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Bioavailability and Analytical Measurement of Copper Residuals in Sediments

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Abstract Analytical measurements are commonly used to screen for toxicity or lack of toxicity from sediment-associated copper. Comparisons of analytical measurements with toxicological responses can be useful for determining the practicality of analytical measurements for assessing the toxicity of copper in sediments. The purpose of this research was to determine the utility of method detection limits (MDLs; i.e., minimum concentration of an analyte such as copper that can be measured with 99 % confidence with a specific analytical method and matrix) to predict the bioavailability of copper in five different sediments. The specific objectives of this research were to (1) select and characterize five sediments with different characteristics, (2) amend and measure a range of copper concentrations in the five sediments to determine MDLs and bioavailability of copper amendments in those sediments, (3) discern relationships with sediment characteristics to MDLs and bioavailability of copper in the five sediments, and (4) compare MDLs and observed toxicity to *Hyalella azteca* Saussure as an indicator of copper bioavailability in the five sediments. The lowest copper concentrations that elicited an observable adverse effect ranged from 15 to 550 mg Cu/kg, and the MDLs ranged from 1.5 to 6 mg Cu/kg. The MDLs and measured copper concentrations were not adequately predictive of the bioavailability and toxicity of copper in the five sediments. No adverse effects were observed for *H. azteca* exposed for 10 days to the sediment from California with simultaneously extractable metals > acid-volatile sulfides. Since the lowest observed effects concentrations of copper in the five sediments ranged two orders of magnitude, the National Oceanic and Atmospheric Administration screening values (threshold and probable effect levels) were not predictive of *H. azteca* responses to the copper-amended sediments.

Keywords Toxicity · Method detection limit · Accumulation · Risks

1 Introduction

There are numerous studies of copper in sediments, but questions still remain regarding measurement and bioavailability of copper residues that accumulate in sediments. There is concern that copper may accumulate in sediments from anthropogenic activities such as parking lot stormwater runoff, mining activities, industrial processes, as well as algaecide and herbicide applications (Teasdale et al. 2003; Gillis and Birch 2006; Jones et al. 2008). To monitor copper accumulation in sediments through time as well as the consequences of those residuals, information is needed regarding the sensitivity of analytical measurements

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and the bioavailability of accumulated copper in sediments.

Analytical measurements of copper residues in sediments can be accomplished if the sediment copper concentration is in excess of a method detection limit (MDL). An MDL is the minimum concentration of an analyte of interest (i.e., copper in this case) that can be measured with 99 % confidence for a specific matrix and analytical method (Kimbrough and Wakakuwa 1993; Creed et al. 1994; APHA 2005). MDLs for copper in sediments can differ due to the sediment matrix and the analytical method used. Reported MDLs for copper in sediments can range from 0.032 to 13 mg Cu/kg depending on the analytical method and sediment matrix (Acar 2006; Enzweiler and Vendemiatto 2004). Because sediment characteristics often range widely from site to site (Suedel and Rodgers 1991), we would expect MDLs for copper residues in sediment to concomitantly differ from site to site. There are apparently no published data that would indicate how sediment characteristics can influence MDLs for copper in sediments. Due to copper's strong affinity for organic matter (OM) and fines in sediments (i.e., clay and silt; Laing et al. 2009), one can hypothesize that organic matter content and particle size, as well as other sediment characteristics, could influence MDLs for copper in sediments. Further, if background sediment copper concentrations are substantially greater than the increase of copper concentration attributed to copper residues in effluents or pesticide applications over time, the likelihood of measuring copper residues would decrease.

The influence of sediment characteristics on the bioavailability of copper sorbed to sediment has been the subject of intense study. Differences in the bioavailability of sediment sorbed copper have been attributed to organic matter type and content (Besser et al. 2003; Milani et al. 2003), acid-volatile sulfides (Allen et al. 1993; DiToro et al. 1990), cation exchange capacity (CEC; Chapman et al. 1998), pH (Burton 1991), and particle size distribution (Hoss et al. 1997). To measure the bioavailability of sediment sorbed copper, an organism is needed that can thrive in sediments with diverse characteristics. *Hyalella azteca* Saussure has been used in sediment toxicity experiments and tolerates a wide range of organic matter contents and particle size regimes. *H. azteca* is commonly used to discern influences of sediment characteristics on the bioavailability of sediment-sorbed copper (Cairns et al. 1984; Suedel et al. 1996; Deaver and Rodgers 1996; Gallagher et al. 2005).

Because the bioavailability and MDLs of sediment sorbed copper differ among sediments, analytical measures may be inadequate to assess exposures of copper residuals in sediments that could elicit adverse effects to benthic organisms. Comparisons of MDLs and toxicological responses [i.e., lowest observed effect concentrations (LOECs), LC50s, and potency slopes] to copper residuals in sediments could provide information regarding the adequacy of analytical methods for measuring sediment copper exposures that may elicit adverse effects to benthic fauna. Further, comparisons between the bioavailability and MDLs of copper amendments to sediments could be useful for determining if analytical measurements (e.g., MDLs) and toxicological responses are related. We hypothesized that there could be an inverse relationship between MDLs and the bioavailability of copper in sediments (i.e., lower MDLs are proportional to more bioavailable copper in sediments; higher MDLs are proportional to less bioavailable copper in sediments).

Monitoring programs to assess risks associated with copper accumulation in sediments may be restricted by analytical methods for measuring copper exposures and methods to detect adverse effects from copper residues in sediments. The purpose of this research was to measure MDLs for copper in sediments with divergent characteristics and to discern relationships for MDLs and bioavailability of copper amendments in sediments. Specific objectives of this study were to (1) select and characterize five sediments with different characteristics, (2) amend and measure a range of copper concentrations in the five sediments to determine MDLs and bioavailability of copper amendments in those sediments, (3) discern relationships with sediment characteristics to MDLs and bioavailability of copper in the five sediments, and (4) compare MDLs and observed toxicity to *H. azteca* Saussure as an indicator of copper bioavailability in the five sediments.

2 Materials and Methods

2.1 Sediment Sampling and Characterization

Five sediments with divergent characteristics were collected from the Mississippi River in Mississippi (32°07′ N, 91°01′ W); an aquaculture pond in South

Carolina (34°68′ N, 82°81′ W); an irrigation pond in Colorado (39°16′ N, 104°53′ W); Lake John Hay in Salem, Indiana (38°61′ N, 86°1′ E); and an urban pond in Buena Park, California (33°87′ N, 117°98′ W). Sediment samples were collected from different physiographic provinces of the contiguous USA based on the ranges of sediment characteristics found in freshwater bottom sediments by Suedel and Rodgers (1991). Approximately 20 L of surficial sediments was collected from each site with a polypropylene scoop acquiring the top 10 cm of sediment. The sediment samples were placed in polyethylene bags prewashed with 10 % technical grade nitric acid (Thermo Fisher Scientific, Inc.). Twenty liters of corresponding surface water were also collected from each site. All samples were shipped on wet ice to a laboratory at Clemson University for analysis. Sediment handling and storage methods followed those specified by Plumb (1981). Surface water samples were stored at approximately 4 °C until analysis. Each sediment sample was placed in a separate container and gently homogenized. Three replicates of each sediment were characterized for particle size distribution (hydrometer method; Gee and Bauder 1986), particle surface area (calculated based on particle size classes; Suedel and Rodgers 1991), organic matter (loss on ignition; Nelson and Sommers 1986), cation exchange capacity (displacement after washing ammonia probe analysis; CEC), pH (probe analysis), percent solids (gravimetric; Plumb 1981), dry bulk density (gravimetric; Blake 1965), acid-volatile sulfides (AVS), and simultaneously extractable metals (SEM; purge and trap; Leonard et al. 1996).

2.2 Measurement of MDLs for Copper in Sediments

The MDLs for copper in the five sediment samples were empirically derived from two bench-scale experiments with a series of copper sulfate pentahydrate ($CuSO_4 \cdot 5H_2O$; Thermo Fisher Scientific, Inc.) amendments. Flasks (125 mL) containing wet sediment (i.e., 30 g dry sediment estimated by percent solids) were used for the experiments to determine MDLs for copper in sediments. Stock solutions were made by diluting a 1,000 mg Cu/L stock solution in 100 mL of nanopure water (18 Ω). The acid soluble copper concentrations in the stock solutions were measured by acidifying the samples with trace metal grade nitric acid (Thermo Fisher Scientific, Inc.) to a pH≤2 for 24 h then filtering samples through a 0.45-μm filter before analysis by inductively coupled plasma–optical emission spectroscopy (ICP-OES; Perkin-Elmer Optima 3100RL; APHA 2005). For sediment copper amendments, 1 mL of stock solution with the targeted mass of copper was added to each flask. Sediment amendments were allowed a contact period of 2 weeks before sediment copper concentration analysis based on a previous study by Murray-Gulde et al. (2002), indicating that copper sulfate partitioned to sediment within 2 weeks. An initial range finding experiment targeted sediment copper amendments of untreated control, 0.5, 1, 2, 4, and 8 mg Cu/kg was used to determine copper amendments for definitive MDL experiments. Based on the results from range finding experiments, different copper amendments (i.e., treatments) were used for each sediment sample for definitive MDL experiments. Targeted copper amendments for definitive experiments determining copper MDLs were as follows: (1) untreated control, 1, 1.5, 2, 2.5, and 3 mg Cu/kg for the Mississippi River sediment sample; (2) untreated control, 3, 4, 5, 6, and 7 mg Cu/kg for the South Carolina aquaculture pond sediment sample; (3) untreated control, 4, 5, 6, 7, and 8 mg Cu/kg for the Lake John Hay (Indiana) sediment sample; (4) untreated control, 3, 4, 5, 6, and 7 mg Cu/kg for the Colorado irrigation pond sediment sample; and (5) untreated control, 5, 6, 7, 8, and 9 mg Cu/kg for the California (Buena Park) urban pond sediment sample.

Sediment copper concentrations were measured three times for each amended sediment sample using a digestion block and ICP-OES (US EPA method 3050b; US EPA 1996). The MDLs of copper in sediments were defined as the lowest amendment with a measured sediment copper concentration greater than background, discerned by ANOVA and Dunnett's multiple range tests (α=0.01) with copper-amended treatments compared to untreated controls. Regression analyses were used to determine correlations of sediment characteristics and MDLs of copper residues in sediments (SAS 9.2 2010).

2.3 Sediment Copper Bioavailability Experiments

Bioavailability of copper in the five sediment samples was measured using copper sulfate pentahydrate amended sediments in toxicity experiments. Sediments were amended using the method outlined by Huggett et al. (1999) and allowed a contact time of

2 weeks prior to organism introduction based on a previous study by Murray-Gulde et al. (2002), indicating that copper sulfate partitions to sediments within 2 weeks. The targeted sediment copper amendments for definitive toxicity experiments were as follows: (1) untreated control, 10, 15, 25, 35, 50, 60, and 70 mg Cu/kg for the Mississippi River sediment sample; (2) untreated control, 75, 100, 125, 175, 250, 450, and 550 mg Cu/kg for the South Carolina aquaculture pond sediment sample; (3) untreated control, 50, 75, 100, 150, 250, 450, and 550 mg Cu/kg for the Indiana Lake John Hay sediment sample; (4) untreated control, 350, 400, 450, 550, 600, 650, and 750 mg Cu/kg for the Colorado irrigation pond sediment sample; and (5) untreated control, 400, 550, 650, 800, 1,000, 1,200, 1,400 mg Cu/kg for the California urban pond sediment sample. Bioavailability of copper in the five amended sediment samples was measured using 10-day static nonrenewable sediment toxicity experiments and second-instar *H. azteca* (approximately 2 to 3 weeks old, collected using a sieving method; Deaver and Rodgers 1996) cultured at Clemson University following the procedures of de March (1981). Sediment toxicity experiments were conducted at 23±1 °C under a 16-h light/8-h dark photoperiod (US EPA 2000). Experiments were initiated with ten *H. azteca* in three replicated 250-mL borosilicate beakers, with 160 mL of overlying site water and 40 mL of sediment (Suedel et al. 1996). *H. azteca* were fed with three 7-mm *Acer rubrum* discs at test initiation (Huggett et al. 1999). Water and sediment samples were collected at the termination of the experiments for measurement of soluble copper concentrations in the overlying water and sediment copper concentrations. Soluble copper concentrations in the overlying water were analyzed by filtering each sample through a 0.45-μm filter, and the filtrates were acidified to a pH≤2 with trace metal grade nitric acid before analysis by ICP-OES (Thermo Fisher Scientific, Inc.; APHA 2005). Sediment copper concentrations were measured using ICP-OES (US EPA method 3050b). Water characteristics (i.e., hardness, alkalinity, pH, conductivity, and temperature) were measured at the initiation and termination of the toxicity experiments to insure that the environmental tolerances of *H. azteca* were satisfied (APHA 2005).

The probit method was used to calculate LC50s with 95 % confidence intervals (SAS 9.2 2010). Analysis of variance and Dunnett's multiple range tests were used to discern differences between treatments and untreated control to estimate the no observed effect concentrations (NOECs) and lowest observed effect concentrations (α=0.05; Suedel et al. 1996; SAS 9.2 2010). Potency slopes were calculated (as change in response of *H. azteca* over increase in sediment copper concentration or change in exposure) to more explicitly evaluate the bioavailability of copper in the five sediments since the potency slopes include a range of response to a range of exposures from the lower threshold to the saturated response (=100 % mortality; Johnson et al. 2008), and differences in slopes (=sensitivity and bioavailability) could be statistically evaluated using analysis of covariance. Potency slopes were calculated for the linear portion of the exposure–response curves (Johnson et al. 2008) to discriminate differences of copper potency with different sediments and to determine relationships with the LOECs and LC50s to the potency of copper-amended sediments (SAS 9.2 2010).

2.4 Relationships of MDLs and Bioavailability of Copper in Sediments

The MDLs for copper in sediments and the observed responses (i.e., LOECs, LC50s, and potency slopes) were used to test for relationships between the MDLs and bioavailability of copper in sediments. Regression analyses were used to determine relationships with the MDLs of copper in sediments and the respective LOECs, LC50s, and potency slopes for the five sediment samples (SAS 9.2 2010).

3 Results and Discussion

3.1 Sediment Characteristics

Characteristics of the five sediments collected from a variety of locations differed widely (Table 1). In particular, the "background" copper concentrations in the five sediment samples ranged from <1.5 to 150 mg Cu/kg (Table 1). Reported background copper concentrations in sediments for physiographic provinces throughout the USA range from 0.8 to 50 mg Cu/kg (Flemming and Trevors 1989). The original purpose for collecting sediments for these experiments was to capture a sufficient range of characteristics, so the results of these experiments may be widely applicable.

Table 1 Characteristics of sediments used in bioavailability experiments

Physical/chemical characteristics	Mississippi River	Aquaculture pond	Lake John Hay	Irrigation pond	Urban pond
Sediment					
Percent solids (%)	81	45	76	71	80
Sediment dry bulk density (g/cm^3)	1.60	0.63	1.51	1.18	1.62
pH	7.15	6.88	6.70	7.45	7.80
% OM ± SD	0.26±0.11	5.39±0.08	2.52±0.07	0.34±0.34	3.04±0.61
CEC (mEq/100 g) ± SD	5.71±3.46	16.93±1.92	18.19±0.04	53.79±9.73	25.18±6.37
% Sand	98	26	66	5	86
% Silt	2	41	27	55	11
% Clay	<1	33	7	34	3
Surface area (cm^2/g)	53	2,600,000	540,000	2,700,000	230,000
Background Cu concentration (mg/kg)	<1.5	10	12	18	150
AVS (μmol/g) ± SD	<0.2	14.8±1.5	7.4±1.9	27.8±4.1	3.32±0.2
SEM (μmol/g) ± SD	0.008±0.0001	0.066±0.011	0.068±0.019	0.066±0.010	10.24±1.91

Average of three replicates ± SD

The percent sand ranged from 5 to 98 %; percent silt ranged from 2 to 55 %; and percent clay ranged from <1 to 34 % (Table 1). Particle surface area ranged from 53 to 2,700,000 cm^2/g. Sediment dry bulk density ranged from 0.63 to 1.62 g/cm^3, and the organic matter content ranged from 0.26 to 5.39 %. The CEC ranged from 5.71 to 53.79 mEq/100 g, and pH ranged from 6.7 to 7.8 SU. AVS and SEM ranged from <0.2 to 27.8 μmol/g and from 0.008 to 10.24 μmol/g, respectively.

3.2 MDLs and Bioavailability of Copper in Sediments

The MDLs (standard deviation) for copper in the five sediments (in sequence from lowest to highest) were 1.5 (0.3) mg Cu/kg (Mississippi River), 4 (0.5) mg Cu/kg (aquaculture pond), 4 (0.6) mg Cu/kg (irrigation pond), 6 (1.9) mg Cu/kg (Lake John Hay), and 6 (3.2) mg Cu/kg (urban pond). The percent recoveries for copper in the five sediments (in sequence from lowest to highest) were 111 % (Mississippi River), 99 % (aquaculture pond), 93 % (irrigation pond), 95 % (Lake John Hay), and 85 % (urban pond). Based on the MDLs for these diverse sediments, the range of MDLs would likely not differ more than one order of magnitude when ICP-OES (US EPA method 3050b) is used. Based on results from these sediments, the analytical method used (ICP-OES with US EPA method 3050b) is relatively sensitive and can detect changes in sediment copper concentrations of approximately 1.5–6 mg Cu/kg.

The toxicity experiments using *H. azteca* indicated that the bioavailability of copper also ranged widely in these sediments. The 10-day LC50s ranged from 26 to 592 mg Cu/kg (a difference of 566 mg Cu/kg; Table 2). Based on measured sediment copper concentrations, the 10-day LOECs for the copper-amended sediments ranged from 15 mg Cu/kg (Mississippi River) to 550 mg Cu/kg (urban pond), and these 10-day LOECs differed by 535 mg Cu/kg (15–550 mg Cu/kg; Table 2). For these copper-amended sediments, 10-day potency slopes ranged from 0.071 to 1.7 % mortality/mg Cu/kg (a difference of 1.629 % mortality/mg Cu/kg; Table 2). Previous studies have noted that toxicity observed from sediments containing copper was related more to copper concentrations in overlying water than to sediment copper concentrations (Cairns et al. 1984; Suedel et al. 1996; Deaver and Rodgers 1996). When the 10-day LC50s and 10-day LOECs were calculated based on soluble copper concentrations in the overlying water, the range was 13–160 μg Cu/L (a difference of 147 μg Cu/L), and the range for 10-day LC50s was 43–167 μg Cu/L (a difference of 124 μg Cu/L). The 10-day potency slopes calculated based on soluble copper concentrations in the overlying water, ranged from 0.095 to 0.48 % mortality/μg/L (a difference of 0.385 % mortality/μg/L). The wide range of 10-day LOECs, 10-day LC50s, and 10-day potency slopes based on sediment copper concentrations compared to the range

Table 2 Measured 10-day NOECs, 10-day LOECs, 10-day LC50s (95 % confidence interval), and 10-day potency slopes based on measured sediment copper concentrations and soluble copper concentrations in the overlying water for *H. azteca* exposed to five copper-amended sediments

Parameter	Mississippi River	Aquaculture pond	Lake John Hay	Irrigation pond	Urban pond
10-day NOEC					
Sediment (mg Cu/kg)	9	57	58	354	395
Overlying water (μg Cu/L)	68	8	26	132	143
10-day LOEC					
Sediment (mg Cu/kg)	15	85	141	394	550
Overlying water (μg Cu/L)	109	13	33	147	160
10-day LC50 (95 % CI)					
Sediment (mg Cu/kg)	26 (22–29)	125 (82–184)	179 (150–208)	426 (262–688)	592 (526–653)
Overlying water (μg Cu/L)	141 (126–156)	91 (18–162)	43 (33–54)	151 (118–160)	167 (155–177)
10-day potency slopes					
Sediment (% mortality/mg Cu/kg)	1.7	0.75	0.2	0.25	0.071
Overlying water (% mortality/μg Cu/L)	0.48	0.095	0.88	0.24	0.45

observed from soluble copper concentrations measured in the overlying water, supports the notion that soluble copper in the overlying water is a more accurate measure of the bioavailable fraction of copper for *H. azteca* in these laboratory sediment toxicity experiments than the bulk sediment copper concentrations.

Based on measured sediment copper concentrations, two negative logarithmic trends were observed with 10-day potency slopes and 10-day LOECs [R^2=0.77; potency slope=−0.425 ln (10-day LOEC)+2.564] and the 10-day potency slopes and 10-day LC50s [R^2=0.78; potency slope=−0.497 ln (10-day LC50)+3.044] for the five copper-amended sediments (Figs. 1 and 2). The observed relationships of 10-day potency slopes and 10-day LOECs and 10-day LC50s demonstrate that the 10-day LOEC or 10-day LC50 increases as the potency of copper decreases in sediments. These relationships are likely due to different binding mechanisms that affect the bioavailability of copper in these sediments. Based on the copper amendments required to elicit observable adverse effects on *H. azteca* in these sediments, increases in sediment copper concentrations of 14–400 mg Cu/kg would be required to measure adverse effects.

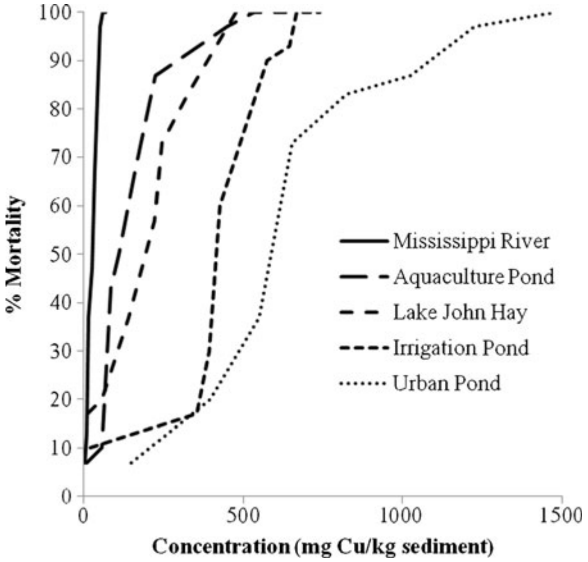

Fig. 1 Concentration–response curves based on measured sediment copper concentrations for *H. azteca* exposed for 10 days in copper-amended sediments

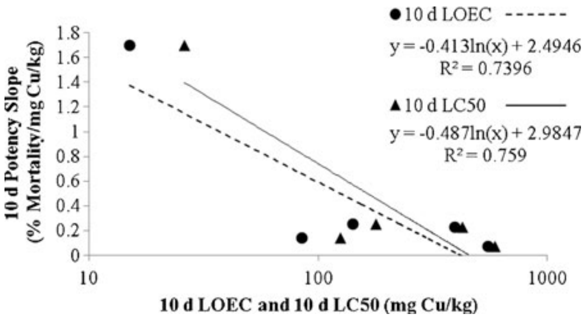

Fig. 2 Trends of the potency slopes and 10-day LOECs and 10-day LC50s for *H. azteca* exposed for 10 days to five copper-amended sediments

Table 3 Correlation coefficients and significance of linear relationships for sediment characteristics and MDLs for copper in sediments

Sediment characteristics	*P* value	R^2
% OM	0.153	0.547
Percent solid (%)	0.283	0.363
Sediment dry bulk density (g/cm^3)	0.346	0.293
Percent sand	0.397	0.244
Percent clay	0.438	0.210
Percent silt	0.762	0.035
CEC (mEq/100 g)	0.811	0.022
pH	0.872	0.010
Surface area (^{2}/g)	0.963	< 0.001
Background sediment copper concentration	0.998	< 0.001

3.3 Relationships with Bioavailability and MDLs of Copper in Sediments and Sediment Characteristics

There were no significant linear correlations (α=0.05) of MDLs of copper in the five sediments with the measured or calculated sediment characteristics in this study (Table 3). Organic matter content had the highest correlation coefficient, but the relationship was not sufficient to be predictive (P=0.153, R^2=0.547; Table 3). Sediments with the highest and lowest background copper concentrations had the highest and lowest measured MDLs, respectively (Fig. 3). A logarithmic relationship was observed for MDLs of copper in the sediments and background sediment copper concentrations (R^2=0.712, y=0.8781 ln(x)+2.0717; Fig. 3) with higher background copper concentrations in sediments associated with higher MDLs for copper.

Several sediment characteristics influence the bioavailability of copper in sediments (Jones et al. 2008). In this study, pH had the greatest correlation with the 10-day NOECs, 10-day LOECs, and 10-day LC50s (Table 4). An AVS/SEM ratio greater than one has been proposed as a predictor of the lack of sediment toxicity due to divalent metals (Ankley et al. 1994; DiToro et al. 1990). In this study, the urban pond sediment had an AVS/SEM of 0.3 (data taken from Table 1), and according to the AVS/SEM hypothesis, divalent metals in this sediment may cause toxicity. Results from the toxicity experiment with the urban pond sediment indicated no background toxicity, and a greater amount of amended copper was required before toxicity could be detected compared to the other sediments in this study. Because the bioavailability of copper in sediments is influenced by several sediment characteristics (e.g., organic matter, CEC, and pH; Jones et al. 2008), the utility of a single sediment characteristic (such as AVS/SEM) to predict the bioavailability and toxicity of copper in sediment is limited (Ankley et al. 1993; Huggett et al. 1999; Jones et al. 2008).

Although sediment characteristics can differ widely, sediment characteristics can be correlated. For example, the percent organic carbon and organic matter are positively correlated with CEC and primarily associated with fine particle-sized sediments (Bailey and White 1964; Suedel and Rodgers 1991). As the CEC and organic matter increase, bioavailability of copper in sediments decreases (Besser et al. 2003; Milani et al. 2003; Cairns et al. 1984). Characteristics correlated with increased bioavailability of copper in sediments such as percent sand (Hoss et al. 1997) decrease as the

Fig. 3 Background sediment copper concentrations and MDLs for copper in the five sediments

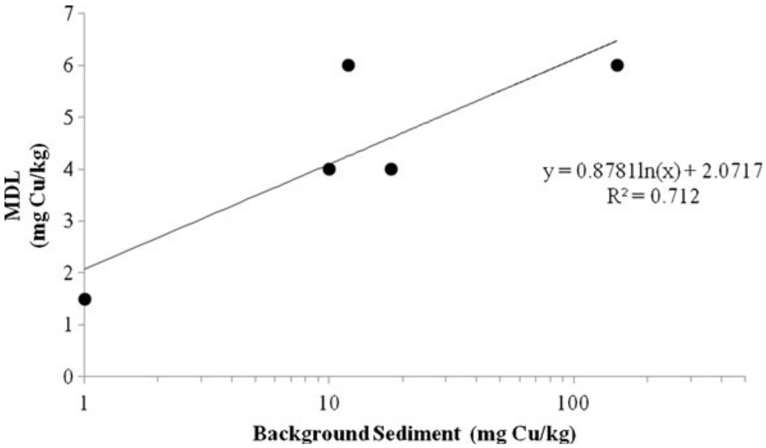

Table 4 Correlation coefficients of linear regressions for sediment characteristics and the 10-day NOECs, 10-day LOECs, 10-day LC50s, and 10-day potency slopes (based on measured sediment copper concentrations)

Sediment characteristics	10-day NOEC	10-day LOEC	10-day LC50	10-day potency slope
% OM	0.023	0.004	<0.001	0.250
Percent sand	0.060	0.015	0.019	0.262
Percent lay	0.028	0.002	0.003	0.185
Percent silt	0.063	0.021	0.027	0.331
CEC (mEq/100 g)	0.430	0.432	0.580	0.329
pH	0.751	0.706	0.671	0.029
Surface area (cm^2/g)	0.029	0.002	0.003	0.182
Background sediment copper concentration	0.526	0.682	0.685	0.202
AVS	0.146	0.060	0.064	0.230

organic matter content and CEC increase (Suedel and Rodgers 1991). Due to the wide range of sediment characteristics expected in the various physiographic provinces, copper concentrations that elicit adverse effects can span at least two orders of magnitude based on the estimated 10-day LOECs from this study. Results of this study indicated that sediment toxicity experiments or other sediment data such as benthic fauna analyses are required to accurately assess the toxicity and bioavailability of copper in sediments.

3.4 Comparisons of MDLs and Bioavailability of Copper in Sediments

The range of MDLs (1.5–6 mg Cu/kg) was less than the range of 10-day LOECs (15–550 mg Cu/kg) by approximately two orders of magnitude. The 10-day LOECs were greater than the MDLs for each of the sediments. Because the range and values of MDLs were less than the 10-day LOECs (toxicological detection limits), the concentrations of copper in sediments eliciting adverse effects to *H. azteca* could be readily measured. Further, *H. azteca* is a sensitive sentinel species recommended by the US EPA to measure the toxicity and bioavailability of sediment-associated copper (Suedel et al. 1996; Kubitz et al. 1995; US EPA 2000). A comparison of LC50s demonstrates that *H. azteca* is more sensitive than the fish *Pimephales promelas* to copper sulfate and is within two orders of magnitude of sensitivity compared to other sentinel species (i.e., *Ceriodaphnia dubia*, *Daphnia magna*, and *Daphnia pulex*) exposed to copper sulfate (Murray-Gulde et al. 2002). MDLs of copper in these sediments and the measured 10-day LOECs were related. However, MDLs were not adequate to predict the 10-day LOECs for the five copper-amended sediments (Fig. 4). A logarithmic relationship was observed with the potency slopes and the MDLs [R^2=0.913, % mortality/mg Cu/kg=−1.128 ln (mg Cu/kg)+2.04; Fig. 5]. The logarithmic relationship illustrated that the accuracy of sediment copper measurements increases as the potency of copper in the five sediments increases.

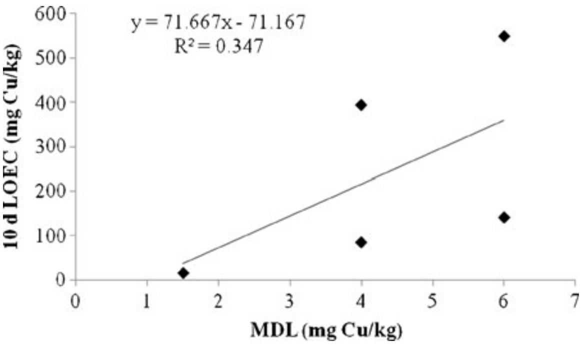

Fig. 4 MDLs and 10-day LOECs of copper for the five sediment samples

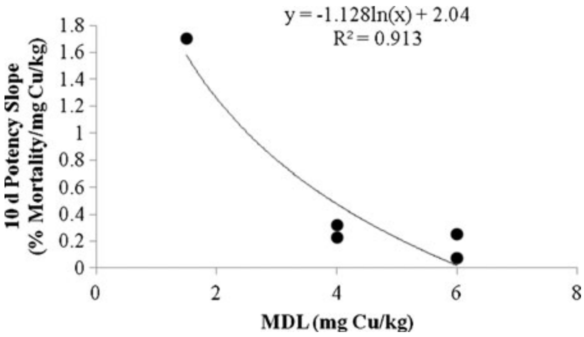

Fig. 5 Trend for MDLs and the 10-day potency slopes for *H. azteca* exposed 10 days to five copper-amended sediments

Because MDLs for copper were one to two orders of magnitude less than the 10-day LOECs for the five sediment samples, sediment copper concentrations that elicited *H. azteca* mortality were readily measured. Analytical measurements have been used to screen sediments for toxicity and predict the toxicological status of sediments (MacDonald et al. 2000; Buchman 2008). The National Oceanic and Atmospheric Administration screening quick reference tables indicate sediment copper concentrations less than 35.7 mg Cu/kg which are likely not toxic [threshold effect level (TEL)], and sediment concentrations greater than 197 mg Cu/kg would have probable adverse effects [probable effect level (PEL); Buchman 2008]. For this experiment, one of the five sediments had a 10-day LOEC less than the TEL (Buchman 2008), and two of the sediments had 10-day LOECs approximately two times greater than the PEL. For some sediments, copper concentrations less than the TEL may be toxic, while some sediments with copper concentrations greater than the PEL may not be toxic. To accurately assess the bioavailability and risks of copper accumulation in sediments for a site, toxicity experiments or other sediment data such as benthic fauna analyses are needed. The analytical method in this study was sufficiently sensitive for measuring the lowest sediment copper concentrations that elicited adverse effects for *H. azteca* exposed in the five sediment samples. However, analytical measurements were not predictive of the bioavailability and toxicity of copper for the five sediment samples.

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