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Biogeochemical redox cycling of arsenic in mine-impacted lake sediments and co-existing pore waters near Giant Mine, Yellowknife Bay, Canada

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ABSTRACT

Lacustrine sediments, submerged tailings, and their pore waters have been collected at several sites in Yellowknife Bay, Great Slave Lake, Canada, in order to investigate the biogeochemical controls on the remobilization of As from mining-impacted materials under different depositional conditions. Radiometric dating confirms that a mid-core enrichment of Pb, Zn, Cu and Sb corresponds to the opening of a large Au mine 60 a ago. This was evident even in a relatively remote site. Arsenic was enriched at mid-core, coincident with mining activity, but clearly exhibited post-depositional mobility, migrating upwards towards the sediment water interface (SWI) as well as down-core. Deep-water (15 m) Yellowknife Bay sediments that contain buried mine waste are suboxic, relatively organic-rich and abundant in microbes with As in pore waters and sediments reaching 585 μ g/L and 1310 mg/kg, respectively. Late summer pore waters show equal proportions of As(III) and As(V) (16–415 μ g/L) whereas late winter pore waters are dominated by As(III) (284–947 μ g/L). This can be explained by As(III) desorption mechanisms associated with the conversion of FeS to FeS₂ and the reduction of As(V) to As(III) hrough the oxidation of dissolved sulfide, both microbially-mediated processes. Processes affecting As cycling involve the attenuating efficiency of the oxic zone at the SWI, sediment redox heterogeneity and the reductive dissolution of Fe(hydr)oxides by labile organic matter, temporarily and spatially variable.

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1. Introduction and study objectives

Yellowknife Bay sediments have potentially received anthropogenic As through at least three pathways: (1) tailings decant discharged via Baker Creek, a tributary to Yellowknife Bay; (2) erosion of submerged tailings stored directly on shore east of the mill; and (3) atmospheric dispersion of roaster stack emissions during mining operations.

Sediment cores extracted from Yellowknife Bay in 1984 had peak As concentrations in the upper 4 cm that ranged from 1010 mg/kg to 2800 mg/kg (Mudroch et al., 1989). These authors estimated that 20 a of additional sediment accumulation would effectively bury these As-enriched upper sediments once mine effluent discharge via Baker Creek ceased. However, Mudroch et al. (1989) did not have sediment pore water data to confirm or refute the presence of a dissolved labile fraction originating from the As-rich surficial sediments. Although Baker Creek inputs may be relatively low in As at present, submerged and buried sediments in Yellowknife Bay that were previously contaminated with As may continue to act as sources to surface waters. If redox conditions are low enough at the sediment–water interface (SWI), a situation that is usually due to the influx of organic matter, As-bearing surficial Fe(hydr)oxides may dissolve. Reductive dissolution of Fe(hydr)oxides would remove this mechanism of attenuating upwardly diffusing As and may release As to bottom-waters (Martin and Pedersen, 2002). This study was designed, in part, to reveal whether the As-rich horizon documented by Mudroch et al. (1989) has remained at depth, migrated upwards or downwards and is a source for dissolved As diffusing vertically.

Previous research (Walker et al., 2005) has indicated that Asbearing minerals in mine waste at Giant Gold Mine, Yellowknife, NWT include both oxide (roaster-generated maghemite and hematite) and sulfide (arsenopyrite) mineral phases. The long-term stability of these materials is highly sensitive to the oxidationreduction state of the environment in which they are placed.

The research reported in this paper is intended to show the variations in redox conditions in lacustrine environments by sampling both sediments and sediment pore waters at high resolution in the vertical direction in environmentally and geochemically diverse locations within the As-enriched sediment footprint in Yellowknife Bay (Moore et al., 1978; Mudroch et al., 1989; Jackson et al., 1996; Mace, 1998; EBA, 2001; Golder, 2002; Walker and Jamieson, 2003). In addition, a site in Akaitcho Bay distal to mining activities was investigated as a potential control site.



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1.1. Geological setting, ore processing and waste management history

Giant Mine operated from 1948 to 1999 on the shores of Great Slave Lake, Northwest Territories, Canada. The local geology of the Yellowknife area is described by Siddorn et al. (2007). Gold in the ore units is intimately associated with sulfides, dominantly pyrite and arsenopyrite, with total sulfide content typically less than 10%. Roasting was used to treat refractory Au microscopically enclosed in arsenopyrite. This process volatilizes As and Sb, transforms the sulfides into porous Fe oxides of maghemite and hematite, amenable to cyanidation, and produces a Au-rich calcine also high in As, Sb, Cu, Pb and Fe. Walker et al. (2005) have shown that the roastergenerated Fe oxides produced at Giant contain as much as 7 wt.% As which includes both As(III) and As(V). Calcine was combined with flotation tailings and discharged with mill and mine water. Arsenic-bearing phases within the Giant tailings include arsenopyrite, roaster-generated maghemite and hematite, and Fe oxyhydroxides as weathering rims on sulfides (Walker et al., 2005).

During the first few years of the mine (1948–1951), tailings were deposited in a small embayment on the shores of Yellowknife Bay east of the mill (Fig. 1). Air photographs of the submerged tailings throughout the life of the mine show sediment plumes extending out from this area suggesting the dominant winds out of the south during the open water season have eroded and transported tailings throughout Yellowknife Bay since initial deposition (Andrade, 2006).



Fig. 1. Study site locations in Yellowknife Bay and Akaitcho Bay, Great Slave Lake, NT. ID = Identification number.

Aerial emissions from the roaster stack were predominantly As_2O_3 and SO_x in the particulate and vapor phase, respectively. The first decade (1948–1958) of operations saw the largest emissions (thousands of kg of As_2O_3 per day) which decreased significantly in subsequent decades due to emission controls (INAC, 2007). Historic roaster stack emissions have potentially impacted all of Yellowknife Bay. However, aerial dispersion combined with currents in the bay make it difficult to predict a net effect of this input at a specific location.

In 1975, Moore et al. (1978) measured As concentrations that ranged from 1500 to 20,400 μ g/L in Baker Creek surface waters, a tributary to Yellowknife Bay. Jackson et al. (1996) found As concentrations in surface sediments of the creek mouth as high as 2550 mg/kg. Mace (1998) recorded As levels in surface sediments upstream of Baker Creek mouth that ranged from 1764 mg/kg to 3821 mg/kg.

Geophysical investigations indicate the submerged tailings apron covers an area of 100,000 m² (Golder, 2002). Bulk geochemical investigations of the submerged tailings (Golder, 2002; EBA, 2001), determined As concentrations were as high as 3685 mg/kg but are typically in the 1000 mg/kg range. Pore water As concentrations obtained from approximately 40 cm below the SWI ranged from 920 μ g/L to 4360 μ g/L (Golder, 2002). The presence of a thin (4-7 cm thick) visibly oxidized zone at the top of cores in submerged tailings suggests possible attenuation of As by sorption onto authigenic Fe(hydr)oxides at the SWI (Walker and Jamieson, 2003). Arsenic-bearing roaster Fe oxides are heterogeneously distributed within these tailings (Walker and Jamieson, 2003) but typically make up less than 1% of them. Although these As-rich roaster oxides make up a small fraction of the submerged tailings, the As content is in the weight percent range (Walker et al., 2005) potentially making them an environmentally significant reservoir. Of interest is the potential for roaster oxides, likely dispersed throughout the bay through wind and wave erosion, to destabilise in the more organic-rich deeper portions of Yellowknife Bay.

2. Methods

2.1. Sampling locations

Sampling at the deep Yellowknife Bay site was done to expand on previously published data gathered by Mudroch et al. (1989). Sampling locations are shown in Fig. 1 and listed in Table 1. The sampling strategy targeted this site in both summer and winter almost two decades after Mudroch's sampling to see whether sedimentation is indeed an effective "natural" remediation scheme for As or if the element is undergoing diagenetic cycling, as documented in other subaqueous sediments (Takamatsu et al., 1985; Petersen and Carpenter, 1986; De Vitre et al., 1991; Mok and Wai, 1990; Wilderlund and Ingri, 1995; Muller et al., 2002; Martin and Pedersen, 2002).

The Submerged Beach Tailings sites are approximately 150 m offshore from the historic tailings that were deposited at the lake's edge during the first few years of mine production. Akaitcho Bay was initially chosen as a control site to determine natural back-

Table 1Sampling locations.

ground elemental concentrations. The sampling location is 10.6 km from the Giant Mine in an area without active or historic mining activity.

2.2. Sampling techniques

Sediment cores were retrieved with a 7.62 cm (ID) gravity corer (Glew, 1989). SCUBA divers were employed for both summer and winter sampling at the deep-water sites. Winter deep-water sampling involved cutting an opening through approximately 1.5 m of ice cover to create access for the divers. Once retrieved, all sediment cores were kept cool with ice packs and transported in the dark to a laboratory in Yellowknife. Cores used for geochemical analyses were extruded and sub-sampled in an ultra-pure N₂-filled glove-bag. Sediment sub-samples were then immediately frozen for transport to Queen's University, then freeze-dried in a Labconco freeze dryer at 1.0 Pa and -50 °C. Those destined for microbiological analyses were sub-sampled in the field under atmospheric conditions using sterile techniques, transported to the laboratory in coolers with ice packs for later analyses at the University of Ottawa.

High-resolution diffusion-based dialysis arrays (commonly known as peepers) were used to record the vertical variation in the chemistry of sediment pore waters (Hesslein, 1976). Prior to field installation, peepers and their cases were cleaned with dilute Sparkleen^{*}, rinsed twice with distilled water, rinsed once with double-distilled water (DDW), soaked in 0.5% ultra-pure HNO₃ for 24 h and rinsed three times with DDW. Peeper cells were then filled with DDW and covered with a polysulphone Gelman^{*} filter membrane (0.45 μ m and 0.22 μ m pore size) in a clean fume hood. Peepers were then sealed in their cases and deoxygenated by either a two-week low-flow ultra-pure N₂ purge or by periodic bubbling of immersed peepers in DDW with ultra-pure N₂ (Carignan and Gachter, 1994).

Two peepers were inserted into the sediments at each site (depth precision estimated to be ± 5 mm) and left for 14 days to equilibrate with sediment interstitial waters. After extraction, peepers were photographed and the SWI was visually verified. Peepers were then immediately wrapped in cling-wrap, sealed in purged cases (ultra-pure N₂) and purged again to avoid oxidation of peeper cell waters by atmospheric contact. Peeper cases were then placed in opaque black plastic bags to avoid photo-oxidation and transported back to the laboratory in Yellowknife for immediate subsampling.

Pore water samples were extracted from peepers by pipetting and transferred into clean 8 mL high density polyethylene (HDPE) bottles in a glove-bag filled with ultra-pure N_2 .

2.3. Analysis

Selected sediment cores were examined for the γ -ray ²¹⁰Pb, ²¹⁴Bi and ¹³⁷Cs signatures in each core in order to determine sediment horizon dates and sedimentation rates using methods described in Binford (1990). Sediment elemental analysis was accomplished by an *aqua regia* digest followed by ICP-MS for a

Site code	Site name	Latitude (DMS)	Longitude (DMS)	Depth (m)
AOBS-03	Akaitcho Bay	N62°23'38.8″	W114°17′2.4″	12
YKBS-03	Yellowknife Bay Summer	N62°29′2.8″	W114°20′47.6″	13
YKBW-04	Yellowknife Bay Winter	N62°29'2.8″	W114°20′47.6″	13
BCS-03	Baker Creek Mouth	N62°29'11.8"	W114°21′32.1″	1.5
BTS1-03	Submerged Beach Tailings 1	N62°29′43.9″	W114°20'39.2″	1.5
BTS2-03	Submerged Beach Tailings 2	N62°29'44.6"	W114°20'37.4″	1.5

36 element suite at ACME Laboratories in Vancouver, BC. Sequential leaches were done on selected sediment horizons at Oueen's University using methods described in Chipley et al. (2003) and MacFarlane et al. (2005). Approximately 5.0 g of leach (distilled deionised water (DDW), 2% HNO3 or 30% HNO3) was added to a 0.5 g sediment sample and placed in an ultrasonic bath for 2 h at room temperature. The sample was then centrifuged for 10 min and 1.0 g of supernatant was pipetted into acid-washed HDPE bottles containing 50.0 g of DDW spiked with ¹¹⁵In (ICP-MS internal standard). Samples were analysed on a high-resolution ICP-MS-equipped with an ESI Teflon nebulizer. Extraction results are intended to show the relative binding strength of measured parameters to their mineral host phase by incrementally stronger acid leaches only and as a tool for identifying mineral host phases as no known mineral standards were run alongside the selected sediment core samples.

Microbiological and related experiments were done at the University of Ottawa and detailed methodology can be found in Praharaj and Fortin (2004). Sulfate-reducing bacteria (SRB) and As-reducing bacteria (AsRB) were enumerated with the most probable number (MPN) techniques (Fortin, 2005; Kuai et al., 2001). *In situ* sulfate reduction rate (SRR) measurements on selected cores were calculated after the methods of Kostka et al. (2002). Iron mono-sulfide and FeS₂ were indirectly determined by measuring acid-volatile sulfide (AVS = FeS + H₂S) and chromium-reducible sulfur (CRS = $S^0 + FeS_2$) after methods in Fossing and Jorgensen (1989).

Pore waters extracted from peeper cells were acidified with ultra-pure HNO₃ and analysed for a suite of elements by ICP-MS. Pore waters were speciated for As $(H_2AsO_4^-, HAsO_4^{2-} and H_3AsO_3^0)$ in an ultra-pure N₂-filled glove-bag using the field method of Le et al. (2000). Organoarsenicals (CH₃AsO₂OH⁻, (CH₃)₂AsOO⁻) were not considered in speciation techniques due to their low relative proportions (<5%) reported in sediment pore waters from lakes in the vicinity of Yellowknife subject to similar historical mining impacts (Bright et al., 1994, 1996). Extracted peeper cell samples were passed through positively charged quaternary amine polymerically bonded silica-based anion exchange (SAX) resin cartridges (500 mg, 0.14 meq/g). SAX cartridges were preconditioned with 5 mL of 50% ACS grade methanol at low-flow (2 mL/min) and kept wet before sample addition for better interaction between analytes (negatively charged As species) and the silica resin. The uncharged As(III) complex (H₃AsO₃) was collected immediately after passing through the SAX cartridge while the negatively charged As(V) complexes ($H_2AsO_4^-$ and $HAsO_4^{2-}$) were subsequently eluted with a counter ion (5 mL 1 M ultra-pure HCl). The As(III)-rich samples were later acidified with ultra-pure HNO₃ to pH 2. Both samples were collected in acid-washed HDPE bottles, stored in the dark at 4 °C and later analysed for total As by ICP-MS. The efficiency of the SAX cartridges was tested by running As spikes through the cartridge. Separate solutions of Na₂HAsO4:7H2O and NaAsO2:4H2O in DDW were passed through the SAX cartridge at low-flow (2 mL/min) and the eluate was collected in acid-washed HDPE bottles. A 1 M HCl solution was then passed through the SAX cartridge at the same flow rate and the eluate was also collected in acid-washed HDPE bottles. The results indicated 89% and 80% efficiency in retaining the negatively charged As(V) oxyanions and passing the neutrally charged As(III) oxyanion, respectively.

Dissolved Fe(II) pore-water concentrations were analysed by colorimetry using the FerroZine[®] method (Viollier et al., 2000). Dissolved sulphide-S pore-water concentrations were determined by colorimetry using Cline's method (Cline, 1969). Dissolved SO₄ sediment pore-water concentrations were determined using the BaSO₄-turbidimetric method (Rodier, 1975).

3. Results and discussion

3.1. Historical record of mining impact

Solid-phase metal(loid) concentrations are relatively low throughout the core profile from Akaitcho Bay (AOBS-03, Fig. 2a), but there is a distinctive mid-core increase in As, Pb, Cu and Zn indicating that the sampling site has been subject to minor inputs. Although this area was selected as a control site remote from mining activities, Pb, Cu and Zn concentrations increase starting at a depth of approximately 16 cm, coincident with the opening of Giant Mine according to radiometric dating (Fig. 2b). Timelines were generated as per methods in Binford (1990). Mudroch et al. (1989) showed metal(loid) contamination from Giant Mine in Yellowknife Bay with sediments SE of Latham Island (Fig. 1) having As and Zn concentrations ranging from 108 to 890 mg/kg and 116 to 200 mg/kg, respectively. Comparisons to concentrations in Akaitcho Bay suggest downstream dilution is likely responsible for the lower metal(loid) concentration magnitudes observed in Akaitcho Bay sediments. Thus, instead of recording natural background concentrations, Akaitcho Bay has very likely been influenced by historical mining activity from Giant Mine as well as other mining and processing activities in the area (Walker, 2006), and can not be considered a control site. In addition, the lower position of the solid-phase As concentration peak relative to those for Pb. Cu and Zn. as well as the near-surface peak for As, suggests that there has been and still is post-depositional remobilization of this element both up- and down-core. This is further supported by the presence of dissolved As concentrations in adjacent pore waters (Fig. 2c).

3.2. Diagenetic remobilization of arsenic

Fig. 3a shows metal(loid) concentrations and the ²¹⁰Pb derived timeline in the core collected in August 2003 in Yellowknife Bay (YKBS-03). Increases in Pb, Sb, Cu and Zn coincide with the opening of Giant Mine (±1SD) in 1948. The concentrations of Pb, Sb and Zn start to decrease in the early 1960s consistent with mine waste management improvements. After approximately 1981, Pb, Sb, Cu and Zn concentrations approach background levels similar to those seen near the bottom of the core. The lack of significant pore-water concentrations of Pb, Sb, Cu and Zn indicate these particular metal(loid)s are not currently being remobilized and sedimentation has indeed isolated these enrichments at depth. Fortuitously, the inert nature of the Pb, Sb, Cu, Zn layer independently confirms ²¹⁰Pb dates and serves as an additional time marker to the ¹³⁷Cs peaks.

In contrast to the Cu, Zn, Pb and Sb solid-phase profiles, As deviates significantly suggesting post-depositional remobilization. A cursory look at Fig. 3a would suggest As inputs into Yellowknife Bay began lower in the sediment column ca. 1922, but this is highly unlikely since mining activity did not commence until 1948. This highlights the pitfalls of using diagenetically mobile elements as time markers in recent sediments. Higher in the sediment profile, As decreases concomitantly with Cu, indicating effective effluent treatment post-1981. However, the surficial sediments show a substantial enrichment in As comparable to mid-core concentrations. Note that the same surficial solid-phase As increasing trend is seen in the Akaitcho Bay core as well.

The dissolved As concentration peak is perched approximately 3 cm above the mid-core enrichment in the solids (compare Fig. 3a and b). Aqueous As is diffusing both upwards and downwards away from the solid-phase mid-core source. Sequential leach data (Fig. 3c) confirms the presence of a labile As source that



Fig. 2. Data from Akaitcho Bay, the remote site, sampled in August 2003. (a) Solid phase metal(loid) concentrations from sediment core. (b) Radiometric dating of sediment core. Error bars equivalent to one standard deviation. (c) As speciation in sediment pore waters.

originates from the mid-core solids as indicated by the DDW leachable portion. This source is, and likely has been, supplying

sediment pore waters with significant dissolved As, establishing a concentration gradient that drives diffusion. Solid-phase As, at



Yellowknife Bay Aug 03 (YKBS-03) and Apr 2004 (YKBW-04)



Fig. 3. Data from Yellowknife Bay (location shown in Fig. 1). (a) Solid phase metal(loid) concentrations from sediment core with associated timeline. (b) Dissolved As and Fe in sediment pore waters. (c) Sequential extractions for As in selected sediment horizons of YKBS-03. (d) Solid-phase As in YKBS-03 and YKBW-04 sediment cores. (e) Solid-phase Fe, Mn, and S in YKBS-03 and YKBW-04 sediment cores.

the mid-core enrichment, may be adsorbed as a loosely bound outer sphere complex. Foster (2003, and references therein) and Goldberg and Johnson (2001) documented physico-sorption (outersphere complexation) of As on smectite and amorphous Fe and Al oxides, respectively. Clay minerals such as these are expected to be present in Yellowknife Bay sediments which include the weathering products of volcanic and granitic rocks in the area (Andrade, 2006).

Higher in the sediment sequence, a concomitant decrease in dissolved As and an increase in solid-phase As suggests an efficient mechanism for As attenuation at the SWI (Fig. 3d and e). Yet, unlike the solid-phase mid-core As source, identified as roaster-generated maghemite and hematite (Andrade, 2006), the As in the surficial sediments is effectively bound as inferred from the lack of released As in the dilute sequential leaches (Fig. 3c). This indicates As may be bonded much "tighter", such as to Fe–Mn (hydr)oxides in an inner-sphere monodentate and/or bidentate configuration, similar to those described in the EXAFS study of Waychunas et al. (1993). In that study, the As oxyanion complexes were chemisorbed to fer-

rihydrite and the FeOOH polymorphs, phases known to precipitate in the oxic portion of lacustrine sediments (Fortin et al., 1993). However, the presences of dissolved As (75 μ g/L) above the SWI indicates not all of the upwardly diffusing As is being attenuated and suggests a finite number of available solid-phase surficial binding sites for dissolved As species.

The dissolved Fe(II) concentration peak (not shown) straddles the SWI, indicating surficial sediments are also reducing and Fe is released from reductively-dissolved Fe(hydr)oxides. This was most likely driven by the summer addition of labile organic matter (5.0 wt.%) to the SWI. Fig. 3d and e indicate a strong correlation between As and Fe as seen in the solid-phase core profile trends and to a lesser extent with S and Mn trends. The As concentrations just above the SWI shown in Fig. 3b are therefore probably a result of the dissolution of Fe(hydr)oxides, and possibly Mn oxides (De Vitre et al., 1991). However, this As release to bottom-waters is small compared to the magnitude of upwardly diffusing As below the SWI and suggests minimal erosion of the Fe–As solid-phase surficial veneer was occurring, at least during

Sequential Leaches of Yellowknife Bay Core (YKBS-03)





the sampling dates. Almost all of the dissolved pore-water As migrating to the SWI is attenuated in the top 1 cm of the sedi-

ment column illustrating the scavenging efficiency of the Fe-Mn(hydr)oxides. Thus, the preservation of this very thin oxic zone should be paramount in As mitigation strategies for the bay.

3.3. Seasonal expansion and contraction of the sedimentary oxic and reducing zones

The deep-water site in Yellowknife Bay was sampled in late summer (YKBS-03) and late winter (YKBW-04) in order to provide insight into seasonal mechanisms. Recall that Fig. 3b showed the measured depths of dissolved As and Fe maxima for summer are shallower (1 cm) than those for the winter (2 cm). It is possible that seasonal variations in primary productivity, subsequent organic matter input and resulting reductive dissolution of As– Fe-rich (hydr)oxides is responsible for this As–Fe depth maxima

-40

0

100

difference. It is more realistic though, that sediment heterogeneity plays a large role in observed vertical geochemical variations. Evidence for this is from triplicate coring done by Mudroch et al. (1989) who found As concentrations ranged from 630 mg/kg to 2800 mg/kg in the top centimeter of sediments while Fig. 3d and e shows the solid-phase As-rich Fe–Mn veneer at the SWI in the summer has approximately half the concentration of As compared to the winter. However, an additional consideration is the fact that the surficial oxic As–Fe-rich skin, where thin enough, could undergo reductive dissolution from the increased O₂ demand of organic input. Considering sediment heterogeneity as an undulating and thin near-surface Fe-redox front (Shimmield and Pedersen, 1990, and references therein) implies a patchy mosaic of oxic and reducing zones, which is the intersection between the undulating redox





Fig. 4. Data from Yellowknife Bay (location shown in Fig. 1). (a) As speciation in pore waters from YKBS-03 and YKBW-04 sampling sites. (b) S speciation in pore waters, from YKBS-03 and YKBW-04 sampling sites. (c) Arsenate and sulfate-reducing bacteria in YKBS-03 and YKBW-04 sediment cores. (d) Sulfate reduction rates in YKBS-03 and YKBW-04 sediment cores, measured with S-35 core injection technique. (e) Acid-volatile sulfide (AVS) and chromium-reducible sulfur (CRS) in sediment core YKBS-03 and YKBW-04 sediment cores.

Dissolved Sulfide (µg/L)

400

500

600

300

200

700

800

900





Fig. 4 (continued)

plane and the relatively flat sediment surface plane. Seasonal variations in organic matter could facilitate the further aerial expansion of the reducing zones during summer primary productivity (i.e., increased sedimentary O_2 demand) and contraction of these zones during the winter (i.e., less sedimentary O_2 demand). This process could not be identified with a high level of confidence given the limited sites sampled and the large variation in As content evident from Mudroch et al. (1989) and this study.

3.4. As(V)/As(III) speciation in pore waters and correlations with microbial activity

Arsenic species are known to exist in disequilibrium in natural and contaminated waters. In this study, As(V):As(III) ratios in sediment pore water vary between 0.1 and 56. Lower ratios (<1) are found in the anoxic portion of sediments, defined as the sediments below the depth where significant dissolved Fe concentrations begin to increase (Stumm and Morgan, 1996). The higher ratios are found in the oxic zone and in the overlying bottom-waters.

At the Yellowknife Bay site, As(V):As(III) ratios are much higher in pore water collected in the summer (YKBS-03) than in the winter. Arsenic(III) dominates in the winter profile (YKBW-04) (Fig. 4a). Another striking difference in seasonal sampling of pore waters is the abundance of dissolved sulfide in the summer and the near depletion in the winter. This is despite the fact that dissolved SO₄ concentrations below the SWI are similar and decrease at the same depth during both sampling seasons which indicates that SO₄ reduction is occurring during both seasons (Fig. 4b). The seasonal As speciation trends may partially be explained by the activity of microbes and the cycling of solid-phase Fe-sulfides, as follows:

Fig. 4c and d shows significant populations of As-reducing bacteria (AsRB) and SO₄-reducing bacteria (SRB) present during both sampling seasons. However, the measured SO₄ reduction rates (SRR) are much higher in the winter (approximately 715 nmol/ cm^3/day maximum) than the summer (approximately 22 nmol/ cm^3/day maximum). This seasonal difference in SRB activity results in the varied distribution of acid-volatile sulfide (AVS, considered to represent FeS) and chromium-reducible sulfur (CRS, considered to represent FeS₂) seen in Fig. 4e. This has a direct bearing on dis-

solved As(III) pore-water concentrations. Bostick and Fendorf (2003) performed adsorption experiments with dissolved As(III) on FeS and FeS₂. Their results showed As(III) adsorption onto FeS is much greater (i.e., 45 μ mol As(III)/g FeS, maximum at pH 9) than on FeS₂ (<8 μ mol As(III)/g FeS at pH 9). Greater As(III) adsorption was also noted at higher versus lower pH for experiments done at pH 9, 7 and 4. Rickard and Luther (1997) contend that the mechanisms involved in the conversion of FeS to FeS₂ are:

$$\operatorname{FeS}_{(s)} \to \operatorname{FeS}_{(aq)}$$
 (1)

$$FeS_{(aq)} + H_2S_{(aq)} \rightarrow FeS_{2(s)} + H_{2(g)}$$

$$(2)$$

In Yellowknife Bay, the increase in the FeS₂ fraction, at the expense of FeS, is hypothesized to result in the desorption of the As(III) oxyanion from the surface of the FeS structure. The pH of sediment pore waters for the two sampling seasons (Fig. 5) is also consistent with the suggestion by Rickard and Luther (1997), who state that slight shifts in pH near the first dissociation constant of H_2S (pH = 6.99) will determine whether the majority of dissolved sulfide will be present as H₂S or HS⁻. This point is critical since Eq. (2) cannot be electrically balanced using HS⁻ (Rickard and Luther, 1997). This may explain why the YKBS-03 pore waters have significant sulfide at higher pH values versus no dissolved sulfide during slightly lower winter pH values (YKBW-04). In addition, the pH and dissolved As(III) distributions also agree with the results of Bostick and Fendorf (2003). Higher pH in the YKBS-03 pore waters results in greater adsorption of the As(III) oxyanion to FeS and FeS₂ than in the YKBW-04 sampling, where As(III) is abundant. A possible control of dissolved As(III) in natural submerged sediments, not previously documented, can be described as an As(III) desorption mechanism:

$$\text{FeS}_{(s)} \sim \text{As}(\text{OH})_3 + \text{H}_2\text{S}_{(aq)} \rightarrow \text{FeS}_{2(s)} + \text{H}_{2(g)} + \text{As}(\text{OH})_{3(aq)}$$
 (3)

The decrease in As(V) pore-water concentrations from the YKBS-03 sampling season to those seen during the YKBW-04 sampling season, however, are not explained by the above-described mechanisms. Hoeft et al. (2004) described a chemoautotroph, different from the heterotrophic SRB and AsRB enumerated in this study, that are able to respire As(V) in the absence of organics using reduced S^{2–} as the electron donor. It is possible that the



Yellowknife Bay Aug 03 (YKBS-03) and Apr 2004 (YKBW-04)

Fig. 5. Data from Yellowknife Bay (location shown in Fig. 1). Pore water pH from sampling sites YKBS-03 and YKBW-04.

 Table 2

 Seasonal variations in redox sensitive species at approximately 10.5 cm depth in Yellowknife Bay August 2003 and April 2004 sampling seasons.

Sampling Season	As(V) (µmol/L)	As(III) (µmol/L)	Sulfide (µmol/L)	Sulfate (µmol/L)
YKBS-03 (summer)	2.27	2.51	22.7	47.9
YKBW-04 (winter)	0.9	5.6	<dl< td=""><td>61.5</td></dl<>	61.5

reduction of As(V) to As(III) is being carried out by chemoautotrophs through the oxidation of dissolved HS⁻ as reported by Hoeft et al. (2004).

In experiments done on the anoxic bottom-waters of Mono Lake, Ca, USA, Hoeft et al. (2004) reported a decrease in As(V) concentrations coincident with increases in both As(III) and SO₄ concentrations during laboratory-based culture experiments. The transformation of As(V) to As(III) using a modified version (i.e., using HS⁻ instead of S²⁻ and the neutral As(III) oxyanion and divalent As(V) oxyanion species) of the equation of Hoeft et al. (2004) indicates that for every 4 mol of As(V) reduced, 1 mol of SO₄ is produced (Eq. (4)). Examining the relevant dissolved reactants and products in Eq. (4) from a particular depth in the sediment pore waters of Yellowknife Bay cores, reveals a consistency with the results of Hoeft et al. (2004), shown in Table 2. Interestingly, a large surplus of sulfide is available during the YKBS-03 sampling for Eq. (4) to proceed and the sum of the As(V) and As(III) in the YKBS-03 sampling is approximately the amount of As(III) observed in the YKBW-04 sampling.

$$4HAsO_{4(aq)}^{2-} + HS_{(aq)}^{-} + 7H^{+} \rightarrow 4H_{3}AsO_{3(aq)}^{0} + SO_{4(aq)}^{2-}$$
(4)

It should be noted here that the MPN method used for the determination of AsRB population is based on assessment by visual inspection, namely the observation of a bright yellow precipitate (As₂S₃) within seconds of sulfide addition. This is the result of biotic reduction of arsenate as observed in the present study. This is in stark contrast to the abiotic reduction of arsenate by sulfide, which, despite being rapid, does not produce visible precipitate under the given conditions until about 1 h after sulfide addition (Kuai et al., 2001). Although there is a positive indication of biotic reduction in the MPN system, there is no conclusive indication that the AsRB are active in the sediments and no information on the rate of arsenate reduction.

Sediment heterogeneity precludes concluding the results of As speciation at the deep Yellowknife Bay site are seasonally induced. It is more likely that the sediments are patchy regarding the distribution of As species and that sampling has captured snapshots of As species redox transformations explaining dissolved pore water geochemistry (i.e., the same site at the sediment pore scale was not sampled more than once). This study describes As speciation and redox transformations in natural systems rather than laboratory systems, and provides insight into possible mechanisms involved in Yellowknife Bay.

3.5. Arsenic diffusion and fluxes

Sediment pore waters are chemically dynamic and are subject to significant vertical ion concentration changes over short time and spatial scales compared to their adjacent solid-phase counterparts. Mathematically, the one dimensional chemical migration of ions due to a concentration gradient, known as diffusion, in sediment pore waters is described by Fick's first law:

$$J_z = -(D^0/F)_i \varphi dc/dz \tag{5}$$

where J_z = diffusive transport rate of the ion (µg/cm²/month), D^{0} = coefficient of diffusion of ion *j* (cm²/s), *F* = formation resistivity factor, accounting for the tortuosity of the ion path in a porous medium, φ = porosity, and *dc/dz* = concentration gradient of ion *j* (μ g/L/cm). Note the expression on the right hand side of the equation is negative, indicating that the flux is in the opposite direction to the concentration gradient. The value D° is calculated from known values for H₂AsO₄⁻ at 298.15 K (Li and Gregory, 1974) and the Stokes–Einstein relation:

$$D_1^0 \eta_1 / T_1 = D_2^0 \eta_2 / T_2 \tag{6}$$

where η = viscosity of water, and *T* = temperature of water in Kelvin.

Fick's first law assumes: (1) dc/dz is linear between the pore water maximum and the bottom-water concentration and (2) wave-induced ion transport, bioturbation and advection are nonexistent. Both these assumptions are violated in the sediments sampled in this study because: (1) arsenic is known to be attenuated close to the SWI by Fe-Mn(hydr)oxides and gradients may be concave upwards instead of linear, resulting in overestimations of As mobility rates towards the SWI (Martin and Pedersen, 2002); (2) the lake bottom at the submerged tailings are physically mixed (observed asymmetrical wave ripples) due to currents resulting in underestimations of As diffusion rates; and (3) suspected advective flow from groundwater sources (Walker and Jamieson, 2003). In addition, the fluxes in this study are calculated for only 30 days and some parameters in Fick's first law change over longer time periods, such as temperature. Nevertheless, estimates of As fluxes towards the SWI are useful when comparing heavily impacted sampling sites in Yellowknife Bay to Akaitcho Bay, a site approaching natural As concentrations for the area (Table 3).

The upward As flux calculated for Akaitcho Bay sediments (AOBS-03) agrees well with As fluxes from other natural sediments in Sweden ($-0.18 \ \mu g/cm^2/month$ in Wilderlund and Ingri, 1995) and the Amazon Shelf ($-0.4 \ \mu g/cm^2/month$ in Sullivan and Aller, 1996). Flux calculations for sites YKBS-03 and YKBW-04, directly influenced by Giant Mine activity, are higher though less than the As fluxes calculated for mining-impacted lacustrine sediments in Balmer Lake, ON ($-25 \ \mu g/cm^2/month$, Martin and Pedersen, 2002). Calculated As fluxes at site YKBS-03 are slightly higher than those for YKBW-04, even though the As concentration maximum in YKBW-04 is twice that of YKBS-03 (Fig. 3b). The shallower concentration peak (1 cm) and warmer sediment temperatures in the Au-

Table 3					
Calculated	diffusive	flux of A	s ⁵⁺ towards	the sediment-	water interface

Site	T (K)	$D^{\rm o} ({\rm cm}^2/{\rm s})^{\rm a}$	dc/dz (µg/L)	$J_z (\mu g/cm^2/month)^*$
AOBS-03	282.7	5.78E-06	42.2	-0.4
YKBS-03	282.7	5.78E-06	331.3	-3.1
YKBW-04	278.7	5.01E-06	212.8	-2.0
BCS-03	282.7	5.78E-06	1419.5	-15.0
BTS1-03	282.7	5.78E-06	268.5	-0.9^{\dagger}
BTS2-03	282.7	5.78E-06	70.2	-0.2^{\dagger}

 $F = \varphi^{-3}$ for sediments with $\varphi \sim 0.7-0.9$ and $F = \varphi^{-2}$ for $\varphi < 0.7$ (Ullman and Aller, 1982).

 φ = 0.9 based on average particle density of 2.65 g cm⁻³ and water content measurements for cores AOBS-03 and YKBS-03.

 a D^{o} = Corrected for temperature using Stokes-Einstein relationship (Li and Gregory, 1974).

* Diffusional flux across SWI calculated for 30 day month. YKBW-04 sampled in April and all other sampling sites sampled in August.

[†] Diffusional flux across SWI calculated using estimated φ (approximately 0.6 for unconsolidated surficial submerged tailings composed of very fine sand with minor silt (Berner, 1980).

gust sampling season both work in conjunction to increase fluxes towards the SWI. Submerged Beach Tailings fluxes are similar to AOBS-03 fluxes due to the lower porosity of the Beach Tailings, which increases *F*, even though As concentration gradients over similar depths in BTS1-03 and BTS2-03 are much greater than in AOBS-03 pore waters.

While the data do support apparent seasonal differences, only two measurements of pore water As were done at the deep Yellowknife Bay site and may not represent seasonality. For example, the data indicate that the redoxcline fluctuates between 1 and 2 cm near the SWI but given the sediment heterogeneity, such measurements more readily imply that the redoxcline is an undulating geochemical plane and may intersect the SWI and bring reduced, soluble As to the surface in a patchy network. Since this flux is non-linear, a large flux for a short time may represent an important loss of As from the sediments despite the fact that it does not appear to be a major loss mechanism during the sampling dates. The differences in flux calculations also highlight the control sediment porosity has on the dissolved mass contribution to overlying waters.

The flux modelling is useful in identifying relative differences, however, calculations are based on single time point measurements of depth profiles. Fluxes could easily change at another point in time if the gradient became steeper or intercepted the SWI. Since the seasonal variation in gradients may change appreciably the flux numbers that are obtained in this study represent fluxes only twice during the year, not a bracketed range of fluxes between which all other values likely reside. Fluxes could be quite significant for the brief times that reducing pore waters reach the water surface. Thus, sediments may actually be an important source of As to the water column, although measurements to date indicate more attenuation at the SWI than release.

4. Conclusions

A significant proportion of measured As and other elemental concentrations in sediments and pore waters in this study exceed Canadian Environmental Quality Guidelines for a freshwater setting (CEQG, 2003). However, it should be noted that the deepest measured concentrations in Akaitcho Bay sediments, thought to represent natural pre-mining background for the area, are higher than the CEQG. This suggests the local geology contributes detrital material that is slightly elevated in As and other elements. In fact, van Hees et al. (1999) measured As, Sb and Pb concentrations in the shear-hosted ore body at Giant as high as 5748, 225 and 398 mg/kg, respectively. The same authors recorded 30 mg As/kg in the metasediments east of Yellowknife Bay. Both these local sources, as well as probable upstream sources, contribute to the natural geochemical composition of the lacustrine sediments investigated in this study.

The sites described here indicate that mine-impacted lacustrine sediments can be both a source and a sink of reactively mobile As with changing seasonal redox conditions. Akaitcho Bay sediments record both the impact of Au mining and the diagenetic remobilization of As. In the case of the Yellowknife Bay site, a very thin undulating oxic zone, can effectively attenuate upwardly diffusing As. Conversely, if the redoxcline is above the SWI, sediments can be actively releasing As by the reductive dissolution of Fe(hydr)oxides. Thus, the input of labile organic matter via primary production in the open water season may be the controlling factor in the efficiency of the oxic zone in attenuating As. The deep Yellowknife Bay sediments are relatively suboxic, organic-rich and abundant in microbes. The aqueous As speciation is complex and thought to be controlled by pH-dependant sorption mechanisms and microbially-driven seasonal transformations of authigenic Fe-sulfides. These factors and others, such as resultant dissolved concentration gradients, sediment porosity and temperature, all occur in conjunction determining temporarily and spatially variable As speciation and fluxes.

4.1. Implications for the remediation of the Giant Mine site

Martin and Pedersen (2002, 2004) documented a similar release of As in mining-impacted Balmer Lake sediments and suggested limiting anthropogenic nutrient inputs that have the potential to increase primary production, rain labile organic matter to aquatic sediments and drive down the redox state of the sediments. Yellowknife City stopped discharging sewage into Niven Lake, a body of water which drains into Back Bay and Yellowknife Bay, in 1981 and started treating sewage before disposal. At present, the combination of a lack of an extensive soil cover in the surrounding area (i.e., low nutrient influx through erosion and transport), the strong physical mixing (i.e., oxygenation of the water column during fall storm events before freeze-up), a relatively small population in Yellowknife City and effective sewage treatment all work together in favour of limiting nutrient inputs to the bay. Yet, as has been shown by Martin and Pedersen (2004), anthropogenic shifts in trophic status triggering redox changes in sediments are possible over time. A seasonal monitoring program for both the water column and sediments, may be warranted due to the relatively thin measured and presumable patchy oxic zone (i.e., millimeters to centimeters) attenuating upwardly diffusing As from sediment pore waters. However, it is likely that natural organic matter input is great enough (even at the control site), that reducing conditions in the sediments could be widespread and is a much more important redox control compared to contributions from anthropogenic sources. Careful monitoring of the water column productivity and pore water elemental cycling are appropriate measures to be implemented as part of any mitigation strategy for Yellowknife Bay sediments. The Baker Creek site is the best candidate for any mitigation given its larger As flux, but more importantly, the near-shore quasi-containment via a breakwater along the shoreline.

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