Ecological assessment of copper and cadmium in surface waters of Chesapeake Bay watershed

Article *in* Environmental Toxicology and Chemistry · June 1998

DOI: 10.1002/etc.5620170626

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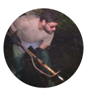

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SETAC PRESS

Environmental Toxicology and Chemistry, Vol. 17, No. 6, pp. 1172–1189, 1998
Printed in the USA
0730-7268/98 $6.00 + .00

Hazard/Risk Assessment

ECOLOGICAL RISK ASSESSMENT OF COPPER AND CADMIUM IN SURFACE WATERS OF CHESAPEAKE BAY WATERSHED

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(*Received* 6 *June* 1997; *Accepted* 23 *September* 1997)

Abstract—This ecological risk assessment was designed to characterize risk of copper and cadmium exposure in the Chesapeake Bay watershed by comparing the probability distributions of environmental exposure concentrations with the probability distributions of species response data determined from laboratory studies. The overlap of these distributions was a measure of risk to aquatic life. Dissolved copper and cadmium exposure data were available from six primary data sources covering 102 stations in 18 basins in the Chesapeake Bay watershed from 1985 through 1996. Highest environmental concentrations of copper (based on 90th percentiles) were reported in the Chesapeake and Delaware (C and D) Canal, Choptank River, Middle River, and Potomac River; the lowest concentrations of copper were reported in the lower and middle mainstem Chesapeake Bay and Nanticoke River. Based on the calculation of 90th percentiles, cadmium concentrations were highest in the C and D Canal, Potomac River, Upper Chesapeake Bay, and West Chesapeake watershed. Lowest environmental concentrations of cadmium were reported in the lower and middle mainstem Chesapeake Bay and Susquehanna River. The ecological effects data used for this risk assessment were derived primarily from acute copper and cadmium laboratory toxicity tests conducted in both fresh water and salt water; chronic data were much more limited. The 10th percentile (concentration protecting 90% of the species) for all species derived from the freshwater acute copper toxicity database was 8.3 μg/L. For acute saltwater copper data, the 10th percentile for all species was 6.3 μg/L copper. The acute 10th percentile for all species in the freshwater cadmium database was 5.1 μg/L cadmium. The acute 10th percentile for all saltwater species was 31.7 μg/L cadmium. Highest potential ecological risk from copper exposures was reported in the C and D Canal area of the northern Chesapeake Bay watershed. Relatively high potential ecological risk from copper exposure was also reported in Middle River. Moderate potential ecological risk from copper exposure was reported in selected locations in the Choptank and Potomac Rivers. Potential ecological risk from copper exposure was either low or data were insufficient to assess ecological risk in the other 14 basins. Potential ecological risk from cadmium exposures was much lower than for copper. Highest potential ecological risk from cadmium exposure was reported in the C and D Canal. Low to moderate potential ecological risk for the most sensitive trophic group (fish) was reported in the Potomac River, upper mainstem bay, West Chesapeake watershed, Choptank River, and Chester River. In the other 12 basins, ecological risk was either judged to be low or insufficient data were available for determining risk.

Keywords—Copper Cadmium Ecological risk assessment Chesapeake Bay watershed

INTRODUCTION

The 1987 Chesapeake Bay Agreement identified the improvement and maintenance of water quality as the most critical elements in the restoration and protection of Chesapeake Bay [1]. This agreement also called for the development and adoption of a Chesapeake Bay basinwide toxics reduction strategy to support research, monitoring, and toxic substance management that were directed to overall chemical reduction in the Chesapeake Bay watershed [1]. One commitment specified the creation of a toxics of concern (TOC) list for Chesapeake Bay. This TOC list was designed to prioritize more than 1,000 chemicals that may be affecting aquatic life or human health in Chesapeake Bay by using a risk-based ranking system and to direct future research efforts and management initiatives.

The first TOC list was completed in 1990 and revised in 1996 [2,3]. The revised TOC list was developed using a chemical ranking system that incorporates sources, fate, exposure, and effects of chemicals on Chesapeake Bay living resources and human health [4]. The TOC list contains a list of primary TOCs as well as a list of secondary TOCs (chemicals of potential concern). For both the 1990 and 1996 lists, copper and cadmium were identified as either primary or secondary TOCs. Both of these metals are found naturally in the environment at low concentrations. Copper is widely discharged in Chesapeake Bay from both point sources (metal plating, industrial and domestic waste facilities, boat paints, and mineral leaching) and nonpoint sources. Cadmium enters Chesapeake Bay primarily through industrial and municipal effluents, landfill leaching, nonpoint source runoff, and atmospheric deposition [5].

Although both of these metals have been identified as TOCs in the Chesapeake Bay watershed, a quantitative probabilistic ecological risk assessment has not been conducted for either metal. The objectives of this study were to use the U.S. Environmental Protection Agency's (U.S. EPA's) Ecological Risk Assessment paradigm to assess ecological risk of copper and cadmium at various locations in the Chesapeake Bay watershed and to rank ecological risk (high to low) for these locations. The procedures used in this assessment are described elsewhere [6–8]. This probabilistic risk assessment characterizes risk by comparing probability distributions of environmental exposure concentrations with the probability distributions of species response data (determined from laboratory studies). The overlap of these distributions is a measure of potential risk to aquatic life in Chesapeake Bay. This approach has a

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number of advantages over a quotient method (comparing the most sensitive species with the highest environmental concentrations) because it allows, if not exact quantification, at least a strong sense for the magnitude and likelihood of potential ecosystem effects of copper and cadmium in Chesapeake Bay. An implied assumption of this approach is that protecting a large percentage of species will also preserve ecosystem structure and function. The 10th percentile (protection of 90% of the species) was selected as the level of protection in this risk assessment based on a previous study [8]. The final result of the risk characterization is expressed as the probability that exposure concentrations of copper and cadmium (within defined spatial and temporal ranges) will exceed concentrations deemed protective of aquatic life in the Chesapeake Bay watershed.

PROBLEM FORMULATION

Three distinct phases of ecological risk assessment were followed: problem formulation, analysis, and risk characterization. The problem formulation phase involves the identification of major issues to be considered in the risk assessment. The analysis phase reviews existing data on exposure (environmental monitoring) and ecological effects (laboratory toxicity studies). The risk characterization phase involves estimation of the probability of adverse effects on aquatic populations and communities in potentially impacted areas of the Chesapeake Bay watershed.

The problem formulation phase of this risk assessment identified the following major issues to be addressed: stressor characteristics, ecosystems at risk, ecological effects, endpoints, temporal concurrence of copper and cadmium, critical ecological periods, and a conceptual model for risk assessment.

Stressor characteristics

The chemical and physical properties of copper and cadmium are described in detail in the Exposure Characterization section. In the problem formulation phase of this risk assessment, the solubility, persistence in water and sediment, and bioconcentration potential of copper and cadmium were considered important.

Copper and its salts (e.g., chloride and sulfate) are soluble in water, are persistent, and may bind to particulates. Aquatic biota bioconcentrate copper in their tissue. Bioconcentration factors (BCFs) as high as 2,000 for freshwater algae and 28,200 for saltwater bivalves have been reported [9].

Cadmium is slightly soluble in water, although its chloride and sulphate salts are freely soluble. Cadmium does not easily degrade in aquatic systems and tends to bind to sediments. This metal is also readily bioaccumulated by aquatic organisms. Bioconcentration factors as high as 12,400 have been reported in freshwater fish and as high as 3,160 for a saltwater polychaete [10]. In both freshwater and salt water, particulate matter and dissolved organic matter may bind a substantial portion of cadmium.

Ecosystems at risk

The aquatic ecosystem addressed in this risk assessment was the Chesapeake Bay watershed. Most of the exposure data for copper and cadmium were reported for the mainstem and tributaries (102 stations in 18 basins/areas) primarily in Maryland waters of Chesapeake Bay (Fig. 1).

Ecological effects

A comprehensive review and synthesis of the literature related to copper and cadmium aquatic toxicity was conducted using literature searches (e.g., AQUIRE, etc.) and various review documents (e.g., U.S. EPA water quality criteria reports [9,10]). Acute copper toxicity data were available for 121 freshwater species and 57 saltwater species. Chronic toxicity data for copper were available for 35 freshwater species and 12 saltwater species. For cadmium, acute toxicity data were reviewed for 139 freshwater species and 88 saltwater species. Chronic cadmium toxicity data were available for 24 freshwater species and 16 saltwater species. Detailed tables summarizing the copper and cadmium data used for this article are available in Hall et al. [11].

A review of the acute toxicity data revealed that effects of copper on aquatic species have been reported at concentrations as low as 1.3 μg/L for *Daphnia* tested in freshwater [12] and 1.2 μg/L for a bivalve tested in saltwater [13]. For cadmium, acute effects in freshwater have been reported at concentrations as low as 0.5 μg/L for rainbow trout [14] and in saltwater for concentrations as low as 1.1 μg/L for a shrimp species [15].

Endpoints

Two types of endpoints defined by the U.S. EPA [7] are assessment endpoints and measurement endpoints. Assessment endpoints are the actual environmental values that are to be protected. Measurement endpoints are the measured responses to a stressor that can be correlated with or used to protect assessment endpoints [16].

The assessment endpoints for this risk assessment are the long-term viability of aquatic communities in Chesapeake Bay (fish, invertebrates, etc.). Specifically, the protection of at least 90% of the species 90% of the time (10th percentile from species susceptibility distributions) from acute copper and cadmium exposures is the defined assessment endpoint. Measurement endpoints include all acute copper and cadmium toxicity data (survival, growth, and reproduction) generated from freshwater and saltwater laboratory toxicity studies.

Temporal concurrence of copper and cadmium and critical ecological periods

The overlap of contaminant exposures and critical ecological periods are key issues in this risk assessment. The presence of copper and cadmium in the Chesapeake Bay watershed was determined from exposure data collected primarily during the spring and summer (1985–1996) at various locations (Fig. 1). Although these data are somewhat biased because of their temporal limitations, the data collected during the spring and early summer are likely to represent worst-case conditions from nonpoint source loading. Spring in the Chesapeake Bay watershed is the period of high freshwater input into various tributaries because of snow melting and spring rains [17]. Therefore, potential loading of copper and cadmium from nonpoint sources exists. Spring is also a critical ecological period for various important aquatic resources of concern in this risk assessment. Various fish species, such as striped bass, white perch, alewife, and blueback herring, spawn in the spring in freshwater areas of various bay tributaries, such as the Potomac River, Choptank River, Nanticoke River, and Upper Chesapeake Bay [18]. Therefore, early life stages of these fish species may be susceptible to direct impacts from metals such as copper and cadmium or to indirect impacts if their food sources

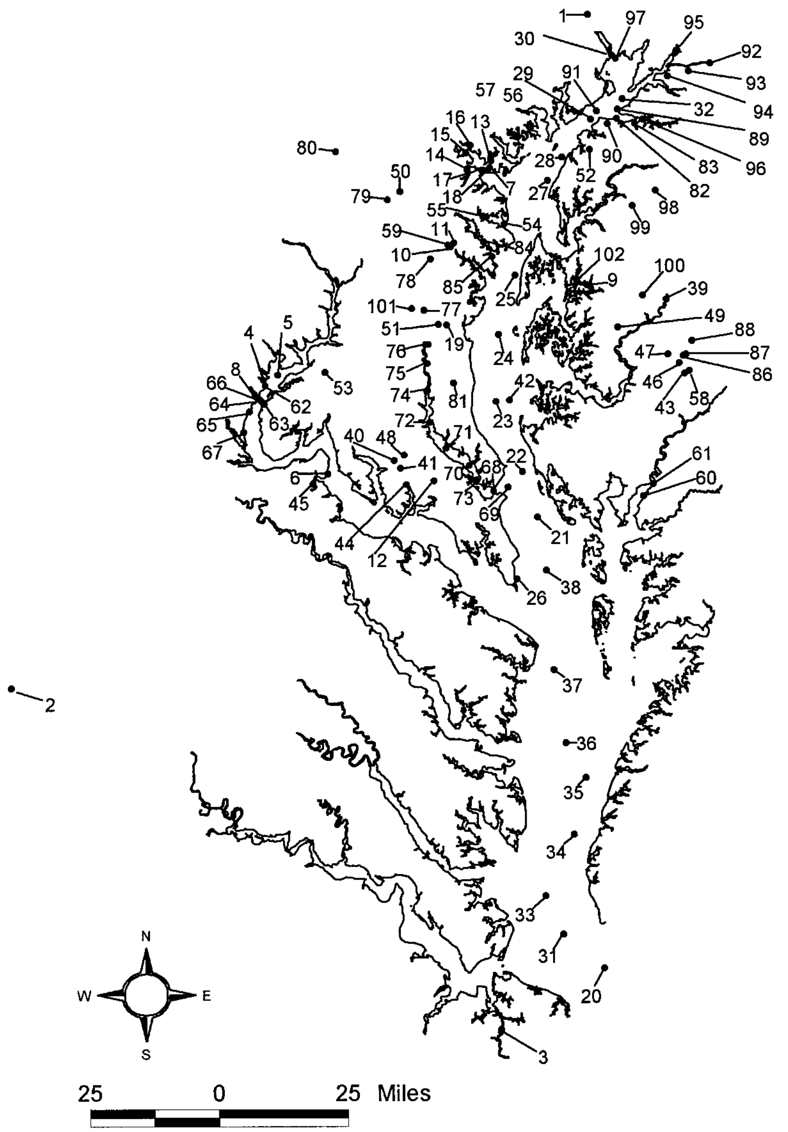

Fig. 1. Location of the 102 stations where copper and cadmium were measured from 1985 to 1996 in the Chesapeake Bay watershed, USA (see Appendix for key to map and station descriptions).

(e.g., zooplankton) are impaired. Spring is also a critical period for zooplankton, the trophic intermediaries between the very productive phytoplankton and the higher trophic groups such as fish. In oligohaline areas of the bay, total microzooplankton numbers reportly peak in May [19]. Spring is also a critical period for the lowest trophic group (phytoplankton) because peak primary production occurs from March through May, followed by a secondary maximum peak during July and August [20].

Conceptual model

Problem formulation is completed with the development of a conceptual model in which a preliminary analysis of the ecosystem at risk, stressor characteristics, and ecological effects are used to define the possible exposure and effects scenarios. The goal is to develop working hypotheses to determine how stressors such as copper and cadmium might affect exposed ecosystems. The conceptual model is based on information about the ecosystem at risk and the relationship between the measurement and assessment endpoints. Professional judgement is used to select risk hypotheses. The conceptual model describes the approach that will be used for the analysis phase and the types of data and analytical tools that will be needed. Specific data gaps and areas of uncertainty are described later in this report.

The hypothesis considered in this risk assessment was as follows: Copper and cadmium may cause permanent reductions at the species and community levels for fish, benthos, zooplankton, or phytoplankton in the Chesapeake Bay watershed, and these reductions may adversely affect community structure and function. The ecological risk of each metal was evaluated separately.

EXPOSURE CHARACTERIZATION

The potential for exposure of aquatic organisms to copper and cadmium is an important component of a probabilistic ecological risk assessment. Exposure data are used in conjunction with effects data (see Ecological Effects) to characterize risk. The exposure analysis for these metals considers use rates, sources, loadings, chemical properties, and a spatial/temporal scale of measured concentrations (data sources, sampling regimes, analytical methods, and data analysis).

Copper and cadmium loading in the Chesapeake Bay watershed

Anthropogenic activities that contribute to copper loading in Chesapeake Bay are municipal and industrial effluents (particularly from smelting, refining, or metal plating industries), nonpoint source runoff (e.g., poultry manure-based fertilizer and pesticides), atmospheric depositions, commercial and recreational boating, and water treatment for algae control [2]. In 1985, the estimated annual urban loading of copper in Chesapeake Bay was 230,000 pounds [21]. Total annual atmospheric deposition loads of copper to tidal waters of Chesapeake Bay were estimated to be 24,000 pounds [21]. Maximum annual loading estimates for copper at stations participating in the Chesapeake Bay Fall Line Toxics Monitoring Program in the Susquehanna and James Rivers in 1990 and 1991 were 479,000 and 150,000 pounds, respectively [22].

Loading of cadmium in the Chesapeake Bay watershed occurs mainly through industrial and municipal effluents, landfill leaching, nonpoint source runoff, and atmospheric deposition [2]. In 1985, the estimated annual urban loading of cadmium in Chesapeake Bay was 14,000 pounds [21]. Total annual atmospheric deposition loads of cadmium to tidal waters of Chesapeake Bay were estimated at 2,700 pounds [21]. Maximum loading estimates for cadmium at the Fall Line monitoring stations in the Susquehanna and James Rivers in 1990 and 1991 were 95,000 and 16,490 pounds, respectively [22].

Chemical properties of copper and cadmium

Copper has two main oxidation states: 1^+ and 2^+. The Cu^{2+} ion is the most environmentally relevant to aquatic systems and is generally considered the most toxic form to aquatic life. Copper is present in both soluble and particulate forms in the environment. For example, copper oxide is very insoluble, whereas copper hydroxide is reasonably soluble and potentially bioavailable. Bioavailability of copper is controlled by the presence of iron and manganese oxides in aerobic environments as well as dissolved organic matter. In anaerobic environments, sulfide chemistry dominates. Processes that control copper reactions with particles are sorption, chelation, coprecipitation, and biological concentration. In freshwater environments, an increase in hardness has been shown to reduce toxicity [9]. Particulate forms of copper may be deposited in bedloads near the source or distributed into adjacent environments. Particle size, currents, and density determine the final deposition of copper in the ecosystem. Aquatic biota have a moderate to high potential to bioconcentrate copper because BCFs as high as 28,200 have been reported for saltwater bivalves [9]. As exposure concentrations of copper decline, BCFs have been reported to increase.

The oxidation state for cadmium is the 2^+ ion. Chloride and sulphate cadmium salts are highly soluble in water, although cadmium is rather insoluble. Soluble forms of cadmium are removed from the water column by interaction or adsorption onto sediments and by biota. Removal of cadmium from the water column is controlled by various factors, such as complexing ligands, other metals, oxidation potential, and pH. Cadmium is not rapidly degraded in aquatic systems and tends to bind to sediment. The inorganic speciation of cadmium is predicted to be dominated by association with chloride ions in saltwater. In freshwater, total cadmium is dominated by free hydrated ion (Cd^{+2}) at pH 6 and partitioned between the free ion and carbonate complexes at higher pH [23]. Increasing hardness (calcium carbonate) reduces the toxicity of cadmium in freshwater. Bioconcentration factors as high as 12,400 have been reported in freshwater fish [5].

Although the potential for sediment-bound copper and cadmium to cause risk to sediment dwelling aquatic biota exists, the focus of this risk assessment was an evaluation of risk to aquatic biota from exposure to surface water concentrations of these metals. Probabilistic risk assessment techniques for assessing risk of aquatic species to sediment exposure is still developmental and contains a higher degree of uncertainty than water column exposure. By using surface water concentrations in this risk assessment, the results can be more closely related to regulatory guidelines, such as the U.S. EPA's water quality criteria for each respective metal.

Measured concentrations of copper and cadmium in the Chesapeake Bay watershed

Data sources and sampling regimes. Dissolved copper and cadmium exposure data from six sources were available from 1985 to 1996 at 102 stations (18 basins) in freshwater and saltwater tributaries and mainstem areas of the Chesapeake Bay watershed (Fig. 1 and Tables 1 and 2). For nearly all samples used in this risk assessment, both copper and cadmium were measured from the same sample. The exception was the Fall Line database, which had more measurements for copper. No planned rain event sampling was conducted to measure these metals because all samples were collected from a predetermined sampling regime. Several data sources were used.

Data from the Ambient Toxicity Testing Program [24–27] were collected over a period of 4 years (1990–1994) on a limited temporal scale (August through October and April 1993) at the following locations: Elizabeth, Potomac, Wye, and Patapsco Rivers in 1990; Patapsco, Potomac, and Wye Rivers in 1991; Middle, Nanticoke, and Wye Rivers in 1992–1993; and Patapsco (Baltimore Harbor), Magothy, Sassafras, and Severn Rivers in 1994.

Data from the Chesapeake Bay Fall Line Toxics Monitoring Program [28,29] were collected at one station each in the Susquehanna and James Rivers monthly from 1990 to 1993.

Data from the National Oceanic and Atmospheric Administration (NOAA) [30] were collected quarterly (May, August, November, and February) at 15 stations along the Patuxent River during 1995 and 1996.

To obtain data for striped bass [31–36], copper and cadmium were measured from 1985 through 1990 in the following tributaries or mainstem areas during April and May as part of an in situ contaminant study: Chesapeake and Delaware (C and D) Canal in 1985, Potomac River in 1986, Choptank River and CD Canal in 1987, Potomac River in 1988, Potomac River and Upper Chesapeake Bay in 1989, and Potomac River and Upper Chesapeake Bay in 1990.

Data from Maryland coastal plain streams [37,38] were collected at 24 stations during five different sampling periods over a 2-year period (1992–1993). Streams from the following basins were sampled for these metals: Nanticoke, Choptank, Chester, West Chesapeake, Patuxent, and Potomac.

Data published by the University of Delaware [39] were collected at 20 stations in mainstem Chesapeake Bay from the mouth of the bay in Virginia to the northern section in Maryland during August 1985.

Metals analysis

Copper and cadmium data reported during the Ambient Toxicity Testing Program were collected from subsurface-

Table 1. Summary of the six copper and cadmium data sources for this risk assessment

Data ID	Total samples (n)	Sample period	Detection limit (μg/L) Cu	Detection limit (μg/L) Cd
AMBTOX90 [24]	12	Aug–Sep 1990	2	1–2
AMBTOX91 [25]	13	Aug–Sep 1991	2	2
AMBTOX93 [26]	14	Oct 1992, Apr 1993	1–2	1–2
AMBTOX94 [27]	12	Oct 1994	1	0.5
Fall line monitoring [28,29]	164	Monthly, 1990–1993	0.02	0.1
NOAA/COASTES[a] [30]	60	Quarterly, 1995–1996	<0.01	<0.001
Striped bass study ’85 [31]	51	Apr 1985	2	0.5
Striped bass study ’86 [32]	39	Apr 1986	5	1
Striped bass study ’87 [33]	40	Apr 1987	1	0.5
Striped bass study ’88 [34]	49	Apr–May 1988	3	3
Striped bass study ’89 [35]	71	Apr–May 1989	1	1
Striped bass study ’90 [36]	36	Apr–May 1990	1	0.5
CPS[b] [37,38]	120	Apr, Jun, Oct 1992–1993	0.5–2.0	0.1–0.5
UDE[c] [39]	20	Aug 1985	<0.4	<0.006

[a] NOAA/COASTES = National Oceanographic and Atmospheric Administration/Complexity and Stressors in Estuarine Systems.
[b] CPS = Maryland coastal plains streams.
[c] UDE = University of Delaware.

depth integrated grab samples (a composite of bottom, middepth, and surface samples). All samples were filtered using a 0.40-μm polycarbonate membrane and preserved in Ultrex®-grade nitric acid. Both metals were analyzed using an atomic absorption–furnace (AA–F) method as outlined by the U.S. EPA [40]. The limit of detection for copper was 1 to 2 μg/L; the detection limit for cadmium ranged from 0.5 to 2 μg/L.

Both metals from the Fall Line Toxics Monitoring Program were measured in grab samples from the James River and Susquehanna River stations using ultraclean sampling procedures. Dissolved concentrations of copper and cadmium were measured using an inductively coupled plasma–mass spectrometry method. The detection limit was 0.02 μg/L for copper and 0.1 μg/L for cadmium.

In the NOAA study, both copper and cadmium were measured from surface-water grab samples using an ultraclean technique. All samples were filtered using 0.45-μm polypropylene capsule filters and preserved using 0.2% Ultrex hydrochloric acid. Metals analysis was conducted using an AA–F method as described in Bruland et al. [41]. Detection limits for copper and cadmium were <0.01 and <0.001 μg/L, respectively.

The copper and cadmium data from the striped bass studies were collected from both subsurface grab samples and composite samples (usually 24 h in duration). All samples were filtered using 0.40-μm polycarbonate membranes and preserved using Ultrex-grade nitric acid. Both metals were analyzed using an AA–F method as outlined by the U.S. EPA [40]. Detection limits for copper ranged from 1 to 5 μg/L (<2 μg/L most of the time). Limits of detection for cadmium were 0.5 μg/L for all years except 1988 (during which it was <3.5 μg/L).

Copper and cadmium measurements from the University of Delaware database were taken from discrete water column depths in the mainstem Chesapeake Bay. All samples were filtered with 0.4-μm acid-cleaned nuclepore membranes, acidified to pH <2, and frozen until analysis. Both metals were analysed using an AA–F method as described in Danielsson et al. [42]. Limits of detection for copper and cadmium were <0.4 and <0.006 μg/L, respectively.

For the Maryland coastal plain streams database, copper and cadmium were measured from grab samples taken seasonally. All samples were filtered using 0.40-μm polycarbonate membranes and preserved in Ultrex-grade nitric acid. Both metals were analyzed using an AA–F method [40]. Limits of detections for copper and cadmium were <0.5 to 2.0 and 0.10 to 0.50 μg/L, respectively.

Data analysis

Various investigators have addressed approaches for handling values below the detection limits, such as assigning these values as zero, one-half the detection limit, or the detection limit [43]. For this risk assessment, copper and cadmium values below the detection limit were assumed to have log-normal distributions. The distribution of exposure data was calculated on the basis of measured values, and the concentrations of the nondetects were assumed to be distributed along a lower extension of this distribution. For example, if 80 of 100 samples were reported as nondetects, the 20 measured values were assigned ranks from 81 to 100, and the frequency distribution was calculated from these 20 values. In some cases in these data sets, actual concentrations were reported even though they were below the detection limits. When this occurred, the concentrations were used in the analysis. For cases where more than one value was available at the same time and station (a very rare occurrence), the highest value was used in the frequency distribution.

For data sets arranged by basin or station with four or more values above the detection limit, log-normal distributions of exposure concentration were determined as follows. The observations in each data set were ranked by concentration, and for each observation the percentile ranking was calculated as $n/(N + 1)$, where n is the rank sum of the observation, and N is the total number of observations, including nondetects. Percentile rankings were converted to probabilities, and a linear regression was performed using the logarithm of concentration as the independent variable and normalized rank percentile as the dependent variable. Although nondetect observations were not included in the regression analysis, they were included in the calculation of the observation ranks. The 90th percentile

Table 2. Summary of copper and cadmium data for all basins and stations[a]

Basin and data ID[b]	Station[c]	Samples (n)		Detections (n)		Concn. (μg/L) Maximum		Concn. (μg/L) 90th Percentile	
		Cu	Cd	Cu	Cd	Cu	Cd	Cu	Cd
Baltimore Harbor									
AMBTOX90,91	Patapsco River	5	5	3	2	3.7	1.4		
AMBTOX94	Bear Creek	1	1	1	0	3.85	BLD[d]		
AMBTOX94	Curtis Bay	1	1	1	0	2.47	BLD		
AMBTOX94	Middle Branch	1	1	1	0	2.40	BLD		
AMBTOX94	Northwest Harbor	1	1	1	0	2.17	BLD		
AMBTOX94	Outer Harbor	1	1	1	0	1.90	BLD		
AMBTOX94	Sparrows Point	1	1	1	0	2.08	BLD		
Baltimore Harbor	All combined	11	11	9	2	3.85	1.4	4.1	
Chesapeake and Delaware Canal									
Striped bass studies	Chesapeake City	37	37	37	36	68	4.3	56	4.2
Striped bass studies	Delaware City	16	16	16	16	64	6.1	73	4.9
Striped bass studies	Courthouse Point	18	18	18	18	53	3.4	50	3.4
Chesapeake and Delaware Canal	All combined	71	71	71	71	68	6.1	70	4.6
Chester									
CPS	URL	5	5	1	3	1.10	1.40		
CPS	USE	5	5	1	1	0.91	0.14		
Chester	All combined	10	10	2	4	1.10	1.40		1.07
Choptank									
Striped bass studies	Martinak	20	20	20	6	40	3.0	24	2.2
CPS	KGC	5	5	2	2	1.30	0.52		
CPS	UTK	5	5	0	1	BLD	0.16		
Choptank	All combined	30	30	22	9	40	3.0	22	1.4
James									
AMBTOX90	Elizabeth River	2	2	2	0	3.7	BLD		
Fall Line Monitoring	02035000	71	23	66	0	9.00	BLD	4.48	
James	All combined	73	25	68	0	9.00	BLD	4.5	
Lower bay mainstem									
UDE	CB1	1	1	1	1	0.48	0.050		
UDE	CB2	1	1	1	1	0.41	0.064		
UDE	CB3	1	1	1	1	0.40	0.028		
UDE	CB5	1	1	1	1	0.48	0.027		
UDE	CB6	1	1	1	1	0.72	0.032		
UDE	CB7	1	1	1	1	1.39	0.047		
UDE	CB8	1	1	1	1	0.63	0.033		
Lower bay mainstem	All combined	7	7	7	7	1.39	0.064	1.27	0.07
Middle bay mainstem									
UDE	CB9	1	1	1	1	0.65	0.016		
UDE	CB10	1	1	1	1	0.51	0.008		
UDE	CB11	1	1	1	1	0.49	0.006		
UDE	CB12	1	1	1	1	0.60	0.009		
UDE	CB13	1	1	1	1	0.68	0.022		
UDE	CB14	1	1	1	1	0.74	0.015		
UDE	CR1D	1	1	1	1	1.14	0.053		
Middle bay mainstem	All combined	7	7	7	7	1.14	0.053	1.08	0.05
Upper bay mainstem									
Striped bass studies	Grove	19	19	19	0	9.5	BLD	6.9	
Striped bass studies	Howell	18	18	18	1	10.0	1.3	6.5	
Striped bass studies	Spesutie	19	19	19	2	67.0	6.7	16.4	
Striped bass studies	Elkton	6	6	5	0	8	BLD	12	
Striped bass studies	Kentmore	5	5	4	0	5	BLD	6	
Striped bass studies	Havre de Grace	6	6	2	0	13	BLD		
UDE	CB15	1	1	1	1	1.13	0.019		
UDE	CB16	1	1	1	1	1.00	0.043		
UDE	CB17	1	1	1	1	1.35	0.060		
UDE	CB18	1	1	1	1	2.47	0.066		
UDE	CB19	1	1	1	1	1.35	0.024		
UDE	CB20	1	1	1	1	1.60	0.053		
Upper Bay mainstem	All combined	79	79	73	9	67	6.7	8	2.4
Magothy									
AMBTOX94	Gibson Island	1	1	1	0	2.66	BLD		
AMBTOX94	South Ferry	1	1	1	0	1.38	BLD		
Magothy	All combined	2	2	2	0	2.66	BLD		

Table 2. Continued

Basin and data ID[b]	Station[c]	Samples (n)		Detections (n)		Concn. (μg/L) Maximum		Concn. (μg/L) 90th Percentile	
		Cu	Cd	Cu	Cd	Cu	Cd	Cu	Cd
Middle									
AMBTOX93	Frog Mortar	3	3	3	0	9.9	BLD		
AMBTOX93	Wilson Point	3	3	3	1	10.1	2.7		
Middle	All combined	6	6	6	1	10.1	2.7	12.9	
Nanticoke									
AMBTOX93	Bivalve	2	2	0	0	BLD	BLD		
AMBTOX93	Sandy Hill Beach	2	2	1	0	2.0	BLD		
CPS	DMP	5	5	0	3	BLD	0.55		
CPS	FBB	5	5	1	3	0.74	0.32		
CPS	FBI	5	5	2	5	2.00	1.00		1.46
CPS	NDB	5	5	0	3	BLD	0.22		
CPS	TLB	5	5	1	2	1.20	0.37		
CPS	UMH	5	5	1	3	1.30	0.78		
Nanticoke	All combined	39	39	6	22	2.0	1.00	1.2	0.95
Patuxent									
CPS	CAB	5	5	0	5	BLD	1.70		3.34
CPS	LYC	5	5	0	5	BLD	1.05		2.72
CPS	SEW	5	5	0	3	BLD	1.01		
NOAA/COASTES	LPXT0173	4	4	4	4	0.60	0.008	0.69	0.012
NOAA/COASTES	PTXCF8747	4	4	4	4	0.90	0.024	1.25	0.029
NOAA/COASTES	PTXCF9575	4	4	4	4	0.89	0.025	1.63	0.039
NOAA/COASTES	PTXDE2792	4	4	4	4	0.80	0.068	0.91	0.010
NOAA/COASTES	PTXDE5339	4	4	4	4	0.74	0.082	1.38	0.114
NOAA/COASTES	PTXDE9401	4	4	4	4	0.79	0.094	0.87	0.134
NOAA/COASTES	PTXDF0407	4	4	4	4	0.83	0.053	1.60	0.074
NOAA/COASTES	PTXED4892	4	4	4	4	1.03	0.117	1.28	0.141
NOAA/COASTES	PTXED9490	4	4	4	4	0.99	0.074	1.17	0.096
NOAA/COASTES	PXT0402	4	4	4	4	1.17	0.086	1.59	0.123
NOAA/COASTES	PXT0494	4	4	4	4	1.43	0.122	1.66	0.193
NOAA/COASTES	PXT0603	4	4	4	4	1.49	0.078	1.79	0.111
NOAA/COASTES	PXT0809	4	4	4	4	1.14	0.014	1.27	0.018
NOAA/COASTES	PXT0972	4	4	4	4	0.47	0.006	0.49	0.008
NOAA/COASTES	WBPXT0045	4	4	4	4	0.88	0.434	1.17	0.895
Patuxent Basin	All combined	75	75	60	73	1.49	1.70	1.11	0.47
Potomac									
AMBTOX90	Freestone Point	1	1	1	1	6.7	1.48		
AMBTOX90	Indian Head	1	1	1	1	5.9	1.32		
AMBTOX90	Morgantown	5	5	2	2	5.5	1.00		
AMBTOX90	Possum Point	1	1	1	0	3.9	BLD		
AMBTOX90	Dahlgren	5	5	3	3	4.5	1.80		
CPS	BTM	5	5	0	3	BLD	1.15		
CPS	CHP	5	5	1	3	2.4	0.66		
CPS	COF	5	5	2	4	2.9	0.88		1.83
CPS	DYN	5	5	0	3	BLD	1.03		
CPS	FOR	5	5	1	5	1.1	1.00		2.00
CPS	MTW	5	5	2	5	2.3	1.20		1.63
Striped bass studies	Cherry Hill	13	13	8	8	47	1.5	32	1.4
Striped bass studies	Maryland	25	25	20	6	10	13.0	7	5.6
Striped bass studies	Mid	26	26	22	4	9	14.0	7	4.9
Striped bass studies	Virginia	32	32	28	8	10	5.0	9	2.9
Striped bass studies	Quantico	13	13	10	9	60	6.6	36	3.4
Striped bass studies	Widewater	13	13	11	7	72	3.4	36	2.7
Potomac	All combined	165	165	165	72	72	14.0	12	2.43
Sassafras									
AMBTOX94	Betterton	1	1	1	0	1.35	BLD		
AMBTOX94	Turners Creek	1	1	1	0	2.26	BLD		
CPS	MLC	5	5	0	2	BLD	0.67		
Sassafras	All combined	7	7	2	2	2.26	0.67		
Susquehanna									
Fall line monitoring	01578310	93	55	90	5	8.0	1.24	3.1	0.78
Severn									
AMBTOX94	Junction Route 50	1	1	1	0	1.39	BLD		
AMBTOX94	Annapolis	1	1	1	0	2.12	BLD		
Severn	All combined	2	2	2	0	2.12	BLD		

Table 2. Continued

Basin and data ID[b]	Station[c]	Samples (*n*)		Detections (*n*)		Concn. (μg/L) Maximum		Concn. (μg/L) 90th Percentile	
		Cu	Cd	Cu	Cd	Cu	Cd	Cu	Cd
West Chesapeake									
CPS	BEB	5	5	0	4	BLD	1.10		2.38
CPS	BRB	5	5	1	3	1.1	0.62		
CPS	NRV	5	5	1	5	1.9	1.40		2.43
West Chesapeake	All combined	15	15	2	12	1.9	1.4		1.55
Wye									
AMBTOX90,91,93	Manor House	7	7	3	0	5.4	BLD		
AMBTOX93	Quarter Creek	2	2	0	0	BLD	BLD		
Wye	All combined	9	9	3	0	5.4	BLD		

[a] Maximum concentrations and 90th percentile values (minimum of four detected concentrations) are presented by basin and station.
[b] See Table 1 for definitions of data IDs.
[c] See Appendix for station definitions.
[d] BLD = below limit of detection.

concentrations (exceedence of a given value only 10% of the time) were calculated for sampling stations (or basins) on the basis of calculated log-normal concentration distributions.

Measured concentrations by basin

The 90th percentile values for copper in the 18 basins presented in Table 2 ranged from a high of 70 μg/L in the C and D Canal to a low of 1.08 μg/L in the middle mainstem Chesapeake Bay. The high 90th percentile value in the C and D Canal was likely related to boating activity (and thus the presence of copper-based antifouling paint) because two of the stations were located near marinas and because all stations were affected by the heavy commercial boating traffic that uses this canal. The second highest 90th percentile value for copper (22 μg/L), measured in the Choptank Basin, was likely related to agricultural activity in the area (poultry manure fertilizer or pesticide use). The third highest 90th percentile value for copper (12.9 μg/L), measured in Middle River, was likely related to boating activities in adjacent marinas or urban runoff. Lower concentrations of copper were generally reported in the mainstem Chesapeake Bay compared with the various freshwater and saltwater tributaries. The 90th percentile values for copper were not calculated for the Severn and Magothy Basins because of a lack of data (only two data points for each basin). These values were not calculated for the Chester, Sassafras, West Chesapeake, or Wye Basins because fewer than four detected concentrations were reported.

The 90th percentile values for cadmium (Table 2) ranged from 4.6 μg/L in the C and D Canal to 0.05 μg/L in the middle mainstem Chesapeake Bay. The high cadmium values in the C and D Canal mirror the high values reported for copper and are likely related to human activity near marinas. The second highest 90th percentile value for cadmium (2.43 μg/L), measured in the Potomac River, is likely related to the proximity of sampling stations near point source discharges from facilities such as Quantico Marine Base, the Possum Point Power Plant, or the Indian Head Military Facility. In general, the 90th percentile values for cadmium were lower in mainstem areas of the Chesapeake Bay than in the various tributaries. The 90th percentile values for cadmium were not calculated for the Severn and Magothy Basins because of the low number of data points (two), nor were they calculated for Baltimore Harbor and the James, Middle, Sassafras, and Wye Basins because fewer than four detected concentrations were reported.

Exposure duration

Exposure data from the C and D Canal (1985 and 1987) and the Potomac River (1986, 1988, 1989, and 1990) were used to examine the duration of exposure for both copper and cadmium because measurements from sequential daily sampling during limited time periods (weeks) were conducted during multiple years at these highest risk (highest 90th percentiles) locations [11]. An examination of exposure duration provided insight on the variability of environmental exposures and frequency of high concentrations.

The exposure duration data for both cadmium and copper in the C and D Canal showed that within a given year values were fairly constant for a given station with occasional spikes occurring (6.1 μg/L cadmium and 68 μg/L copper), particularly in 1985 (Table 2 and Hall et al. [11]). Because the available data are limited, it is not possible to provide any further insight on the implication of these spikes, although it is unlikely that the few measurements that were made would have detected the highest concentrations present in this area.

Cadmium and copper exposure duration data from the Potomac River also showed that occasional spikes occurred for these metals from 1986 to 1990 [11]. Maximum concentrations of 14 μg/L cadmium and 72 μg/L copper were reported (Table 2). Although the frequency of these spikes is limited, the likelihood that maximum values occurring in this river were measured is remote. A comparison of spike values for both metals also suggests that, at least in a few cases in which maximum values were reported at the same location and on the same date, a common source may be involved [11].

Summary of exposure data

The highest environmental concentrations of copper (based on 90th percentiles) in the Chesapeake Bay watershed were reported in the C and D Canal, Choptank River, Middle River, and Potomac River. Sources of copper responsible for these exposures cannot be identified with certainty, but human activities such as watercraft antifouling paint, nonpoint source runoff (fertilizer), and industrial and municipal effluents are likely candidates. As expected, the lowest concentrations of copper were reported in areas with the least amount of direct human activity, such as the lower and middle mainstem Chesapeake Bay and the Nanticoke River. Analysis of multiple-year sets of exposure duration data from the C and D Canal and the Potomac River demonstrated that copper concentrations can remain fairly constant for several days but that spikes occasionally occurred in both of these systems (~70 μg/L).

Based on the calculation of 90th percentiles, cadmium concentrations were highest in the C and D Canal, Potomac River, Upper Chesapeake Bay, and West Chesapeake watershed. The high exposures were likely related to human activities, such as industrial and municipal effluents, nonpoint source runoff, and atmospheric deposition, although a direct link cannot be established with the available data. As reported above for copper, the lowest environmental concentrations were reported in areas with the least amount of direct human impact, such as the lower and middle mainstem Chesapeake Bay and Susquehanna River.

ECOLOGICAL EFFECTS

To characterize the ecological effects of copper and cadmium, we address the following areas: modes of toxicity, toxicity data analysis, effects from laboratory toxicity tests, and microcosm studies.

Modes of toxicity

Both copper and cadmium are broad spectrum enzyme inhibitors that impact various trophic groups of aquatic species. Modes of toxicity for each metal are addressed below.

Copper. Copper is a minor nutrient for both plants and animals at low concentrations and is toxic to aquatic life at concentrations approx. 10 to 50 times higher. The toxic effects of copper are avoided in living organisms (1) by developing an active process for eliminating excess copper ingested in the diet, (2) by reducing the thermodynamic activity of copper ions virtually to zero by using the metal only as a prosthetic element tightly bound to specific copper proteins, and (3) by the interaction between zinc and copper [44]. Although little is known about the primary mode of copper toxicity in plants, the inhibition of photosynthesis and disruption of plant growth are suspected to be the major insults resulting from copper exposure. Morel et al. [45] suggested that one of the targets of copper in diatoms is silica metabolism, which leads to disruption of cell division.

Copper adversely affects fish by causing histological alterations in the gill, kidney, hematopoietic tissue, mechanoreceptors, chemoreceptors, and other tissues [46]. Reproductive effects from copper exposure, such as reduced egg production in females, abnormalities in newly hatched fry, and reduced survival of young, have also been reported [46].

Cadmium. Cadmium is a nonessential element that can be both carcinogenic and toxic to aquatic biota [47]. In algae, cadmium has been reported to increase cell volume, lipid relative volume, and vacuole relative volume [48]. Cadmium has been shown to adversely affect invertebrates by inhibiting calcium influx [49]. In fish, cadmium has been shown to adversely affect several enzyme systems, such as those systems involved with neurotransmission, transepithelial transport, intermediary metabolism, and mixed-function oxidase/antioxidant activity [47]. Skeletal deformities in fish from low-level exposure to cadmium have also been reported [50]. In general, a common result of cadmium exposure in vertebrates is hypocalcemia, which is likely related to the inhibition of calcium influx [51].

Toxicity data analysis

For freshwater toxicity studies with both copper and cadmium, hardness (concentrations of calcium and magnesium) is one water quality variable that significantly influences toxicity. As hardness increases, the toxicity of the trace metal to biota generally decreases due to reduced bioavailability of the metal or alteration of the osmoregulatory capacity of the organism. The U.S. EPA addresses the influence of hardness on both copper and cadmium toxicity in their development of freshwater quality criteria [9,10]. For the copper and cadmium toxicity data used in this risk assessment, hardness was also considered in the ranking of sensitivities of various freshwater species. To realistically compare freshwater toxicity data among species, all data were standardized to a hardness of 50 mg/L $CaCO_3$. This value was selected because it is the mean hardness value of 24 Maryland coastal plains streams sampled five times over a 2-year period from 1992 to 1993 [37,38]. If hardness data were not available with the freshwater toxicity values for a given species, then the toxicity data were not used in the analysis. The following equation was used to adjust the freshwater acute and chronic toxicity data:

$$\mathrm{LC50}_{\mathrm{standardized}} = \ln \mathrm{LC50}_{\mathrm{observed}} - (b[1]\ln \mathrm{hardness}_{\mathrm{observed}} - \ln \mathrm{hardness}_{\mathrm{standardized}})$$

where $\mathrm{hardness}_{\mathrm{standardized}}$ = 50 mg/L as $CaCO_3$; $b[1]$, or the slope, = 0.942 for copper acute data, 0.855 for copper chronic data, 1.128 for cadmium acute data, and 0.785 for cadmium chronic data.

The primary toxicity benchmark used for this risk assessment was the 10th percentile of species sensitivity (protection of 90% of the species) from acute exposures. The implied assumption when using this benchmark is that protecting a large percentage of the species assemblage will preserve ecosystem structure and function. This level of species protection is not universally accepted, especially if the unprotected 10% are keystone species and have commercial or recreational significance. However, protection of 90% of the species 90% of the time (10th percentile) has been recommended by the Society of Environmental Toxicology and Chemistry [6] and others [8]. Recent mesocosm studies have reported that this level of protection is conservative [8,52].

Copper and cadmium toxicity data were each analyzed as a distribution on the assumption that the data represented the universe of species. An approximation was made because it is not possible to test the universe of species in Chesapeake Bay. This approximation assumes that the number of species tested (N) is one less than the number in the universe. To obtain graphic distributions for smaller data sets that are symmetrical (normal distributions), percentages were calculated from the formula $[100 \times n/(N + 1)]$, where n is the rank number of the datum point, and N is the total number of data points in the set [53]. This formula compensates for the size of the data sets, because small (uncertain) data sets will give a flatter distribution with more chance of overlap than larger (more certain) data sets. In cases in which there were multiple data points for a given species, the lowest value was used in the regression analysis of the distribution. Data were plotted using SigmaPlot [54].

Effects of copper and cadmium from laboratory toxicity tests

Acute and chronic copper and cadmium toxicity data used in this risk assessment were obtained from the AQUIRE da-

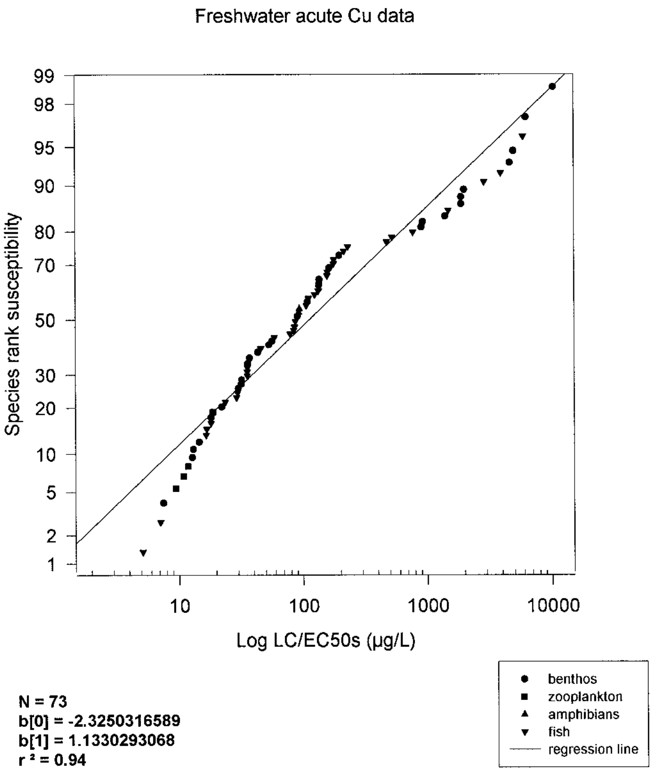

Fig. 2. Distribution of acute median lethal and effects concentrations (LC/EC50s) for freshwater copper toxicity data.

tabase through 1995, from U.S. EPA water quality criteria documents [9,10], and from manual searches of literature from academic, industry, and government sources. A summary of copper and cadmium acute and chronic toxicity data by water type (freshwater and salt water) are discussed below. Detailed tabular presentations of these data are available in Hall et al. [11].

Acute toxicity of copper. Acute freshwater copper toxicity data were available for 121 species, primarily benthos and fish. Hardness data were available for 73 species, and the distribution of these data is presented in Figure 2. The range of acute toxicity values was from 1.3 μg/L for *Daphnia* to 13,000 μg/L for an aquatic sowbug [55]. Within the fish trophic group, the Cyprinidae and Salmonidae families contained species that were more sensitive to acute copper exposures than the other eight families of freshwater fish. The benthic species most sensitive to acute copper exposure was gastropods, followed by amphipods. Despite the variability in sensitivities of the various species and trophic groups, the acute freshwater 10th percentile values for all species together (8.3 μg/L) and by trophic group (6.9–10.8 μg/L) were somewhat similar, as shown in Table 3.

The distribution of acute copper saltwater toxicity data from 57 species is shown in Figure 3. As reported for the acute copper freshwater toxicity studies, most of the data were available for benthos and fish. Acute copper toxicity values ranged from 1.2 μg/L for a bivalve [13] to 346,700 μg/L for a crab species [56]. The fish families with the species most sensitive to saltwater copper exposure were Pleuronectidae, Antherinidae, and Moronidae. The acute saltwater 10th percentile values for all species, phytoplankton, zooplankton, benthos, and fish were 6.3, 2.1, 9.3, 4.1, and 16.1 μg/L, respectively (Table 3).

Table 3. The 10th percentile intercepts for freshwater and saltwater copper toxicity data by test duration and trophic group (values represent protection of 90% of the test species)

Water type	Data type	Trophic group	n	10th Percentile (μg/L)
Freshwater[a]	Acute	All species	73	8.3
		Zooplankton	4	7.0[b]
		Benthos	31	6.9
		Fish	36	10.8
	Chronic	All species	21	3.8
		Zooplankton	3	0.8[b]
		Benthos	7	3.8[b]
		Fish	10	3.9
Saltwater	Acute	All species	57	6.3
		Phytoplankton	3	2.1[b]
		Zooplankton	7	9.3[b]
		Benthos	30	4.1
		Fish	15	16.1
	Chronic	All species	4	6.4[b]

[a] Hardness-adjusted values (50 mg/L) were used.
[b] Because of the small data sets ($n < 8$), these values have a high degree of uncertainty and were therefore not used for risk estimates.

Chronic toxicity of copper. Chronic copper toxicity data were available for 35 freshwater species, and hardness data were available for 21 of these species (Fig. 4). Chronic values ranged from 3.9 μg/L for the brook trout [57] to 60.4 μg/L for the Northern pike [58]. The lowest freshwater 10th percentile value (0.8 μg/L) was for zooplankton (Table 3). The 10th percentile values for all species, benthos, and fish were similar (≈3.8 μg/L). The 10th percentile value for all species from chronic tests (3.8 μg/L) was approximately half the 10th percentile value reported from all freshwater species from acute tests (8.3 μg/L). These data are supportive of the very low acute/chronic ratios (ACRs) generally reported for trace metals [59].

Saltwater chronic toxicity data were limited to 12 species,

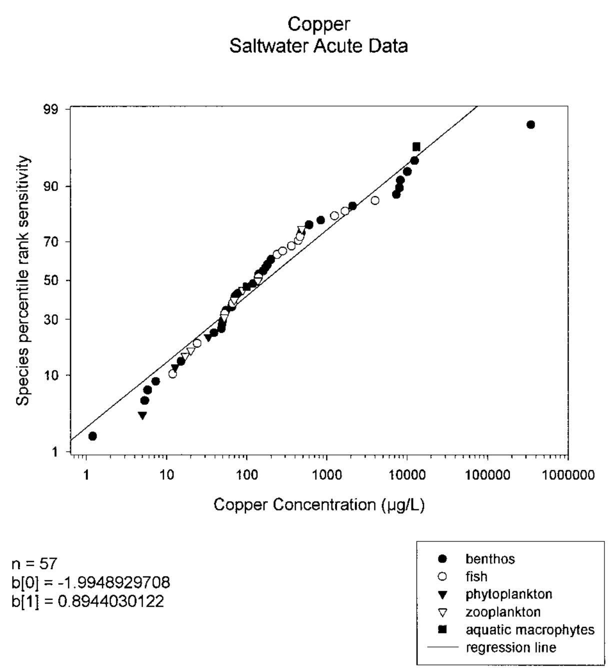

Fig. 3. Distribution of acute median lethal and effects concentrations for saltwater copper toxicity data.

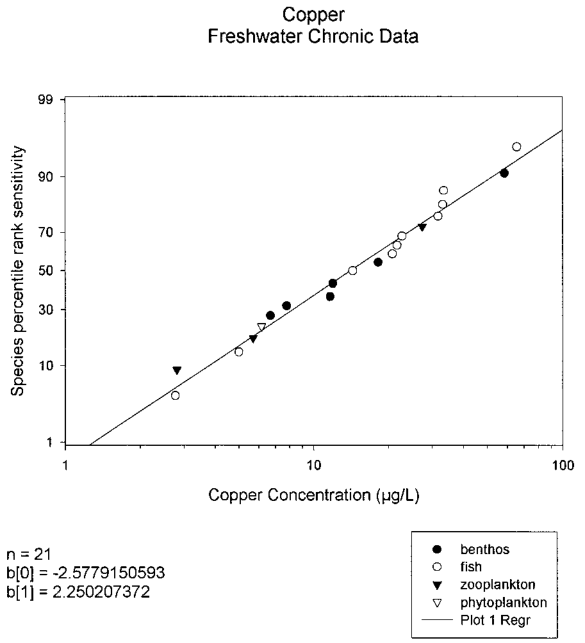

Fig. 4. Distribution of chronic freshwater copper toxicity data.

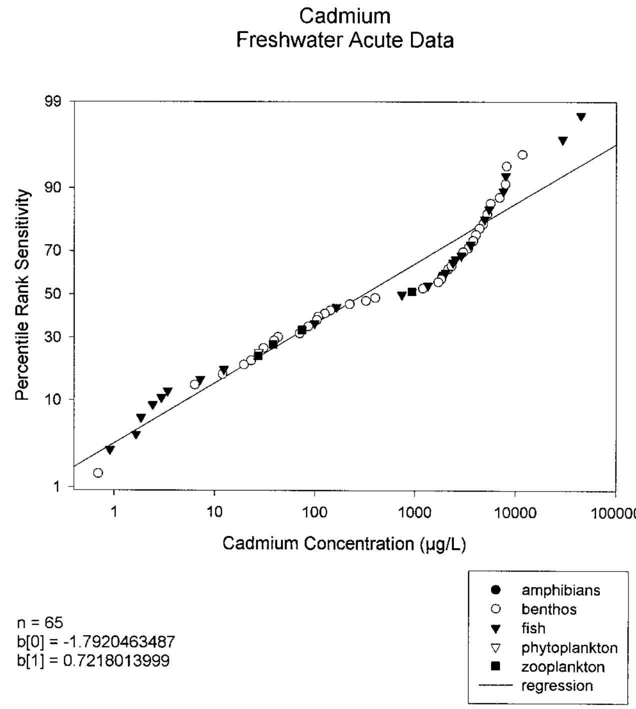

Fig. 6. Distribution of acute median lethal and effects concentrations for freshwater cadmium toxicity data.

and actual chronic values were reported only for the mysid (54 µg/L) and a copepod (64 µg/L) (Fig. 5). The other two values were the lowest-observed-effect concentration (LOEC) and the no-observed-effect concentration (NOEC). The 10th percentile value for the saltwater chronic toxicity data was 6.4 µg/L (Table 3).

Acute toxicity of cadmium. Acute freshwater cadmium toxicity data were available for 139 species (65 species with hardness data), with benthos and fish the most predominant trophic groups represented (Fig. 6). Acute cadmium toxicity values ranged from 0.5 µg/L for rainbow trout [14] to 18,000,000 µg/L for an alterfly [60]. Within the benthic trophic group, various species of amphipods were more sensitive than others. The 10th percentile values for all species, zooplankton, benthos, and fish were 5.1, 4.0, 12.3, and 0.9 µg/L, respectively (Table 4).

Acute cadmium saltwater toxicity data were available for 88 species (Fig. 7). Toxicity values ranged from 1.1 µg/L for the grass shrimp [15] to 135,000 µg/L for an oligochaete worm [61]. Moronidae was the fish family most sensitive to acute saltwater cadmium exposures. Copepods appeared to be the most sensitive zooplankton. The saltwater 10th percentile values for all species, phytoplankton, zooplankton, benthos, and fish were 31.7, 17.0, 15.0, 23.3, and 163 µg/L, respectively (Table 4).

Chronic toxicity of cadmium. Freshwater cadmium toxicity data from chronic exposures were reported for 24 species; 18

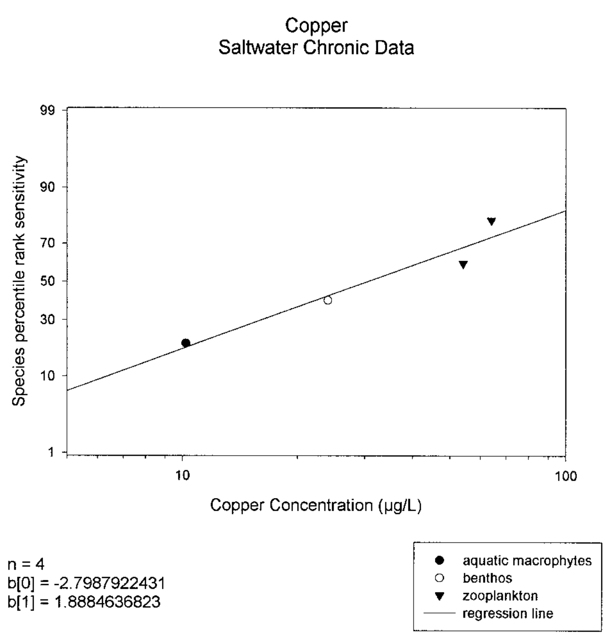

Fig. 5. Distribution of chronic saltwater copper toxicity data.

Table 4. The 10th percentile intercepts for freshwater and saltwater cadmium toxicity data by test duration and trophic group (values represent protection of 90% of the test species)

Water type	Data type	Trophic group	*n*	10th Percentile (µg/L)
Freshwater[a]	Acute	All species	65	5.1
		Zooplankton	4	4.0[b]
		Benthos	35	12.3
		Fish	24	0.9
	Chronic	All species	18	0.4
		Zooplankton	4	0.03[b]
		Fish	13	1.8
Saltwater	Acute	All species	88	31.7
		Phytoplankton	5	17.0[b]
		Zooplankton	7	15.0[b]
		Benthos	58	23.3
		Fish	17	163
	Chronic	All species (benthos)	4	0.25[b]

[a] Hardness-adjusted values (50 mg/L) were used.
[b] Because of the small data sets ($n < 8$), these values have a high degree of uncertainty and were therefore not used for risk estimates.

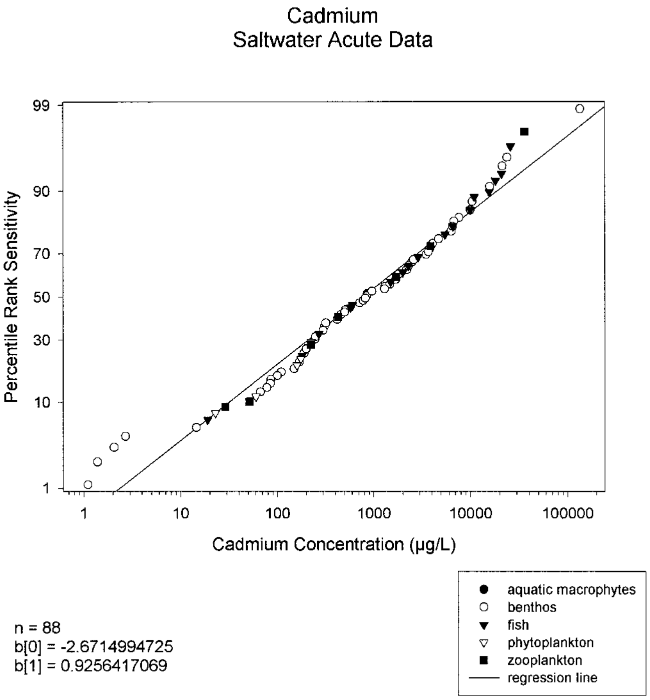

Fig. 7. Distribution of acute median lethal and effects concentrations for saltwater cadmium toxicity data.

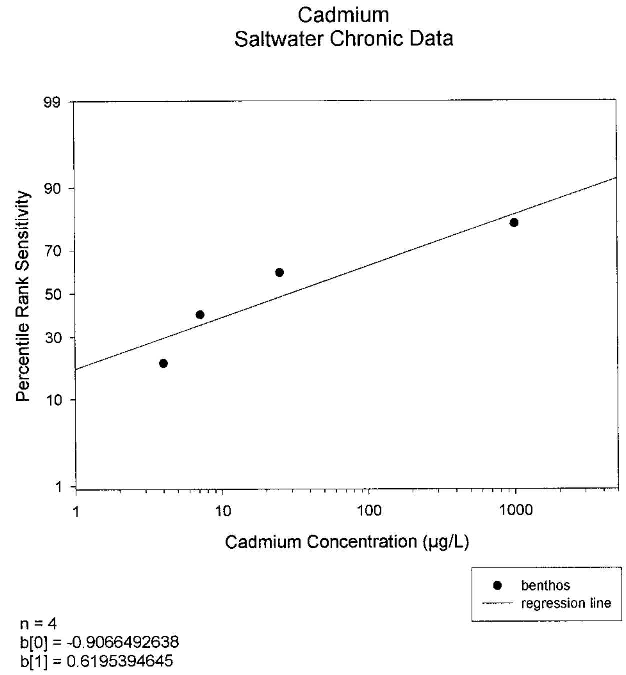

Fig. 9. Distribution of chronic saltwater cadmium toxicity data.

chronic values and/or NOECs were available with hardness data (Fig. 8). Chronic values ranged from 0.15 μg/L for a cladoceran [62] to 60 μg/L for a rotifer [63]. The 10th percentile values reported for chronic exposures were 0.4 μg/L for all species, 0.03 μg/L for zooplankton, and 1.8 μg/L for fish (Table 4).

Chronic saltwater cadmium toxicity data were available for 16 species; however, only four of these data points were either chronic values, NOECs, or LOECs (Fig. 9). The range of values was rather wide as a 28-d NOEC of 4 μg/L was reported for the mysid [64] and a 120-h LOEC of 1,000 μg/L was reported for a nematode [65]. The 10th percentile value for all species (four benthic species) was 0.25 μg/L (Table 4).

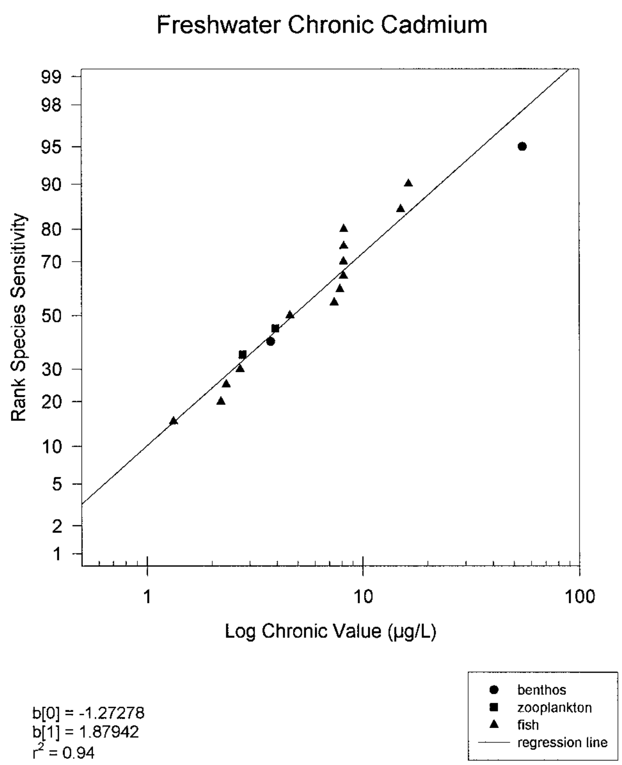

Fig. 8. Distribution of chronic freshwater cadmium toxicity data.

Microcosm studies

Copper and cadmium microcosm studies with reported maximum acceptable toxic concentration (MATC), LOEC, or NOEC values were very limited. Pratt et al. [66] reported NOEC, MATC, and LOEC values of 6.6, 9.2, and 12.7 μg/L copper, respectively, for freshwater protozoan communities exposed to copper for 21 d. The MATC of 9.2 μg/L is similar to the 10th percentile value reported for all freshwater species subjected to acute copper exposures (8.3 μg/L) (see ''Acute toxicity of copper'' section). In another copper microcosm study, Balczon and Pratt [67] reported an LOEC of 20.2 to 42.8 μg/L in artificial communities (measuring community structure) and an LOEC of 24 to 98.5 μg/L in littoral microcosms. Lowest-observed-effect concentrations for measures of community processes ranged from 42.8 to 310.3 μg/L. The various copper benchmarks used by Balczon and Pratt [67] were generally higher than the various 10th percentile values listed by trophic group in Table 3.

Only one microcosm result was reported for cadmium. Niederlehner et al. [68] reported an NOEC of 5.6 μg/L cadmium for colonization rates for protozoan communities. This value is similar to the 10th percentile value for all species (acute freshwater data) of 5.1 μg/L reported in Table 4.

Summary of effects data

Effects from copper were reported at concentrations slightly above 1 μg/L from acute freshwater exposures, although effects at this low range were rare. The 10th percentile value for all species derived from the freshwater acute copper toxicity database was 8.3 μg/L. Similar freshwater acute 10th percentile values (6.9 to 10.8 μg/L) were reported among the various trophic groups. The 10th percentile value for all species in the freshwater chronic database was 3.8 μg/L copper. This value is approximately half the 10th percentile value for the acute freshwater data. These data are supportive of the very low ACR for copper previously documented. The 10th percentile value for all species exposed to acute saltwater copper exposures was 6.3 μg/L. This concentration is similar to the acute copper freshwater 10th percentile value (8.3 μg/L) reported above. Saltwater chronic data with copper were limited to four species; a 10th percentile value of 6.4 μg/L was determined from these data.

The 10th percentile for all species derived from the freshwater acute cadmium toxicity data base was 5.1 μg/L. Acute toxicity values as low as 0.5 μg/L cadmium were reported for rainbow trout. The 10th percentile value for all species in the freshwater chronic toxicity database was 0.4 μg/L. A comparison of the acute and chronic 10th percentile values shows an ACR of approx. 13. The 10th percentile value for all species in saltwater acute cadmium toxicity data set was 31.7 μg/L. This value is six times higher than the 10th percentile value for freshwater acute cadmium. These data suggest that cadmium is much less toxic in salt water than freshwater. Saltwater chronic cadmium toxicity data were very limited (four species). Based on these limited data points, the 10th percentile value was 0.25 μg/L.

RISK CHARACTERIZATION

Characterizing risks

One simple and commonly used method for characterizing risks to aquatic biota is the use of risk quotients. Risk quotients are simple ratios of exposure and effects concentrations where the susceptibility of the most sensitive species is compared with the highest environmental exposures. If the exposure concentration equals or exceeds the effects concentration, then an ecological risk is suspected. The quotient method is a valuable first-tier assessment that allows determination of worst-case effects and exposure scenarios for a particular contaminant. However, some of the major limitations of the quotient method for ecological risk assessment are that it fails to consider variability of exposures among individuals in a population, ranges of sensitivity among species in the aquatic ecosystem, and the ecological function of these individual species. The probabilistic approach addresses these various concerns because it expresses the results of an exposure or effects characterization as a distribution of values rather than a single point estimate. Quantitative expressions of risks to aquatic communities are therefore determined by using all relevant single-species toxicity data in conjunction with exposure distributions. A detailed presentation of the principles used in a probabilistic ecological risk assessment are presented by Solomon et al. [8].

The following sections summarize the results of the risk characterization phase of this probabilistic ecological risk assessment of copper and cadmium in the Chesapeake Bay watershed. The toxicity benchmark used for the risk characterization is either the freshwater or saltwater acute 10th percentile value for each metal, depending on whether freshwater or salt water is present within the basin. The acute 10th percentile value was selected for the following reasons: (1) based on laboratory experimental data, dissolved and bioavailable copper and cadmium are in the water column of the aquatic environment for only short periods of time that are more closely related to acute exposures that chronic exposures; (2) exposure duration data presented in the ''Exposure Characterization'' section showed that spike concentrations of copper and cadmium are short-lived (hour to days) in the environment (e.g., copper rapidly complexes with natural organic particulates [69]); and (3) toxicity data are much more numerous and represent a wider range of trophic groups for acute studies than chronic studies. In addition to using the acute 10th percentile value for all species in freshwater or salt water, the trophic group with the lowest acute 10th percentile value (most sensitive trophic group) with at least eight data points was also used as an additional benchmark (more conservative approach) to assess possible ecological risk. The U.S. EPA uses a minimum value of eight species for development of acute numeric water quality criteria [70].

Table 5. Probability of exceeding the copper acute freshwater or saltwater 10th percentile for all species[a]

Location	Acute 10th percentile (μg/L)	Probability of exceeding 10th percentile (%)
C and D Canal	8.3 (benthos, 6.9)	86 (90)
Middle River	6.3 (benthos, 4.1)	47 (74)
Choptank River	8.3 (benthos, 6.9)	29 (32)
Potomac River	8.3 (benthos, 6.9)	16 (20)
Upper mainstem bay	8.3 (benthos, 6.9)	9.3 (13)
James River	8.3 (benthos, 6.9)	1.4 (2.8)
Baltimore Harbor	6.3 (benthos, 4.1)	1.2 (10)
Susquehanna River	8.3 (benthos, 6.9)	0.3 (0.7)
Lower mainstem bay	6.3 (benthos, 4.1)	<0.1 (<0.1)
Nanticoke River	8.3 (benthos, 6.9)	<0.1 (0.2)
Patuxent River	6.3 (benthos, 4.1)	<0.1 (<0.1)
Middle mainstem bay	6.3 (benthos, 4.1)	<0.1 (<0.1)

[a] Values in parentheses are for the most sensitive trophic group with more than eight species.

Risk characterization of copper in the Chesapeake Bay watershed

Potential ecological risk from copper exposure (and cadmium) was characterized by using freshwater acute effects data for freshwater areas and saltwater effects data for saltwater areas. The highest potential ecological risk area for copper exposures in the Chesapeake Bay watershed was reported in the C and D Canal (Table 5). The probability of exceeding the acute freshwater 10th percentile value for all species was 86%. For the most sensitive trophic group (based on acute freshwater exposures), the probability of exceeding the 10th percentile value for benthos was even higher (90%). The second highest risk area for copper exposures in the watershed was the Middle River (Table 5). The probability of exceeding the 10th percentile value for all species and the probability of exceeding the 10th percentile value of the most sensitive trophic group with at least eight species (based on acute saltwater exposures) was 47 and 74%, respectively. The third highest risk area for copper exposures was the Choptank River. The probability of exceeding the 10th percentile value for all species and most sensitive trophic group with at least eight species (benthos, 6.9 μg/L) was 29 and 32%, respectively. The Potomac River was the fourth highest area for ecological risk. The probability of exceeding the 10th percentile value for all species and the most sensitive trophic group with at least eight species (benthos) was 16 and 20%, respectively. The rankings of the fifth, sixth, and seventh highest ecological risk areas were as follows: upper mainstem bay, James River, and Baltimore Harbor.

Table 6. Probability of exceeding the cadmium acute freshwater or saltwater 10th percentile for all species[a]

Location	Acute 10th percentile (μg/L)	Probability of exceeding 10th percentile (%)
C and D Canal	5.1 (fish, 0.9)	7.5 (88)
Upper mainstem bay	5.1 (fish, 0.9)	3.4 (29)
Chester River	5.1 (fish, 0.9)	3.3 (11)
Potomac River	5.1 (fish, 0.9)	2.8 (33)
Choptank River	5.1 (fish, 0.9)	1.5 (17)
West Chesapeake watershed	5.1 (fish, 0.9)	1.4 (20)
Nanticoke River	5.1 (fish, 0.9)	0.5 (11)
Susquehanna River	5.1 (fish, 0.9)	<0.1 (6.2)
Patuxent River	5.1 (fish, 0.9)	0.5 (5)
Lower mainstem bay	31.7 (benthos, 23.3)	<0.1 (<0.1)
Middle mainstem bay	31.7 (benthos, 23.2)	<0.1 (<0.1)

[a] Values in parentheses are for the most sensitive trophic group with more than eight species.

The probability of exceeding the 10th percentile value for all species ranged from 1.2 to 9.3% for these three areas. The other 11 basins evaluated had either very low ecological risk (e.g., Susquehanna River, lower mainstem bay, Nanticoke River, Patuxent River, or middle mainstem bay) or insufficient data to determine whether ecological risk existed (Table 2).

Risk characterization of cadmium in the Chesapeake Bay watershed

The highest potential ecological risk area for cadmium in the Chesapeake Bay watershed was the C and D Canal area (Table 6). The probability of exceeding the acute freshwater 10th percentile value for all species was only 7.5% in the C and D Canal; however, the probability of exceeding the 10th percentile value for the most sensitive freshwater trophic group (fish, 0.9 μg/L) was 88%. The five next highest areas for ecological risk based on the 10th percentile value for all species were the upper mainstem bay, Chester River, Potomac River, Choptank River, and West Chesapeake watershed. The potential of ecological risk in these five areas was low (<3.5% using the 10th percentile value for all species). Using the 10th percentile value for the most sensitive trophic group (fish) with at least eight species increased the potential risk (11–33%) for these areas. However, this level of risk was still judged to be low to moderate. The ecological risk for the other 12 basins was either very low or data were inadequate to assess possible ecological risk (Table 2).

Uncertainty in ecological risk assessment

Uncertainty in ecological risk assessment has three basic sources: (1) lack of knowledge in areas that should be known, (2) systematic errors resulting from human or analytical error, and (3) nonsystematic errors resulting from the random nature of the ecosystem (i.e., Chesapeake Bay watershed). The following sections will address specific uncertainty from the above three sources as associated with exposure data, effects data, and risk characterization.

Uncertainty associated with exposure characterization

Copper and cadmium exposure data used for this risk assessment were obtained from six data sources from 1985 to 1996 as previously described. The spatial scale of these data (102 stations in 18 basins or mainstem areas) was somewhat limited considering that there are at least 50 major rivers that discharge into the Chesapeake Bay. Exposure data from basins in Virginia waters of Chesapeake Bay were particularly limited because only the James River Basin and the lower mainstem bay were represented. The temporal scale (sampling frequency) of the available data for the watershed was even more limited. In many cases, only a few measurements were made for these metals at various stations. Rain event sampling for these metals in tributaries and streams was not considered in the sampling designs of the various monitoring studies. Although rain event sampling is more relevant for pesticides applied on agricultural crops that enter aquatic systems during runoff, such events may be important for copper loading resulting from fertilizer use on crops or copper and cadmium loading from urban stormwater discharges or municipal and industrial overflow. The sampling frequency of the present exposure data for both metals is clearly inadequate for rain event sampling.

The copper and cadmium analysis associated with the six laboratories introduces uncertainty because analytical procedures differed among the laboratories. Specific differences in sample collection, filtering, and detection limits for these metals occurred among laboratories.

Uncertainty associated with ecological effects data

Because of the relatively small number of species that can be routinely cultured and tested in laboratory toxicity studies, there is uncertainty when extrapolating these toxicity data to responses of natural taxa found in the Chesapeake Bay watershed. In the case of copper in the Chesapeake Bay watershed, freshwater and saltwater acute toxicity were available for 73 and 57 species, respectively, for use in the calculation of the 10th percentile value. Although these data seem adequate for all species, the distribution among the various trophic groups was weighted more with fish and benthos. Acute copper data were particularly limited for plants (phytoplankton and macrophytes), zooplankton, and amphibians. Chronic data were limited for both types of water but particularly for saltwater species ($n = 4$).

Acute cadmium toxicity data used for the calculation of the 10th percentile value were available for 65 freshwater species and 88 saltwater species. The freshwater acute data were limited for zooplankton, and no data were available for aquatic plants. The saltwater acute cadmium database did not include any macrophyte data, and the phytoplankton and zooplankton data were also limited. The freshwater cadmium chronic data did not include any plants or benthos. The saltwater chronic database did not include any fish or plants (only benthos).

In addition to more data with an expanded list of species, more ecologically relevant copper and cadmium toxicity data are needed to reduce uncertainty and to address comparisons of laboratory and field data. Metal speciation, dissolved organic carbon, suspended particulates, and bedded sediments should be considered with laboratory-to-field extrapolations. The role of organic complexation in reducing the toxic form of these metals available to aquatic biota is particularly critical.

Acute freshwater and saltwater copper and cadmium toxicity data were used in the risk characterization as previously discussed. The use of acute data for predicting ecosystem effects is often questioned and assumed to be an area of significant uncertainty. However, Slooff et al. [71], in their review of single species and ecosystem toxicity for various chemical compounds, reported that there is no solid evidence that predictions of ecosystem level effects from acute tests are unreliable. The results of Slooff et al. [71] coupled with the use of a distribution of acute toxicity data reduce some of the uncertainty associated with using acute data.

Although single-species laboratory toxicity tests are valuable in risk assessment, microcosm and mesocosm data provide the following useful information for assessing the impact of a stressor on aquatic communities in an ecosystem: aggregate responses of multiple species, observation of population and community recovery after exposure, and indirect effects resulting from changes in food supply. Unfortunately, microcosm and mesocosm studies that determined NOECs were limited for both copper and cadmium.

Uncertainty associated with risk characterization

Many of the uncertainties associated with the variability in the exposure and effects characterizations discussed above are incorporated in the probabilistic approach used in this risk assessment [6]. Quantitative estimation of risks are analyzed as a distribution of exposure and effects data.

Ecological uncertainty includes the effects of confounding stressors, such as other contaminants, and the ecological redundancy of the functions of affected species. In the Chesapeake Bay watershed, numerous contaminants may be present simultaneously in the same aquatic habitats; therefore, joint toxicity may occur. The concurrent presence of various contaminants along with copper and cadmium makes it difficult to determine the risk of each metal in isolation.

Ecological redundancy is known to occur in aquatic systems. Field studies have shown that resistant taxa tend to replace more sensitive species under stressful environmental conditions [8,52]. The resistant species may replace the sensitive species if it is functionally equivalent in the aquatic ecosystem, and the impact on overall ecosystem function is reduced by these species shifts. For this risk assessment, information on the ecological interactions among species would help to reduce this area of uncertainty.

CONCLUSIONS AND RESEARCH NEEDS

Potential ecological risk from copper exposure was greater than for cadmium in the Chesapeake Bay watershed. Potential ecological risks from copper exposures were reported to be greatest in the C and D Canal area, with relatively high risk also predicted in the Middle River. Other areas where potential ecological risks from copper exposures were judged to be moderate were the Choptank River and Potomac River. For the other 14 basins, the ecological risk from copper exposures was either low or data were insufficient to assess ecological risk. As reported above for copper, the area with the highest potential ecological risk from cadmium exposures was the C and D Canal area. Low to moderate potential ecological risk from cadmium exposures to the most sensitive trophic group (fish) was reported in the Potomac River, upper mainstem bay, West Chesapeake watershed, Choptank River, and Chester River. In the other 12 basins, ecological risk from cadmium exposures was either low or insufficient data were available for assessing ecological risk.

The goal of this study was to determine ecological risk in the Chesapeake Bay watershed for both copper and cadmium independently. However, because both copper and cadmium were measured from the same sample, joint toxicity and possible enhanced potential ecological risk may be present in the higher risk areas, such as the C and D Canal and selected areas of the Potomac River, in which both metals are common. Previous laboratory toxicity studies with mixtures of copper and cadmium suggest additive toxicity that would support the possibility of increased ecological risk in these selected areas [72].

The following research is recommended to supplement existing data for assessing the ecological risks of copper and cadmium in the Chesapeake Bay watershed.

Exposure assessments for copper and cadmium using randomly selected stations are needed on a broad spatial and temporal scale in the Chesapeake Bay watershed. On a spatial scale, copper and cadmium data are needed for the major rivers (tributaries) and representative freshwater streams where these data are lacking, particularly in Virginia waters of the Chesapeake Bay watershed (e.g., Rappahannock and York Basins). Exposure assessments with increased sampling frequency covering all seasons of the year at representative locations in the Bay watershed (including some of the basins in this article where data are lacking) are also needed to improve our ability to determine risk of aquatic biota to these metals. Specifically, rain event sampling (e.g., samples every 2–4 h during the event) and subsequent measurement of metals in streams or tributaries near known sources of copper and cadmium are needed. All exposure assessments of copper and cadmium should be conducted by laboratories using the most updated analytical methods (with documented and approved quality assurance/quality control procedures) with detection limits slightly below the toxicity thresholds for the most sensitive species.

An extensive spatial and temporal exposure assessment of both copper and cadmium is recommended in the C and D Canal area over multiple years. Because the C and D Canal was the highest risk area for these metals based on data collected in 1985 and 1987, the obvious question is whether this area still has concentrations that may pose a risk to aquatic biota. Biological communities should also be sampled in the C and D Canal area to determine whether they are impaired compared with communities in similar habitats.

Acute toxicity data for various trophic groups for both metals in freshwater and saltwater are recommended for improving the current toxicity database. Specifically, acute freshwater and saltwater toxicity data for copper are needed for plants (phytoplankton and macrophytes). For cadmium, acute freshwater toxicity data are needed for zooplankton and aquatic plants; acute saltwater cadmium data are lacking for macrophytes, phytoplankton, and zooplankton.

Microcosm/mesocosm toxicity data that include the calculation of NOEC, LOEC, and chronic values for both copper and cadmium in freshwater and saltwater environments are needed to provide insight on the interaction of aggregate species assemblages during metals exposure, recovery potential of exposed species, and possible indirect effects on higher trophic groups. These studies should be designed to simulate environmentally realistic pulsed exposures of these metals documented to occur in the environment.

Assessments of biological communities (index of biotic integrity for fish, invertebrates, etc.) in aquatic systems that receive the highest exposures of copper and cadmium are recommended to determine whether the predicted ecological risk for these metals can be confirmed with actual field data.

Acknowledgement—We acknowledge the Chesapeake Bay Program Office, U.S. EPA, for funding this study (grant CB993438010). The Toxics of Concern Workgroup of the U.S. EPA Toxics Subcommittee is also acknowledged for its support. The following individuals provided data: Gerhardt F. Reidel, Joseph R. Scudlark and Christy Stoll. We thank Mary Hancock for typing this manuscript.

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APPENDIX

Key to map for Figure 1[a]

Station	Description	Latitude	Longitude
1	Susquehanna River fall line (1578310)	39.6586	76.1744
2	James River fall line (2035000)	37.6708	78.0861
3	Elizabeth River	36.8081	76.2933
4	Freestone Point	38.5833	77.2667
5	Indian Head	38.6000	77.2167
6	Morgantown	38.3337	77.0157
7	Patapsco River	39.2167	76.5000
8	Possum Point	38.5362	77.2920
9	Wye River (Manor House)	38.9028	76.1298
10	Bell Branch (BEB)	38.9917	76.6333
11	Bacon Ridge Branch (BRB)	38.9992	76.6136
12	Burnt Mill Creek (BTM)	38.3322	76.6369
13	Bear Creek	39.2358	76.4961
14	Curtis Bay	39.2064	76.5803
15	Middle Branch	39.2528	76.5883
16	North West Harbor	39.2767	76.5742
17	Outer Harbor	39.2089	76.5247
18	Sparrows Point	39.2081	76.5075
19	Cabin Branch (CAB)	38.7694	76.6528
20	CB1	36.9950	75.9467
21	CB10	38.2467	76.2617
22	CB11	38.3717	76.3233
23	CB12	38.5633	76.4317
24	CB13	38.7517	76.4350
25	CB14	38.9183	76.3883
26	CB15	38.0717	76.3233
27	CB16	39.1883	76.2883
28	CB17	39.2567	76.2400
29	CB18	39.3683	76.1433
30	CB19	39.5500	76.0800
31	CB2	37.0833	76.0950
32	CB20	39.4300	76.0333
33	CB3	37.1883	76.1633
34	CB5	37.3650	76.0750
35	CB6	37.5267	76.0433
36	CB7	37.6200	76.1200
37	CB8	37.8217	76.1750
38	CB9	38.1000	76.2200
39	Martinak	38.8750	75.8417
40	Chaptico Creek (CHP)	38.3817	76.7822
41	Coffee Hill (COF)	38.3614	76.7578
42	CR1D	38.5700	76.3833
43	Davis Millpond (DMP)	38.6708	75.7639
44	Dynards Run (DYN)	38.3164	76.7344
45	Dahlgren	38.3012	77.0660
46	Faulkner's Branch/Bradley Road (FBB)	38.6989	75.7853
47	Faulkner's Branch, Ischer Road (FBI)	38.7214	75.8261
48	Forest Hall (FOR)	38.3989	76.7492
49	Kings Creek (KGC)	38.7897	76.0094
50	LPXT0173	39.1333	76.8183
51	Lyons Creek (LYC)	38.7689	76.6239
52	Mill Creek (MLC)	39.2825	76.1436
53	Mattawoman Creek (MTW)	38.6161	77.0486
54	Gibson Island	39.0600	76.4350
55	South Ferry	39.0767	76.5014
56	Frog Mortar	39.3083	76.4028
57	Wilson Point	39.3083	76.4125
58	North Davis Branch (NDB)	38.6783	75.7478
59	North River (NRV)	38.9878	76.6233
60	Bivalve	38.3214	75.8894
61	Sandy Hill Beach	38.3567	75.8558
62	Cherry Hill	38.5667	77.2583
63	Maryland	38.5167	77.2583
64	Mid	38.5222	77.2667
65	Virginia	38.4917	77.3083
66	Quantico	38.5278	77.2750
67	Widewater	38.4333	77.3250
68	PTXCF8747	38.3133	76.4222
69	PTXCF9575	38.3265	76.3713
70	PTXDE2792	38.3800	76.5150
71	PTXDE5339	38.4243	76.6008
72	PTXDE9401	38.4940	76.6645
73	PTXDF0407	38.3413	76.4858
74	PTXED4892	38.5828	76.6783
75	PTXED9490	38.6582	76.6845
76	PTX0402	38.7118	76.6858
77	PXT0494	38.8062	76.7075
78	PXT0603	38.9500	76.6950
79	PXT0809	39.1083	76.8617
80	PXT0972	39.2350	77.0583
81	Sewell Branch (SEW)	38.6083	76.5867
82	Betterton	39.3742	76.0503
83	Turners Creek	39.3631	75.9842
84	Junction Route 50	39.0056	76.5067
85	Annapolis	38.9669	76.4717
86	Tull Branch (TLB)	38.7194	75.7719
87	Twiford Meadow (TWM)	38.7236	75.7625
88	Tributary to Marshyhope Creek (UMH)	38.7631	75.7431
89	Grove	39.4000	76.0500
90	Howell	39.3583	76.0833
91	Spesutie	39.3917	76.1250
92	Delaware City	39.5417	75.7250
93	Chesapeake City	39.5167	75.8000
94	Courthouse Point	39.5000	75.8750
95	Elkton	39.5667	75.8500
96	Kentmore	39.3750	75.9583
97	Havre de Grace	39.5417	76.0667
98	Tributary to Red Lion Branch (URL)	39.1767	75.8992
99	Tributary to Southeast Creek (USE)	39.1308	75.9794
100	Tributary to Tuckahoe Creek (UTK)	38.8831	75.9269
101	WBPXT0045	38.8085	76.7507
102	Quarter Creek	38.9167	76.1667

[a] Stations where copper and cadmium were sampled from 1985 to 1996 in the Chesapeake Bay watershed, USA. Latitude and longitude coordinates are given in degrees.