



Seasonal variation of arsenic and antimony in surface waters of small subarctic lakes impacted by legacy mining pollution near Yellowknife, NT, Canada



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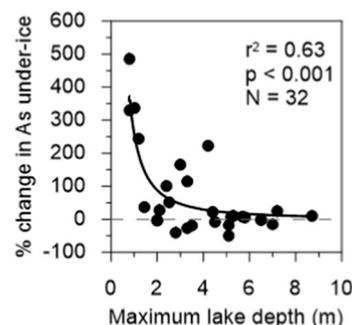
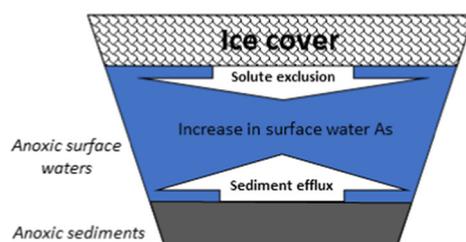
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HIGHLIGHTS

- As and Sb concentrations in waters of subarctic lakes in Canada were investigated.
- Seasonality influenced lake water concentrations.
- Arsenic increased in winter with water column anoxia and cryoconcentration.
- Large difference between open-water and under-ice As in lakes <4 m deep
- No increase in surface water Sb in winter suggests no coupling with Fe/Mn cycling.

GRAPHICAL ABSTRACT



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ABSTRACT

The seasonal variation in lake water arsenic (As) and antimony (Sb) concentrations was assessed in four small (<1.5 km²) subarctic lakes impacted by As and Sb emissions from legacy mining activities near Yellowknife, Northwest Territories, Canada. Substantial variation in As concentrations were measured over the two-year period of study in all but the deepest lake (maximum depth 6.9 m), including a four-fold difference in As in the shallowest lake ([As]: 172–846 µg L⁻¹; maximum depth 0.8 m). Arsenic concentrations were enriched following ice cover development in the three shallowest lakes (50–110%) through a combination of physical and biogeochemical processes. Early winter increases in As were associated with the exclusion of solutes from the developing ice-cover; and large increases in As were measured once oxygen conditions were depleted to the point of anoxia by mid-winter. The onset of anoxic conditions within the water column was associated with large increases in the concentration of redox sensitive elements in lake waters (As, iron [Fe], and manganese [Mn]), suggesting coupling of As mobility with Fe and Mn cycling. In contrast, there was little difference in Sb concentrations under ice suggesting that Sb mobility was controlled by factors other than Fe and Mn associated redox processes. A survey of 30 lakes in the region during fall (open-water) and late-winter (under-ice) revealed large seasonal differences in surface water As were more common in lakes with a maximum depth <4 m. This threshold highlights the importance of winter conditions and links between physical lake properties and biogeochemical processes in the chemical recovery of As-impacted subarctic landscapes. The findings indicate annual

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remobilization of As from contaminated lake sediments may be inhibiting recovery in small shallow lakes that undergo seasonal transitions in redox state.

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1. Introduction

Atmospheric metal(loid) pollution from industrial sources is a global concern (e.g. Matschullat, 2000) and the legacy of these activities can persist in aquatic environments decades after emissions are reduced or eliminated (Blais et al., 1999; Houben et al., 2016; Keller et al., 2007). Arsenic (As) and antimony (Sb) are metalloids of particular interest because of the associated human and ecological health risks (Bhattacharya et al., 2007; Filella et al., 2009), and are considered priority pollutants by the United States Environmental Protection Agency (EPA, 2014). High concentrations of these metalloids often exist together in mining waste streams due to the co-occurrence in hydrothermal mineral deposits (Fawcett et al., 2015; Serfor-Armah et al., 2006). Considerable research has been directed at understanding the biogeochemistry of As, because of its widespread occurrence in the environment and toxicity (Bhattacharya et al., 2007; Smedley and Kinniburgh, 2002). In contrast, processes that influence Sb mobility and sequestration remain relatively poorly understood, and there are fewer field studies directed at understanding Sb biogeochemical processes in aquatic systems (Filella et al., 2009).

The biological and chemical recovery of lakes from metalloid pollution is complex and is influenced by multiple factors, including the physical and hydrological properties of the lake and its basin, and the biogeochemical cycling of the pollutant (Belzile et al., 2004; Greenaway et al., 2012; Martin and Pedersen, 2002). Understanding recovery processes in small waterbodies is important because small lakes (<1 km²) dominate the global distribution of fresh waters and many aquatic processes are amplified in smaller lakes and ponds (Downing et al., 2006). The influence of benthic fluxes of metal(loid)s is magnified in small, shallow lakes due to the typically higher ratio of sediment surface area to lake volume (Orihel et al., 2017). In lakes that have received inputs of As waste, recovery of surface waters may be delayed or confounded by the internal loading of As to the water column from As stored in the sediments (Martin and Pedersen, 2004, 2002). The seasonal and long-term fate of As is often coupled with the biogeochemical cycling of iron (Fe), and may vary throughout the year dependent on changes in redox conditions near the sediment boundary (Couture et al., 2008; Martin and Pedersen, 2002; Senn et al., 2007). Iron (oxy)hydroxides form under oxic conditions in near-surface lake sediments and can sequester As from the dissolved fraction through co-precipitation or adsorption (Dixit and Hering, 2003). The development of anoxia in sediments results in the reductive dissolution of Fe (oxy)hydroxides, releasing sorbed As to porewaters and the overlying water column (Arsic et al., 2018; Bennett et al., 2012). This process has been demonstrated for a variety of events that may induce anoxic conditions near the sediment boundary, including: lake eutrophication (Azizur Rahman and Hasegawa, 2012; Hasegawa et al., 2009) and the seasonal thermal stratification of the hypolimnion (Hollibaugh et al., 2005; Senn et al., 2007).

The biogeochemical cycling of Sb is less well understood than for As and conflicting examples exist regarding the mobility of Sb in oxidized surficial environments. Many field and laboratory-based studies demonstrate the importance of Fe (oxy)hydroxides in controlling Sb mobility in soils and lake sediments (e.g. Chen et al., 2003; Mitsunobu et al., 2010, 2006). In contrast, recent studies from contaminated environments have shown increased mobility of Sb under oxic conditions and suggest the competitive advantage of aqueous As(V) over Sb(V) for sorption sites on Fe (oxy)hydroxides (Fawcett et al., 2015) or Sb(III) oxidation and release of Sb(V) driven by the precipitation of Fe (oxy)

hydroxides as a mechanism (Ren et al., 2019). In several studies, the limited mobility of Sb observed in anoxic environments has been attributed to the precipitation of Sb(III) with reduced organic or inorganic sulfur to form solid phase species (Arsic et al., 2018; Bennett et al., 2017; Fawcett et al., 2015; Ren et al., 2019). Majzlan et al. (2016) discussed the apparent disagreement in the literature on whether Sb is mobile in the near-surface environment and suggested this was due to variable solubility of oxidation products of primary Sb minerals.

In light of this previous research there has been little consideration of how winter processes in subarctic environments may influence the mobility of As and Sb because most field studies have been undertaken in temperate or tropical locations or restricted to the open-water season (e.g. Chen et al., 2003; Hollibaugh et al., 2005; Senn et al., 2007). Shallow subarctic lakes may be ice covered for more than half the year, which can strongly affect the physical and chemical properties of surface waters. The development of an ice cover may lead to the onset of seasonally anoxic conditions when the oxygen demand in the sediments exceeds the oxygen budget in the water column (Deshpande et al., 2015; Mathias and Barica, 1980) and the exclusion of dissolved solutes and gases from the ice matrix can increase solute concentrations in underlying waters (Bergmann and Welch, 1985; Hobbie, 1980; Pieters and Lawrence, 2009). Understanding the seasonality of water quality in small subarctic lakes is important because cryoconcentration and increased sediment efflux may increase As and Sb exposure to aquatic organisms or in some cases contribute to the delayed recovery of these systems.

This study examined the seasonal variation of As and Sb in four small subarctic lakes that were impacted by atmospheric deposition of contaminants from gold mining in the Yellowknife area. The primary elements of focus were As and Sb because these metalloids were released in large quantities from historical ore roasting operations and often exhibit contrasting geochemical behavior in the environment (Arsic et al., 2018; Fawcett et al., 2015). The objective of this study was to quantify the extent of seasonal variation in surface water quality of shallow subarctic lakes impacted by legacy mineral processing and to investigate the roles of physical (cryo- and evapo-concentration) and biogeochemical (sediment efflux) controls on surface water concentrations of As and Sb. We used a combination of frequent sampling at four lakes close to historical mining operations and a series of regional lake surveys to evaluate seasonality at the lake scale and a broader regional scale.

2. Materials and methods

2.1. Environmental setting and background

The study area is located within the southern portion of the Slave Geological Province of the Canadian Shield (Fig. 1). Small lakes are common in the region and remnant from the recession of Glacial Lake McConnell and ancestral Great Slave Lake within the last 10,000 years (Wolfe et al., 2017). The climate of the region is continental subarctic and characterized by long, cold winters (−25.6 °C January mean) and short, warm summers (17.0 °C July mean) (Environment Canada, 2018). Temperatures typically drop below freezing in early October and remain below 0 °C until mid-to-late April (Environment Canada, 2018). Consequently, small lakes such as those investigated in this study may be ice-covered for half of the year. Air temperatures during the study period were similar to climate normals (1980–2010) for

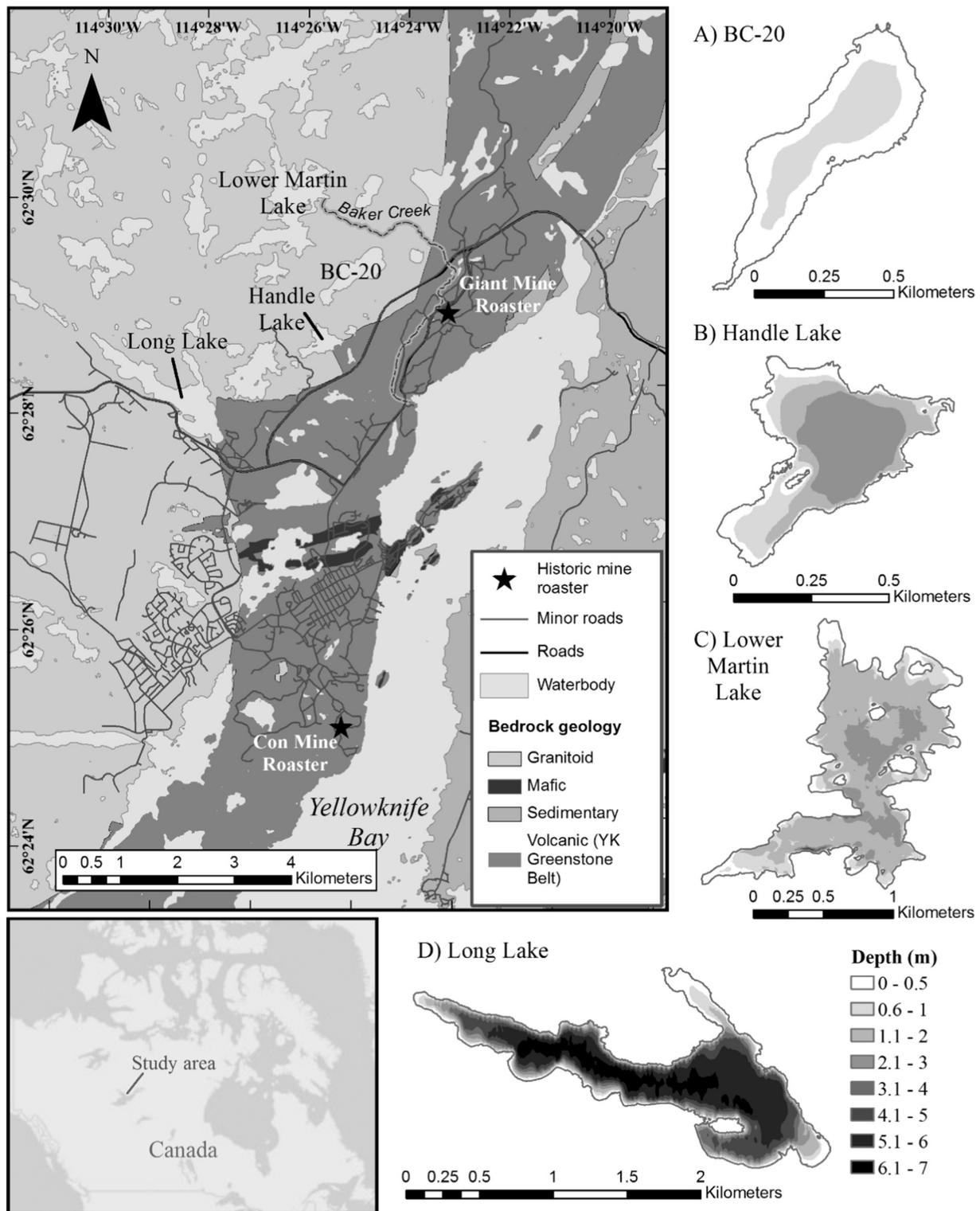


Fig. 1. Study area (left panel) and bathymetry of the four study lakes: a) BC-20; b) Handle Lake; c) Lower Martin Lake; and d) Long Lake.

Yellowknife, except for the winter of 2015–16 that was slightly warmer than average (Fig. A.1) (Environment Canada, 2018).

2.1.1. Arsenic and antimony pollution in the Yellowknife area, NT, Canada

The Yellowknife area was one of the most productive gold mining regions in Canada. >13.5 million ounces of gold were produced between 1938 and 2004, predominately from the two largest mines: Giant Mine (1949–2004) and Con Mine (1938–2003) (Moir et al., 2006). Roasting of gold-bearing arsenopyrite (FeAsS) resulted in emissions of a volatile

gas phase of As ($\text{As}(\text{OH})_3$ or As_4O_6) that condensed to arsenic trioxide (As_2O_3) dust upon release from the roaster stacks and was subsequently distributed across the surrounding landscape (Hocking et al., 1978; Hutchinson et al., 1982; Walker et al., 2015). More than 20,000 t of As_2O_3 were released during operations at Giant Mine, and most of these emissions (>84%) occurred during the first 10 years of production prior to the installation of more efficient roasting technologies (Bromstad et al., 2017). The roasting of arsenopyrite was less extensive at Con Mine but was used as part of operations intermittently between

1942 and 1970, and an estimated 2500 t of As_2O_3 were released to the atmosphere from the Con Mine roaster. Stibnite (Sb_2S_3) and antimony (Sb)-bearing sulphosalts were also present in the ore roasted at Giant Mine and the roasting of these minerals resulted in the production of a unknown gaseous phase of Sb that was incorporated into the structure of the As_2O_3 (Fawcett and Jamieson, 2011; Riveros et al., 2000). These large releases of As_2O_3 resulted in an enduring environmental legacy in the region, and concentrations of As and Sb remain elevated in regional lake waters (Houben et al., 2016; Palmer et al., 2015), lake sediments (Dushenko et al., 1995; Galloway et al., 2017; Schuh et al., 2018) and soils (Bromstad et al., 2017; Jamieson et al., 2017) >60 years after the bulk of these emissions were released.

2.1.2. Study lakes

Detailed field investigations were completed in four lakes within 5 km of the now decommissioned roaster at Giant Mine, Yellowknife, NT (Fig. 1). All four lakes are natural waterbodies located beyond mine lease boundaries and downwind (prevailing easterly winds) from Giant Mine. The lakes are underlain by granitoid bedrock west of the Yellowknife Greenstone Belt that is composed of Archean metavolcanic rocks that hosted the Con and Giant mineral deposits (Moir et al., 2006). The study lakes were selected to investigate the influence of lake physical properties on seasonal changes in surface water quality, and thus lakes vary in surface area, volume, and hydrological characteristics (Table 1).

All four study lakes are characterized by relatively simple basin morphology, including a single basin with relatively consistent depth across its extent (Fig. 1). Long Lake (max. depth 6.9 m) (62.476°N, 114.436°W) and Lower Martin Lake (max. depth 2.9 m) (62.512°N, 114.421°W) are fish-bearing, although fish were only present in Lower Martin Lake during the open-water season due to the onset of anoxic conditions in the water column in early winter, which forced the migration of fish from Lower Martin or resulted in winterkill. Long Lake has no discernable inflow or outflow and is surrounded by steep exposed bedrock outcrops on the northern and eastern shores. Lower Martin Lake is part of the Baker Creek watershed that drains an area of approximately 155 km² and is the final lake in the Baker Creek system before flowing through the Giant Mine property and ultimately discharging into Yellowknife Bay in Great Slave Lake. Discharge from Lower Martin Lake has been monitored by the Water Survey of Canada since 1983 (station number 07SB013), and historical records indicate outflow from the lake typically occurs throughout the year, although average daily discharge is normally small (<0.2 m³/s) between late September and the start of freshet in early May. Discharge from Lower Martin was extremely low during the study period, driven by abnormally low water levels, and flow was non-existent except for a small period during freshet (Fig. A.1). Handle Lake (62.491°N, 114.397°W) is a small bedrock-bound lake (max. depth 3.0 m) with no channelized inflow or outflow located 2.5 km from the historic roaster at Giant Mine. BC-20 (unofficial name; 62.503°N, 114.393°W) is a small shallow (<1.0 m) pond adjacent to the lower reaches of Baker Creek above the Giant Mine site. In both sampling years, BC-20 was frozen to bottom sediments by early January. The lake edge and the surrounding bedrock outcrops are buffered by wide expanses of peatlands (50–100 m wide) and the presence of exposed

and vegetated lake bottom sediments around the margin of the lake suggest the water level has receded in the recent past. No channelized flow exists between BC-20 and the surrounding watershed, however, ephemeral drainage to Baker Creek is expected during freshet and extremely wet periods through a series of wetlands at the north end of the lake.

2.2. Lake morphometry

Lake morphometry was determined for Long Lake, Handle Lake and BC-20 in June 2016 and Lower Martin Lake in September 2017 using a Garmin Fishfinder 250™ or Lowrance HDS5™ depth sounder and chart plotter attached to a canoe. Bathymetric maps were constructed in ArcMap v.10.4 (ESRI, Redlands, California) for each of the study lakes using the individual point data (location and depth) collected during the surveys and converting to a raster. Lake volume estimates were calculated from the raster files using the surface volume tool in the 3D analyst extension in ArcMap v.10.4.

Changes in the volume of Handle Lake during the study period were estimated to support As and Sb mass balance models. Water level was recorded during summer on each site visit from a benchmark using a stadia rod and level. Lake volume on the open-water sampling dates was calculated by subtracting the difference in water level from the raster generated for the original bathymetric survey that was conducted on June 10 using the surface volume tool in the spatial analyst extension of ArcMap (v. 10.4). Winter water volume was estimated by removing the ice cover from the bathymetry raster using the same approach. The ice-cover thickness was adjusted by 9.05% to compensate for the increase in volume of ice over water due to phase change.

2.3. Water and sediment sampling

2.3.1. Frequent surface water sampling of the four study lakes

Lake water chemistry was sampled regularly at the four study lakes between July 2014 and September 2016. Samples were consistently collected at the same location in the center of the lakes. In the open-water season, surface water samples were collected from just below the surface (approx. 0.15 m) in acid-washed 250 mL polyethylene containers that had been rinsed three times with lake water. During winter, surface samples were collected 10-cm below the base of the ice cover through a 20-cm diameter hole drilled through the ice. Sampling at multiple intervals in the water column was conducted at Long Lake and Handle Lake in February, April, May/June and July 2016 to assess the vertical profile of water quality during the ice-covered and ice-free seasons. No interval sampling was conducted in the two shallowest lakes (BC-20 and Lower Martin Lake) and no thermal stratification of the water column was observed at any of the lakes during the summer sampling periods (Figs. A.2 and A.3). Water samples during winter and through the water column were collected using a peristaltic pump attached to Teflon™ line that was pre-washed with 5% HCl solution and rinsed with ultrapure water prior to each sampling trip. The lines were flushed with lake water from each sampling depth for 2 min prior to sample collection between sites and depth intervals. All metal(loid) data presented in this study refer to the filtered fraction (<0.45 μm) of the

Table 1
Physical characteristics of the four study lakes.

| Study lake | Lake area (km ²) | Maximum depth (m) | Lake volume (m ³) | Sediment surface area: lake volume | End of winter ice thickness (m) | Distance to Giant Mine roaster (km) |
|-------------------|------------------------------|-------------------|-------------------------------|------------------------------------|--|-------------------------------------|
| BC-20 | 0.23 | 0.8 | 82,930 | 2.79 | Frozen to bottom | 1.8 |
| Handle Lake | 0.21 | 3.0 | 316,005 | 0.67 | 0.78 ^a , 0.59 ± 0.01 ^c | 2.5 |
| Lower Martin Lake | 1.21 | 2.9 | 1,693,859 | 0.80 | 0.84 ^a , 0.66 ± 0.01 ^c | 3.0 |
| Long Lake | 1.13 | 6.9 | 4,331,913 | 0.26 | 1.0 ^a , 0.65 ± 0.03 ^b | 4.9 |

^a End of April 2015.

^b End of April 2016 (mean and standard error of 5 measurements).

^c End of April 2016 (mean and standard error of 3 measurements).

sample, unless otherwise noted, and all samples were filtered immediately in the field and preserved with nitric acid (HNO₃) to 2% (v/v). Following collection, water samples were stored in a cooler with ice packs and delivered the same day to an accredited government laboratory (Taiga Laboratory, Yellowknife, NT).

Water samples were analyzed for general chemistry (including major ions, dissolved organic carbon and nutrients), and 25 total and dissolved metal(loid)s. Dissolved organic carbon was measured by high temperature combustion on a total carbon analyzer (SM5310) (APHA, 1992). Concentrations of major cations and anions were determined by ion chromatography (SM4110) (APHA, 1992). Phosphorous was measured colorimetrically (SM4500P) (APHA, 1992). Total (unfiltered) and dissolved (filtered <0.45 µm) metal(loid) concentrations were determined by inductively coupled plasma mass spectrometry (ICP-MS) following EPA method 200.8 (Creed et al., 1994). In addition to ICP-MS metal(loid) analyses, a subset of water samples were analyzed for total inorganic arsenic and arsenite [As(III)] via hydride generation quartz furnace atomic absorption spectrometry (HG-AAS) at ALS Laboratories in Kelso, WA, according to EPA method 1632. Arsenate [As(V)] was estimated by difference between total inorganic As and As(III). The minimum reporting limit for As(III) and total inorganic As was 0.02 µg L⁻¹. Water for As speciation was filtered to <0.45 µm and preserved with hydrochloric acid in the field (McCleskey et al., 2004). Water chemistry results from individual sites are presented in the Supplementary information (Tables A.2–A.5). Field blanks and field duplicates were collected as part of quality assurance and quality control measures in the study. All samples collected as field blanks (N = 12) reported values below method detection limits (MDL) of 0.2 and 0.1 µg L⁻¹ for As and Sb, respectively. The mean relative percent difference (RPD) between field duplicates (N = 13) was 4% (st. dev. = 3.9%) and 2% (st. dev. = 2.7%) for As and Sb, respectively.

2.3.2. Regional lake water and sediment surveys

In addition to the detailed investigation of seasonal variation in 4 lakes, surface water from 31 lakes was sampled in March 2015. These lakes were part of a group of 86 lakes within 30 km of Yellowknife that were originally sampled in September 2012 and September 2014 as part of a broad survey of surface water and near-surface sediment quality that was conducted to assess the distribution of legacy pollutants in the region (Palmer et al., 2015; Galloway et al., 2017). The re-sampling reported in this paper was designed to capture late-winter water chemistry in the region and to explore the influence of lake physical properties on seasonal differences in surface water concentrations of As and Sb. Lakes represented a range of size (i.e. surface area and depth) and distance from legacy point sources of pollutants. Sample collection methods and analytical methods are similar to those reported in Palmer et al. (2015) and used in the repeated sampling of the four lakes in this study (Section 3.2.1.) (see Supplemental information). Relationships between surface water and near-surface sediment conditions were explored to examine potential influences of sediment properties on lake water chemistry. In brief, and as described in Galloway et al. (2017), near-surface sediments were collected with an Ekman grab sampler and the top 2–5 cm were retained for analyses. Sediments were analyzed for element concentrations by ICP-MS following aqua regia digestion. Total organic carbon (TOC%) was determined by Rock-Eval 6 pyrolysis as the sum of S1, S2, S3, and residual carbon fractions (Lafargue et al., 1998). These data are reported in Galloway et al. (2017).

2.4. Water column oxygen depletion

On each sampling date, in-situ measurements of dissolved oxygen, pH, and temperature were made with a YSI 6920 multiprobe sonde (Yellow Springs Inc., Yellow Springs, Ohio) calibrated with certified reference solutions within 24 h of field sampling. The rate and timing of oxygen depletion in Handle Lake and Lower Martin Lake was measured with MiniDOT® dissolved oxygen loggers (Precision Measurement

Engineering Inc., Vista, California) during the 2015–16 ice-covered and ice-free seasons. The loggers were installed 1-m above the sediment surface to record water column oxygen levels and temperature at 10-min intervals. This information was compiled into daily mean conditions and data presented in the figures represent these daily mean levels. The temperature range of the sensors is 0 to 35 °C with an accuracy of ±0.1 °C. In this study water column measurements of <0.5 mg L⁻¹ O₂ are considered to represent anoxic conditions following Zogorski et al. (2006).

2.5. Measuring solute exclusion from lake ice

Lake ice thickness was recorded on each winter sampling date using a calibrated hooked rod through a hole drilled in the ice. Results from late April 2015 and 2016 are presented in Table 1. The extent of solute exclusion from the lake ice cover was assessed by collecting ice chips from augered holes in each of the lakes. The lake ice at two of the sites consisted of a thin layer of white ice overlying a thick layer of black ice. No melting of the snow cover was observed prior to the April sampling periods, therefore it is assumed that white ice represents water that was redistributed to the ice surface through cracks or near the shoreline and subsequently mixed with the snow cover prior to freezing (i.e. overflow), whereas black ice represents lake water frozen in-situ. Ice samples were collected from both ice types in Ziploc™ bags, melted, and stored in high density polyethylene bottles prior to general chemical analyses and metal(loid) analyses at Taiga Laboratories in Yellowknife, NT following the methods described in Section 2.3.1.

2.6. Data analysis

Seasonal enrichment factors were calculated for each of the study lakes to evaluate the change in water chemistry during the period of ice cover and during the open-water season, and to test the hypothesis that element concentrations in shallow lakes increase over winter as a result of solute exclusion and increased sediment efflux of redox sensitive elements. Water chemistry data from the end of the winter season (April) were divided by results from the last sampling period prior to freeze-up (typically October) to yield a winter enrichment factor. The summer enrichment factor was calculated by dividing results from end of summer (September) by early open-water season conditions (June). It was assumed that changes in redox state near the sediment boundary would have little effect on the flux of the cations and anions Ca²⁺, K⁺, Mg²⁺ and Cl⁻ across the sediment boundary, therefore winter enrichment in the sum of these major ions (Σ major ions) was expected to primarily represent cryoconcentration and was used to compare with changes in the redox sensitive elements of interest (Fe, Mn, As, and Sb) that were expected to respond to cryoconcentration and changes in sediment efflux.

For the regional lake water surveys, the percent difference between late-winter and open-water surface water elemental concentrations was used to assess whether there were identifiable physical thresholds that controlled the difference in surface water chemistry between seasons, following:

$$\left(\frac{[\text{Late winter}] - [\text{Fall}]}{[\text{Fall}]} \right) \times 100\% \quad (1)$$

where [Late winter] and [Fall] represent the concentration of elements from the regional water quality surveys in March and September, respectively. It was expected that, at a regional scale, larger seasonal differences in surface water concentrations would be observed for shallow lakes, where the surface area to lake volume ratio was large, in contrast with deep lakes, where the influence of solute exclusion and sediment diffusive fluxes would be dampened by large water volumes.

2.6.1. Assessing the relative influence of summer and winter processes in Handle Lake

The relative influence of physical (cryo- and evapoconcentration) and biogeochemical (sediment efflux) processes on As and Sb concentrations across seasons were assessed in Handle Lake using water column profile sampling and a mass balance approach. It was assumed that differences in the mass of As and Sb in Handle Lake between sampling periods would be the net result of sedimentation and sediment efflux processes, whereas changes in concentration without any corresponding changes in mass were the result of cryo- or evapoconcentration. This approach assumed no input or output of elements via groundwater or from the surrounding catchment. Concentrations of As, Sb, Fe and Mn were measured at 3–4 depth intervals through the water column on February 16, April 14, May 9, and July 27, 2016 and the depth-weighted mean concentration was calculated to obtain a lake-wide estimate of As and Sb concentrations for these dates. The depth-weighted mean concentration was combined with the lake volume estimate (see Section 2.2) for the sampling dates to generate an estimate of As and Sb mass.

The influences of cryo- and evapoconcentration on water concentrations of As and Sb were modelled for the under-ice and open-water seasons using the data generated in the mass balance estimates. The expected concentrations of As and Sb due to cryoconcentration were modelled as the mass of the elements prior to freeze-up (September) divided by the changing lake volume over the winter period. The influence of evapoconcentration on lake water concentrations of As and Sb was modelled using a similar approach, and the mass of As and Sb calculated for early June was divided by the adjusted volume for late July to yield an estimated concentration due to evapoconcentration.

The statistical analyses were conducted using the software program R v.3.4.1 (R core team, 2017) and results of statistical tests were deemed significant at $p < 0.05$.

3. Results

Concentrations of dissolved As (filtered fraction $<0.45 \mu\text{m}$) were above Canadian and World Health Organization guidelines of $10 \mu\text{g L}^{-1}$ for the maximum allowable concentration for drinking water

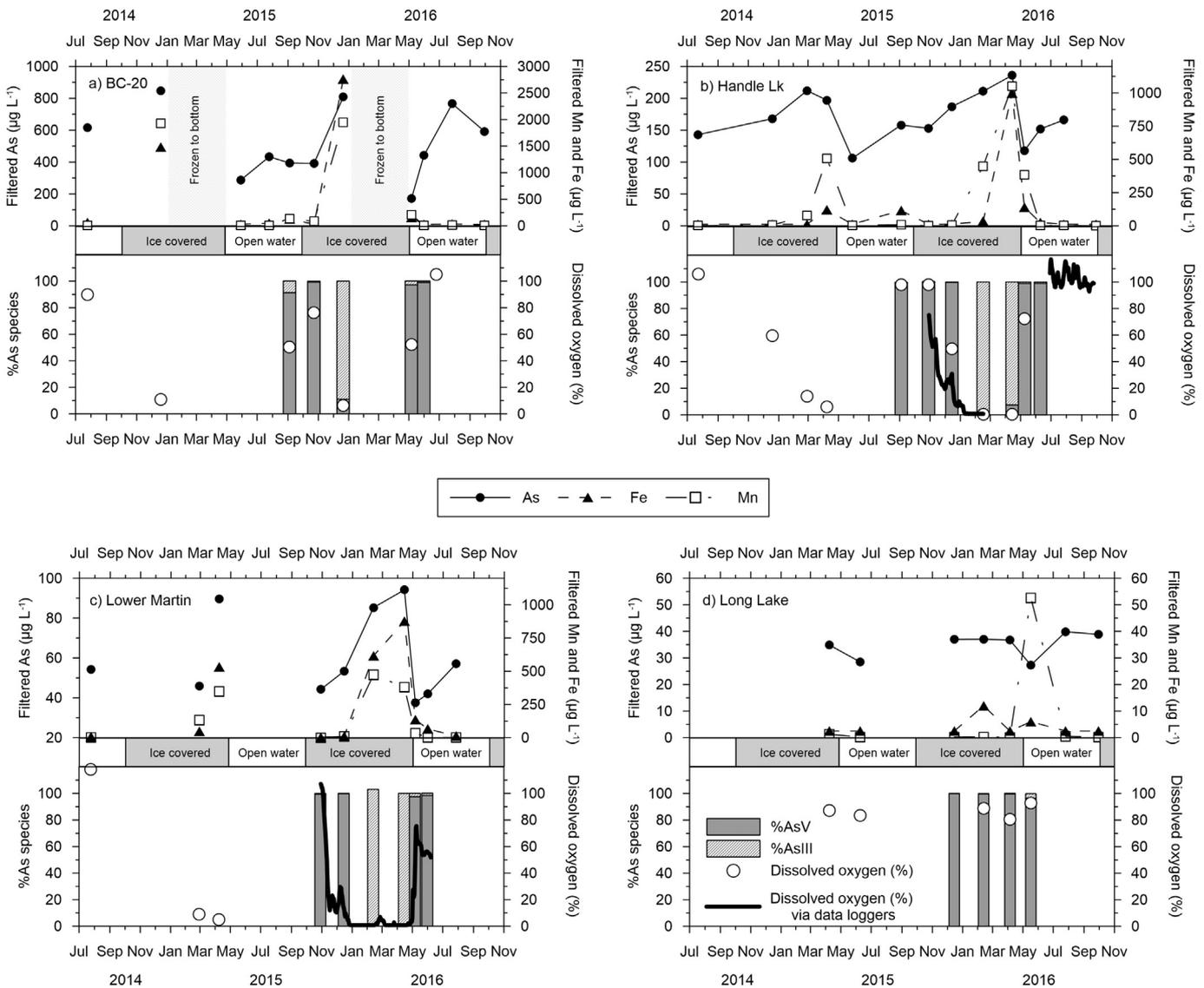


Fig. 2. The seasonal variation in As, Fe, Mn, and dissolved oxygen (saturation %) and the proportion of inorganic arsenic species in surface waters of the four study lakes, July 2014 to September 30, 2016. The top panel of each plot represents the concentration of As, Fe, and Mn in the filtered fraction ($<0.45 \mu\text{g L}^{-1}$) of surface waters of the four detailed study lakes, including: a) BC-20; b) Handle Lake; c) Lower Martin Lake; and d) Long Lake. The lower panels in each plot show the proportion of each of the inorganic species of arsenic (As(III) and As(V)) present in the filtered fraction ($<0.45 \mu\text{m}$) of surface waters at different sampling periods and the amount of dissolved oxygen (saturation %) measured in situ. Note difference in scale amongst the figures.

in all study lakes during all sampling periods (Health Canada, 2017; WHO, 2011) (Fig. 2). Dissolved Sb concentrations were below the 20 $\mu\text{g L}^{-1}$ WHO guideline for drinking water quality in all lakes during the entire study (WHO, 2011) (Fig. 3). Dissolved As and Sb concentrations were highest in BC-20 (max As: 846 $\mu\text{g L}^{-1}$; max Sb: 10.1 $\mu\text{g L}^{-1}$), followed by Handle Lake (max As: 236 $\mu\text{g L}^{-1}$; max Sb: 7.5 $\mu\text{g L}^{-1}$), Lower Martin Lake (max As: 94.2 $\mu\text{g L}^{-1}$; max Sb: 2.1 $\mu\text{g L}^{-1}$), and Long Lake (max As: 39.9 $\mu\text{g L}^{-1}$; max Sb: 2.1 $\mu\text{g L}^{-1}$), respectively (Table 2). Arsenic and Sb in surface waters from the study lakes were predominately in the dissolved fraction (Table 2).

3.1. Seasonal changes in water column dissolved oxygen

BC-20, Handle Lake, and Lower Martin Lake all experienced periods of winter anoxia in the water column (Fig. 2). In both study years, the water column in these three lakes was typically oxygen depleted ($<0.5 \text{ mg L}^{-1} \text{ O}_2$) by early January, although interannual variation between sites and years was noted (Fig. 2). The rate of oxygen depletion was greater in Lower Martin Lake than Handle Lake, and oxygen levels were below 0.5 mg L^{-1} by December 25, 2015 at Lower Martin Lake and January 8, 2016 at Handle Lake (Fig. 2). Dissolved oxygen was not measured continuously at BC-20, but dissolved oxygen levels were below 5% during sampling on December 21, 2015. Surface waters at Long Lake remained well oxygenated throughout the entire study (Fig. 2). Oxygen levels decreased at depth ($>3 \text{ m}$) during winter sampling in February and April but did not reach anoxic conditions within 0.5 m of the sediment boundary (Fig. A.2).

3.2. The concentration of arsenic and major ions in lake ice

Water chemistry of black ice samples indicated that almost all ($>95\%$) major ions and total unfiltered As and Sb were excluded during black ice development (Table A.1). Conversely, concentrations of total unfiltered As and Sb were comparable or higher in white ice than in lake waters collected prior to freeze-up at Lower Martin Lake and BC-20, respectively (Table A.1). This difference likely reflects the source and mechanism of white ice development, since white ice forms from the freezing of lake waters that have been redistributed to the ice surface. If white ice forms after substantial ice development, the sourced

water represents lake waters that may have been elementally enriched by solute exclusion.

3.3. Seasonal changes in surface water chemistry

Seasonal differences in concentrations of As, Sb, Fe, Mn, and Σ major ions were observed in surface waters of all four study lakes (Figs. 2 & 3), although the pattern of change in Long Lake was different than the other three lakes. In the three shallow lakes (BC-20, Handle Lake and Lower Martin Lake) concentrations of these elements typically increased under ice and were highest during late winter. The winter enrichment factor was greatest for the redox sensitive elements Fe and Mn, except in Long Lake, where no increase in elemental concentrations of Fe and Mn was observed over winter (Table 2). A large decrease in element concentrations was observed in BC-20, Handle Lake and Lower Martin Lake in association with spring snowmelt and the loss of the ice cover in early May (Figs. 2 & 3).

The variation in elemental concentrations of surface waters was low in Long Lake, the deepest and largest volume lake in the study, which did not experience anoxia in the water column. There was no evidence of under ice enrichment in concentrations of As, Sb, Fe, Mn, or Σ major ions (Figs. 2 & 3; Table 2). Similar to the other three sites, concentrations of As, Sb, and Σ major ions decreased at Long Lake during freshet (Figs. 2 & 3). In contrast to the three shallow sites, a large increase in surface water Mn was measured in Long Lake during freshet sampling.

Seasonal changes in surface water As concentrations were greatest in the shallowest and lowest volume lake in the study (BC-20), and surface water As varied >4 -fold over the entire study period (172–846 $\mu\text{g L}^{-1}$). Large winter increases in surface water As in the three shallowest lakes were associated with the depletion of oxygen from the water column and large increases in Fe and Mn (Fig. 2). When data from all four study lakes were included, the winter enrichment factor was more strongly correlated with the surface area to lake volume ratio (Spearman rank order correlation, $r_s = 0.95$; $p = 0.051$) than lake volume alone ($r_s = -0.63$; $p = 0.367$). Increases in surface water As concentrations were also measured during the open-water season at BC-20, Handle Lake, and Lower Martin Lake; however, concentrations of Fe and Mn remained low. In these three shallow lakes, the concentrations of As in surface waters were lowest in May post-snowmelt and gradually increased over the course of the open-water season, although

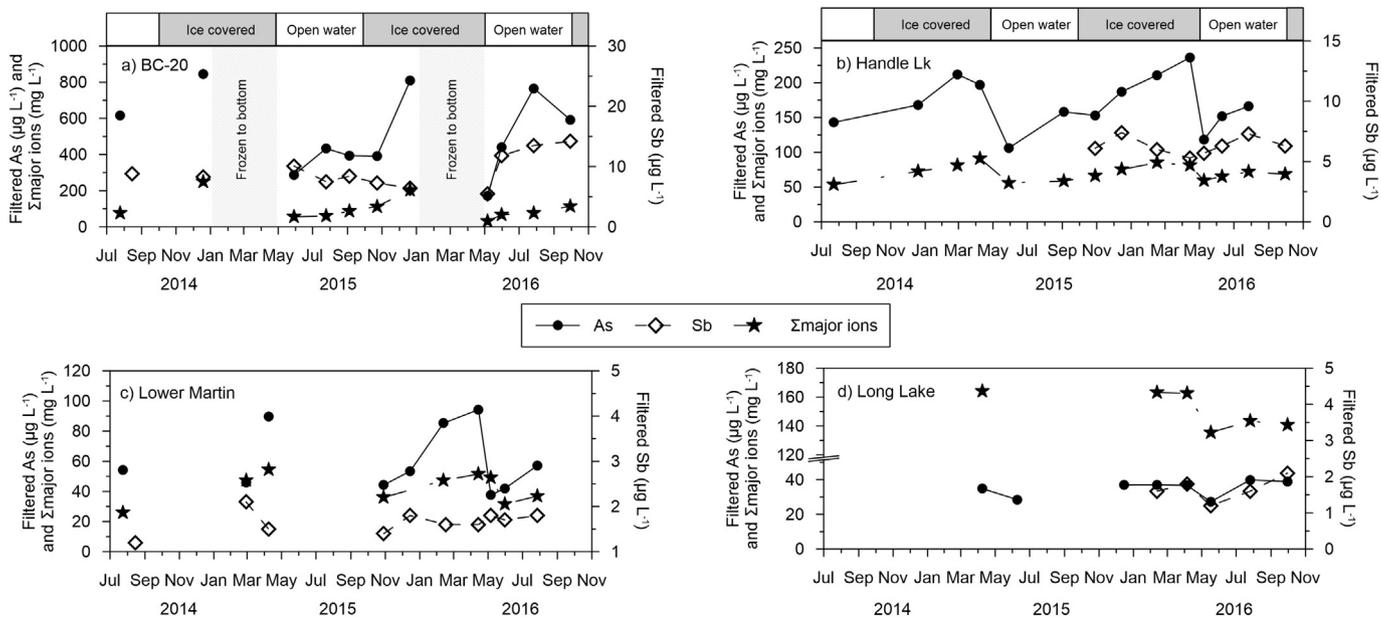


Fig. 3. Concentrations of As, Sb and the sum of major ions in the filtered fraction ($<0.45 \mu\text{m}$) of surface waters for each of the study sites, July 2014 to November 2016.

Table 2

Summary statistics for select elements and water quality parameters at the four detailed study sites. The total metal(loid) concentration in the dissolved fraction (<0.45 μm) represents the mean from all sampling periods and the standard deviation is reported in parentheses. The winter enrichment factor represents the increase in surface water concentration during the ice-covered season (October to April) and the open-water season (June to September). For sites with more than one year of data, the enrichment factor represents the year with the greatest increase in concentration.

| Site | Surface water concentration (filtered <0.45 μm) | | | | Proportion of total metal(loid) in dissolved fraction (stdev) | Maximum winter enrichment factor | Maximum summer enrichment factor |
|---|---|---------|---------|----|---|----------------------------------|----------------------------------|
| | Mean | Maximum | Minimum | N | | | |
| As ($\mu\text{g L}^{-1}$) | | | | | | | |
| BC-20 | 522 | 846 | 172 | 11 | 0.99 (0.15) | 2.1 | 1.3 |
| Handle Lk | 170 | 236 | 106 | 14 | 0.99 (0.05) | 1.5 | 1.1 |
| Lower Martin Lk | 60 | 94 | 38 | 10 | 0.88 (0.18) | 2.1 | – |
| Long Lk | 35 | 40 | 27 | 8 | 0.96 (0.04) | 1.0 | – |
| Sb ($\mu\text{g L}^{-1}$) | | | | | | | |
| BC-20 | 9.3 | 14 | 5.5 | 11 | 0.98 (0.12) | 0.9 | 1.2 |
| Handle Lk | 6.3 | 7.5 | 5.3 | 13 | 0.96 (0.08) | 0.9 | 1.1 |
| Lower Martin Lk | 1.7 | 2.1 | 1.2 | 10 | 0.93 (0.11) | 1.1 | – |
| Long Lk | 1.7 | 2.1 | 1.2 | 5 | 0.99 (0.05) | 0.9 | – |
| Fe ($\mu\text{g L}^{-1}$) | | | | | | | |
| BC-20 | 433 | 2760 | 23 | 11 | 0.44 (0.26) | 95 | 0.9 |
| Handle Lk | 23 | 208 | <5.0 | 14 | 0.18 (0.23) | 83 | 0.5 |
| Lower Martin Lk | 231 | 876 | <5.0 | 10 | 0.48 (0.38) | 350 | – |
| Long Lk | 4.1 | 12 | <5.0 | 8 | 0.25 (0.18) | 1.0 | – |
| Mn ($\mu\text{g L}^{-1}$) | | | | | | | |
| BC-20 | 396 | 1950 | 4.2 | 11 | 0.59 (0.37) | 23 | 1.2 |
| Handle Lk | 178 | 1050 | 0.5 | 14 | 0.32 (0.42) | 2100 | 0.2 |
| Lower Martin Lk | 138 | 473 | 0.4 | 10 | 0.53 (0.51) | 950 | – |
| Long Lk | 7.0 | 53 | <0.2 | 8 | 0.08 (0.16) | 0.5 | – |
| Σ Major ions (mg L^{-1}) | | | | | | | |
| BC-20 | 103 | 249 | 31 | 11 | – | 1.8 | 1.7 |
| Handle Lk | 70 | 91 | 53 | 14 | – | 1.2 | 1.1 |
| Lower Martin Lk | 42 | 54 | 26 | 9 | – | 1.4 | – |
| Long Lk | – | – | – | – | – | NA | – |
| Specific conductivity ($\mu\text{S cm}^{-1}$) | | | | | | | |
| BC-20 | 470 | 1090 | 166 | 11 | – | 1.7 | 1.7 |
| Handle Lk | 314 | 423 | 242 | 14 | – | 1.3 | 1.2 |
| Lower Martin Lk | 185 | 244 | 131 | 10 | – | 1.4 | – |
| Long Lk | 431 | 475 | 384 | 7 | – | 1.1 | – |

to a lesser extent than during the ice-covered season (Table 2). Conditions during the summer of 2016 at BC-20 were the exception, when the surface water As concentration measured in July was $766 \mu\text{g L}^{-1}$, a value comparable to late winter concentrations measured in the lake (Fig. 2).

Data presented in Fig. 4 highlight the relationship between elemental concentrations of surface waters and dissolved oxygen levels during the development of the ice cover. In the three shallow lakes, concentrations of As, Fe, and Mn were highest under anoxic conditions and the relationship is best described by a logarithmic or exponential model. In contrast, the relationship between concentrations of major ions and dissolved oxygen in the water column is best represented by a linear model, and lacks a large increase in major ions in association with the development of anoxia.

Compared to large changes in As, Fe, and Mn in the three shallowest lakes, there was less variation in surface water Sb concentrations over the study period and no large increases in Sb were associated with the onset of anoxia in the water column (Fig. 3). Although somewhat limited by the frequency of sampling in the study, the data in Fig. 3 suggest that the concentration of Sb in surface waters at Handle and Lower Martin Lake increased between the two early-winter sampling periods (November – December), and subsequently decreased later in the winter after the onset of anoxia in the water column (Fig. 3).

3.4. Seasonal As and Sb mass loading in Handle Lake

Water column profiling during winter in Handle Lake revealed a depth gradient in As, Sb, Fe, and Mn concentrations, with concentrations

of all elements increasing closer to the sediment boundary (Fig. A.4). No water column gradient was observed for As, Sb, Fe, or Mn during open-water sampling in May and July (Fig. A.4).

Lake volume decreased 19% over the winter period with the development of an ice-cover and there was a subsequent 42% increase in the estimated lake-wide mean concentration of As (Table 3). Model estimates for cryoconcentration influence on water column As concentrations were similar to measured values in early winter (December), but underestimated concentrations of As in February and April by approximately 12% (Table 3). Water column mass of As was also relatively similar between the end of the open-water season and early winter, but increased approximately 15% between December and February with the onset of water column anoxia. The mass increase in As between December and April represented an estimated sediment efflux of $273 \mu\text{g m}^{-2} \text{day}^{-1}$ over that period (Table 3). In contrast with As, no sediment efflux of Sb was observed in Handle Lake in winter. Water column concentrations of Sb decreased <10% over the ice-cover period and did not correspond with expected concentrations from the cryoconcentration model (Table 3). The total Sb load in the Handle Lake water column also decreased over the ice-cover period by approximately 25%, corresponding to an estimated flux of $18 \mu\text{g m}^{-2} \text{day}^{-1}$ Sb from the water column to lake sediments between December and April 2016 (Table 3).

Lake volume decreased in Handle Lake over the open water season (approximately 8%) and concentrations of As were similar to model estimates for evapoconcentration. Lake-wide mass of As was consistent between the two summer sampling periods and the estimated sediment-water efflux of As was low ($7.8 \mu\text{g m}^{-2} \text{day}^{-1}$). The concentration and mass of Sb in the water column increased over the open-

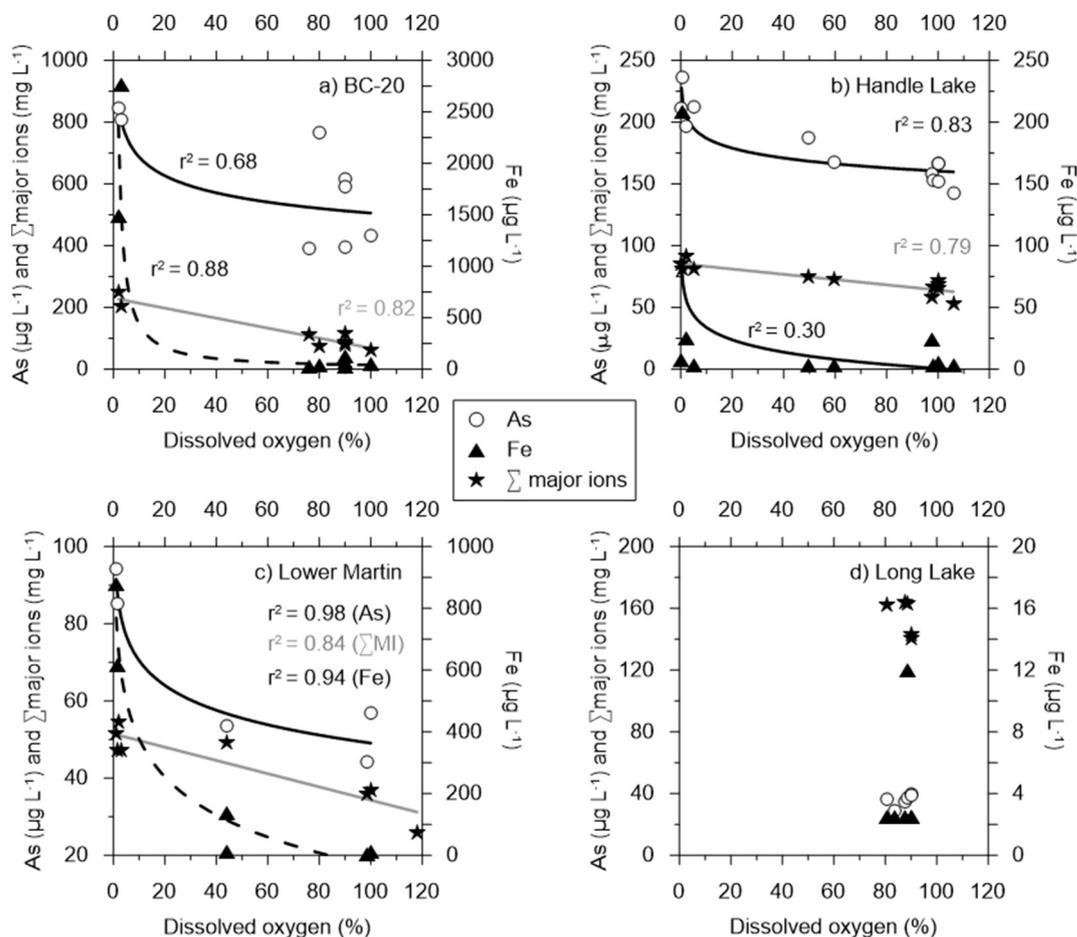


Fig. 4. Relationships between selected elements (As, Fe, and the sum of major ions) and dissolved oxygen in surface waters for: a) BC-20; b) Handle Lake; c) Lower Martin Lake; and d) Long Lake. Reported data are from sampling periods between July and the end of April. Data collected during snowmelt period are excluded. The coefficients of determination (r^2) presented in figures represent linear and logarithmic regression models with $p < 0.001$. Note the different concentration scales between panels. All metal(loid) and ion data refer to the filtered fraction ($<0.45 \mu\text{m}$) in surface waters.

water season, but the increase was small compared to changes observed for As over winter and suggested a low rate of Sb release from lake sediments during summer ($<3 \mu\text{g m}^{-2} \text{day}^{-1}$) (Table 3).

3.5. Seasonal changes in inorganic arsenic speciation of surface waters

In all four lakes, the proportion of inorganic As species was dominated by arsenate [As(V)] (>90%) during the open-water season and

early in the ice-cover season when surface water conditions remained well oxygenated (Fig. 2). During the ice-covered season of 2015–16 the relative proportion of arsenite [As(III)] increased in the three shallowest lakes in association with the depletion of oxygen from surface waters. In these three lakes there was a rapid return to As(V) as the dominant inorganic species following snowmelt and the erosion of the ice cover (Fig. 2). In Long Lake, As(V) accounted for >96% of the total inorganic As in all sampling periods.

Table 3

Mass balance, cryo- and evapo-concentration model, and sediment-water flux estimates in Handle Lake for As and Sb.

| Sampling date | Ice thickness (m) | Lake volume (m^3) | Arsenic | | | Antimony | | | |
|---|--|------------------------------|---|---|-----------|---|---|-----------|--------|
| | | | Concentration ($\mu\text{g L}^{-1}$) ^a | Modelled concentration ($\mu\text{g L}^{-1}$) | Mass (kg) | Concentration ($\mu\text{g L}^{-1}$) ^a | Modelled concentration ($\mu\text{g L}^{-1}$) | Mass (mg) | |
| Winter | September 4, 2015 | – | 292,012 | 158 | – | 46.1 | 7.5 | – | 2190 |
| | December 15, 2015 | 0.30 | 241,017 | 187 | 191 | 45.1 | 7.4 | 9.1 | 1784 |
| | February 16, 2016 | 0.51 | 208,082 | 253 | 222 | 52.6 | 5.8 | 10.5 | 1207 |
| | April 14, 2016 | 0.59 | 196,284 | 265 | 235 | 52.0 | 6.8 | 11.2 | 1335 |
| | Percent change (Dec.–April) | | –18.6% | 41.7% | 23.0% | 15.4% | –8.1% | 23.1% | –25.2% |
| Sediment - water flux ($\mu\text{g m}^{-2} \text{day}^{-1}$) (Dec.–April) | | | | | | 273.3 | | | –17.7 |
| Summer | June 10, 2016 | – | 316,005 | 152 | – | 48.0 | 6.3 | – | 1991 |
| | July 27, 2016 | – | 292,012 | 166 | 164 | 48.5 | 7.3 | 6.8 | 2132 |
| | Percent change | | –7.6% | 9.2% | 7.9% | 0.9% | 15.9% | 7.9% | 7.1% |
| | Sediment - water flux ($\mu\text{g m}^{-2} \text{day}^{-1}$) | | | | | 7.8 | | | 2.5 |

^a Depth-weighted mean.

3.6. Potential influence of snowmelt on surface water As concentrations and speciation

Sampling of Lower Martin Lake on 6 May 2016, three days prior to the loss of lake ice, provided an opportunity to evaluate the influence of snowmelt on the concentration and speciation of As in surface waters in a shallow lake in the region. On that day, most of the snow cover had melted from the surrounding catchment and a small area of open water was present between the lake shore and floating ice cover ($[As] = 26.5 \mu\text{g L}^{-1}$). Surface waters collected from below the ice cover reflect snowmelt input to the lake, were oxygenated ($>40\%$ DO saturation) and represented the lowest concentrations of As measured in Lower Martin Lake during the study ($[As] = 37.6 \mu\text{g L}^{-1}$). As(V) accounted for 98% of inorganic As species in surface waters in contrast to three weeks earlier when As(III) was the predominant species under anoxic water column conditions (Fig. 2).

3.7. Seasonal differences in As, Sb, Fe, and major ions in the regional lake surveys

A steep decrease in surface water As concentration was observed with greater distance from the historic Giant Mine roaster in the open-water and under-ice sampling periods (Fig. A.5), consistent with previous studies in the region (Houben et al., 2016; Palmer et al., 2015). Seasonal differences in surface water As between the two sampling periods were not correlated with distance from the mine roaster (Spearman rank order correlation: $r_s = 0.02$; $p = 0.44$; $n = 31$). Therefore, distance was not integrated as a covariate in subsequent analyses related to the influence of physical lake properties on seasonal differences in surface water As.

Late-winter element concentrations were typically higher than during the open-water sampling period and lake depth had an important influence on these seasonal differences. The largest changes in As and Fe between the late-winter and open-water seasons were typically in lakes with a maximum depth <4 m (Fig. 5). Measured differences were as high as $125 \mu\text{g L}^{-1}$ As and $5757 \mu\text{g L}^{-1}$ Fe within a lake. Large seasonal differences in Sb were only measured in lakes shallower than 2 m and, in contrast with As and Fe, surface water Sb was higher in the open water season for 33% of the lakes (Fig. 5c).

3.8. Relationship between surface water and near-surface sediment chemistry

Surface water and sediment concentrations of As were positively correlated during the open-water sampling period (Fig. A.6a). Furthermore, the highest concentrations of surface water As were measured in lakes with high sediment TOC (Fig. A.6b).

4. Discussion

Concentrations of As and Sb remain elevated in surface waters of small lakes near the historic roaster at Giant Mine 50 years after the bulk of roaster emissions were deposited across the landscape. High concentrations of As and Sb in regional surface waters have been previously reported in the literature over the last 40 years (Houben et al., 2016; Palmer et al., 2015; Wagemann et al., 1978). These studies present surface water results collected during the open-water season and were primarily developed to assess the magnitude and regional distribution of legacy pollutants in surface waters. In this study we build on this previous work by demonstrating that concentrations of surface water As can vary >5 -fold between open-water and ice-covered seasons

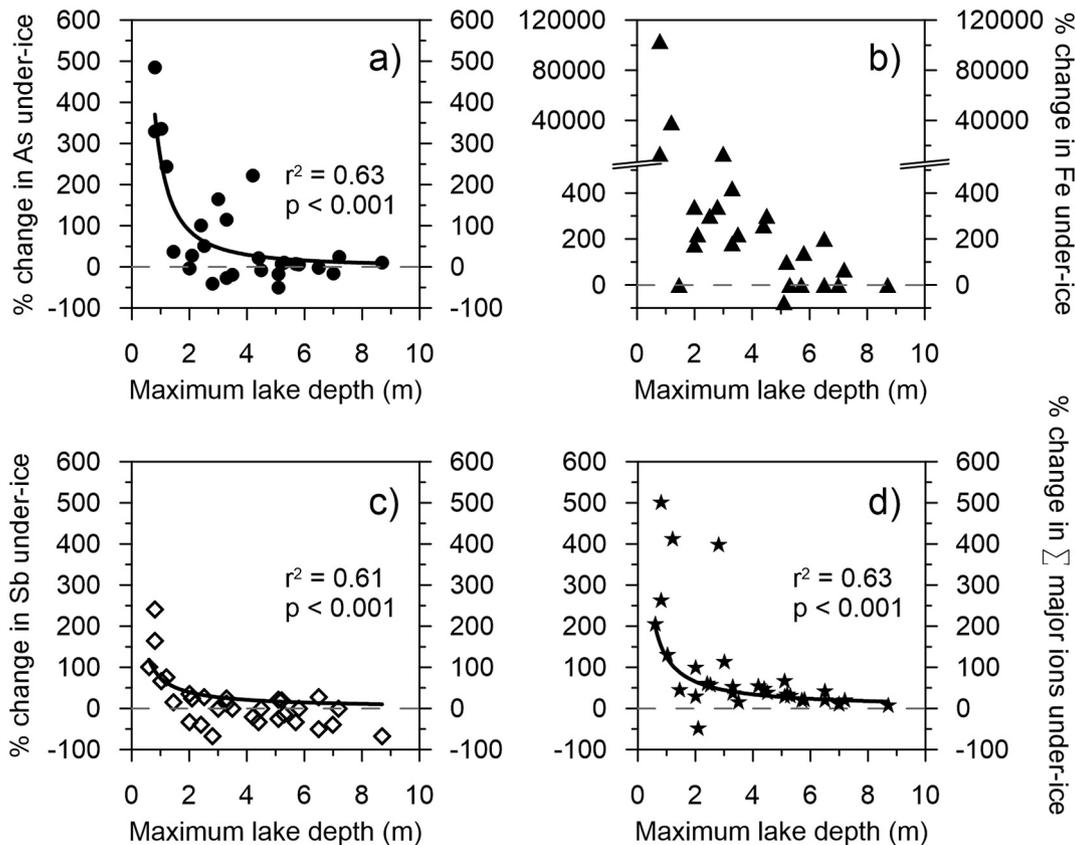


Fig. 5. Relationships between seasonal change in surface water concentrations of elements (as the percent change in water chemistry between fall and late winter) and maximum lake depth in 31 lakes within 30 km of Yellowknife, including: a) As; b) Fe; c) Sb; and d) sum of major ions. Only lakes with maximum depth <10 m were included. All metal(loid) and ion data refer to the filtered fraction ($<0.45 \mu\text{m}$) in surface waters.

and are greatest for lakes with a maximum depth <4 m (Fig. 5). We also found evidence that seasonal variation in under-ice water chemistry is likely driven by a combination of solute exclusion during ice formation and lake-bottom biogeochemical processes.

4.1. Seasonal changes in surface water As influenced by a combination of physical and biogeochemical processes

Regular sampling of four lakes near the historic Giant Mine roaster and seasonal sampling of 31 lakes across the region highlight substantial variation in surface water quality of shallow lakes in the region. Seasonal differences varied in magnitude, and increased or decreased dependent on the element of interest, which underlines the complex interactions that influence the seasonal variability of legacy pollutants in lakes in the region. The development of ice-cover strongly enriched surface water concentrations of As, Fe, Mn, and major ions of the three shallowest lakes (Figs. 2 and 3). The measurement of low elemental concentrations in lake ice (Table A.1) indicated that the development of the ice cover was effective in excluding solutes during its development and early winter increases in surface water As and major ions, likely reflect the influence of cryoconcentration. The similarity in modelled and measured concentrations of As during early winter in Handle Lake support the suggestion that early season concentration increases are due to solute exclusion and cryoconcentration (Table 3).

Large increases in surface water As, Fe, and Mn in association with the onset of anoxia in the water column in the three shallowest lakes indicated an increase in the sediment efflux of these elements due to seasonal oxic-anoxic transitions (Figs. 2 and 4). Results from under ice water column sampling and As mass balance estimates for Handle Lake indicated: 1) an increase in concentrations of As, Fe, and Mn towards the sediment boundary (Fig. A.4), consistent with sediment efflux of these elements; and 2) an increase in mass of As in the water column coinciding with the onset of anoxic conditions in the water column (Table 3).

In BC-20, Handle Lake, and Lower Martin Lake, rapid oxygen depletion from the water column was facilitated by the relatively high ratio of sediment surface area to lake volume (>0.6) and the high sediment oxygen demand of the organic-rich bottom sediments (BC-20: 17% TOC; Handle: 28% TOC; Lower Martin: 25% TOC) (Table 1; Fig. 2). Previous solid phase speciation of As in sediments in the study lakes has shown that near-surface Fe (oxy)hydroxides may host a substantial amount of As (3–4 wt%) (Schuh et al., 2018; Van Den Berghe et al., 2018). Therefore, late-winter increases in surface water As were likely due to seasonal desorption/dissolution from Fe (oxy)hydroxides following the removal of the oxic boundary in near-surface sediments. While the aerobic zone in near-surface sediments may be quite thin (<2 cm), this layer can be an effective barrier to diffusion of As across the sediment-water boundary for much of the year (Andrade et al., 2010; Bennett et al., 2012; Martin and Pedersen, 2004). Lakes close to historic roasting operations in the Yellowknife region contain large reservoirs of As stored in lake sediments at depths between 10 and 30 cm (Schuh et al., 2019, 2018; Thienpont et al., 2016; Van Den Berghe et al., 2018). The continued dissolution of As at depth that is primarily derived from legacy As₂O₃, results in steep porewater gradients that drive the upward diffusion of As(III) towards the sediment surface (Schuh et al., 2018; Van Den Berghe et al., 2018). High porewater concentrations of As just below the sediment Fe(III) redoxcline under oxic conditions are an additional source of aqueous As available for release to overlying waters with the onset of anoxia at the sediment boundary during prolonged ice cover. The data presented here suggest that increased sediment efflux of As with change in redox state at the sediment boundary is likely an important mechanism in controlling seasonal changes in the surface water quality of shallow lakes. Further, the positive correlation between surface water and sediment As concentrations supports the hypothesis that elevated surface water As is sustained by the continued internal loading from contaminated sediments (Fig. A.6a).

In contrast to large changes measured in the three shallowest lakes, changes in lake water chemistry were small over winter in the deepest lake (Long Lake) (Fig. 2). Similarly, we found that differences in As between the two regional surface water surveys were low for lakes with a maximum depth >4 m (Fig. 5). This threshold is similar to the findings of Leppi et al. (2016) from a series of lakes in northern Alaska that showed minimal oxygen depletion in lakes with a maximum depth >4 m. Considerable variation in late winter dissolved oxygen conditions has been noted in shallow arctic and subarctic lakes, which has been attributed to differences in landscape (lake surface area, littoral area) and limnological (trophic status) properties (Leppi et al., 2016; Mathias and Barica, 1980) that may contribute to the extent of seasonal change in surface water As concentrations for lakes <4 m deep (Fig. 5). As pointed out by Mathias and Barica (1980) the empirical relationship between oxygen depletion rate and lake depth primarily reflects differences in the sediment surface area to lake volume ratio with changing lake depth.

Temporal changes in surface water concentrations of As were also measured over the open-water season in the three shallowest lakes although differences in As were typically small and not associated with increases in Fe and Mn or low oxygen conditions (Fig. 2). The diffusion of As across the sediment-water boundary during the open-water season has been estimated in Long Lake and for a littoral area in Lower Martin Lake by applying Fick's First Law of diffusion to sediment porewater information (Schuh et al., 2019; Van Den Berghe et al., 2018). These studies suggest internal loading of As from lake sediments occurs during the open-water season. Across the study region, surface water As was highest in lakes with organic-rich surficial sediments highlighting a potential link between internal As loading and organic matter accumulation (Fig. A.6b). Organic matter accumulation at the sediment boundary alters the position of the Fe(III) redoxcline in lake sediments by increasing sediment oxygen demand and microbial respiration rates. The thinning of the aerobic zone in near-surface sediments limits the area where upwardly mobile As may be scavenged by adsorption on Fe oxy(hydroxides), thus leading to higher rates of sediment efflux (Martin and Pedersen, 2004). Sediment temperature has also been shown to influence sediment efflux rates of As through increased microbial respiration rates, thinning of the oxic layer and reductive dissolution of Fe-oxyhydroxides (Barrett et al., 2019). A temperature effect may explain why large increases in summer concentrations of surface water As were noted in BC-20, the shallowest and warmest study lake (Fig. 2). Daily mean sediment temperatures in BC-20 were well above 20 °C for much of July 2016 (Fig. A.7).

Hydrological processes may also have an important influence on surface water As during the open-water season. In particular, evaporative fluxes are high in the region during summer and lakes typically have a negative water balance during this period when evaporative fluxes can greatly exceed precipitation (Gibson et al., 1998; Spence, 2006). Although there is limited understanding of the water balance of the study lakes, the large surface area to volume ratio in BC-20, Handle and Lower Martin suggests evapoconcentration of solutes may also contribute to summer enrichment of As concentrations in these lakes that is supported by similar summer enrichment factors for Σ major ions and specific conductivity (Table 2).

4.1.1. The relative influence of biogeochemical processes vs cryo- and evapoconcentration in controlling As concentration and loading in Handle Lake

The arsenic mass balance estimates for Handle Lake were used to elucidate the relative influence of winter and summer processes on the flux and concentration of As in shallow lakes in the region. These data suggest that increases in surface water concentrations of As during summer were predominately attributed to a decrease in lake volume driven by evaporative processes, since there was little change in As mass between the two sampling periods and 86% of the summer increase in As concentration can be attributed to the evapoconcentration

estimate (Table 3). These data also suggest that winter processes have a greater influence on water column concentrations (42% increase in [As]) and loading of As (+7 kg As) compared to open water processes and were driven by a combination of cryoconcentration and sediment As release with the onset of anoxia in the water column (Fig. A.4; Table 3). The influence of these two processes on lake water concentrations of As was relatively equal, since the cryoconcentration estimate accounted for approximately 56% of the increase in surface water As concentration between December and April (Table 3). While the results from Handle Lake are instructive for a general understanding of the partitioning of summer and winter processes driving water column As concentrations and mass balance, it is difficult to generalize the results across the wider region, since variation in lake biophysical properties, such as depth and surface area to volume ratio, sediment organic content, and sediment temperature will alter the relative influence of these processes.

4.2. Periods of seasonal anoxia alter the oxidation state of surface water arsenic

In fresh waters, As typically exists as inorganic oxyanions of arsenate [As(V)] and arsenite [As(III)]. (Smedley and Kinniburgh, 2002; Wang and Mulligan, 2006). Arsenate tends to dominate in oxidizing environments, whereas As(III) is more stable under reducing conditions (Smedley and Kinniburgh, 2002). Results from this study follow this expected pattern. Inorganic As was measured predominately as As(V) in all study periods when the lakes were well oxygenated, whereas As(III) was the dominant inorganic As species after lake waters were depleted of oxygen (Fig. 2). In the winter of 2015–16, the measurement of As(III) as the dominant species in the water column corresponded with the onset of anoxic conditions and is likely the result of both the reduction of lake water As(V) to As(III) and the mobilization of As(III) from sediment porewaters to overlying lake waters. The oxidation of As(III) to As(V) occurred rapidly in spring upon removal of the ice cover. In Lower Martin Lake, this transition occurred in association with snowmelt inputs to the lake from the landscape prior to the loss of ice cover (Fig. 2). The mechanisms controlling the rapid oxidation of As(III) under ice warrant additional attention, since abiotic oxidation of As(III) under circumneutral conditions is expected to be slow compared to microbially and photochemically mediated As(III) oxidation with intense sunlight (Asta et al., 2012; Hug et al., 2001), as would be expected in subarctic locations in early May.

4.3. Changes in surface water Sb concentrations across seasonal redox transitions

In the four lakes studied in detail, the seasonal enrichment factors showed that concentrations of Sb were relatively unchanged over the duration of winter and increased in the open water season, contrary to the patterns of seasonal enrichment factors for As, Fe, and Mn (Figs. 2 & 3; Table 2). In the regional dataset, surface water Sb concentration changed little between open-water and under-ice seasons. Antimony concentrations were frequently lower under ice except for the shallowest lakes (<2 m) (Fig. 5). Further, Sb mass balance estimates in Handle Lake indicated a 25% decrease in lake wide mass of Sb over the duration of winter, and a slight increase in mass of Sb in the water column between the two summer sampling periods (Table 3). These data suggest that Sb mobility does not increase in association with the transition from oxic-anoxic conditions in the lakes, a finding that is consistent with several recent studies that have highlighted the contrasting mobility of As and Sb in contaminated lake sediments (Arsic et al., 2018; Fawcett et al., 2015). Water column sampling under ice at Handle Lake, however, presented conflicting results, as Sb concentrations increased with proximity to the sediment boundary in association with increases in concentrations of Fe and Mn (Fig. A.4), suggesting that Sb may be released from lake sediments with the removal of the oxic boundary. The use of surface water chemistry to explore questions

pertaining to biogeochemical processing within lake sediments has limitations. Whether the water column profile data indicate contrasting geochemical behavior, settling of colloidal fractions (<0.45 μm) of Sb from the water column, or are simply a limitation of attempting to use changes in low concentrations of trace metalloids in surface waters to understand biogeochemical processes occurring within lake sediments remains unresolved. Detailed porewater and mineralogical analyses are warranted to help elucidate the processes controlling Sb retention and release from sediments to inform the long-term fate of this element.

5. Conclusions and directions for future research

Concentrations of surface water As remain high in lakes close to point sources of legacy mining emissions because sediments are a persistent source of As to overlying waters that are seasonally re-cycled. Observed seasonal changes were greatest for lakes with a maximum depth <4 m and were driven by a combination of physical and biogeochemical processes. Lake depth control was apparent in the regional study lakes distal from the point source of contamination, suggesting that this physical parameter is an important control in lakes with a seasonal ice cover regardless of contamination.

Knowledge gaps persist regarding the long-term fate of As and Sb in lakes in the region and important directions for future research include:

- Further work to clarify the biogeochemical processes controlling Sb mobility, including detailed porewater analyses and solid-phase speciation of near surface sediments;
- Exploring the role of repeated redox oscillations at the sediment-water boundary on the biogeochemical cycling of As and Sb to determine the long-term net gain or loss of these elements from the water column. The influence of oscillating redox conditions on As-bearing floodplain soils has been explored experimentally using laboratory bioreactors (Parsons et al., 2013), and a similar approach may help to explain long-term (i.e. decadal) changes in shallow lakes that experience seasonal redox oscillations in contaminated lake sediments;
- Detailed studies directed at understanding the role of snowmelt processes on As cycling in subarctic lakes. Results from this study suggest that large winter additions of As to the water column may be offset by the rapid oxidation of aqueous As(III) and the precipitation and sedimentation of As-bearing minerals.
- Experimental work to investigate the influence of temperature in controlling sediment-water fluxes of metal(loid)s. This is important for gaining a better understanding of how summer sediment diffusive fluxes may vary temporally in shallow lakes where sediment and water temperatures can change quickly and spatially between lakes with different physical and biological characteristics. Temperature investigations are also important in light of expected lake warming associated with climate change (Williamson et al., 2009).

Finally, this study highlights the importance of winter processes for understanding the chemical and biological recovery in shallow subarctic lakes from metalloid pollution. The interpretation of surface water and sediment geochemistry in areas with transient redox conditions requires investigations across the spectrum of redox conditions. Clearly, sampling in the open-water season, when most environmental research takes place in the subarctic, does not account for a critical period in the annual cycling of As and Sb.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.scitotenv.2019.05.258>.

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