U. S. DEPARTMENT OF THE INTERIOR
U. S. GEOLOGICAL SURVEY

Preliminary estimates of benthic fluxes of dissolved metals in Coeur d'Alene Lake, Idaho

by

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Open-File Report 98-793

1998

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ABSTRACT

This report presents porewater and selected water column data collected from Coeur d'Alene Lake in September of 1992. Despite probable oxidation of the porewater samples during collection and handling, these data are used to calculate molecular diffusive fluxes of dissolved metals (i.e., Zn, Pb, Cu, and Mn) across the sediment-water interface. While these data and calculations provide preliminary information on benthic metal fluxes in Coeur d'Alene Lake, further work is needed to verify their direction and magnitude.

The benthic flux calculations indicate that the sediment is generally a source of dissolved Zn, Cu, Mn, and, possibly, Pb to the overlying water column. These benthic fluxes are compared with two other major sources of metals to Coeur d'Alene Lake – the Coeur d'Alene and St. Joe Rivers. Comparisons indicate that benthic fluxes of Zn, Pb, and Cu are generally less than half of the fluxes of these metals into the lake from the Coeur d'Alene River. However, in a few cases, the calculated benthic metal fluxes exceed the Coeur d'Alene River fluxes. Benthic fluxes of Zn and, possibly, Pb may be greater than the corresponding metal fluxes from the St. Joe River. These results have implications for changes in the relative importance of metal sources to the lake as remediation activities in the Coeur d'Alene River basin proceed.

INTRODUCTION

The Coeur d'Alene mining district is located in the northern panhandle of Idaho. Total production records indicate that this area ranks as one of the world's largest producers of silver (Ag) and one of the United States' major producers of lead (Pb) and zinc (Zn). Mining began in the district in the late 1800's. Over ninety mines now exist in this region and most of them are located along the South Fork of the Coeur d'Alene River and its major tributaries (Bennett and others, 1988). Only four of these mines are currently operating.

In the early days of the mining district, ore separation methods were not very efficient and the resulting jig tailings were highly enriched in Zn. Later development of more efficient flotation methods resulted in tailings with lower metal concentrations. It has been estimated that about 115 million tons of mine tailings were produced and about 60% of those tailings entered the Coeur d'Alene River system (Javorka, 1991).

The major repositories of the discharged mine tailings were the channel and floodplain of the lower Coeur d'Alene River and Coeur d'Alene Lake. The material that is located in the channel and floodplains is re-distributed during periodic floods within the Coeur d'Alene River basin. This process also results in continued transport of metal enriched sediment downstream to Coeur d'Alene Lake. Horowitz and others (1993, 1995) studied the composition of the surface and subsurface sediments in Coeur d'Alene Lake. They found that large portions of the near surface sediments in the central and northern parts of the lake are significantly enriched in Ag, arsenic (As), cadmium (Cd), mercury (Hg), Pb, antimony (Sb), and Zn, and somewhat enriched in copper (Cu), iron (Fe), and manganese (Mn) relative to the nearby non-mineralized St. Joe River basin. They estimated that 83 million tons of metal enriched sediment are in the lake.

There are concerns that diagenetic reactions in the near surface sediment of the lake have the potential to remobilize metals from the particulate to the dissolved phase. If dissolved metal concentrations in the porewater of near surface sediments are greater than those in the overlying waters, then diffusion processes could transport the dissolved metals from the sediment into the overlying water column. This benthic flux of dissolved metals could contribute to the water quality of the lake as well as be an important source of biologically available metals.

A study that determined the composition of porewater in the sediments of Coeur d'Alene Lake was done late in the summer of 1992. This work was part of a much larger effort that examined the general limnology of Coeur d'Alene Lake and its hydrologic, nutrient, and trace element budgets (Woods and Beckwith, 1997). Data from the porewater study were never formally published, although an unpublished manuscript by Kristin Dennen was written that summarized the methods and some of the data. In addition, a letter written by one of the investigators (Nancy Simon) contained additional data and more information about methods.

The U. S. Environmental Protection Agency is currently in the process of developing a Remedial Investigation/Feasibility Study for the entire Coeur d'Alene River Basin. Part of this process involves collating and synthesizing data on the composition of waters and sediments and the processes controlling metal distributions and concentrations in the basin. This report fills a data gap by providing information about the composition of porewaters and the direction and magnitude of benthic fluxes of dissolved metals in Coeur d'Alene Lake.

This report has several objectives. The first is to formally publish the data collected in the porewater study in 1992. The second is to assess the data and then use it to calculate benthic fluxes of metals in Coeur d'Alene Lake. These fluxes will then be compared to river fluxes of metals into the lake in order to estimate the relative importance of these two different sources of metals. Knowing the relative magnitude of the sources of metal to the lake is important for developing remediation plans and directing and prioritizing remediation activities.

SAMPLING AND ANALYTICAL METHODS

Samples of the water column and interstitial waters were collected from five sites located throughout the lake during the week of September 2, 1992 (Figure 1). The latitude, longitude, and water column depth at each of the sites are summarized in Table 1.

Water column samples were collected in acid-washed, plastic 125 or 250 mL bottles by scuba divers. Bottles were opened a few inches either below the surface of the lake or above the sediment-water interface. Upon returning to the surface, each sample was filtered through a 0.4 μm cellulose acetate filter into glass vials. The water samples were preserved with nitric acid (2% v/v).

Porewater within the top 30 cm of the sediment column was collected by two methods. The first method utilized diffusion-controlled equilibrator samplers. These samplers also are known as peepers or dialyzers. The specific samplers that were used are described in Simon, Kennedy, and Masoni (1985) and are based on the design given in Hesslein (1976). Briefly, the acrylic samplers had individual cells that were spaced at 1 cm intervals from 1 to 2 cm above the sediment-water interface, at the interface, and up to 20 cm below the interface. The samplers were immersed in a de-oxygenated, very dilute solution of NaCl (i.e., less than half the concentration of Na or Cl in the lake water). The solution was purged with nitrogen to minimize the effect of oxygen on anoxic porewater. The cells were then covered with 0.2 μm polycarbonate membranes, and transported to the field in the degassed solution. The samplers were inserted by scuba divers. Two samplers, designated as either A or B, were deployed at each site except for the Delta site where only one porewater sampler was inserted. The samplers remained in place for 6 weeks during which time the contents of the cells came to equilibrium with the dissolved constituents external to the sampler. The porewater samplers were retrieved and then returned to the laboratory under a blanket of nitrogen gas. All further sampling was done in a glove bag to maintain anoxic conditions. The 10 mL porewater samples from the samplers were preserved with nitric acid (2% v/v) and stored in sealed glass vials.

The second method used to recover porewater was collecting cores, sectioning them, and separating the porewater from the sediment by centrifugation. Divers collected sediment cores using polycarbonate core liners. The cores were transported to the laboratory and placed in a nitrogen-filled glove bag for sectioning. The cores were divided into 2 cm intervals and the wet sediment was placed into centrifuge tubes. After centrifugation, the tubes were returned to the glove bag where the supernatant was filtered through 0.2 μm polycarbonate filters. The porewater samples were acidified using nitric acid (2% v/v) and stored in sealed glass vials.

Dissolved calcium (Ca), magnesium (Mg), silicon (Si), Fe, Mn, and Zn concentrations in the porewaters were determined using direct current plasma atomic emission spectrometry (DCP-AES). Dissolved Pb, Cu, and chromium (Cr) concentrations in the porewaters were determined using graphite furnace atomic absorption spectrometry (GFAAS). Palladium nitrate was used as a modifier for the Pb analyses. Magnesium nitrate was used as a modifier for the Cr analyses. Sulfate (SO_4) and chloride (Cl) concentrations were determined by ion chromatography (IC).

Precision of the metal analyses was determined by analyzing ten replicates of a standard. Precision was better than or equal to 4.3%, except for Cr where precision was 7.1% (Table 2).

Detection limits for each metal were determined by measuring ten replicates of samples with concentrations near the detection limits. The detection limits were calculated as twice the standard deviation of these measurements and are summarized in Table 2.

Standard reference water (National Institutes of Standards and Technology reference material 1643b) was used to assess the accuracy of the metal measurements. The measurements and the most probable values reported for the reference standard agreed to better than or equal to 5.3% (Table 2).

The porosity of the sediment at each site was determined by measurements of the water content of the sediments. Pre-weighed wet sediment was dried and re-weighed. The porosity was calculated as follows:

$$\text{wet weight (g)} - \text{dry weight (g)} = \text{water weight (g)} \qquad (1)$$

$$\text{dry weight}/\rho_{sed} = \text{cm}^3 \text{ dry sediment} \qquad (2)$$

$$\text{water weight}/\rho_{water} = \text{cm}^3 \text{ water} \qquad (3)$$

$$\Phi = \text{porosity} = [\text{cm}^3 \text{ water}/(\text{cm}^3 \text{ water} + \text{cm}^3 \text{ dry sediment})] \qquad (4)$$

where ρ_{sed} is the density of the sediment and is approximately 2.65 g cm^{-3} (Pedersen, 1983) and ρ_{water} is the density of water (1.0 g cm^{-3}).

RESULTS

The data are summarized in a series of Tables. Metal concentrations at the top and bottom of the water column are given in Table 3. These data are from a table in the unpublished manuscript by Dennen. The concentrations of elements in the diffusion-controlled samplers are given in Table 4. The concentrations of Ca, Mg, Si, Fe, Mn, Zn, Pb, and Cu are from tables in the unpublished manuscript by Dennen. The data for Cl and SO_4 were digitized from graphs included with the letter from Simon. The water content, porosity of the sediment, pH of the porewater, and concentrations of elements in the interstitial porewaters of the cores are given in Table 5. The water content, pH, and concentrations of Fe, Mn, Zn, Pb, Cu, Cr, and Cd are from tables and the concentrations of Ca, Mg, Cl, and SO_4 were digitized from graphs included with the correspondence from Simon.

The concentrations of six constituents of the porewater from the samplers and cores are plotted for each station in Figures 2-6. In general, the concentrations of these species, with the possible exception of sulfate, are greater in the porewater from the cores than from the diffusion-controlled samplers. One might argue that these differences are due to heterogeneity of the sediments and associated porewater at any given site. If this were the case, then the data from the two samplers should not match as well as they do and the core data should not always be greater in concentration than that from the samplers.

Carignan and others (1985) did a comparison of the in-situ dialysis and centrifugation methods. They found good agreement between the methods for Fe, Mn, cobalt (Co), nickel (Ni), and Cr when the samples were centrifuged at 5,000 rpm and then filtered through 0.45 μm Millipore membranes. However, concentrations of Zn, Cu, and dissolved organic carbon were higher by centrifugation than by dialysis. They suggested that these elements were not completely separated during filtration of the supernatant. When the centrifugation speed was increased to 11,000 rpm and 0.2 or 0.03 μm Nuclepore membranes were used, the results for Zn, Cu, and the other trace elements were comparable for the two methods. Thus, Carignan and others (1985) concluded that the two methods give comparable results, if care is taken to avoid contamination from particles in the centrifugation method. The use of 0.2 μm filters during the processing of the Coeur d'Alene porewaters from the cores should have precluded contamination by colloidal particles.

Carignan (1984) examined potential problems in the use of diffusion-controlled samplers. One important finding was that the presence of oxygen either in the solution filling the cells or within the plastic of the samplers before they were inserted into anoxic sediments significantly affected the concentrations of dissolved Mn, Fe, and reactive phosphate in the samples. Lower concentrations of dissolved Mn and Fe, due to oxidation and precipitation of oxyhydroxide phases, were observed in samplers that were not deaerated before deployment in anoxic sediments. Scavenging of metals (e.g., Zn, Pb, and Cu) by these phases also would reduce the concentrations of other dissolved metals in the samplers. Carignan (1984) suggested that samplers be stored in an inert environment while not in use, that their exposure to oxygen be minimized, that samplers and solution be deaerated for 24 to 48 hours before insertion into the sediment, and that all subsampling of the cells occurs quickly upon retrieval of the samplers. Although precautions against oxygen exposure were taken during the deployment and retrieval of porewater samples in Coeur d'Alene Lake, lower concentrations of metals in the porewater from the samplers compared to the cores suggest that dissolved Mn and Fe may have oxidized and precipitated in the samplers and scavenged dissolved Zn, Pb, Cu, and other metals. In contrast to cations, anions, such as sulfate and chloride, are not strongly adsorbed by Fe and Mn oxide phases at the near neutral to basic pH values observed in the porewater. Hence, their concentrations are generally comparable between the two methods (Tables 4 and 5, Figure 7).

It is probable that interstitial water data collected from both samplers and cores in Coeur d'Alene Lake during September 1992 were compromised. Recent correspondence with Nancy Simon, the principle investigator for the porewater work, states that "iron oxidation occurred in the interstitial water samples (and associated sediment) during the time of their collection. The glove bag was not anaerobic enough to prevent the transformation of ferrous iron in the interstitial water to ferric iron and subsequent iron oxyhydroxides".

Despite apparent oxidation problems, all data are presented and benthic fluxes are calculated based on both methods. This approach provides a starting point for assessing the direction and magnitude of benthic metal fluxes in Coeur d'Alene Lake. However, it is likely that these calculated benthic fluxes for Zn, Cd, Cu, and Mn are underestimates of the actual metal fluxes because of metal scavenging by Fe oxide phases precipitated during sample handling. Further work needs to be done to confirm the direction and, especially, the magnitude of benthic metal fluxes in the lake.

DISCUSSION

Redox state of Coeur d'Alene Lake sediments and associated trace metal mobilization

The flux of dissolved elements across the sediment-water interface is the result of the coupling of physical, chemical, and biological processes (Santschi and others, 1990). Molecular and eddy diffusion can transport dissolved elements that have been mobilized from solid phases by biologically mediated chemical reactions. One of the most important biochemical reactions in the upper sediments of aquatic environments is the oxidation of organic matter. This process affects the partitioning of certain elements between solid and dissolved phases. Studies of the diagenesis of organic matter in freshwater and marine sediments indicate that the oxidation of organic matter proceeds using a thermodynamically predictable sequence of oxidants – oxygen, nitrate, Mn oxyhydroxides, Fe oxyhydroxides, and sulfate (Froelich and others, 1979; Berner, 1980; Pedersen and Losher, 1988; Luther and others, 1998). These reactions are reflected in the composition of the porewater as a function of depth. With increasing depth, the observations include the disappearance of oxygen and nitrate, followed by the appearance of dissolved Mn and Fe, and then the disappearance of sulfate. Oxygen is the primary oxidant of organic matter in the oxic zone. Suboxic conditions occur when oxygen concentrations are very low and nitrate, Mn oxyhydroxides, and Fe oxyhydroxides are used as oxidants. The location of this zone in the upper sediments of Coeur d'Alene Lake is of particular interest because the oxidation of Mn and Fe oxyhydroxides can result in the release of associated metals to the dissolved phase (e.g., Zn, Pb, Cu, or Cd). No oxygen and oxidation of organic matter by sulfate characterize anoxic conditions. Sulfate reduction results in the production of sulfide. This sulfide either appears in the porewater or is precipitated as a metal sulfide, if there are sufficient concentrations of dissolved metals (e.g., primarily Fe, but possibly Zn, Pb, Cu, and Cd). The depth scale where these reactions occur can be large (meters) or small (millimeters to centimeters) depending on parameters such as the supply of organic matter, bottom water anoxia, and sedimentation rates.

Although there are no data concerning oxygen concentrations in the sediments of Coeur d'Alene Lake, the work of Woods and Beckwith (1997) indicated that oxygenated waters overlaid the sediments at all stations, except Chatcolet, during September 1992. The bottom waters at Chatcolet during this time had no oxygen indicating that the boundary between oxic and anoxic conditions had moved from the sediments into the bottom of the water column. Another indication of anoxic conditions in the sediments at the Chatcolet site is the low concentrations of sulfate in the porewaters (Figure 2). For the other sites, the transition from oxic to anoxic conditions, as delineated by decreases in sulfate concentrations, occurs either in the upper 1 cm of the sediment or 2 to 5 cm below the interface (Figures 3-6). Thus, the depth scale in which the redox state changes from oxic to anoxic in the sediments of Coeur d'Alene Lake is compressed into less than a centimeter to a few centimeters just below the sediment-water interface. This transition zone goes through the suboxic region where Mn and Fe oxyhydroxide phases should be reduced. Accordingly, the porewater data from the cores indicate large increases in dissolved Mn and Fe concentrations below the sediment-water interface.

The oxidation and mobilization of Mn and Fe oxyhydroxides should release other trace elements associated with these phases. Profiles of dissolved Zn, Pb, and Cu in the interstitial waters of the sediments of Coeur d'Alene Lake are also presented in Figures 2-6. Dissolved Zn concentrations are higher below the sediment-water interface than in the overlying water at all sites. Dissolved Pb concentrations also increase from the overlying water to the porewater at all sites except Chatcolet where concentrations are at or below the detection limit. Both Zn and Pb may be associated with Mn and Fe oxyhydroxide phases and released as these phases are oxidized. Indeed, the leaching studies of Horowitz and others (1993) suggest that many trace elements, including Zn and Pb, in the surface sediments of Coeur d'Alene Lake primarily are associated with an operationally defined Fe oxide phase. In contrast, dissolved Cu concentrations either increase (Chatcolet and East Point), decrease (Delta and Valhalla), or show little to no change (Harlow Point) below the sediment-water interface.

Benthic flux calculations

The flux of dissolved elements across the sediment-water interface by molecular diffusion is calculated using Fick's First Law; i.e.,

$$J_s = -\Phi\, D_s\, [\delta C/\delta x] \qquad (5)$$

where J_s is the benthic flux (g cm^{-2} d^{-1}), Φ is the porosity just below the sediment-water interface, D_s is the diffusion coefficient for the element in the sediment (cm^2 d^{-1}), and $\delta C/\delta x$ is the concentration gradient of the element across the sediment-water interface (g cm^{-4}) (Berner, 1980).

Diffusion coefficients in the sediment (D_s) are related to molecular diffusion coefficients in water (D_0) as follows:

$$D_s = D_0/(\Phi\, F) \qquad (6)$$

where F is the sediment resistivity. For high porosity sediments, as in Coeur d'Alene Lake, F can be approximated as Φ^{-3} (Ullman and Aller, 1982). Therefore,

$$D_s = D_0/\Phi^{-2} \qquad (7)$$

Values of D_0 at infinite dilution for a variety of ions are tabulated in Li and Gregory (1974). These values depend on the speciation of the metals. Metal speciation is a function of pH, redox potential, and the presence of complexing ligands such as carbonate, dissolved organic carbon, and sulfide (Turner, Whitfield, and Dickson, 1981; Xue, Kistler, and Sigg, 1995; Luther and others, 1996). Because we have no data on dissolved organic carbon or sulfide concentrations in the porewaters of Coeur d'Alene Lake, the diffusion coefficients used in the benthic flux calculations are chosen based on inorganic speciation calculations for metals in near neutral, oxic freshwater. These calculations indicate that the dominant species of dissolved Zn, Pb, Cu, and Mn for these conditions are the free metal ions (Zn^{2+}, Pb^{2+}, Cu^{2+}, and Mn^{2+}) (Turner, Whitfield, and Dickson, 1981). The D_0 values for Zn^{2+}, Pb^{2+}, Cu^{2+}, and Mn^{2+} at 25^0C are, respectively, 0.618, 0.816, 0.633, and 0.594 cm^2 d^{-1} (Li and Gregory, 1974). These diffusion coefficients also are a function of temperature. The Stokes-Einstein relationship is used to temperature correct the diffusion coefficients to in-situ conditions as follows:

$$(D_0\eta^0/T)_{T1} = (D_0\eta^0/T)_{T2} \qquad (8)$$

where η^0 is the viscosity of water and T is absolute temperature ($T^0C + 273.15$). The temperature dependence on the viscosity of water is tabulated in Dorsey (1940). The temperature at the base of the water column at each sampling site during September 1992 was estimated from the work of Woods and Beckwith (1997). These temperatures and the diffusion coefficients in the sediments used in the calculations of the fluxes at each site are summarized in Table 6.

The concentration gradient ($\delta C/\delta x$) across the sediment-water interface is calculated as:

$$\delta C/\delta x = [(Me^{2+})_{BW} - (Me^{2+})_{PW}]/\Delta d \quad (9)$$

where $(Me^{2+})_{BW}$ is the concentration of the dissolved metal (Me^{2+}) at the bottom of the water column just above the interface (g cm^{-3} or g L^{-1}), $(Me^{2+})_{PW}$ is the concentration of dissolved metal in the porewater just below the interface (g cm^{-3} or g L^{-1}), and Δd is the distance between the location of the bottom water and porewater sample (cm). For flux calculations using metal data from the diffusion-controlled samplers, we used average concentrations of the samples at 0 and –1 cm from the samplers as the concentration of $(Me^{2+})_{BW}$, metal concentrations in the 1 cm cell for the $(Me^{2+})_{PW}$ values, and a Δd of 0.5 cm. For flux calculations involving the porewater data from the cores, we used metal concentrations in bottom waters collected by scuba divers a few inches from the interface, metal concentrations in the porewater from the 0-2 cm interval, and a Δd value of 1 cm.

There are several limitations in determining fluxes using the above approach. First, the flux calculations assume that molecular diffusion is the only process affecting transport of elements across the interface. Other physical and chemical process that could either increase or decrease transport, such as bioturbation or mineral precipitation at the interface, are not taken into account in the calculations. Second, the calculations assume that there are linear gradients in metal concentrations across the interface. Given the data that are available to us, the method for calculating the gradients is essentially a two-point calculation. The thickness of the sampling interval is critical for elements that have large changes in concentration with depth, as the measured metal concentration is the average for that depth interval. With greater sampling resolution near the sediment-water interface, an exponential model can be used to quantify the gradient (Klump and Martens, 1981). This model generally indicates that the diffusive flux is underestimated by the linear gradient assumption. Hence, the measured gradient in the porewater of Coeur d’Alene Lake may be less than the actual gradient because of sampling limitations for the depth interval just below the sediment-water interface. And third, these calculations indirectly determine the flux. There are methods, such as benthic flux chambers and core incubations, that directly determine fluxes (Devol, 1987; Berelson and others, 1990; Kuwabara and others, 1996; Smith and others, 1997). Direct determinations of fluxes eliminate uncertainties due to bioturbation or non-linear gradients. In addition, porewater to overlying water gradients might indicate metal fluxes where none exist. For example, dissolved Fe concentrations may be high in porewaters and low in overlying waters suggesting a flux out of the sediment. However, if there is a very thin oxic zone at the sediment-water interface, Fe can be trapped at the interface due to oxidation and precipitation processes.

River flux calculations

The flux of a metal due to inflowing rivers is calculated as follows:

$$J_{inflow} = L_{Me}/A \quad (10)$$

where J_{inflow} is the flux of metal due to inflow (g cm^{-2} d^{-1}), L_{Me} is the annual load of the metal (g d^{-1}), and A is the surface area of the lake (cm^2). The annual loads of total recoverable Zn, Pb, and Cu for the two major rivers (i.e., Coeur d’Alene and St. Joe Rivers) flowing into the lake were obtained from Woods and Beckwith (1997). Because the level of Coeur d’Alene Lake varies during the year due to water control at the Post Falls dam, the surface area of the lake used in the calculations is the average of the values at full pool (129 km^2) and at the limit of drawdown (122 km^2) (Woods and Beckwith (1997).

Benthic fluxes of dissolved metals in Coeur d'Alene Lake

Benthic fluxes of dissolved Zn, Pb, Cu, and Mn are presented in Figures 8-11. Benthic fluxes for dissolved Cd and Cr were not calculated as the necessary data were either not available (i.e., bottom water concentrations for Cd) or below detection limits (i.e., Cr). Positive values indicate fluxes of dissolved metals from the porewater to the overlying water column or, in other words, the sediment acts as a source of dissolved metal to the lake water. A value of zero indicates no flux. A negative flux indicates transport from the overlying water to the porewater. In this case, the sediment is a sink for dissolved metals. All flux data are summarized in Table 7.

Nine out of 14 flux determinations for dissolved Zn indicated that the sediment in Coeur d'Alene Lake is a source of dissolved Zn to the water column (Figure 8). These fluxes ranged from 3 to 451 μg Zn cm^{-2} y^{-1}. Three of the determinations were zero indicating no transport across the sediment-water interface. Only data from sampler B at East Point indicated a small flux into the sediments. The porewater data from the cores indicated higher fluxes for Zn than from the samplers, in accordance with the higher metal concentrations observed in the porewater data from the cores.

All benthic fluxes of dissolved Pb were either zero or positive (Figure 9). One half of the determined Pb fluxes indicated that the sediment in Coeur d'Alene Lake is a source of dissolved Pb. These fluxes ranged from 3.5 to 87 μg Pb cm^{-2} y^{-1}. The other half of the determinations indicated no transport of dissolved Pb across the sediment-water interface. All determined fluxes were zero at Chatcolet. Sampler data indicate higher benthic fluxes of dissolved Pb than did porewater data from cores at Delta and East Point (i.e., sampler A only). Otherwise, fluxes of Pb from cores were greater than fluxes calculated from the samplers.

Nine determinations (i.e., the majority) of benthic fluxes of dissolved Cu in Coeur d'Alene Lake were positive indicating that the sediment is a source of dissolved Cu to the lake water (Figure 10). These fluxes ranged from 0.2 to 11 μg Cu cm^{-2} y^{-1}. Four out of the 14 determinations indicated that the sediment acts as a sink for Cu. Three of these negative fluxes were very close to zero. Only the flux that was determined from sampler B at Chatcolet indicated no transport across the interface. The dissolved Cu fluxes determined from the core data were larger than those determined from the sampler data, except at Delta where they were equal.

All determinations of the benthic flux of dissolved Mn, except for sampler A at Chatcolet, were zero or positive (Figure 11). Eleven of the 14 determinations indicated that the sediment is a source for dissolved Mn. These fluxes ranged from 0.4 to 1411 μg Mn cm^{-2} y^{-1}. Benthic fluxes for dissolved Mn determined from core data were always larger than from sampler data.

Comparisons between benthic and river fluxes of metals in Coeur d'Alene Lake

The hydrologic budgets for Coeur d'Alene Lake during 1991 and 1992 indicated that the St. Joe and Coeur d'Alene Rivers supplied about 92-93% of the inflow to the lake. The St. Joe River contributed about 52% of the inflow while the Coeur d'Alene River accounted for about 40-41% of the inflow (Woods and Beckwith, 1997). Sediments in the St. Joe watershed have substantially lower concentrations of Zn, Pb, and other elements than sediments in the Coeur d'Alene River watershed (Horowitz, Elrick, and Cook, 1993). Hence, the fluxes of metals into Coeur d'Alene Lake from these two sources are substantially different for Zn and Pb (Table 7). During 1991 and 1992, the flux of Zn from the Coeur d'Alene River into the lake was 9 to 10 times greater than from the St. Joe River while Pb fluxes were 6 to 10 times greater. The fluxes for Cu into the lake were about the same for the two rivers (Table 7). No loading data for Mn from the rivers are available, so no river fluxes can be calculated.

The relative importance of the benthic fluxes as compared to the river fluxes of Zn, Pb, and Cu to the lake during 1992 is presented in Figures 12-14. A value of 1 in these plots indicates that the benthic flux is equal to the river flux. A value greater than 1 indicates that the benthic flux is greater than the river flux. Alternately, a value less than 1 indicates that the river flux is greater than the benthic flux.

The benthic fluxes for Zn calculated from the cores are greater, by factors of 1.6 to 13, than the flux of Zn from the St. Joe River. The opposite is true for the benthic fluxes calculated from the sampler data; i.e., there either are no benthic fluxes or they are about equal to or only a fraction (i.e., 0.09 to 0.67) of the St. Joe River flux. In contrast, the benthic fluxes for Zn calculated from the samplers were <12% of the Coeur d’Alene River flux, while the fluxes calculated from the cores at Chatcolet, Delta, Harlow Point, and East Point ranged from 17-32% of the Coeur d’Alene River flux. However, the core data from Valhalla indicated that the benthic flux of Zn was 1.38 times larger than the Coeur d’Alene River flux during 1992.

The majority (i.e., 9 out of 14 determinations) of Pb fluxes from the sediment in Coeur d’Alene Lake was less than the St. Joe River flux. All benthic fluxes of Pb, except that calculated from the sampler data at Delta, were smaller (benthic flux/river flux < 0.6) than the Coeur d’Alene River flux during 1992. The flux of Pb that was calculated from the sampler data at the Delta site was 1.9 times the flux of Pb from the Coeur d’Alene River.

Because the fluxes of Cu from the two rivers were approximately the same during 1992, the relative importance of the benthic flux as compared to either river flux is the same. The Cu fluxes calculated from the sampler data were <14% of either river flux. The fluxes calculated from the core data were <57% of either river flux at all sites except East Point. The East Point benthic flux for Cu determined from the porewater data from the cores was 35 to 40% greater than either of the river fluxes.

SUMMARY AND CONCLUSIONS

1) Lower concentrations of dissolved Mn, Fe, Zn, Pb, and Cu were observed in porewaters collected from Coeur d’Alene Lake in 1992 using diffusion-controlled samplers as compared to sectioning and centrifuging cores. These differences generally were not observed in the concentrations of sulfate or chloride. A plausible explanation for the lower concentrations of certain elements is that the samplers were exposed to oxygen during sampling and handling. Correspondence from Nancy Simon indicates that all samples were likely exposed to oxygen during sample handling in the glove bags. This exposure resulted in the oxidation and precipitation of dissolved Mn and Fe and subsequent scavenging of dissolved Zn, Pb, and Cu by the metal oxyhydroxide phases. Elements that are conservative or not prone to significant scavenging at higher pH, such as chloride and sulfate, were not affected.

2) Although the bottom waters generally are oxygenated, the sediments of Coeur d’Alene Lake are anoxic within the first few centimeters below the sediment-water interface. The transition from oxic to anoxic conditions near the sediment-water interface results in the mobilization of metals into the dissolved phase that have the potential to be transported across the interface into the overlying water column.

3) Benthic metal fluxes in Coeur d’Alene Lake calculated using porewater data collected in September 1992 are likely underestimates because of oxidation during the handling of porewater samples. Despite this problem, molecular diffusive flux calculations indicate that the

sediments of Coeur d'Alene Lake are generally a source of dissolved Zn, Cu, and Mn to the water column. Half of the determinations indicated that the sediment is also a source for dissolved Pb. The other half of the determinations indicated no flux of dissolved Pb across the sediment-water interface.

4) The magnitude of the benthic source of Zn, Pb, and Cu is generally less than that from the Coeur d'Alene River. However, if the benthic fluxes that were calculated from the cores are considered to be more reliable, then benthic fluxes for Zn, and in some cases, for Pb are greater than their corresponding fluxes from the St. Joe River. This observation has implications for the relative importance of the various sources of Zn and Pb once remediation activities improve the water quality of the Coeur d'Alene River.

5) Because of probable oxidation of porewater samples collected during September 1992 and indirect determinations of benthic fluxes from porewater profiles, alternative methods that directly measure fluxes, such as benthic flux chambers or core incubations, should be used to confirm the direction and magnitude of benthic fluxes of dissolved metals in Coeur d'Alene Lake.

ACKNOWLEDGEMENTS

The effort that went into collecting and analyzing this porewater data by Nancy Simon, Paul Woods, and associates (USGS) is gratefully acknowledged. Paul Woods encouraged me to determine the benthic fluxes using this porewater data and supplied me with the unpublished paper by Kristen Dennen and the letter and graphs from Nancy Simon. Nancy Simon graciously contributed her insights regarding the handling of the porewater samples. EPA financially supported the time that I used to collate and interpret the porewater data. Jim Kuwabara and Larry Miller (USGS) provided helpful reviews of an earlier draft of this work.

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Table 1. Latitude, longitude, and water column depth at sample sites in Coeur d'Alene Lake.

Site	Latitude	Longitude	Water depth m
Chatcolet	47^0 21' 43"	116^0 45' 03"	11.1
Delta	47^0 27' 15"	116^0 48' 47"	16.6
Harlow Point	47^0 27' 13"	116^0 49' 27"	17.1
East Point	47^0 28' 06"	116^0 51' 24"	21.2
Valhalla	47^0 36' 26"	116^0 48' 38"	29.3

Table 2. Precision, detection limits, and accuracy of analytical measurements

Element	Precision %	Detection Limits $\mu g\ L^{-1}$	Accuracy %
Ca	3.1	10	1.3
Cr	7.1	5	3.8
Cu	2.9	2	5.2
Fe	3.2	12	0.2
Mg	1.8	2	4.5
Mn	1.2	10	0.5
Pb	4.3	6	3.2
Si	4.1	80	2.3
Zn	4.2	20	5.3

Table 3. Dissolved element concentrations at the top and bottom of the water column (WC) in Coeur d'Alene Lake.

Site	Location in WC	Ca $mg\ L^{-1}$	Mg $mg\ L^{-1}$	Si $mg\ L^{-1}$	Fe $mg\ L^{-1}$	Mn $mg\ L^{-1}$	Zn $\mu g\ L^{-1}$	Pb $\mu g\ L^{-1}$	Cu $\mu g\ L^{-1}$
Chatcolet	top	8	1.9	5.3	<0.012	<0.01	<20	<6	2
Chatcolet	bottom	7.7	1.84	4.93	<0.012	0.065	<20	<6	7
Delta	top	6.7	1.97	6.3	<0.012	0.011	65	<6	5
Delta	bottom	6.2	1.95	7.6	<0.012	0.031	103	<6	9
Harlow Point	top	7.1	2.06	6.7	<0.012	<0.01	69	<6	5
Harlow Point	bottom	6.7	2.02	7.3	<0.012	<0.01	71	<6	4
East Point	top	7.1	2.09	6.4	<0.012	<0.01	57	<6	5
East Point	bottom	6.1	1.85	7.2	<0.012	<0.01	94	<6	2
Valhalla	top	6.3	1.88	6.1	<0.012	<0.01	69	<6	2
Valhalla	bottom	6	1.82	7.3	<0.012	0.013	96	<6	4

Table 4. Interstitial porewater data from the diffusion-controlled samplers deployed in Coeur d'Alene Lake. n.m. = not measured. n.d. = no data given in unpublished reports.

CHATCOLET SITE

Depth cm	Ca mg L^{-1} sampler A	Ca mg L^{-1} sampler B	Mg mg L^{-1} sampler A	Mg mg L^{-1} sampler B	Si mg L^{-1} sampler A	Si mg L^{-1} sampler B	Cl mg L^{-1} sampler A	Cl mg L^{-1} sampler B	SO_4 mg L^{-1} sampler A	SO_4 mg L^{-1} sampler B
-1	1.8	2.47	0.369	0.494	1.34	1.97	0.086	0.102	n.d.	n.d.
0	2.35	2.59	0.484	0.528	1.87	1.93	0.151	0.103	n.d.	n.d.
1	2.21	2.63	0.452	0.551	1.84	2	0.108	0.105	n.d.	n.d.
2	2.44	2.99	0.503	0.625	1.99	2.23	0.108	0.109	n.d.	n.d.
3	2.72	3.06	0.571	0.649	2.19	2.26	0.102	0.136	n.d.	n.d.
4	2.78	3.12	0.623	0.671	2.39	2.28	0.101	0.111	n.d.	n.d.
5	2.61	3.01	0.592	0.65	2.92	2.3	0.124	0.094	n.d.	n.d.
6	2.84	2.92	0.7	0.63	2.78	2.31	0.1	0.102	n.d.	n.d.
7	2.91	2.9	0.614	0.635	2.39	2.3	0.11	0.125	n.d.	n.d.
8	2.92	2.92	0.62	0.635	2.51	2.33	0.107	0.116	n.d.	n.d.
9	2.91	2.89	0.626	0.63	2.47	2.35	0.104	0.136	n.d.	n.d.
10	2.94	2.94	0.631	0.637	2.5	2.5	0.103	0.109	n.d.	n.d.
15	3.02	2.95	0.658	0.658	2.59	2.44	0.106	0.128	n.d.	n.d.
20	3.13	3.03	0.693	0.678	2.58	2.44	0.123	0.151	n.d.	n.d.

Depth cm	Fe mg L^{-1} sampler A	Fe mg L^{-1} sampler B	Mn mg L^{-1} sampler A	Mn mg L^{-1} sampler B	Zn µg L^{-1} sampler A	Zn µg L^{-1} sampler B	Pb µg L^{-1} sampler A	Pb µg L^{-1} sampler B	Cu µg L^{-1} sampler A	Cu µg L^{-1} sampler B
-1	1.7	2.58	0.308	0.389	<20	<20	<6	<6	2	3
0	2.4	2.75	0.394	0.379	<20	<20	<6	<6	3	3
1	2.4	2.95	0.334	0.386	<20	<20	6	<6	2	3
2	2.61	3.49	0.362	0.443	<20	<20	<6	<6	2	6
3	3.08	3.44	0.422	0.47	<20	<20	<6	<6	2	2
4	3.37	3.62	0.455	0.493	<20	<20	6	<6	4	3
5	3.43	3.61	0.456	0.486	<20	<20	n.m.	<6	3	2
6	4.26	4.08	0.508	0.482	26	<20	8	<6	7	5
7	4.2	3.96	0.498	0.487	n.m.	<20	n.m.	<6	8	4
8	4.57	4.44	0.509	0.504	<20	<20	<6	<6	2	4
9	4.7	4.45	0.523	0.501	<20	<20	<6	<6	2	6
10	5	4.51	0.538	0.514	<20	<20	14	<6	2	15
15	5.61	4.79	0.543	0.514	<20	<20	<6	<6	14	2
20	5.49	5.23	0.537	0.508	<20	<20	<6	<6	3	3

Table 4. (continued) Interstitial porewater data from the diffusion-controlled samplers deployed in Coeur d'Alene Lake. n.m. = not measured. n.d. = no data given in unpublished reports.

DELTA SITE

	Ca	Mg	Si	Cl	SO_4
Depth cm	mg L^{-1} sampler A	mg L^{-1} sampler A	mg L^{-1} sampler A	mg L^{-1} sampler A	mg L^{-1} sampler A
-1	0.67	0.186	1	0.112	0.459
0	0.69	0.186	1.8	0.106	0.422
1	0.93	0.234	1.04	0.104	0.422
2	1.66	0.382	1.1	0.107	0.176
3	2.45	0.545	1.31	0.132	0.049
4	2.86	0.642	1.17	0.113	0.042
5	3.21	0.71	1.19	0.136	0.057
6	3.5	0.776	1.25	0.119	0.051
7	3.81	0.842	1.34	0.195	0.422
8	4.09	0.886	1.37	0.114	0.019
9	4.3	0.936	1.46	0.505	0.019
10	4.44	0.97	1.58	0.12	0.051
15	4.96	1.12	1.55	0.128	0.06
20	4.95	1.17	1.54	0.152	0.08

	Fe	Mn	Zn	Pb	Cu
Depth cm	µg L^{-1} sampler A	µg L^{-1} sampler A	µg L^{-1} sampler A	µg L^{-1} sampler A	µg L^{-1} sampler A
-1	<12	<10	123	<6	3
0	0.06	<10	136	n.m.	4
1	2.64	0.156	326	562	3
2	2.76	0.454	235	535	3
3	4.03	0.647	212	265	2
4	4.58	0.726	239	141	2
5	4.95	0.767	269	85	3
6	5.72	0.83	264	88	2
7	6.56	0.94	285	131	<2
8	7.22	1	289	178	2
9	7.74	1.07	290	168	3
10	8.12	1.12	312	231	3
15	9.6	1.23	440	356	2
20	10.1	1.27	451	515	4

Table 4. (continued) Interstitial porewater data from the diffusion-controlled samplers deployed in Coeur d'Alene Lake. n.m. = not measured. n.d. = no data given in unpublished reports.

HARLOW POINT SITE

	Ca	Ca	Mg	Mg	Si	Si	Cl	Cl	SO$_4$	SO$_4$
Depth	mg L^{-1}	mg L^{-1}	mg L^{-1}	mg L^{-1}	mg L^{-1}	mg L^{-1}	mg L^{-1}	mg L^{-1}	mg L^{-1}	mg L^{-1}
cm	sampler A	sampler B	sampler A	sampler B	sampler A	sampler B	sampler A	sampler B	sampler A	sampler B
-1	0.69	0.68	0.187	0.184	1.5	0.88	0.121	0.129	0.391	0.572
0	0.7	0.7	0.186	0.188	1.06	0.83	0.127	0.121	0.534	0.547
1	0.89	0.72	0.227	0.191	1.19	0.83	0.103	0.152	0.441	0.557
2	0.99	0.86	0.244	0.223	1.77	0.93	0.092	0.109	0.254	0.461
3	1.14	0.93	0.271	0.237	1.8	1.27	0.102	0.108	0.103	0.235
4	1.36	1.08	0.309	0.255	2.13	1.28	0.116	0.102	0.073	0.146
5	1.4	1.3	0.323	0.293	2.08	1.54	0.108	0.14	0.053	0.044
6	1.53	1.43	0.34	0.323	2.14	1.83	0.1	0.131	0.057	0.042
7	1.54	1.51	0.341	0.338	2.15	1.86	0.116	0.152	0.046	0.05
8	1.55	1.51	0.351	0.343	2.3	2.02	0.112	0.108	0.044	0.042
9	1.56	1.58	0.353	0.359	2.23	2.06	0.127	0.105	0.049	0.032
10	1.59	1.64	0.363	0.367	2.14	2.02	0.115	0.131	0.047	0.045
15	1.73	1.79	0.396	0.405	2.39	2.16	0.131	0.11	0.042	0.057
20	1.72	1.94	0.402	0.439	2.39	2.21	0.291	0.134	0.047	0.016

	Fe	Fe	Mn	Mn	Zn	Zn	Pb	Pb	Cu	Cu
Depth	mg L^{-1}	mg L^{-1}	mg L^{-1}	mg L^{-1}	μg L^{-1}	μg L^{-1}	μg L^{-1}	μg L^{-1}	μg L^{-1}	μg L^{-1}
cm	sampler A	sampler B	sampler A	sampler B	sampler A	sampler B	sampler A	sampler B	sampler A	sampler B
-1	0.023	0.013	0.013	<10	28	81	<6	<6	4	2
0	0.033	0.014	0.018	<10	28	102	11	<6	3	2
1	0.182	0.013	0.722	0.66	47	132	61	<6	10	3
2	0.77	0.177	0.82	0.622	51	177	97	41	2	3
3	1.85	0.77	1.18	0.798	35	173	205	34	3	2
4	2.55	1.38	1.43	0.93	59	183	195	216	2	7
5	2.79	2.36	1.55	1.27	38	161	143	236	2	2
6	3.06	2.78	1.65	1.52	43	188	180	207	3	4
7	2.83	2.74	1.66	1.63	61	193	119	166	2	2
8	2.59	2.54	1.69	1.68	42	187	84	24	2	7
9	2.56	2.47	1.71	1.75	78	173	70	63	2	3
10	2.53	2.36	1.78	1.78	81	170	66	32	2	2
15	2.64	2.48	1.94	2.06	60	255	46	32	3	<2
20	2.81	2.95	1.96	2.27	64	342	n.m.	57	4	2

Table 4. (continued) Interstitial porewater data from the diffusion-controlled samplers deployed in Coeur d'Alene Lake. n.m. = not measured. n.d. = no data given in unpublished reports.

EAST POINT SITE

	Ca	Ca	Mg	Mg	Si	Si	Cl	Cl	SO_4	SO_4
Depth	mg L^{-1}	mg L^{-1}	mg L^{-1}	mg L^{-1}	mg L^{-1}	mg L^{-1}	mg L^{-1}	mg L^{-1}	mg L^{-1}	mg L^{-1}
cm	sampler A	sampler B	sampler A	sampler B	sampler A	sampler B	sampler A	sampler B	sampler A	sampler B
1	0.7	0.65	0.19	0.185	0.86	0.78	0.096	0.079	0.572	0.608
0	0.69	0.66	0.198	0.185	0.88	0.83	0.091	0.088	0.555	0.607
-1	0.76	0.64	0.196	0.181	1.2	0.8	0.095	0.103	0.4	0.604
-2	0.97	0.67	0.238	0.186	1.6	0.9	0.098	0.086	0.058	0.612
-3	1.12	0.89	0.269	0.235	1.83	1.45	0.094	0.096	0.077	0.328
-4	1.17	1.08	0.281	0.274	2.07	1.7	0.099	0.087	0.058	0.164
-5	1.18	1.09	0.281	0.278	2.1	1.8	0.122	0.091	0.056	0.087
-6	1.24	1.13	0.301	0.281	2.24	2.01	0.091	0.082	0.051	0.059
-7	1.17	1.09	0.286	0.283	2.19	2.1	0.096	0.088	0.053	0.058
-8	1.25	1.15	0.301	0.289	2.33	2.12	0.002	0.093	0.055	0.044
-9	1.26	1.31	0.306	0.292	2.36	2.16	0.088	0.109	0.042	0.049
-10	1.28	1.37	0.307	0.297	2.38	2.2	0.097	n.d.	0.056	n.d.
-15	1.44	1.31	0.34	0.315	2.34	2.31	0.098	0.098	0.043	0.054
-20	1.52	1.38	0.361	0.335	2.34	2.14	0.104	0.106	0.039	0.606

	Fe	Fe	Mn	Mn	Zn	Zn	Pb	Pb	Cu	Cu
Depth	mg L^{-1}	mg L^{-1}	mg L^{-1}	mg L^{-1}	µg L^{-1}	µg L^{-1}	µg L^{-1}	µg L^{-1}	µg L^{-1}	µg L^{-1}
cm	sampler A	sampler B	sampler A	sampler B	sampler A	sampler B	sampler A	sampler B	sampler A	sampler B
1	0.017	<12	<10	<10	101	112	<6	<6	3	2
0	0.21	<12	<10	<10	84	119	9	<6	3	<2
-1	0.75	<12	0.89	<10	319	106	134	<6	7	3
-2	0.84	<12	2.35	0.03	204	145	46	<6	4	3
-3	1.06	<12	2.8	1.24	135	290	73	<6	8	6
-4	1.07	0.133	2.8	2.38	121	142	51	18	7	3
-5	1.03	0.327	2.92	2.69	98	99	45	12	2	2
-6	0.94	0.98	3.12	2.78	104	131	51	17	3	4
-7	0.86	0.86	3.09	2.84	124	92	40	14	5	3
-8	0.94	0.75	3.06	2.9	116	68	27	17	2	2
-9	1.27	0.68	3.03	3.03	165	102	33	13	4	2
-10	1.31	0.9	2.98	3.04	161	123	32	10	2	2
-15	1.97	1.33	3.06	2.85	276	144	99	21	4	3
-20	2.21	1.2	3.3	3.25	289	180	104	26	3	3

Table 4. (continued) Interstitial porewater data from the diffusion-controlled samplers deployed in Coeur d'Alene Lake. n.m. = not measured. n.d. = no data given in unpublished reports.

VALHALLA SITE

Depth cm	Ca mg L^{-1} sampler A	Ca mg L^{-1} sampler B	Mg mg L^{-1} sampler A	Mg mg L^{-1} sampler B	Si mg L^{-1} sampler A	Si mg L^{-1} sampler B	Cl mg L^{-1} sampler A	Cl mg L^{-1} sampler B	SO$_4$ mg L^{-1} sampler A	SO$_4$ mg L^{-1} sampler B
-1	0.7	0.66	0.187	0.183	0.8	0.85	0.087	0.133	0.388	0.478
0	0.68	0.67	0.187	0.187	0.87	0.95	0.078	0.089	0.384	0.529
1	0.67	0.66	0.181	0.177	0.84	1.11	0.091	0.081	0.457	0.481
2	0.63	0.67	0.176	0.176	0.97	1.38	0.08	0.083	0.469	0.419
3	0.69	0.75	0.188	0.199	1.4	2.1	0.089	0.087	0.439	0.223
4	0.73	0.82	0.193	0.212	1.84	2.22	0.1	0.082	0.525	0.096
5	0.79	0.85	0.198	0.22	2.16	2.29	0.1	0.101	0.343	0.091
6	0.84	0.9	0.213	0.233	2.29	2.43	0.096	0.091	0.134	0.05
7	0.86	0.92	0.223	0.238	2.36	2.39	0.109	0.104	0.109	0.044
8	0.97	1	0.247	0.25	2.46	2.48	0.099	0.1	0.021	0.043
9	0.98	0.99	0.247	0.247	2.31	2.49	0.096	0.047	0.032	0.019
10	0.97	0.99	0.25	0.252	2.27	2.47	0.088	0.119	0.038	0.039
15	1.06	1.12	0.272	0.279	2.17	2.3	0.091	0.104	0.045	0.037
20	1.17	1.15	0.291	0.29	2.18	2.25	0.091	0.11	0.024	0.043

Depth cm	Fe mg L^{-1} sampler A	Fe mg L^{-1} sampler B	Mn mg L^{-1} sampler A	Mn mg L^{-1} sampler B	Zn µg L^{-1} sampler A	Zn µg L^{-1} sampler B	Pb µg L^{-1} sampler A	Pb µg L^{-1} sampler B	Cu µg L^{-1} sampler A	Cu µg L^{-1} sampler B
-1	0.014	0.016	<10	<10	120	97	<6	<6	<2	7
0	0.031	0.015	<10	0.01	100	80	<6	<6	<2	7
1	0.013	0.031	<10	0.089	110	177	<6	<6	4	3
2	0.013	0.029	0.13	0.91	210	251	<6	<6	<2	5
3	0.025	0.034	0.575	2.14	251	91	<6	<6	<2	3
4	0.143	0.081	1.63	2.51	113	52	15	<6	<2	3
5	0.326	0.239	2.28	2.74	58	57	7	13	<2	2
6	0.364	0.5	2.5	2.87	58	58	10	7	<2	2
7	0.411	0.67	2.61	2.84	71	67	12	12	<2	2
8	0.432	0.75	2.87	2.88	<20	79	12	15	<2	3
9	0.442	0.8	2.84	2.8	81	110	13	9	5	2
10	0.52	0.91	2.8	2.74	112	105	16	8	2	2
15	0.57	1.27	2.93	2.67	147	164	51	38	2	3
20	0.81	0.87	2.97	2.94	145	174	73	23	3	2

Table 5. Water content and interstitial porewater data from cores collected in Coeur d'Alene Lake.
n.d. = no data given in unpublished reports.

CHATCOLET SITE

Depth interval	wet weight	dry weight	porosity	pH	Ca	Mg	Cl	SO$_4$	Fe	Mn	Zn	Pb	Cu	Cr	Cd
cm	g	g			mg L^{-1}	mg L^{-1}	mg L^{-1}	mg L^{-1}	mg L^{-1}	mg L^{-1}	μg L^{-1}	μg L^{-1}	μg L^{-1}	μg L^{-1}	μg L^{-1}
0-2	1.4	0.369	0.881	7.5	3.111	1.007	0.092	0.064	4.628	1.828	1027	<6	37	<5	0.5
2-4	0.5	0.201	0.798	7.06	4.023	1.398	0.102	0.03	13.236	2.116	436	<6	76	<5	0.42
4-6	0.92	0.728	0.411	6.95	7.182	1.207	0.106	0.036	13.154	2.288	1893	<6	7	<5	14
6-8	3.46	1.518	0.772	6.96	7.121	1.397	n.d.	n.d.	17.336	2.684	1110	<6	58	<5	2.2
8-10	0.63	0.568	0.224	6.98	9.268	1.399	0.136	0.029	20.056	2.524	3970	<6	64	<5	0.43
14-16	1	0.662	0.575	6.85	8.239	1.987	0.18	0.038	20.868	3.624	3000	<6	433	<5	0.42
19-21	1.4	0.996	0.518	6.83	9.39	1.802	0.174	0.03	15.022	2.974	910	<6	84	<5	9.7

DELTA SITE

Depth interval	wet weight	dry weight	porosity	pH	Ca	Mg	Cl	SO$_4$	Fe	Mn	Zn	Pb	Cu	Cr	Cd
cm	g	g			mg L^{-1}	mg L^{-1}	mg L^{-1}	mg L^{-1}	mg L^{-1}	mg L^{-1}	μg L^{-1}	μg L^{-1}	μg L^{-1}	μg L^{-1}	μg L^{-1}
0-2	4	1.841	0.757	8.09	7.466	1.804	0.273	0.227	3.451	3.705	1041	52	8	<5	3.8
2-4	2.7	1.072	0.801	8.22	9.023	1.8	0.731	0.198	6.872	3.214	666	95	5	<5	4
4-6	4	2.292	0.664	8.3	16.831	2.004	n.d.	n.d.	8.607	3.246	603	191	4	<5	2
6-8	2.2	1.125	0.717	8.47	10.263	1.602	n.d.	0.172	11.936	4.452	1073	60	8	<5	2.9
8-10	2.3	1.2	0.708	8.52	4.397	1.999	n.d.	0.317	11.571	8.048	409	77	<2	<5	2
14-16	1.2	0.461	0.809	8.57	4.219	1.206	n.d.	n.d.	17.377	5.778	1538	115	4	<5	2.4
19-21	3.1	1.177	0.812	8.45	7.084	2.003	n.d.	n.d.	17.377	7.6	837	59	3	<5	11

HARLOW POINT SITE

Depth interval	wet weight	dry weight	porosity	pH	Ca	Mg	Cl	SO$_4$	Fe	Mn	Zn	Pb	Cu	Cr	Cd
cm	g	g			mg L^{-1}	mg L^{-1}	mg L^{-1}	mg L^{-1}	mg L^{-1}	mg L^{-1}	μg L^{-1}	μg L^{-1}	μg L^{-1}	μg L^{-1}	μg L^{-1}
0-2	2.35	0.802	0.836	8.45	n.d.	n.d.	n.d.	n.d.	1.969	1.48	1224	251	16	<5	2.4
2-4	1.97	0.696	0.829	8.61	n.d.	n.d.	n.d.	n.d.	5.4	7.49	<20	74	<2	<5	2.5
4-6	2	0.646	0.847	8.65	n.d.	n.d.	0.209	0.099	15.996	1.243	1235	94	33	<5	3.2
6-8	2.6	0.988	0.812	8.63	n.d.	n.d.	0.355	0.131	15.225	12.982	725	147	22	<5	22
8-10	1.64	0.744	0.761	8.62	n.d.	n.d.	0.244	0.107	18.676	15.056	700	876	53	<5	22
14-16	1.08	0.486	0.764	8.37	n.d.	n.d.	0.273	0.205	10.718	17.576	630	382	173	<5	14
19-21	1.58	0.793	0.725	8.7	n.d.	n.d.	0.187	0.15	15.266	16.594	4750	129	236	<5	22

Table 5. Water content and interstitial porewater data from cores collected in Coeur d'Alene Lake.
n.d. = no data given in unpublished reports.

EAST POINT SITE

Depth interval cm	wet weight g	dry weight g	porosity	pH	Ca mg L^{-1}	Mg mg L^{-1}	Cl mg L^{-1}	SO$_4$ mg L^{-1}	Fe mg L^{-1}	Mn mg L^{-1}	Zn μg L^{-1}	Pb μg L^{-1}	Cu μg L^{-1}	Cr μg L^{-1}	Cd μg L^{-1}
0-2	2.8	0.852	0.858	7.32	n.d.	n.d.	n.d.	n.d.	4.06	17.038	1162	142	122	<5	8.6
2-4	1	0.35	0.831	6.99	n.d.	n.d.	n.d.	n.d.	4.304	20.91	609	113	57	<5	2.5
4-6	1.47	0.604	0.792	7.3	n.d.	n.d.	0.112	0.175	3.37	19.71	2451	126	18	<5	1.7
6-8	1.32	0.463	0.831	7.2	n.d.	n.d.	0.108	0.053	3.898	20.858	3153	26	151	<5	1.9
8-10	1.28	0.569	0.768	7.25	n.d.	n.d.	0.111	0.041	9.005	22.4	307	376	125	<5	5.6
14-16	2.32	1.176	0.721	7.4	n.d.	n.d.	0.151	0.342	15.103	19.348	1863	40	39	<5	10.8
19-21	2.25	0.907	0.797	7	n.d.	n.d.	0.142	0.079	22.04	15.93	748	221	73	<5	3.6
29-31	1.76	0.77	0.773	7	n.d.	n.d.	0.152	0.103	19.075	14.328	885	69	90	<5	0.34

VALHALLA SITE

Depth interval cm	wet weight g	dry weight g	porosity	pH	Ca mg L^{-1}	Mg mg L^{-1}	Cl mg L^{-1}	SO$_4$ mg L^{-1}	Fe mg L^{-1}	Mn mg L^{-1}	Zn μg L^{-1}	Pb μg L^{-1}	Cu μg L^{-1}	Cr μg L^{-1}	Cd μg L^{-1}
0-2	1.87	0.25	0.945	7.23	n.d.	n.d.	0.11	0.283	3.085	8.144	4234	31	<2	<5	2.2
2-4	1.66	0.25	0.937	7.5	n.d.	n.d.	0.101	0.15	2.639	14.234	204	17	<2	<5	14
4-6	1.59	0.244	0.936	7.44	n.d.	n.d.	0.097	0.044	3.898	19.266	923	52	<2	<5	26
6-8	1.76	0.272	0.935	7.55	n.d.	n.d.	0.157	0.025	5.178	24.732	473	91	<2	<5	1.2
8-10	2.09	0.305	0.939	7.43	n.d.	n.d.	0.108	0.051	7.349	24.845	1542	7	<2	<5	11
14-16	2.6	0.819	0.852	7.11	n.d.	n.d.	0.121	0.019	14.129	22.005	283	287	<2	<5	11
19-21	2.82	0.719	0.886	7.79	n.d.	n.d.	0.121	0.034	13.073	15.89	8188	142	<2	<5	3.5
24-26	1.6	0.173	0.956	7.82	n.d.	n.d.	0.129	0.044	11.449	10.635	579	291	<2	<5	0.11

Table 6. Summary of in-situ diffusion coefficients (D_s) at bottom water temperatures used in molecular diffusive calculations.

Site	Temperature ^0C	D_s for Zn^{2+} $cm^2\ d^{-1}$	D_s for Pb^{2+} $cm^2\ d^{-1}$	D_s for Cu^{2+} $cm^2\ d^{-1}$	D_s for Mn^{2+} $cm^2\ d^{-1}$
Chatcolet	14	0.329	0.435	0.337	0.316
Delta	9.5	0.214	0.282	0.219	0.206
Harlow Point	9.5	0.261	0.345	0.268	0.251
East Point	9.5	0.275	0.363	0.282	0.265
Valhalla	7.5	0.316	0.418	0.324	0.304

Table 7. Summary of molecular diffusive benthic fluxes and river fluxes for metals in Coeur d'Alene Lake. n.d. = no data available for metal loading.

Site		Zn flux $\mu g\ cm^{-2}\ y^{-1}$	Pb flux $\mu g\ cm^{-2}\ y^{-1}$	Cu flux $\mu g\ cm^{-2}\ y^{-1}$	Mn flux $\mu g\ cm^{-2}\ y^{-1}$
Chatcolet	sampler A	0	0	-0.11	-3.5
Chatcolet	sampler B	0	0	0	0
Chatcolet	core	106	0	3.3	179
Delta	sampler A	23	87	-0.06	17
Delta	core	55	3.6	-0.06	209
Harlow Point	sampler A	3	11	1.1	108
Harlow Point	sampler B	6.5	0	0.16	100
Harlow Point	core	92	26	1	113
East Point	sampler A	39	29	0.71	146
East Point	sampler B	-1.6	0	0.18	0
East Point	core	92	15	11	1411
Valhalla	sampler A	0	0	0.45	0
Valhalla	sampler B	19	0	-0.89	17
Valhalla	core	451	3.6	4.4	853
St. Joe River	1991	66	21	16	n.d.
St. Joe River	1992	35	8	7.8	n.d.
CdA River	1991	678	218	16	n.d.
CdA River	1992	327	46	7.6	n.d.

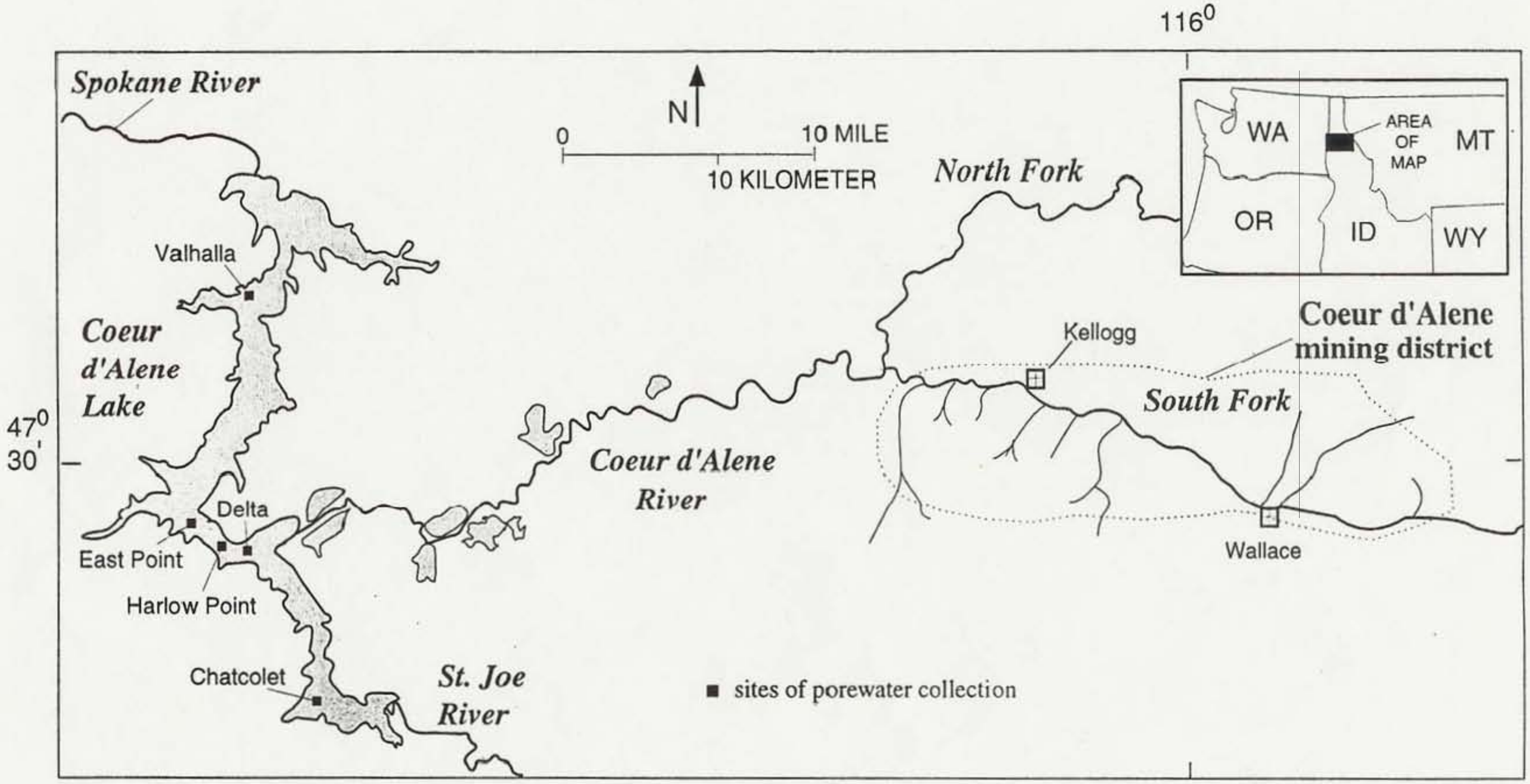

Figure 1. Location of Coeur d'Alene Lake and sites of porewater collection.

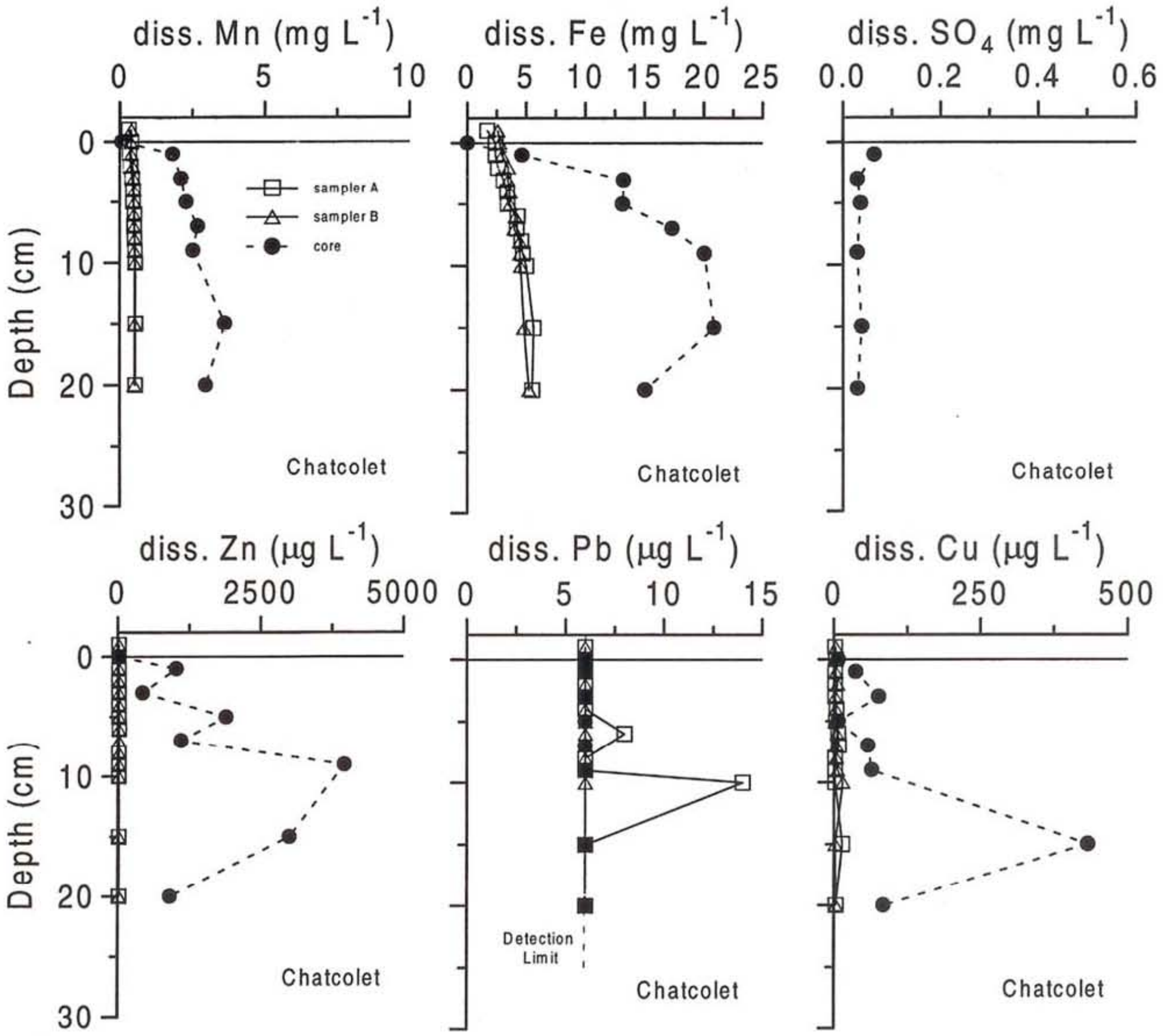

Figure 2. Porewater profiles of Mn, Fe, SO_4, Zn, Pb, and Cu at the Chatcolet site.

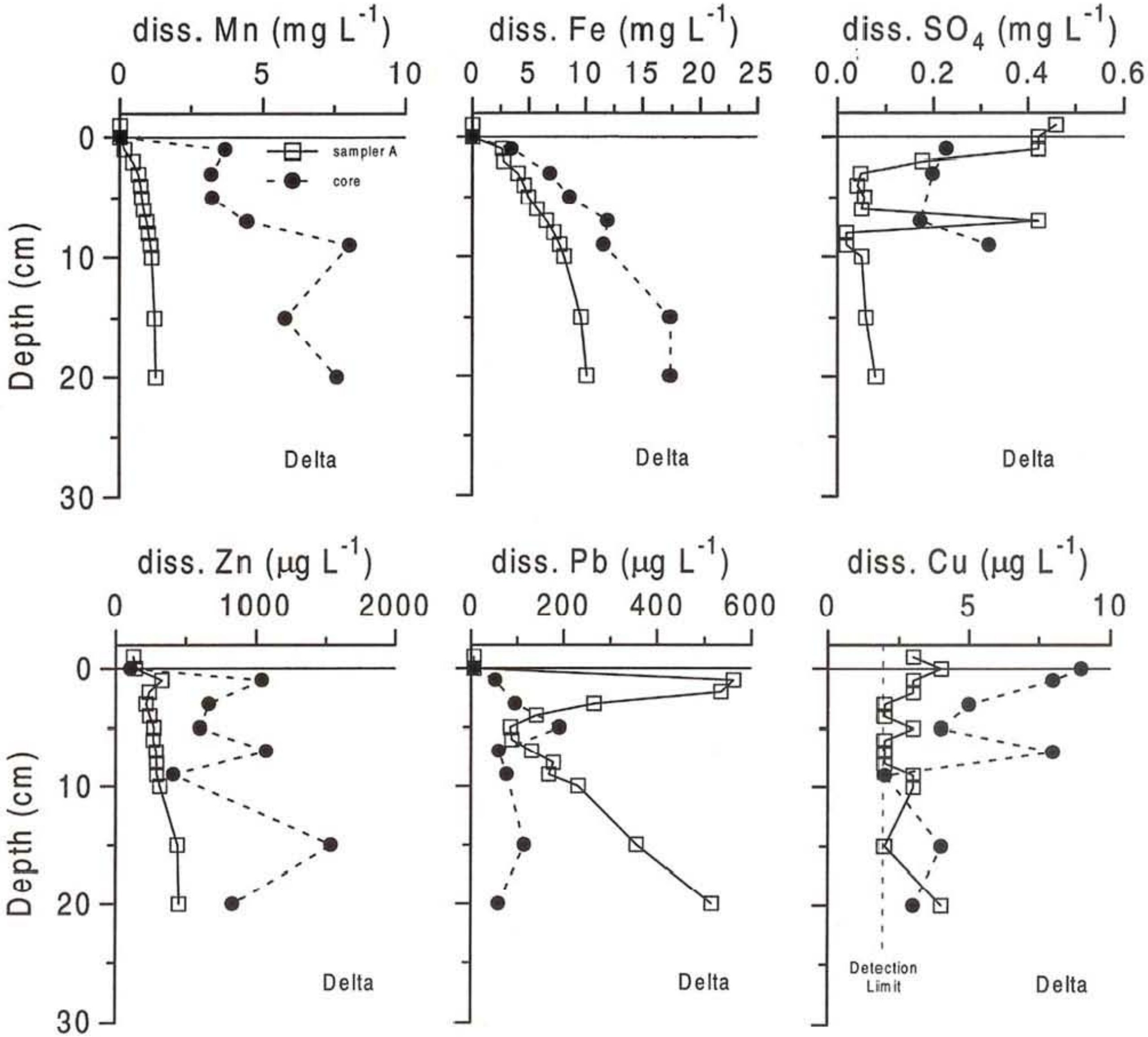

Figure 3. Porewater profiles of Mn, Fe, SO_4, Zn, Pb, and Cu at the Delta site.

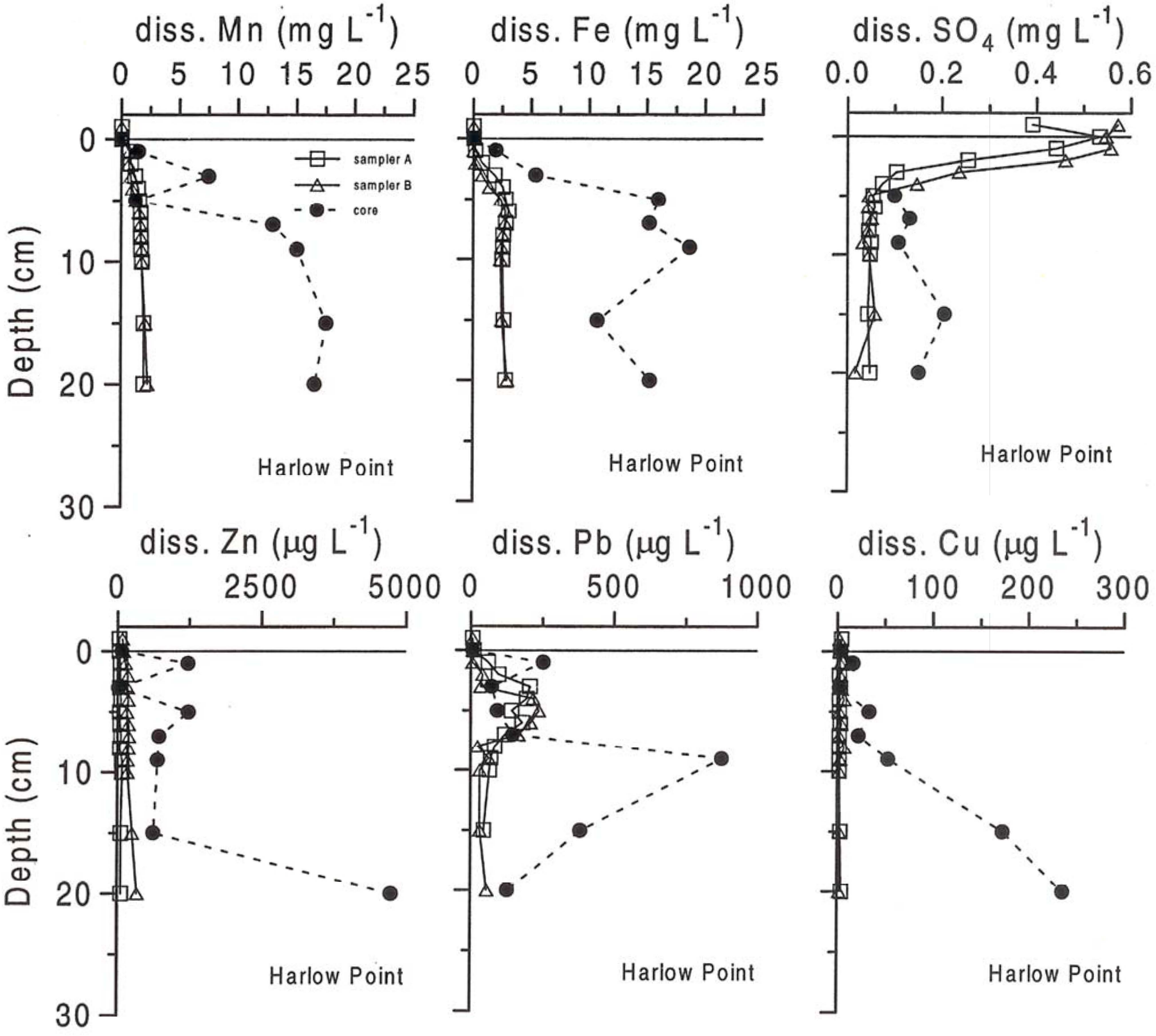

Figure 4. Porewater profiles of Mn, Fe, SO$_4$, Zn, Pb, and Cu at the Harlow Point site.

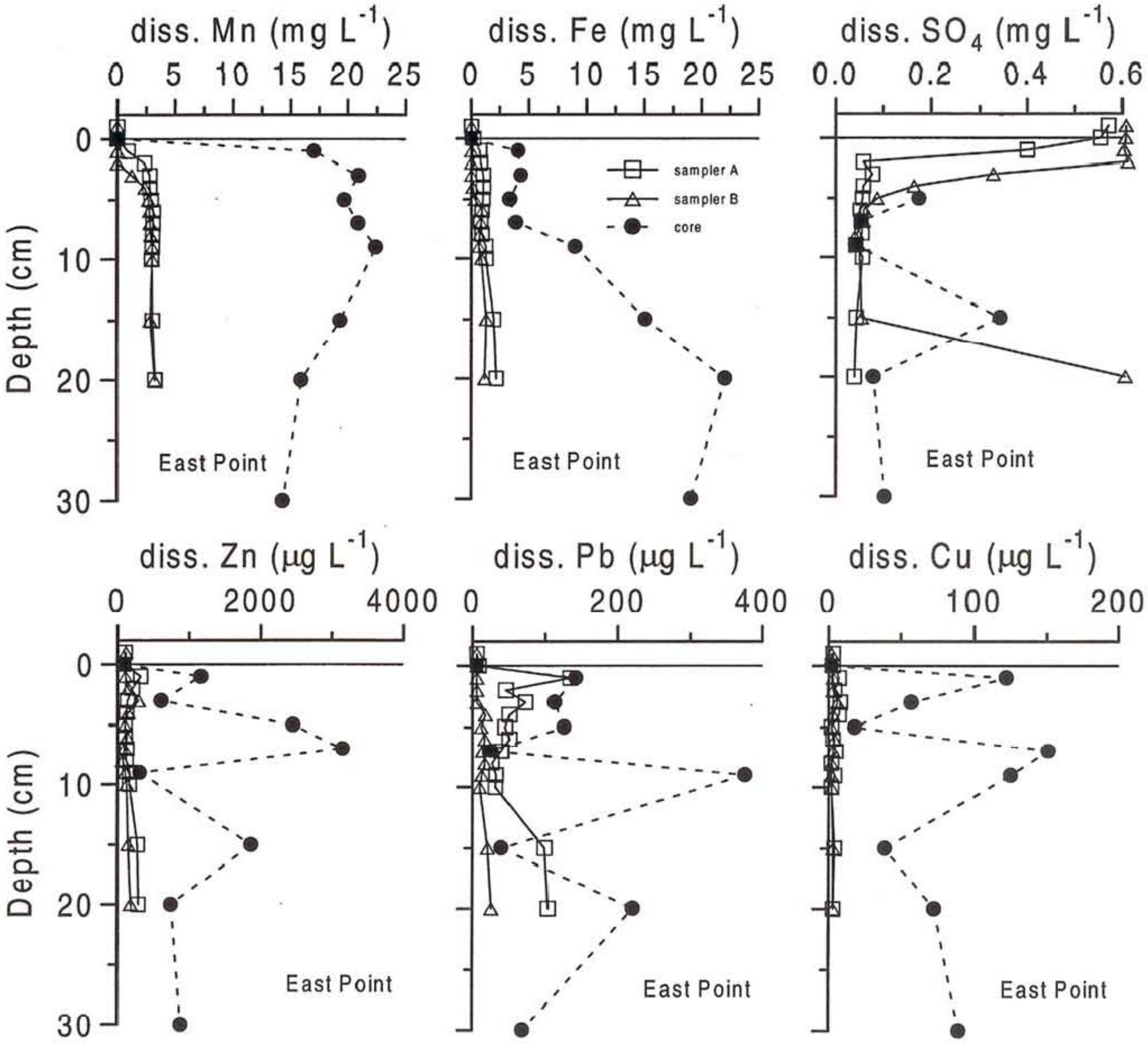

Figure 5. Porewater profiles of Mn, Fe, SO_4, Zn, Pb, and Cu at the East Point site.

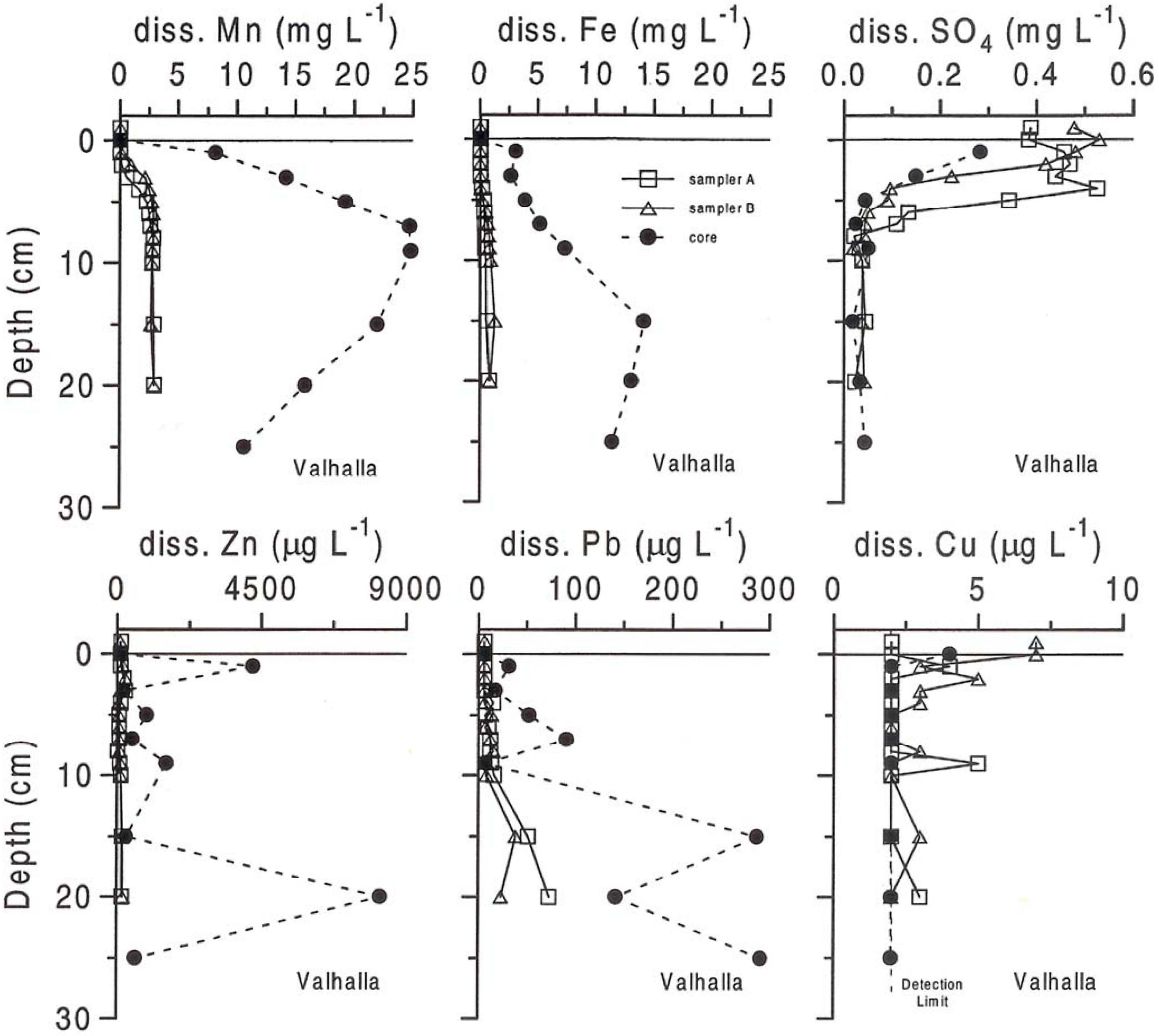

Figure 6. Porewater profiles of Mn, Fe, SO$_4$, Zn, Pb, and Cu at the Valhalla site.

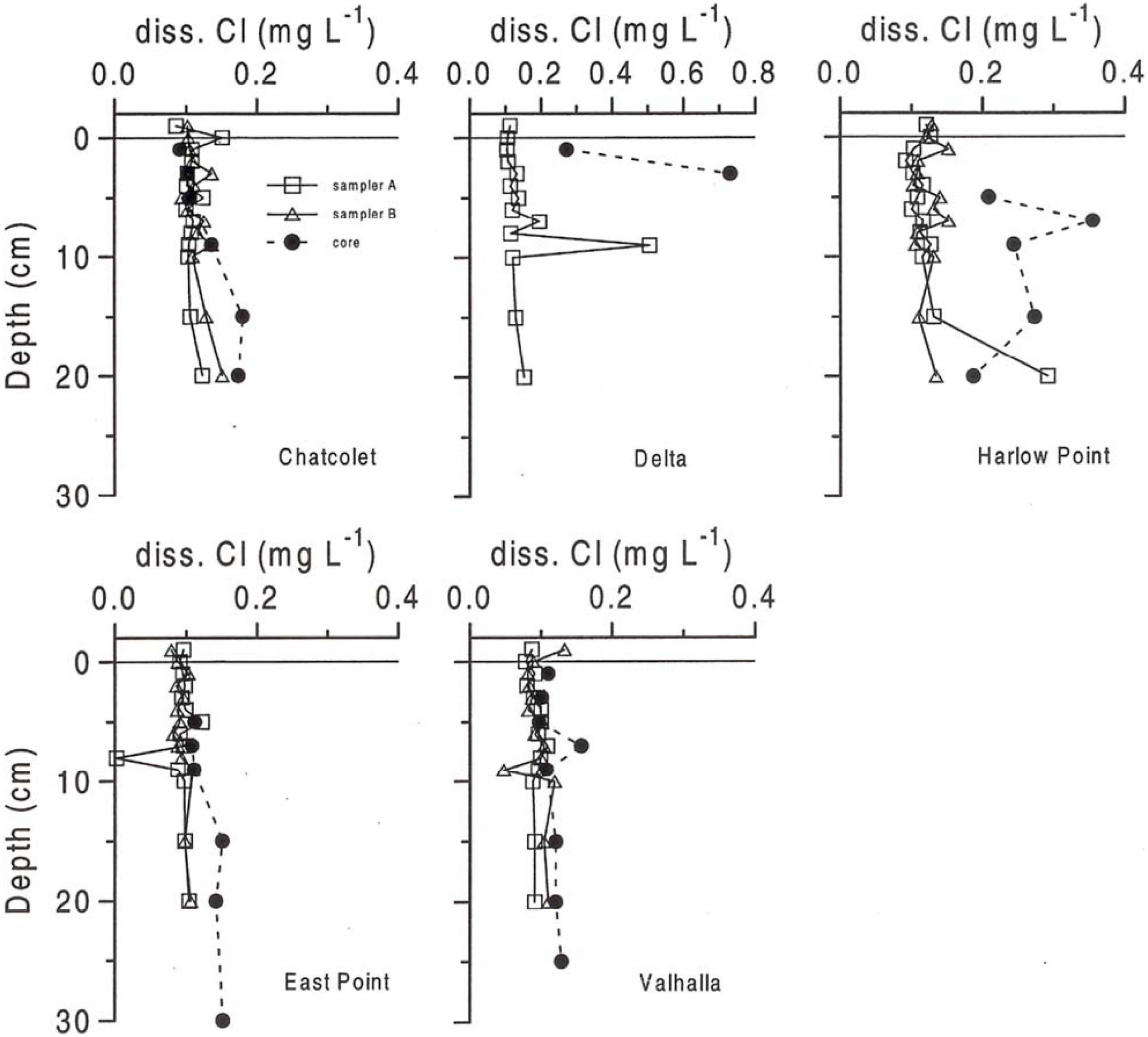

Figure 7. Porewater profiles of Cl at all sites.

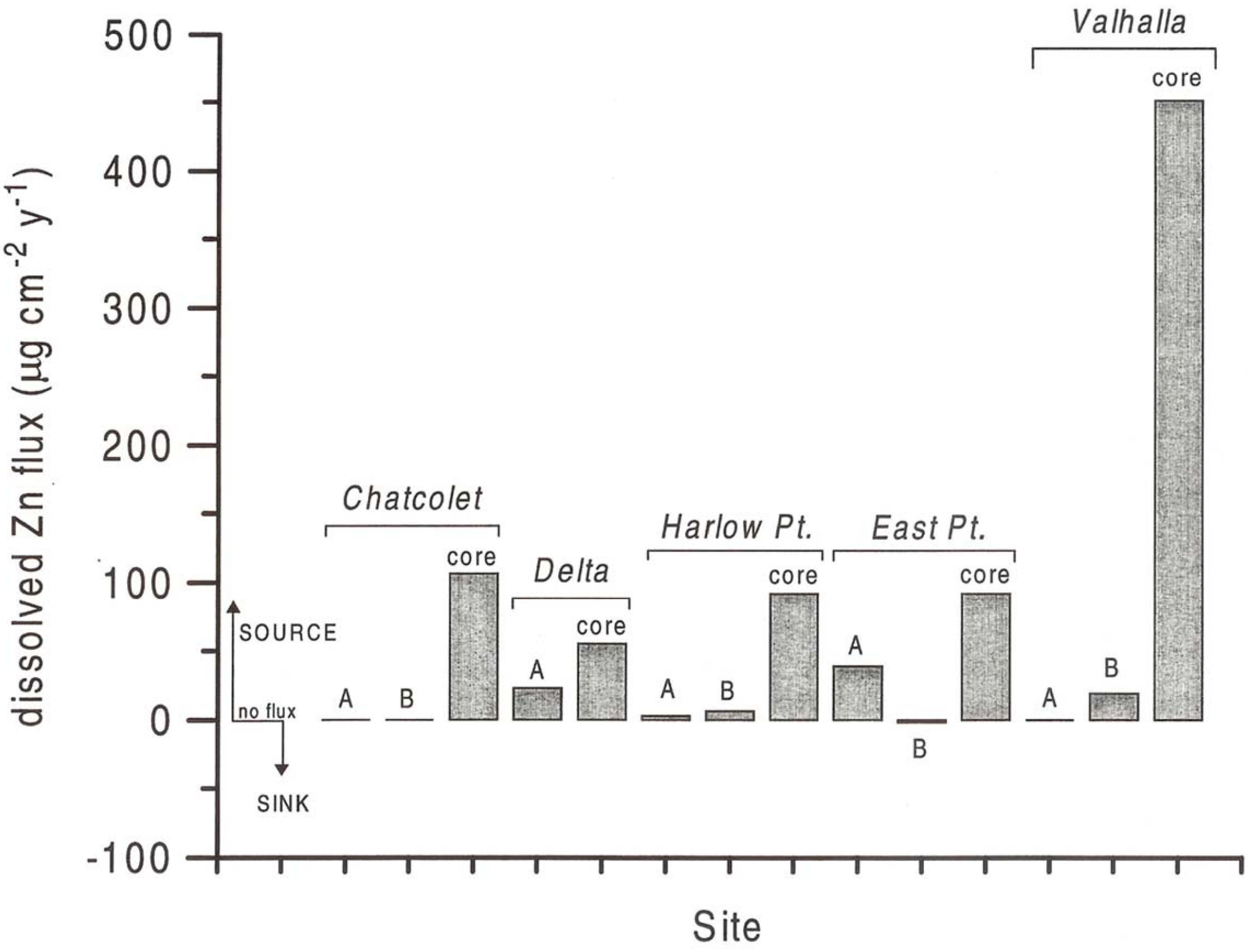

Figure 8. Molecular diffusive fluxes of Zn across the sediment-water interface in Coeur d'Alene Lake.

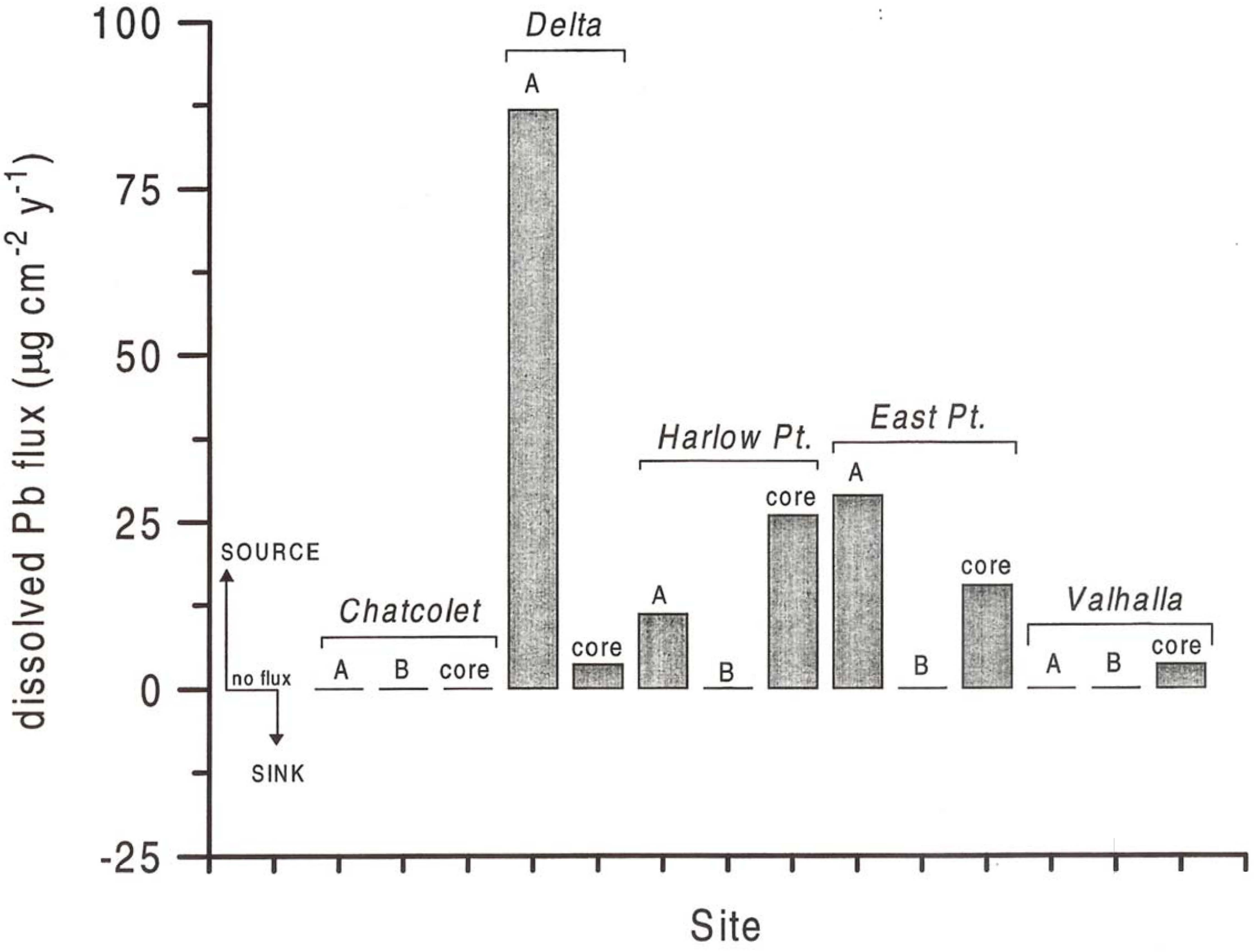

Figure 9. Molecular diffusive fluxes of Pb across the sediment-water interface in Coeur d'Alene Lake.

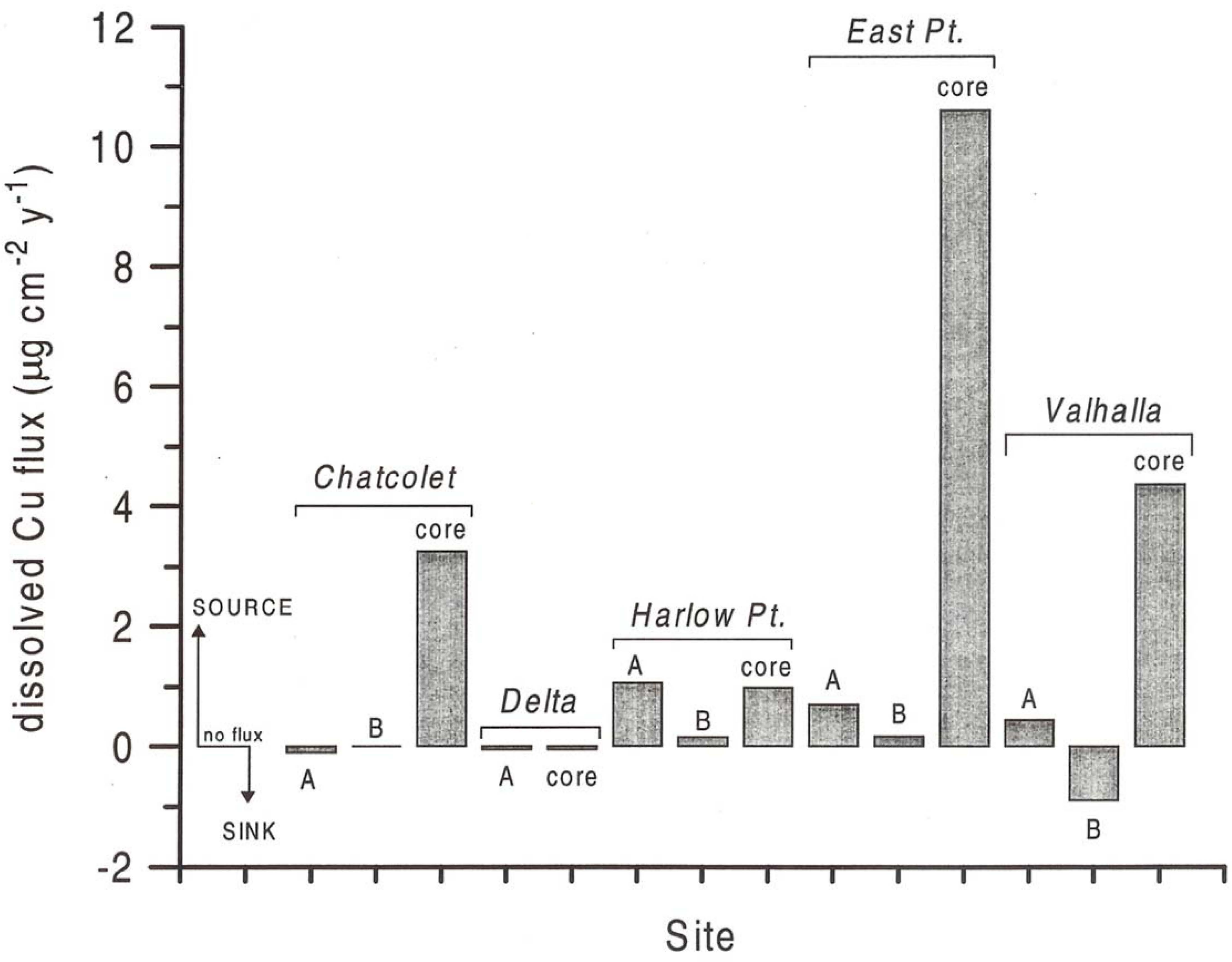

Figure 10. Molecular diffusive fluxes of Cu across the sediment-water interface in Coeur d'Alene Lake.

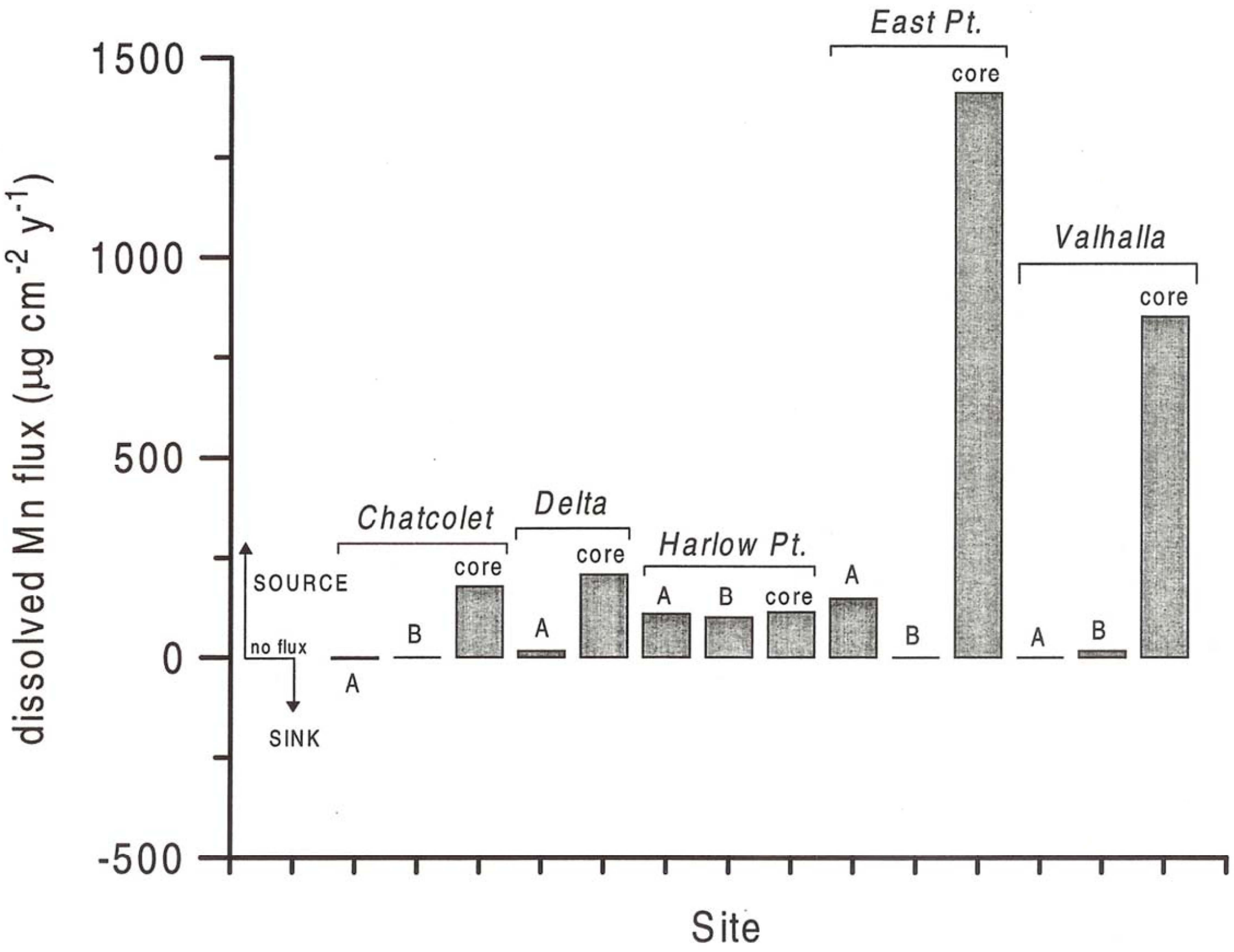

Figure 11. Molecular diffusive fluxes of Mn across the sediment-water interface in Coeur d'Alene Lake.

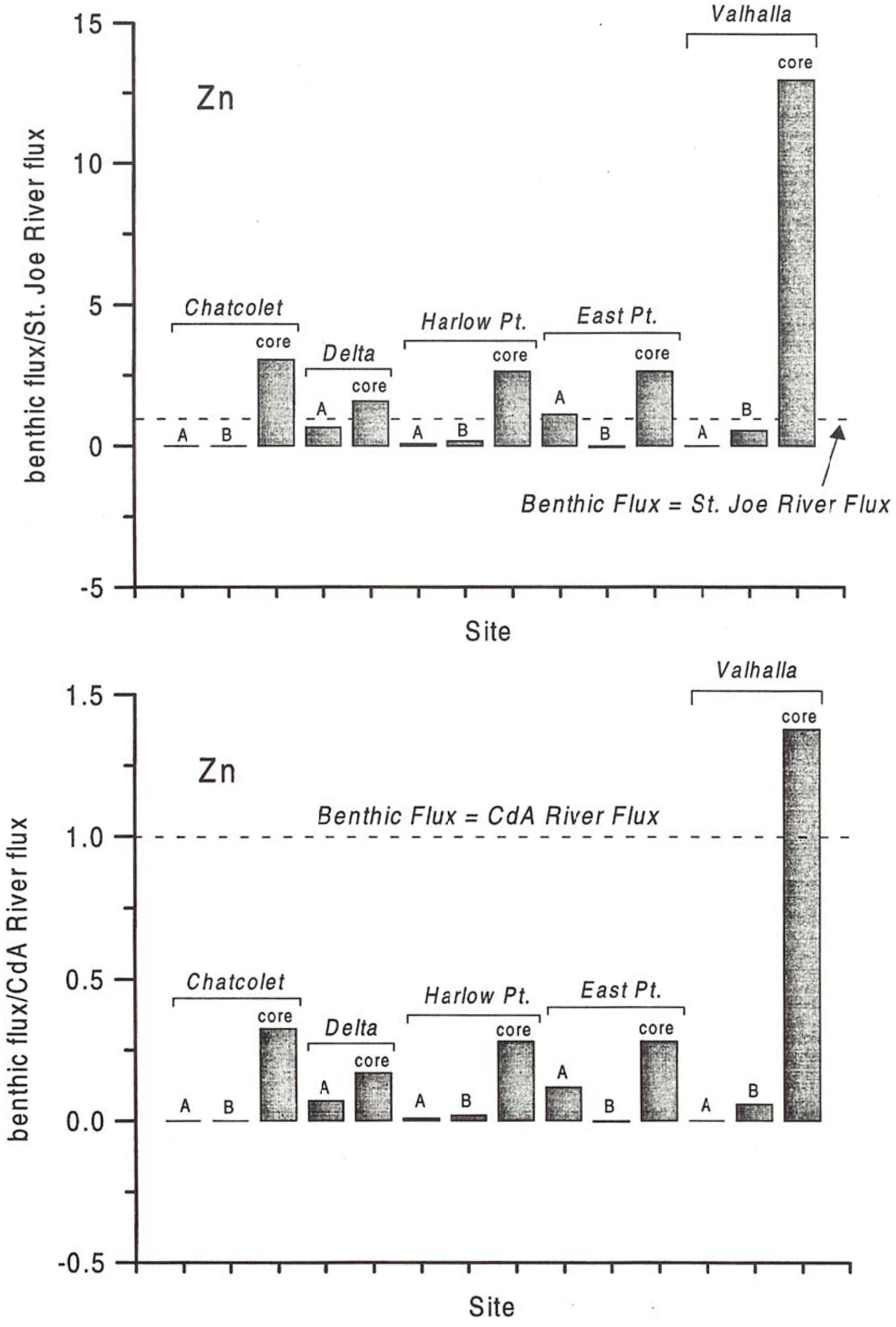

Figure 12. Ratio of benthic fluxes to river fluxes for Zn during 1992.

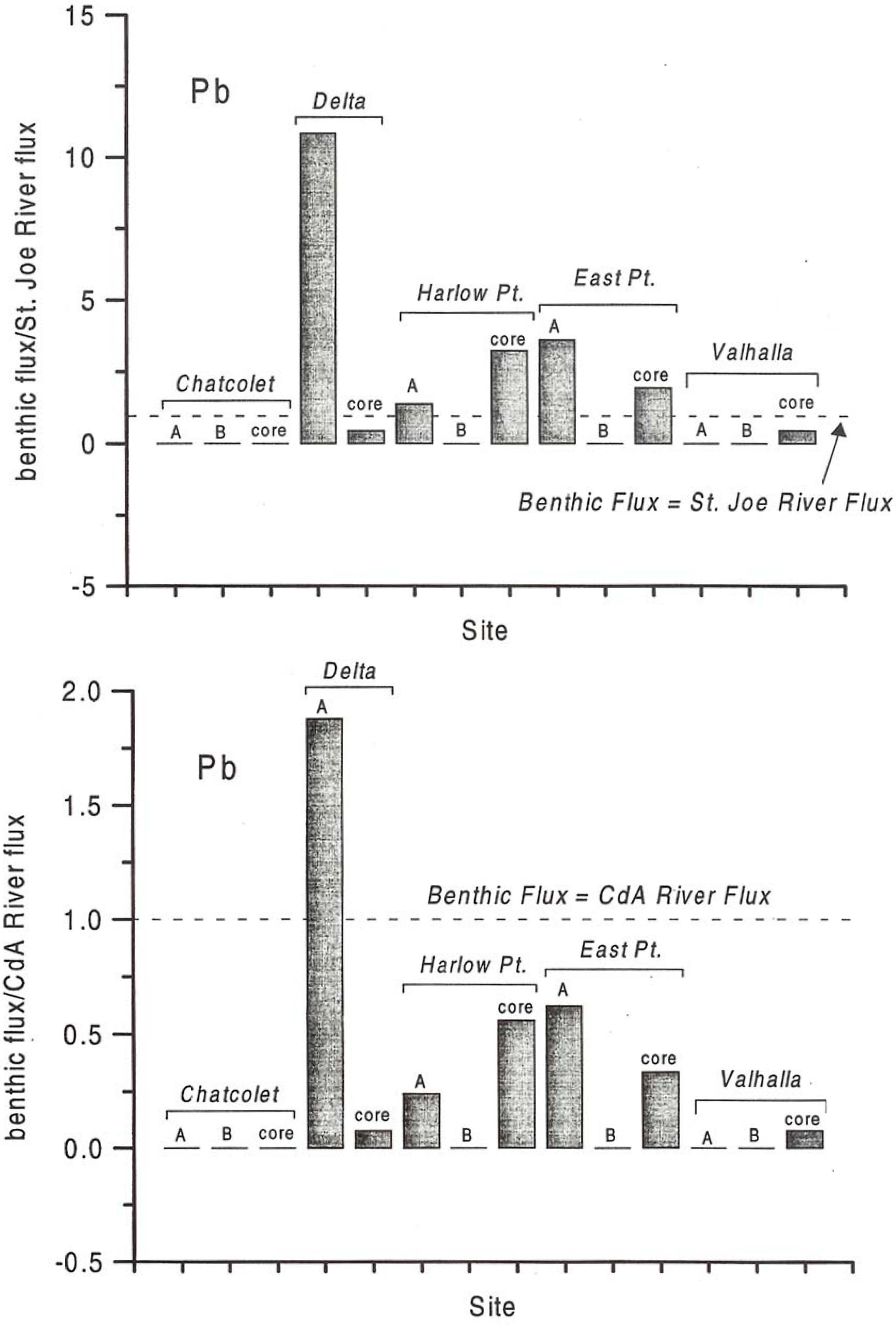

Figure 13. Ratio of benthic fluxes to river fluxes for Pb during 1992.

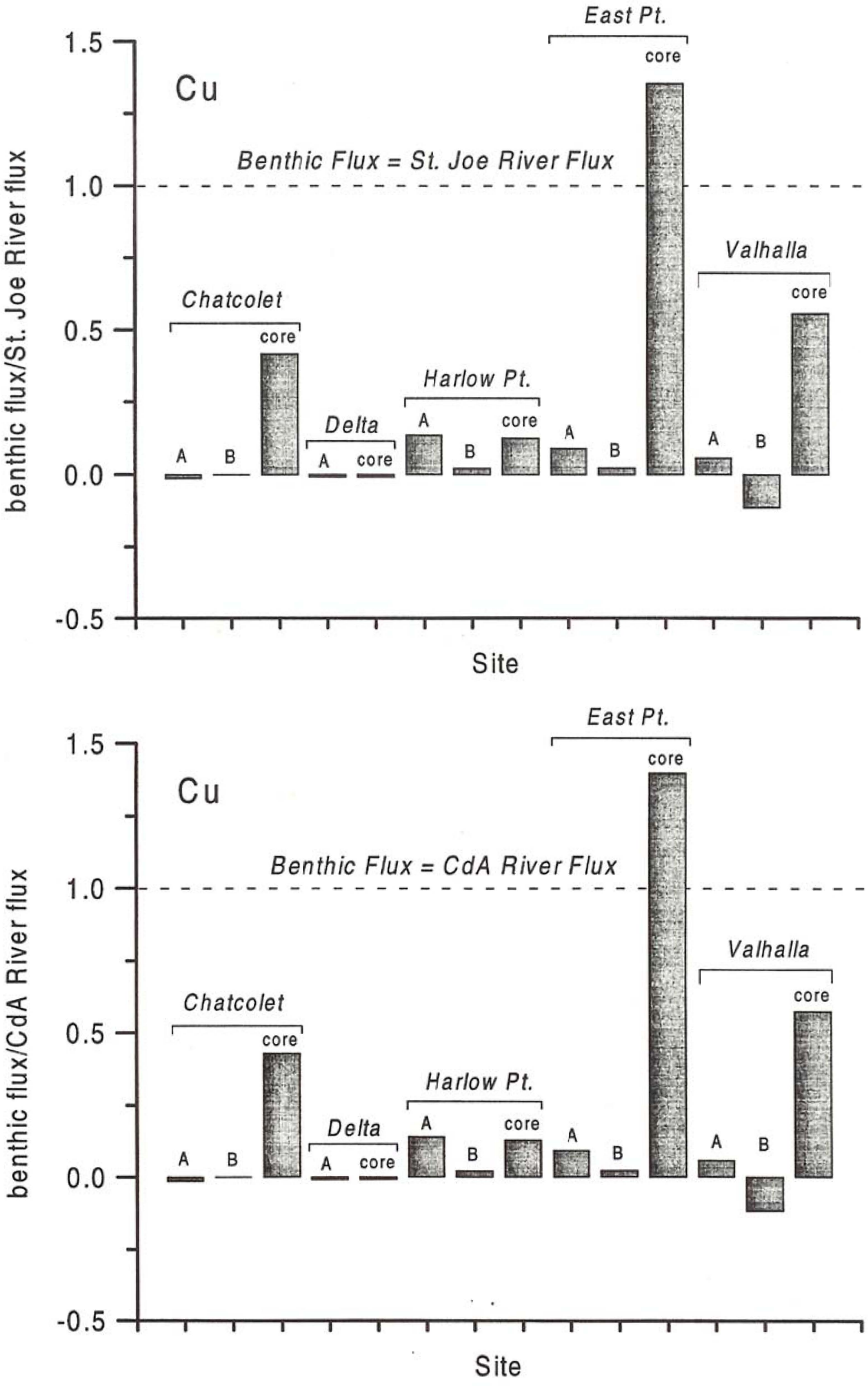

Figure 14. Ratio of benthic fluxes to river fluxes for Cu during 1992.