

# Biological and Chemical Characterization of Metal Bioavailability in Sediments from Lake Roosevelt, Columbia River, Washington, USA

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**Abstract** We studied the bioavailability and toxicity of copper, zinc, arsenic, cadmium, and lead in sediments from Lake Roosevelt (LR), a reservoir on the Columbia River in Washington, USA that receives inputs of metals from an upstream smelter facility. We characterized chronic sediment toxicity, metal bioaccumulation, and metal concentrations in sediment and pore water from eight study sites: one site upstream in the Columbia River, six sites in the reservoir, and a reference site in an uncontaminated tributary. Total recoverable metal concentrations in LR sediments generally decreased from upstream to downstream in the study area, but sediments from two sites in the reservoir had metal concentrations much lower than adjacent reservoir sites and similar to the reference site, apparently due to erosion of uncontaminated bank soils. Concentrations of acid-volatile sulfide in LR sediments were too low to provide strong controls on metal bioavailability, and selective sediment extractions indicated that metals in most LR sediments were primarily associated with iron and manganese oxides. Oligochaetes (*Lumbriculus variegatus*) accumulated greatest concentrations of copper from the river sediment, and greatest concentrations of arsenic, cadmium, and lead from reservoir sediments. Chronic toxic effects on amphipods (*Hyalella azteca*; reduced survival) and midge larvae (*Chironomus dilutus*; reduced growth) in whole-sediment exposures were

generally consistent with predictions of metal toxicity based on empirical and equilibrium partitioning-based sediment quality guidelines. Elevated metal concentrations in pore waters of some LR sediments suggested that metals released from iron and manganese oxides under anoxic conditions contributed to metal bioaccumulation and toxicity. Results of both chemical and biological assays indicate that metals in sediments from both riverine and reservoir habitats of Lake Roosevelt are available to benthic invertebrates. These findings will be used as part of an ongoing ecological risk assessment to determine remedial actions for contaminated sediments in Lake Roosevelt.

Lake Roosevelt (LR) is a long (about 160 km), narrow reservoir created by the impoundment of the upper Columbia River behind Grand Coulee Dam in the State of Washington, USA for power generation, irrigation, and flood control. Bed sediments of LR are contaminated by trace elements, including arsenic (As), cadmium (Cd), copper (Cu), mercury (Hg), lead (Pb), and zinc (Zn). Concentrations of As, Cu, and Zn are greatest in sediments of the riverine reach upstream of LR, and concentrations of Cd, Pb, and Hg are greatest in reservoir sediments (Bortleson et al. 2001; Cox et al. 2004). Elevated concentrations of trace elements in Lake Roosevelt sediments have been attributed primarily to downstream transport of metals released from a lead–zinc smelter in Trail, British Columbia, Canada. This smelter discharged large quantities of metal-contaminated slag from smelter operations into the Columbia River until 1995 and it continues to discharge metals in effluents from its wastewater system. Another source of trace elements in

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the LR watershed is the Spokane River, which enters the lower reach of LR and transports trace elements from mining areas in its watershed (Yake, 1979). Previous studies have documented biological effects associated with metal-contaminated LR sediments, including elevated metal concentrations in aquatic biota and toxic effects of sediment and pore water (Bortleson et al. 2001; Era and Serdar, 2001). A recent study of sediment cores concluded that sediment metal concentrations in LR have decreased over time, but substantial quantities of metals remain in the bottom sediments of the reservoir (Cox et al. 2004).

Controls on metal mobility and bioavailability in the LR system remain poorly understood. Potential influences on metal bioavailability in LR sediments include differences in the nature and proximity of metal sources (*e.g.*, solid and liquid smelter wastes vs. historic mining activities), weathering and dilution of metal-contaminated particles within the river and reservoir, dewatering of sediments due to reservoir operations, and physical–chemical characteristics of bed sediments, notably concentrations of metal-binding phases such as sulfides, organic matter, and iron/manganese hydrous oxides (Ankley et al. 1996). In 2004, the US Geological Survey conducted concurrent geochemical and toxicological studies to characterize the sources, mobility, and bioavailability of metals in bed sediments from LR. Geochemical studies reported metal concentrations in sediment and pore water from sediment cores, including selective sediment extractions, and evaluated release of metals from in-place and resuspended sediments (Paulson and Cox 2007; Paulson et al. 2006). The objective of the toxicology study was to characterize spatial patterns in bioavailability and toxicity of metals in LR sediments as they relate to known or suspected metal sources and to differences in sediment characteristics and metal-binding phases. We report results of laboratory bioaccumulation and toxicity tests with benthic invertebrates exposed to LR sediments, along with determinations of metal concentrations in whole sediments and pore waters and of other sediment characteristics that modify metal bioavailability.

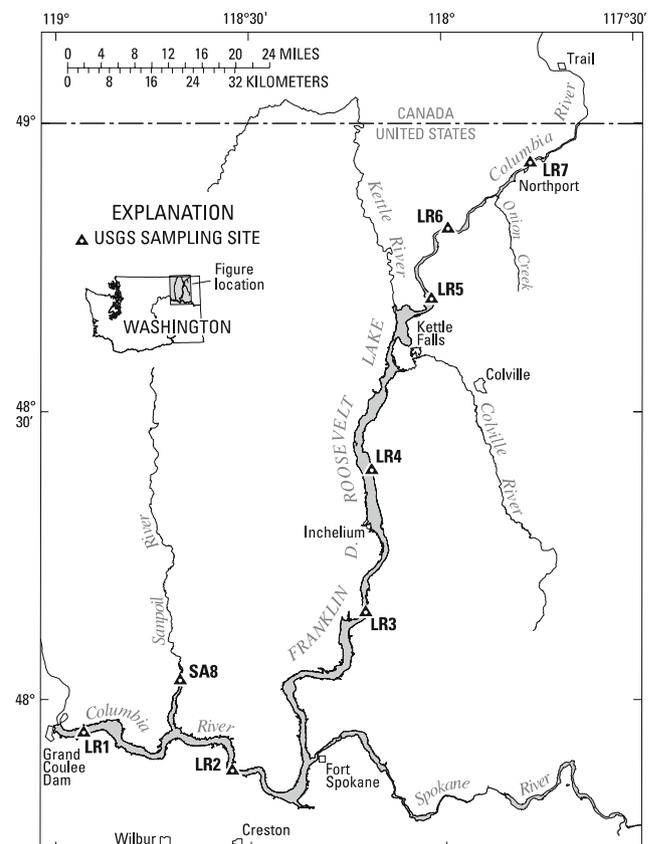
## Methods

### Sediment Collection

Bed sediments were collected in September 2004 from eight sites in the vicinity of LR (Fig. 1). Six sites in the impounded reach of LR (reservoir sites) were numbered from LR1, closest to the dam, through LR6. We refer to sites LR1 through LR4 as “lower reservoir” sites and sites LR5 and LR6 as “upper reservoir” sites. Site LR7 was

located in the free-flowing reach of the Columbia River upstream of the impoundment, about 30 km downstream from the Trail smelter. A reference site, SA8, was located in the upper Sanpoil River arm of LR, an area unaffected by metal inputs from the smelter. Sediments from these eight sites are referred to collectively as LR sediments. Additional information about sampling sites is provided by Paulson et al. (2006).

Sediments were collected from minimum water depth of 12 m (at a reservoir elevation of about 388 m above sea level) at locations known to have been under water for at least 2 years before sampling, to reduce effects of reservoir drawdown. At each sample site, 10-L composite sediment samples were made up of from multiple cores collected with a stainless-steel box corer (diameter: 20 cm). Penetration of the box core ranged from 4 to 6 cm, except for site LR2, where penetration was up to 10 cm. Composite samples were mixed on-site using Teflon blades, placed in polyethylene containers, and refrigerated. Portions of each composite sample were shipped to the Columbia Environmental Research Center, Columbia, MO, where they were stored in the dark at 4 °C for 10–18 days before the start of toxicity and bioaccumulation tests. Remaining



**Fig. 1** Map of Lake Roosevelt study area, showing sediment sampling sites

portions were freeze-dried for additional analyses, including selective sediment extractions (Paulson et al. 2006).

#### Chemical and Physical Characterization

Metal concentrations were determined in samples of whole sediment, pore water, and oligochaete tissues. Total recoverable (TR) metals were extracted from freeze-dried, homogenized sediment samples and freeze-dried oligochaete tissues using a microwave nitric/hydrochloric digestion method based on EPA method 3015A (USEPA 1998a). Acid-volatile sulfide (AVS) and simultaneously extracted metals (SEM; Cu, Zn, Ni, Pb, and Cd) were extracted in 1N HCl at room temperature following methods described by Brumbaugh and Arms (1996). Pore waters were prepared by centrifugation of whole sediments for 30 min at 7000 g, with supernatants filtered through 0.45- $\mu\text{m}$  polypropylene cartridge filters and acidified to 1% HNO<sub>3</sub> (v/v). All filtrates were subjected to microwave digestion with ultrapure nitric acid, followed by dilution to 50 mL with ultrapure water (USEPA 1998a). Trace element concentrations (As, Cd, Cu, Ni, Pb, and Zn) were determined in sediments, pore waters, and oligochaete tissues by inductively coupled plasma–mass spectrometry (ICP-MS; PE/SCIEX Elan 6000 with CETAC ADX-500 autosampler/autodiluter; May et al. 1997). Freeze-dried samples of homogenized sediments and oligochaete tissues were also analyzed for Hg using combustion–amalgamation atomic absorption spectrophotometry (EPA method 7473; USEPA 1998b).

Whole sediments and pore waters were also analyzed for physical–chemical characteristics that affect metal bioavailability. Particle-size distribution was determined by the hydrometer method (ASTM 2007c). Total organic carbon (TOC) of sediments was estimated by dividing loss-on-ignition data (Paulson et al. 2006) by an empirical

conversion factor of 2.13 (Dean 1974). Pore waters were analyzed for conductivity, pH, alkalinity, hardness, ammonia, and dissolved sulfides by standard methods (APHA 2005). Dissolved organic carbon (DOC) was analyzed in pore waters from archived (refrigerated) core samples from six of eight LR sites in July 2005 by wet oxidation and colorimetric analysis (Technicon Auto-Analyzer II).

#### Bioaccumulation and Toxicity Tests

Whole-sediment bioaccumulation and toxicity tests were conducted based on standard methods (ASTM 2007a; ASTM 2007b; USEPA 2000). Test systems were maintained at 23 °C, with overlying water (well water diluted with deionized water; hardness 140 mg/L as CaCO<sub>3</sub>) renewed automatically at a rate of two volume-additions per day. Sediments were added to test chambers and water replacements were started 24 h before the start of each test. Bioaccumulation and toxicity tests included both the SA8 reference sediment and the control sediment, a wetted soil from Florissant, MO (FL) that has been used for many sediment tests with midges and amphipods in our laboratory (Table 1). The control sediment was used to document test acceptability (ASTM 2007b; USEPA 2000). Statistically significant reductions in tests end points were determined by comparisons with the reference sediment.

The bioaccumulation test was a 28-day exposure with *Lumbriculus variegatus*. Test chambers were 6-L glass aquaria containing 1 L of sediment, with four replicates for each sediment. Oligochaetes were not fed during the test. At the end of the test, oligochaetes from each chamber were transferred to clean water for 6 h to allow purging of sediment from gut contents before metal analyses. Oligochaetes from each replicate were processed and analyzed

**Table 1** Physical and chemical characteristics of Lake Roosevelt sediments

ID <sup>a</sup>	Sand (%)	Silt (%)	Clay (%)	Moisture (%)	TOC (%)	AVS ( $\mu\text{mol/g}$ )
FL [C]	<1	32	68	24	0.42	0.2
SA8 [R]	24	32	44	48	1.9	0.40
LR1	82	15	3	27	0.33	0.04
LR2	34	39	27	73	2.7	3.1
LR3	7	39	54	56	1.8	0.6
LR4	80	13	7	27	0.23	0.01
LR5	43	14	44	52	1.6	1.4
LR6	82	13	5	55	1.5	7.4
LR7	92	9	<1	26	0.28	11

TOC = total organic carbon; AVS = acid-volatile sulfide

<sup>a</sup> [C], control sediment; [R], reference sediment

separately, except that tissue from multiple replicates for each sediment were combined into one composite sample of each sediment for Hg analysis. No sample for Hg analysis was collected from the LR1 sediment due to insufficient biomass. Toxicity tests included a 28-day test with *Hyalella azteca* and a 12-day test with *Chironomus dilutus*. Test chambers for toxicity tests were 300-mL beakers with 100 mL of sediment, with eight replicates per sediment. Survival and growth were determined at the end of each test. Amphipod growth was determined by digital measurement of the length of each surviving individual (Ingersoll et al. 2002) and midge growth was determined by a single measurement of ash-free dry weight for each replicate (ASTM 2007b; USEPA 2000).

### Statistical Analysis

Toxicity and bioaccumulation data were analyzed by SAS/STAT software (version 9.1). Metal concentrations were log-transformed before statistical analysis to improve homogeneity of variance. Differences in toxicity end points among sediments were tested by analysis of variance (ANOVA) on rank-transformed data. Differences between LR sediments and the reference sediment (SA8) were evaluated using Dunnett's test. Pearson correlation analysis was used to evaluate patterns of association of toxicity and bioaccumulation end points with physical and chemical constituents of sediment and pore waters. Bivariate plots of these variables were examined to identify artifacts such as strongly nonlinear relationships and excessive influence of outlying data points. Statements of statistical significance refer to a probability of type I error of 5% or less ( $p \leq 0.05$ ).

## Results and Discussion

### Characterization of Sediment and Pore Water

Physical characteristics of composite sediment samples varied widely among locations in LR (Table 1). Sediments from four sites (LR1, LR4, LR6, LR7) were dominated by sand-sized particles and contained less than 10% clay-sized particles. Sediments from site LR7, located closest to the smelter, had the highest proportion of sand-size particles (92%), including black slag particles, and had almost no clay-sized particles. The remaining LR sites contained less than 50% sand particles, with the LR3 sediment containing the greatest proportion of fine particles (93% silt and clay). The organic carbon content of most LR sediments fell in the range 1.5–2.7%, but the TOC in sediments from LR7 and from two reservoir sites (LR1 and LR4) was much

lower (0.23–0.33%). The AVS content of LR sediments was also low, except for sediments from the two most upstream sites, LR6 and LR7 (Table 1). Characteristics of the SA8 reference sediment were similar to sediments from the lower reservoir.

Pore waters of composite sediment samples had similar physical–chemical characteristics (Table 2). Pore waters were slightly alkaline (pH 7.5–8.0) and moderately hard (120–180 mg/L as  $\text{CaCO}_3$ ). Conductivity ranged from 150  $\mu\text{S}/\text{cm}$  in LR3 to 370  $\mu\text{S}/\text{cm}$  in LR4. Concentrations of total ammonia (<2 mg/L) and free sulfide (<0.3 mg/L) posed little or no risk of toxicity to amphipods or midges (ASTM 2007b; USEPA 2000). Detectable sulfide and elevated concentrations of dissolved iron in pore waters from LR2, LR3, LR5 and LR6 probably indicate reducing conditions in these sediments at the start of toxicity tests. DOC concentrations in pore waters [determined from archived sediment cores (2–13-cm depths)] were high (>15 mg/L) in all samples analyzed, with the highest concentration (120 mg/L) in pore water from LR5. Dissolved oxygen in overlying water ranged from 6.0 to 7.7 mg/L during toxicity tests.

### Metal Concentrations in Sediment

Total recoverable metal concentrations in sediments varied widely along the length of LR (Table 3). Concentrations of most elements of concern (Zn, Cu, Pb, and As) were greater in sediments from LR7, and to a lesser extent LR6, than in sediments collected further downstream, but the greatest concentrations of Cd and Hg occurred in sediments from the lower reservoir (Table 3). Concentrations of Pb, Zn, and Cu were consistently high in sediments from three sites in the reservoir (LR2, LR3, and LR5), but sediments from two other reservoir sites (LR4 and LR1) had much lower metal concentrations that were similar to the SA8 reference sediment. This difference in metal concentrations, together with differences in physical characteristics (e.g., higher sand content and lower TOC), suggests that sediments from LR1 and LR4 might have been recently deposited into the reservoir by landslides of bank soils, as has been reported by other investigators (Bortleson et al. 2001; Jones et al. 1961; Paulson et al. 2006). Concentrations of one or more metals exceeded probable effect concentrations [PECs; concentrations associated with an increased frequency of adverse effects on sediment-dwelling organisms (MacDonald et al. 2000)] at five of the seven nonreference sites in LR (Table 3). Concentrations of Cu, Zn, and Pb in sediments from LR7 exceeded PECs by factors ranging from 9 (for Cu) to 57 (for Zn). Concentrations of these three metals were lower in reservoir sites, with Cu concentrations below PECs at all sites

**Table 2** Water quality of pore waters from composite samples of Lake Roosevelt sediments at the start of toxicity and bioaccumulation tests

ID <sup>a</sup>	pH	Conductivity ( $\mu\text{S}/\text{cm}$ )	Alkalinity ( $\text{mg}/\text{L}$ as $\text{CaCO}_3$ )	Hardness ( $\text{mg}/\text{L}$ as $\text{CaCO}_3$ )	Mn ( $\text{mg}/\text{L}$ )	Fe ( $\text{mg}/\text{L}$ )	Ammonia ( $\text{mg N}/\text{L}$ )	Sulfide ( $\text{mg}/\text{L}$ )	DOC ( $\text{mg}/\text{L}$ )
FL [C]	7.97	2800	150	1200	5.8	47	1.6	0.11	nm <sup>b</sup>
SA8 [R]	7.59	290	130	130	2.5	4.0	0.7	0.01	25
LR1	7.97	270	120	160	0.93	0.5	0.3	<0.004	nm
LR2	7.48	210	120	150	11	72	1.1	0.22	32
LR3	7.55	150	100	140	7.4	83	0.4	0.14	19
LR4	7.93	370	110	180	0.97	0.6	0.3	<0.004	27
LR5	7.46	280	110	130	1.0	2.3	1.9	0.04	120
LR6	7.91	240	110	120	0.61	3.5	1.6	0.13	44
LR7	7.94	250	110	120	0.03	0.5	0.2	<0.004	15

Note: All analyses were performed on pore waters from composite sediments, except dissolved organic carbon (DOC) analyses were performed on archived sediment cores

<sup>a</sup> [C], control sediment; [R], reference sediment

<sup>b</sup> nm = not measured

downstream of LR6. However, concentrations of Zn and Pb remained above PECs as far downstream as LR2, and Cd concentrations only exceeded the PEC in sediments from the lower reservoir.

Concentrations of Zn, Cu, Cd, and Pb in SEM fractions of LR sediments followed patterns similar to those for TR metals (Table 4). SEM Cu concentrations were much lower than TR Cu concentrations, especially at upstream sites, but SEM Pb concentrations closely approximated TR Pb concentrations. For all four metals, SEM metal concentrations were lowest, as a proportion of TR metals, in sediments from LR7, suggesting that a greater proportion

of metals in this sediment were associated with less labile sediment phases. The molar sum of metal concentrations in SEM extracts ( $\Sigma\text{SEM}$  = sum of Cu, Zn, Ni, Pb, and Cd) from all eight LR sediments exceeded the available binding capacity of AVS. The fraction of SEM metals in excess of AVS ( $\Sigma\text{SEM} - \text{AVS}$ ), which can be considered “potentially bioavailable” (Ankley 1996; USEPA 2005), was greatest at LR7 (260  $\mu\text{mol}/\text{g}$ ) and decreased to 10  $\mu\text{mol}/\text{g}$  at several sites in the reservoir (LR5, LR3, and LR2). The three least contaminated sites had much lower levels of potentially bioavailable metals (0.3–0.4  $\mu\text{mol}/\text{g}$ ). The  $\Sigma\text{SEM} - \text{AVS}$  fraction was divided by the organic carbon fraction of sediments to generate an index of metal bioavailability based on influence of both AVS and TOC ( $\Sigma\text{SEM} - \text{AVS}/f_{\text{OC}}$ ) that is the basis for equilibrium partitioning-based sediment benchmarks (ESBs; USEPA 2005). This ESB index indicated a 6-fold to 10-fold greater range in metal bioavailability between the low-organic carbon sediment from LR7 and the more organic-rich sediments from the lower reservoir (LR2 and LR3).

The bioavailability of solid-phase metals in the LR sediment composites was further characterized by Paulson *et al.* (2006), who conducted a series of selective sediment extractions (SSEs). The four fractions generated by these extractions are reported here as follows: F1 (acetic acid extract), metals sorbed to surfaces of sediment particles; F2 (hydroxylamine hydrochloride extract), metals associated with Fe and Mn oxide coatings; F3 (hydrogen peroxide/nitric acid extract), metals associated with organic matter and sulfide coatings; and F4 (dissolution by four-acid digestion), residual metals in crystalline mineral particles. Although these fractions are operationally defined and cannot be assumed to contain only these metal phases, the sequence of fractions from F1 to F4 represents a shift of

**Table 3** Total-recoverable (TR) metal concentrations in Lake Roosevelt sediments

Sediment <sup>a</sup>	TR metal concentration ( $\mu\text{g}/\text{g}$ dry wt)						PEQ <sup>b</sup>
	Cu	Zn	As	Hg	Cd	Pb	
FL [C]	14	60	8.8	0.03	0.26	16	0.13
SA8 [R]	22	120	8.4	0.03	0.48	16	0.89
LR1	10	81	8.6	0.003	0.3	10	0.65
LR2	84	970*	22	0.84	7.7*	270*	7.0
LR3	68	910*	13	1.1*	7.1*	400*	7.4
LR4	12	54	2.8	0.01	0.2	9	0.39
LR5	78	940*	8.6	0.65	4.3	220*	5.4
LR6	290*	3,100*	9.9	0.32	4.3	200*	11
LR7	2800*	26,000*	32	0.02	4.3	1,110*	85
PEC	149	459	33	—	5.0	128	—

Note: Asterisks indicate concentrations that exceed probable effect concentrations (PECs; MacDonald *et al.* 2000)

<sup>a</sup> [C], control sediment; [R], reference sediment

<sup>b</sup>  $\Sigma\text{PEQ}$  = sum of probable effect quotients, [metal concentration/PEC], excluding Hg

**Table 4** Simultaneously extracted metal (SEM) concentrations in Lake Roosevelt sediments

Sediment <sup>a</sup>	SEM concentration (µg/g dry wt)					ΣSEM – AVS <sup>b</sup> (µmol/g)	ESB index <sup>c</sup> (µmol/g OC)
	Cu	Zn	As <sup>b</sup>	Cd	Pb		
FL [C]	4.0	8.2	0.60	0.19	8.6	0.03	4
SA8 [R]	7.7	38	3.0	0.38	17	0.42	22
LR1	1.7	21	1.5	0.23	5.0	0.36	110
LR2	46	713	6.1	6.5	240	9.9	360
LR3	38	613	5.4	6.5	380	11	620
LR4	2.5	16	0.8	0.18	5.0	0.32	140
LR5	50	710	3.1	3.1	210	11	710
LR6	180	2,500	4.3	1.8	200	35	2,400
LR7	99	16,000	13	1.2	590	260	92,000*

Note: Asterisks indicate values of equilibrium-partitioning sediment benchmark (ESB) index that indicate high risk of toxicity (>3000 µmol/g OC; USEPA 2005)

<sup>a</sup> [C] indicates control sediment; [R] indicates reference sediment

<sup>b</sup> ΣSEM – AVS was calculated using sums of molar concentrations of Cu, Zn, Ni, Cd, and Pb in SEM extracts. SEM – Ni concentrations were low (≤20 µg/g)

<sup>c</sup> ESB index = ΣSEM – AVS/ $f_{OC}$

chemical associations from more labile to more resistant and from greater to lesser biological availability (Luoma 1989; Tessier et al. 1984). The distribution of metals among SSE fractions was not uniform among locations or among metals. In sediments from the most contaminated sites, metals were primarily associated with the “resistant” F3 and F4 fractions at upstream sites (LR7, LR6), whereas the “labile” F1 and F2 fractions predominated at downstream sites (LR5, LR3, and LR2; Fig. 2). The percentage of total sediment metals in resistant fractions at LR7 ranged from 52% for Zn to 99% for Cu. Pb fractions showed the greatest differences between upstream and downstream sites, with distribution shifting from 91% resistant at LR7 to 90% labile at LR2. Cd and Zn also occurred predominantly (77–93%) in labile phases at sites LR3 and LR2, but over 50% of Cu remained in resistant phases at these sites. SSE profiles for the three least contaminated sites (SA8, LR1, and LR4) indicated greater proportions of all four metals in residual fraction, compared to other sites in the reservoir. This difference in SSE profiles suggests that sediments from these three sites represent regional background metal concentrations rather than anthropogenic inputs. Because metal concentrations in these sediments are so much lower than those from other LR sediments (Table 3), even a small loading of labile metals from upstream sources would be sufficient to alter this SSE profile.

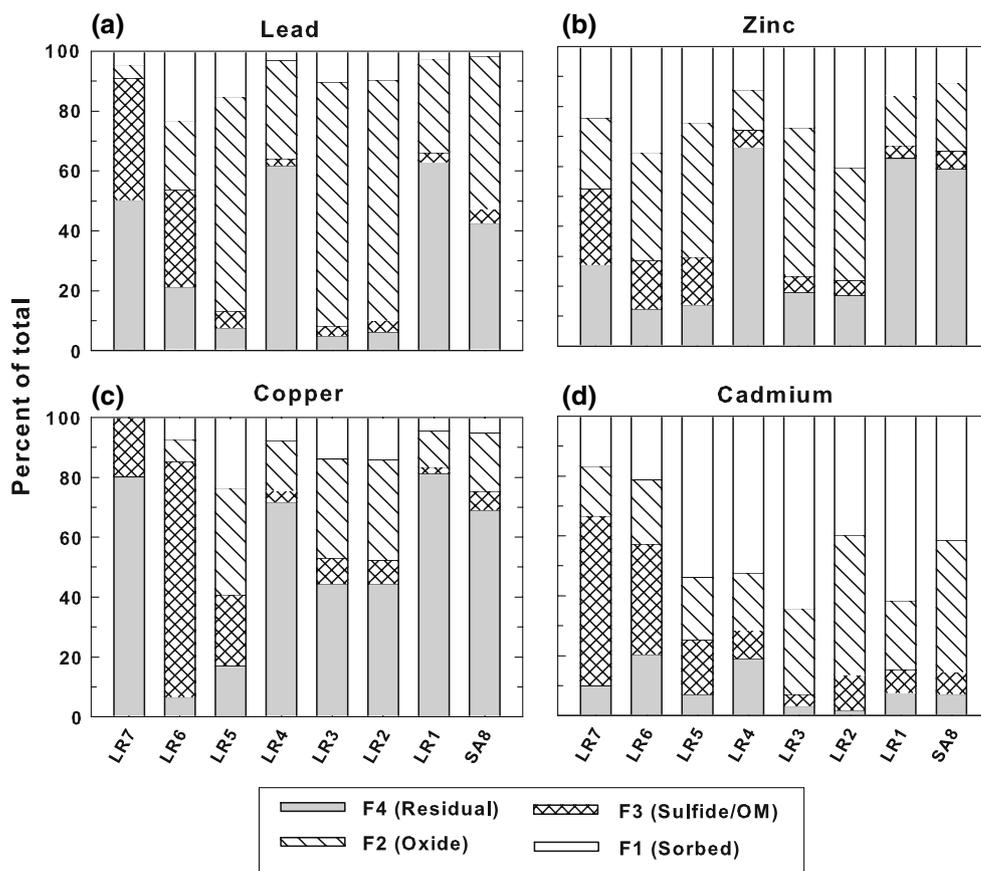
This observed upstream–downstream gradient in metal-binding phases is consistent with the hypothesis that metals in these sediments are weathered as they move downstream through LR, resulting in a shift from crystalline minerals and sulfide coatings to more labile associations with phases

such as hydrous oxides of Fe and Mn. Cox et al. (2004) reported evidence of weathering of surfaces of slag particles from the upstream reach of LR. Alternatively, the predominance of labile metals in sediments from LR5, LR3, and LR2 could result from preferential sorption and/or settling of dissolved and colloidal components of liquid smelter effluents onto these fine-textured sediments (Cox et al. 2004). The similarities of sediment metal concentrations and SSE profiles across these three sites, which include sites both upstream and downstream of the confluence of the Spokane River, suggests that neither metal concentrations nor metal bioavailability in LR sediments are strongly influenced by metals entering the reservoir via the Spokane River.

#### Metal Concentrations in Pore Water

Metal concentrations in pore waters of composite sediment samples followed different trends than those observed for whole-sediment metal concentrations (Table 5). Metal concentrations in pore waters from several reservoir sediments were substantially greater than those in sediments from the upriver site, LR7, which had greatest concentrations of TR and SEM metals. Maximum concentrations of all five elements studied were measured in pore waters from LR2 or LR3 sediments (Table 5). Metal concentrations in pore waters from the four metal-contaminated reservoir sites (LR2, LR3, LR5, LR6) exceeded US EPA (2004) chronic water quality criteria by factors as great as 17 (for Zn), 50 (for Cu), 400 (for Cd) and 580 (for Pb). Paulson et al. (2006) reported much lower metal

**Fig. 2** Distribution of metals among four selective sediment extraction fractions in LR sediments. Fractions are expressed as a percent of the total mass of each metal recovered from each sediment



concentrations in pore waters from surficial layers (0–2 cm) of sediment cores collected at the same locations and dates. Paulson and Cox (2007) reported that pore waters from surficial layers of LR2 and LR3 sediments had metal

concentrations one to three orders of magnitude less than those in our composite pore waters and that concentrations of Pb and Cd in surficial pore waters exceeded chronic criteria by factors of 3 or less. In contrast to results for the reservoir sites, pore-water metal concentrations from the LR7 sediment were similar for composite and surficial samples.

**Table 5** Metal concentrations in pore waters of Lake Roosevelt sediment (composite samples)

Site <sup>a</sup>	Pore water metal concentration ( $\mu\text{g/L}$ )					$\Sigma\text{TU}^b$
	Cu	Zn	As	Cd	Pb	
FL [C]	<4.1	<44	2.5	0.87*	0.76	0.7
SA8 [R]	4.0	<44	36	0.45*	8.9*	2.3
LR1	<4.1	<44	2.5	0.32	1.5	1.4
LR2	350*	1700*	94	28*	1400*	240
LR3	600*	2600*	64	130*	3800*	1100
LR4	<4.1	<44	1.4	<0.17	1.0	0.6
LR5	48*	<44	7.1	3.3*	180*	46
LR6	110*	300*	8.4	2.6*	250*	60
LR7	15	<44	1.7	<0.17	7.1	3.0

Note: Asterisks indicate concentrations exceeding hardness-adjusted chronic water quality criteria (USEPA 2004). TU = toxic unit (pore-water metal concentration/water quality criterion)

<sup>a</sup> [C], control sediment; [R], reference sediment

<sup>b</sup>  $\Sigma\text{TU}$  = sum of toxic units for Cu, Zn, As, Cd, and Pb

Differences in pore-water metal concentrations between composite and surficial sediment samples might reflect both differences in the composition of these sediments and geochemical changes occurring during storage of the composites. High metal concentrations in pore waters of composite sediment samples might reflect the greater metal concentrations in deeper sediment layers (depths up to 10 cm) included in composite samples (Cox et al. 2004). Paulson et al. (2006) reported that concentrations of Cd, Cu, Pb, and Zn in whole sediment from deep (5–10 cm) sections of cores from LR2 and LR3 were about twice as high as concentrations in surface (0–1 cm) sections of these cores. In addition, changes occurring in the composite samples during the 2-week storage period might have influenced the metal concentrations in pore waters from the reservoir sediments. Pore waters from LR2 and LR3 composites contained high concentrations of Fe and Mn and detectable concentrations of sulfide (Table 2),

**Table 6** Bioaccumulation of metals ( $\mu\text{g/g}$  dry wt) from Lake Roosevelt sediments by the oligochaete, *L. variegatus*

Site <sup>a</sup>	Cu		Zn		As		Cd		Pb	
FL [C]	4.6	(0.16)	210	(5)	2.0	(0.1)	0.05	(0.01)	0.25	(0.07)
SA8 [R]	7.5	(2.1)	290	(6)	28	(3.5)	0.14	(0.02)	0.87	(0.16)
LR1	15	(2.8)*	320	(8)*	3.2	(0.8)	2.4	(0.1)*	1.1	(0.5)
LR2	17	(4.5)*	320	(36)	30	(1.4)	4.8	(4.6)*	9.8	(7.8)*
LR3	16	(3.4)*	320	(25)*	8.5	(0.4)	6.6	(2.2)*	19	(18)*
LR4	16	(1.6)*	300	(3)	3.2	(1.0)	4.2	(1.2)*	0.84	(0.20)
LR5	7.5	(0.6)	280	(8)	28	(2.1)	0.48	(0.19)*	5.2	(0.6)*
LR6	8.4	(1.2)	280	(6)	7.4	(0.3)	0.24	(0.03)	4.4	(1.3)*
LR7	150	(18)*	320	(18)*	2.4	(0.5)	0.70	(0.05)*	4.9	(2.4)*
ANOVA:	$p < 0.0001$		$p = 0.0011$		$p < 0.0001$		$p < 0.0001$		$p < 0.0001$	

Note: Means, with standard deviations in parentheses;  $n = 4$ . ANOVA results ( $p$ -values) are from analysis of log-transformed data, excluding data from control (FL). Asterisk indicates means significantly greater than reference site (SA8) by Dunnett's test

<sup>a</sup> [C] indicates control sediment; [R] indicates reference sediment

suggesting that reducing conditions led to dissolution of Fe and Mn oxides (Van Cappellen and Gaillard 1996). The high concentrations of metals in pore waters of composite samples from LR2 and LR3 are also consistent with the high proportion of metals associated with sorbed and oxide fractions in these sediments, which could have been solubilized under reducing conditions (Fig. 2). In contrast, pore waters from LR7 had low concentrations of Zn, despite very high Zn concentrations in labile sediment fractions. LR7 pore waters contained no detectable sulfide and had low concentrations of dissolved Fe and Mn, suggesting that this sediment remained oxidized during storage, with Zn remaining bound to Fe/Mn oxide particles. The occurrence of high metal concentrations in composite pore waters, especially those from LR2 and LR3, suggests that reducing conditions developed in some sediments during storage. Alternatively, some portion of the metals present in these samples could have remained in solution as metal–humic complexes or passed through the 0.45- $\mu\text{m}$  filter membranes as freshly precipitated colloids (e.g., hydrous oxides).

### Metal Bioaccumulation

The 28-day bioaccumulation test with *L. variegatus* demonstrated that organisms in LR sediments experienced significantly greater metal exposure than those in the SA8 reference sediment. Bioaccumulation of Cu, Zn, As, Cd, and Pb from the SA8 reference sediment was greater than bioaccumulation from the control sediment, apparently reflecting a general enrichment of background metal concentrations in the study area (Bortleson et al. 2001). Bioaccumulation of all five elements differed significantly among sites, with oligochaetes in three or more LR sediments accumulating concentrations of Cu, Cd, Pb, and

Zn that were significantly greater than those accumulated from the reference sediment (Table 6). Bioaccumulation of Cu, Cd, and Pb showed the greatest increases, with maximum bioaccumulation of these metals exceeding bioaccumulation from the reference sediment by factors of 20 for Cu (LR7), 22 for Pb (LR3), and 47 for Cd (LR3). In contrast, maximum bioaccumulation of Zn from LR sediments was only 10% greater than bioaccumulation from the reference sediment, suggesting that differences in Zn bioavailability among locations were minimal or that oligochaetes were able to regulate internal Zn concentrations across the range of Zn exposure in LR sediments. Bioaccumulation of As also differed significantly among sediments, but no LR sediments had As bioaccumulation significantly greater than the reference sediment. Limited data (single composite samples from seven of eight sediments; data not shown) indicated a wide range of Hg bioaccumulation from LR sediments, with lowest bioaccumulation from SA8, LR4, and LR5 sediments (0.03–0.05  $\mu\text{g/g}$ ) and highest bioaccumulation from LR2 sediments (0.57  $\mu\text{g/g}$ ).

Patterns of metal bioaccumulation from LR sediments differed among the metals studied. Sediment from LR7 caused the greatest bioaccumulation of Cu—an order of magnitude greater than bioaccumulation from reservoir sediments—and intermediate bioaccumulation of Cd and Pb. Sediments from the upper reservoir did not produce remarkable bioaccumulation of any metals, but sediments from the lower reservoir produced the greatest bioaccumulation of both Pb and Cd and intermediate bioaccumulation of Cu. High bioaccumulation of Cd and Pb from lower-reservoir sediments corresponded to high levels of these metals in composite pore waters and was consistent with the prevalence of labile fractions of Pb and Cd in selective extractions from these sediments. In

**Table 7** Survival and growth of amphipods (*H. azteca*) and midges (*C. dilutus*) during sediment toxicity tests

ID <sup>a</sup>	Amphipod test (28-day)				Midge test (12-day)			
	Survival (%)		Total length (mm)		Survival (%)		Ash-free dry wt (mg)	
FL [C]	85	(3)	3.7	(0.05)	90	(4)	1.92	(0.08)
SA8 [R]	98	(2)	3.2	(0.08)	81	(6)	1.03	(0.05)
LR1	94	(3)	3.6	(0.09)	96	(3)	0.99	(0.07)
LR2	99	(2)	3.6	(0.11)	90	(3)	0.82	(0.04)*
LR3	90 <sup>b</sup>	(2)	3.4	(0.06)	88	(5)	0.67	(0.05)*
LR4	84 <sup>b</sup>	(16)	3.7	(0.22)	95	(4)	1.21	(0.07)
LR5	90 <sup>b</sup>	(6)	3.2	(0.10)	89	(2)	0.87	(0.05)
LR6	98	(2)	3.6	(0.05)	89	(7)	0.82	(0.05)*
LR7	71	(5)*	3.2	(0.10)	90	(3)	0.41	(0.08)*
ANOVA	$p < 0.0001$		$p < 0.0001$		$p = 0.57$		$p < 0.0001$	

Note: Means, with standard deviations in parentheses ( $n = 8$ , except where noted). ANOVA results ( $p$ -values) from analyses of rank-transformed data, excluding control. Asterisks indicate means determined to be significantly less than the SA8 reference sediment, by Dunnett's test

<sup>a</sup> [C], control sediment; [R], reference sediment

<sup>b</sup> Means and statistical analyses exclude replicates with zero survival ( $n = 5$  for LR4,  $n = 7$  for LR3 and LR5; see text). With all replicates included, mean percent survival (with standard errors) for these sediments was as follows: LR3, 79 (11); LR4, 53 (18); and LR5, 79 (12)

contrast, bioaccumulation of Cu was only moderately increased in the lower reservoir, despite high Cu concentrations in composite pore waters from LR2 and LR3.

### Sediment Toxicity

Three of the four end-points in sediment toxicity tests (amphipod survival, amphipod growth, and midge growth) differed significantly among the sediments tested (Table 7). Tests with amphipods and midges met test acceptability criteria for survival and growth endpoints (ASTM 2007a; USEPA 2000) in both the control sediment and the reference sediment. Raw data indicated low amphipod survival (71%) in the upstream LR7 sediment and low, but highly variable, survival in sediments from three sites (LR3, LR4, and LR5) in the middle reservoir (Table 7). Although amphipods exposed to sediment from LR4 had the lowest overall mean survival (53%), survival varied widely among the eight replicates of this sediment, with 100% survival in four replicates and 0–20% survival in the other four replicates. Low amphipod survival in the LR4 sediment was surprising because of the near-background metal concentrations in LR4 sediment and pore water. Single replicates from the LR3 and LR5 sediments also had zero survival, whereas all other replicates from these sediments had high survival (60–100%). There were no replicates with zero survival in the other sediments tested. Based on observations of unidentified benthic organisms in some LR sediments during incubation studies (Paulson and Cox 2007; Anthony Paulson, USGS, personal communication), we suspect that the 100% amphipod

mortality in these five replicates was caused by predation by indigenous organisms rather than by highly variable sediment toxicity or by multiple technical errors. When replicates with zero survival were excluded from calculations, the mean amphipod survival ranged from 84% to 90% for sediments LR3, LR4, and LR5 (Table 7). With all replicates included, mean survival for LR7, and LR3 were significantly less than means for the SA8 reference site, but with zero-survival replicates excluded, only the mean for LR7 was significantly less than the reference site (Table 7). Growth of amphipods also differed significantly among sediments tested, but the range of mean amphipod length among LR sediments (3.2–3.7 mm) was identical to the range for the control and reference sediments and no LR sediments had amphipod growth that was significantly less than the reference sediment.

Midge growth, but not survival, was significantly affected by exposure to LR sediments (Table 7). Survival did not differ significantly among treatments, with midge survival in LR sediments overlapping broadly with the range for control and reference sediments. There was no evidence of predation of midge larvae in sediments from LR3, LR4, and LR5. In contrast, midge growth differed significantly among sediments tested and showed clear reductions in several LR sediments. Midge growth in the SA8 reference sediment was less than that in the control but was similar to growth in the two least contaminated LR sediments (LR1 and LR4), suggesting that growth in these three sediments (range: 0.99–1.2 mg ash-free dry weight) represents a normal reference range for the LR area. Midge growth in the remaining four LR sediments (LR7, LR6, LR3, and LR2) was reduced by 20% (for LR2 and LR6) to

60% (for LR7), relative to the reference sediment. Midge growth in these four treatments was significantly reduced relative to the reference sediment, indicating significant toxic effects of metals in these sediments.

Responses of amphipods and midges in this study are consistent with findings of other recent toxicity studies with LR sediments and pore waters. A 1994 study reported toxic effects on amphipods (reduced survival) in whole sediments collected from the riverine reach (including a site near LR7) and toxic effects on daphnids in pore waters from both the riverine reach (reduced survival and reduced reproduction) and the lower reservoir (reduced reproduction) (Bortleson et al. 2001). A 2005 study (Stefanof et al. 2006) conducted toxicity tests with LR pore waters (7-day tests with daphnids) and sediments (10-day tests with midge larvae and 28-day tests with amphipods) and reported results that were similar to both the 1994 study and the current study, notably the reduced survival of amphipods in sediments from the riverine reach and reduced growth of midges in sediments from both the riverine reach and the lower reservoir. Another similarity between the 2005 study and the current study was the finding that sediments from several sites throughout the reservoir had little or no toxicity to any of the species tested, suggesting deposition of uncontaminated bank sediments.

#### Associations Between Biological and Chemical Assays

Metal bioaccumulation had few strong associations with metal concentrations in pore waters or solid phases of LR sediments (Table 8). Bioaccumulation of Cd and Zn had no significant associations with concentrations of these metals in either pore water or sediment. Bioaccumulation of Cu had significant positive correlations with Cu concentrations in surficial pore water (Paulson and Cox 2007) and in the F4 sediment fraction, although both of these correlations reflect the strong influence of data from a single site (LR7). Bioaccumulation of As was significantly correlated with As concentrations in both surficial and composite pore-water samples. Bioaccumulation of Pb had significant correlations with Pb concentrations in both pore-water samples, as well as those in all sediment extracts except the F4 fraction. The only significant correlations between bioaccumulation and toxicity end points were between Cu bioaccumulation and amphipod survival, again reflecting the influence of data from LR7, and between Pb bioaccumulation and midge growth.

Toxicity end points had no significant correlations with sediment and pore-water characteristics listed in Tables 1 and 2 (results not shown), but they had significant correlations with metal bioaccumulation and metal

concentrations in sediment and pore water (Table 8). Amphipod growth and midge survival, which did not differ significantly between LR sediments and the reference sediment, had no significant correlations with sediment or pore-water metals. Amphipod survival (with zero-survival reps excluded) had significant correlations with As concentrations in pore water (reflecting high As concentrations in LR7 pore water) and with Cu bioaccumulation. Midge growth had significant correlations with concentrations of all five elements in one or more sample types, including broad-based sediment fractions (TR and/or SEM) of all five elements, labile (F1 and F2) and resistant (F3 and F4) fractions of Pb and Zn, and resistant fractions of Cu. In contrast to these broad-based associations with metal concentrations in sediment, midge growth had only one significant correlation with metal concentrations in pore waters—with Zn concentrations in surficial pore water. Overall, midge growth had the weakest associations with Cd and the strongest and most broad-based associations with Pb, Cu, and Zn. The many significant associations of midge growth with concentrations of all five elements studied suggest that the observed effects might reflect contributions of multiple metals.

Risks of toxicity from metal mixtures in sediments can be estimated from measured metal concentrations in sediment or pore water. Using TR metal concentrations, we estimated risks of metal toxicity using PECs recommended by MacDonald et al. (2000). Concentrations of metals of interest were divided by PECs to produce probable effect quotients (PEQs) and PEQs were summed for the elements of interest in LR sediments ( $\Sigma$ PEQ = sum of PEQs for As, Cd, Cu, Pb, and Zn) to reflect cumulative risks of metal toxicity. Ingersoll et al. (2001) reported a greater than 50% frequency of toxicity to midges and amphipods in sediments with mean PEQs of 1.0 or greater, which corresponds to  $\Sigma$ PEQ values of 5.0 or greater for the LR sediment data. Values of  $\Sigma$ PEQ in LR sediments (Table 3) ranged from less than 1.0 for three low-metal sediments (LR1, LR4, and SA8) to 85 for the most contaminated sediment, LR7. Of the four sites with intermediate  $\Sigma$ PEQ values, sediment from LR5 ( $\Sigma$ PEQ = 5.4) was not toxic to midges and the remaining sediments ( $\Sigma$ PEQ from 7.0 to 12) caused significant reductions in midge growth (and, for LR7 sediments, reduced amphipod survival). Across the eight LR sediments,  $\Sigma$ PEQ for metals accurately predicted observed toxic effects on midge growth ( $r^2 = 0.90$ ; Fig. 3a).

Risks of metal toxicity were also evaluated using the ESB index,  $\Sigma$ SEM  $-$ AVS/ $f_{OC}$  (USEPA 2005). Sediments with values of the ESB index less than 130  $\mu$ mol/g organic carbon (OC) are predicted to be nontoxic and those with values greater than 3000  $\mu$ mol/g OC are predicted to be

**Table 8** Correlations (*r*) among toxicity, metal bioaccumulation, and metal concentrations in Lake Roosevelt sediments and pore waters (*n* = 8)

Variable <sup>a</sup>	Bioaccumulation	Amphipod survival	Amphipod growth	Midge survival	Midge growth
Arsenic					
BIO	—	0.66	−0.36	−0.66	0.16
PW(S)	0.93*	0.73*	−0.26	−0.67	0.39
PW(C)	0.77*	0.64	−0.15	−0.63	−0.11
SEM	0.14	−0.25	−0.52	−0.45	−0.93*
TR	0.08	−0.21	−0.42	−0.26	−0.89*
Cadmium					
BIO	—	−0.11	0.52	0.59	0.17
PW(S)	0.62	−0.04	0.25	0.42	−0.25
PW(C)	0.36	0.49	0.001	−0.30	−0.61
SEM	0.18	0.15	−0.26	−0.34	−0.77*
TR	0.04	−0.01	−0.31	−0.32	−0.61
F1	0.27	0.45	−0.06	−0.26	−0.23
F2	0.11	0.48	−0.12	−0.43	−0.35
F3	−0.16	0.06	−0.20	−0.25	−0.62
F4	−0.17	0.20	−0.03	−0.24	−0.34
Copper					
BIO	—	−0.83*	0.17	0.25	−0.69
PW(S)	0.87*	−0.56	0.20	0.45	−0.67
PW(C)	−0.05	0.24	−0.08	−0.31	−0.53
SEM	0.51	−0.38	−0.46	−0.32	−0.89*
TR	0.65	−0.52	−0.42	−0.22	−0.89*
F1	−0.20	0.23	−0.20	−0.37	−0.43
F2	0.38	0.44	−0.20	−0.48	−0.27
F3	0.41	−0.34	−0.39	−0.32	−0.79*
F4	0.89*	−0.70	−0.46	−0.15	−0.86*
Lead					
BIO	—	−0.02	−0.19	−0.20	−0.71*
PW(S)	0.73*	−0.22	−0.06	0.08	−0.62
PW(C)	0.90*	0.37	−0.12	−0.41	−0.43
SEM	0.89*	−0.21	−0.45	−0.38	−0.86*
TR	0.88*	−0.32	−0.42	−0.27	−0.90*
F1	0.93*	−0.10	−0.26	−0.20	−0.73*
F2	0.93*	0.18	−0.30	−0.37	−0.49
F3	0.73*	−0.35	−0.42	−0.28	−0.90*
F4	0.44	−0.70	−0.39	−0.07	−0.89*
Zinc					
BIO	—	−0.37	0.25	0.38	−0.43
PW(S)	0.27	−0.21	−0.24	0.09	−0.79*
PW(C)	0.35	0.40	0.27	−0.17	−0.31
SEM	0.12	−0.38	−0.40	−0.23	−0.90*
TR	0.17	−0.45	−0.40	−0.21	−0.92*
F1	0.15	−0.36	−0.33	−0.19	−0.90*
F2	0.10	−0.33	−0.43	−0.29	−0.91*
F3	0.04	−0.48	−0.44	−0.21	−0.87*
F4	0.27	−0.06	−0.42	−0.16	−0.90*

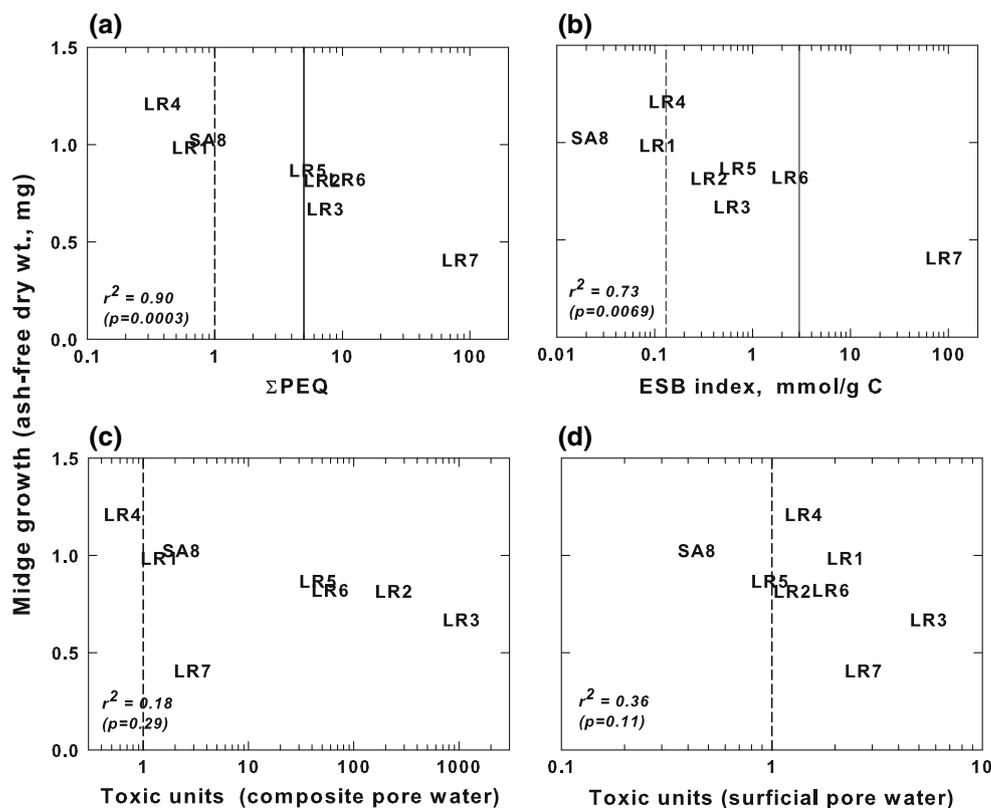
Note: Asterisks indicate significant correlations

<sup>a</sup> Variables: BIO = bioaccumulation; PW(S) = pore water from surficial sediments; PW(C) = pore water from sediment composite; SEM = simultaneously extracted metals; TR = total recoverable; F1 to F4 = selective extraction fractions (see text)

toxic, with intermediate values indicating uncertain toxicity. These guidelines predict that sediments from LR7 would be toxic, that sediment from SA8, LR1, and LR4

would be nontoxic, and that toxicity of sediments from LR3, LR3, LR5, and LR6 would be uncertain (Table 4; Fig. 3b). These classifications corresponded closely to

**Fig. 3** Relationships between midge growth and indexes of toxicity risk in LR sediments. AFDW = ash-free dry weight;  $\Sigma$ PEQ = sum of (TR metal concentration/probable effect concentration); ESB index =  $\Sigma$ SEM - AVS/*foc*; Toxic Units = sum of pore-water toxic units (TU = metal concentration/chronic water quality criterion). Dashed lines indicate lower thresholds for toxicity; solid lines indicate threshold for probable toxicity (see text)



observed significant toxic effects on midge growth determined by ANOVA. Values of the ESB index were significantly correlated with midge growth ( $r^2 = 0.73$ ; Fig. 3b), although this correlation was weaker than the correlation with  $\Sigma$ PEC.

Another approach for evaluating risks of sediment toxicity from metal mixtures is based on metal concentrations in pore water (Ankley et al. 1996; USEPA 2005). We calculated pore-water toxic units (TU = metal concentration/chronic water quality criterion) and summed these toxic units to create an index of the toxicity of the metal mixture ( $\Sigma$ TU). This approach assumes that sediment metals will be nontoxic if  $\Sigma$ TU is less than 1.0. Although no specific benchmark for toxicity is specified, this approach assumes that toxicity should increase with increasing  $\Sigma$ TU values of 1.0 or greater (USEPA 2005). Separate  $\Sigma$ TU values were calculated for composite and surficial pore water samples for each sediment. Composite pore waters from all LR sediments except LR4 had  $\Sigma$ TU values greater than 1.0, indicating some risk of metal toxicity (Table 5). Midge growth gradually decreased with increasing  $\Sigma$ TU for composite pore waters, except for LR7, the most toxic site, which had a  $\Sigma$ TU similar to that for the reference site (Fig. 3c). Toxicity indexes calculated from surficial pore-water samples were lower than those calculated from composite samples and had a stronger (but not significant) correlation with midge

growth (Fig. 3d). The two sites with lowest surficial  $\Sigma$ TU values (SA8 and LR5) were nontoxic and the two sites with the highest  $\Sigma$ TU values were toxic (LR7 and LR3), but the remaining four sites had similar  $\Sigma$ TU values but variable effects on midge growth. These results suggest that metal concentrations in surficial pore waters, which were analyzed immediately after sampling and were presumably closer to equilibrium with overlying waters, were a better representation of metal concentrations in surface sediments inhabited by midge larvae during the toxicity tests. Sampling of pore waters during the course of toxicity tests, rather than immediately after the storage period, might be necessary to reduce uncertainty about pore-water metal exposure.

#### Metal Bioavailability in Lake Roosevelt Sediments

The results of this study demonstrate that bioavailability of metals in sediments differed substantially among the sites sampled in LR. Sediments from the upstream site, LR7 contained greatest concentrations of solid-phase metals and caused toxic effects on both midges and amphipods. Sediments from the lower reaches of LR (e.g., sites LR2 and LR3) contained much lower total metal concentrations but had substantial concentrations of metals in forms that were chemically labile and biologically available, as

demonstrated by significant increases in metal bioaccumulation and significant reductions in midge growth.

Measurements of metal concentrations in multiple sediment and pore-water fractions improved our understanding of processes controlling metal bioavailability in LR sediments. Estimates of toxicity risk based on both  $\Sigma$ PEQ (calculated from total-recoverable metal concentrations) and the ESB index (calculated from SEM, AVS, and TOC) were both strongly correlated with metal toxicity (midge growth) in LR sediments. The inability of the ESB index to improve predictions of bioavailable metals, relative to  $\Sigma$ PEQ, reflects the low AVS concentrations and narrow range of TOC concentrations in LR sediments. Additional studies are underway in our laboratory to compare the ability of PEQ and ESB indexes to predict metal bioavailability and toxicity across a wider range of sediment characteristics. Measurement of metal concentrations in selective sediment extracts and in sediment pore waters did not improve predictions of metal bioavailability, but the predominance of metals in labile sediment fractions of some reservoir sediments was consistent with high pore-water metal concentrations and with significant toxic effects in these sediments, despite relatively low total-recoverable metal concentrations. The broad suite of chemical analyses performed for this study might not be practical for routine sediment quality assessments, but careful consideration of available information of physico-chemical characteristics of sediments, such as particle size distribution, redox status, and organic content, can aid in selection of appropriate measures of metal bioavailability in freshwater sediments.

Relationships among metal concentrations in sediment and pore water, metal bioaccumulation, and toxic effects suggest that that sorption and/or coprecipitation of metals to Fe and Mn hydrous oxides is a dominant control on metal bioavailability in LR sediments under oxidizing conditions. Bioavailability of metals associated with hydrous oxides might be increased under reducing conditions, which might have developed during storage of some LR sediments. Studies of lake sediments that undergo seasonal anoxia have documented seasonal dissolution of Fe and Mn oxides and mobilization of associated toxic metals (Balistrieri et al. 1992). This hypothesis is consistent with recent findings that low levels of metal were released from LR sediments during studies with surficial LR sediments under aerobic conditions (Paulson and Cox 2007). Our laboratory is evaluating the use of a longer period for equilibration of metal-contaminated sediments in test chambers before toxicity tests (*i.e.*, 1 week rather than 1 day) to reduce the influence of any changes occurring during sediment storage. Although anoxic conditions might not occur in surficial sediments of LR, changes in the depth of the redox interface, in response to seasonal

patterns of temperature and primary production or to changes in pool level of the reservoir (Cox et al. 2004), could affect metal bioavailability and toxicity to benthic organisms. Additional studies of spatial and temporal variation of metal bioavailability in LR are needed to adequately characterize risks of metal toxicity from LR sediments.

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