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Need for Environmental Quality Guidelines Based on Ambient Freshwater Quality Criteria in Natural Waters—Case Study "Zinc"

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The Environmental Engineering Laboratory (EEL) at Merck & Co., Inc. and Syracuse Research Corporation (SRC) investigated the toxicity of zinc bromide ($ZnBr_2$) to the freshwater crustaceans Daphnia magna and Ceriodaphnia dubia under static exposure conditions, and the chronic toxicity to fathead minnow, Pimephales promelas, under renewal. The 48-hr LC_{50} and EC_{50} of zinc (as $ZnBr_2$), based on measured concentrations of zinc to Daphnia magna, were 1.22 (1.01-1.48) and 0.86 (0.73-1.02) mg Zn/L, and to Ceriodaphnia dubia, 0.50 (0.41-0.62) and 0.36 (0.30-0.44) mg Zn/L, respectively. The 7-d LC_{50} and EC_{50} of zinc (as $ZnBr_2$) to fathead minnow, based on measured concentrations of zinc were 0.78 (0.65-0.89) and 0.76 (0.66-0.85) mg Zn/L, respectively. These studies were performed by Syracuse Research Corporation.

The definitive assays indicate that Ceriodaphnia dubia was the most sensitive species tested. Measured concentrations of zinc at the end of the tests demonstrated a reduction in soluble zinc of up to 41%, due to the combined effects of alkaline pH (8.3-8.7) and hardness (190-224 mg/L as $CaCO_3$) of the standard laboratory water. In natural waters, suspended solids and dissolved organic compounds are likely to contribute to additional removal of bioavailable zinc. The EPA national ambient freshwater quality criteria for zinc is 47 µg/L as a 24-hr average. It fails to account for the effect of site-specific water quality parameters and resident aquatic ecosystem sensitivity. Inclusion of both site-specific water quality parameters and resident aquatic ecosystem sensitivity into the ambient freshwater quality criteria will result in scientifically valid approaches that rely less on generic numerical values.

The "Interim Guidance on Interpretation and Implementation of Aquatic Life Criteria for Metals by the U.S. EPA (1992)" provides a Water-Effects Ratio (WER). The WER compares the toxicity of a pollutant in the actual site water to its toxicity in laboratory water, for two or more aquatic species. Because a metal's toxicity in water in the laboratory is the basis of the national criterion, the WER will be used as an adjustment to obtain a site-specific value. Adjustment may either increase or decrease the numeric value of the criterion.

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MATERIALS AND METHODS

A fresh, 500 g sample of 'Baker Analyzed' granular $ZnBr_2$ (lot# B41704) was used to conduct the tests described within this paper. The sample was held at room temperature (20°C) in the dark until testing. All studies were conducted under Good Laboratory Practices (GLPs) and followed U.S. EPA "Methods For Measuring The Acute Toxicity of Effluents to Freshwater and Marine Organisms (1985)". Test solutions for the screening and definitive tests were prepared from dilutions of 5,000 and 2,500 mg/L stock solutions, respectively, in hardness-adjusted standard laboratory water (SLW). SLW was obtained by filtration of City of Syracuse tapwater through a pair of activated charcoal filters. Hardness of the SLW was increased by the addition of 576 mg Na_2CO_3, 360 mg $CaSO_4 \cdot 2H_2O$, 360 mg $MgSO_4$, and 24 mg KCl to 8 L SLW to achieve a total hardness ranging from 180-200 mg/L as $CaCO_3$. Water temperature, pH, and hardness of fresh and aged test solutions were measured daily in several screening and definitive test beakers. Hardness and alkalinity were determined by standard USEPA procedures (U.S. EPA 1983). Zinc concentrations in test solutions were also determined for each treatment at the beginning of the definitive tests and for replicate solutions in each beaker either when 100% mortality was observed or at the end of the study. Zinc concentrations in the test solutions were measured with a Perkin-Elmer Model 373 Flame Atomic Absorption Spectrophotometer. Zinc metal, dissolved in 6N HCl, was utilized as the standard. The spectrophotometer wavelength was set at 213.9 nm utilizing an air-acetylene flame. The instrument detection limit was 0.005 mg/L Zn with a sensitivity of 0.02 mg/L Zn and an optimum Zn concentration range of 0.05 - 2 mg/L. The percent recovery for Zn in the test treatments ranged from 45.5 to 100%.

The static acute assays with *Ceriodaphnia dubia* were conducted in 30-mL glass beakers each containing 15 mL of test solution. Test beakers were held in a temperature-controlled environmental chamber for approximately 1 hr before initiation of a test. Five ceriodaphnids were transferred to test solutions in each beaker after test solutions had warmed to ~25°C. Four replicates were used at each test concentration, providing a total of 20 ceriodaphnids in each treatment. The presence of mortality and effects among test organisms were recorded daily.

Screening and definitive assays with *Daphnia magna* were conducted in 250-mL glass beakers, each containing 200 mL of test solution. Test containers were held in a temperature-controlled environmental chamber for approximately 1 hr before initiation of a test. Ten daphnids were transferred to test solutions in each beaker in both screening and definitive tests approximately 1 hr after the preparation of test solutions. Test concentrations in both assays were replicated.

Renewal chronic (seven-day) toxicity tests with larval fathead minnows were conducted in 1-L glass beakers each containing 800 mL of test solution. Test beakers were held in a temperature-controlled environmental chamber for approximately 1 hr before initiation of the test. Ten minnows were transferred to test solutions in each beaker after test solutions had warmed to 25°C. Test solutions were renewed every 24 hr by siphoning 600 mL of used solution from the exposure vessel and adding equal volume of freshly prepared test solution back into the vessels. Two replicates were tested in each treatment. Mortality and effects among test fish were recorded daily.

Ceriodaphnia data analysis generated LC_{50}s and EC_{50}s, estimated by computerized versions of the parametric probit (Computer Sciences Corporation 1988) and nonparametric Spearman-Karber procedures. *Daphnia magna* data analysis generated LC_{50} and EC_{50} and were estimated by a computerized version of the non-parametric Spearman-Karber procedure.

Pimephales promelas data analysis generated LC_{50} and EC_{50} and were estimated by computerized versions of the parametric probit and non-parametric Spearman-Karber procedures. Comparisons of mean dry weights of control and $ZnBr_2$-treated larval minnows were accomplished with a computerized version of Dunnett's Procedure (Computer Sciences Corporation 1988). The no-observed-effect-concentration (NOEC) and lowest-observed-effect-concentration (LOEC), based on growth of minnows after seven days, were used to calculate the chronic value (ChV) derived from the geometric mean of the NOEC and LOEC.

RESULTS AND DISCUSSION

The 48-hr LC_{50} and EC_{50} static acute toxicity values of zinc bromide to *Daphnia magna*, based on measured concentrations of zinc, were 1.22 (1.01-1.48) and 0.86 (0.73-1.02) mg Zn/L, respectively. There were no observable effects among daphnids exposed to 0.34 mg/L zinc after 48 hr. The 48-hr LC_{50} and EC_{50} static acute toxicity values of zinc bromide to *Ceriodaphnia dubia*, based on measured concentrations of zinc, were 0.50 (0.41-0.62) and 0.36 (0.30-0.44) mg Zn/L, respectively. The 7-d LC_{50} and EC_{50} chronic toxicity values of zinc bromide to the fathead minnow, based on measured concentrations of zinc, were 0.78 (0.65-0.89) and 0.76 (0.66-0.85) mg Zn/L, respectively. The lowest-observed-effect-concentration (LOEC) for growth among minnows after seven days was 0.63 mg Zn/L. The chronic value (ChV) derived from the geometric mean of the NOEC and LOEC for growth of larvae was 0.43 mg Zn/L.

The definitive assays indicated that *Ceriodaphnia dubia* was the most sensitive species tested to zinc bromide. Measured concentrations of zinc at the end of the tests demonstrated a reduction in soluble zinc concentration of up to 41%. The data are summarized in Tables 1 - 3. The reduction in measured zinc concentration was due likely to the hardness of the standard laboratory water. Zinc speciation and the formation of insoluble precipitates is much more complex in natural waters than in standard laboratory water. In natural waters, suspended solids and dissolved organic compounds are likely to contribute to the reduction of bioavailable zinc to aquatic organisms. The U.S. EPA published zinc acute toxicity test results for thirty freshwater species (U.S. EPA 1980). The median toxicity values ranged from

Table 1. Measured zinc bromide concentrations of test solutions in a definitive toxicity test with *Ceriodaphnia dubia* exposed to nominal concentrations of zinc bromide.

Nominal Zinc Conc. (mg/L)	Measured Zinc Concentration (mg/L) 0 hr	Measured Zinc Concentration (mg/L) 48 hr	Percent Of Nominal Zinc 0 hr	Percent Of Nominal Zinc 48 hr
0	<0.1	<0.1	---	---
0.12	<0.1	<0.1	<83.3	<83.3
0.22	0.16	0.10	72.7	45.5
0.39	0.28	0.18	71.7	46.2
0.70	0.57	0.53	81.4	75.7
1.22	1.06	0.77	86.9	63.1
2.18	2.10	1.30	96.3	59.6

Table 2. Measured zinc bromide concentrations of test solutions in a definitive toxicity test with *Daphnia magna* exposed to nominal concentrations of zinc bromide.

Nominal Zinc Conc. (mg/L)	Measured Zinc Concentration(mg/L) 0 hr	Measured Zinc Concentration(mg/L) 48 hr	Percent Of Nominal Zinc 0 hr	Percent Of Nominal Zinc 48 hr
0	<0.001	0.083	---	---
0.22	0.21	0.22	95.5	100
0.34	0.32	0.36	94.1	100
0.54	0.52	0.52	96.3	96.3
0.84	0.78	0.82	92.9	97.6
1.26	1.2	0.96	95.2	76.2
1.95	1.8	1.3	92.3	66.7
3.00	2.8	---	93.3	---

Table 3. Measured zinc bromide concentrations of test solutions in a definitive toxicity test with *Pimephales promelas* exposed to nominal concentrations of zinc bromide.

Nominal $ZnBr_2$ Conc. (mg/L)	Nominal Zinc Conc. (mg/L)	Cumulative Average Zinc Exposure Concentration (mg/L) 24 hr	48 hr	96 hr	168 hr	Percent Nominal Zinc At 168 hr
0	0	<0.1	<0.1	<0.1	<0.1	---
1.8	0.52	0.31	0.33	0.29	0.29	55.8
2.8	0.81	0.60	0.66	0.62	0.63	77.8
4.2	1.22	0.99	1.02	1.01	1.01	82.8
6.5	1.89	1.77	1.72	1.70	1.66	87.8
10.0	2.90	2.6	2.6	2.6	2.6	89.7

90 to 58,100 µg/L. Chronic tests with six species resulted in values from 47 to 852 µg/L. With nine different plant species, the results ranged from 30 to 67,700 µg/L. A chronic value of 47 µg/L was obtained with both a sensitive invertebrate (*Daphnia magna*) in hard water and a medium sensitive fish (flagfish) in soft water. For total recoverable zinc, the criterion to protect freshwater aquatic life as derived using the EPA Guidelines is 47

μg/L as a 24-hr average and the concentration (in μg/L) should not exceed the numerical value given by $e^{(0.83[\ln(\text{hardness})]+1.95)}$ at any time. The criterion maximum concentration (CMC) is expressed in terms of a 1 hr average concentration. The criterion continuous concentration (CCC) is expressed as a 4-d average. Neither is to be exceeded more than once every three years on the average. The CMC and CCC are intended to protect the aquatic environment against acute and chronic impacts, respectively.

For zinc, the CMC is 117 μg/L and the CCC is 106 μg/L. These are based on a water hardness of 100 mg/L as $CaCO_3$. The National Water Quality Criteria for metals have been generated from data published in literature and reviewed by the EPA. Several publications (Mount and Norberg 1984) and (Norberg and Mount 1985) on effluent testing provided the basis for the testing protocols and discharge limits. The aquatic toxicity evaluation performed at SRC involved a receiving stream with a hardness of 200 mg/L. Using the EPA criteria specified as a function of hardness to calculate the CMC and CCC for zinc at 200 mg/L hardness gave values of 211 and 191 μg/L, respectively (U.S. EPA 1986). These criteria values are quite different from those derived experimentally in this study.

Patterson et al. (1977) provided extensive theoretical and experimental studies elucidating the removal of zinc by precipitation. Their data revealed low water solubilities of the carbonate and hydroxides of zinc in surface waters. Brown et al. (1983) found that most U.S. soil and drinking water contain between 10 - 300 mg/L and 0.003 - 2 mg/L zinc, respectively. These findings suggest that exceeding the EPA CCC for zinc by several fold would not effect the ecosystem health of many surface waters due to the ubiquitous nature of zinc in the environment. O'Donnel et al. (1985) found zinc complexes are much less toxic than zinc metal ion to freshwater organisms. Zinc toxicity was found to be a function of complexation and the resulting water solubilities of those complexes are a function of water quality parameters. Parkerton et al. (1989), in a study using indicator species to derive site-specific criteria for zinc in three rivers, concluded that differences in bioavailability of zinc in the rivers was attributable to differences in water hardness and sorption characteristics. Chapman (1991) recommends the use of guidelines instead of criteria. In this testament, the measure of ecosystem health becomes the focus. The presence, absence or condition of multiple species, but never a single species, becomes the evaluation guideline. Site specific guidelines ought to take into account resident ecosystem health, it's sensitivity and water quality parameters.

The present study raises a number of questions as to the universal applicability of the EPA water quality criteria for zinc. Analytical difficulties have influenced both the development of water criteria and the evaluation of water quality in surface waters. There are no standard methods for measuring zinc speciation in natural waters. Flame atomic absorption spectrometry used in this study does not have the sensitivity required for the analysis of zinc in the low parts per billion levels. Because of these analytical constraints, much of the existing surface water quality monitoring data for zinc is reported as below detection limits that are higher than applicable water quality standards and are of limited value. In the studies performed at SRC, the percent recovery for zinc in the laboratory environment was highly variable. The measured aqueous concentration of zinc (regardless of speciation) was significantly reduced due to the formation of insoluble particulates. It is apparent that there is a need to predict the fate of zinc in aquatic environments and to develop permit limits that are protective to aquatic life, but not so overly restrictive that they are economically or technically unachievable. There is sufficient knowledge of the mechanisms of zinc toxicity and the behavior of zinc in natural waters to discount for non-bioavailability in regulatory actions and decision making.

The EPA has recently incorporated a Water Effects Ratio (WER) into the calculation of the numeric value for the Water Quality Criterion for Metals (U.S. EPA 1992). The EPA document utilizes the WER which considers the bioavailability and toxicity of metals in receiving waters to adjust the National criterion. The WER is the ratio of either: (1) aquatic life acute toxicity test results conducted in receiving stream water to the acute toxicity test results conducted in laboratory dilution water, (2) aquatic life chronic toxicity test results conducted in receiving water to the chronic toxicity test results conducted in laboratory dilution water, or (3) both. Bioavailability defines that portion of the metal which is biologically available under a given physical, chemical or biological condition that may cause or contribute to acute or chronic impairment of aquatic life. A wastewater discharger has the option of developing a site-specific WER to protect designated fish and aquatic life when they can demonstrate there exist physical, chemical or biological conditions of receiving waters which differ from conditions upon which National Ambient Water Quality Criterion for Metals are established (U.S. EPA 1986). The WER is used as an adjustment to obtain site-specific values which may either increase or decrease the numeric value of the criterion. The approach is intended to address the issue of metals toxicity to fish and aquatic life in a direct manner and will assure the protection of receiving streams. The Water Quality Criteria (U.S. EPA 1992) of zinc for fish and other aquatic life at continuous concentrations (µg/L) is now defined as **"[Exp(0.8473[ln(hardness)]+ 0.7614)]x [WER]"**. This EPA guidance document addresses the issue of bioavailability and toxicity of site-specific receiving water.

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