Importance of Sediment-Water Interactions in Coeur d'Alene Lake, Idaho, USA: Management Implications

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ABSTRACT / A field study at Coeur d'Alene Lake, Idaho, USA, was conducted between October 1998 and August 2001 to examine the potential importance of sediment-water interactions on contaminant transport and to provide the first direct measurements of the benthic flux of dissolved solutes of primary concern in this lake. Because of potential ecological effects, dissolved zinc and orthophosphate were the solutes of primary interest. Results from deployments of an in situ flux chamber indicated that benthic fluxes of dissolved zinc and orthophosphate were comparable in magnitude to riverine inputs. Tracer analyses and benthic-community metrics provided evidence that solute benthic flux was diffusion controlled at the flux-chamber deployment sites. That is, affects of biomining (or bioturbation) and groundwater interactions did not strongly influence benthic fluxes. Remediation efforts in the river might not produce desired water-quality effects in the lake because imposed shifts in concentration gradients near the sediment-water interface would generate a benthic feedback response. Therefore, development of water-quality models to justify remediation strategies requires consideration of contaminant flux between the water column and underlying sediment in basins that have been affected by long-term (decadal) anthropogenic activities.

Coeur d'Alene Lake is downstream of the Bunker Hill Superfund site in Idaho, the second largest Superfund site in the United States (Figure 1). It has served as receiving waters for solutes associated with silver and zinc mining for approximately a century. Two rivers are the major inputs to the lake: the St. Joe River to the south, and the Coeur d'Alene River draining mining areas to the east. Outflow from the lake is through the Spokane River. Horwitz and others (1996b) reported that mining-associated sediments are ubiquitously distributed in the lake, even up-gradient of the Coeur d'Alene River plume, and postulated that various constituents would diffuse out of the sediment column. Solutes of particular ecological interest are zinc and orthophosphate, because: (1) unlike many other particle-reactive solutes, dissolved zinc remains at elevated concentrations in this pH-neutral lake downstream of the Coeur d'Alene River plume, and (2) under terms of primary productivity, the lake water column has phosphorus limited (Woods and Beckwith 1997).

Solute transport through a lake may conceptually be represented by a number of transport processes. For example, riverine sources and sinks represent processes that have been examined, quantified, and sometimes regulated for decades. In contrast, direct measurements of benthic flux, the transport of solutes (i.e., metals, ligands, toxicants, or nutrients) between the water column and the underlying sediment, are typically scarce or totally absent. Yet recent studies have consistently indicated that processes like benthic flux must be incorporated into water-quality models to generate quantitatively accurate results (Wood and others 1995, Topping and Kuhabara 2003).

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Near the sediment-water interface, interdependent physical, chemical, and biological processes form vertical geochemical gradients that can induce a benthic flux that is positive (out of the sediment) or negative (consumed by the sediment). (Boudreau and Jorgensen 2001; Topping and Kuwabara 2003). This flux may be enhanced by the presence of macroinvertebrates that bioturbate the surficial sediments (Caffrey and others 1996).

This study poses the following questions: "Is benthic flux significant in magnitude relative to other major sources and sinks to the water column of Coeur d'Alene Lake? If so, what are the implications of this process on the development of remedial strategies for this and other mining-impacted lakes and reservoirs?" These questions are motivated by a number of factors. First, pore-water profiles for dissolved zinc suggest a significant diffusive flux in certain parts of the lake (Balazsner 1996). Second, metal–distribution studies in the lake have clearly indicated elevated concentrations of particle-reactive solutes in the lake bottom sediment (Horowitz and others 1996b). For example, sediment-associated zinc concentrations in the lake down-gradient of the Coeur d'Alene River plume are, on average, 50 times greater than background concentrations. Background concentrations of zinc in sediments are strongly influenced by regional geology, and in the vicinity of Coeur d'Alene Lake, have been reported to range between 110 and 118 μg/g (Horowitz and others 1995a). Although this background range exceeds the average crustal concentration for zinc (71 μg/g) (Taylor and McLeannan 1985), a particular Zn concentration of 119 μg/g was reported for remote lakes (Fonnet and Wittman 1981). Finally, there is a growing body of scientific evidence that suggests that changes in redox conditions and nutrient availability near the sediment-water interface can dramatically alter the mobility of metals and ligands associated with the bottom sediment (La Force and others 1998). The current study reports on the first direct measurements of the benthic flux of dissolved zinc and orthophosphate from deployments of an in situ flux chamber in this lake and discusses their implications on water quality and remediation strategies.

Methods and Materials

In Situ Flux Chamber Deployments

A benthic flux chamber (Berelson and others 1992), specifically designed for trace-element studies, was deployed by boat multiple times between 16 and 27 August 1999, at each of two lake sites. One site was in the main-channel of the lake, 7 km down-gradient of the mouth of the Coeur d'Alene River (53 m depth; Figure 1). The second deployment site was in Mica Bay, 17 km down-gradient of the mouth of the Coeur d'Alene River (27 m depth). The flux chamber was deployed down with the help of scuba divers to minimize flux-chamber disturbance of the surficial sediments and so that a rectangular acrylic chamber on the bottom of this device would penetrate the sediment but still remain an overlying water. This overlying water was isolated from the ambient lake water by closure of a lid, which initiated the incubation of approximately 1500 cm² of lake-bottom sediment surface. The deployments ranged from about a half day to two days. Before each deployment, the flux chamber was programmed to sample the overlying water within the chamber at six specified times during the chamber incubation. For trace-element and nutrient analyses, sampled water was stored in fluorinated polyethylene polymer columns until the flux chamber was retrieved. The time-series of solute concentrations from a deployment was used to determine benthic flux. The term "dissolved" in this study operationally refers to samples filtered using membranes with 0.2-μm pore size to correspond with previous trace-metal studies in the lake (Woods and Beekworth 1997). Based on dissolved-bromide concentrations by flow-injection colorimetry, the overlying water volumes in the chamber were approximately 11.4 and 15.0 liters for the two Mica Bay replicate deployments, and 17.1, 19.7, and 19.2 liters for the three main-channel replicate deployments.

During flux-chamber deployments, dissolved-oxygen fluxes were measured using electrodes (Yellow Springs Inc., model 5780) mounted inside and outside the chamber that were modified to operate in the pulsed mode with a precision of 1% (Hammond and others 1996). Bromide (Br⁻) and radon (Ra) were used as tracers of hydrologic transport between chamber water and sediment pore-water. At the beginning of each deployment, a dissolved-Br⁻ solution was injected into the chamber as a conservative tracer to: (1) determine the volume of incubated water in the chamber, and (2) based on Br⁻ loss from the water during the incubation, provide a measure of bioturbation (often referred to as bioturbation) effects or potential ground-water interactions. Depending on the volume of overlying water, bromide concentrations in the chamber after the injection ranged from 300 to 600 μM, while the ambient bottom-water concentration was consistently < 5 μM. As samples were removed, bottom water flowed into the chamber, so the use of bromide as a conservative tracer allowed for sample-dilution corrections (Berelson and others 1992). Radon flux was also estimated following the determination of radon emanation strength of lake sediments. Emanation rate was established by incubating a few tens of milliliters of lake sediment in a jar.
Table 1. Specifications for chemical analytical methods used in this study

<table>
<thead>
<tr>
<th>Analyte</th>
<th>Detection limit</th>
<th>Precision</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zinc</td>
<td>0.5 mg/l</td>
<td>± 2%</td>
</tr>
<tr>
<td>Orthophosphate</td>
<td>2.5 mg/l</td>
<td>1.0 mg/l</td>
</tr>
<tr>
<td>Dissolved oxygen</td>
<td>0.5 mg/l</td>
<td>± 3%</td>
</tr>
<tr>
<td>Bromide</td>
<td>0.2 mg/l</td>
<td>± 8%</td>
</tr>
<tr>
<td>Radon</td>
<td>1 dpm/l</td>
<td>± 5%</td>
</tr>
</tbody>
</table>

filled with lake water. The sediment was incubated long enough for the radon to reestablish equilibrium with the radium contained within the sediment. Radon diffusive flux was then estimated according to procedures described by Breckson and others (1982).

Dissolved orthophosphate, from water-column samples and flux-chamber deployments, was refrigerated in darkness until analyses were performed by automated spectrophotometry. Trace-metal samples were filtered, acidified with quartz-distilled nitric acid to 0.03 N, then refrigerated in darkness until their analyses by direct-injection inductively coupled plasma mass spectrometry (ICP/MS) using external standardization. Quality-control specifications for each analysis have been documented (Woods and others 1999) and methodological specifications summarized (Table 1).

Water-Colunm Sampling

In preparation for benthic-flux studies, initial water-column samples were collected from the main-channel site on 15 October 1998, 2 m below the surface and 2 m above the bottom. At both flux-chamber deployment sites, water-column samples were collected between 16 and 27 August 1999 for analysis of dissolved macronutrients and dissolved trace metals. Samples were pumped from three depths (2 m below the surface, mid-depth, and 2 m above the bottom) using a high-displacement peristaltic pump and a tethered length of rigid fluorotyrene polymer tubing. On 7 August 2001, supplementary water-column samples were collected from the flux-chamber deployment sites as well as two other profundal sites where Ruard (1996) reported the highest macroinvertebrate abundances.

Sediment Coring

From each flux-chamber incubation site, six replicate cores with a surficial area of 77 cm² were used to characterize the sediment moisture content and benthic biology. Cores were taken using a device fabricated from nonmetallic parts (Savill Corporation, Minneapolis, MN, USA). For moisture content, approxi- mately 10 ml of surficial sediments was collected from each sediment core, then bottled, and refrigerated in darkness. Wet weight and dry weight after desiccation were measured to calculate moisture content.

Biological Measurements

The benthic biological community at each flux-chamber deployment site was characterized from the replicate sediment cores in the following way:

1. Bacterial abundance in surficial sediment was determined using subsamples taken with a syringe corer. Approximately 10 ml of surficial sediment was collected and fixed with 0.5 ml of 37% formalin. Samples were then refrigerated in darkness. Benthic bacterial concentrations were microscopically determined by direct epifluorescent counts using acridine-orange prepration and determined on the basis of sediment dry weight. Three replicate preparations were each counted 16 times yielding a standard error of approximately 2 × 10⁴ cells/g.

2. Benthic chlorophyll-a was determined from surficial sediment sampled with a chambered 1 cm-ID acrylic tube and then collected on a 50 μm glass-fiber filter and buffered with magnesium carbonate (Thompson and others 1981). Triplicate samples from each core were then frozen in darkness until spectrophotometrically analyzed (Franzén 1968) yielding a standard error of approximately 0.7 μg/cm².

3. Macroinvertebrate densities were estimated from the remaining sediment that was sieved at 500 μm, fixed with 10% buffered formalin, and stained with rose bengal solution. Samples were then sorted at ×10 magnification and macroinvertebrates were identified to the lowest practicable taxonomic level. No subsampling was used.

Flux-chamber incubation studies represented a pilot effort with a primary goal of determining the potential importance of sediment-water interactions in affecting solute transport in the lake. A clear limitation to any pilot study is the constraint of temporal and spatial coverage. For example, it is reasonable to question how representative the two incubation sites were of the lake. Active, thriving benthic communities observed and reported by Ruard (1996) in certain parts of the lake, particularly sites C3 and C4 in the main channel, suggest high spatial variability in the distribution of benthic invertebrates that may significantly affect benthic flux. To address this issue, the benthic community and water column were again sampled at four lake sites on 7 August 2001 (Figure 1). Benthic invertebrates were sampled using a Ponar grab (cross-sectional area of 0.025 m²) matching the surficial area of the Eckman
device used by Rudd (1996). Unlike the replicate sediment cores taken in August 1999, Posidonia grazers were not replicated at each site. The water column was sampled as previously described. Two of the four sites were the same as initially sampled in October 1998 and August 1999. The other two locations were referred to as C3 and C4 by Rudd (1996) where elevated benthic macroinvertebrate densities were observed in October 1995, down-wind of the Coeur d'Alene River plume. The objectives of this supplementary sampling were: (1) determine whether the sites sampled by Rudd in 1995 contained higher benthic invertebrate densities than our flow-chamber deployment sites, and (2) determine if water-column gradients at these sites indicate profiles consistent with those of August 1999.

Results and Discussion

Surficial sediment at both embayments (Mica Bay and main-channel near mouth of Coeur d'Alene Spur) sites was consistently high in moisture content, ranging from a mass ratio of 0.90 to 0.97 at the sediment-water interface. This is consistent with direct observations of unconsolidated surficial material in sediment cores, but the composition of the surficial material was quite different among the sites. Every sediment core from the main-channel site was dominated by inorganic, ferric-oxide-coated particles. The authigenic (localized or in place) formation of iron oxides in the lake was previously noted by Horowitz and others (1995). In contrast, every core from the Mica Bay site was dominated by detrital material, presumably from the littoral zones.

Minimal Biomixing Effects

At all four sampling sites, sediments were characterized by an orange oxidized surficial layer < 1 cm thick, overlaid by alternating biogenic and lithogenic layers. Such "varving" is often indicative of minimal sediment reworking (i.e., low biomixing and surficial mixing) by the benthic community. Varving is sufficiently stable and widespread that it has been used to date the onset of metal enrichment to the lake (Horowitz and others 1995b). Low densities of benthic macroinvertebrates and benthic algae were observed during our flow-chamber deployments in 1999 relative to other published values (Table 2). As initially observed in October 1998 and quantified in August 1999 and 2001, macroinvertebrate densities were consistently too low to generate biomixing effects that could, in turn, enhance benthic flux at these locations. Macroinvertebrate densities in Mica Bay and the main channel outside Rockford Bay during our benthic-flux experiments in 1999 averaged 98 ± 125 macroinvertebrates/m² from the 12 cores. Horowitz and others (1995) also noted the virtual absence of living macroinvertebrates at their profundal sites in Coeur d'Alene Lake in 1989.

Although a number of benthic biological studies have been conducted in oligotrophic and mesotrophic lakes (Ricker 1952, Reimers and others 1955, Dermott and others 1977, Lindegaard and Jonasson 1979, Rudd 1996), results from these studies reflect a high variability in methods used to estimate macroinvertebrate densities. Aside from an earlier benthic study in Coeur d'Alene Lake (Rudd 1996), comparable methods, and hence comparable results, were only found in one other study. Reimers and others (1955), using an Eckman dredge of identical cross-sectional area and a 500-μm sieve, observed macroinvertebrate densities that ranged from 900 to 4700 macroinvertebrates/m² in 10 oligotrophic lakes in Cowichan Creek Basin, California, USA. Although macroinvertebrate densities in Coeur d'Alene Lake were generally higher in 2001 than in 1999 (Table 2), all densities were consistently lower than those reported for the same sites in the late summer of 1995 (10,000–95,695 macroinvertebrates/m²) in the Coeur d'Alene River delta and the main channel outside Carlin Bay; identified as sites C3 and C4, respectively by Rudd (1996). That is, using methods similar to Rudd, our density estimates were consistently lower even at the two profundal sites where the highest densities were observed in 1995. These extremely low densities suggest that biomixing was minimal during all our sampling periods in 1998, 1999, and 2001. Although results from this study do not reflect benthic densities as high as those reported by Rudd (1996), current knowledge of the system does not preclude the possibility of enhanced benthic flux due to biomixing effects if densities similar to those observed by Rudd

<table>
<thead>
<tr>
<th>Sites</th>
<th>Minimum density (individuals/m²)</th>
<th>Maximum density (individuals/m²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fluxchamber sites</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1999</td>
<td>0</td>
<td>260</td>
</tr>
<tr>
<td>2001</td>
<td>170</td>
<td>490</td>
</tr>
<tr>
<td>Rudd Sites C3 and C4</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1995</td>
<td>10,000</td>
<td>99,000</td>
</tr>
<tr>
<td>2001</td>
<td>130</td>
<td>1200</td>
</tr>
<tr>
<td>Oligotrophic lakes in Cowichan Creek Basin, California</td>
<td>900</td>
<td>4790</td>
</tr>
</tbody>
</table>


occur. Therefore, estimates of benthic fluxes presented in this study could be conservative if densities of bio-
turbating macroinvertebrates are significantly higher during other seasons or other locations.

Consistent with our observations of low macroinver-
tebrae densities in Coeur d'Alene Lake, benthic chlo-
rophyll concentrations during flux-chamber deploy-
ments only ranged from 1.3 to 3.5 μg/cm². Studies
reporting benthic chlorophyll concentrations in mes-
sotrophic and oligotrophic lakes are not common, but
significantly higher concentrations (15-35 μg/cm²)
were observed in Lake Erken by Goekkoel and John-
son (1996).

Oxygen consumption by profundal lake sediments in this study was consistent with low biological activity by the macrofauna and benthic algae as described above. Ratios measured during flux-chamber deploy-
ments were similar among stations and deployments (combined range of 0.19-0.50 g O₂/m³/day (Table 5). By comparison, Cornwall and Kippin (1992) deter-
mined an average 0.24 g O₂/m³/day flux into Table 5. Lake sediments in Alaska and characterized it as "ex-
tremely low rates of benthic oxygen consumption for a lake environment." For the oligotrophic Maukaoka Lakes, Walker and Snodgrass (1986) calculated values for sediment oxygen demand between 0.13 and 0.59 g O₂/m³/day, while the profundal sediments of the meso-
trophic Lake Vechten generated an oxygen flux of 0.86 g O₂/m³/day (Stwerta and others 1991). With a water-residence time of 180 days (Woods and Beckwith 1997), physical conditions may favor benthic flux in Coeur d'Alene Lake being controlled by diffusion or bioturbation, as opposed to low-residence-time systems (e.g., low-order streams) where benthic flux due to hyperbolic exchange or groundwater/surface-water
interactions can dominate (Stream Solute Workshop 1990). Low rates of loss of bromide from the overlying water in the chamber (Table 5) and radon benthic flux were consistent with benthic biological analyses indicat-
ing minimal bioturbation effects (i.e., diffusive controls on benthic flux) (Berenson and others 1982). The dif-
finite flux of radon at the Mica Bay and main-channel

<table>
<thead>
<tr>
<th>Sampling site</th>
<th>Deployment number</th>
<th>DO flux (g/m³/day)</th>
<th>Bromanide flux (μg/cm²/yr)</th>
<th>Radon flux (atoms/m²/sec)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mica Bay</td>
<td>2</td>
<td>-0.50</td>
<td>-9.2 ± 3.7</td>
<td>198 ± 30</td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>-0.23</td>
<td>-19.5 ± 2.0</td>
<td>99 ± 20</td>
</tr>
<tr>
<td></td>
<td>1</td>
<td>-0.28</td>
<td>-0.0 ± 0.6</td>
<td>105 ± 30</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>-0.19</td>
<td>-19.4 ± 1.6</td>
<td>242 ± 50</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>-0.24</td>
<td>-13.5 ± 2.7</td>
<td>242 ± 50</td>
</tr>
</tbody>
</table>

Table 3. Physical transport characteristics reflected in the benthic flux of dissolved oxygen (DO), injected bromide, and radon at flux-chamber deployment sites in Coeur d'Alene Lake.

sites calculated from sediment radium measurements, was approximately 110 and 155 atoms/m²/year, respec-
tively. The agreement between the calculated diffusive flux of radon and the measured benthic fluxes (99-242 atoms/m²/year; Table 3) clearly indicates that diffusion is the primary transport mechanism for exchange of dis-
solved species between the bottom sediment and over-
lying water column. In summary, there are multiple lines of evidence that the benthic flux of dissolved
solutes like zinc and orthophosphate was diffusion con-
trolled during our sampling periods.

In contrast to macroinvertebrate and benthic algal
abundance, benthic bacterial concentrations were of
the order of 10⁶-10⁷ cells/g dry surficial sediment, similar to those previously observed for the lake (Har-
rington and others 1998a). These concentrations fall
within a wide range of published concentrations for
lake sediments from approximately 10⁵-10⁷ cells/g
lake sediment using direct counts (Jones and others 1979, Harrington and others 1998a). Estimated sulfate-
reducing bacteria concentrations as high as 10⁶ cells/g
weight are among the highest reported (Har-
rington and others 1998b). Based on the low benthic
algal and macroinvertebrate abundances consistently
observed in this study, the carbon source that supports these high microbial abundances is not evident, partic-
ularly in the main channel. These microbial communi-
ties are critical in establishing radon gradients that
regulate the remobilization, transformation and subse-
quent transport of sediment-associated contaminants (Harrington and others 1998b, Llavekko and others
1998, Cummings and others 1999).

Water-Column Gradients

Near the surface (75 m water depth), concentrations for dissolved Zn ranged between 38 and 58 μg/liter for
all sampling dates and locations, and all surface or-
thophosphate concentrations were below the detection limit (< 1 μg/l). These near-surface concentrations have remained stable over decadal time scales. Moni-
toring efforts throughout the lake between 1991 and 1994 indicated a dissolved Zn range of 38-66 μg/l; and

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toring efforts throughout the lake between 1991 and 1994 indicated a dissolved Zn range of 38-66 μg/l; and
an orthophosphate range of < 1–3 μg/l (Woods and Beckwith 1997). Both dissolved Zn and orthophosphate concentrations were elevated near the sediment-water interface relative to the shallower depths during our flux-chamber deployments in August 1999 (Figure 2). This trend is not indication that remineralization and accumulation of a chemical species in pore waters can result in a release of these solutes into the overlying water, generating a positive benthic-flux. Seasonal trends in thermal stratification and water-column chlorophyll concentrations (Woods and Beckwith 1997) tend to discount the possibilities that elevated bottom-water concentrations were generated by remineralization of settled detrital material or by a density-driven, horizontal, riverine source. Elevated bottom-water concentrations observed for dissolved Zn (Figure 2A) at all sampling locations and dates provide circumstantial evidence consistent with direct measurements that a benthic source to the overlying water is significant relative to other solute-transport processes. In contrast to the temporal stability of dissolved Zn profiles in the lake water column at the two flux-chamber deployment sites, the elevated orthophosphate concentrations observed in bottom waters in August 1999 were absent in August 2001 (Figure 2B). Although beyond the scope of our benthic flux study, factors generating these interannual shifts in water-column gradients, particularly for a limiting nutrient like phosphorus, will be important to identify in generating predictive models for the lake.

Benthic Accumulation of Zn and P

A comparison of major riverine inflows and outflows of solutes through Coeur d’Alene Lake in 1999 indicates a net accumulation of particle-associated metals such as Zn and ligands such as orthophosphate during the period of our benthic studies. Loading data for 1999 (Woods unpublished) indicated that phosphorus entered the lake primarily bound to suspended particles (only 24% dissolved using a discharge-weighted average from the Coeur d’Alene and St. Joe Rivers) while zinc primarily entered in dissolved form (81% dissolved from those two major riverine inputs). Annual riverine inputs to the lake for dissolved Zn and orthophosphate were 380 and 19.5 Mg/yr, respectively, while riverine losses from the lake for the same two solutes were 480 and 16.9 Mg/yr. Based on daily discharge data and 12 samples for concentration over the full range of the hydrograph, errors associated with these load estimates are approximately 10% about the mean. Therefore, only the input−output difference for dissolved Zn is statistically significant. However, differences for both Zn and P are consistent with the idea of a loss of solute to the lake bed. Total (dissolved and particulate) Zn loss to the Spokane River (490 Mg/yr) was nearly identical to the dissolved Zn loss. This sug
Table 4. Comparison of benthic-flux measurements from flux-chamber deployments for dissolved Zn and orthophosphate with area-averaged riverine flux and calculated diffusive flux for zinca

<table>
<thead>
<tr>
<th>Source</th>
<th>Zn flux (tonnes/km²/yr)</th>
<th>Orthophosphate flux (tonnes/km²/yr)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Benthic Flux</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mica Bay</td>
<td>3.5 ± 1.5</td>
<td>0.20 ± 0.20</td>
</tr>
<tr>
<td>Main Channel</td>
<td>2.8 ± 0.8</td>
<td>0.07 ± 0.02</td>
</tr>
<tr>
<td>Diffusive estimate</td>
<td>1.3 ± 0.3</td>
<td>_</td>
</tr>
<tr>
<td>Cour d’Alene River</td>
<td>5.5</td>
<td>0.00</td>
</tr>
<tr>
<td>St. Joe River</td>
<td>0.04</td>
<td>0.00</td>
</tr>
</tbody>
</table>

*aErrors associated with the coarse flux estimates are approximately 50% of the mean.

bConcentration data not available.

gests the predominance of dissolved-phase transport for Zn out of the lake and an accumulation of particle-associated solute within the lake during that year. Therefore, the lake bed is not only where solutes have historically accumulated, but it is also where solutes continue to accumulate as a pool for subsequent benthic transport.

Riverine discharge into the lake in 1999 was 120% of the long-term (1902-1999) mean (US Geological Survey 2005), and floodplain sediments were not transported during peak flows. Zinc and total phosphorus concentrations associated with suspended sediments during peak flows ranged from 2400 to 3100 µg/g and from 650 to 850 µg/g, respectively. The average Zn and total P concentrations for riverine lake sediments (3069 and 1300 µg/g, respectively) (Horowitz and others 1993, Woods and Beckwith 1997) were slightly higher than suspended-sediment concentrations and consistent with the notion of a continued source of solute to the lake bed.

Particle enriched in Zn and P deposit on the lake bed at a rate of about 2 cm/yr (Horowitz and others 1995a). Using zinc concentrations from lake sediments that were spatially averaged over 12 lake zones, Horowitz and others (1993) estimated 2900 tonnes/km² of zinc in the lake bed over an area of 108.2 km² that displayed trace-element-enriched sediments. A similar method of spatial averaging, but with coarser resolution of only six lake zones (Woods and Beckwith 1997) provides an estimate of 900 tonnes/km² for the mass of phosphorus in enriched lake sediments.

Benthic-Flux Comparisons

Riverine sources of dissolved Zn to the lake are dominated by the Cour d’Alene River (Table 4). The magnitudes of the measured benthic fluxes for both dissolved orthophosphate and zinc (approximately 0.1 and 3 tonnes/km²/yr, respectively) are similar to, and certainly significant relative to the riverine fluxes (Table 4). A diffusive flux estimate for dissolved Zn for Mica Bay (Baltrieri 1998) lends further support to the conclusion that benthic flux was diffusion controlled in the lake.

Based on previous oxygen profiles in the lake (Woods and Beckwith 1997), it was hoped that timing flux-chamber deployments in the late summer would facilitate examining the effects of epibenthic conditions in the hypolimnion in relation to the immobilization and benthic flux of orthophosphate and zinc. Unfortunately, the water column was not stratified during our flux-chamber deployments. Ambient dissolved-oxygen concentrations in bottom waters at both deployment sites were consistently near saturation (80 ± 1% saturation, 9.5-9.7 mg/L), and did not get below 50% saturation in the flux chamber during any deployment. Despite unexpectedoxic conditions in the lake bottom waters, a rather tightly grouped range of dissolved oxygen consumption rates (Table 3), higher consumption rates were coincident with enhanced sediment release of dissolved Zn and orthophosphate (ρ² = 0.93 and 0.43, respectively). Our study cannot specify a cause for this empirical relationship, but one might reasonably speculate, based on work by others (Cummins and others 1999, Zachara and others 2001), that increased microbial respiration in the lake bed generated reducing conditions near the sediment-water interface that favored increased ferrous iron solubility over ferric iron species, and hence the release of particle-associated Zn and orthophosphate from ferric-oxide surfaces.

Cour d’Alene Lake is considered a traditional mesotrophic/oligotrophic system. In an oligotrophic system the concept of a limiting nutrient is fragile, because dissolved-solute concentrations are typically balanced in such a way that minimal changes in concentration of one solute can alter nutrient limitation. Under theoxic, pH neutral (7.5-8.0) conditions observed for the lake water column, orthophosphate has a high affinity for metal-oxide surfaces (Goldberg 1985,
Arai and Sparks (2001). Depending on the chemical characteristics of the particle surface, varying levels of solute competition for adsorption sites occur, including competition by biological surfaces that may cause the re-partitioning of orthophosphate from inorganic particles to algal cells (Kawasbara and others 1986). Without adhesion competition, only about 1 mg/l of ferric oxide particles in suspension, equivalent to 0.03 m2 of particulate coating (using the approximate surface area for goethite determined by Goldberg (1985)), would be required to adsorb dissolved-or-

thophosphate concentrations typical for the lake (i.e., 0.3 mM). In a phosphorus-limited system like Coeur d'Alene Lake, where orthophosphate can interact with fluvial and re-suspended sediments coated with ferric oxides, adsorption/desorption reactions potentially can regulate internal cycling and bioavailability of the limiting nutrient (Kawasbara 1992).

The mechanism of zinc toxicity to aquatic primary producers is a disruption of phosphorus assimilation (in particular an interference with phosphorylation re-
actions) (Bates and others 1982). Inhibitory effects of Zn(II) activity on algal growth, as observed in Coeur d'Alene Lake (Woods and Beckwith 1997), are there-
fore dependent on orthophosphate concentrations (Kawasbara 1985). As Zn(II) activity increases, cell division is suppressed and phosphorus accumulates intra-

cellularly. Therefore, as zinc bioavailability increases, phosphate utilization is inhibited. Conversely, when phosphate bioavailability increases, zinc toxicity effects are alleviated. The lake has been designated a phosphorus-limited system, based on bloom dynamics results and riverine loads (Woods and Beckwith 1997). For example, riverine inputs of nitrogen to phosphorus to the lake in 1999 were near a molar ratio of 32 (as mass ratio of 14). This is twice the Redfield ratio of 16 in tidal units (or 7 in mass units) that describes the relative proportions of those essential nutrients re-
quired by phytoplankton as gain energy (Redfield 1958).

In average, average molar ratios of benthic flux for dissolved nitrogen to orthophosphate, determined from flux-chamber deployments, were 70 ± 29 and 41 ± 23 (for the main channel and embayment sites, re-
spectively (or 52 ± 9 and 19 ± 6 in mass units), all considerably higher than the Redfield ratio. Given the importance of the lake sediments as a source of dis-

solved orthophosphate to the water column relative to riverine sources (Table 1), our results strongly suggest that the lake sediments could significantly effect or-

thophosphate availability and hence zinc toxicity in the water column by sorption/desorption reactions.

Management Implications

The significance of sediments-water interactions in Coeur d'Alene Lake suggests important management implications (Figure 3). An existing concentration gra-

dient for a contaminant across the sediment-water in-
terface in the lake drives the release of solute from the lake bed into the water column. (Table 4) that, in the case of Coeur d'Alene Lake, is similar in magnitude to riverine flux. Up-gradient remediation attempts to de-

crease solute loads and concentrations. However, a management-designed decrease in water-column concen-

trations can potentially elevate the importance of benthic flux relative to riverine inputs. The graphical example provided for dissolved zinc in Figure 3 illus-

trates that with a large initial concentration gradient, as observed in Coeur d'Alene Lake (Balistreri and others 2002), only a marginal (< 10%) increase in the mag-

nitude of benthic flux would be expected in response to upstream remediation at this historically contami-
nated site that accomplished a 50% decrease in water-

column concentrations. This marginal effect is due to the fact that benthic flux is already an important con-


taminant transport process before upstream remedia-


tion is implemented. In contrast, a mining-affected sys-

tem like Butte Lake (Pederson 1985) exhibits similar

pore-water and water-column contaminant concen-

trations, both being much lower than Coeur d'Alene

Lake. In such a system, a remedial 50% decrease in water-column concentration may have pronounced ef-


effects on benthic flux (> 50% increase; Figure 3), but these less-impacted sites would probably be prioritized

Figure 3. Calculated changes in diffusive-controlled benthic

flux due to 50% decrease in dissolved Zn concentrations in

the lake. Curves represent changes in benthic flux for lake

environments that reflect contrasting pore-water quality.
lower for remedial action. Finally, in a situation like that found at Terrace Reservoir (Balistreri and others 1996), pore-water and water-column concentrations may both be elevated but similar in magnitude. Under these conditions, diffusive benthic flux is not initially significant unless hydrologic inputs are low (i.e., where water residence times are of the order of months or greater). However, upstream remediation to decrease water-column concentrations effectively shifts and increases the vertical concentration gradient, thereby increasing the driving force for enhanced benthic flux (Figure 3). Therefore, remediation efforts upgradient of a lake or reservoir may produce unexpected and possibly unfavorable results due to a benthic response. When water-quality models are developed to justify remediation strategies in basins that have been historically affected by anthropogenic activities, it would be unwise to disregard sediment sources and sinks in lakes (or reservoirs).

As with Coeur d'Alene Lake, studies in other aquatic environments have consistently indicated that the point-source load for a dissolved contaminant (Lps) is often similar in magnitude to the diffusive or biotrans- ported benthic load to the water column (Lbenthic) (Wood and others 1995, Topping and Kawabara 2003, Kawabara and others 2002). Those loads may be expressed as:

\[ L_{ps} = [\text{Solute}]_{ps} \cdot Q_{ps} = (\Delta[\text{Solute}] / \gamma_{s}) / (H' \cdot A_{ps}) \]

where: Qps and Aps are overall riverine discharge and benthic surface area for the aquatic system, \( \Delta[\text{Solute}] / \gamma_{s} \) is the change in solute concentration during a flux-chamber deployment, \( H' \) is a characteristic height (e.g., water-column height in the flux chamber), and \( \gamma_{s} \) is a characteristic time (e.g., diffusion of the flux-chamber incubation). Because \( (A_{ps} / Q_{ps}) / H' \) reflects a bottom-water residence time for the aquatic system (Rw), the terms in the equation can be rearranged and simplified into the following form:

\[ (\Delta[\text{Solute}] / [\text{Solute}]_{ps}) \cdot \gamma_{s} = \gamma_{s} / R_{w} \]

The equation indicates an inverse relationship between the relative change in the solute concentration and the normalized bottom-water residence time associated with an aquatic system (Rw/\( \gamma_{s} \); Figure 4). The injection, where Rw equals \( \gamma_{s} \), suggests a final solute concentration at the end of the incubation to be approximately twice the initial overlying-water concentration in order that the magnitude of the benthic flux be similar to external loads. As one shifts from riverine systems to estuaries to lakes and reservoirs, and residence times generally increase, the equation suggests a decrease in the threshold change in solute concentration required for benthic flux to be a primary solute-transport process (Figure 4). That is, in lentic systems with high residence times, even a small (submicromolar) concentration gradient for a contaminant across the sediment-water interface could generate conditions where benthic flux becomes quantitatively important. Furthermore, benthic interactions remain significant at the other end of the hydrologic spectrum in lotic systems with low residence times, e.g., lower-order stream environments where Rw <\( \gamma_{s} \), because diffusive controls give way to hyporheic exchange or ground and surface-water interactions (Kawabara and others 1984, Stream Solute Workshop 1990). A growing body of evidence suggests that benthic fluxes may, in fact, be inherently important in virtually all types of aquatic systems because, over the long term, these systems restructure concentration gradients at the sediment-water interface to respond to changes in vertical and horizontal solute fluxes (Boudreau and Jorgensen 2001).

Conclusions
Benthic flux of both dissolved orthophosphate and zinc in Coeur d'Alene Lake, Idaho, was significant in magnitude relative to major riverine sources of those dissolved solutes. Because both solutes are biologically reactive and surface reactive, particularly in this lake, the ecological and management implications of these results may be far reaching, in lakes and reservoirs where benthic flux is diffusion controlled, response of
the lake bed to upstream remediation efforts is depe-
dendent on the initial concentration gradient at the sedi-
ment-water interface and can potentially increase the 
driving force to enhance contaminant transport be-
tween the sediment and overlying water column. It may 
be prudent to consider these sediment-water interac-
tions when formulating management models to design 
and predict the effects of upstream remedial actions for 
all aquatic systems.

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References

Arul, Y. and D. L. Sparks. 2001. ATR/FTIR spectroscopic 
investigation of phosphate adsorption mechanisms at the 
ferrohydrite-water interface. Journal of Colloid and Interface 
Science 241:317-326.

Bal Санов, L. S. 1998. Preliminary estimates of benthic flux of 
dissolved nutrients in Cour d’Alene Lake, Idaho. US Geologi-

Bal Санов, C. S., Orlov, R. F., Briggs, P. H., Elrick, K. A. 
and Edelman, P. 1996. Metal fluxes across the sediments-water 
interface in Terrace Reservoir, Colorado. US Geological Survey 

Bal Санов, L. S., Box, S. E., Beuskens, A. A., Hopper, R. L. 
and Mahewy J. B. 2002. Impacts of historical mining in the 
Cour d’Alene River Basin. Pages 1-34 in Bal Санов L.S. 
and Stapp L.L. (eds.) Pathways of metal transfer from 
mineralized sources to bioreceptors: a synthesis of the min-
eral resources program’s past environmental studies in the 
western United States and future research directions. US 


Zinc adsorption and transport by Chlamydomonas reinhardtii and 
Sedentaria rhodopensis (Chlorococcales) grown in semi-

222 as a tracer for mixing in the water column and benthic 
exchange in the southern California borderland. Earth and 

Bourgeois, B. P., and A. J. Borgens. 2001. The benthic 

Caillere, J., D. Hammont, J. Kubara, L. Miller, and K. 
Duffey. 1980. Benthic processes in San Francisco Bay: the 
role of organic inputs and biodegradation. Pages 429-442 in 
T. Hollibaugh Edic, San Francisco Bay: the ecosystem. Ameri-
can Association for the Advancement of Science, Pacific 
Division, San Francisco.

of manganese and iron-rich sediments in Toxik Lake, Alaska. 
Hydrobiologia 240:45-49.

Cummings, D. E., J. C. Carreau, J. S. Fedoroff, and R. F. Rosen-
zweig. 1999. Arsenic mobilization by the diatomary 
F(N)-lilucing bacterium Schizochytrium alga BrV. Environ-
mental Science and Technology 33:729-739.

Production of Chlamydomonas, Protococcus, and Chlorella at 
different levels of phytoplankton biomass in Lake Mem-
phresinag. Quebec-Vermont, Journal of the Fisheries Research 

aquatic environment. Springer-Verlag, New York 488.

Frenzen, M. A. H. 1985. Standard Methods for the Examina-
tion of Water and Wastewater. 16 ed. Method 10085C, 
"American Public Health Association, American Water 
Works Association, Water Pollution Control Federation, 
Washington, DC 1268.

coupling. Profoundal benthic community response to spring 
dinotrophic deposition in monothrix Lake Erken. Limnology 
and Oceanography 41:636-647.

Goldberg, S. A. 1985. Chemical modeling of union competi-
tion on goethite using the constant capacitance model. Soil 

Pope. 1996. Early diagnosis of organic carbon in the equa-

Harrington, J., W. Rember, L. Alfair, S. Fedoroff, and R. 
Rosenzweig. 1998. Phase associations and mobilization of 
iron and trace elements in Cour d’Alene Lake, Idaho. 
Environmental Science and Technology 32:690-699.

Basic geotropism of arsenic (III) in metal(lo)-contami-
nated ferrohynite lake sediments. Environmental Science and 
Technology 32:2420-2430.

mining and related activities on the sediment trace element 
geochemistry of Lake Cour d’Alene, Idaho, USA, Part I: 
1995a. Effect of mining and related activities on the sedi-
mant trace element geochemistry of Lake Coret d'Aleure, 
Idaho, USA. Part II: subsurface sediments. Hydrological Pro-
cess 9:955-96.
1995b. A summary of the effects of mining and related 
activities on the sediment-trace element geochemistry of 
Lake Coret d'Aleure, Idaho, USA. Journal of Geochemical 
Exploration 52:135-144.
microbial study of sediments from the Cumbrian Lakes. 
Kowalska, J. S. 1985. Phosphorusrich interactive effects on 
growth by Selenastrum capricornutum (Chlorophyta). Environ-
mental Science and Technology 19:417-421.
Kowalska, J. S. 1992. Associations between benthic flora and 
diet changes in dissolved arsenic, phosphorus, and related 
physicochemical parameters. Journal of the North American 
Benthological Society 11:218-228.
Kowalska, J. S., H. V. Leland, and K. E. Bencala. 1984. Copper 
transport along a Sierra Nevada stream. Journal of Environ-
growth response to particle-bound orthophosphate and 
Kowalska, J. S., M. T. Smith, D. Pasquale, M. Prakins, W. 
Byron, E., Topping, B. R., C alike, L. L., Fend, S. V., 
disolved mercury across the sediments-water interface in 
Lakhotan Reservoir, Nevada. US Geological Survey Water 
La Force, M. J., S. E. Fendorf, C. G. Li, G. M. Schnieder, and 
R. F. Roeserewing. 1998. A laboratory evaluation of trace 
element mobility from flooding and nutrient loading of 
Coret d'Aleure River sediments. Journal of Environmental 
Quality 27:318-328.
Lindegard, C., and F. M. Jonasson. 1979. Abundance, popu-
lation dynamics and production of zoobenthos in Lake 
Pederen, T. F. 1983. Dissolved heavy metals in a lacustrine 
mine tailings deposit—Buntle Lake, British Columbia. Ma-
Reimer, N. J., J. Macie and, E. P. Pater. 1955. Limnologi-
cal study of the lakes of Convict Creek Basin, Mono Coun-
ty, California. Fishery Bulletin of the U.S. Fish and Wildlife 
Service 56:457-503.
Ricker, W. E. 1952. The benthos of Cuyahoga Lake. Journal of the 
Fisheries Research Board Canada 9:304-315.
community of a trace elements enriched lake and an 
uncontaminated lake in north Idaho. The effects of mine 
Eastern Washington University, Cheney, Washington 65.
assessing whole streams in dynamic ecosystems. The 
Cagenberg. 1991. Oxygen-consuming processes at the 
 profundal and littoral sediment-water interface of a small 
meso-eutrophic lake (Lake Vechtela, The Netherlands). 
Limnology and Oceanography 50:1124-1135.
crust: its composition and evolution. An examination of the 
geochronological record preserved in sedimentary rocks. 
Distribution of benthic chlorophyll in San Francisco Bay, 
Topping, B. R., Kowalska, J. S. (2005) "Dissolved nickel and 
 benthic flux in south San Francisco Bay: A potential for 
 natural sources to dominate." Bulletin of Environmental 
Toxicology and Chemistry 71: 46-56.
 oxygen demand in lakes. Journal of Environmental 
Engineering 12:25-23.
Weidel, R. G. 1983. Limnology, 2 ed. Saunders College Pub-
lishing, New York. 767.
1995. Diagnostic modeling of trace metal partitioning in 
 south San Francisco Bay. Limnology and Oceanography 
40:345-348.
Wood, P. F. and Beckwith. M. A. 1997. Nutrient and trace-
element enrichment of Coret d'Aleure Lake, Idaho. US 
 assurance project plan for US Geological Survey studies in 
support of Spokane River: Basin R/FS US Environmental 
Protection Agency, Seattle, Washington, and US Geological 
Solvability of Fe(III) oxide-bound trace metals by a 
dissimilatory Fe(III) reducing bacterium. Geochimia et 
Cosmochimica Acta 65:7-93.