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Remobilization of legacy arsenic from sediment in a large subarctic waterbody impacted by gold mining

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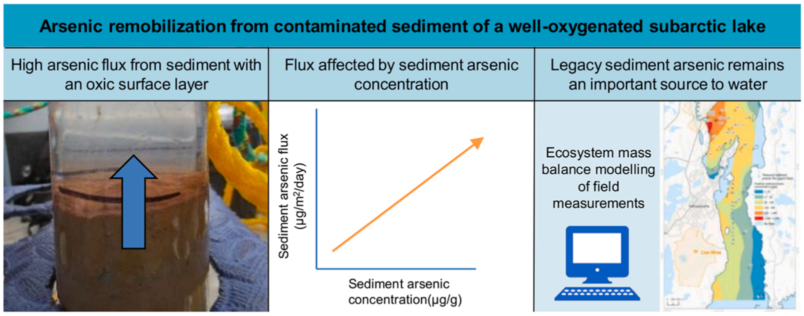
HIGHLIGHTS

- High arsenic flux from contaminated sediment to oxygenated surface water.
- Aqueous arsenic at the sediment-water interface was predominately as arsenate.
- Low seasonal variation of sediment arsenic flux occurred in summer and winter.
- Arsenic flux increased with sediment solid-phase arsenic concentration.
- Arsenic release from sediment was an important source to surface water.

GRAPHICAL ABSTRACT



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ABSTRACT

Arsenic contamination from mining poses an environmental challenge due to the mobility of this redox-sensitive element. This study evaluated arsenic mobility in sediments of Yellowknife Bay (Canada), a large subarctic water body impacted by gold mining during the 20th century. Short-term measurements of arsenic flux from sediment, arsenic profiling of the water column and sediment porewater, and mass balance modelling were conducted to assess the importance of sediment as an arsenic source. Sediment arsenic fluxes were highly variable throughout Yellowknife Bay and ranged from – 65–1520 µg m^{-2} day^{-1}. Elevated fluxes measured near the mine site were among the highest published for well-oxygenated lakes. Redox boundaries were typically 2–3 cm below the

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Mass balance
Mining

sediment surface as indicated by porewater profiles of iron, manganese, and arsenic, with arsenic maxima of 65–3220 μg L^{-1} predominately as arsenite. Sediment arsenic flux was positively related to its solid-phase concentration. Modelling indicated sediment was a principal source of arsenic to the water column. Adsorption and precipitation processes in the oxidizing environment of near-surface sediments did not effectively attenuate arsenic remobilized from contaminated sediments. Internal recycling of legacy arsenic between sediment and surface water will impede a return to background conditions in Yellowknife Bay for decades.

1. Introduction

Environmental contamination of arsenic has occurred at historic mine sites in Canada [23,33,61] and around the world [13,35,42]. Many of these mines were in operation when government regulations and mitigation measures for pollution were limited [33,40]. Legacy contamination of arsenic from mining and ore processing remains an environmental challenge due to the post-depositional mobility of arsenic, which results in slow recovery of impacted aquatic ecosystems [40,51,7] and on-going potential risks to ecological and human health [16,17,37].

Arsenic is a redox-sensitive element, and its environmental behavior in sediments is strongly tied to the cycling of iron and sulfur [20,34,62], and in some cases manganese [12]. Recent research has also identified associations between organic matter and arsenic in sediments, including reduced sulphur compounds (thiols), which compete with iron oxyhydroxides for sorption of arsenic [21,24,38,45]. Mining-derived minerals deposited in sediments can release arsenic to porewater; the fate of arsenic associated with these minerals is dependent on mineral stability and surrounding environmental conditions. Arsenic-bearing sulphide minerals may oxidize in the surface sediment layers, typically releasing some arsenic to pore water and retaining some arsenic in secondary iron oxyhydroxides. In oxygen-poor environments, or on burial, reductive dissolution of arsenic-bearing iron oxides and oxyhydroxides is an important mechanism for arsenic release to sediment porewaters [54]. Dissolved arsenic in porewater can diffuse within the sediment profile and bind to sulphides, organic matter or iron oxyhydroxides depending on the surrounding biogeochemical conditions in the sediment [20,45,54]. In oxygenated surface sediments, iron oxyhydroxides act as an adsorption barrier to upward diffusion of arsenic, while iron dissolution following the progressive burial and onset of reducing conditions releases arsenic into surrounding water [44,50]. Arsenic in porewaters is predominately inorganic arsenate (As^{+5}) or arsenite (As^{+3}) as oxyanions ($HAsO_4^{-2}$ or H_3AsO_3, respectively), depending on sediment redox and pH conditions [59]. The mobility and long-term fate of arsenic in sediment is controlled by complex biogeochemical interactions involving arsenic with iron, sulfur and organic matter, which may differ among ecosystems.

Remobilization of arsenic from lake, river and estuarine sediments has been reported following the onset of anoxia and dissolution of iron oxides and oxyhydroxides [10,35,44]. The sediment efflux of arsenic is impeded in systems where oxic conditions extend from the water column into sediments due to adsorption and precipitation with iron oxyhydroxides in surface sediment and particles settling out of the water column [19,22,25,3,36,43,70]. Even though the sediment efflux of arsenic is impeded by the presence of an oxic boundary, sediments can still be a source of arsenic in well-oxygenated lakes if the upward diffusion of arsenic from sediment exceeds the attenuation capacity of the surface layer [32,55,7], though the broader importance of this process remains unclear and is potentially influenced by organic matter interactions with arsenic and iron [12,19,9]. Methodological uncertainties also limit our broader understanding of sediment flux processes because sediment arsenic fluxes are commonly estimated from porewater concentration gradients and theoretical calculations such as Fick's Law of diffusion and diagenetic modelling [2,41,44]. Field measurements of arsenic flux by incubation of lake sediments provide validation of theoretical estimates because they account for the net effects of chemical and biological processes not considered in diffusion calculations [39]. Information is currently limited on the extent to which mining-contaminated lake sediments are a source of arsenic in well-oxygenated systems and the environmental controls on this flux.

For six decades, Yellowknife Bay (Northwest Territories, Canada) received arsenic-bearing wastes from several different sources including atmospheric emissions from gold-ore roasting, direct discharge of tailings, and mine site effluent via Baker Creek. Mine-related loads of arsenic continue to enter Yellowknife Bay via treated mine water released from the Giant Mine property (which is currently being decommissioned) and catchment erosion from contaminated soils [52]. Earlier investigations of arsenic profiles in sediments and porewaters of Yellowknife Bay showed evidence of post-depositional mobilization and likely diffusion of arsenic from sediment [2,15], though the importance of this flux was unclear.

The main objective of this study was to evaluate the stability of legacy arsenic contamination by measuring arsenic diffusion rates and the influence of potential environmental drivers of arsenic diffusion from sediments of Yellowknife Bay, a large water body impacted by gold mining. The study combined several approaches, including field measurements of arsenic flux by incubation of intact sediments, profiling of porewater arsenic concentrations in sediment, profiling of water column arsenic concentrations, and ecosystem mass balance modelling to evaluate the spatial and seasonal contributions of arsenic release from contaminated sediments to surface waters. Environmental characteristics of Yellowknife Bay sediments were measured to evaluate controls on arsenic flux. Parallel research by Paudyn et al. [52] on arsenic mineralogy and solid-phase element profiles in Yellowknife Bay sediments provides important complementary information on the current mineral hosts of arsenic in sediments and the post-depositional fate of mining-derived arsenic. The current study presents novel findings on the importance of arsenic remobilization from mining-contaminated sediments under well-oxygenated conditions in a subarctic water body.

2. Materials and methods

2.1. Study site

Yellowknife Bay is in the North Arm of Great Slave Lake in the Northwest Territories, Canada (Fig. 1). The City of Yellowknife (population ~20,000) is located on the western shore of Yellowknife Bay, and two Yellowknives Dene First Nation communities (Ndilo and Dettah) are also located on its shores. During the 20th century, Yellowknife Bay received arsenic, antimony, and metals from gold mining operations at Con Mine (1938–2003), Negus Mine (1939–1952), and Giant Mine (1948–2004). Contamination to Yellowknife Bay occurred via several sources, including atmospheric deposition of ore roasting emissions from all three operations, the majority of which was released from Giant Mine during early years of operation when stack emissions were uncontrolled [33]. Ore roasting generated arsenic trioxide and roaster-generated iron oxides containing up to 6% arsenic [64,65], which were dispersed into the receiving environment. In addition, effluent was discharged into the north end of Yellowknife Bay via Baker Creek during summer throughout the life of Giant Mine (Fig. 1). Effluent was untreated prior to the construction of a water treatment plant in 1980, and treated effluent continued to be discharged until after mine closure up to the time of this study. Tailings from Giant Mine were deposited on the north shore of Yellowknife Bay between 1948 and 1951, and they subsequently eroded and were redistributed by wave action and currents [27] (Fig. 1). These sources of mining contamination have enriched arsenic in Yellowknife Bay sediments by more than two orders of magnitude above background (25 ± 10 μg g^{-1}), with maximum concentrations of 1300–8656 μg g^{-1} reported at sites near Giant Mine [15,2,52].

Yellowknife Bay is a relatively large water body with a surface area of approximately 20 km^2 and a maximum water depth of approximately 30 m at the south end of the bay. In this subarctic environment (latitude 62.4°N), sub-freezing temperatures maintain ice cover on Yellowknife Bay for much of the year, from November to June. Summer warming leads to thermal stratification of the water column for a brief period in July and August, particularly at the north end of the bay, which is more protected from wind. The Yellowknife River and Baker Creek, with mean annual discharges of 59 and 0.2 m^3 s^{-1} [67], respectively, are the dominant inflows, and wind-driven circulation also brings water from the main body of Great Slave Lake into the bay.

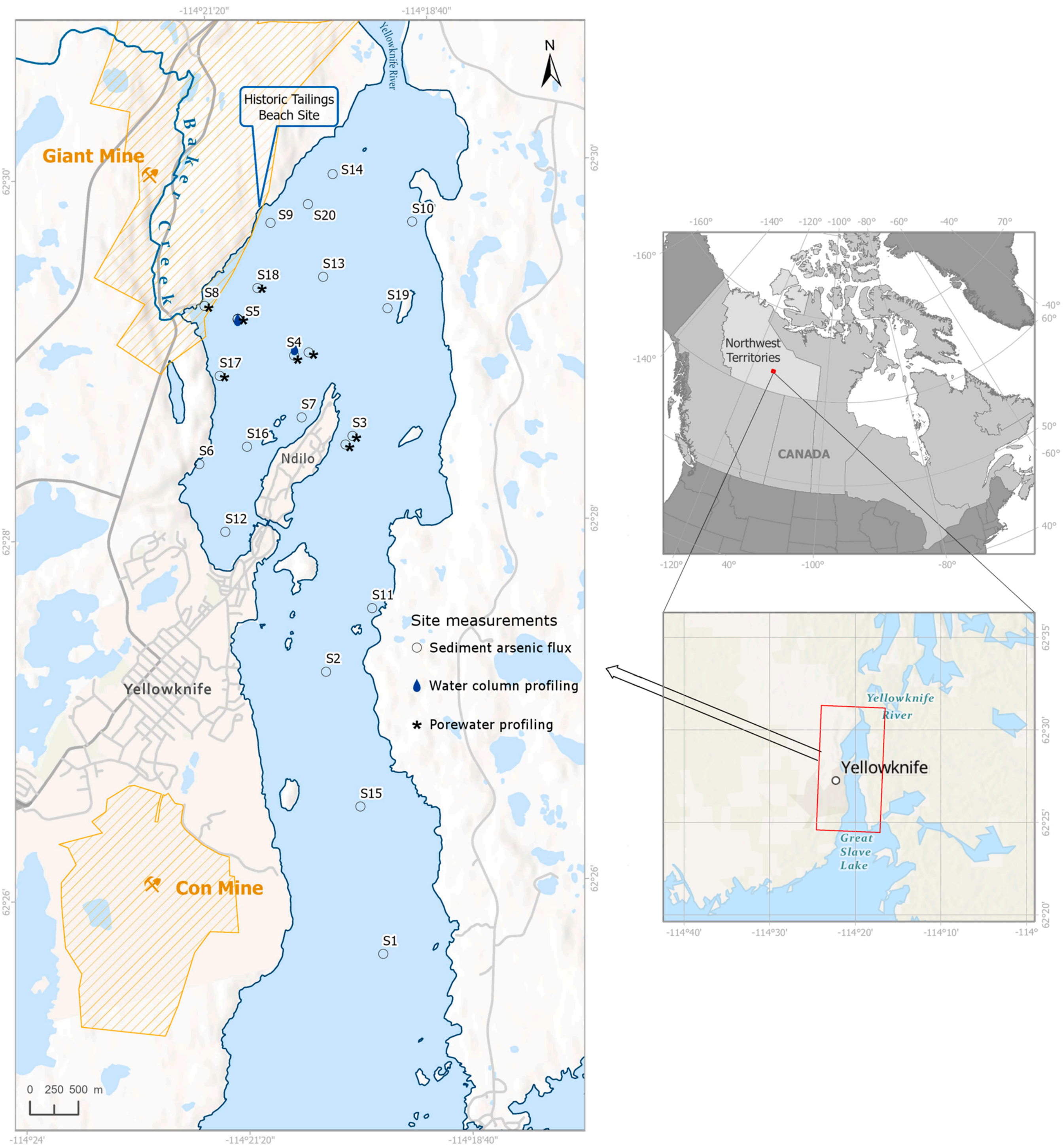

Fig. 1. Map of Yellowknife Bay and its location adjacent to the City of Yellowknife on Great Slave Lake in the Northwest Territories, Canada. The left panel presents the 20 sites where 28 sediment cores were collected for arsenic flux measurements as well as the locations for water column and porewater profiling. Map created using ArcGIS software by Esri and the Esri Canada Topographic basemap.

2.2. Field sampling

Field sampling was conducted on Yellowknife Bay in August 2018 (late summer), March 2019 (winter), and the beginning of July 2019 (early summer) to measure diffusion of arsenic from intact sediment cores. Over the three sampling periods, a total of 28 sediment cores were collected from 20 sites throughout the bay. Some of the sampling sites were the same as those reported in Paudyn et al. [52], although the site names are different. Both sets of identifiers as well as geographic coordinates and other site details are provided in Table S1 of the Supplemental Information. Duplicate cores were collected at two sites in August and two sites in March to estimate within-site variability, and four of the sites were sampled in both August and March to examine seasonal variability. The remaining sites were only sampled on one occasion. Sites were selected to represent both a range of depths as well as a gradient in sediment arsenic contamination (which decreased with greater distance from the Giant Mine property) (Fig. 1). Shallow sites were higher energy environments due to wave action, while deeper sites were low energy depositional areas.

Sediment cores were collected with a gravity corer, ensuring a sufficient volume of overlying water remained to conduct water sampling during the incubation experiments. To estimate the water volume, the height of the overlying water (mean ± standard deviation = 21 ± 7 cm, $n = 28$ cores) was measured at four places across the core surface due to the uneven surface of the sediment. Smaller 6.6 cm diameter core tubes were used to collect more compact, coarser nearshore sediment, while 8.6 cm diameter core tubes were used for offshore finer sediment. Overlying water volumes varied among the 28 cores (mean ± standard deviation = 1.1 ± 0.5 L), which was taken into account in the flux determination.

Short-term incubation experiments were conducted on the cores to measure changes in arsenic concentrations of overlying water over time. Water sampling was conducted with trace metal clean protocols including use of acid-washed materials and clean hands, dirty hands protocol. Overlying water was sampled at the start of the experiment (day 0) on the day of core collection and roughly every 24–48 h for 2–6 days (Supplemental Fig. S1). Initial experiments were 5–6 days in August 2018 and March 2019, and then the length was reduced to 2 days for the final field program in July 2019 because of adequate flux detection over the shorter time period. Exact times for sampling were noted to determine the duration between water sampling events. During the experiment, sediment cores were either incubated in the lake at the epilimnetic or hypolimnetic temperature (depending on collection depth) using a core holder system (similar to [48]) or in a laboratory refrigerator in Yellowknife, adjusted to near-ambient lake temperatures. The overlying water of the cores was not mixed or stirred during the incubation, which may have resulted in the formation of a boundary layer at the sediment-water interface (SWI). Temperature loggers were placed adjacent to the cores to record water temperature during the experiments. For each sampling event, 5 mL of filtered (0.2 μm) overlying water was collected with an acid-washed rhizon sampler (Rhizosphere Research Products, Wageningen, the Netherlands) and a syringe, preserved with 2% vol/vol HNO_3 in a 15 mL metal-free tube, and stored in a refrigerator until laboratory analysis. A total of 108 water samples, 15 field duplicates, 11 field blanks and 4 travel blanks were collected during the field program. At the end of the incubation, overlying water was removed from each core with an extruder, and sediment profiles of percent dissolved oxygen were measured at 0.5 cm intervals from the surface with a microsensor (Microx 4 oxygen meter, Presens, Regensberg, Germany). The top 3 cm of surface sediment was then collected with an extruder for analysis of organic matter content and solid-phase element concentrations. Sediment samples were frozen in clean sampling bags.

Sediment porewater was separately sampled from eight cores (3 sites in August 2018, 3 sites in March 2019, and 2 sites in July 2019; Fig. 1). Two of the sites sampled in March were the same sites from August, in order to examine seasonal variability of porewater profiles. Profiles of sediment porewater (dissolved fraction, 0.2 μm) were sampled using acid-washed rhizons inserted into pre-drilled ports in core tubes at depths of 1 cm above the SWI, at the SWI (0 cm depth), and 1–6 cm below the SWI at 1 cm intervals, similar to Shotbolt [58] and Seeberg-Elverfeldt et al., [56]. At each depth in the sediment profile, a clean acid-washed syringe (attached to the rhizon sampler) was used to retrieve 3 mL of porewater for arsenic, iron and manganese (preserved with 2% vol/vol HNO_3) and 2 mL for inorganic arsenic speciation (preserved with 1.25 mM EDTA and 87 mM glacial acetic acid). Preservatives were placed in the syringes prior to sampling so that element speciation was fixed as the porewater entered the syringe. A total of 64 porewater samples, 1–2 field duplicate (1 for metals, 2 for inorganic arsenic), and 3 field blanks were collected during the field program. Dissolved oxygen profiles in sediment were measured with the PreSens microsensor in some of the cores sampled for porewater.

The water column was profiled for inorganic arsenic speciation at two sites on Yellowknife Bay near Baker Creek (Fig. 1) during the August, March and July field work. Water was collected at the surface then every metre of the water column to the lake bottom using an acid-washed Teflon line and a peristaltic pump. At each depth, 15 mL of water was filtered in-line using a high capacity 0.45 μm filter and transferred to a 15 mL metal-free tube already containing 1.25 mM EDTA and 87 mM glacial acetic acid preservative. A total of 57 surface water samples and 7 field duplicates were collected during the field program. Water column profiles of temperature, dissolved oxygen, and conductivity were also measured using a YSI sonde (YSI Inc., Yellow Springs, Ohio, USA) at the time of water sampling. Additional water chemistry data for Yellowknife Bay are available in Chételat et al. [15].

2.3. Laboratory analysis

Filtered surface water (from the incubation experiments) and sediment porewater were analyzed for arsenic, iron, and manganese concentrations at the Taiga Environmental Laboratory in Yellowknife by inductively coupled plasma mass spectrometry (ICP-MS) according to EPA method 200.8. Analytical detection limits were < 0.2 μg L^{-1}, < 5 μg $L^{-1}$and < 0.1 μg L^{-1} for arsenic, iron, and manganese, respectively. Field and travel blank results ($n = 18$) were below or at detection limits and were less than 10% of reported concentrations in samples. Field duplicate measurements for arsenic in surface water and porewater had, on average, a relative standard deviation (RSD) of 3% ($n = 16$).

Filtered surface water (from water column profiling) and sediment porewater were analyzed for inorganic arsenic speciation (arsenite, arsenate) at the Laboratory of Environmental Geochemistry at the Université de Montréal (Montreal, Quebec, Canada). Total inorganic arsenic and arsenite were analyzed by hydride generation atomic fluorescence spectrometry (HG-AFS) for August and March samples. Arsenate was estimated by the difference between total inorganic arsenic and arsenite. Samples collected in July were analyzed for arsenite and arsenate by liquid chromatography ICP-MS, and total inorganic arsenic was estimated from the sum of arsenite and arsenate. A subset of samples was analyzed by both the HG-AFS and LC-ICP-MS methods, demonstrating high comparability of arsenite concentrations (Pearson $r = 0.99$, $p < 0.001$, $n = 38$). The analytical detection limit for arsenite was 0.1 μg L^{-1}, and field blanks ($n = 3$) and travel blanks ($n = 2$) were below detection. Field duplicate measurements for arsenite in surface water or porewater had, on average, a RSD of 6% ($n = 3$) except for samples with concentrations near analytical detection, in which case duplicates were within 0.2 μg L^{-1} of each other ($n = 4$).

Surface sediment from the incubation experiments ($n = 28$) was freeze-dried and homogenized for chemical analysis. Total organic carbon (TOC) of sediment was measured as a percent of dry weight by combustion and acid evolution infrared methods at RPC Laboratories (Fredericton, New Brunswick, Canada). Element concentrations (arsenic, manganese, iron, sulphur) in sediment were analyzed by ICP-

MS following digestion in aqua regia solution at Bureau Veritas (Vancouver, British Columbia, Canada). Detection limits were 0.1 μg g^{-1}, 1 μg g^{-1}, 0.1 mg g^{-1}, and 20 μg g^{-1} for arsenic, manganese, iron and sulphur, respectively, and analytical blanks ($n = 5$) were below or at the detection limits. Average recoveries of those elements from a certified reference material (OREAS 262, method aqua regia, OREAS North America Inc, Sudbury, Canada) were between 92% and 100% ($n = 4$). Analytical duplicates of sediment were < 5% ($n = 4$).

2.4. Data analysis

The arsenic flux (μg m^{-2} day^{-1}) between sediment and overlying water was measured from the incubation experiments by the change over time of arsenic mass in water overlying the sediment cores as follows:

Flux = (arsenic_mass$_{end}$ - arsenic_mass$_{start}$)/(surface area)(incubation period).

Where water arsenic mass at the start and end of the incubation was calculated from the water arsenic concentrations (μg L^{-1}) multiplied by the water volume (L), the sediment surface area was estimated using the diameter of the core tube, and the incubation period was the time in days between the two sampling events (measured to nearest 0.5 h). All fluxes were calculated based on 2-day incubations, since the duration of the incubation (i.e. 2 versus 5–6 days) had a minor effect on some flux estimates, perhaps influenced by the formation of a boundary layer at the sediment surface (Supplemental Fig. S1). A negative flux value indicated net transport from water to sediment, while a positive flux indicated net diffusion from the sediment to overlying water.

Sediment arsenic fluxes were mapped on top of modelled arsenic concentrations of Yellowknife Bay surface sediments (~ top 3–5 cm) to provide spatial reference for the gradient in arsenic contamination. Spatial estimates of sediment arsenic concentrations in Yellowknife Bay were generated by kernel interpolation with the Geostatistical Wizard in ArcGIS Pro (Esri Canada, Toronto, ON, Canada) using 136 concentration measurements from Golder [27], Stantec [60], Chételat et al. [15], and Paudyn et al. [52]. The data were log transformed for interpolation and then back-transformed for presentation.

The influence of environmental conditions on arsenic sediment flux was evaluated with Spearman correlations due to non-linearity of some relationships. The environmental variables included in the analysis were water temperature (°C), site water depth (m), sediment concentrations of arsenic, iron, manganese and sulfur (μg g^{-1} or mg g^{-1}), dissolved oxygen at 1 cm depth in the sediment (%), and sediment total organic carbon.

A mass balance model was developed using Stella Professional 2.01 (ISEE SYSTEMs Inc., Lebanon, NH, USA) to evaluate the contribution of sediment arsenic load to surface water arsenic concentrations in Yellowknife Bay. The modelled inputs of arsenic to Yellowknife Bay were arsenic diffusion from sediment, and inflows from the Yellowknife River and Baker Creek. Direct surface runoff from the shorelines was not included in the model. Modelled loss processes of arsenic were particle settling from the water column and exchange with the main body of Great Slave Lake. Yellowknife Bay was divided into 8 cells (Supplemental Fig. S2) and bi-directional mixing was included between all cell-to-cell boundaries. All cells were divided into an epilimnion and a hypolimnion by the epilimnion depth, with separate cell-to-cell mixing in the epilimnion and the hypolimnion. Seasonal variation in epiliminion depth and discharge of the Yellowknife River and Baker Creek were incorporated into the model. In addition, seasonal variation in water arsenic concentration of Baker Creek was included due to high variability. There was a strong gradient in water conductivity (a conservative tracer) between the main inflow (the Yellowknife River) and the main body of Great Slave Lake (~55–220 μS cm^{-1}). Calibration of the exchange parameters in the model was carried out by first adjusting the mixing rates between cells to match available conductivity data for the bay. Measured sediment arsenic fluxes from this study were used as the gross flux term in the model providing a conservative estimate of the arsenic contribution from sediment. A higher flux value (800 ± 460 μg m^{-2} day^{-1}, rounded mean ± SD of 8 measurements) was applied to the area near the Baker Creek inflow and a lower value (120 ± 90 μg m^{-2} day^{-1}, rounded mean ± SD of 13 measurements, positive fluxes only) applied to the rest of Yellowknife Bay (see Results). Uncertainty in the contribution of sediment load was evaluated using the standard deviation of flux means as upper and lower bounds. Details of other model parameters and sources of data used in the model are provided in the Supplemental Information (Table S2). The model was used to estimate annual loads of arsenic to Yellowknife Bay from three sources (Baker Creek, the Yellowknife River, and lake sediment) and then to estimate water-column arsenic concentrations at three model cells in the bay (nearfield area near Baker Creek inflow, a midfield area of north Yellowknife Bay, and a farfield area of south Yellowknife Bay; see Supplemental Fig. S2 for exact locations). Water arsenic concentrations were estimated using the full model and the relative influence of arsenic sources was evaluated by estimating independent contributions from sediment, Baker Creek and the Yellowknife River. Modelled water arsenic concentrations at the three locations in Yellowknife Bay (presented as means of the epiliminion and hypoliminion) were compared with field measurements of inorganic arsenic concentrations from this study and previously published work [15].

3. Results

3.1. Sediment arsenic fluxes

Diffusion of arsenic from sediment to overlying water (a positive flux) was observed at 65% of sites sampled in Yellowknife Bay (Fig. 2). Short-term arsenic fluxes ranged from − 65–1520 μg m^{-2} day^{-1} ($n = 28$ cores from 20 sites; Table 1), with positive fluxes measured at 13 of 20 sites and negative fluxes at 7 sites. Dissolved oxygen measurements in the sediment cores, after short-term incubations were completed, indicated that an overlying oxic layer was maintained in surficial sediments throughout the incubations (Table 1). Relatively high precision was obtained for field measurements of arsenic flux; duplicate cores collected from the same site and sampling event showed low variation (RSD = 21 ± 9%, $n = 4$ pairs) compared to between-site differences. Among cores with a negative arsenic flux, the rate of influx to sediment from the water column averaged − 41 ± 16 μg m^{-2} day^{-1} ($n = 7$ cores), while cores with a positive arsenic flux had an average diffusion rate from sediment of 395 ± 442 μg m^{-2} day^{-1} ($n = 20$ cores). Only one sediment core had a flux of zero. Negative sediment arsenic fluxes tended to occur at shallower sites and sites farther away from the Giant Mine property (Fig. 2). The greatest arsenic fluxes from Yellowknife Bay sediment were observed at sites closest to the mine property (Fig. 2).

3.2. Sediment porewater profiles

Porewater profiles of arsenic in 8 cores from Yellowknife Bay showed concentration gradients indicative of diffusion from sediment (Figs. 3, 4). Oxic conditions were typical at the SWI. At 1 cm sediment depth, dissolved oxygen saturation in porewater averaged 15 ± 12% ($n = 22$ cores). The lowest porewater arsenic concentrations were observed at the SWI, and concentrations increased with sediment depth to maxima at 3–6 cm. The maximum arsenic concentration in each of the porewater profiles ranged from 65 to 3220 μg L^{-1}. Arsenic, iron, and manganese redox boundaries were all likely within 2–3 cm of the sediment surface in the cores as indicated by a rapid downward increase of iron and manganese concentrations in the porewater as well as a shift towards arsenic predominately as arsenite (Figs. 3, 4). There were exceptions to those patterns, such as at site S4 (Fig. 4), where porewater arsenite concentrations did not increase appreciably with sediment depth, and site S17, where arsenite was the dominant form of inorganic arsenic in porewater even at the SWI (Fig. 3).

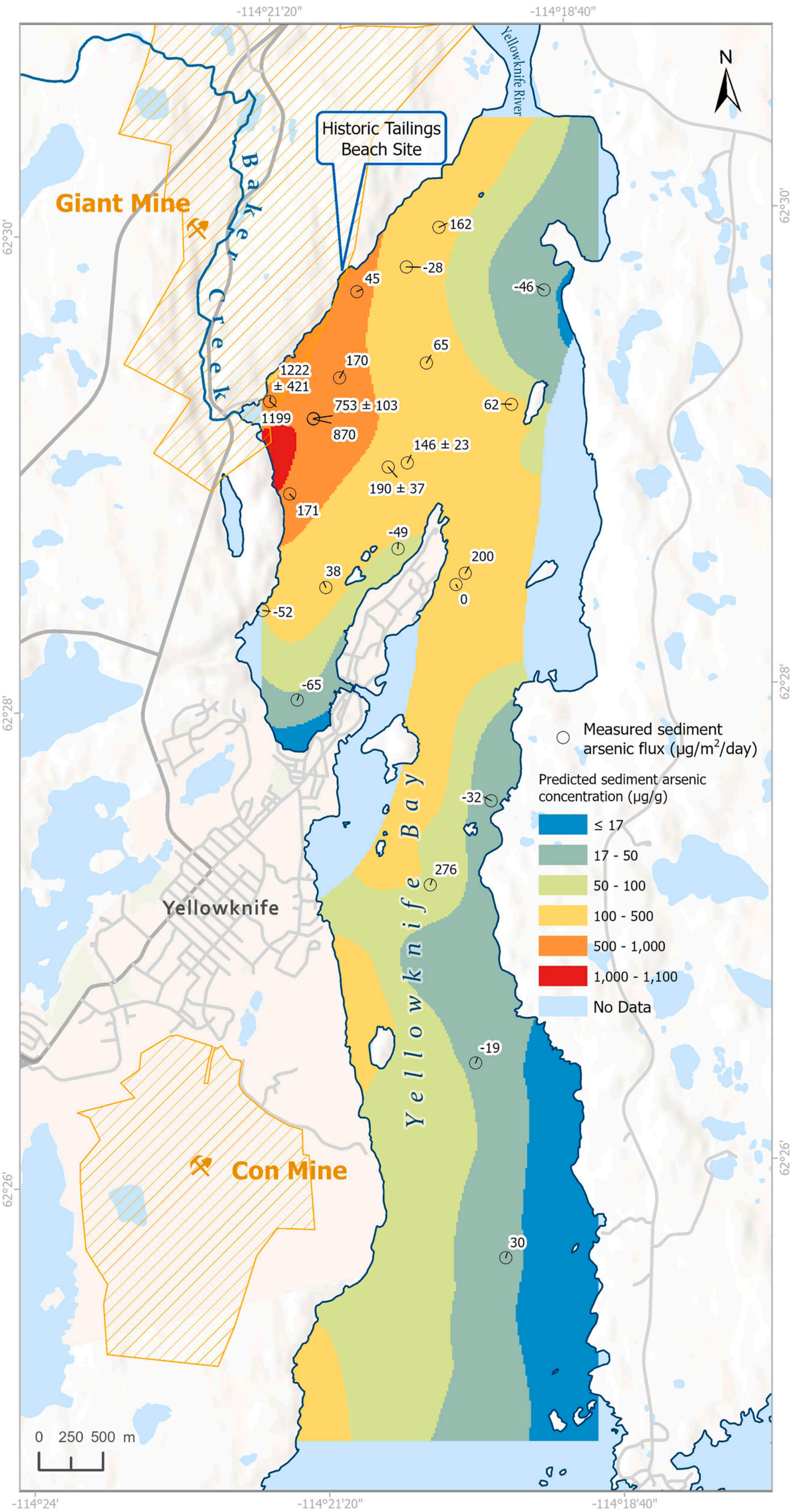

Fig. 2. Sediment arsenic fluxes at 20 sites in Yellowknife Bay. Means (± 1 standard deviation) are presented for duplicate measurements on the same sampling date. Sediment arsenic fluxes were mapped over modelled arsenic concentrations of Yellowknife Bay surface sediments to provide spatial reference for the gradient in arsenic contamination (see the data analysis section for interpolation details). Map created using ArcGIS software by Esri and the Esri Canada Topographic basemap.

Table 1
Sediment characteristics (0–3 cm) and arsenic fluxes in 28 sediment cores collected from 20 sampling sites in Yellowknife Bay in 2018 and 2019.

Characteristic ($n = 28$)	Mean (± SD)	Range
Arsenic flux (μg m^{-2} day^{-1})	272 ± 420	− 65 – 1520
Arsenic concentration (μg g^{-1})	638 ± 834	10 – 3206
Iron concentration (mg g^{-1})	33.5 ± 6.7	16.3 – 43.1
Manganese concentration (μg g^{-1})	1622 ± 1086	235 – 4173
Sulphur concentration (μg g^{-1})	496 ± 244	200 – 1200
Total organic carbon (%)	1.6 ± 0.4	0.3 – 2.4
Dissolved oxygen saturation (%) at 1 cm sediment depth[a]	15 ± 12	1 – 40
Water depth at collection site (m)	8.6 ± 5.4	1.1 – 19.8
Water temperature (°C)	11 ± 4	4 – 19

[a] $n = 22$

3.3. Seasonal variation of arsenic fluxes and porewater concentrations

Little seasonal variation in sediment arsenic flux was observed at four sites sampled in both August and March with a range of bottom water temperature of ~2–12 °C between those two months (Fig. 5). Three of the sites showed slightly lower arsenic fluxes in March (under ice conditions), although the seasonal variation was small relative to the between-site differences in flux. For the one site (S4) where duplicate measurements were available, there was no difference between March and August (Mann-Whitney test, $p = 0.33$, $n = 4$). Porewater measurements at two of the sites similarly showed little seasonal variation in arsenic concentration profiles, consistent with the flux observations (Fig. 4). Together, the arsenic fluxes and porewater profiles showed good site fidelity between the late summer and winter sampling events, with potentially minor declines in winter flux.

3.4. Water column arsenic concentrations

Vertical profiles of inorganic arsenic concentration in the water column of Yellowknife Bay showed little depth variation throughout the year (Fig. 6). The filtered water concentrations of inorganic arsenic were generally low, averaging 2.4 ± 2.5 μg L^{-1}, though higher concentrations of 7.3 μg L^{-1} and 19.5 μg L^{-1} were observed mid-depth and near the lake bottom, respectively, at site S5 in March (Fig. 6). Thermal stratification of the water column was most apparent in August, while conductivity gradients were observed in the water column in August and March. The water column was well-oxygenated in all seasons with dissolved oxygen > 10 mg L^{-1} (> 70% saturation). Arsenite accounted for < 50% (mean ± SD = 22 ± 14%) of surface water arsenic in March and July, with little depth variation. In contrast, arsenite dominated in the epilimnion at both sites in August, representing the majority (67 ± 10%) of the water inorganic arsenic. Overall, the water column profiles indicated rapid mixing and dilution of arsenic diffusing from sediment.

3.5. Environmental influences on sediment arsenic flux

Arsenic fluxes from sediment were best explained by the more than two-order magnitude variation of solid-phase arsenic concentrations in the sediment surface layer (top 3 cm). Higher arsenic fluxes occurred from sediments containing more arsenic, although the association was not strongly linear (Spearman *rho* = 0.73, Holm's $p < 0.001$, $n = 28$; Fig. 7). Considerable variation in arsenic flux was observed for sediments with arsenic concentrations > 500 μg g^{-1}, suggesting that additional environmental factors were important. A similar positive correlation was found between arsenic flux and sediment iron concentration, though slightly weaker (Spearman *rho* = 0.68, Holm's $p < 0.001$, $n = 28$). Correlations with other environmental factors were not statistically significant (Holm's $p > 0.05$), including site water depth, water temperature, dissolved oxygen saturation (%) at 1 cm depth in the sediment, as well as sediment content of TOC, manganese and sulfur. Although no correlation was found between site depth and sediment arsenic flux, shallow sites (≤ 4 m depth, median = −39 μg m^{-2} day^{-1}) had lower fluxes than deeper sites (> 4 m depth, median = 170 μg m^{-2} day^{-1}) (Mann-Whitney test, $p = 0.002$, $n = 28$). Sediment organic carbon content was relatively low in all the sediment samples (TOC <2.4%, Table 1), consistent with an earlier survey of sediment characteristic for the north end of Yellowknife Bay (Supplemental Fig. S3). This earlier survey also showed clay was the dominant particle type in surface sediment near the mouth of Baker Creek, with lesser contributions of silt, where the highest arsenic concentrations and fluxes were measured (Supplemental Fig. S3). Silt and sand dominated sediments in Yellowknife Bay near the mouth of the Yellowknife River, likely reflecting river loads of suspended sediment.

3.6. Modelled arsenic loads to Yellowknife Bay

Modelling results indicated sediment fluxes were an important source of arsenic to Yellowknife Bay surface waters. The annual load of arsenic from sediments was estimated at 1180 kg, which was comparable to the annual load from mine discharge to Yellowknife Bay via Baker Creek (1270 kg) and more than 1.5 times the load from the Yellowknife River (720 kg). The upper and lower bounds for the annual load of arsenic from sediment were estimated at 360–2000 kg based on the uncertainty of the mean flux (see methods), reflecting large variation in fluxes among sites. Model estimates of mean water arsenic concentrations were comparable (within 0.4 μg L^{-1}) to measured concentrations in the nearfield area adjacent to Baker Creek and in the farfield area at the south end of Yellowknife Bay (Fig. 8). However, the model substantially underestimated the mean water arsenic concentration by 1.5 μg L^{-1} in a mid-field area of north Yellowknife Bay. Model estimates of individual source contributions to water column arsenic concentrations indicated the influence of each load varied in different areas of Yellowknife Bay. In the nearfield area, the arsenic loads from Baker Creek and sediment contributed roughly equally to the water arsenic concentration, while farther away in midfield and farfield areas, loads from Yellowknife Bay sediment and the Yellowknife River were the dominant arsenic sources.

4. Discussion

4.1. Importance of sediment arsenic flux to surface waters of Yellowknife Bay

Sediments of Yellowknife Bay are a leaky reservoir of legacy arsenic contamination, resulting in a sustained release of arsenic to overlying water. Sediment was a source of arsenic at many sites throughout the bay during both summer and winter, with the highest fluxes found in the nearfield area close to the Giant Mine site. This diffuse flux from sediment represents a significant load of arsenic to Yellowknife Bay that is comparable to the point-source load of arsenic (including treated effluent) from the contaminated mine site via Baker Creek.

The maximum sediment arsenic flux measured in Yellowknife Bay was the second highest among published studies compiled for lakes with a well-oxygenated water column (Table 2). Out of 19 water bodies, only a tailings storage facility for a gold mine in the Solomon Islands had a higher maximum flux of 4500 μg m^{-2} day^{-1} compared with Yellowknife Bay (1520 μg m^{-2} day^{-1}). Similarly, the average arsenic flux of 800 μg m^{-2} day^{-1} for a subset of eight Yellowknife Bay sites near Baker Creek was higher than maximum fluxes of the other waterbodies (except the tailings facility). In addition, the high arsenic fluxes of Yellowknife Bay sediments (with oxic overlying water) were comparable to those of five lakes with hypoxic/anoxic bottom waters (Table 2), where the presence of reducing conditions at the SWI and through the water column likely promoted reductive dissolution of arsenic-bearing iron

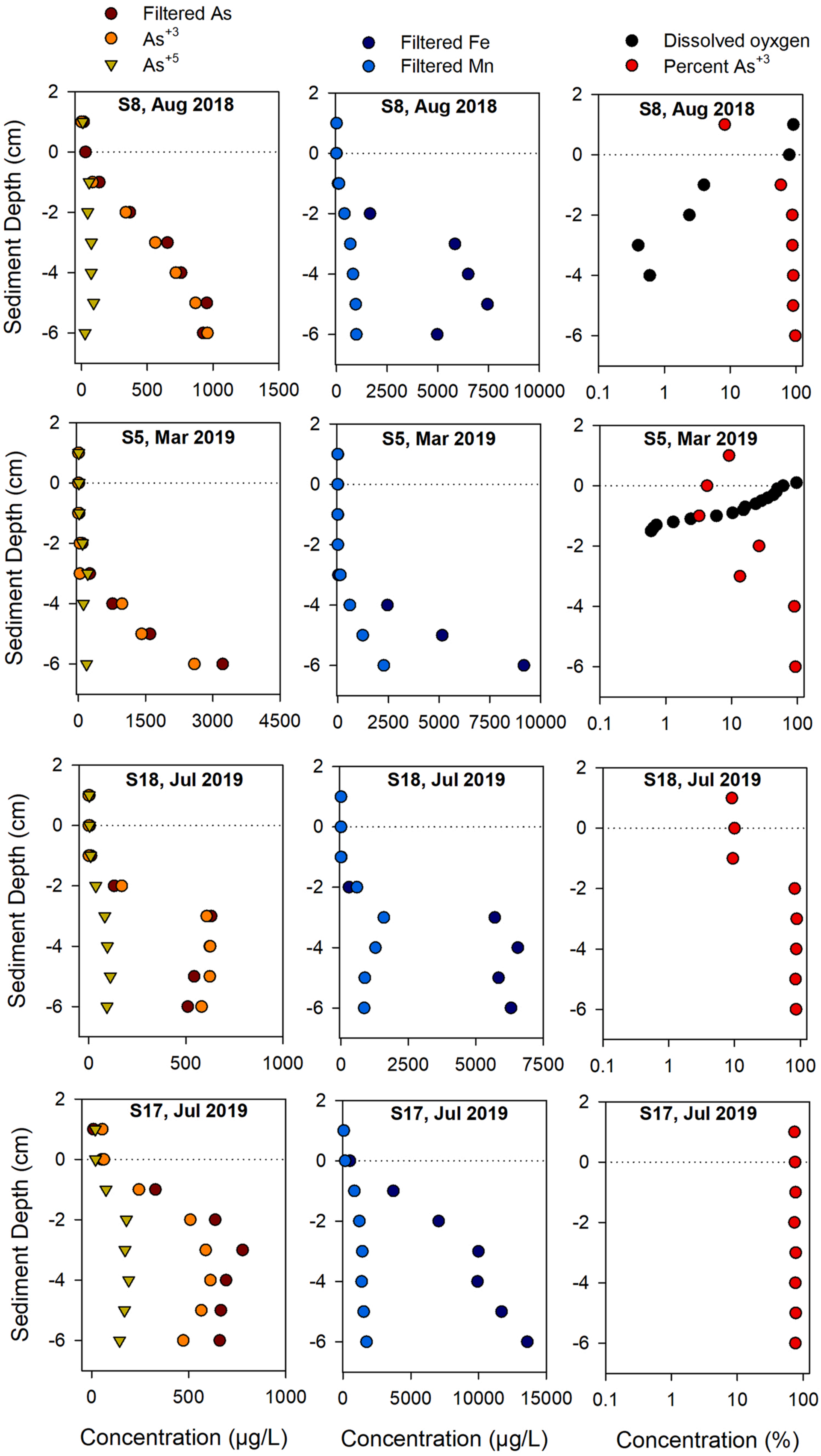

Fig. 3. Profiles of filtered arsenic, iron and manganese concentrations at the SWI and in porewater (to a sediment depth of 6 cm) at four sites representing a range of conditions in Yellowknife Bay. Inorganic arsenic concentrations (arsenite, arsenate, percent arsenite) and porewater dissolved oxygen saturation (for two cores) are also presented. Note the logarithmic scale of the panels on the right.

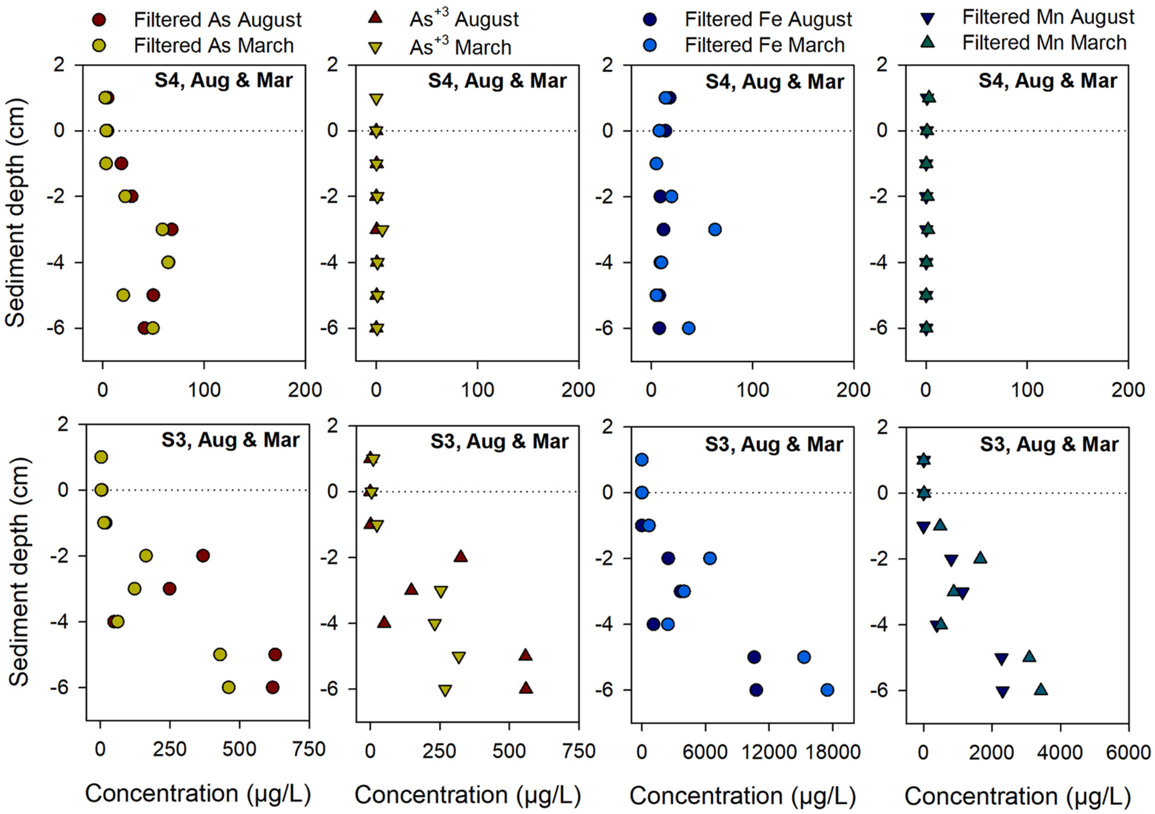

Fig. 4. Comparison between summer and winter profiles of filtered concentrations of arsenic, arsenite, iron and manganese at the SWI and in porewater (to a sediment depth of 6 cm) at two sites in Yellowknife Bay.

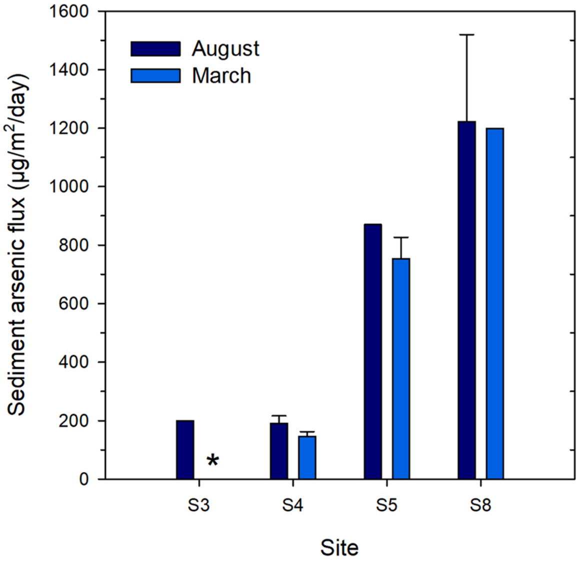

Fig. 5. Comparison of sediment arsenic fluxes between August 2018 and March 2019 at four sites. Measurement precision of duplicates is provided for a subset of fluxes. The asterisk indicates a flux of zero for site S3 in March.

oxyhydroxide minerals and unconstrained diffusion of dissolved arsenic from deeper in the sediments [6,50]. The elevated fluxes in Yellowknife Bay are likely related to the high degree of sediment contamination, as indicated by higher porewater arsenic concentrations than most sites (Table 2). Together, this comparison with other studies indicated exceptional arsenic fluxes from Yellowknife Bay sediments relative to other lakes in the region and internationally.

Surface water concentrations of arsenic are relatively low in Yellowknife Bay despite the high sediment flux to the water column. Dissolved arsenic was typically $< 5\ \mu g\ L^{-1}$ (which is below the World Health Organization drinking water guideline of $10\ \mu g\ L^{-1}$) [68]. The low net effect of sediment efflux is due to the large water volume of Yellowknife Bay (approximately 150 million cubic metres), as well as high hydrological connectivity and mixing with the main body of Great Slave Lake. Nevertheless, surface water arsenic concentrations in Yellowknife Bay are approximately 3–5 fold higher than background concentrations ($\sim 0.5\ \mu g\ L^{-1}$) in the Yellowknife River and the main body of Great Slave Lake [15].

Water column arsenic concentrations were relatively homogenous across depths and seasons. A depth gradient in water arsenic concentration might be expected given the high sediment arsenic flux but was not observed near the sediment surface (with the exception of a site in winter). This suggests relatively rapid dispersion of arsenic in the water column, which is facilitated by the large volume, currents, and wind (during the open-water season) typical of a great lake. Unpublished high frequency temperature profiling of the Yellowknife Bay water column (Supplemental Fig. S4) indicated thermal stratification is weak during the open-water season and frequent mixing occurs over a short time period (i.e. days). Water column mixing did not allow for a build-up of arsenic near the SWI in summer, in contrast to small lakes with a stable hypolimnion (e.g., [6]).

4.2. Environmental controls on arsenic diffusion

Observations of high arsenic fluxes from Yellowknife Bay sediments support earlier conclusions that arsenic mobility can be important in lakes with well-oxygenated surface water [2,32,55,7]. While redox state and iron biogeochemistry play a fundamental role in controlling arsenic mobility, an oxic SWI is not always a sufficient barrier to impede arsenic diffusion to overlying water, as sometimes reported [10,3,62]. This

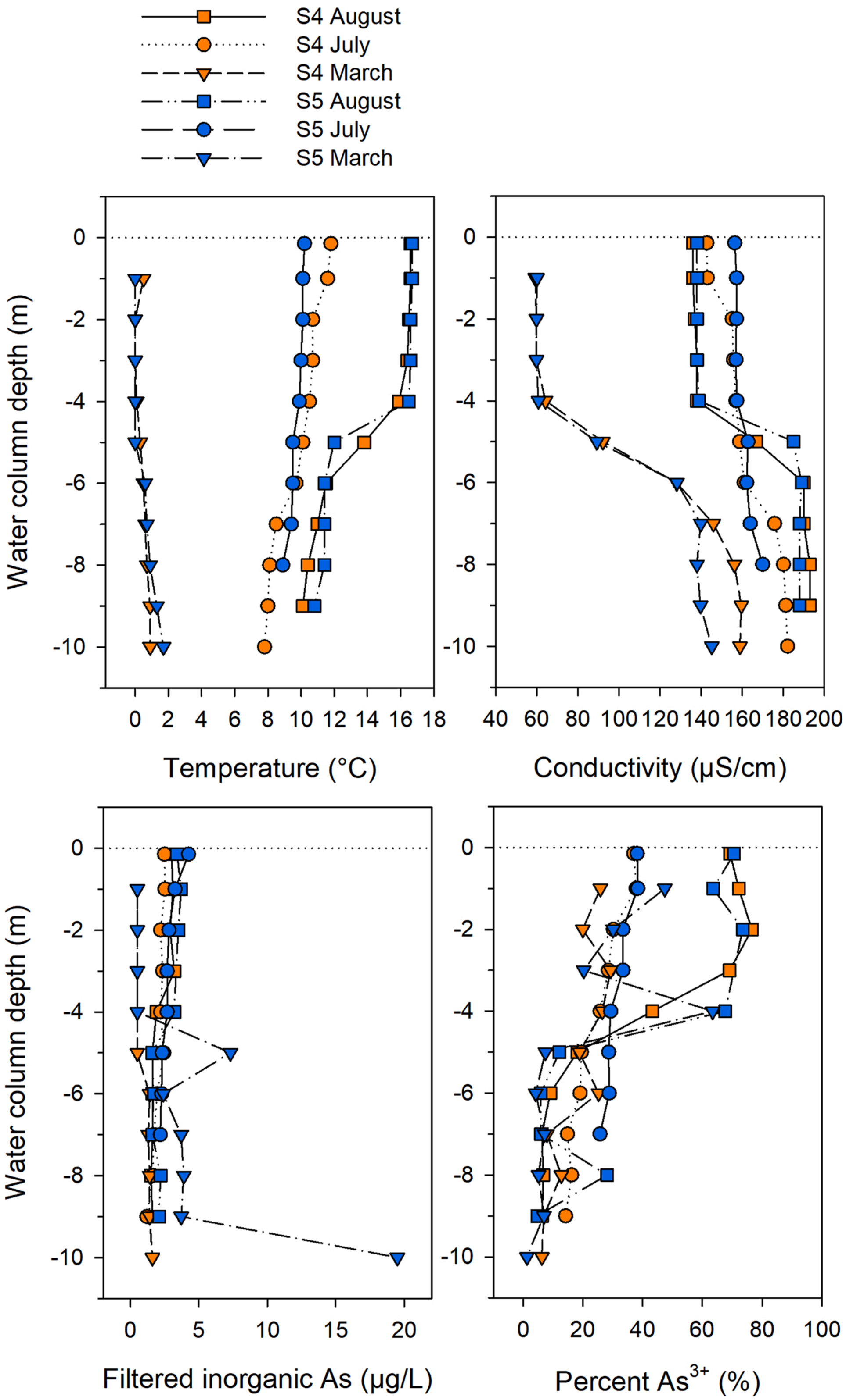

Fig. 6. Water column profiles of temperature, conductivity, filtered inorganic arsenic and percent arsenite in Yellowknife Bay. Measurements were taken at 1 m intervals between the water surface and lake bottom at two sites in August 2018, March 2019 and July 2019.

study examined the environmental conditions allowing for sediment arsenic fluxes in an oxidizing environment.

The solid-phase arsenic concentration of surface sediment was the environmental characteristic most strongly correlated with arsenic flux. This positive influence is likely due to the presence of more arsenic-bearing material that undergoes dissolution and supplies dissolved arsenic to porewater. However, large variation in arsenic flux was found among sediments with similarly high solid-phase arsenic concentrations, which is likely influenced by differences in mineralogy (and the stability) of arsenic source materials. A parallel study by Paudyn et al.

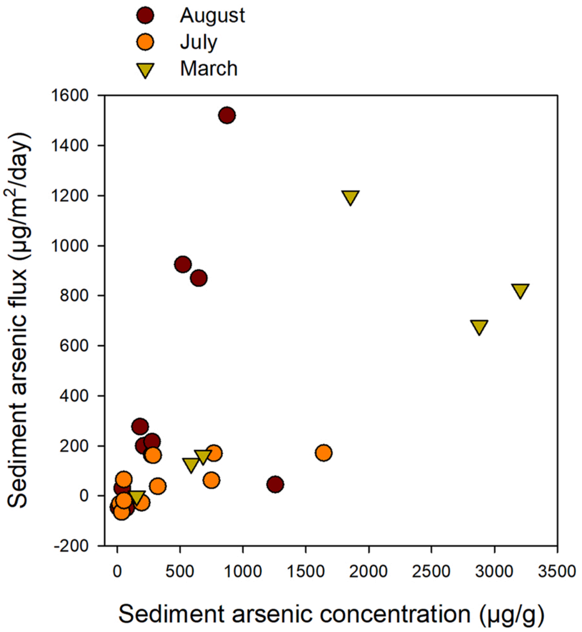

Fig. 7. Positive correlation between solid-phase arsenic concentration in surface sediment and arsenic flux (Spearman *rho* = 0.73, Holm's $p < 0.001$, $n = 28$).

[52] examined in detail the arsenic mineralogy of Yellowknife Bay sediments. They found sub-surface peaks of solid-phase arsenic at approximately 2–5 cm below the SWI associated with iron concentration maxima and the presence of authigenic iron oxyhydroxides and roaster-generated iron oxides. Considerable spatial variation was observed in the proportions of arsenic-hosting minerals both among sites and with depth in Yellowknife Bay sediment. Variable amounts of arsenopyrite (from mine tailings) were also present in the oxic surface layer of sediments, which could slowly release arsenic through oxidative dissolution. Iron oxides and oxyhydroxides release arsenic as sediments are progressively buried and the iron redox-cline migrates upwards. If limited sorption sites are available, iron oxyhydroxides may not prevent diffusion of high porewater concentrations of arsenic towards the sediment surface [14]. Arsenic trioxide was present in surface sediments and is another source of arsenic given its relatively high solubility in water [47]. The two sites with the highest arsenic fluxes (S5, S8) contained a mix of arsenic-bearing minerals in the sediment surface layer (1–2.5 cm) consisting of iron oxyhydroxides, arsenopyrite, roaster-generated iron oxides and arsenic trioxide [52]. Additional geochemical research is needed to evaluate which mining wastes contribute more to the sediment arsenic flux via oxidative dissolution (in oxic sediments) or reductive dissolution (in deeper sediments).

Yellowknife Bay sediments have very low organic carbon content (<2.5%), which may have implications for arsenic mobility in Yellowknife Bay. Limited availability of organic substrates for microbial metabolism results in low biological oxygen demand. Water currents driven by wind and the Yellowknife River inflow may also contribute to replenishment of dissolved oxygen at the sediment surface. These processes allow for the maintenance of a thick oxic surface layer, where the co-precipitation and/or adsorption of arsenic can occur with iron (and other metal) oxyhydroxides. Sediment organic matter can also affect arsenic mobility through its complexation with sulphur or oxygen functional groups [11,66], which can reduce arsenic binding to soil and sediment particles including iron oxides [8]. Yellowknife Bay sediments may have limited capacity for arsenic sequestration with organic matter, in contrast with other subarctic lakes in the region with higher sediment

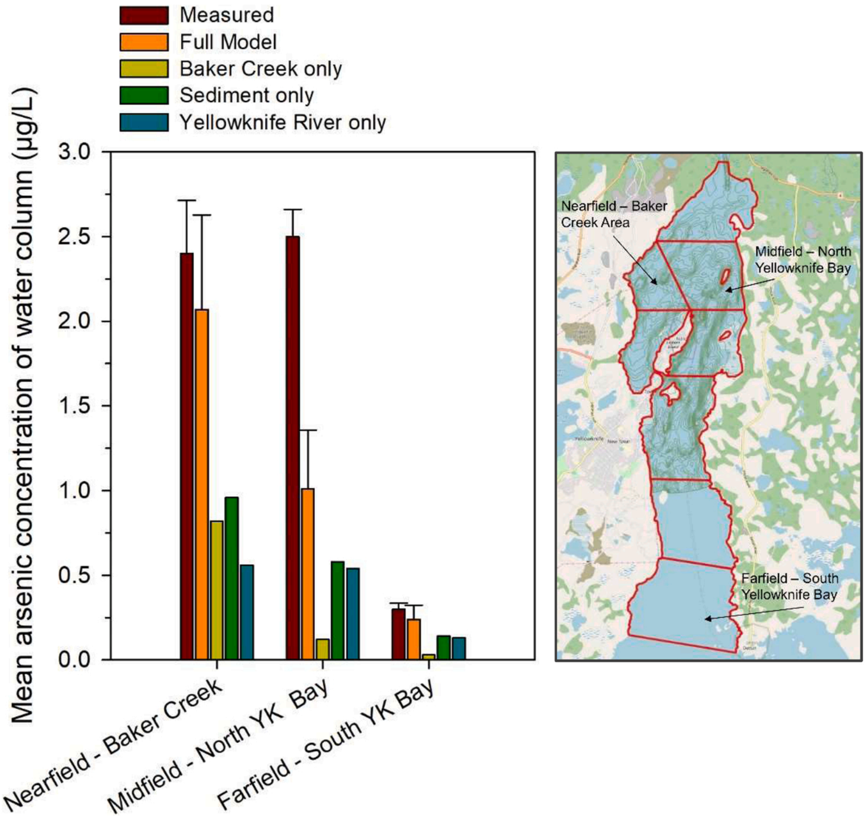

Fig. 8. Comparison of model estimates of water column arsenic concentrations with field measurements in three areas of Yellowknife Bay. Arsenic contamination declines with increasing distance from the Baker Creek inflow and Giant Mine site (see inset map). Water arsenic concentrations were estimated using the full model and contributions from individual loads of sediment, the Yellowknife River, and Baker Creek.

Table 2

Comparison of arsenic porewater concentrations and sediment fluxes of lakes reported in the literature. Fluxes are differentiated by dissolved oxygen conditions in the water column (oxic versus hypoxic/anoxic), and water bodies are ranked by maximum sediment flux for oxic waters.

Water body	Location	Peak porewater [arsenic] ($\mu g\ L^{-1}$)	Arsenic flux ($\mu g\ m^{-2}\ day^{-1}$)		Source
			Oxic	Hypoxic/ anoxic	
Gold Ridge Mine tailings storage facility	Solomon Islands	~2000 – 17,000	720 – 4500[a]	1020 – 7010[a]	Jacob-Tatapu et al.[32]
Yellowknife Bay, Great Slave Lake	Northwest Territories, Canada	65 – 3220	– 65 – 1520		This study
Yellowknife Bay, Great Slave Lake	Northwest Territories, Canada	~500 – 1100	67 – 1033[a, b]		Andrade et al.[2]
Balmer Lake	Ontario, Canada	~800 – 8000	55 – 411[a]	4904 – 10,411[a]	Martin et al. (2002)
Long Lake	Northwest Territories, Canada	~500 – 600	5 – 247[a]		Schuh et al.[55]
Lower Martin Lake	Northwest Territories, Canada	~500	168[a]		Van den Berghe (2018)
Lower Martin Lake	Northwest Territories, Canada	120 – 160	86 – 154	595 ± 123	Palmer et al.[50]
Akaitcho Bay, Great Slave Lake	Northwest Territories, Canada	~70 (arsenite)	133[a]		Andrade et al.[2]
Angle Lake	Washington, USA	43 ± 4	127	11 – 14	Barrett et al.[6]
Moira Lake	Ontario, Canada	~160 – 240	21 – 105[a]		Azcue, Dixon[5]
Killarney Lake	Washington, USA	948 ± 121	15	873 – 1302	Barrett et al.[6]
8 unnamed lakes (NW10 to NW80)	Northwest Territories, Canada	49 – 112	– 1 – 13		Leclerc et al.[41]
Poyang Lake	Jiangxi Province, China	4 – 56	2 – 11		Deng et al.[22]
Handle Lake	Northwest Territories, Canada	260	8	273	Palmer et al. [51], Van Den Berghe et al.[63]
Spy Pond	Massachusetts, USA	~300 – 900		451 – 1354	Senn et al. [57], (2005)

a Converted from different units reported in original study (e.g., $\mu g\ cm^{-2}\ year^{-1}$), [b] Negative values reported in original study indicate efflux

organic carbon of 9–22% [45]. It is also possible that spatial variation of sediment arsenic flux in north Yellowknife Bay was influenced by differences in clay, silt and sand composition, as clay content was higher in sediments closer to Baker Creek, while silt and sand content dominated on the northeast side close to the inflow of the Yellowknife River. Similarly, the low sediment arsenic flux at the historic Tailings Beach (site S9) was likely due to high compaction and low porosity of the submerged tailings composed of very fine particles [2].

Particle scavenging is a loss process that transports arsenic from the water column to sediment [6,18]. Under oxic conditions, arsenate is readily sorbed to metal oxide particles, including iron oxyhydroxides, which settle out of the water column. Yellowknife Bay is an oligotrophic water body with very low total suspended solids (< 4 mg L), and therefore, sedimentation is likely low. Note that measurements of sediment arsenic flux in this study (based on changes in overlying water in cores) were net fluxes that reflected both sediment diffusion and water column sedimentation. A loss of arsenic was observed in overlying water of cores at seven sampling sites in Yellowknife Bay (averaging −41 ± 16 $\mu g\ m^{-2}\ day^{-1}$). Those sites were generally in shallow waters where wave action may have increased particulates in the water column at the time of sampling. In comparison, much higher arsenic sedimentation rates of – 174 to – 964 $\mu g\ m^{-2}\ day^{-1}$ were observed in eutrophic Killarney Lake (Washington, USA), where setting of phytoplankton biomass was important for arsenic removal from the water column [6].

Low seasonal variation of sediment arsenic flux and associated porewater profiles was observed in Yellowknife Bay, suggesting year-round diffusion to overlying water. This finding is consistent with Paudyn et al. [52], who found little change in solid-phase profiles of arsenic and iron in Yellowknife Bay sediments between summer and winter. Andrade et al. [2] found a higher flux in summer (1033 $\mu g\ m^{-2}\ day^{-1}$) than winter (667 $\mu g\ m^{-2}\ day^{-1}$) at one site in Yellowknife Bay, though with limited sampling the influence of sediment heterogeneity and seasonal variation could not be distinguished. Seasonal variation in arsenic mobility may be influenced by water temperature, sedimentation of labile organic matter, microbial metabolism, and migration of the iron redox-cline in the sediment profile [42,6,69]. We posit that low seasonal variation of sediment arsenic flux occurs in Yellowknife Bay due to the oligotrophic state of this water body, the low microbial oxygen demand, the maintenance of oxic conditions in the water column and surface layer of sediment, and frequent mixing of the water column (limiting thermal stratification in the bay). A laboratory experiment conducted on slurries (top 15 cm) of Yellowknife Bay sediment showed that short-term warming treatments from 7° to 21°C did not enhance arsenic fluxes [4]. In contrast, high seasonal variability of arsenic flux has been observed with the onset of anoxia through the water column in small, shallow subarctic lakes under ice in winter [50,51] and in the hypolimnion of more productive temperate lakes during summer [44,57,6].

4.3. *Inorganic arsenic speciation*

Aqueous arsenic speciation was influenced by processes in the water column and the sediment. Inorganic arsenic (as arsenate and arsenite) dominates in surface water of Yellowknife Bay with limited formation of organic arsenic species [15]. The highest arsenite concentrations were observed in deeper anoxic porewaters (> 3 cm below the SWI) associated with reducing conditions and the dissolution of arsenic minerals. Arsenate was the dominant inorganic form at the SWI (generally accounting for ~90%), although two sites (S3 and S17) exceptionally had > 50% arsenite in oxic waters at the surface. Similarly, water column arsenic near the lake bottom was predominately as arsenate. These observations suggest arsenate is the dominant inorganic arsenic species to diffuse out of Yellowknife Bay sediments. In August 2018, water column arsenic speciation varied with depth despite consistent redox conditions through the water column. Arsenite dominated in oxic epilimnetic waters whereas arsenate was the predominant species in the hypolimnion. Since porewaters near the SWI suggest that arsenic efflux from the sediments is predominately as arsenate, arsenate reduction in the epilimnion was likely mediated by algal metabolic processes [29–31]. Arsenate, which is chemically similar to the limiting nutrient phosphate, can be rapidly taken up by phytoplankton, then reduced to arsenite and excreted, presumably as a detoxification mechanism [29]. The stability of algal reduced arsenite is likely limited, and several processes in the water column, such as photo-oxidation of arsenite to arsenate counter-acts algal arsenate reduction [1].

4.4. *Arsenic mass balance for Yellowknife Bay*

Remobilization of legacy arsenic contamination from sediments delivers an important annual load to the water column of Yellowknife Bay and contributes to water arsenic concentrations above background. At the ecosystem level, this diffuse source of arsenic is comparable to the point source load of arsenic from Baker Creek on the mine site. In the nearfield area alone, model estimates indicated elevated water arsenic concentrations are due to roughly equal contributions from sediment fluxes in Yellowknife Bay and Baker Creek inputs, while outside the nearfield area, the sediment contribution has a dominant influence on water arsenic concentrations. More complex hydrodynamic modelling of Yellowknife Bay by Golder [28] estimated complete dilution of Baker Creek inputs of arsenic at a distance of $<$ 2 km into Yellowknife Bay (i.e. within the nearfield cell of our model). This is consistent with our finding that sediment flux is the dominant anthropogenic source of arsenic to Yellowknife Bay surface water outside the nearfield area. These findings highlight the importance of spatial variation in contributions of different arsenic sources and effects on water concentrations within a large water body.

The arsenic mass balance model for Yellowknife Bay was based on average conditions and did not account for inter-annual variability in fluxes. Sediment arsenic fluxes measured over a decade earlier at two sites in Yellowknife Bay [2] were comparable though smaller in range than those from the broader spatial survey of this study (Table 2). In contrast, arsenic fluxes from Baker Creek and the Yellowknife River are strongly dependent on discharge, which varies widely among years. A separate analysis generated estimates of arsenic annual loads from Baker Creek ranging between 404 and 1279 kg during the years 2011–2018 [26], in comparison with our estimate of 1270 kg. Arsenic delivered to Yellowknife Bay from Baker Creek originates from multiple contamination sources including watershed transport of atmospherically-deposited arsenic, summer-time releases of treated effluent from tailings ponds, and legacy tailings in the creek bed [26]. In addition, watershed transport of arsenic in Baker Creek varies between low and high flow years [26,49]. During dry years when low stream flow in Baker Creek results in smaller arsenic loads of ~500–700 kg [26], Yellowknife Bay sediments likely contribute the greatest arsenic load to Yellowknife Bay surface waters.

Overall, our model estimates of water arsenic concentrations were in agreement with empirical measurements along the gradient in mining contamination. However, the model substantially underestimated the average water arsenic concentration in an area of north Yellowknife Bay. The sediment arsenic flux may have been underestimated, potentially because of high spatial variation throughout the bay and the limited number of measurements. Terrestrial runoff from contaminated soils near the shoreline may be an additional relevant source of arsenic that was not accounted for in the model. Arsenic trioxide was found in surface sediments at all sampling sites of Yellowknife Bay within 2 km of the roaster [52]. Since this mineral arsenic host was released during ore roasting (which ceased in 1999), the presence of arsenic trioxide in surface sediments is an indication of catchment transport of legacy contamination from atmospheric deposition of roaster emissions [49,52,55,63].

4.5. Implications for ecosystem recovery from mining contamination

Peak loads of mining contamination were deposited to Yellowknife Bay sediments during the 1950–1970 s with subsequent declines as pollution mitigation measures improved [15,2,53]. A sediment investigation in the 1980 s noted the reduction of arsenic load to sediment due to better pollution controls, though the assessment concluded the contamination would be buried in 20 years with no acknowledgement of potential post-depositional mobility [46]. More recent sediment profiles indicated that mining-derived metals and antimony – but not arsenic – are gradually declining towards background concentrations through burial of uncontaminated sediment [15,52,53]. In contrast, arsenic concentration peaks are currently found in surface sediments (within the top 5 cm) almost five decades later due to remobilization of this redox-sensitive element [52]. Arsenic is slowly being sequestered through precipitation with sulphur to form arsenic-sulphide minerals (e.g. realgar) in deeper anoxic sediments [52]. Internal recycling of arsenic across the sediment-water continuum and catchment transport will continue to impede the return to background arsenic conditions in Yellowknife Bay for decades. While surface water arsenic concentrations are low, elevated porewater concentrations within a few centimetres of the sediment surface are a potential risk for sediment dwelling biota in the nearfield area [27]. Sediment disturbance could mobilize high concentrations of arsenic from porewaters into the water column. In addition, this subarctic region is experiencing environmental change due to climate warming [71], and long-term monitoring is warranted to track ecosystem changes that may enhance the remobilization of arsenic such as greater sedimentation of organic matter and altered redox conditions. Upward migration of the redox cline and development of anoxia at the SWI would likely increase arsenic fluxes to the water column.

5. Conclusions

The study contributes to the complex literature on arsenic remobilization from mining contamination by demonstrating the occurrence of high sediment arsenic fluxes in a well-oxygenated system and identifying associated environmental conditions. The highly contaminated sediments of Yellowknife Bay are a leaky reservoir of legacy arsenic, resulting in a slow, continuous release of arsenic to overlying water. A suite of factors likely contributes to high sediment arsenic fluxes, including elevated solid-phase and porewater arsenic concentrations in sediments, the mineralogy of arsenic mining-wastes, and the low productivity of this large subarctic water body. A next step is to experimentally investigate arsenic fluxes of Yellowknife Bay sediments through redox transitions in the water column and to compare fluxes between sediments with contrasting arsenic mineralogy. A more detailed coupling of arsenic mineralogy to flux measurements is needed to evaluate the mining wastes undergoing dissolution. Internal recycling of legacy arsenic between sediment and the water column will maintain surface water above pre-mining conditions, and future environmental changes under a warming climate may impact the trajectory for recovery of Yellowknife Bay.

Environmental implication

Arsenic is a hazardous material, and point-source releases from industrial activities pose environmental and human health risks. This study found sediment efflux of arsenic adjacent to a closed mine was elevated for a well-oxygenated lake. Many studies have reported effective attenuation of upwardly diffusing arsenic by adsorption and/or co-precipitation with iron and manganese minerals in oxic surface sediments. In Yellowknife Bay, porewater arsenic diffusion to overlying water was not fully attenuated, likely in part because of high porewater arsenic concentrations. Legacy arsenic contamination deposited in sediments decades ago remains an important arsenic source to surface water in this system.

CRediT authorship contribution statement

John Chételat: Conceptualization, Funding, Investigation, Formal analysis, Writing – original draft, Writing – review & editing. **Michael J. Palmer:** Conceptualization, Investigation, Writing – review & editing. **Katrina Paudyn:** Investigation. **Heather Jamieson**: Conceptualization, Funding, Supervision, Writing – review and editing. **Marc Amyot:** Investigation. **Reed Harris:** Funding, Investigation. **Raymond Hesslein**: Investigation, Writing – original draft. **Nicolas Pelletier:** Investigation. **Ines Peraza**: Investigation.

Declaration of Competing Interest

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests. John Chetelat reports financial support was provided by Environment and Climate Change Canada. John Chetelat reports financial support was provided by Government of the Northwest Territories. John Chetelat reports financial support was provided by Natural Sciences and Engineering Research Council of Canada.

Data Availability

Data will be made available on request.

Acknowledgements

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Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.jhazmat.2023.131230.

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