RELEASE OF ELEMENTS TO NATURAL WATER FROM SEDIMENTS OF LAKE ROOSEVELT, WASHINGTON, USA

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Abstract—Reservoir sediments from Lake Roosevelt (WA, USA) that were contaminated with smelter waste discharged into the Columbia River (BC, Canada) were examined using three measures of elemental release reflecting varying degrees of physical mixing and time scales. Aqueous concentrations of Cd, Cu, Pb, and Zn in the interstitial water of reservoir sediments, in the gently stirred overlying waters of incubated sediment cores, and in supernatants of aggressively tumbled slurries of reservoir sediments generally were higher than the concentrations from a reference site. When compared to chronic water-quality criteria, all three measures of release suggest that slag-contaminated sediments near the U.S.–Canadian border are potentially toxic as a result of Cu release and Pb release in two of the three measures. All three measures of Cd release suggest potential toxicity for one site farther down the reservoir, probably contaminated as a result of transport and adsorption of Cd from smelter liquid waste. Releases of Zn and As did not appear to be potentially toxic. Carbonate geochemistry indirectly affects the potential toxicity by increasing water hardness.

Keywords—Interstitial Pore water Incubation Sediments Lake Roosevelt, Washington

INTRODUCTION

The widespread metal contamination of sediments of the 240-km-long reservoir behind Grand Coulee Dam in the State of Washington (USA), commonly known as Lake Roosevelt (Fig. 1), has been described previously [1–5]. The sediment contamination has been attributed to the discharges of slag and liquid wastes from a Pb-Zn smelter in British Columbia (Canada). A number of approaches have attempted to predict the bioavailability of solid-phase metals by examining solid phases including metal sulfides [6] and weakly adsorbed phases [7]. In laboratory studies, the toxicity of sediments to organisms correlated with the Cd concentrations in the interstitial water of sediments [8,9]. Limited data [5,10] suggest that the concentrations of a number of elements are elevated in the interstitial waters of Lake Roosevelt relative to control sites, but it is unclear if the bioavailability of elements in slag follows the same pattern as those predicted from other types of metal discharges. Weakly acidic leaching of weathered slag in dumps resulted in solutions containing mg/L quantities of Cd, Cu, Pb, and Zn [11,12]. Whereas the concentrations of Cd, Cu, Pb, and Zn in seepage from exposed dumps in Australia reached 236, 184, 58, and 10,200 μg/L, respectively [13], seepage collected from an intermittently flooded dump in California (USA) during the annual drawdown of a reservoir contained lower concentrations (0.61, 11, 0.53, and 250 μg/L, respectively). Previous efforts in Lake Roosevelt have focused on the horizontal [1–4] and vertical [5] extent of sediment contamination, but limited data from sediment bioassays [2,10] suggest evidence of lethal and sublethal toxicity. The release of elements from Lake Roosevelt sediments to interstitial wa-

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became fully operational in 1999 [15]. The distribution of elements between slag and liquid effluent has been shown to affect the transport of each element to the sediment column of the Columbia River and Lake Roosevelt [2,5].

Hydraulic and sediment depositional conditions vary substantially in the 240-km length of Lake Roosevelt. The 60-km reach between the U.S.–Canadian border and Onion Creek, Washington, USA, named the riverine reach (RR), is characteristically fluvial in nature with swift and comparatively shallow (depth, <20 m) flow over an armored river bed composed of cobbles, boulders, and coarser materials, such as slag. In this reach, sandier deposits are restricted to sheltered areas protected from the main river flow. Because all the Cu and approximately 90% of the Zn were discharged with the slag (G3 Consulting, London, UK, personal communication), these elements have been found at high concentrations in RR sediments. Being a volatile element, Cd was emitted primarily in gas streams (75%), and very little Cd (<10%) was discharged to the Columbia River as slag in 1995.

Conditions are more lake-like (lacustrine) throughout the remainder of the reservoir, which for the purposes of the present study is divided into two sections: The upper reach (UR), and middle and lower reaches (MLR). The UR, which extends from Onion Creek to near Kettle Falls (WA, USA) is the transitional reach between fluvial and lacustrine conditions. As the channel cross-sectional area increases because of the broad-
Table 1. Physical properties and elemental concentrations (µg/g dry wt) of solid samples from this and previous studies

<table>
<thead>
<tr>
<th>Site</th>
<th>Reach</th>
<th>Water depth (m)</th>
<th>Sediment thickness (cm)</th>
<th>Sand (%)</th>
<th>TOC (%)b</th>
<th>Elemental concentrations in sediments</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Ca</td>
</tr>
<tr>
<td>Sanpoil Arm</td>
<td>REF</td>
<td>NA</td>
<td>2</td>
<td>&gt;50</td>
<td>1–2</td>
<td>NA</td>
</tr>
<tr>
<td>Tributaries</td>
<td>REF</td>
<td>NA</td>
<td>3</td>
<td>&gt;25</td>
<td>2–5</td>
<td>NA</td>
</tr>
<tr>
<td>SA-8</td>
<td>REF</td>
<td>18</td>
<td>6</td>
<td>24.0</td>
<td>0.53</td>
<td>18,800</td>
</tr>
<tr>
<td>LR-1</td>
<td>MLR</td>
<td>12</td>
<td>4</td>
<td>82.0</td>
<td>0.04</td>
<td>13,700</td>
</tr>
<tr>
<td>LR-2</td>
<td>MLR</td>
<td>26</td>
<td>10</td>
<td>33.8</td>
<td>0.92</td>
<td>11,300</td>
</tr>
<tr>
<td>LR-3</td>
<td>MLR</td>
<td>14</td>
<td>6</td>
<td>6.9</td>
<td>0.88</td>
<td>15,400</td>
</tr>
<tr>
<td>LR-4</td>
<td>MLR</td>
<td>14</td>
<td>4</td>
<td>79.6</td>
<td>0.36</td>
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</tr>
<tr>
<td>LR-4A</td>
<td>MLR</td>
<td>30</td>
<td>2</td>
<td>1.3</td>
<td>NA</td>
<td>16,700</td>
</tr>
<tr>
<td>LR-5</td>
<td>UR</td>
<td>13</td>
<td>4</td>
<td>43.0</td>
<td>ND</td>
<td>32,600</td>
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<tr>
<td>LR-5A</td>
<td>UR</td>
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<td>50.6</td>
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<tr>
<td>LR-6</td>
<td>UR</td>
<td>14</td>
<td>4</td>
<td>81.7</td>
<td>0.07</td>
<td>43,400</td>
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<tr>
<td>LR-7 (avg.)</td>
<td>RR</td>
<td>14</td>
<td>4</td>
<td>90.7</td>
<td>0.12</td>
<td>83,550</td>
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<tr>
<td>RM743g</td>
<td>RR</td>
<td>0</td>
<td>2</td>
<td>&gt;99</td>
<td>0.1</td>
<td>95,400</td>
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<tr>
<td>Riverine Slug</td>
<td>RR</td>
<td>0</td>
<td>2</td>
<td>100</td>
<td>NA</td>
<td>NA</td>
</tr>
<tr>
<td>Upstream of Northport</td>
<td>RR</td>
<td>3</td>
<td>NA</td>
<td>NA</td>
<td>NA</td>
<td>45,000</td>
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<tr>
<td>At Northport [24]</td>
<td>RR</td>
<td>2</td>
<td>NA</td>
<td>NA</td>
<td>NA</td>
<td>45,000</td>
</tr>
</tbody>
</table>

a See Figure 1 for location of sites. NA = not analyzed; ND = not detected; Ref = reference site; MLR = middle and lower reaches; UR = upper reach; RR = riverine reach.
b TOC = total organic carbon as a percentage of dry weight (J. Besser, U.S. Geological Survey, personal communication).
c Median from three samples taken from the Sanpoil Arm (% fines between 48 and 92%) [2].
d Three tributary samples in which the percentage fines were greater than 75% and TOC was between 2 and 5% [4].
e Loss on ignition of LR4 was 0.05% dry weight, whereas loss of ignition of LR4A was 5.57%.
f Values for loss of ignition of LR5 and LR5A were approximately 3.40 and 3.47% dry weight, respectively.
g RM743 = unsorted river bank sediment from River Mile 743, on which the tumbling experiment was performed; TOC from Bortleson et al. [2].h Visually identifiable slag particles from RM743 after sorting to greater than 1 mm and drying; designated as RSS743 [5].

Materials

A deep box corer (length, 13.5 cm; width, 13.5 cm; depth, 23 cm; Wildlife Supply Company, Buffalo, NY, USA) was used to collect samples between September 21 and 28, 2004. Most samples were collected below elevations that were not exposed during reservoir drawdown since 2001 (12-m water depth in Table 1). All sampling at LR-2 was moved to deeper water (depth, 26 m), where finer-grained sediments allowed adequate sediment penetration of the box corer. Intact cores for the incubation experiments and for subsequent use in the tumbling experiment also were collected in deeper water at alternative sites LR-4A (depth, 30 m) and LR-5A (depth, 25 m). Composite samples of surface sediments collected up to a thickness of 10 cm were used to measure grain-size distribution and the elemental composition of the solid sediments, including total organic carbon (TOC). Replicate composite samples and intact cores were collected at LR-7 and are labeled 7R. All plastic ware for sampling and processing was acid-cleaned before sampling. The lot of acid-cleaned, 25-mm Millipore Durapore in-line filters (pore size, 0.45 µm; Millipore, Burlington, MA, USA) was pretested for contamination with all-plastic syringes before conducting the field sampling. A more detailed description of methods, the complete data set,
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and the results of laboratory and field quality-assurance samples can be found elsewhere [15].

**Extraction of interstitial water**

Sediment plugs from the top 2 cm of multiple box cores from each site (the number of samples ranged between two and five) were sealed in 50-ml polypropylene centrifuge tubes. Dissolved oxygen concentration at depths shallower than 12 m in Lake Roosevelt does not drop below 7.1 mg/L during September [16]. High dissolved oxygen concentrations in the water column and the likely exchange between the water column and coarse sediments sampled during this project suggest that the redox conditions of the interstitial waters would not change dramatically between the time the sealed samples were packed on ice in the field and less than 8 h later, when they were centrifuged at 2,000 rpm for 20 min. Within a portable laminar flow hood at the field laboratory at Fort Spokane (WA, USA), each supernatant in the centrifuge tubes was filtered through an in-line filter and preserved with Optima HNO₃ (pH <2; Fisher Scientific, Fair Lawn, NJ, USA) in 15-ml high-density polyethylene (HDPE) bottles. Eight samples of reservoir water were collected either from the surface or from the water overlying cores within the box corer. The Pb weights on the outside of the box core may have contaminated two water samples overlying the core sediment with dissolved Pb (2.5 and 5.5 μg/L), and these two Pb values were not included in the statistical analysis.

**Core incubation experiments**

An acrylic core liner was inserted through the overlying water into the sediment. The intact core with its overlying water was isolated from the rest of the sediment in the corer, and the core liner was sealed at both ends. At LR-7, the core liners had to be presealed, loaded with sediment, and filled with reservoir water from the site, because the gritty nature of this sediment easily broke the bottom seal. Each evening in the field laboratory, the intact core within the core liner was placed in an incubator (14–18°C) to match bottom water temperatures. A polypropylene paddle attached to an external motor set at 4 rpm was inserted to mid-depth (>2 cm from the sediment water interface) of the overlying water (140–380 ml) through an oversized hole in a polypropylene beaker cover that was sealed over the top of the core. After approximately 1 h, 11 ml of the overlying water was sampled with a Teflon syringe tip and was filtered as described for interstitial water. Replacement reservoir water from the site (11 ml) was then slowly added to the overlying water to minimize the headspace. The temporary headspace of 11 ml of air during the withdrawal of each water sample, the dissolved oxygen contained in the replacement water added after each sample, and the limited exchange with the atmosphere through the small gap in the hole in the beaker cover through which the paddle was inserted maintained a small supply of oxygen to the overlying water.

The overlying water was sampled and replaced with site water at approximately 2, 4, 8, 16, and 32 d. Quality-control measurements included analyzing duplicate samples taken from each core experiment at approximately 16 d and a control incubation experiment containing a mixture of water from MLR sites with no added sediment that was mixed with the paddle. After 35 d of stirring, concentrations of major ions and Sb in triplicate samples from the control experiment were not statistically different from those at the beginning of the experiment, and the concentrations of As, Cd, and Pb were not detectable. After 35 d of stirring, one of the triplicate samples had a Cu concentration of 1.0 μg/L, and the average Zn concentration was 3.3 μg/L. Given these results, the reporting level for Zn values in the incubation experiments was set at 3.3 μg/L.

**Tumbling experiments**

At the end of the month-long incubation experiment (November 3, 2004), the top 2 cm of each incubation core (~66 ml) was extruded into a 125-ml wide-mouth HDPE bottle. The next day, approximately 30 ml of reservoir water from each site were added to each bottle, which trapped approximately 30 ml of air in the sealed container. In addition, approximately 80 ml of water from LR-7 was added to two dried samples (~150 g) of unsorted beach sand from site RM743 collected as part of a previous study [5]. The bottles containing the sediment slurries were then tumbled end-over-end seven times per minute for 15 min. The slurries were allowed to settle, and 11 ml of supernatant were withdrawn and filtered. The slurries were then sealed, tumbled for 43 d, and sampled again. The decomposition of organic matter in the sealed containers likely consumed significant amounts of dissolved oxygen, especially in the MLR sediments from sites LR-2, LR-3, and LR-4A, which contained higher TOC concentrations than the UR and RR sediments.

**Analysis of liquid samples**

The total elemental concentrations of sediment were obtained by analysis of the acid extractant after digestion of the sediments by hydrochloric, nitric, perchloric, and hydrofluoric acids by inductively coupled plasma–mass spectrometry on a PerkinElmer Elan 6000 (Norwalk, CT, USA) at the Geology laboratory of the U.S. Geological Survey in Denver (CO, USA) [17]. The results of the total elemental concentrations generally were within the certified ranges when compared to blind Standard reference materials PACS-2 (National Research Council of Canada, Ottawa, ON, Canada) and IAEA-405 (International Atomic Energy Agency, Vienna, Austria). Analysis of field duplicates at LR-7 generally resulted in relative percentage differences of less than 10%, except for the 15% value for Cd.

Filtered reservoir water, interstitial waters, water overlying the incubation cores, and supernatants from the tumbled sediment slurries were diluted by a factor of 5.0 with 0.16 N Ultrasolve grade HNO₃ (J.T. Baker, Phillipsburg, NJ, USA) before analysis by inductively coupled plasma–mass spectrometry methods [18]. The quality of the elemental analysis of liquid samples was examined by submission of eight double-blind standard reference materials with a wide range of elemental concentrations (e.g., 1–89 μg Cu/L). The recoveries of these standard reference materials generally were within 10% of certified values, but the Cu recovery in the low-concentration SLRS-3 (National Research Council of Canada) was low (72%).

**RESULTS**

**Site characterization**

The elemental concentrations at the reference site (SA-8) in the Sanpoil Arm (Table 1) in the present study were similar to those in samples collected from the Sanpoil Arm in 1992 [2] and in three samples with similar grain-size distribution collected from tributaries to Lake Roosevelt in 2001 [4].

The RR sediments were predominately sand and contained little TOC (<0.12% dry wt). Concentrations of Fe, Cu, and
Zn averaged 220,000, 2,630, and 18,100 μg/g, respectively, for the duplicate composite sediment samples (LR-7 and LR-7R). The relatively large concentrations of Fe and Ca in LR-7 sediments likely reflect the contributions of Fe and limestone used as flux in the smelting process that produced the slag, which was discharged to the Columbia River. Riverine slag particles contained very little Cd (<0.004 μg/g), and the average Cd concentration in LR-7 sediments (average, 1.3 μg/g) seemed to be controlled by transport of RR suspended matter (13–18 μg/g), onto which Cd that was discharged from the smelter as liquid effluent adsorbed. Likewise, the Pb concentrations at LR-7 (average, 820 μg/g) were more like the Pb concentration of RR suspended matter (490–840 μg/g) than the Pb concentration of riverine slag (400 μg/g). The amount of slag in each RR and UR sample was estimated by assuming that Zn sediment concentrations in the sediments were the weighted average of riverine slag from site RM743 and of RR suspended matter (taken from literature data in Table 1). These mass-balance calculations suggest that LR-7 sediment and the field duplicate (LR-7R) sample contained approximately 70% slag.

Compared to RR sites, UR sediments (LR-6, LR-5, and LR-5A) were finer grained, and mass-balance calculations suggest UR sediments contained approximately 5% slag. Concentrations of Ca from UR sediments were twice the concentrations in Lake Roosevelt reference sediments and likely reflected the presence of carbonate-rich sedimentary material in this reach (Fig. 1). The Zn and Cu concentrations in UR sediments from LR-6 and LR-5A were approximately a factor of 10 lower than those from RR but still elevated relative to sediments from MLR and reference sites. Concentrations of Cd increased with decreasing slag content from 1.3 μg/g within the RR to between 3.4 and 4.2 μg/g at UR sites LR-6, LR-5, and LR-5A. Concentrations of Pb in the UR (167–212 μg/g) decreased fourfold from those in the RR but remained approximately 10-fold greater than those of the reference samples.

Sediment from two MLR sites (LR-1 and LR-4) had lower elemental concentrations than those of the reference site. The lower concentrations of Al, Ca, Mg, and TOC in these coarse sediments relative to other LR sites likely reflect dilution by terrestrial soils from bank erosion or landslides [5]. Besides being from different source material than the fine-grained sediments at other MLR sites, the coarser material at LR-1 and LR-4 likely adsorbs less dissolved metals during their transport through the water column. Because the TOC of other MLR sediments approached 1% dry wt and contained less sand (<33% vs approximately 80% for LR-1 and LR-4), the results from LR-1 and LR-4 will be disregarded for the purposes of regional comparison. Concentrations of Cu, Pb, and Zn of MLR sediments were significantly higher than those of the reference site but were lower than concentrations from UR sites. Sediment from MLR sites LR-2 and LR-3 also had the two highest concentrations of Cd found in the present study (6.8 and 6.7 μg/g, respectively). Cadmium found in MLR sediments could not have originated from slag particles and likely was adsorbed from the aqueous phase onto organic-rich, fine-grained particles, which were transported and deposited downstream [2,5]. Elevated concentrations of Cu, Pb, and Zn in MLR sediments resulted from anthropogenic inputs, most likely smelter emissions, because all measures of reference sediment contained lower concentrations. These elevated concentrations could have resulted from either the transport of small fragments of slag from UR sediments or adsorption of aqueous-phase elements. Sites LR-1 and LR-2 are downgradient from the confluence of the Lake Roosevelt with the Spokane Arm, and additional inputs of dissolved Cd and Zn could have been transported through the Spokane River from the Coeur d’Alene mining district in Idaho (USA) [19]. In general, the spatial trends in the total concentrations of As, Cu, Cd, Pb, and Zn in sediments from Lake Roosevelt were similar to those found in previous studies [2–5].

**Hardness as an indicator of dissolution of basic minerals**

The hardness in interstitial waters from near-surface RR sediments (depth, 0–2 cm) of LR-7 (hardness, 69.8 mg/L as CaCO₃ in Table 2) was similar to the hardness in the water column (62 mg/L), suggesting an active exchange of water between interstitial water of this coarse-grained sediment and the reservoir water in this turbulent reach. Hardness values in UR interstitial water reached 150 mg/L at LR-5. In contrast, the hardness of MLR interstitial water ranged from 61 to 91.9 mg/L. Similar to interstitial water, the highest values of hardness (128–147 mg/L) in water overlying incubation cores were observed in the two cores from the UR sites (hereafter, cores from site LR-X will be referred to as core LR-X). Of the three types of water, the supernatants of the sediment slurries after 43 d of tumbling contained the highest values of hardness for each of the seven sites. Basic minerals continued to dissolve during the 43 d of subsequent tumbling, and the hardness of supernatants of tumbled UR sediment slurries increased from 140 to approximately 450 mg/L. The hardness of the supernatants from LR-7 averaged 284 mg/L after 43 d of tumbling. The hardness of supernatants of MLR sediments increased from approximately 90 mg/L at the beginning of the tumbling to between 227 and 264 mg/L after 43 d of tumbling. In all three measures of release, aqueous solutions in contact with UR sediments contained the highest values of hardness, likely resulting from dissolution of dolomite or other carbonate minerals that dominate the geology of this region.

**Dissolved iron as an indicator of reducing conditions**

A detectable concentration of dissolved Fe can be an indicator of a reducing condition. Median interstitial Fe concentrations as high as 3.02 (single value) and 1.24 mg/L were measured in the interstitial waters at sites LR-5A and SA-8, respectively. The absence of detectable dissolved Fe in the interstitial water from RR site LR-7 and in 14 of 15 individual interstitial water samples from MLR sites suggest that any Fe released during the weathering of slag precipitated as Fe oxide while oxygen in the overlying water diffused into the sediments. Detectable concentrations of Fe were not measured in any sample overlying RR cores, and low concentrations of Fe (0.25–0.33 μg/L) were detected in half the samples of water overlying incubation UR core 5A. Only 1 of 21 water samples overlying MLR cores contained a detectable Fe concentration (0.27 mg/L for core 4A at 17 d). Under the experimental conditions of the core incubation experiments for which the Fe oxidation rates are estimated to be on the order of minutes [20], any Fe that was mobilized within the sediments was immediately oxidized at the sediment–water interface while oxygen from the overlying water diffused into the sediment. The loading of organic matter likely depleted the oxygen concentrations in the closed tumbling bottles for some samples and, thus, led to releases of Fe. Dissolved Fe was detectable...
Table 2. Concentrations of waters in contact with Lake Roosevelt (WA, USA) sediments

<table>
<thead>
<tr>
<th></th>
<th>RR</th>
<th>UR</th>
<th>MLR</th>
<th>REF</th>
<th>All reaches</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>LR-7</td>
<td>LR-7R</td>
<td>RM743</td>
<td>RM743R</td>
<td></td>
</tr>
<tr>
<td>No. of samples</td>
<td>2</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>2</td>
</tr>
<tr>
<td>Hardness (mg/L)</td>
<td>69.8</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>4</td>
</tr>
<tr>
<td>Cu (µg/L)</td>
<td>&lt;0.25</td>
<td>—</td>
<td>&lt;0.25</td>
<td>—</td>
<td>&lt;0.25</td>
</tr>
<tr>
<td>Zn (µg/L)</td>
<td>18.8</td>
<td>—</td>
<td>12.5</td>
<td>—</td>
<td>13.4</td>
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<tr>
<td>Cd (µg/L)</td>
<td>&lt;0.1</td>
<td>—</td>
<td>&lt;0.1</td>
<td>—</td>
<td>0.48</td>
</tr>
<tr>
<td>Pb (µg/L)</td>
<td>2.7</td>
<td>—</td>
<td>4.9</td>
<td>—</td>
<td>3.8</td>
</tr>
<tr>
<td>As (µg/L)</td>
<td>&lt;1</td>
<td>—</td>
<td>3.3</td>
<td>—</td>
<td>1.5</td>
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<tr>
<td>Volume of water (ml)</td>
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<td>142</td>
<td>—</td>
<td>214</td>
<td>174</td>
</tr>
<tr>
<td>Hardness (mg/L)</td>
<td>86.1</td>
<td>—</td>
<td>128</td>
<td>—</td>
<td>147</td>
</tr>
<tr>
<td>Fe (mg/L)</td>
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<td>&lt;0.25</td>
<td>&lt;0.25</td>
<td>—</td>
<td>0.33</td>
</tr>
<tr>
<td>Cu (µg/L)</td>
<td>4.9</td>
<td>10.1</td>
<td>5.2</td>
<td>—</td>
<td>1.5</td>
</tr>
<tr>
<td>Zn (µg/L)</td>
<td>9.7</td>
<td>13</td>
<td>46</td>
<td>—</td>
<td>12</td>
</tr>
<tr>
<td>Cd (µg/L)</td>
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<td>&lt;0.1</td>
<td>0.16</td>
<td>—</td>
<td>&lt;0.1</td>
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<tr>
<td>Pb (µg/L)</td>
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<td>1.8</td>
<td>0.7</td>
<td>—</td>
<td>1.3</td>
</tr>
<tr>
<td>As (µg/L)</td>
<td>&lt;1</td>
<td>2</td>
<td>&lt;1</td>
<td>—</td>
<td>&lt;1</td>
</tr>
<tr>
<td>Ratio of solids to liquids (kg/L)</td>
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<td>1.65</td>
<td>2.00</td>
<td>1.78</td>
<td>0.85</td>
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<tr>
<td>Hardness (mg/L)</td>
<td>238</td>
<td>329</td>
<td>140</td>
<td>149</td>
<td>458</td>
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<tr>
<td>Fe (mg/L)</td>
<td>&lt;0.25</td>
<td>&lt;0.25</td>
<td>&lt;0.25</td>
<td>—</td>
<td>0.77</td>
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<tr>
<td>Cu (µg/L)</td>
<td>30</td>
<td>94</td>
<td>56</td>
<td>140</td>
<td>0.6</td>
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<tr>
<td>Zn (µg/L)</td>
<td>60</td>
<td>176</td>
<td>45</td>
<td>118</td>
<td>5.4</td>
</tr>
<tr>
<td>Cd (µg/L)</td>
<td>0.19</td>
<td>0.34</td>
<td>0.13</td>
<td>0.31</td>
<td>&lt;0.1</td>
</tr>
<tr>
<td>Pb (µg/L)</td>
<td>1.6</td>
<td>18.7</td>
<td>4.5</td>
<td>17.4</td>
<td>1.6</td>
</tr>
<tr>
<td>As (µg/L)</td>
<td>2</td>
<td>2</td>
<td>4</td>
<td>5</td>
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- Washington, USA. See Figure 1 for locations. RR = riverine reach; UR = upper reach; MLR = middle and lower reaches; REF = reference site; — = not applicable.
- Field replicate.
- Laboratory replicate.
- Affected by landslide material.
- Median concentration of N replicates.
- Median of eight sites and LR-5A.
- Hardness as CaCO₃; does not include two samples thought to be contaminated.
- Maximum concentration during the incubation experiment.
- Concentration after 43 d of tumbling.
only in two of the four supernatants of tumbled sediments from RR sites LR-7 and RM734. High Fe concentrations of 3.75 and 9.96 mg/L were measured in the supernatants from tumbled sediments from LR-6 (UR) and from LR-4A (MLR), respectively. The trends in Fe release were not consistent among methods. Reduction–oxidation chemistry under different time scales, physical exchange rates with atmospheric and aqueous sources of oxygen, and solution chemistry probably were responsible for the differences.

Dissolved copper and zinc as indicators of slag dissolution

The median concentrations of interstitial Cu from LR-7 was 9.2 µg/L, and median concentrations from UR sites (<0.5–1.9 µg/L) were significantly lower than RR concentrations (Fig. 2). Concentrations of Cu in MLR interstitial waters were higher than concentrations from the reference site (median, 0.55 µg/L), with the highest median MLR concentration (2.4 µg/L) being measured at LR-1. Maximum Cu concentrations in the water overlying UR cores 6 and 5A were 5.2 and 1.5 µg/L, respectively, whereas Cu concentrations in the water overlying MLR core 2 reached a maximum concentration of 4.5 µg/L. The release of 56 to 140 µg/L of Cu from unsorted RR beach sands containing slag from RM734 suggests that the slag was primarily responsible for the release of 30 to 94 µg/L of Cu from LR-7 sediments during the tumbling experiment. Copper concentrations in the supernatants of UR and MLR sediments were greater than those of the reference sediments but less than 5 µg/L. The three methods were consistent in indicating that RR sediments released the largest amounts of Cu.

The median concentrations of interstitial Zn (Table 2) from LR-7 was 18.8 µg/L, whereas median concentrations from UR sites ranged from 3.3 to 12.5 µg/L. Maximum Zn concentrations in water overlying duplicate RR cores were 9.7 and 13.3 µg/L (Table 2). Water overlying UR core 6 contained the highest Zn concentration (46 µg/L) measured in all incubation experiments. The highest Zn concentrations in the supernatants among the reaches were found in the RR supernatant from the LR-7 and RM734 sediments (45–176 µg/L). Concentrations of Zn in interstitial water, overlying water, and supernatants of MLR sediments were less than 15 µg/L. The highest Zn concentrations in interstitial waters (18.8 µg/L) and in the supernatants of tumbled sediment slurries (176 µg/L) were measured in RR sediments, but the highest Zn concentration in water overlying cores (46 µg/L) was measured in the experiment with UR core 6.

Dissolved cadmium and lead: Indicators of liquid effluent discharges

Concentrations of Cd in interstitial water from RR and UR sites were at or below the reporting level (Table 2). In contrast, MLR site LR-3 contained the highest interstitial Cd concentrations (maximum, 0.97 µg/L) (Fig. 3). Concentrations of Cd in water overlying RR core 7R were below the reporting level, and only one water sample overlying core 7 contained a detectable Cd concentration (0.14 µg/L). A maximum Cd concentration of 0.16 µg/L was measured in waters overlying UR core 6 and was below the reporting level in water overlying UR core 5A. The core from MLR site LR-3 at the end of the experiment contained the highest Cd concentrations in overlying water (0.3 µg/L) measured in the present study. Dissolved Cd concentrations in the duplicate supernatants of tumbled sediments of RR sediments varied considerably and averaged 0.26 µg/L. The highest Cd concentration from the tumbling experiment (0.68 µg/L) was measured in the supernatant from MLR site LR-3. The samples from MLR site LR-3 contained the highest Cd concentrations in interstitial water, the highest Cd concentrations in the water overlying incubation cores, and the highest Cd concentrations in supernatants of tumbled sediment. In contrast, no Cd was detected in interstitial waters or the water overlying the RR cores.
Concentrations of Pb in RR interstitial water (LR-7) had a median concentration of 2.7 μg/L, and were considerably higher than those of the reference site (Fig. 4). Median Pb concentrations in interstitial water from UR sites (2.4–4.9 μg/L) were higher than those from the reference site and generally higher than those from RR sites. Concentrations of Pb in MLR interstitial waters were greater than those from the reference site (median, 0.53 μg/L) and highly variable. In all incubation cores sampled in the present study, maximum Pb concentrations of less than 2 μg/L were found at the beginning of the experiments, and Pb decreased to concentrations near or below the reporting level. Concentrations of Pb in supernatants of tumbled slurries of RR sediments were highly variable, with a maximum concentration of 18.7 μg/L. The concentration of Pb in the MLR supernatant of tumbled sediment slurry from LR-3 was 5.9 μg/L, which was considerably higher than concentrations in supernatants from UR and other MLR tumbled sediments. Concentrations of Pb in the interstitial water and supernatants of tumbled slurries of RR sediments were the highest among all reaches, but other results among methods were highly variable. These differences may have been a result of experimental artifacts, such as possible adsorption during the incubation experiment.

**Dissolved arsenic**

Median concentrations of interstitial As (Table 2) ranged from less than 1 to 20.8 μg/L, with the reference site having the highest median concentration. Only four of the eight incubation experiments contained detectable As concentrations, with the maximum concentration of 8 μg/L being measured in water overlying MLR core LR-4A. Concentrations of As in supernatants ranged between 2 and 5 μg/L, and were not grouped by reach. Concentrations of As were small, and no consistent geographic pattern was observed.

**DISCUSSION**

The correlation between toxicity of sediments to benthic organisms and the elemental concentrations in interstitial water suggests that the index termed interstitial water criteria toxic unit (IWCTU) [21] might represent the potential toxicity of each element measured in the present study. The IWCTUs for As, Cd, Cu, Pb, and Zn are the ratios of the median interstitial water concentration to a water-quality criterion. The IWCTU index could be used to rank the relative toxicity of specific elements within a system or the relative toxicity of sediments from specific sites. The chronic water-quality criteria were calculated on the basis of the median hardness of interstitial water at each site and the conversion factors between total and dissolved concentrations of Cd and Pb (http://www.epa.gov/waterscience/criteria/nrwqc-2006.pdf). It should be noted that the calculated chronic water-quality criteria used in Table 3 are much lower than the concentrations for which biological effects were observed in the references cited [22]. An IWCTU greater than 1.0 would suggest potential toxicity. Although the toxicities of metals such as Cd, Cu, Pb, and Zn are thought to be additive to some extent, the Cd reporting level (0.10 μg/L), which in many cases exceeded 50% of the chronic water-quality criteria, precluded meaningful summation of toxic units.

The IWCTUs for Cu and Pb were 1.6 in RR sediments, indicating potential toxicity from Cu and Pb. The IWCTUs for Pb of greater than 1.0 were calculated at two MLR sites (Fig. 5). At UR sites LR-5 and LR-5A, IWCTUs for Pb were less than 1.0 because of the higher calculated chronic water-quality criteria as a result of the higher hardness of UR interstitial water (104–150 mg/L) relative to the median hardness among all sites (83 mg/L). Potential toxicity from Cd is indicated for MLR sediments from two sites, where the IWCTUs for Cd were 1.5 and 2.8. The IWCTU for As (0.14) at the reference site (SA-8) was highest among the sites, whereas the IWCTUs for Pb and Zn for the reference site were 0.24 and 0.04, respectively. The highest IWCTU for Zn (0.22) was calculated for RR sediments.

The concentration of an element in water overlying the incubation core also can be normalized to a chronic water-quality criterion to provide a measure of potential toxicity to pelagic organisms dwelling near the sediment–water interface, such as white sturgeon. This measure, here termed incubation water-quality toxic units, would reflect maximum exposure, because the maximum concentration in the overlying water during the experiment was used in the calculation, and the incubation experiment does not reflect the flushing of the bottom boundary layer of the water column by natural turbulence.
slurries that were tumbled end-over-end for 43 d. Aqueous cores incubated for one month, and supernatants of sediment interstitial water in the sediments, gently stirred water overlying mixing. The three types of natural waters were ambient in-tensions of these elements in natural waters in contact sediments of Lake Roosevelt were measured by determining concentra-
sions associated with liquid effluent discharged by a British Columbia smelter (Cu and Zn), tran-
5. Cox SE, Bell PR, Lowther JS, VanMetre PC. 2005. Vertical distribution of trace-element concentrations and occurrence of met-

in river and reservoir systems. Like IWCTU, a value of the incubation water-quality toxic unit of greater than 1.0 suggests the potential for toxic response by benthic organisms assuming an environmental condition similar to that represented by the incubation experiment. A maximum incubation water-quality toxic unit for Cu of greater than 1.0 was found only for the RR core. The Cd concentration in water overlying the MLR core 3 at the end of the incubation experiment exceeded the chronic water-quality criterion. No other incubation water-quality toxic unit value exceeded 1.0.

The environment of the high solids to liquids ratio and the extended contact time of water with sediment in the closed system in which the sediment slurries were tumbled would reflect conditions found in the interstitial water of sediment buried deep in the sediment column. The aggressive mixing of water and sediment in the tumbling experiments would accelerate the diagenetic reactions, but the closed system could lead to changes in aqueous chemistry, including redox conditions. Potential toxicity of Cu and Pb were inferred for RR sediments, and potential toxicity from Cd release was suggested for sediments from MLR site LR-3. Supernatant concentrations do not suggest potential toxicity of As and Zn.

CONCLUSION

The release of constituents contributing to hardness, easily reducible metals (Fe), transition metals associated with slag discharged by a British Columbia smelter (Cu and Zn), trans-
ition metals associated with liquid effluent discharged by smelter (Cd and Pb), and metalloid (As) from the sediments of Lake Roosevelt were measured by determining concentrations of these elements in natural waters in contact sediments under three conditions varying in time and degree of physical mixing. The three types of natural waters were ambient interstitial water in the sediments, gently stirred water overlying cores incubated for one month, and supernatants of sediment slurries that were tumbled end-over-end for 43 d. Aqueous concentrations of Cd, Cu, Pb, and Zn in contact with Lake Roosevelt sediments generally were higher than the concentrations obtained from waters in contact with reference sediments.

An index of potential toxicity, called a toxic unit, was calculated for each type of natural water by comparing the aqueous concentration of an element to the chronic water-quality criterion that was corrected for water hardness. The three measures generally provided consistent indications of potential toxicity of Cu and Cd for sites in which the aqueous concentrations exceeded the water-quality criteria. All three measures indicated potential toxicity by the release of Cu from sediments at two sites in the RR of Lake Roosevelt (near the U.S.–Canadian border). Likewise, all three measures indicate potential toxicity by the release of Cd from the sediments collected at one site (LR-3) in the middle reach of the Lake Roosevelt. Results of two of the three measures indicate potential toxicity by the release of Pb from the sediments in the RR, with the differences among the results possibly caused by differences in experimental conditions or artifacts. Higher concentrations of hardness in water in contact with sediments in the UR of Lake Roosevelt, which likely is caused by the differences in the carbonate geology, resulted in higher chronic water-quality criteria for this reach, thereby lessening the potential toxicity of Pb releases. Concentrations of Zn and As did not exceed the chronic water-quality criteria in any experiment. Given that the total concentrations of As, Cd, Cu, Pb, and Zn in Lake Roosevelt sediments determined in this and previous investigations are consistent with elemental transport from the liquid effluent and slag discharged from the smelter, the trends in the releases of elements reported here suggest that future studies should focus on the release of Cu from the RR sediments and the release of Cd from the MLR.

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