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

Management Implications

(Short title: Sediment-Water Interactions in Coeur d'Alene Lake**)**

James S. Kuwabara[*1], Paul F. Woods[2], William M. Berelson[3], Laurie S. Balistrieri[4],

James L. Carter[1], Brent R.Topping[1], and Steven V. Fend[1]

[1] U.S. Geological Survey, 345 Middlefield Road, Menlo Park, CA 94025, * corresponding

    author, kuwabara@usgs.gov

[2] U.S. Geological Survey, 230 Collins Road, Boise, ID 83702

[3] University of Southern California, Department of Geological Sciences, 3651 Trousdale

    Parkway, Los Angeles, CA 90089

[4] U.S. Geological Survey, University of Washington, P.O. Box 355351, Seattle, WA 98195

ABSTRACT

A field study at Coeur d'Alene Lake, Idaho, 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 environmental 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 Zn and orthophosphate were comparable in magnitude to riverine inputs. Tracer analyses and benthic-community metrics provided evidence that solute benthic flux were diffusion-controlled at the flux-chamber deployment sites. That is, effects of biomixing (or bioturbation) and ground-water interactions did not strongly influence benthic flux. 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 feed-back 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.

Keywords: water-quality management, benthic flux, sediment-water interactions, non-point sources, contaminant transport, phosphate limitation

INTRODUCTION

Coeur d'Alene Lake is down-gradient of the Bunker Hill Superfund Site in Idaho, the second largest Superfund site in the U.S.A. (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. Horowitz and others (1995b) 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) in terms of primary productivity, the lake water column is 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 others 2001).

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 others 2001). 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 (Balistrieri 1998). Second, metal-distribution studies in the lake have clearly indicated elevated concentrations of particle-reactive solutes in the lake bottom sediment (Horowitz and others 1995b). For example, sediment-associated zinc concentrations in the lake down-gradient of the Coeur d'Alene River plume are, on average, 32 times greater than background concentrations. Background concentrations for 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 ug-g^{-1} (Horowitz and others 1995b). Although this background range exceeds the average crustal concentration for zinc (71 ug-g^{-1}; Taylor and McLennan 1985), a particulate-Zn concentration of 118 ug-g^{-1} was reported for remote lakes (Forstner 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

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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:

An *in-situ* benthic-flux chamber (Berelson and others 1982), specifically designed for trace-element studies, was deployed by boat multiple times between August 16 – 27, 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 (33 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 guided 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 retain some overlying water. This overlying water was isolated from the ambient lake water by closure of a lid, which initiated the incubation of approximately 1500 cm^2 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 6 specified times during the chamber incubation. For trace-element and nutrient analyses, sampled water was stored in fluoroethylene 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 Beckwith 1997). Based on dissolved-bromide concentrations by flow-injection colorimetery, the overlying water volumes in the

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chamber were approximately 11.4 and 15.0 L for the two Mica Bay replicate deployments, and 17.1, 19.7, and 19.2 L for the three main-channel replicate deployments.

During flux-chamber deployments, dissolved-oxygen fluxes were measured using electrodes (Yellow Springs Inc., Model 5730) 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 biomixing (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 1982). 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 filled with lake water. The sediment was incubated long enough for the radon to re-establish equilibrium with the radium contained within the sediment. Radon diffusive flux was then estimated according to procedures described by Berelson 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 0.03N, 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-column sampling:

In preparation for benthic-flux studies, initial water-column samples were collected from the main-channel site on October 15, 1998, 2 m below the surface and 2 m above the bottom. At both flux-chamber-deployment sites, water-column samples were collected between August 16 – 27, 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 fluoroethylene-polymer tubing. On August 7, 2001, supplementary water-column samples were collected from the flux-chamber-deployment sites as well as two other profundal sites where Ruud (1996) reported the highest macroinvertebrate abundances.

Sediment coring:

From each flux-chamber incubation site, 6 replicate cores with a surficial area of 77 cm^2 were used to characterize the sediment moisture content and benthic biology. Cores were taken using a device fabricated from non-metallic parts (Savillex Corporation, Minnetonka, MN). For moisture content, approximately 10 mL of surficial sediment was collected from each sediment-core, then bottled, and refrigerated in darkness. Wet weight and dry weight after lyophilization 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 sub-samples 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 preparations and determined on the basis of sediment dry weight. Three replicate preparations were each counted 16 times yielding a standard error of approximately 2×10^8 cells-g^{-1}.

(2) Benthic chlorophyll-*a* was determined from surficial sediment sampled with a chamfered 1 cm ID acrylic tube then collected on a 47 mm 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 (Franson 1985) yielding a standard error of approximately 0.7 μg-cm^{-2}.

(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 8× 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 Ruud (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 August 7, 2001 (Figure 1). Benthic invertebrates were sampled using a Ponar grab

(cross sectional area of 0.023 m^2) matching the surficial area of the Eckman device used by Ruud

(1996).   Unlike the replicate sediment cores taken in August 1999, Ponar Grabs 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 Ruud (1996) where elevated benthic

macroinvertebrate densities were observed in October 1995, down-gradient of the Coeur d'Alene

River plume. The objectives of this supplementary sampling were to: (1) determine whether the

sites sampled by Ruud in 1995 contained higher benthic invertebrate densities than our flux-

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 embayment (Mica Bay) and main-channel (near mouth of Coeur

d'Alene River) 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 (1993). 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 less than 1 cm in thickness overlying 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 flux-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 experiment in 1999 averaged 98 ± 125 macroinvertebrates-m^{-2} from the 12 cores. Horowitz and others (1993) 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, Ruud 1996), results from these studies reflect a high variability in methods used to estimate macroinvertebrate densities. Aside from an earlier benthic study in Coeur

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d'Alene Lake (Ruud 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-m^{-2} in 10 oligotrophic lakes in Convict Creek Basin, California. 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 – 98,695 macroinvertebrates-m^{-2}) in the Coeur d'Alene River delta and the main channel outside Carlin Bay; identified as Sites C3 and C4, respectively by Ruud (1996). That is, using methods similar to Ruud, 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 Ruud (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 Ruud occur. Therefore, estimates of benthic fluxes presented in this study could be conservative if densities of bioturbating macroinvertebrates are significantly higher during other seasons or other locations.

Consistent with our observations of low macroinvertebrate densities in Coeur d'Alene Lake, benthic-chlorophyll concentrations during flux-chamber deployments only ranged from 1.3 to 3.5 μg-cm^{-2}. Studies reporting benthic-chlorophyll concentrations in mesotrophic and oligotrophic lakes are not common, but significantly higher concentrations were observed in Lake Erken by Goedkoop and Johnson (1996; 13 to 33 μg-cm^{-2}).

Oxygen-consumption by profundal lake sediments in this study was consistent with low biological activity by the macrofauna and benthic algae as described above. Rates measured during flux-chamber deployments were similar among stations and deployments (combined range of 0.19 to 0.30 g O_2–m^{-2}-d^{-1}, Table 3). By comparison, Cornwell and Kipphut (1992) determined an average 0.24 g O_2–m^{-2}-d^{-1} flux into Toolik Lake sediments in Alaska and characterized it as "extremely low rates of benthic oxygen consumption for a lake environment". For the oligotrophic Muskoka Lakes, Walker and Snodgrass (1986) calculated values for sediment oxygen demand between 0.13 and 0.59 g O_2–m^{-2}-d^{-1}, while the profundal sediments of the meso-eutrophic Lake Vechten generated an oxygen flux of 0.86 g O_2–m^{-2}-d^{-1} (Sweerts and others 1991). With a water-residence time of 180 d (Woods and Beckwith 1997), physical conditions may favor benthic flux in Coeur d'Alene Lake being controlled by diffusion or biomixing, as opposed to low residence-time systems (e.g., low-order streams) where benthic flow due to hyporheic exchange or ground-water/surface-water interactions can dominate (Stream Solute Workshop 1990). Low rates of loss of bromide from the overlying water in the chamber (Table 3), and radon benthic flux were consistent with benthic-biological analyses indicating minimal biomixing effects (i.e., diffusive controls on benthic flux; Berelson and others 1982). The diffusive flux of radon at the Mica Bay and main-channel sites calculated from sediment-radium measurements, was approximately 110 and 133 atoms-m^{-2}-s^{-1} , respectively. The agreement between the calculated diffusive flux of radon and the measured benthic fluxes (99-242 atoms-m^{-2}-s^{-1}; Table 3) clearly indicates that diffusion is the primary transport mechanism for exchange of dissolved species between the bottom sediment and overlying water

column. In summary, there are multiple lines of evidence that the benthic flux of dissolved

solutes like zinc and orthophosphate was diffusion controlled during our sampling periods.

In contrast to macroinvertebrate and benthic-algal abundance, benthic-bacterial

concentrations were of the order of 10^8 - 10^9 cells-g^{-1} dry surficial sediment, similar to those

previously observed for the lake (Harrington and others 1998a). These concentrations fall within

a wide range of published concentrations for lake sediments from approximately 10^6 - 10^{10} cells-

g^{-1} lake sediment using direct counts (Jones and others 1979, Harrington and others 1998a).

Estimated sulfate-reducing bacteria concentrations as high as 10^6 cells-g^{-1} wet weight are among

the highest reported (Harrington 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, particularly in the main channel. These

microbial communities are critical in establishing redox gradients that regulate the

remobilization, transformation and subsequent transport of sediment-associated contaminants

(Harrington and others 1998b; La Force and others 1998; Cummings and others 1999).

Water-column gradients – Near the surface (2 m water depth), concentrations for

dissolved Zn ranged between 38 and 58 µg-L^{-1} for all sampling dates and locations, and all

surface orthophosphate concentrations were below the detection limit (<1 µg-L^{-1}). These near-

surface concentrations have remained stable over decadal time scales. Monitoring efforts

throughout the lake between 1991 and 1994 indicated a dissolved-Zn range of 33 to 66 µg-L^{-1},

and an orthophosphate range of <1 to 3 µg-L^{-1} (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

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trend is one indication that remobilization and accumulation of a chemical species in pore waters can result in a release of those 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, 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 inter-annual 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 the Lake in 1999 indicates a net accumulation of particle-associated metals like Zn and ligands like 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 580 and 19.5 Mg-yr^{-1}, respectively, while riverine losses from the lake for

the same two solutes were 480 and 16.9 Mg-yr^{-1}. 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^{-1}) was nearly identical to the dissolved Zn loss. This

suggests 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 (90 year) mean (U.

S. Geological Survey 2003), and flood-plain 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^{-1} and from 630 to 850 μg-g^{-1}, respectively. The average

Zn and total P concentrations for surficial lake sediments (3600 and 1300 μg-g^{-1}, 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.

Particles enriched in Zn and P deposit on the lake bed at a net rate of about 2 cm-yr^{-1}

(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-km^{-2} of zinc in

the lake bed over an area of 108.2 km^2 that displayed trace-element enriched sediments. A

similar method of spatial averaging, but with coarser resolution of only 6 lake zones (Woods and Beckwith 1997) provides an estimate of 900 tonnes-km^{-2} for the mass of phosphorus in enriched lake sediments

Benthic-flux comparisions – Riverine sources of dissolved Zn to the lake are dominated by the Coeur d'Alene River (Table 4). The magnitudes of the measured benthic fluxes for both dissolved orthophosphate and zinc (approximately 0.1 and 3 tonnes-km^{-2}-yr^{-1}, respectively) are similar to, and certainly significant relative to the riverine fluxes (Table 4). A diffusive-flux estimate for dissolved Zn for Mica Bay (Balistrieri 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 suboxic conditions in the hypolimnion in relation to the remobilization 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 $\pm$ 1% saturation, 9.5-9.7 mg-L^{-1}), and did not get below 50% saturation in the flux chamber during any deployment. Despite unexpected oxic conditions in the lake bottom waters, and 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 (r^2 = 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 (Cummings 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.

Coeur d'Alene Lake is considered a transitional 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 oxic, pH neutral (7.5 to 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 repartitioning of orthophosphate from inorganic particles to algal cells (Goldberg 1985; Kuwabara and others 1986). Without adsorbate competition, only about 1 mg-L^{-1} of ferric-oxide particles in suspension, equivalent to 0.03 m^2 of particulate coating (using the approximate surface area for goethite determined by Goldberg (1985)), would be required to adsorb dissolved-orthophosphate concentrations typical for the lake (i.e., <0.3 µM). In a phosphorus-limited system like Coeur d'Alene Lake, where orthophosphate can interact with fluvial and resuspended sediments coated with ferric-oxides, adsorption/desorption reactions potentially can regulate internal cycling and bioavailability of the limiting nutrient (Kuwabara 1992).

The mechanism of zinc toxicity to aquatic primary producers is a disruption of phosphorus assimilation (in particular an interference with phosphorylation reactions; Bates and others 1982). Inhibitory effects of Zn-ion activity on algal growth, as observed in Coeur d'Alene Lake (Woods and Beckwith 1997), are therefore dependent on orthophosphate concentrations

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(Kuwabara 1985). As Zn-ion activity increases, cell division is suppressed and phosphorus accumulates intracellularly. Therefore, as zinc bioavailability increases, phosphate utilization is inhibited. Conversely, when phosphate bioavailability increases, zinc toxicity effects are mitigated. Coeur d'Alene Lake has been designated as a phosphate-limited system, based on bioassay results and riverine loads (Woods and Beckwith 1997). For example, riverine inputs of nitrogen to phosphorus to the lake in 1999 were at a molar ratio of 32 (or mass ratio of 14). This is twice the Redfield ratio of 16 in molar units (or 7 in mass units) that describes the relative proportions of those essential nutrients required by phytoplankton to generate tissue (Wetzel 1983). In addition, average molar ratios of benthic flux for dissolved nitrogen to orthophosphate, determined from flux-chamber deployments, were 70 ± 20 and 41 ± 13 for the main channel and embayment sites, respectively (or 32 ± 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 dissolved orthophosphate to the water column relative to riverine sources (Table 4), our results strongly suggest that the lake sediments could significantly affect orthophosphate availability and hence zinc toxicity in the water-column by sorption/desorption reactions.

MANAGEMENT IMPLICATIONS

The significance of sediment-water interactions in Coeur d'Alene Lake suggests important management implications (Figure 3). An existing concentration gradient for a contaminant across the sediment-water interface 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 decrease solute loads and concentrations. However, a management-designed decrease in water-column concentrations can

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potentially elevate the importance of benthic flux relative to riverine inputs. The graphical

example provided for dissolved zinc in Figure 3 illustrates that with a large initial concentration

gradient, as observed in Coeur d'Alene Lake (Balistrieri and others 2002), only a marginal

(<10%) increase in the magnitude of benthic flux would be expected in response to upstream

remediation at this historically contaminated 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 contaminant transport process before upstream remediation is implemented. In

contrast, a mining-affected system like Buttle Lake (Pederson 1983) exhibits similar pore-water

and water-column contaminant concentrations, both being much lower than Coeur d'Alene Lake.

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

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

be prioritized lower for remedial action. Finally, in a situation like that found at Terrace

Reservoir (Balistrieri 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 up-gradient of a lake

or reservoir may produce unexpected and possibly unsatisfactory 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 (L_{riv}) is often similar in magnitude to the diffusive or bioturbated benthic load to the water column ($L_{benthic}$) (Wood and others 1995; Topping and others 2001; Kuwabara and others 2002). Those loads may be expressed as: $L_{riv} = [Solute]_{sys} * Q_{sys} \simeq (\Delta[Solute]/T^*)(H^*A_{sys}) = L_{benthic}$, where: Q_{sys} and A_{sys} are overall riverine discharge and benthic surface area for the aquatic system, $\Delta[Solute]$ 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 T^* is a characteristic time (e.g., duration of the flux-chamber incubation). Because $(A_{sys}/Q_{sys})H^*$ reflects a bottom-water residence time for the aquatic system (R_{sys}), the terms in the equation can be rearranged and simplified into the following form: $(\Delta[Solute] / [Solute]_{sys}) \simeq T^*/R_{sys,}$. 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 (R_{sys}/T^*; Figure 4). The inflection, where R_{sys} equals T^*, 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

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systems with low residence times, e.g., lower-order stream environments where $R_{sys} << T^*$, because diffusive controls give way to hyporheic exchange or ground and surface-water interactions (Kuwabara 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 dependent on the initial concentration gradient at the sediment-water interface, and can potentially increase the driving force to enhance contaminant transport between the sediment and overlying water column. It may be prudent to consider these sediment-water interactions when formulating management models to design and predict the effects of upstream remedial actions for all aquatic systems.

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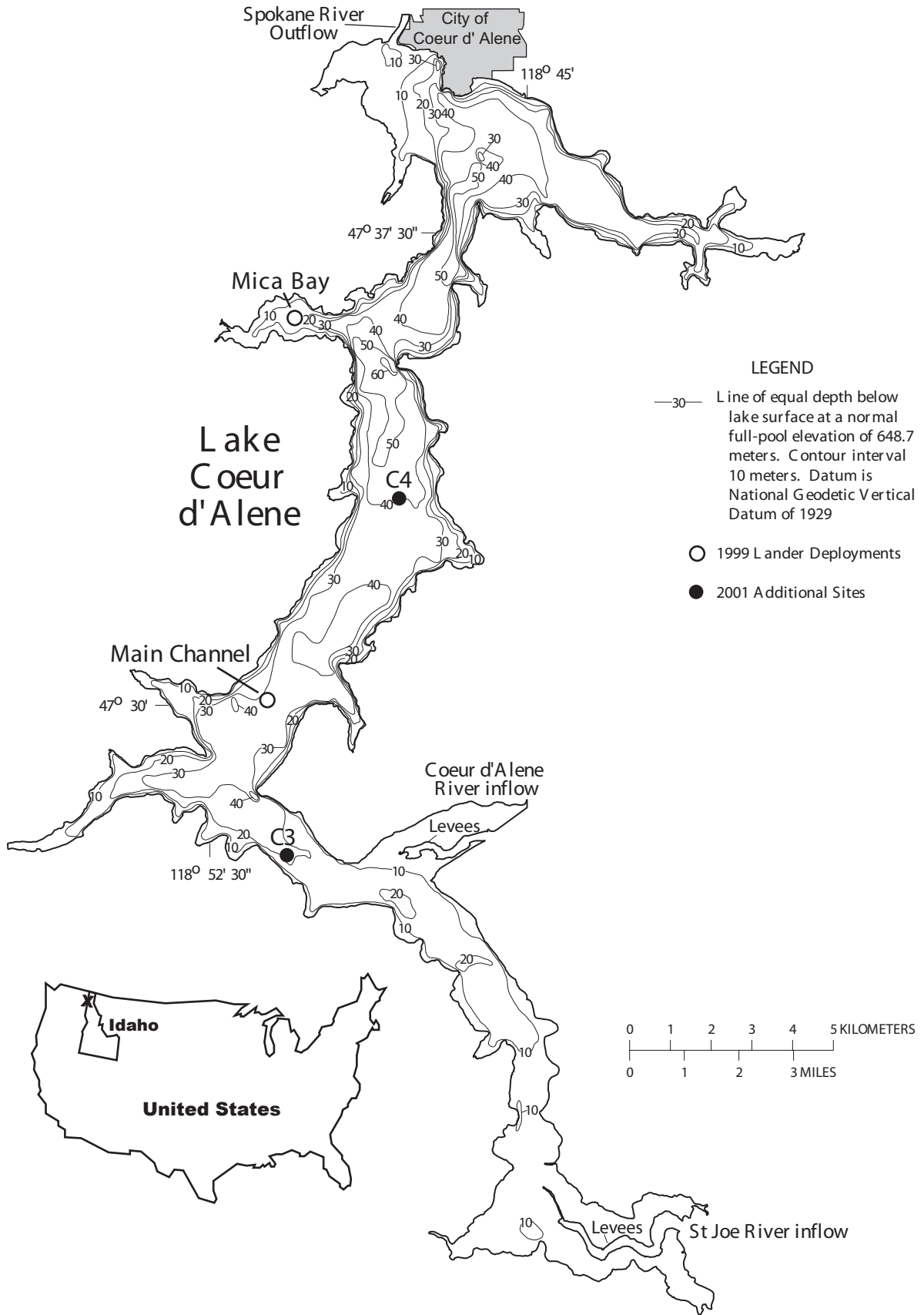
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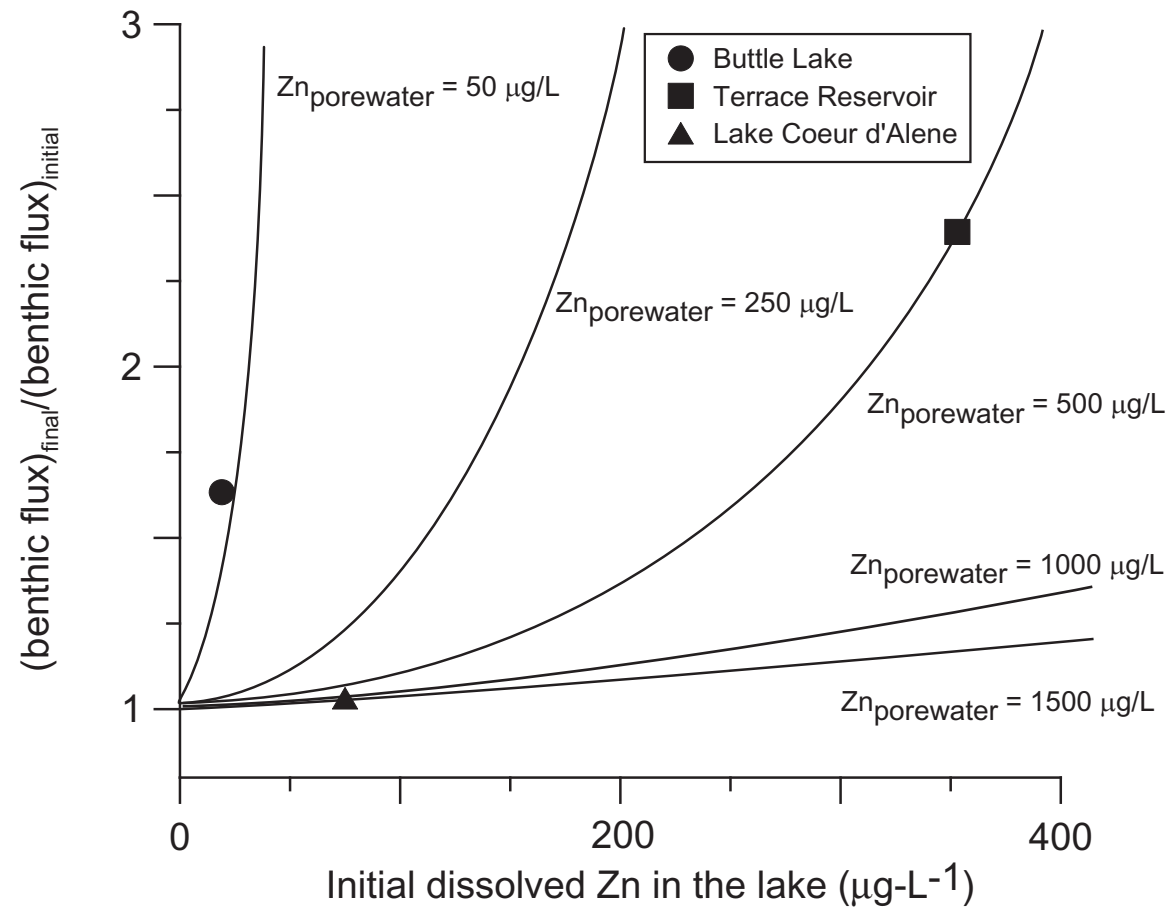
FIGURE CAPTIONS

Figure 1. Coeur d'Alene Lake sampling sites. Open circles indicate water-column and flux-chamber deployment sites sampled between October 1998 and August 2001. Closed circles indicate additional sites sampled in August 2001, replicating profundal sites C3 and C4 with elevated macroinvertebrate abundance in late summer 1995 (Ruud 1996). Bathymetric map modified from Woods and Beckwith (1997).

Figure 2. Temporal variability in water-column concentration gradients for (A) dissolved zinc and (B) orthophosphate. Concentrations are normalized to values at the surface.

Figure 3. Calculated changes in diffusion-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.

Figure 4. Importance of diffusion-controlled benthic flux based on an inverse relationship between threshold contaminant gradients and hydrologic residence time. Transitions between types of aquatic systems reflect broad generalities about their relative residence times.

Spokane River
Outflow

City of
Coeur d' Alene

10 30
118° 45'

10
20
30 40

30
40
50 40

30
20
30 10
47° 37' 30"

50

Mica Bay

10 20 30
40
40
50
30
60
50

Lake
Coeur
d'Alene

20
50
10

C4
40

30
20 10

30 40

30

Main Channel

10
20
30 40
47° 30'

20
30

30
20
30

10

40

30

Coeur d'Alene
River inflow

Levees

20
10
C3

118° 52' 30"

10

20
10

20

Idaho

United States

LEGEND

—30— Line of equal depth below
lake surface at a normal
full-pool elevation of 648.7
meters. Contour interval
10 meters. Datum is
National Geodetic Vertical
Datum of 1929

○ 1999 Lander Deployments

● 2001 Additional Sites

0 1 2 3 4 5 KILOMETERS

0 1 2 3 MILES

10

10

10

St Joe River inflow

Levees

Table 1. Specifications for chemical analytical methods used in this study.

Analyte	Detection Limit	Precision
Zinc	0.5 ug/L	+/- 2%
Ortho-Phosphate	2.5 ug/L	1.0 ug/L
Dissolved Oxygen	0.5 mg/L	+/- 3%
Bromide	0.2 mg/L	+/- 8%
Radon	1 dpm/L	+/- 6%

Table 2. Comparison of macroinvertebrate areal densities determined in this study with published values from oligotrophic/mesotrophic lakes using similar sampling methodologies (Reimers and others 1955, Ruud 1996)

Sites	Minimum Density (Individuals-m^{-2})	Maximum Density (Individuals-m^{-2})
Flux-chamber Sites 1999	0	260
Flux-chamber Sites 2001	170	4900
Ruud Sites C3 and C4 1995	10,000	99,000
Ruud Sites C3 and C4 2001	130	1200
Oligotrophic lakes in Convict Creek Basin, California	900	4700

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.

Sampling Site	Deployment Number	DO Flux $(g\text{-}m^{-2}\text{-}d^{-1})$	Bromide Flux $(mg\text{-}cm^{-2}\text{-}yr^{-1})$	Radon Flux $(atoms\text{-}m^{2}\text{-}s^{-1})$
Mica Bay	2	-0.30	-36.2 ± 3.7	128 ± 30
	4	-0.23	-19.5 ± 2.0	99 ± 20
Main Channel	1	-0.28	-0.0 ± 6.6	103 ± 30
	2	-0.19	-19.4 ± 1.6	105 ± 20
	3	-0.24	-13.5 ± 2.7	242 ± 50

Table 4. Comparison of benthic-flux measurements from flux-chamber deployments for

dissolved Zn and orthophosphate with areally averaged riverine flux and calculated

diffusive flux for zinc. Symbol "-" indicates that concentration data is not available.

Errors associated with the riverine flux estimates are approximately 10% of the mean.

Source	Zn Flux (tonnes-km^{-2}-yr^{-1})	Orthophosphate Flux (tonnes-km^{-2}-yr^{-1})
Mica Bay Benthic Flux	3.5 ± 1.5	0.20 ± 0.20
Main Channel Benthic Flux	2.8 ± 0.8	0.07 ± 0.02
Diffusive Estimate	1.3 ± 0.3	-
Coeur d'Alene River	5.3	0.09
St. Joe River	0.04	0.09