guidelines (1985), and using the data shown in the revised Table 3.

In general, based upon the above, the SMAV of 9.625 ug/L dissolved copper for Mytilus edulis would be used as the FAV for copper. However, the IC50s for Mytilus edulis at all Harbor sampling areas range from 16.6 ug/L - 23.6 ug/L dissolved copper, and the site-specific SMAV for Mytilus edulis throughout the Harbor complex was calculated to be 19.06 ug/L dissolved copper. Because these NY/NJ Harbor-specific toxicity testing endpoints occur at concentrations higher than the calculated FAV of 10.58 ug/L, the calculated endpoint is protective for NY/NJ Harbor waters. Therefore, it is appropriate to use the calculated FAV of 10.58 ug/L dissolved copper to recalculate the national acute copper criterion specifically for the waters of the New York/New Jersey Harbor.

The final recalculated acute copper criterion is therefore expressed as follows:

Recalculated acute criterion = FAV/2
Recalculated acute criterion = 10.58/2
Recalculated acute criterion = **5.29 ug/L dissolved copper.**

The recalculated acute copper criterion value of 5.29 ug/L dissolved copper will be multiplied by the FWER of 1.5 to yield the final acute criterion for NY/NJ Harbor.

Acute Site-Specific Criterion = Recalculated Acute Copper Criterion X WER

Acute Site-Specific Criterion = 5.29 ug/L dissolved X 1.5

Acute Site-Specific Criterion = **7.9 ug/L dissolved copper.**

Calculation of a Chronic Copper Criterion

Although toxicity tests of acute duration formed the basis for this study, the FWER can be used to adjust both the national acute <u>and</u> chronic criteria values. This is because any factors which result in differing copper toxicity between site and laboratory waters may be assumed to affect acute and chronic toxicity equally.

The most common method of deriving a chronic criterion requires the development of an acute-to-chronic ratio (ACR) by conducting both acute and full life cycle chronic tests on acutely sensitive species and dividing the FAV (or in the case of copper the SMAV) by the calculated ACR. At the time the copper criteria document (EPA 1984b) was published, sufficient chronic test data on acutely sensitive marine species were not available. The marine acute criterion was based on the SMAV derived from a <u>Mytilus edulis</u> embryo-larval test. Since full life cycle chronic tests had not been conducted on such sensitive marine molluscs, nothing was known about the chronic effects of copper or other metals on such sensitive species. However, because the embryo-larval life stage of an organism is generally the most sensitive life stage, the assumption was made that the sensitivities of embryo-larval molluscs would determine the results of life cycle tests. Under this assumption, acute tests conducted with embryo-larval molluscs could serve as surrogates for life-cycle chronic tests. Therefore, the EPA aquatic life criteria development guidelines (1985) recommended that for substances for which the lowest available SMAVs were determined with embryo-larval molluscs, the ACR should be assumed to be 2 ("factor of 2" assumption), so that the chronic criterion equals the acute criterion. This "factor of 2" assumption was supported by the comparison of early life stage acute test results of fishes with ACRs developed using chronic full life cycle tests with fishes. The copper criteria document (EPA 1984b) utilized the factor of 2 assumption and accordingly the acute criterion (SMAV÷2 = 5.8 ÷ 2 = 2.9 ug/l) was equivalent to the chronic criterion (SMAV÷ACR = 5.8 ÷ 2 = 2.9 ug/l).

David J. Hansen of EPA's ERL-N, EPA's national marine water quality criteria development expert, indicated that based on the following information he believes the factor of 2 assumption is no longer valid, and that an ACR may be developed using data contained in the 1984 copper criteria document (Hansen 1994a and 1994b). Hansen's recommendation is based on post-1984 data which demonstrate chronic effects of tributyltin (TBT) on bivalve and gastropod molluscs, and comparison of these data with acute effects data. Acute values for embryo-larval mollusc tests from Table 1 of the national TBT draft water quality criteria document

(EPA 1987) occur near 1.5 ug/l (Mercenaria mercenaria [hard clams]: 1.13 ug/l and 1.65 ug/l; Crassostrea gigas [Pacific oyster]: 1.56 ug/l). Although no acute data was observed for Ostrea edulis (european oyster), because species within a genus generally have acute values within a factor of two, it is reasonable to assume that the acute value for Ostrea would also be about 1 ug/l. If the ACR of 2.0 were generically appropriate to derive acceptable concentrations for molluscs, no chronic effects would be expected at concentrations lower than approximately 0.5 ug/l (the approximate acute value of 1 divided by 2). That is not what the actual data show. Growth of Mercenaria was reduced at concentrations between 0.01 and 0.5 ug/l, for Crassostrea at 0.02 to 0.2 ug/l, and for Ostrea at 0.02 to 2.0 ug/l. Shell thickening, a TBT specific response, was observed at 0.02 to 2.0 ug/l and 0.01 to 0.05 ug/l in two laboratory studies and about 0.018 to 0.060 ug/l in the field. Mortality of Crassostrea occurred at 0.24 ug/l. These data demonstrate that the previously assumed ACR of 2.0 may not be protective of chronic impacts, even for such sensitive life stages as embryo-larval molluscs.

Based on the above data Hansen concluded that the factor of 2 assumption used in the 1984 copper criteria document to develop the chronic marine criterion is no longer valid. After consultation with Hansen and review of the data he supplied to support his recommendations (Hansen 1994b), EPA and the States of New York and New Jersey agreed that an ACR based on the factor of 2 assumption is no longer valid.

It was therefore necessary to use an appropriate ACR for copper in marine waters. Based on the review of the information provided by Hansen (1994b) the States and EPA proposed, and the WQS/TMDL/WLA workgroups agreed, to use the freshwater ACR of 2.823 obtained from the copper criteria document (EPA 1984b). The States and EPA chose this approach because ACRs are transferrable between fresh and marine water data and because no new data on the chronic toxicity of copper to sensitive marine organisms were found in the recalculation literature search. This method, while a departure from the factor of 2 based ACR, uses only the data contained in the copper criteria document, which were determined to be acceptable to calculate an ACR. In keeping with the EPA aquatic life criteria development guidelines (1985), the ACR of 2.823 is based on the geometric mean of the ACRs for Daphnia magna (ACR = 2.418) and Gammarus pseudolimnaeus (ACR = 3.297), the two species with SMAVs closest to the freshwater FAV.

The recalculated chronic copper criterion is therefore calculated as follows:

Recalculated chronic criterion = (FAV/ACR)
= (10.58 ug/l / 2.823)
= 3.75 ug/l dissolved copper

The recalculated chronic copper criterion value of 3.75 ug/l dissolved copper will be multiplied by the FWER of 1.5 to calculate the final chronic criterion for NY/NJ Harbor.

Chronic Site-Specific Criterion = Recalculated Chronic Criterion X WER
= 3.75 ug/l X 1.5
= 5.6 ug/l dissolved copper.

Conclusion

The site-specific acute and chronic copper criteria for the New York/New Jersey Harbor complex are:

Site-specific acute copper criterion = 7.9 ug/l dissolved copper

Site-specific chronic copper criterion = 5.6 ug/l dissolved copper.

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