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Phase Associations and Mobilization of Iron and Trace Elements in Coeur d'Alene Lake, Idaho

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Sediments of Coeur d'Alene Lake, ID, are heavily contaminated with mine tailings that contain high levels of iron, lead, zinc, arsenic, and other trace elements. These tailings originate from the Silver Valley mining district drained by the South Fork of the Coeur d'Alene River. The possibilities that either lake eutrophication or the development of a seasonally anoxic hypolimnion could mobilize trace elements from sediments into overlying waters led us to evaluate their phase associations. Analysis of ∼0.5 m gravity cores reveals these sediments to be highly reduced, and the trace elements therein predominantly associated with an operationally defined sulfidic phase. Vertical patterns of metal distribution suggest that Fe, Mn, and As have mobilized toward the sediment−water interface; these patterns are consistent with diagenetic solubilization. This is not the case for Zn, Pb, and other trace elements whose maximum abundance is generally found in deeper sediments. We postulate that metal sulfide formation and metal binding with organic material restricts mobilization of most trace elements. The abundance of redox-active elements such as As, Fe, and Mn is highly correlated by depth. The abundance of less redox-sensitive elements such as Pb and Zn is also highly correlated; however, the two groups correlate poorly with one other.

Introduction

Coeur d'Alene Lake, ID: General Description. Coeur d'Alene Lake is Idaho's second largest lake, covering about 129 km^2. Fed in the south by two rivers, the St. Joe (SJR) and the Coeur d'Alene (CDAR) and drained in the north by the Spokane River, Coeur d'Alene (CDA) Lake has become a collecting bed for sediments produced by human activities in its two major drainages (see Figure 1). These activities are predominantly mining and ore processing, logging, and agriculture along the CDAR, and logging and agriculture along the SJR (*1*). Mining and mineral processing on the south fork of the CDAR has affected water and sediment quality to the extent that trace element concentrations in the sediment pore water are characterized as acutely toxic to freshwater biota, and the sediment quality has been classified as severely affected by arsenic, cadmium, lead, and zinc (*1*). Horowitz et al. (*2*) surveyed (∼1 sample/km^2) surficial lake sediments for trace element contamination and concluded that the vast majority of the lake sediment surface was enriched with Ag, As, Cd, Cu, Fe, Hg, Mn, Pb, Sb, and Zn, as compared with uncontaminated sediments. This agrees with the conclusions reached by many other researchers (e.g., refs *3* and *4*).

CDA Lake appears to be variable in trophic status as inferred from total nitrogen and phosphorus levels. On the basis of 1991−92 data, the southern end near Lake Chatcolet was classified as mesotrophic-eutrophic, while the rest of the lake was determined to be oligotrophic-mesotrophic (*1*). However, at times during the 1970s, anoxic conditions were reported in many parts of the lake (*5*), suggesting eutrophication. Recent studies have reported a decrease in both nitrogen and phosphorus loading by the St. Joe (SJR) and Coeur d'Alene Rivers (CDAR) relative to that observed in the 1970s and 1980s (*1, 5*). Nonetheless, many authors have raised a concern (e.g., refs *1* and *2*) that eutrophication and the concomitant development of a seasonally anoxic hypolimnion could combine to significantly raise concentrations of toxic trace elements, as well as soluble N and P in CDA Lake waters. Release of such elements would severely impact aquatic organisms and imperil the six community water supply systems that utilize CDA Lake water (*1*).

Seasonal anoxia is not the only mechanism that might favor the release of sediment nutrients and/or toxic trace metals. Redox transformation of trace elements by metal-respiring bacteria can change the solubility and, hence, mobility of these elements within the sediment environment (*6*−*8*). Metals may also be immobilized as sulfides consequent to the release of H_2S by sulfate-reducing bacteria (SRB) (*7*). In addition, Baccini (*9*) has shown that lake sediment iron concentration strongly influences phosphorus flux from sediments. Indeed, a lake with high sediment Fe concentration and a hypoxic hypolimnion may have phosphorus release into its overlying waters equivalent to another lake with low Fe concentrations and an oxic hypolimnion (*9*). We note that to the extent that iron-reducing bacteria (IRB) control the relative abundance of oxidized iron within sediments, these organisms may indirectly affect sediment phosphorus flux. Clearly, many factors besides trophic status need to be examined in order to evaluate the risk posed by contaminated CDA Lake sediments under conditions of local and/or seasonal eutrophication.

The Nature of Trace Element Enrichment in Coeur d'Alene Lake Sediments. There is a consensus in the literature that CDA Lake sediments are contaminated and that the CDAR continues to act as the principal source for trace element-rich sediments. Although tailings ponds have been constructed in the mining district, influx of metal into the lake from the CDAR continues as a result of resuspension of tailings-rich stream sediments (*2, 3, 10*). Information about the phase partitioning of metals within these sediments is limited to two studies. Mok and Wai (*11*) measured dithionite-reducible iron in CDAR sediments in order to assess their potential for binding As. They reported an average of 2500 mg of Fe/kg of sediment in that phase. Iron extractable by dithionite is usually present as Fe(III) (hydr)oxides, compounds which have been shown to have high affinities for As (*11*). Horowitz et al. (*2*) performed sequential dissolution on four grab samples from surface sediments of CDA Lake. A 0.25 M hydroxylamine hydrochloride extraction was used to estimate iron oxide-associated metals, and an H_2O_2−HNO_3 extraction was used to estimate metal bound to organic/sulfidic phases. These workers determined that ∼95% Pb,

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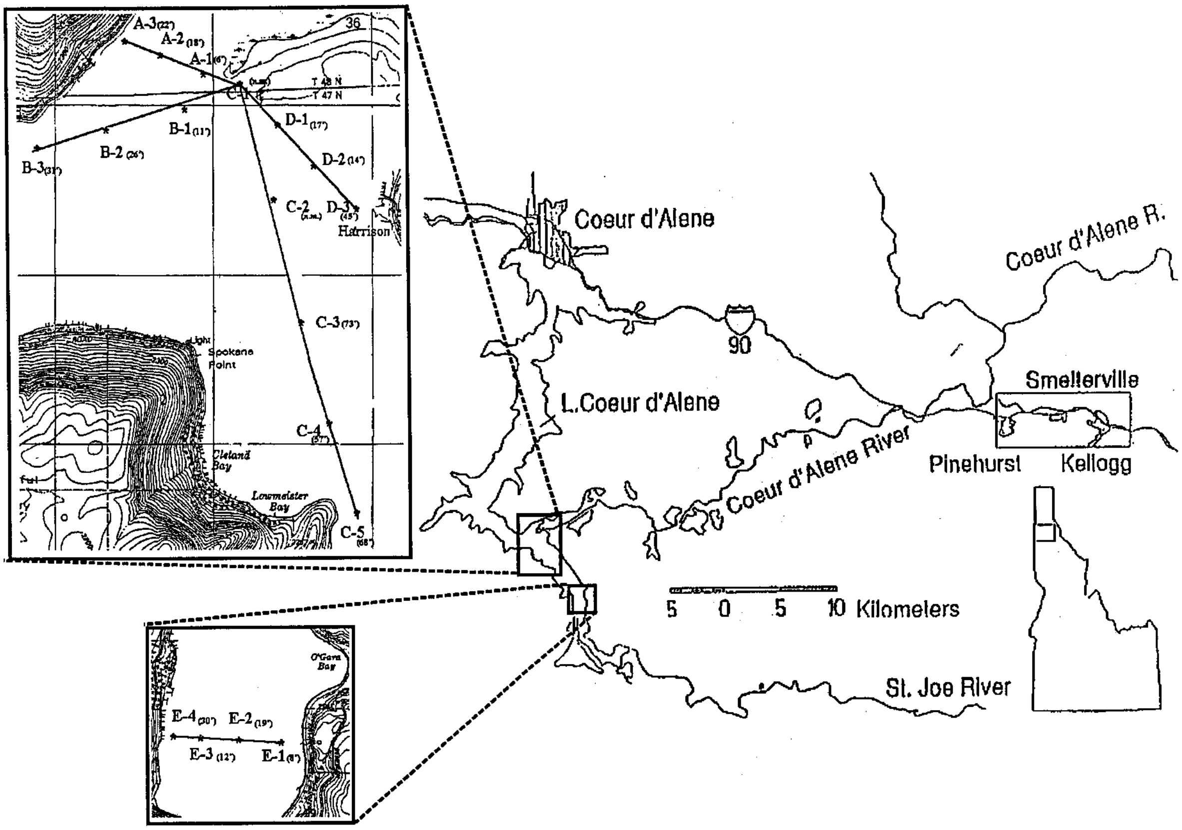

FIGURE 1. Study site showing the region of North Idaho (top), CDA Lake near the contaminated CDAR delta (bottom left), and CDA Lake near the pristine SJR delta (bottom right).

90% Cd, 80% Zn, 75% As, and 55% Cu were released by the first extraction. Horowitz et al. (*2*), therefore, concluded that Fe and Mn oxides represented the dominant hosts for trace metals in surface sediments.

The results presented by Horowitz et al. (*2*) have been criticized by Pedersen (*12*) because sample processing was conducted under aerobic conditions. Pedersen (*12*) also criticizes the two-step procedure utilized by Horowitz on the basis that it was designed for aerobic sediments, not anaerobic sediments. Furthermore, inasmuch as carbonates were not removed prior to oxide dissolution, the selectivity of the extraction procedure is questionable (*12, 13*). Hence, these results must be interpreted with caution. Sequential extraction of sediments below the top 2 cm was not performed by Horowitz et al. (*14*) because evidence of oxidation was observed in the cores shipped back to the laboratory.

To date, only visual or inferential evidence (e.g., color, vertical metal distribution) has been offered to assess the redox status of CDA Lake sediments (*14, 15*). Furthermore, detailed phase-partitioning of the sediments has not been performed (*3, 10, 14*). Reduction potential measurements and phase partitioning analyses are necessary prerequisites to establishing whether trace elements are likely to remain permanently buried or subject to postdepositional remobilization. Such data would also help disclose whether oxide formation in CDA Lake sediments is authigenic, or whether these oxides have been formed primarily on the CDAR plain and banks, as suggested by Horowitz et al. (*2, 14*). If measurement of these parameters reveals metals to be bound predominantly in reduced phases, such as metal sulfides, the threat of metal release postulated under eutrophic or seasonally anoxic conditions may require reevaluation.

In this study, we seek to extend and clarify understanding of the phases and associations of trace elements in CDA Lake, and to help provide a rational basis for predicting their interactions within the sediments and overlying waters. Sequential dissolution analyses, redox and pH measurements, estimates of bacterial densities, as well as correlation analyses of trace element abundance by depth are combined with previous data to describe phase associations and mobilities of trace elements in CDA Lake sediments. On the basis of these findings, we speculate on the relative potentials for trace metal burial or resolubilization within these environments.

Materials and Methods

Sediment Sampling. Deep sediment cores [$x = 46 \pm 9$ cm (SD)] were removed from CDA Lake (Figure 1) using a gravity-coring device (*16*). Sediments processed for measurement of total trace element abundance and sequential dissolution analysis were frozen immediately in dry ice, then stored in the laboratory at −80 °C (March 1994). Sediment cores were cut in half while frozen solid; one side was used for total metal analyses, the other for sequential dissolution analyses. Cores were subsampled from homogenized 4 cm intervals for total metal analysis, and homogenized 8 cm intervals for sequential dissolution analysis. Care was taken not to sample from the cut surfaces of the cores. Sediment cores collected for Eh/pH measurements and estimates of bacterial density were stored vertically at 4 °C, and purged continuously with N_2(g) (March 1995). Cores were assayed within 12 h of collection.

Estimates of pH, Reduction Potential, and Microbial Abundance. Redox potentials were measured by platinum electrode on cores freshly extruded in a positive pressure nitrogen atmosphere, and adjusted to the standard hydrogen electrode (SHE). pH measurements were performed on these same cores with a portable pH probe and meter (Cole Palmer). Bacterial densities were estimated by epifluorescence microscopy using acridine orange (*17*).

TABLE 1. Mean Values (mg/kg) of Selected Elements in CDA Lake and SJR Delta Cores

		Pb ± SE (range)	Zn ± SE (range)	Mn ± SE (range)	Fe ± SE (range)	As ± SE (range)	P ± SE (range)
SJR delta cores	*N* = 42	78 ± 15 (294−20)	751 ± 41 (1744−100)	349 ± 32 (618−208)	27 642 ± 364 (3560−2260)	12 ± 3 (17−3)	681 ± 92 (1290−510)
CDA Lake cores	*N* = 206	3820 ± 241 (21 413−42)	2995 ± 125 (11 169−103)	5953 ± 173 (9208−409)	82 486 ± 1694 (123 200−21 500)	201 ± 11 (568−2)	560 ± 18 (1320−190)
Fold increase		49	4	17	3	17	0.8
CDA Lake cores below contaminated zone[a]	*N* = 19	124 ± 14 (200−2)	156 ± 22 (342−2)	781 ± 48 (1018−142)	37 618 ± 457 (55 670−22 100)	10 ± 1 (17−1)	1074 ± 121 (1610−670)

[a] Refers to a sediment depth where lead concentrations are at or below 200 ppm.

Analytical Techniques. Total iron and trace element abundance was determined by ICP (inductively coupled plasma) analysis of aqua regia-digested sediment. Metal content of operationally defined phases obtained by selective dissolution was also determined by ICP. Every 20th sample was duplicated, and less than 10% error between samples was detected.

Sequential Extraction Analysis. Selective extractions are common procedures that provide useful information on trace element partitioning within sediment (*18−20*). One should note that sequential extractions are based on operational definitions, and the values generated by such procedures should be interpreted with caution (*21*, *22*). The use of sequential extractions for trace-element partitioning in soils and sediments has drawbacks owing to readsorption of metals onto other sediment fractions (*19*, *23−26*). However, the effects of readsorption may not be as problematic as once thought (*26*). Thus, sequential extractions do allow for a useful comparison between materials, and provide the opportunity to study large numbers of samples, unlike many spectroscopic or microscopic methods.

A sequential extraction procedure was employed that utilized sodium pyrophosphate to remove an organic phase, ammonium oxalate (run in the dark) to remove a phase associated with amorphous inorganic materials such as hydrous iron and manganese compounds, citrate-bicarbonate-dithionite to remove a phase associated with crystalline iron and manganese (hydr)oxides and perchloric acid-boiling nitric acid to dissolve remaining sulfidic compounds. Total metal recovery from the sum of the four fractions was 96 ± 8.2% (SD) compared to the metals measured by aqua regia digest.

Pyrophosphate Extraction. This first extraction (*27*) was performed on sediment samples from which pore water had been extruded using 1 atm positive pressure N_2(g). Fifty milliliters of 0.1 M sodium pyrophospate was added to 1 g (wet weight) samples. The resulting suspensions were placed in 50 mL conical centrifuge tubes, oriented at 45°, then shaken at room temperature in the dark for 12 h at 150 rpm. One drop of Superfloc7 was added, and the suspensions were allowed to settle for 1 h. Centrifugation at 3560*g* for 15 min resulted in separation of liquid and solid phases. The liquid phase was refrigerated at 4 °C until ICP analysis.

Oxalate Fraction. To the solid-phase obtained above, 200 mL of 0.2 M ammonium oxalate (adjusted to pH 3.0 with concentrated HCl) was added. Sediment suspensions were placed in aluminum foil-wrapped tubes, and shaken at 150 rpm for 2 h (*20*). Liquid and solid phases were separated by centrifugation at 3560*g* for 15 min, and the supernatant was refrigerated at 4 °C until ICP analysis.

CBD Fraction. To the remaining sediment, 20 mL of 0.3 M sodium citrate and 2.5 mL of 1 M sodium bicarbonate were added. Suspensions were vortexed vigously, then heated in a water bath to 80 °C. A total of 0.5 g of sodium dithionite was added as a powder, and the solution stirred intermittently while held at 80 °C for 10 min. The solution was then centrifuged at 3560*g* for 15 min. This process was repeated, beginning with the addition of sodium citrate. After the second extraction, a room-temperature wash with citrate-bicarbonate was performed. All three fractions were combined, acidified with 1 mL of concentrated HCl, and diluted to 250 mL (*28*). In using sodium dithionite to extract metals associated with crystalline iron oxides, it is noteworthy that available dithionite reagent contains metal impurities, particularly zinc, that can be as high as 400 ppm (*29*).

Sulfidic Fraction. To the remaining sediment, 1 g of $KClO_3$ was added, followed by 20 mL of concentrated HCl (*30*). This mixture was incubated at 25 °C for 30 min, after which 20 mL of glass distilled H_2O was added. The mixture was vortexed, centrifuged at 3560*g* for 15 min, and the supernatant separated into a second flask. To the pellet, 20 mL of 4 N HNO_3 was added, and the mixture boiled for 20 min in a water bath. Twenty milliliters of a 0.5 g/L KH_2PO_4 solution was then added, and the mixture was allowed to stand at room temperature for 10 min with occasional vortexing. The sample was then centrifuged at 3560*g* for 15 min, and the supernatant was mixed with the previous supernatant and diluted to 200 mL. All extracts were filtered through 0.2 μm nylon filters before ICP analysis.

Results and Discussion

CDA Lake sediments near the mining-impacted CDAR are highly enriched in Fe, Mn, As, Pb, Zn, and other trace elements compared to the relatively pristine sediments obtained near the SJR (see Table 1, Appendix 1, Supporting Information). *Mean* total metal concentrations (in milligrams per kilogram dry weight sediment) for Fe, Mn, As, Pb, and Zn in contaminated sediments are 82 486, 5953, 201, 3820, and 2995, respectively. Mean values (milligrams per kilogram sediment) for Fe, Mn, As, Pb, and Zn in tailings-free sediments are 27 642, 349, 11, 78, and 751, respectively. *Maximum* total metal concentrations detected in contaminated sediments are Fe, 123 200; Mn, 9200; As, 568; Pb, 21 493; and Zn, 11 169.

Examination of the vertical profile of total metal abundance in CDA Lake sediments reveals that different elements have characteristic patterns of distribution. For example, peak abundance of As and Fe is consistently bimodal, whereas Zn and Pb typically show single peaks (Figure 2, panels a and b). Enrichment of As within 15 cm of the sediment−water interface is evident in nearly every core examined. By contrast, maximal values for Zn and Pb are consistently observed at depths ≥30 cm. About half of the cores taken were not deep enough to reveal maxima for Pb and Zn [compared to Horowitz et al. (*14*)]. Not unexpectedly, cores with deeper Pb and Zn peak values were extracted nearer the CDAR delta, where past sampling has shown a much thicker tailings layer (*3*, *14*). Fe shows a bimodal distribution. The major Fe peak generally coincides with the As maximum found near the sediment−water interface, while the minor peak occasionally coincides with Pb and Zn peaks found in deeper sediments.

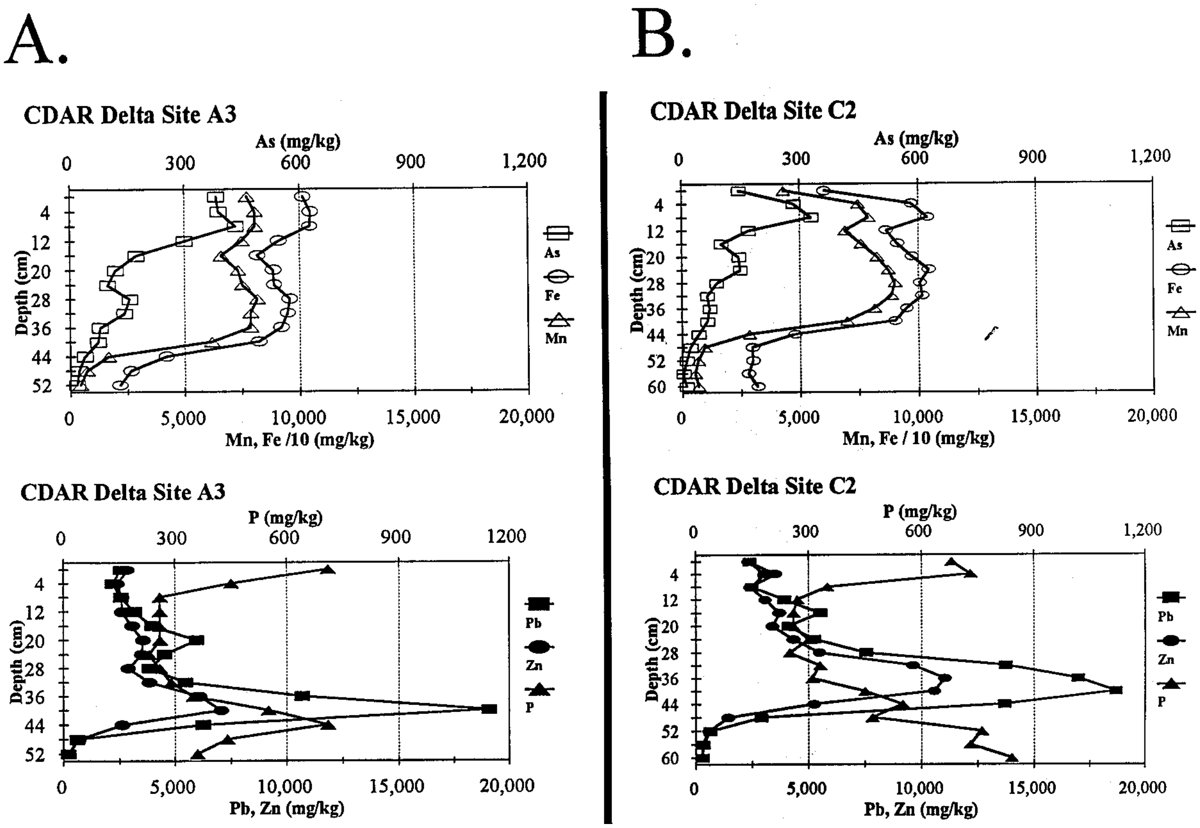

FIGURE 2. CDA Lake sediment cores extracted near the CDAR showing the phenomenon where redox-active (Fe, Mn, As) and redox-inactive (Pb, Zn) elements demonstrate distinct patterns of total abundance. Redox-active elements consistently have surficial maxima, and redox-inactive elements show deeper maxima. (A) Site A-3, (B) site C-2.

TABLE 2. Correlation (*r*) between Selected Elements

	Pb	Zn	Mn	Fe	As	P
		A. CDA Lake Cores (A_1–O_3)[a]				
Pb	1					
Zn	0.90	1				
Mn	0.30	0.55	1			
Fe	0.22	0.46	0.97	1		
As	−0.13	0.07	0.74	0.82	1	
P	−0.21	−0.30	−0.53	−0.48	−0.33	1
		B. SJR Delta Cores (E_1–E_4)[b]				
Pb	1					
Zn	0.69	1				
Mn	0.18	0.55	1			
Fe	0.68	0.71	0.53	1		
As	0.06	−0.10	−0.24	0.01	1	
P	0.78	0.69	0.48	0.83	−0.15	1

[a] $N = 206$. Includes only values where metal contamination exceeds SJR metal concentrations. [b] $N = 42$.

In the contaminated sediments, Fe correlates strongly (Table 2a) by depth with Mn and As ($r = 0.97$ Fe:Mn, $r = 0.82$ Fe:As). These values are in agreement with Horowitz et al. (*14*). Zinc and Pb also correlate strongly with each other by depth ($r = 0.90$). In contrast with the findings of Horowitz et al. (*14*), our data indicate that Fe correlates weakly with Pb ($r = 0.22$) and Zn ($r = 0.46$), and that As correlates very poorly with both Pb ($r = -0.13$) and Zn ($r = 0.07$).

Our data also indicate that, regardless of depth, metals are predominantly associated with an operationally defined sulfidic phase. For Pb and Zn, this fraction represents 49.3 ± 1.4% (SE) and 63.3 ± 1.2% (SE) of the total sediment metal content; for Fe and As, this fraction comprises 67.7 ± 1.4% and 73.3 ± 2.3% (see Figure 3 and Appendix 2, Supporting Information). The next largest fraction of Pb associates with the organic phase [~27.8 ± 1.9% (SE)], in contrast with As, Fe, and Zn whose next largest fractions partition with the amorphous oxide phase (10.3 ± 1.5%, 16.6 ± 1.2%, and 17.2 ± 0.9%, respectively). These results are not directly comparable to those published by Horowitz et al. (*2, 14*) inasmuch as those workers employed a two-step procedure wherein iron oxides were removed prior to the removal of any organic phase. Our method consisted of a five-step procedure wherein the organic phase was removed as the first step in sediment dissolution. Additionally, our samples were frozen in an anaerobic environment and stored at −80 °C until sequential extractions were performed.

CDA Lake sediments near the SJR and CDAR contain abundant bacterial populations. Direct counts reveal a gradient in estimated density from ~10^8 cells/g (wet weight) in the surficial sediments to ~10^6 cells/g (wet weight) in deeper sediments (see Appendix 3, Supporting Information). Our estimates are similar to those observed in other freshwater lake environments (*31*). The average pH of the sediments we examined was generally lower at the surface (pH 5.5), and increased with increasing depth [pH 6.4 (Appendix 3, Supporting Information)]. Bacterial sulfate reduction directly raises pH (*7*). Moreover, utilization of organic acids as electron donors in metal reduction would also serve to increase pH in deeper sediments.

In general, we found CDA Lake sediments to be highly reduced, with most redox potentials measured well below 0 mV (relative to the SHE; see Appendix 3, Supporting Information). At sites distant from the mouth of the CDAR, sediment redox potentials were consistently below zero, even in the uppermost 2 cm. In sediments close to the CDAR, the Eh gradient was less steep. However, no redox potential was recorded higher than +100 mV.

Gross Metal Deposition. The horizontal deposition patterns of trace elements within the CDAR delta are similar

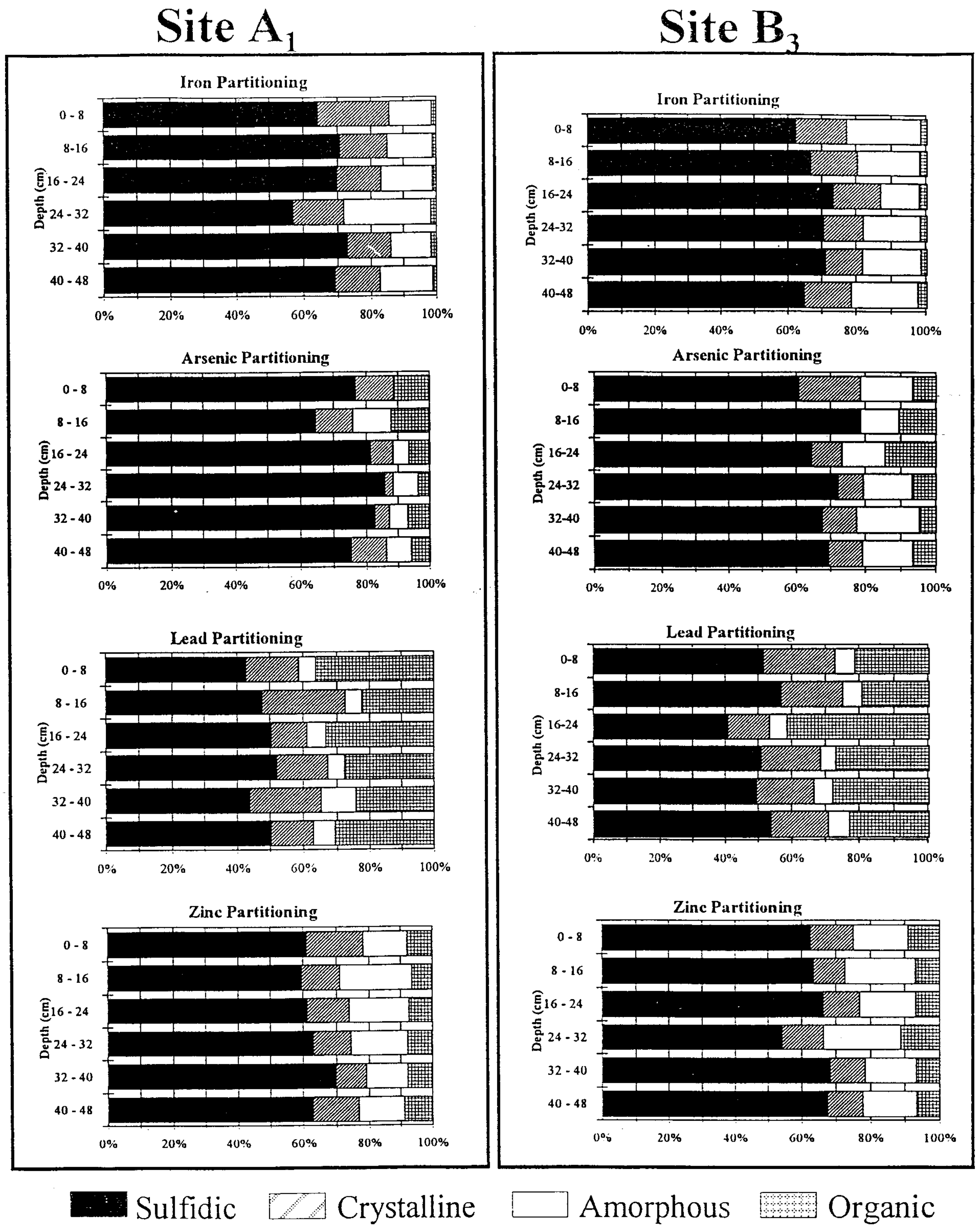

FIGURE 3. Phase partitioning in two CDA Lake cores obtained near the CDAR delta. Phases are sulfidic (black), crystalline (striped), amorphous (white), and organic (hatched).

to those described by Maxfield et al. (*3*) and Horowitz et al. (*2*, *14*). In addition, we observe that the thickness of contaminated sediments decreases along a transect running from the CDAR toward the SJR (transect “C” in Figure 1 and Appendix 1, Supporting Information). The zone of metal contamination at site C-2 extends to approximately 52 cm, 32 cm at site C-3, 24 cm at site C-4, and 20 cm at site C-5.

We observed two distinct subsurface maxima for iron and trace elements: one characteristic of As, Fe, and Mn, another characteristic of Pb and Zn. Generally, maximal abundance of the redox-active elements (As, Fe, Mn) occurs near the sediment−water interface in the region of the redox boundary (2−6 cm). This pattern suggests diagenetic cycling of these elements by oxidation−reduction reactions. It has been noted that large quantities of iron oxides are not required to bind substantial quantities of As or P (*9*, *11*). Moreover, As solubility should be highest where Fe is reduced and sulfate reduction is not active (*32*). The reduction potentials we recorded (see Appendix 3, Supporting Information) indicate that these conditions likely exist just below the top few centimeters. Indeed, oxidized iron has only been reported to occur in the top 2 cm of CDA Lake sediments (*2*). Altogether, the accumulation of As and P near the sediment−water interface is to be expected given the occurrence of a redox boundary in the uppermost region of these sediments.

Iron and phosphorus are negatively correlated in CDA Lake sediments where lead or zinc concentrations are elevated (at least more than twice the SJR delta sediment concentrations). Oxidized Fe in freshwater lake sediments typically acts as a phosphate sink (*9*). Our correlation data therefore suggest that Fe (and, necessarily, Mn) in these regions is reduced enough so that phosphate or arsenate are not bound efficiently. Thus, we believe that the >80% correlation of As and Fe abundance, as well as the high As in the sequential extraction sulfide phase, can be explained by postulating that the majority of As is present as an Fe−As sulfide (e.g., FeAsS).

The >90% correlation between Pb and Zn suggests similar patterns of deposition, as well as similar patterns of cycling (or lack thereof). Interestingly, sequential extraction analyses show that of the metals examined, Pb and Zn, have the smallest fraction bound as sulfides. Our data indicate that significant amounts of both elements partition with the operationally defined organic phase. This is consistent with other studies which have demonstrated that Pb and Zn are easily sequestered by a variety of complex organic compounds including bacterial exo-polysaccharides (*21*) and humic acids (*33*). While Zn has been described as capable of diagenetic remobilization (*23*), the vertical profiles we describe within the sediment column indicate that remobilization by this process has not occurred.

In order of absolute magnitude, Fe > Mn > Pb > Zn > As are the trace elements most enriched within contaminated regions of CDA Lake (see Table 1). CDA sediments collected below the zone of metal contamination, however, do not differ significantly from pristine SJR delta sediments in Pb or As content. Sediments collected near the SJR appear to have higher Zn and lower P content than sediments found below the zone of metal pollution near the CDAR. Low P concentrations in the contaminated zone suggest that recent levels of phosphorus loading (per unit sediment) by the CDAR may be lower than levels that existed prior to the onset of mining.

Metal Phase Partitioning. In contaminated sediments, 60−70% of all Fe is associated with an operationally defined sulfidic phase, while much of the remainder is split between the amorphous and crystalline (hydr)oxide phases. The organic phase contains the least amount of Fe, typically less than 10%. In contrast, two divalent metals, Pb and Zn, partitioned comparatively less with the sulfidic phase (Pb, 40−50%, and Zn, 55−65%), and more with the organic phase (Pb, 20−40%, and Zn, 8−12%). More Zn than Pb appears to be sequestered in the amorphous (hydr)oxide phase, a finding which may help explain why this trace element has been released into the overlying waters (*1*). Zn in this phase could be readily solubilized consequent to iron reduction. Arsenic also shows variable levels of binding to the amorphous oxide phase, with core A-1 half the levels observed for core B-3.

We may infer from the relative quantities of metal bound as sulfides that bacterial sulfate reduction, particularly below the top 4 cm, may be an important mechanism for trace element sequestration. The inference of sulfate-reduction activity is also supported by the low redox potentials registered at these depths (Appendix 3, Supporting Information), the relatively high pH values observed in these zones (pH 6.25), as well as most probable number (MPN), estimates (*34*) that confirm the presence of cultivable SRB in densities ranging from 10^6 to 10^4 cells/g wet weight sediment (Harrington et al. Unpublished results).

SRB can participate in metal-reducing reactions and, by their production of sulfides, in trace element sequestration (*7*). The activities of SRB were once thought to be limited to strictly anaerobic environments. Additionally, bacterial communities in lake sediments have been postulated to be stratified with respect to dominant community members. In this scenario, SRB were believed to predominate in strata below dissimilatory iron-reducing bacteria (DIRB) (*35*). However, recent work has shown that SRB numbers can be high in more aerobic regions of sediments, and that iron and sulfate reduction can occur at the same depth and time (*36*). Further, it has also been shown that, as a group, SRB can support growth using a variety of terminal electron acceptors, including Fe(III), U(VI), Se(VI), and As(V) (*7*). SRB may therefore be active in the upper sediments, perhaps as high as 4 cm from the sediment−water interface.

Our data indicate that reducing conditions prevail in CDA Lake sediments, and that trace elements are chiefly associated with an operationally defined sulfidic phase. Spring runoff and flooding within the CDAR Valley continues to introduce iron and trace elements into CDA Lake. Since these materials are transported as resuspended streambank sediments, it has been proposed that they are introduced into CDA Lake in a predominantly oxidized state (*2, 14*). Our findings suggest that, if this in indeed the case, considerable metal reduction and sequestration takes place within the lake sediments secondary to deposition. We also observe that the fraction of trace elements bound by organic matter is significant, particularly with respect to Pb and Zn. Thus, we concur with Pedersen (*12*) that the risk of release of Pb and Zn into overlying waters under eutrophic conditions may be exaggerated. The biogeochemical cycling of As in CDA Lake requires further study in regard to bacterial formation and dissolution of arsenic sulfides.

Acknowledgments

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Supporting Information Available

Three tables (3 pages) will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the Supporting Information from this paper or microfiche (105 × 148 mm, 24× reduction, negatives) may be obtained from Microforms Office, American Chemical Society, 1155 16th St. NW, Washington, DC 20036. Full bibliographic citation (journal, title of article, names of authors, inclusive pagination, volume number, and issue number) and prepayment, check or money order for $12.50 for photocopy ($14.50 foreign) or $12.00 for microfiche ($13.00 foreign), are required. Canadian residents should add 7% GST. Supporting Information is also available via the World Wide Web at URL http://www.chemcenter.org. Users should select Electronic Publications and then Environmental Science and Technology under Electronic Editions. Detailed instructions for using this service, along with a description of the file formats, are available at this site. To download the Supporting Information, enter the journal subscription number from your mailing label. For additional information on electronic access, send electronic mail to si-help@acs.org or phone (202)872-6333.

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