Seasonal and Interannual Mobility of Arsenic in a Lake Impacted by Metal Mining

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Detailed examination of the water column, sediments, and interstitial waters was conducted in Balmer Lake, Ontario, Canada, in 1993−1994 and 1999 in order to assess the seasonal and interannual controls governing the behavior of As. High-resolution profiles of dissolved ($<$0.45 μm) Fe, Mn, SO_4^{2-}, and ΣH_2S across the sediment−water interface indicate the presence of reducing conditions in close proximity to the benthic boundary during ice-free periods, which are characterized by fully oxygenated bottom waters. Dissolved As is remobilized as As(III) in suboxic sediment horizons via the redox-controlled dissolution of Fe (and perhaps Mn) oxide phases. During 1993−1994, As fluxes to the water column were relatively low (2−15 μg cm^{-2} year^{-1}) and contributed between 2 and 18% of the water column inventory. Dissolved As in the lake waters was derived primarily from external mining-related loadings during this period. Between 1993 and 1999, external loadings of As to Balmer Lake decreased while $[As]_{aq}$ within the lake increased, suggesting an increase in the proportion of sediment-derived As. Indeed, benthic dissolved As fluxes in 1999 ranged from 179 to 380 μg cm^{-2} year^{-1}, representing $\sim$33−60% of the water column burden. The relatively recent importance of sedimentary arsenic sources is suggested to reflect changes to sediment redox conditions associated with a postulated increase in lake primary productivity. Ironically, the increased contribution of dissolved arsenic to the water column appears to have resulted from an otherwise improved in water quality. Reduced loadings of Cu, Zn, and Ni to the lake since 1994 appear to have allowed increased phytoplankton production that has stimulated arsenic release.

Introduction

The mining and smelting of arsenic-bearing ores has contributed greatly to the global anthropogenic input of arsenic to air, soil, and aquatic reservoirs (1). More specifically, the common occurrence of arsenopyrite (AsFeS) in base-metal and gold-bearing ores has resulted in significant loadings of arsenic to the environment from ore-milling practices (2). Lakes often present the ultimate site of deposition for mining-derived arsenic due to the input of mill tailings, wasterock, tailings-pond overflow, and/or acidic seepages (2−6). Accordingly, a knowledge of the processes governing arsenic mobility in contaminated environments is required to develop scientifically defensible and cost-effective remediation strategies.

The impetus behind the research presented here was to investigate the poorly constrained sediment−water cycling of arsenic within the mining-impacted system of Balmer Lake, Ontario, Canada. The particular objectives were to (1) assess the biogeochemical controls governing the mobility and speciation of arsenic in Balmer Lake sediments, (2) determine the direction and magnitude of sediment−water exchanges of dissolved arsenic, and (3) assess the spatial and temporal variability in arsenic mobility over both seasonal and interannual time scales. In particular, it was desired to link periods of seasonal anoxia and the influence of redox-related reactions on arsenic mobility and diagenetic chemistry. The results of this study are broadly applicable to a spectrum of aquatic systems.

Environmental Setting and Background

Balmer Lake is a small, shallow, boreal lake situated in the Canadian Shield of northwestern Ontario (51° 04′ 34″ N, 94° 44′ 43″ W) (Figure 1). The waterbody is 260 ha in area, has an estimated mean depth of 3.0 m, and a maximum basin depth of $\sim$4.0 m. The lake is nutrient replete and hosts organic-rich sediments (7). The shallow water column is well-mixed during the ice-free season from late spring through fall. Periods of bottom water anoxia develop in the winter months in deeper areas ($>$2.5 m) when the lake is ice covered (7).

Balmer Lake has served as a repository of mining-related wastes for two underground gold mines since 1960 (Figure 1). Prior to 1970, flotation tailings derived from roaster processing were discharged directly to the lake. Since that time, the basin has received a combination of treated and untreated tailings-pond overflow. Both mines process high-grade ores rich in Ni, Cu, Zn, and As, and as a result, concentrations of these metals are significantly enriched in the lacustrine sediments.

Sampling and Analytical Methods

Field investigations were carried out in Balmer Lake in 1993−1994 encompassing summer (July 1993), fall (October 1993), and spring (May 1994), as well as in February and August of 1999.

The postdepositional cycling of metals and nutrients in the lake sediments and their exchange with the overlying water column were assessed by sub-centimeter (6.3 mm) resolution sampling of the porewaters and bottom waters using dialysis arrays (peepers). Peepers have been shown to be a reproducible method for the sampling of porewaters in Canadian Shield lakes (8). Peeper design, preparation, and subsampling were identical to those described in Martin et al. (6) and carefully followed protocols outlined by Carignan et al. (9). A Gelman HT-450 filter membrane (polysulfone, 0.45 μm pore size) was used to facilitate dialysis and exclude particles from the water-filled wells.

Peeper deployment was performed using a combination of diver insertion (July 1993, May 1994, and August 1999), aluminum landers (October 1993), and PVC deployment rod assemblies (Februay 1999). For SCUBA deployments, precise ($\pm$0.3 cm) determinations of peeper penetration depth were determined visually upon deployment. The aluminum landers are cube-shaped support structures (1 m $\times$ 1 m $\times$ 0.8 m), which ensured vertical insertion to a specific sediment

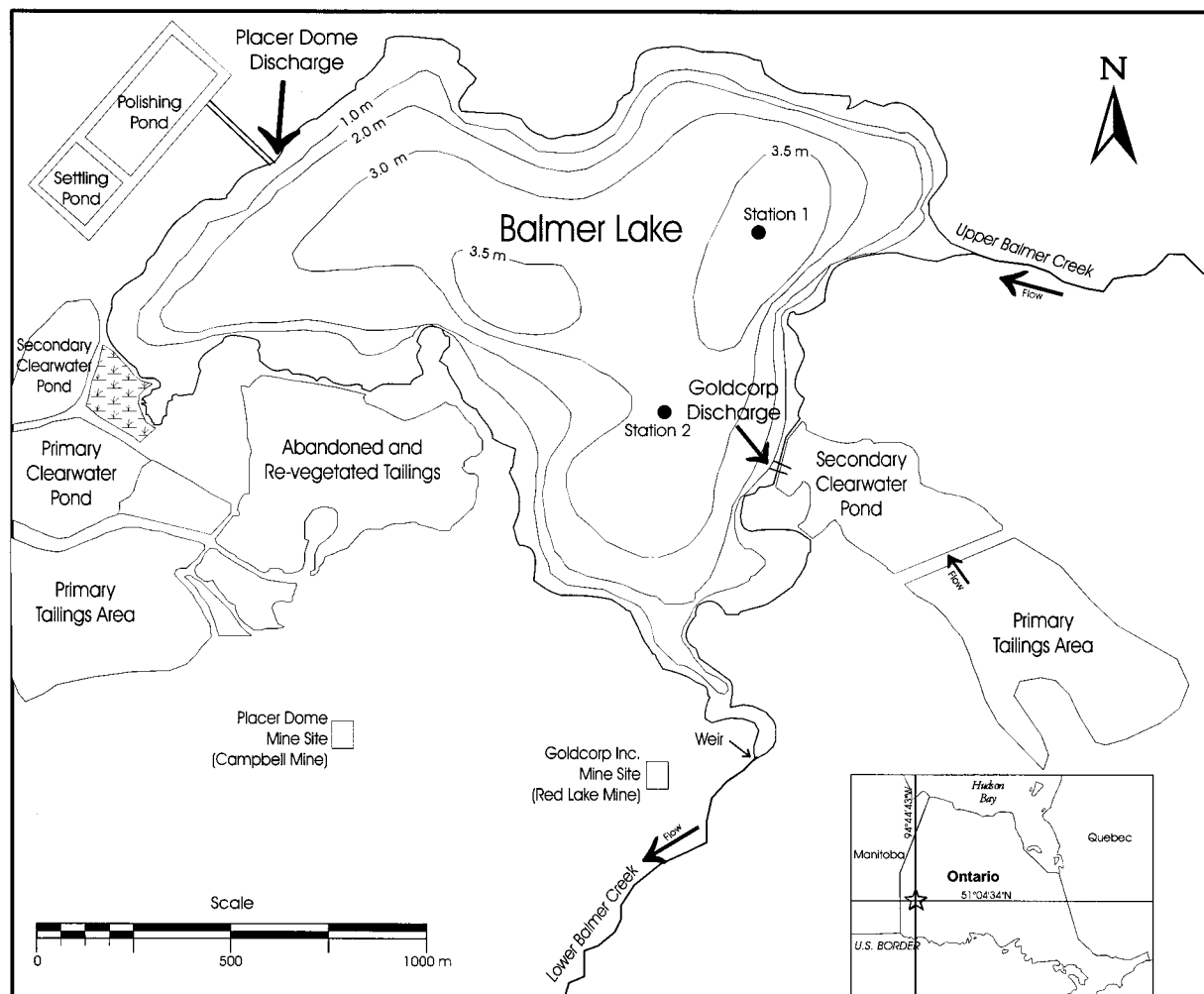* Corresponding author phone: (604) 688-7173; fax: (604) 688-7175; e-mail: ajm@lorax.bc.ca.

FIGURE 1. Site location map of Balmer Lake, ON, Canada.

depth. The peeper—lander assembly remained in situ during the equilibration period; uncertainty associated with the position of the peeper with respect to the sediment—water interface was estimated to be ±1.5 cm. For through-ice deployments, each peeper was attached to a PVC lander assembly and slowly inserted into the sediments via a 5 m long PVC rod. An underwater camera, mounted to the assembly, was used to verify the position of the peeper with respect to the sediment—water interface. Precision associated with insertion depth was estimated to be better than ±0.5 cm. Independent water column samples were collected with a peristaltic pump and acid-cleaned Tygon tubing.

Duplicate sediment cores at station 1 were obtained using a lightweight stainless steel gravity corer in March 1994 (*10*). The corer was lowered through augured holes in the ice from a meter-block and tripod. Cores were carried by hand to the laboratory and immediately subsectioned.

Determinations of As and Mn concentrations in the water column and pore waters were performed via inductively coupled plasma mass spectrometry (ICP-MS) as outlined in Martin et al. (*6*). Precision (1σ rsd) of the As and Mn measurements was estimated to be 2.0 and 2.5%, respectively. Fe concentrations were determined by graphite furnace atomic adsorption spectroscopy (GFAAS) using a Varian Spectra AA300 with a Zeeman background correction (precision = 2.0%). Sulfate concentrations were measured by ion chromatography using a chemically suppressed conductivity detector (Dionex). Precision (1σ rsd) was estimated to be better than ±0.5%. Total sulfide (ΣH_2S) was determined in

pore waters using a diamine reagent (*11*) and measured spectrophotometrically using a Bausch and Lomb Spectronic 2000 analyzer (detection limit = 3 $\mu g\, L^{-1}$). Arsenic speciation was determined via HPLC and ICP-MS. Identification of arsenicals [arsenate, arsenite, monomethylarsonic acid (MMAA), and dimethylarsinic acid (DMAA)] in samples was made by comparison of retention times with those of standards. Arsenic standards obtained as sodium arsenate ($Na_2HAsO_4 \cdot 7H_2O$), arsenic trioxide (As_2O_3), methanearsonic acid [$CH_3AsO(OH)_2$], and cacodylic acid [$(CH_3)_2AsO(OH)$] were dissolved in distilled deionized water to make the standard solutions. Methanol (HPLC grade), tetraethylammonium hydroxide (TEAH, 20% in water), malonic acid (BDH), concentrated phosphoric acid, and ammonium hydroxide (1 M, Fluka) were used as reagents for mobile phases and extractions.

Metal concentrations were determined in the solid phase by X-ray fluorescence spectrometry (Philips 1400 fully automated X-ray spectrometer) using pressed powders, as described by Calvert (*12*). An aliquot of each freeze-dried sediment sample was ground in a tungsten—carbide mill prior to preparation for XRF measurements. Total carbon and sulfur concentrations were determined by combustion/ gas chromatography using a Carlo-Erba NA-1500 elemental analyzer (1σ rsd = 0.6 and 3.5%, respectively) as described by Pedersen et al. (*13*). Carbonate carbon was determined by coulometry. Organic carbon was determined from the difference between the total and carbonate carbon values (combined precision of 1.9%). Accuracy of the elemental
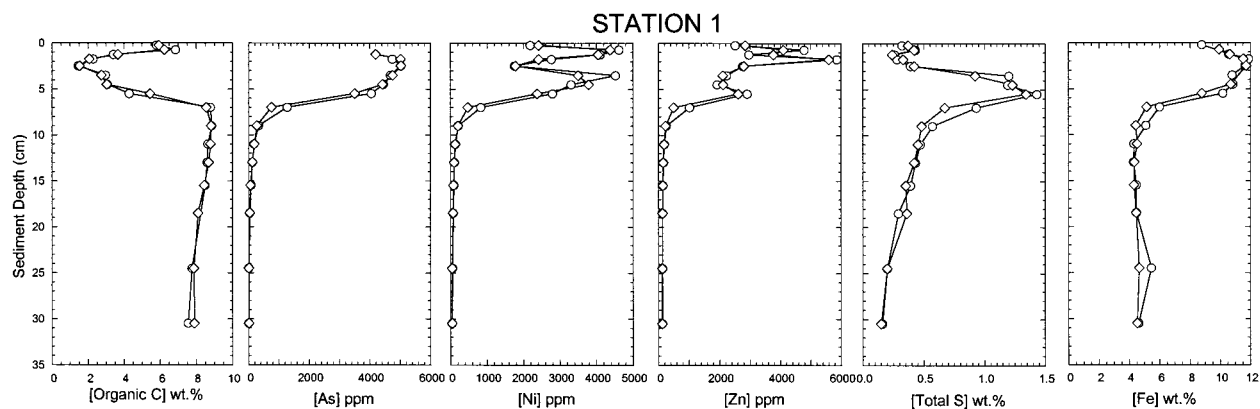
FIGURE 2. Solid-phase distributions from duplicate cores of organic carbon, As, Ni, Zn, S, and Fe at station 1.

analyses was monitored by including aliquots of the standard sediment references MESS-1, BCSS-1, and PACS-1 with each batch of samples.

Results and Discussion

Sediment Geochemistry. The sediments in Balmer Lake comprise both natural and mining-related deposits. Below $\sim$10 cm depth, the sediments consist of essentially tailings-free, organic-rich sediments as shown by the C_{org}, Ni, Cu, Zn, and As distributions (Figure 2). Trace metal concentrations in the lower stratum are low and represent background values (14). Extraordinarily high metal concentrations in the top several centimeters, reaching $\sim$0.5 wt % Ni, 0.6 wt % Zn, and 0.5 wt % As, demonstrate that the upper 10 cm of the sediment column comprises a mixture of tailings material and natural deposits. Profiles for S and Fe suggest these elements are also enriched in the tailings component (Figure 2).

The deposition of flotation tailings in Balmer Lake occurred prior to 1970, during which time roaster tailings products were introduced to both the east and west sides of the basin. Detailed mineralogy of the roaster tailings solids generated at Campbell Mine indicate that these deposits are composed mainly of dolomite, quartz, and chlorite, with minor muscovite, talc, amphibole, and albite (15). Arsenic is present as primary sulfides (arsenopyrite) as well as in roaster oxidation products, including maghemite (γ-Fe$_2$O$_3$) and hematite (α-Fe$_2$O$_3$). The latter oxidation products have been shown to occur as porous grains ($\sim$20$-$50 μm) hosting high concentrations of arsenic (15). Such phases are predicted to represent the principal source of labile As in the subaqueous tailings in Balmer Lake.

Redox Geochemistry. The redox regime in Balmer Lake sediments was assessed by examination of dissolved ($<$0.45 μm) SO_4^{2-}, Fe, Mn, and ΣH_2S profiles across the sediment$-$water interface. During the summer and fall of 1993, sulfate profiles imply sulfate reduction was occurring in the near-surface porewaters; concentrations decrease nonlinearly throughout the sampled horizons (Figures 3 and 4). The similarity between the sulfate profiles at stations 1 and 2 during July 1993 is indicative of lakewide homogeneity. The subsurface sulfate maximum observed in the spring (May 1994) represents the remnant of an interfacial SO_4^{2-} excess associated with the buildup of effluent-derived sulfate in the winter bottom waters (7). The implied reduction of SO_4^{2-} in the May 1994 profile below 10 cm, combined with diffusional transport, indicates that the subsurface peak is in a state of progressive decay. Indeed, the minor subsurface maxima observed in the summer of 1993 at station 1 most likely reflect remnants of a more pronounced spring peak present earlier in the year (Figure 3). In February and August 1999, sulfate reduction in the upper decimeter of the sediment column

liberates H$_2$S to pore solution (Figures 6 and 7). The presence of H$_2$S in the upper 5 cm during these months is consistent with the concavity of the SO_4^{2-} profiles. Although ΣH_2S was not measured in 1993$-$1994, the evidence of sulfate reduction during these periods suggests that fully anoxic conditions were likely present within $\sim$10 cm of the sediment$-$water interface (Figures 3$-$5). The sulfate distributions observed in 1999 (Figures 6 and 7) do not differ markedly from those observed during the summer, fall, and spring of 1993$-$1994. The presence of an H$_2$S maximum at a depth of 2 cm in August 1999 demonstrates that reducing conditions continue to be established in close proximity to the benthic boundary during the late summer/fall period (Figure 7).

During the ice-free periods in Balmer Lake, the porewater distributions of dissolved Fe and Mn are characterized by sharp subsurface concentration gradients in the shallow porewaters, suggesting that the reductive dissolution of Fe- and Mn-bearing oxyhydroxides is occurring in the near-surface sediments (Figures 3$-$5 and 7). The uniform profiles of circum-neutral pH measured at station 1 in May 1994, February 1999, and August 1999 suggest that the increased mobility of Fe and Mn is governed by pϵ.

The depth of Mn(IV) reduction, as defined where d^2[Mn]/dz^2 > 0, migrates from between 5.5 and 8.5 cm in July (1993) to $\sim$3 cm in September (1993), suggesting that the Mn redoxcline migrates upward throughout the summer months (Figures 3 and 4). Such trends are consistent with the sulfate data, which also suggest the development of more reducing conditions over the summer period. The development of reducing conditions over the ice-free months may reflect an increase in oxygen demand associated with the progressive accumulation of labile organic matter over the active period of primary production. Assuming that the Fe(III) redoxcline migrates in accordance with Mn, it can be proposed that the sorptive capacity of the surficial sediments for As decreases through the summer, fall and winter, and increases again in the spring. The depth of Mn reduction in August 1999 of $\sim$1.8 cm is consistent with the presence of highly reducing conditions in the late summer months (Figure 7).

The available evidence suggests that authigenic sulfide precipitation presents a significant control on the distribution of Fe in Balmer Lake porewaters. During the summer period, concavity in the Fe profiles between $\sim$8 and 20 cm depth at stations 1 and 2 implies removal from pore solution (Figure 3). Sulfide precipitation is implicated as a likely Fe sink. Such mechanisms were proposed to account for similarly shaped Fe profiles in another Canadian Shield lake (16, 17). The pronounced decreases of dissolved Fe in the deep porewaters in August and February 1999 support a sulfide removal process (Figures 6 and 7); equilibrium calculations using PHREEQC (18) indicate near saturation with respect to amorphous FeS (SI = 0.41) at the 10 cm depth.
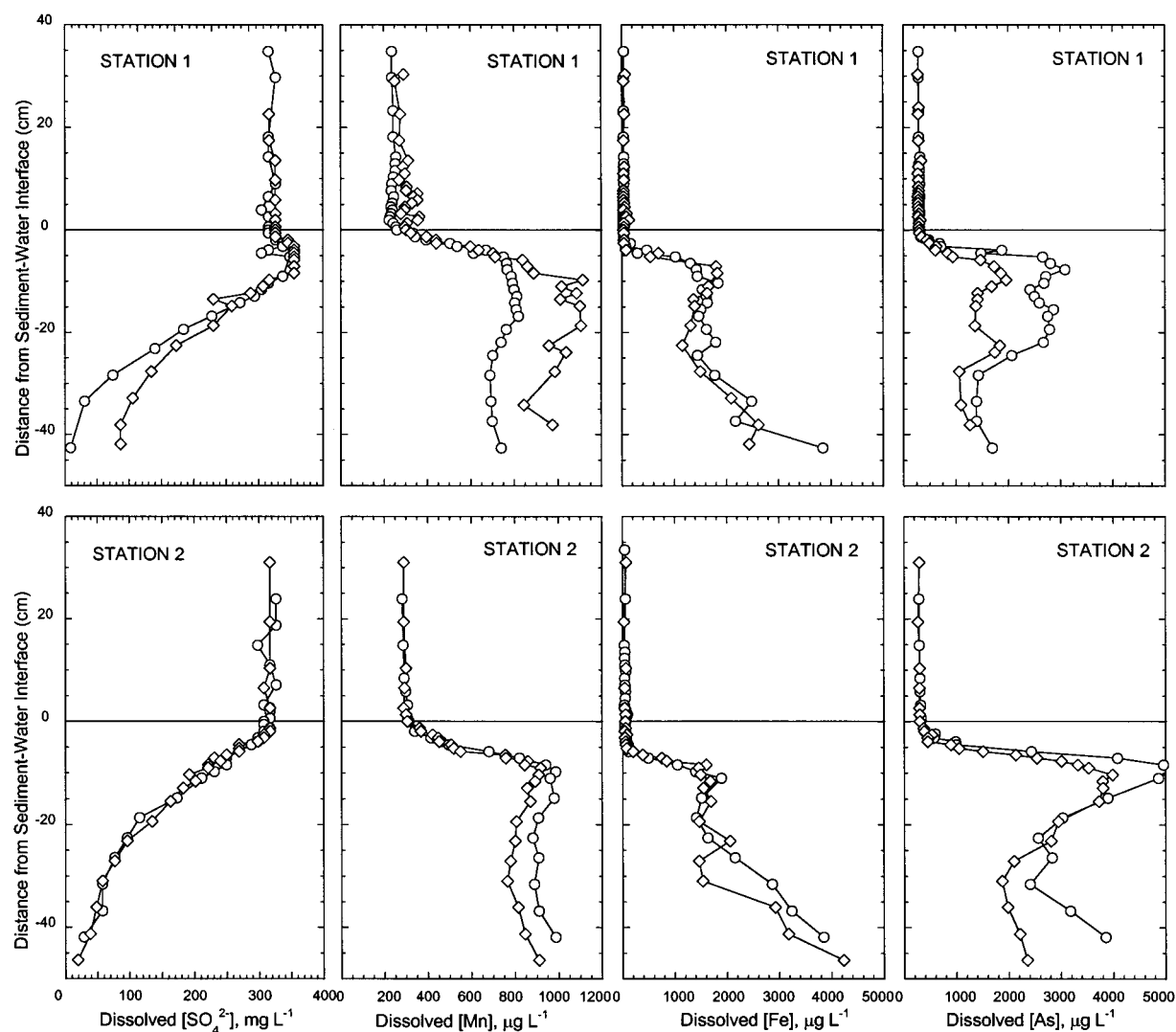
FIGURE 3. Duplicate peeper profiles of dissolved sulfate, Fe, Mn, and As at stations 1 and 2, summer (July) 1993.

Arsenic Mobility. Profiles of dissolved As across the sediment−water interface suggest that two principal controls govern As distributions in Balmer Lake porewaters: (1) intense remobilization at shallow sediment depths indicated by a redox-controlled release from labile, As-bearing particulates; and (2) consumption of As as authigenic sulfide phases at depth.

The summer (1993) distributions of dissolved As closely track Fe and Mn at both stations (Figure 3). Concomitant increases in As levels result in large subsurface maxima of 2000−5000 μg L^{-1} within 10 cm of the sediment−water interface. The parallels between the trace element distributions at stations 1 and 2 reflect a high degree of spatial homogeneity. The arsenic porewater data for the fall (1993) period are comparable to the summer results (Figure 4). Dissolved Fe, Mn, and As porewater distributions are nearly parallel, both of which follow a redox pattern of dissolution in the suboxic zone, upward diffusion, and precipitation near the sediment−water interface.

Sampling conducted in the spring following ice breakup yielded bottom water and porewater distributions of dissolved As comparable to those observed during the well-mixed periods of the previous summer and fall (Figure 5). The shapes of the As profiles observed in Balmer Lake are similar to those observed in other arsenic-contaminated lakes (*8, 19,*

20). However, the magnitudes of the porewater maxima observed in Balmer Lake are considerably greater than those measured in other systems.

Profiles collected in February 1999 are consistent with the 1993−1994 data. The data demonstrate that As is intensely remobilized in the upper decimeter of the sediment column to maximal values exceeding 5000 μg L^{-1} (Figure 6). The close parallels between the As and Fe profiles suggest As is concomitantly remobilized during the reductive dissolution of Fe-oxides. The dissolved As distribution for August 1999 is characterized by a sharp maximum in the near-surface porewaters (~3 cm depth), with concentrations reaching >8000 μg L^{-1} (Figure 7). The large maximum reflects a high degree of diagenetic intensity in the surface sediments, presumably fueled by the oxidation of abundant, fresh organic matter. The As peak is consistent with the interstitial maxima observed for Fe and Mn at this site.

Evidence for As-rich oxidation products (porous texture hematite and maghemite) associated with the tailings discharged to Balmer Lake (*15*) suggests that hydrous As-bearing iron oxides present the principal source of labile As in Balmer Lake sediments. The As associated with the flotation tailings has been shown to be released to pore solution within the saturated zone of a proximal subaerial tailings deposit via reductive dissolution of these iron oxide phases (*15*). The
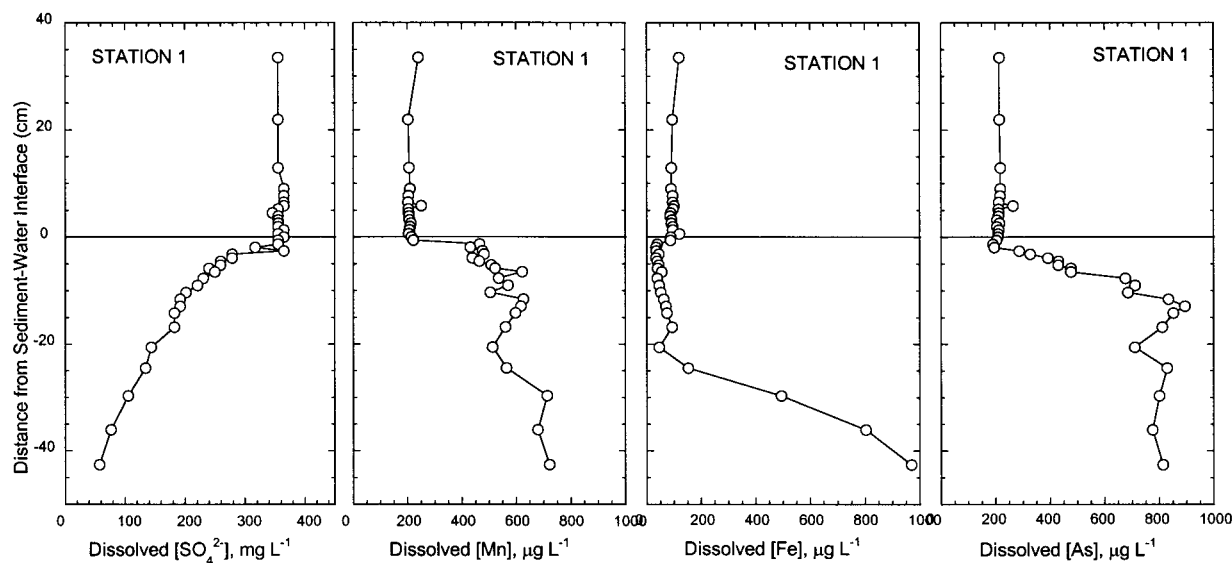
OCTOBER 1993

FIGURE 4. Peeper profiles of dissolved sulfate, Fe, Mn, and As at station 1, fall (October) 1993.
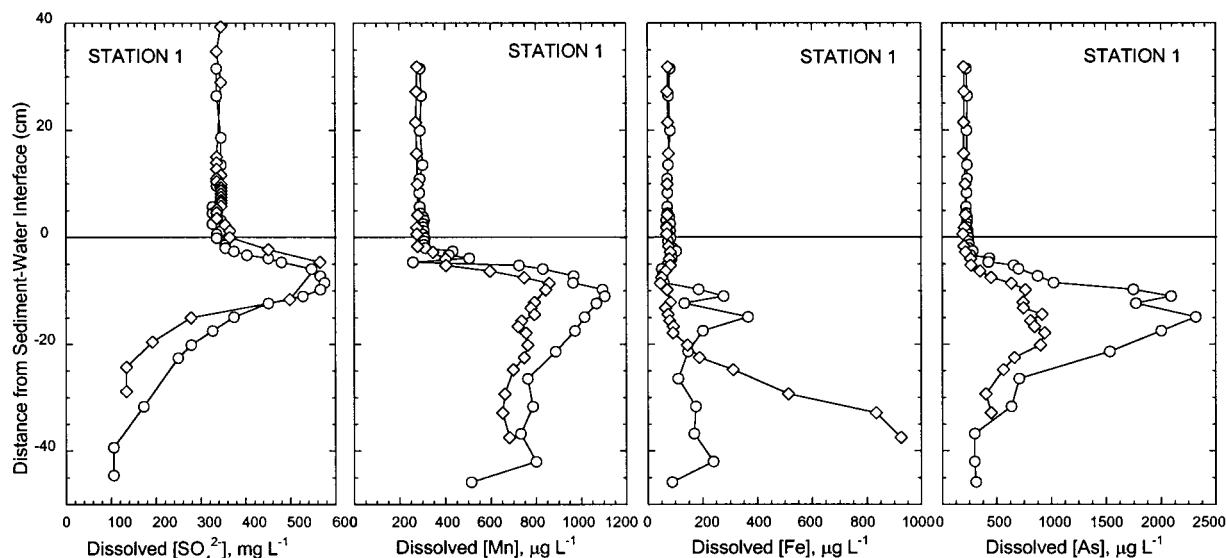
MAY 1994

FIGURE 5. Duplicate peeper profiles of dissolved sulfate, Fe, Mn, and As at station 1, spring (May) 1994.

porewater data for Balmer Lake suggest that similar controls are governing the mobility of arsenic within the lacustrine system.

The decreases in As concentrations observed below the depth of the porewater maximum in some profiles in Balmer Lake likely reflect the precipitation of As-bearing sulfide phases (Figures 3 and 5−7). Although the precipitation of As_2S_3 and mixed Fe−As sulfides has generally not been distinguished in sediments, the coprecipitation/adsorption of As with Fe monosulfides has been clearly shown to be an important removal mechanism in Canadian Shield lakes (8). Similar controls have also been invoked to account for arsenic removal in an arsenic-contaminated reservoir (21), arsenic-rich tailings deposits (15), and coastal marine sediments (22).

The respective remobilization depths of As, Mn, and Fe in Balmer Lake suggest that the cycling of Mn exerts some influence on As behavior. For example, summer (1993) profiles indicate that As and Mn are remobilized at depths

1.5−2.5 cm shallower than Fe (Figure 3), suggesting that the dissolution of Mn solid phases is responsible for the porewater additions of dissolved As above the Fe(III) redox boundary. Arsenic associations with manganese oxides have been shown to become more important in the presence of high concentrations of divalent metal cations (23). Specifically, the binding of divalent metals has been shown to increase the point of zero charge of the manganese oxide surface and hence enhance the sorption of negatively charged arsenate (23). Alternatively, the release of arsenic to porewaters above the Fe(III) redoxcline may result from the reduction of As(V) associated with iron(III) oxide phases to As(III) and the release of the latter to pore solution before the oxides undergo reductive dissolution (24).

Arsenic Speciation. The speciation of arsenic in the bottom waters and porewaters was determined in 1999 to establish the relative importance of different arsenic species (arsenate, arsenite, MMAA, and DMAA). Thermodynamic
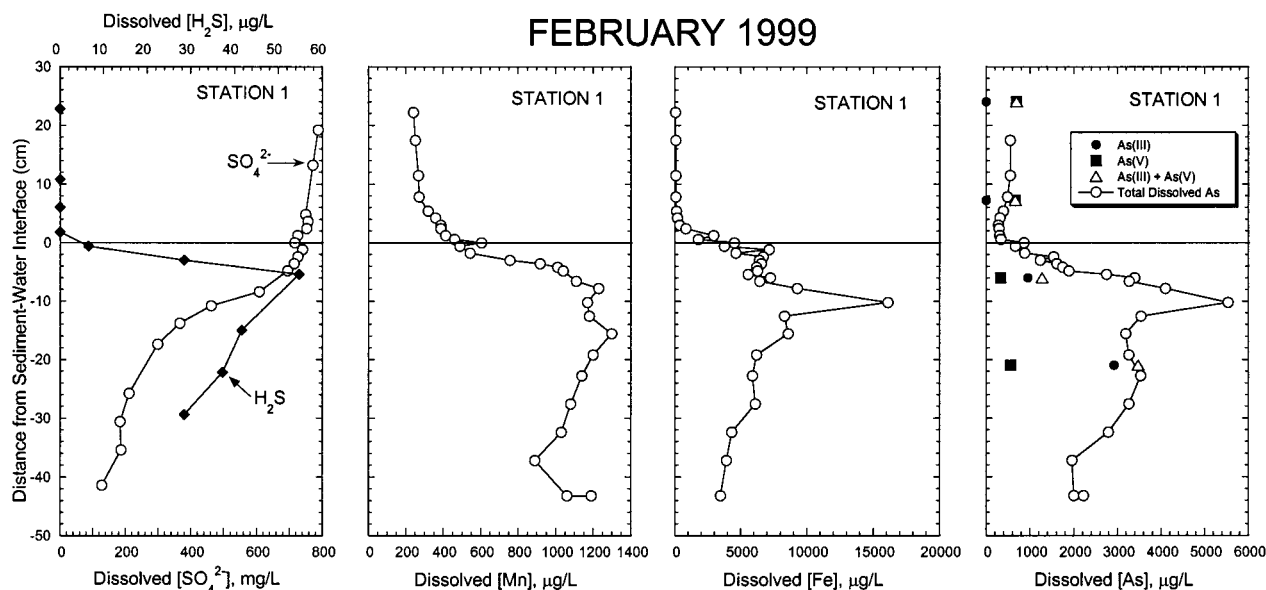
FIGURE 6. Peeper profiles of dissolved ΣH_2S, sulfate, Mn, Fe, total dissolved As, As(III), and As(V) at station 1, winter (February) 1999.
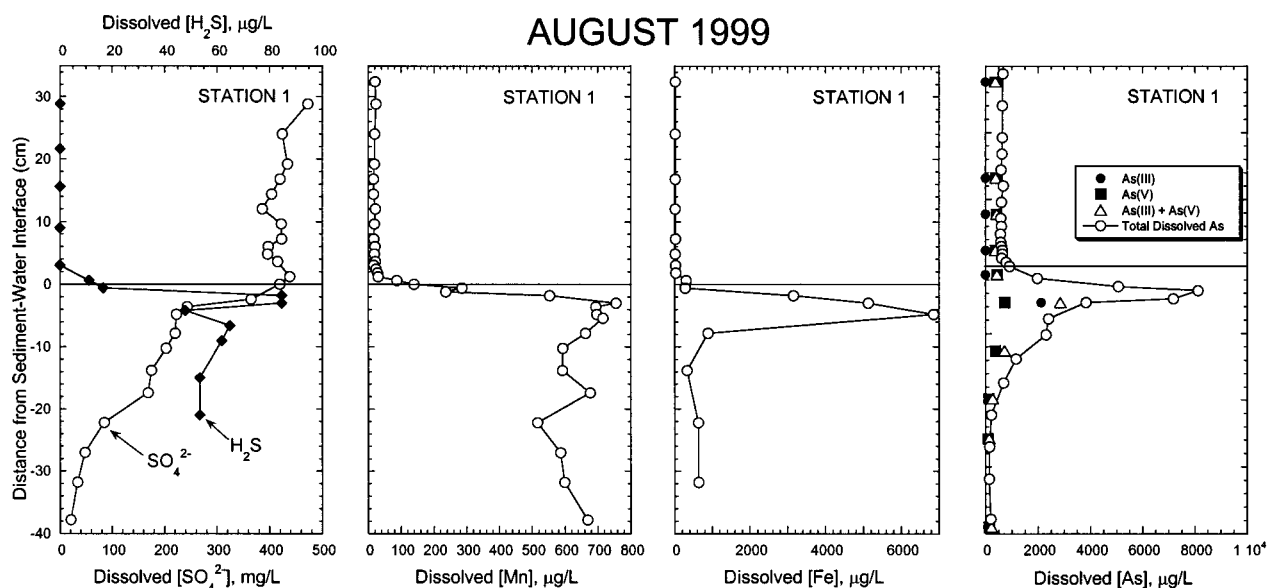

FIGURE 7. Peeper profiles of dissolved ΣH_2S, sulfate, Mn, Fe, total dissolved As, As(III), and As(V) at station 1, summer (August) 1999.

arguments suggest that inorganic As in oxidized aquatic systems should be present as arsenate [As(V)] (25), whereas arsenite [As(III)] typically predominates in anoxic interstitial waters (19, 26–28). Sediments can also be host to a suite of organoarsenicals generated via biologically mediated methylation. These compounds include MMAA, DMAA, trimethylarsine oxide (TMAO), and their reduced analogues monomethylarsine (MMA), dimethylarsine (DMA), and trimethylarsine (TMA) (25).

In February and August 1999, concentrations of As(V) exhibited minor variability across the sediment–water interface (Figures 6 and 7). Above the interface, concentrations of As(V) accounted for >99% of the sum of As(III) + As(V). The As(V) values are also consistent with the independent water column measurements of total dissolved As. Conversely, concentrations of As(III) were characterized by significant increases with depth in Balmer Lake porewaters. The results imply that As(III) is the principal species remobilized in the suboxic porewaters. Such observations are consistent with previous studies of As speciation, which

have also demonstrated the dominance of As(III) in reducing porewaters (27, 29, 30). Collectively, the data demonstrate that the bottom waters in Balmer Lake are dominated by arsenate As(V). The relative dearth of As(III) in the water column implies that upward-diffusing arsenite is oxidized near the sediment–water interface and that the kinetics of As(III) oxidation are sufficiently rapid to prevent its accumulation in bottom waters (31). The progressive development of bottom water anoxia over the winter months, however, may result in an increase in the water column inventory of As(III). In both surveys, DMAA and MMAA were not detected.

Arsenic Fluxes. Large subsurface porewater gradients in Balmer Lake sediments support year-round upward diffusion of dissolved As toward the sediment–water interface. Concentration gradients of dissolved As were used to calculate (1) rates of As remobilization and (2) rates of diffusive transport across the sediment–water interface (Table 1). The rate of As remobilization was inferred from the maximum rate of upward diffusive transport, which was in turn

TABLE 1. Input Values for Calculations of Arsenic Remobilization Rate and Diffusion Rate of Arsenic across the Sediment—Water Interface (Efflux)[a]

sampling period	station	peeper[b]	$D^{\circ}{}_{j}$ (cm^2 s^{-1})	remobilization rate[c] (μg cm^{-2} year^{-1})	efflux[d] (μg cm^{-2} year^{-1})	impact to water column[e] (μg L^{-1})	measured water column[f] [As]$_{aq}$ (μg L^{-1})
July 1993	1	1	7.50E−06	−148	−6	12	286
July 1993	1	2	7.50E−06	−120	−7	15	286
July 1993	2	1	7.50E−06	−148	−15	31	280
July 1993	2	2	7.50E−06	−134	−11	24	280
Oct 1993	1		4.79E−06	−8	−3	6	205
May 1994	1	1	6.08E−06	−53	−2	4	225
May 1994	1	2	6.08E−06	−17	−2	5	225
Feb 1999	1		4.79E−06	−139	−85	179	540
Aug 1999	1		7.50E−06	−305	−181	380	630

[a] Negative flux values imply upward diffusive transport. [b] Refers to stations with duplicate peepers in Figures 3 and 5 (peeper 1 = open circles; peeper 2 = open diamonds). [c] Rate of diffusive transport toward sediment—water interface. [d] Rate of diffusive transport from the sediments into the overlying water column. [e] Steady-state water column [As] predicted from efflux. [f] Measurements obtained from discrete water column samples.

calculated using the linear concentration gradients above the porewater maximum. Conversely, the diffusive input of As to the water column was calculated using an assumed linear concentration gradient across the sediment—water interface. In reality, As concentration gradients adjacent to the benthic boundary are likely to be nonlinear (i.e., concave upward) due to As scavenging in the oxic surface horizons. Therefore, the assumption of linearity results in an overestimation of the magnitude of the concentration gradient. The rate of diffusive transport can be estimated using Fick's first law

$$J_z = \frac{D^{\circ}{}_j}{F} \phi \frac{dc}{dz}$$

where J_z is the flux; $D^{\circ}{}_j$ = in situ diffusion coefficient; F = formation factor of 1.4 for silty clay (32); ϕ = porosity of 0.9, assuming an average particle density of 2.65 g cm^{-3}; and dc/dz = the concentration gradient. The porosity value is based on measurements taken from Martin (7). The formation factor is a measure of tortuosity and takes into account the convoluted path ions and molecules must follow as they diffuse around sediment particles (33). Diffusion coefficients reflect those for free metal ions (34). Diffusive efflux calculations do not take into account random transport mechanisms such as bioturbation and irrigation, which can increase the net diffusive flux by a factor of 2−6 (35). In addition, physical processes such as wave-induced transport and gas ebullition have been ignored. Therefore, the diffusive effluxes in Table 1 likely provide conservatively low estimates of the total benthic flux.

During 1993−1994, As remobilization rates exhibited considerable variability, with values ranging from 8 to 148 μg cm^{-2} year^{-1} (Table 1). The high rates of remobilization in the summer of 1993 reflect the large porewater maxima observed during this period. The As remobilization rate calculated for February 1999 is comparable in magnitude to the 1993−1994 results (Table 1). However, the rate for August 1999 (305 μg cm^{-2} year^{-1}) is considerably greater than rates observed during previous surveys. The large concentration gradient during August 1999 reflects a high rate of As remobilization in the near-surface horizons. The maximum rates of upward As diffusion measured in Balmer Lake are considerably greater than those measured in a temperate estuary (2.2 μg cm^{-2} year^{-1}) (36) and various coastal and lake sediments (0.37−2.4 μg cm^{-2} year^{-1}) (27).

The generally invariant concentration gradients of As across the sediment—water interface in the summer, fall, and spring periods of 1993−1994 demonstrate that a large proportion of the upward-migrating As was reprecipitated in the near-surface horizons with Fe and Mn oxyhydroxides.

As a result, diffusive effluxes of As into the water column during these periods were considerably less than the respective remobilization rates (Table 1). The effluxes measured during 1993−1994 (2−15 μg cm^{-2} year^{-1}) are similar to those measured in a mine-polluted lake (0.77−3.85 μg cm^{-2} year^{-1}) (30) and much greater than those reported for the Laurentian Trough (0.07−0.24 μg cm^{-2} year^{-1}) (37). Assuming an average water column depth of 3 m, and a residence time of 230 days (38), the calculated diffusive inputs over 1993−1994 translate to steady-state water column concentrations of 4−31 μg L^{-1}. This exercise demonstrates that the sediments were contributing to a relative small fraction of the water column inventory during 1993−1994 (Table 1). During this period, the water column As burden was largely derived from loadings from the adjacent mining operations, which were contributing on the order of 4000 kg of dissolved As year^{-1}. Assuming conservative As behavior, a pond volume of 7.8×10^9 L, and the 230 day residence time, 4 tonnes of As per year could contribute ~320 μg L^{-1} to the water column. Although seasonal water column impacts were often based on a single profile, the homogeneity between the flux rates calculated at stations 1 and 2 in July 1993 suggests that the fluxes in Table 1 are representative of lakewide conditions.

The 1999 data yield significantly greater rates of As diffusion into the water column than the measurements made in 1993−1994. Effluxes for February and August translate to steady-state water column concentrations of 179 and 380 μg L^{-1}, respectively (Table 1). In summary, although *rates* of As remobilization have not changed considerably since 1993, diffusive *fluxes* to the water column appear to have increased in recent years. The hypothesis of an increased contribution of As to the water column from the sediments is supported by As loading data from the adjacent mine sites. Specifically, from 1996 to 2000, improved water treatment and management practices resulted in dramatic decreases in As loadings to Balmer Lake; loadings had decreased to <600 kg year^{-1} by 1996. Collectively, the decrease in external As loadings over the 1993−1999 period, and the commensurate increase in the dissolved As concentration in the water column (Table 1), suggest that the relatively recent persistence of high dissolved As concentrations in the water column stems from sedimentary sources.

A shift in the redox state of Balmer Lake sediments toward more reducing conditions represents one possible mechanism to account for the apparent increase in sediment-derived As. Indeed, the shallow depth of As remobilization (~2.5 cm) under conditions of fully oxygenated bottom waters in August 1999 suggests that more reducing conditions (i.e., enhanced oxygen demand) have developed in the lake system. Alteration to sediment redox conditions may reflect a trend toward increasing primary production in the lake

TABLE 2. Dissolved Metal and Nutrient Concentrations in the Balmer Lake Water Column for May 1994, February 1999, and August 1999

parameter	May 1994	Feb 1999	Aug 1999
dissolved metals (μg/L)			
Fe	80	70	22
Mn	260	250	20
As	225	540	620
Cu	195	24	12
Ni	395	94	29
Zn	60	7	2
nutrients (mg/L)			
NO_3^-	17	7.1	23
NH_4^+	2.5	0.35	0.11
PO_4^{3-}	ND[a]	0.43	0.34

[a] Not determined.

system. Analysis of total P, total N, and chlorophyll a in Balmer Lake since 1999 indicates that the system has shifted from oligotrophic conditions premining to a state of eutrophy (Placer Dome, unpublished data). However, during 1993–1994, productivity may have been limited in Balmer Lake by the high concentrations of dissolved Cu, Ni, and Zn (Table 2). By 1999, dissolved metal concentrations in the water column had decreased significantly in response to decreased inputs of effluent-derived metals (Table 2). This shift may have altered the productivity regime in the lake. A shift to higher plankton productivity, for example, would result in a greater flux of labile organic matter to the bottom sediments, increased oxidation rates in the surface sediments, and a decrease in the thickness of the oxic sediment veneer (39). The presence of less "toxic" conditions in Balmer Lake is supported by the extensive natural recolonization of benthic macrophytes in littoral zones since 1994 (Placer Dome Inc., personal communication)

The biochemical evolution of Balmer Lake over the past decade suggests that reducing nutrient loadings to the lake should have a beneficial effect on reducing loadings of sediment-derived As. Such a decrease could be predicted to occur as a consequence of diminished settling fluxes of labile organic matter and reduced sediment oxygen demand in the sediments. This would promote the establishment of a thicker aerobic zone in the upper sediment column and enhanced scavenging of upward-diffusing As species. In contrast, pushing the system to a more reducing state as a potentially viable remediation strategy would likely prove to be ineffective. Indeed, the detection of free sulfide near the sediment–water interface in August 1999 indicated that the sediments were already in an advanced state of anoxia despite being in contact with fully oxygenated bottom waters. Even under these highly reducing conditions in which arsenic sulfides were actively precipitating, the removal kinetics were too slow to sufficiently limit arsenic transfer into the water column.

Acknowledgments

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