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Lake-specific controls on the long-term stability of mining-related, legacy arsenic contamination and geochemical baselines in a changing northern environment, Tundra Mine, Northwest Territories, Canada

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ABSTRACT

Climate change is influencing the biogeochemistry of northern lake ecosystems. These changes may affect the mobility of naturally occurring metal(loid)s and long-term stability of anthropogenic contaminants. Arsenic (As) concentrations in lake sediments in the Courageous Lake Greenstone Belt, Northwest Territories, Canada, are elevated from the operation of two high-grade, low-tonnage historical gold mines (Tundra Mine and Salmita Mine) and the weathering of mineralized bedrock. In sensitive sub-Arctic environments, it is not currently known how the cumulative effects of resource extraction and climate warming will impact geochemical baselines and the long-term stability of legacy contaminants. In this study, measurements of As concentration and speciation in waters and sediments are combined with multivariate analyses of climate proxies (sediment particle size and organic matter composition) from five lakes downstream of the former Tundra Mine site. Data from lake sediment cores were divided into geochemically distinct populations using a combination of radiometric dating and constrained incremental sum-of-squares cluster analysis to define geochemical baselines, examine the lake-specific controls on As distribution, and determine climate-related factors that may influence the long-term stability of As. Median As concentrations in near-surface impacted sediments (median: 110 mg kg^{-1}; range: 31–1,010 mg kg^{-1}; $n = 22$) and pre-mining sediment (median: 40 mg kg^{-1}; range: 28–170 mg kg^{-1}; $n = 102$) exceed the Canadian Council of the Ministers of the Environment Probable Effects Level of 17 mg kg^{-1}. Near the Tundra Mine, the long-term stability of As in the near-surface sediment is influenced by the source of As (direct disposal and weathering of waste rock, tailings overtopping and seepage, discharge of treated tailings effluent, weathering and airborne deposition of tailings and waste rock, and natural weathering of mineralized bedrock), lithology of the sediment, and composition of sediment organic matter. This study demonstrates that in lakes impacted by weathering of waste rock and mineralized bedrock, As in sediments is primarily hosted by Fe-(oxy) hydroxides and may be more susceptible to remobilization with climate warming relative to those lakes impacted by direct discharge of mine wastes where As-bearing sulphides are the most abundant As host. Continued climate warming is expected to increase the natural loading of metal(loid)s and organic matter to lake sediments; however, the effects of these changes on the long-term stability of legacy contaminants will vary between lakes.

1. Introduction

Geochemical baselines and background values provide guidance for monitoring mining impacts in the environment and are used in the development of remediation objectives upon mine closure. Presently, mine site remediation projects in Canada commonly rely on regional

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geochemical baseline values or guidelines based on national average metal(loid) concentrations in environmental media (CCME, 2001a, b; Environment Canada, 2012). As metal(loid) concentrations in lakes reflect local variations of elements in the environment, naturally occurring concentrations in water and sediment may exceed national averages in mineralized areas. In Canada's North, low and highly variable sedimentation rates in lakes also contribute to local variations in the distribution and concentration of metal(loid)s in sediments (Salminen and Tarvainen, 1997; Macumber et al., 2011; Crann et al., 2015). At northern latitudes, climate change is profoundly affecting the seasonality, biological productivity, and hydrology of lakes and has been shown to impact the mobility of certain metal(loid)s, such as mercury (Hg), and influence geochemical baselines (Macdonald et al., 2005; Outridge et al., 2007, 2011; 2017; McGuire et al., 2009; Jiang et al., 2011; Sanei et al., 2012). The thawing of permafrost, as a result of climate warming, has also increased the flux of organic carbon and loading of metal(loid)s (*i.e.* Hg) into sub-Arctic surface waters (Guo et al., 2007; McGuire et al., 2009; Rydberg et al., 2010). However, the influence of climate change on the mobility of other elements, such as As, is not well established, leading to uncertainty in the determination of geochemical baselines and the long-term monitoring of mining-derived contaminants in mineralized regions.

In northern Canada, Archean orogenic gold (Au) deposits are often hosted in metamorphosed mafic to ultramafic volcanic sequences with associated sedimentary rocks known as greenstone belts (Goldfarb et al., 1995; Groves et al., 1998). The Au-mineralization in these deposits commonly occurs in quartz veins containing carbonates, sericite, pyrite and arsenopyrite (FeAsS). Due to the occurrence of As-bearing sulphides in association with these deposits, mining and processing of Au may result in increased As concentrations in sediments and surface waters surrounding both modern and historical mine sites in the Northwest Territories (Wagemann et al., 1978; Groves et al., 1998; Bright et al., 1994, 1996; Golder Associates Ltd., 2005; Andrade et al., 2010; Galloway et al., 2012, 2017; AECOM, 2015; Palmer et al., 2015; Houben et al., 2016; Jamieson et al., 2017; Van Den Berghe et al., 2018). Numerous studies have examined mechanisms influencing As mobility in mining-impacted lake systems to better understand implications for human and environmental health and to establish regional baselines (*e.g.* Mudroch et al., 1989; Azcue et al., 1994; Bright et al., 1994; Thornton, 1996; Martin and Pedersen, 2002). These studies demonstrate that controls on As speciation and mobility differ locally within lakes and between studied lakes due to factors such as water depth and morphology, seasonal thermal stratification, water residence time, primary productivity, sediment organic and inorganic geochemistry, and catchment bedrock lithology (Martin and Pedersen, 2002; Hollibaugh et al., 2005; Wang and Mulligan, 2006; Andrade et al., 2010; Hasegawa et al., 2010; Campbell and Nordstrom, 2014; Galloway et al., 2017; Schuh et al., 2018, 2019; Van Den Berghe et al., 2018; Barrett et al., 2019; Palmer et al., 2019). As a result of lake-specific controls, the dispersion and long-term stability of mining-related As contamination in lacustrine environments may also vary within the scale of a single mining district. Detailed characterization of lake sediment can help to accurately monitor the environmental impacts of mining activities and evaluate the efficacy of mine site remediation projects.

Two high-grade, low-tonnage historical gold mines have operated in the Courageous Lake Greenstone Belt (CLGB) of the Northwest Territories (NT): Tundra Mine (1964–1968) and Salmita Mine (1983–1987) (Fig. 1). During both phases of mining, gold was recovered through mercury amalgamation and cyanidation at the Tundra Mine mill (Silke, 2009). Gold in the region is free-milling and associated with arsenopyrite from hydrothermal mineralization (Ransom and Robb, 1986). As a result, historical mining and milling activities led to the accumulation of As-bearing waste rock, tailings, and impacted waters on site (Fig. 1; URS, 2005; Golder Associates Ltd., 2008). The Tundra Mine was in care and maintenance mode from 1999–2007 under the ownership of the Contaminants and Remediation Directorate (CARD) of Crown-Indigenous Relations and Northern Affairs Canada (CIRNAC). Remediation activities occurred from 2007–2018 including: removal of on-site buildings, dam and landfill repairs, geotechnical inspection of dams, tailings water treatment and disposal, waste rock and tailings kinetic testing, capping and lining of waste rock and tailings, and water quality monitoring (Golder Associates Ltd., 2005, 2008, 2016, 2017; INAC, 2005, 2008; URS, 2005; SENES Consultants, 2006, 2008, 2011; Lorax Environmental, 2007; AANDC, 2010, 2012, 2013, 2014; AECOM, 2015). Waste rock at the former mine site contains 0.07%–6.5% sulphides, with arsenopyrite, pyrite (FeS_2), and pyrrhotite ($Fe_{1\text{-}x}S$) as the primary sulphide minerals (URS, 2005). In tailings, As concentrations range from 70 to $> 10{,}000\,\mathrm{mg\,kg^{-1}}$ (median $= 1{,}630\,\mathrm{mg\,kg^{-1}}$; $n = 35$) with arsenopyrite accounting for 60–98% of total As (Miller et al., unpublished data). Analysis of surface waters, groundwaters and sediment grab samples during environmental monitoring shows that weathering of waste rock and overtopping and seepage of waters from the tailings confinement area (TCA) have resulted in contamination of lakes up to 4 km downstream of the former mine site (INAC, 2005; URS, 2005; SENES Consultants, 2006; Lorax Environmental, 2007). Lakes of the Tundra Mine region may contain elevated As from both hydrothermal mineralization and legacy gold mining activities. However, no baseline data were collected prior to exploration and the initial development of Tundra Mine in 1951, thus, delineating mining impacts and monitoring the long-term effectiveness of remediation remains a challenge (Moore, 1978; Hatfield Consulting, 1982). Following the completion of remediation activities in August 2018, the site is presently in an adaptive management and long-term monitoring phase (AECOM, 2018). The CLGB is located within the Tłı̨chǫ Land Claim Agreement and the North Slave Metis traditional lands and is also highly prospective for future mineral development (Seabridge Gold Inc., 2010; Tetra Tech-Wardrop, 2012; Government of the Northwest Territories, Executive and Indigenous Affairs, 2007).

Through combined geochemical, mineralogical, and limnological techniques, the present study aims to characterize legacy mining impacts in lakes downstream of the former Tundra gold mine and determine the lake-specific controls on the mobility of As. The main objective of this study is to assess the implications of continued climate warming on the long-term stability of mining-derived As contamination in sub-Arctic lakes to help inform long-term monitoring activities and support sustainable development of mineral resources in northern Canada.

2. Study location

2.1. Physiography

Tundra Mine (64.042448° N, 111.169942° W) is located approximately 240 km NE of Yellowknife on the eastern shore of Matthews Lake (Fig. 1). In winter months the site is accessible by a spur road off the Tibbitt to Contwoyto Winter Road. A landing strip near the mine site provides access during the summer. Located within the boreal forest-open tundra zone 80 km north of the treeline, the landscape of the region is characterized by low relief and slightly rounded topography of the Canadian tundra (Hatfield Consulting, 1982). Temperatures in the region range from - 31 to 10 °C with an average annual temperature of - 12 to - 9 °C (SENES Consultants, 2006). Open water season ranges from 94–126 days with break-up in late June and freeze-up in September (INAC, 2005).

2.2. Geological setting

The Tundra Mine deposits and other regional gold showings of the CLGB are associated with the northwest-trending Yellowknife Supergroup of the Central Slave Geological Province (Henderson, 1970; McGlynn and Henderson, 1970; Dillion-Leitch, 1981; Ransom and

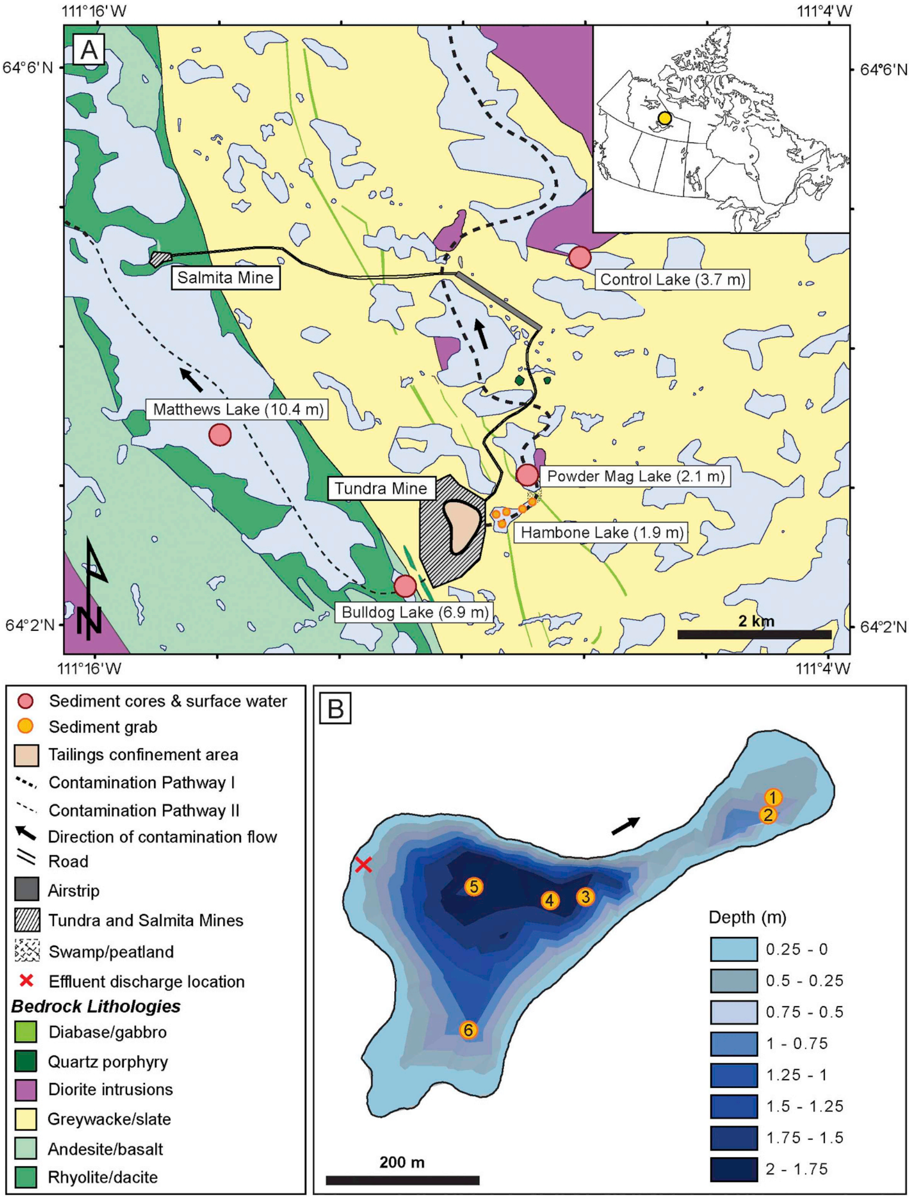


Fig. 1. A) Map showing simplified bedrock geology, sediment gravity core sampling locations, predominant mine drainage pathways originating from the former Tundra Mine site, and lake depths at sampling locations (in brackets) (geology modified from Folinsbee and Moore (1955) & Thompson and Kerswill (1994)); B) Bathymetry map of Hambone Lake with numbered locations of sediment grab samples (bathymetry map rendered from 50 water depth measurements).

Robb, 1986). In the Courageous Lake region, the CLGB unconformably overlies thin, discontinuous sequences of volcanic, clastic, and banded iron formations of the Central Slave Basement Cover Group (~2.39 Ga) and diorite to tonalite gneiss of the Central Slave Basement Complex (~3.325 Ga) (Bleeker et al., 1999). The CLGB is flanked to the east by conformably overlying turbiditic metasedimentary rocks (Fig. 1; Folinsbee and Moore, 1950, 1955; Moore, 1951). Multiple gold showings have been discovered throughout the CLGB. In the Tundra/Salmita Mine region, Au-mineralization is primarily free-milling and hosted in quartz-carbonate–bearing shear zones that occur at the contact between finely laminated argillaceous metasediments of the Burwash Formation and Banting Group volcanics, or in quartz stringers filling narrow shear zones within the metasediments (Ransom and Robb, 1986). In mineralized bedrock of the CLGB, arsenopyrite is found as stringers within quartz veins, in zones of disseminated sulphides within felsic to intermediate tuffaceous rocks, in association with carbonatization and silicification of mafic volcanic rocks, and in trace amounts within slate (Ransom and Robb, 1986) (Fig. 1).

3. Methods

3.1. Sampling locations and sample preparation

Two primary surface water flow paths, originating from the former Tundra Mine site, have been identified by environmental monitoring activities (Fig. 1) (INAC, 2005, 2008; SENES Consultants Ltd., 2006, 2008, 2011; AANDC, 2010, 2012, 2013, 2014). Two lakes from each flow path (Pathway I: Hambone Lake, Powder Mag Lake; Pathway II: Bulldog Lake, Matthews Lake) were sampled for the present study (Fig. 1). One additional sampling site, Control Lake, is not connected to the hydrological flow paths originating at the mine site and has been used as a background (unimpacted) reference for ongoing monitoring activities (Golder Associates Ltd., 2005, Fig. 1).

In March 2016, sediment cores, porewaters, and surface water samples were collected through the ice from Powder Mag, Bulldog, Matthews, and Control lakes. In July 2016, near-surface sediment samples were collected from Hambone Lake (Fig. 1). Prior to collection of sediment cores, surface water samples were collected from the middle of the water column using a Kemmerer water sampler. At each site, water quality variables (dissolved oxygen (DO), temperature, and conductivity) were measured in-situ using a YSI sonde (Professional Plus with a Quattro Probe Cable) and pH was measured with a handheld pH meter (HACH H138 MiniLab ISFET). Surface water samples were placed in a 1-L High-Density Polyethylene (HDPE) bottle, triple-rinsed with sample water, and transported to a clean indoor location for filtering and preservation within 12 h of collection. Samples for dissolved cations and anions were filtered ($< 0.45\,\mu m$) into 60 mL HDPE bottles using an all-plastic 50 mL syringe (Norm-Ject® Sterile Luer-Lock Syringe) and Sterivex® capsule filters. No evidence of Fe oxidation was observed in the samples in the time between collection and filtration. Cation samples were acidified to $pH < 2$ using ultrapure nitric acid. Samples for total As (unfiltered) and inorganic As speciation were collected in amber-coloured 60 mL HDPE bottles (Nalgene® 2106-0002). Samples for As speciation were acidified with 300 µL concentrated acetic acid and preserved with 600 µL of 0.25 M EDTA; total As samples were preserved with 2% HCl. Duplicate surface water samples were collected at one of the four lakes. Travel blanks, acid blanks, and sample blanks were included for analysis. All samples were then refrigerated at 4 °C and stored in a dark location prior to shipment.

Due to the remote location of the Tundra Mine site, transport of sediment cores from the sampling location had the potential to disturb the sediment and result in the oxidation of redox-sensitive elements, such as As. Sediment cores were therefore collected in the winter to allow for the transport of nitrogen (N_2) to the site and subsampling of sediment cores on the frozen lake surface. Sediment cores were collected using a gravity corer and transparent polycarbonate core tubes (7.5 cm × 60 cm). To account for the influence of sediment focusing (Blais and Kalff, 1995) and to avoid sediment disturbance caused by seasonal grounding of lake ice, all sediment cores were collected from the deepest location in each lake (Z_{max}) which was determined based on previous bathymetric surveys (Golder Associates Ltd., 2005). Immediately following collection, sediment cores were vertically extruded and subsampled at 1-cm resolution in a high purity (99.998%) N_2-filled glove bag. Sediment was subsampled into N_2 flushed 50 mL polypropylene centrifuge tubes (Corning® Falcon®) and refrigerated pending shipment to the Geological Survey of Canada – Atlantic (GSC-A) in Dartmouth, NS, for porewater extraction.

Surface sediment grab samples were collected in July 2016 from Hambone Lake using an Ekman dredge sampler. Samples were collected along a traverse from the TCA effluent discharge location to the outlet into Powder Mag Lake (Fig. 1). As the near-surface sediment in Hambone Lake likely freezes during winter months, the collected sediment samples were frozen and sent to Queen's University, Kingston, ON, for subsampling and preparation.

To separate porewater from the sediment, samples were centrifuged (Thermo Scientific Sorvall Legend™ XF Centrifuge) at 4,400 RPM for 30 min (centrifugal force of 4221 Gs) at GSC-A. Porewater was then pipetted from the sample tubes in a high purity (99.998%) N_2-filled glove bag. Samples were prepared following the protocol described above for filtered cations, filtered anions, total As, and total inorganic As speciation. For each sample pH was measured but due to low water content, Eh could not be measured. Following porewater extraction, sediment samples were refrigerated at 4 °C and stored in a dark location prior to shipment to Queen's University for preparation and geochemical analysis.

3.2. Analyses

3.2.1. Surface and porewater chemistry

Surface water samples were analyzed for anions, alkalinity, dissolved organic carbon (DOC), and a 64-element suite of metal(loid)s at the Inorganic Geochemical Research Laboratory of the Geological Survey of Canada. Analyses of major elements were performed by Inductively Coupled Plasma – Atomic Emission Spectroscopy (ICP-AES) using a Perkin-Elmer 3000 DV. Trace elements were analyzed using ICP-MS with a Thermo Corporation X-7 Series II. Anion concentrations were measured using a Dionex DX-600 ion chromatograph using an AS-18 column and gradient elution. Dissolved organic carbon was measured on a Shimadzu TOC-5000 analyzer following removal of inorganic carbon using phosphoric acid. Alkalinity measurements were completed using a PC-Titrate system. For each sample set, analyses were completed on laboratory duplicates, blanks, and certified standards (SLRS-5). For laboratory duplicates, relative standard deviation (RSD) ranges from 0.08%–1.40% and mean percent difference (MPD) ranges from 0.12%–1.98% for As. For field duplicates RSD and MPD are higher for unfiltered samples (2.44% and 3.45%, respectively) than filtered samples (2.05% and 2.90%). Arsenic was below detection limit ($0.1\,\mu g\,L^{-1}$) in all field blanks ($n = 4$). Inorganic As speciation was analyzed by hydride generation-atomic fluorescence spectrometry (HG-AFS; model PSA 10.055 Millennium Excalibur) at the Université de Montréal. Dissolved As speciation by HG-AFS is comprised of three constituents: inorganic As (III) and As (V), and a residual fraction ($As_R = As_{Total} - (As\,(V) + As\,(III))$). The residual fraction includes As species that are not detected using HF-AFS, including thioarsenates in sulfidic waters and non-reducible organoarsenic compounds (Planer-Friedrich and Wallschläger, 2009; PS Analytical, 2018). Standard solutions and certified inter-calibration samples were used to assess accuracy and precision. Trace amounts of As ($0.12, 0.16\,\mu g\,L^{-1}$) were detected in two blanks analyzed for total As, however, As was not detected in the other ($n = 6$) duplicate blanks.

3.2.2. Chronology and sedimentation rates

Near-surface sediment was dated using gamma spectrometry for the four cores collected. Samples for gamma dating were prepared following Schelske et al. (1994). Analysis was completed at the Paleoecological Environmental Assessment Research Laboratory (PEARL, Queen's University) using an Ortec High Purity Germanium Gamma Spectrometer. Total ^{137}Cs, ^{214}Bi, ^{210}Pb, and ^{214}Pb results were processed using ScienTissiME 2.1.2 software.

3.2.3. Sediment geochemistry

Freeze dried sediment sub-samples ($n = 211$) were submitted to Acme Analytical Laboratories (Bureau Veritas), Vancouver, BC, for geochemical analyses. A modified *aqua regia* digestion protocol (1:1:1 $HCl:HNO_3:H_2O$ at 95 °C for one hour) was used prior to elemental analysis via inductively coupled plasma – mass spectroscopy (ICP-MS) (AQ250-EXT package (53 elements)). Near-total (4-acid) digestions were not used as they involve high-temperature fuming with hydrofluoric acid that may volatilize As, antimony (Sb), Hg, and sulphur (S), which are key elements of interest in this study (Parsons et al., 2012, 2019). Sediments were pulverized to approximately 200 mesh size (74 µm) prior to digestion.

One field duplicate was submitted for every 10 samples to assess sampling accuracy and precision. In duplicate samples, RSD ranges from 0.21%–7.22% and MPD ranges from 0.29%–10.21% for As. Certified reference materials (STSD-3 (Lynch, 1990)) and laboratory standard reference materials (STD DS10, STD OREAS45EA) were included with each sample set to assess analytical accuracy and precision. For STSD-3 mean measured As concentration was $24.34 \pm 0.81\,mg\,kg^{-1}$ ($n = 8$) vs. an expected concentration of $22\,mg\,kg^{-1}$ for As following *aqua regia* digestion (RSD 3.3%). Mean measured As concentration for STD DS10 was $42.3 \pm 0.77\,mg\,kg^{-1}$ ($n = 8$) vs. an expected concentration of $46.2\,mg\,kg^{-1}$ As following *aqua regia* digestion.

3.2.4. Characterization of As-bearing solid phases

The distribution of As-bearing solids in lake sediment was characterized using Environmental Scanning Electron Microscopy (SEM) coupled with Automated Mineralogy and integrated Energy-Dispersive

X-ray Spectroscopy (EDS) analyses at Queen's University, Kingston, ON. Through a combination of backscatter electron (BSE) image analysis and EDS, SEM-based Automated Mineralogy was used to identify and quantify relative abundance of common As-bearing minerals (Gu, 2003; Fandrich et al., 2007; Buckwalter-Davis, 2013; Van Den Berghe et al., 2018). Sparse phase liberation analysis (SPL) mode with a user-defined BSE greyscale range of 120–255 was used to selectively identify As-hosting phases, therefore does not provide bulk mineralogy information (Fandrich et al., 2007). Solid phases thought to contain trace concentrations of As were analyzed using a JEOL JXA-8230 electron microprobe operating in wavelength-dispersive (WDS) mode. The relative contribution of each As-hosting phase to bulk sediment As concentrations was calculated using the average As concentration of each phase and the fraction of each As-bearing species obtained by SEM-based automated mineralogy following the methods of Van Den Berghe et al. (2018).

3.2.5. *Sediment textural and organic characteristics*

Sedimentary grain size was determined using a Beckman Coulter LS 13320 laser diffraction particle size analyzer fitted with a Universal Liquid Module over a measurement range between 0.4 and 2000 μm. Followings methods outlined in van Hengstum et al. (2007), Donato et al. (2009), and Murray (2002) sediments were treated with 10% HCl to remove authigenic carbonate particles and 35% H_2O_2 to remove organic matter. Results were processed with the software package GRADISTAT v8.0 (Blott and Pye, 2001) to calculate grain size statistical parameters. Garnet15 (mean diameter 15 ± 2 μm), an accuracy standard supplied by Beckman Coulter, was run once per month. To assess instrumental precision, an in-house mud sample (Cushendun Mud; mean diameter = 20.5 ± 0.76 μm) was run at the start of every session.

Stepwise pyrolysis (Rock-Eval ® 6) was used to characterize the type and source of organic matter (OM) in the sediment samples (*e.g.* Sanei et al., 2005; Carrie et al., 2012). Sediment sub-samples were analyzed to determine the proportion of reactive OM (defined as pyrolysable carbon). Pyrolysable carbon is comprised of: (i) the S1 fraction; composed of small, readily degradable, volatile molecules (*e.g.* biolipids); (ii) the S2 fraction; composed in part of larger molecules of hydrocarbons derived from kerogen (*e.g.* algal cell wall detritus); and, (iii) the S3 fraction; derived from oxygen-containing organic molecules (Sanei et al., 2005; Sanei and Goodarzi, 2006). A standard reference material (Internal 9107 shale standard, Geological Survey of Canada, Calgary; Ardakani et al., 2016) was run every 5th sample and demonstrates < 1% RSD for Total Organic Carbon (TOC), < 3% RSD for S1 and S2 fractions, and 11% RSD for S3. The lower precision for S3 in bulk samples is expected due to poor peak integration and distinction between S3 organic matter and S3 carbonates (siderite in shale standard) (Ardakani et al., 2016). A duplicate sample was run every 10th sample; the majority of duplicate samples demonstrate a RSD of < 5% for all parameters and a MPD of < 15%.

3.2.6. *Statistical analysis of controls on As distribution*

Elements with concentrations below instrumental detection limits in 25% or more of the samples (B, Ge, Hf, In, Pd, Pt, Re, Ta, Te) and those that demonstrated little down-core variability (Ga, K, Na, Th, Tl) were removed prior to statistical analyses. One half of the lower detection limit (LDL) was used for element concentrations below the LDL for retained data (Reimann et al., 2008). No element concentrations exceeded upper detection limits.

Stratigraphically constrained incremental sum of squares cluster analysis (CONISS) compared against a broken stick model using the rioja package in R (R Core Team, 2014; Juggins, 2017) was used to isolate distinct geochemical populations and delineate impacted (MI, I) from background (BG) sediment. Both Anderson Darling and Shapiro-Wilk tests demonstrate a highly non-normal distribution of As ($p < 0.0005$ and $p < 0.0005$, respectively) in sediment samples; therefore, non-parametric tests were chosen for statistical analysis. For cluster analysis, data were log-transformed and converted to standardized values (Davis, 2011).

4. Results

4.1. *Surface water*

4.1.1. *Physiochemical characteristics and major dissolved species*

Surface waters in all four lakes sampled were oxic (range: 3.60–12.8 mg L^{-1}) with circumneutral pH (range: 6.58–7.01). Dissolved oxygen concentrations during winter sampling in 2016 were lowest in Powder Mag Lake and lower than reported during the previous summer in Bulldog (range: 8.0–16 mg L^{-1}) and Powder Mag lakes (range: 3.0–18 mg L^{-1}) (AANDC, 2014). Specific conductance was highest in lakes directly impacted by discharge and disposal associated with mining activities (Powder Mag Lake and Bulldog Lake) and decreased with distance from the TCA. Dissolved organic carbon was highest in Powder Mag Lake, historical monitoring also demonstrates high DOC (16 mg L^{-1}) concentrations in Hambone Lake (INAC, 2005). Concentrations of major dissolved species are consistent with measured trends in specific conductance and reflect decreased loading of metals and SO_4 with increasing distance from the TCA (Table 1; Supplemental Data ST1). These trends are similar to those reported by annual water quality monitoring at Tundra Mine that show decreasing concentrations of dissolved species with increasing distance from point sources of contamination.

4.1.2. *Metal(loid)s and total As speciation*

Concentrations in filtered (< 0.45 μm) and unfiltered surface water samples are similar for all elements with the exception of Al, Mn, Pb and Fe, which demonstrated higher concentrations in unfiltered samples. Analysis of surface waters in Powder Mag Lake demonstrates increased total metal(loid) concentrations with respect to other lakes sampled (Table 1; Supplemental Data ST1). At the time of sampling, As and Fe concentrations exceeded CCME Water Quality Guidelines in Powder Mag Lake. No other elements were measured at concentrations exceeding these guidelines. Total As concentrations are highest in surface waters impacted by tailings effluent and lowest in surface waters farthest from the former mine site (Table 1). The highest percentage of As_R is observed in Control Lake (68%) (Table 1).

4.2. *Chronology and sedimentation rates*

Sediment ages and sedimentation rates were calculated using the constant rate of supply model (Appleby, 2001; Supplemental Data ST7 to ST10). Based on the ^{210}Pb decay profile for each lake, disturbance or mixing (*i.e.* bioturbation, occurrence of slump deposits, sampling error) between sampling intervals was determined to be minimal. Average sedimentation rates in near-surface sediment vary between lakes, ranging from 52–20 yr cm^{-1}. The fastest sedimentation rates are observed in the near-surface sediment of Powder Mag Lake (2.0 yr cm^{-1}) and Control Lake (1.75 yr cm^{-1}); the lowest sedimentation rates in near-surface sediment are observed in the largest lake, Matthews Lake (130 yr cm^{-1}). The lower sedimentation rates observed in Matthews Lake are similar to those reported by Crann et al. (2015) for similar sized lakes in tundra settings.

4.3. *Geochemically distinct groupings*

As northern lacustrine systems are typically characterized by low sedimentation rates, defining the precise onset of anthropogenic activities in the sediment cores is not possible at the sampling resolution used in this study (1 cm) (Gasiorowski, 2008; Crann et al., 2015; Macumber, 2015). To delineate impacted (MI, I) sediment from background (BG), individual sediment cores were divided into distinct

Table 1
Selected surface water physicochemical parameters, anions (dissolved, filtered), alkalinity (as $CaCO_3$), total (unfiltered) concentrations of selected major and trace elements, and inorganic As speciation from surface waters of lakes of the Tundra Mine region.

	Units	CCME[a]	Powder Mag Lake	Bulldog Lake	Matthews Lake	Control Lake
Date of Sampling	–	–	11-Mar-16	10-Mar-16	13-Mar-16	12-Mar-16
Physical Parameters (field measurements)						
Sample Depth	m	–	1.0	3.5	5.7	1.8
Temperature	° C	–	0.20	3.40	2.90	2.50
Specific Conductance	$\mu S\cdot cm^{-1}$	–	833	86.2	49.3	30.7
pH	S.U.	6.5–9.0	7.01	6.75	6.90	6.58
DO	$mg\cdot L^{-1}$	–	3.60	7.80	10.4	12.8
Anions, Alkalinity and DOC						
SO_4	$mg\cdot L^{-1}$	–	257	7.87	4.17	1.29
Alkalinity (as $CaCO_3$)	$mg\cdot L^{-1}$	–	113	23.5	13.9	9.60
DOC	$mg\cdot L^{-1}$	–	16.6	6.90	4.80	7.50
Major and Trace Elements						
Fe	$mg\cdot L^{-1}$	0.30	***0.39***	0.06	0.02	0.02
As[b]	$\mu g\cdot L^{-1}$	5.0	***19.4***	3.01	0.95	0.81
Ba	$\mu g\cdot L^{-1}$	–	47.1	5.30	3.10	4.00
Sr	$\mu g\cdot L^{-1}$	–	238	15.6	13.0	9.60
Zn	$\mu g\cdot L^{-1}$	7.0	2.40	1.20	0.70	3.20
Arsenic Speciation						
As (III)[b]	$\mu g\cdot L^{-1}$	–	0.80	0.17	< 0.09	0.15
As (V)[b]	$\mu g\cdot L^{-1}$	–	15.4	2.57	0.56	0.11
As_R[b]	$\mu g\cdot L^{-1}$	–	3.17	0.28	0.35	0.55

[a] CCME Water Quality Guidelines for the protection of aquatic life (CCME, 2001b), bold and italicized values exceed guidelines.

[b] Concentration reported based on HF-AFS analysis.

geochemical groupings using a combination of cluster analysis, multivariate element profiles, and radiometric dating (Fig. 2). These combined methods allowed for the identification of changes in sediment geochemistry attributed to the onset of mining activities in each of the sediment cores. In lakes proximal to the mine site (Powder Mag Lake and Bulldog Lake) mining impacts are delineated on Fig. 2a by the groupings P-MI and B-MI, respectively. Increases observed in As concentration in sediment pre-dating mining activities in these two lakes are attributed to post-depositional As mobility across the redox interface (RI) and are denoted by P-RI and B-RI (Fig. 2a). In lakes more distal to the former mine site impacts are delineated by the groupings ML-MI and CL-I in the Matthews Lake and Control Lake sediment cores, respectively (Fig. 2b). In all lakes, geochemical groupings in background sediment are apparent from cluster analysis (Fig. 2a and b). These groupings (BG) indicate changes in sediment geochemistry that reflect natural fluctuations in geochemical baselines.

4.4. Sediment geochemistry

Arsenic concentrations range from 31–1,010 mg kg^{-1} in near-surface, impacted sediment (MI & I) and 28–170 mg kg^{-1} in background sediment (BG) (Fig. 3; Supplemental Data ST2 to ST6). In all lakes, the highest solid phase As concentrations (As_{sed}) are evident in mining-impacted sediment, with maximum values observed in Bulldog Lake (median: 570 mg kg^{-1}; range: 200–1,010 mg kg^{-1}; $n = 7$) (Fig. 2a and b; Supplemental Data SF1). The lowest As concentrations in mining-impacted sediment are observed in Matthews Lake (range: 31–90 mg kg^{-1}; median: 48 mg kg^{-1}; $n = 13$). Control Lake is currently used as a background reference for environmental monitoring activities and is the farthest lake from the former Tundra Mine site; As concentrations in the near-surface sediment of Control Lake range from 110–220 mg kg^{-1} (Fig. 3). The highest median background As concentration is observed in Control Lake (CL-BG) (120 mg kg^{-1}) (Fig. 3). In all lakes studied, increased As concentrations in shallow sediment are associated with increases in the concentration of other elements enriched in the ore body or used in processing and refining (Zn, Pb, Ag, Au, Hg, Sb, W, and Sr) (Fig. 2).

In lakes proximal to the former Tundra Mine site, peaks in As concentration occur just below the sediment-water interface (SWI) (Fig. 2). Sediment As concentrations in the shallow sediment of Powder Mag and Bulldog lakes demonstrate profiles similar to S. Sediment concentrations of S in shallow, mining-impacted sediment demonstrate maximum concentrations at 2–3 cm and are 1–2 orders of magnitude higher in Bulldog Lake (median: 0.58%; range: 0.35–1.02%; n = 7) and Powder Mag Lake (median: 1.28%; range: 1.06–1.29%; n = 3) compared to lakes farther from the former mine site (Fig. 2a). Conversely, in more distal lakes, peaks in As concentration occur at the SWI and have profiles similar to Fe and Mn (Fig. 2b). In both Control Lake and Matthews Lake, concentrations of As, Fe, and Mn have maxima at the SWI and gradually decrease in the near-surface sediment.

In Hambone Lake, sediment As concentrations are highest in the two samples collected from the northeastern end of the lake (Fig. 1). Concentrations of other elements enriched in tailings and used in mineral processing (Ag, Au, Hg, Pb, W, Zn) also follow this trend (Table 2).

4.5. Porewater geochemistry

Arsenic porewater concentrations in near-surface sediment are highly variable, ranging from 0.75–383 μg L^{-1} (median: 13.5 μg L^{-1}; $n = 22$; Fig. 3). Dissolved As concentrations in the mining-impacted sediment of Powder Mag Lake (range: 29–383 μg L^{-1}) are an order of magnitude higher than those observed in other lakes sampled.

The concentrations and distributions of dissolved Fe, Mn, and S in porewaters vary between lakes studied as does the relationship between these elements and porewater As concentrations (Fig. 3). The distribution of dissolved As in porewaters in Bulldog and Control Lakes is directly related to the redox behavior of Mn, Fe and S. Conversely, in Matthews Lake, the concentrations of all three elements (Fe, Mn, S) increase at depths in porewaters just below the SWI and no variations in dissolved As are observed in the shallow sediment. Low porewater volumes in deeper sediment of Matthews Lake (below 20 cm) precluded elemental analysis. Profiles of dissolved Fe, Mn, and S are notably different in Powder Mag Lake. No surface enrichment of these elements is observed; however, increases in Fe, Mn, S, and Zn concentrations occur with depth in the sediment column ($n = 30$) (Fig. 3).

The pH of porewaters from both mining-impacted (range: 5.3–7.5; median: 5.7; $n = 21$) and background sediment (range: 4.8–6.7; median: 5.7; $n = 85$) range from slightly acidic to circumneutral. The highest pH values were observed in Powder Mag (range: 5.9–7.5) and are attributed to the annual disposal of alkaline treated tailings effluent

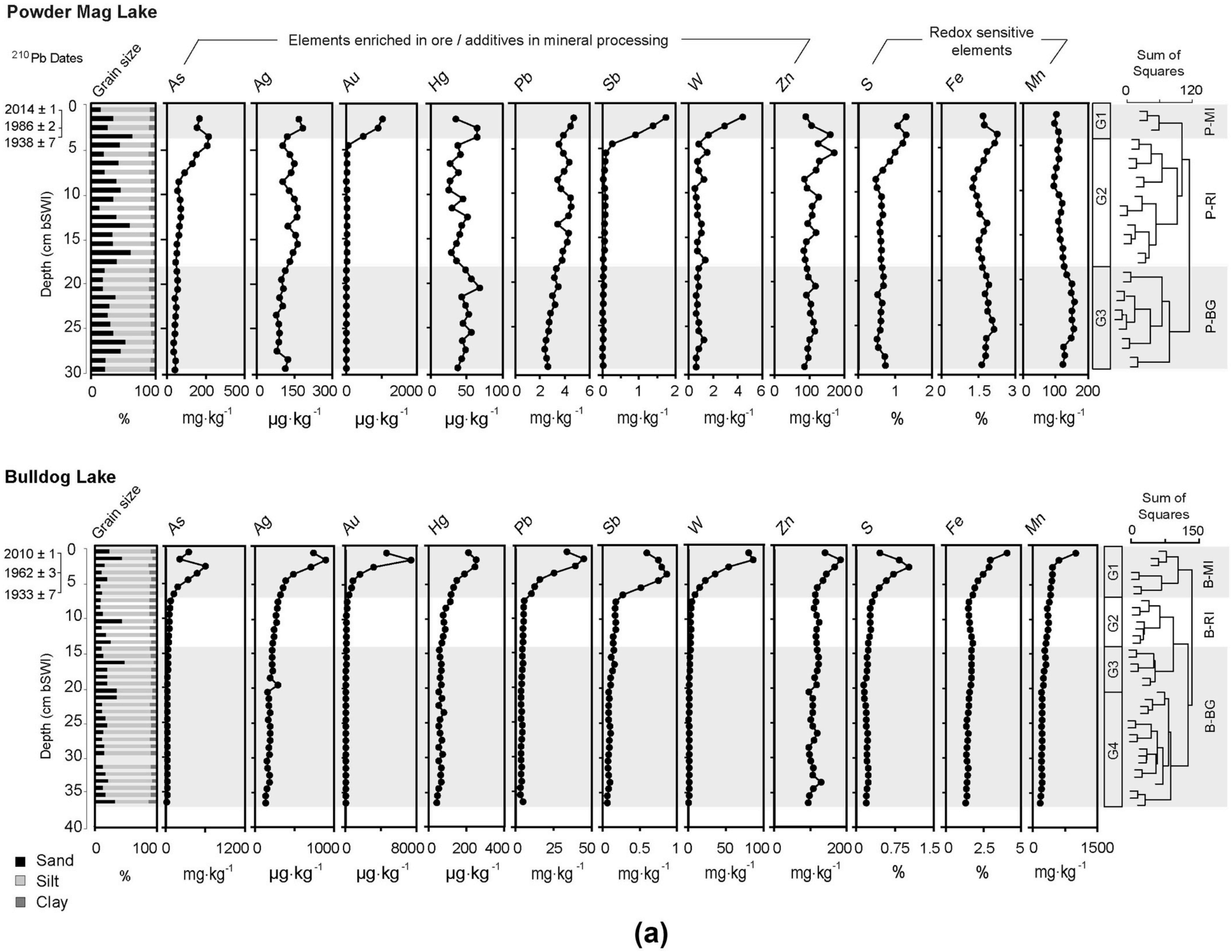


Fig. 2a. Sediment grain size and solid-phase concentrations of As, elements enriched in ore and used in mineral processing (Ag, Au, Hg, Pb, Sb, W, Zn) and redox sensitive elements (S, Fe, and Mn) from sediment cores extracted from Powder Mag Lake and Bulldog Lake. Element concentration profiles are plotted on different scales and scales differ between lakes. Shaded intervals separate mining-impacted (I) and background (BG) geochemical populations identified using CONISS (G1-G4), ^{210}Pb dating, and multivariate element profiles.

along this drainage pathway (pH range: 7.54–8.61; Golder Associates Ltd., 2016). Hambone Lake, located upstream of Powder Mag Lake and also influenced by treated effluent, had high pH values in the water column during past environmental monitoring (range: 6.4 –8.3; AANDC, 2014; Golder Associates Ltd., 2016). The lowest porewater pH was observed in Matthews Lake sediments (range: 4.8–5.8).

As shown in Fig. 3, no consistent trend in inorganic As speciation is apparent in sediment porewaters of the lakes studied near Tundra Mine. In Powder Mag, Bulldog and Matthews lakes As (V) is the predominant aqueous species in porewaters. Conversely, As (III) is the most abundant inorganic species of As in porewater samples analyzed from the Control Lake sediment core. The difference between total As and the sum of As (III) and As (V) is substantial in porewaters of Powder Mag, Matthews, and Control lakes, suggesting that there may be other As species present (*e.g.* thioarsenates, organoarsenic species) in addition to inorganic As (Fig. 3). Further analyses would be required to identify these species.

4.6. *Characterization of As-bearing solid phases*

Six As-hosting solid phases were identified by combined SEM-based automated mineralogy and EMPA analysis in the near-surface sediments of Hambone, Powder Mag, Bulldog, Matthews, and Control lakes. The abundance of these minerals varies between lakes and with depth in the sediment as shown by the horizontal bar graphs on Fig. 5 (Supplemental Data ST11 to ST15).

Arsenopyrite was identified in the near-surface sediment of lakes proximal to the former mine site (Fig. 4). Arsenopyrite grains range in size from 1–25 µm, with the largest and most abundant grains present at 5–6 cm depth in the Bulldog Lake sediment core. In the near-surface sediment of Bulldog Lake, FeAsS accounts for up to 40% of total As. Trace arsenopyrite was also identified in Powder Mag Lake (20% of total As) and Hambone Lake (2% of total As), but no arsenopyrite was observed in the shallow sediment of Matthews Lake or Control Lake.

Authigenic Fe-oxyhydroxides are more prevalent than detrital Fe-oxides in near-surface sediments of all lakes studied. These two phases were differentiated based on grain morphology, using BSE images; detrital particles have sharper edges and more well-defined grain boundaries than authigenic particles which tend to intergrow with surrounding grains (Fig. 4). EPMA of demonstrates that these phases host similar proportions of As (mean = 0.50 wt %, and 0.60 wt %, respectively; combined mean = 0.50 wt %). In the near-surface sediments of Matthews and Control lakes, As is predominantly hosted by Fe-(oxy) hydroxides, accounting for 98–100% of total As. In the near-surface sediments of Bulldog, Hambone, and Powder Mag lakes, authigenic Fe-

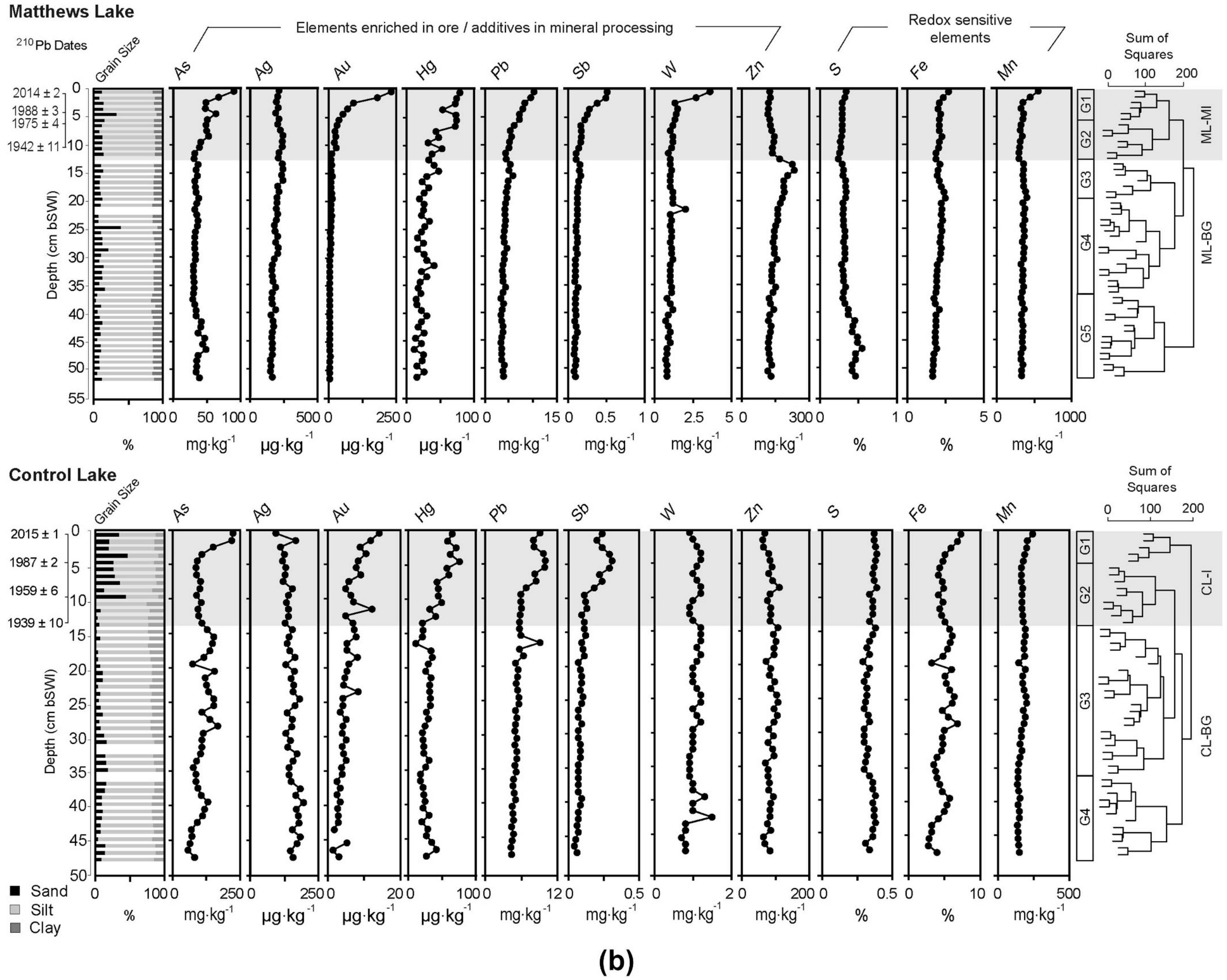


Fig. 2b. Sediment grain size and solid-phase concentrations of As, elements enriched in ore and used in mineral processing (Ag, Au, Hg, Pb, Sb, W, Zn) and redox sensitive elements (S, Fe, and Mn) from sediment cores extracted from Matthews Lake and Control Lake. Element concentration profiles are plotted on different scales and scales differ between lakes. Shaded intervals separate impacted (I) and background (BG) geochemical populations identified using CONISS (G1-G5), ^{210}Pb dating, and multivariate element profiles.

(oxy)hydroxides were identified, but account for a smaller percentage of total As (5–50% of total As).

The main host of As near the redox interface of Bulldog Lake and Powder Mag Lake is a fine grained aggregate of poorly crystalline Fe-(oxy)hydroxide and iron monosulphide (FeS_x/FeO). SEM-based automated mineralogy and EPMA reveal that this phase is heterogeneous in nature with a wide range of morphologies and chemical compositions. Sulphur content of this phase ranges from 0.25–27 wt % ($n = 37$). Arsenic associated with this phase ranges from < D.L. to 0.50 wt % (mean = 0.20 wt %; 20 particles; 27 spots). In the mining-impacted sediment of lakes proximal to the former mine site, this phase accounts for 20–65% of total As (Fig. 5).

In lakes close to Tundra Mine, a discrete As-sulphide phase was identified by SEM-based automated mineralogy. This phase is distinguishable from FeAsS as the Fe content is markedly lower, as determined through EDS spectra (Supplemental Data SF2). The small grain size precludes the use of EPMA to definitively identify this phase as realgar (As_4S_4) or orpiment (As_2S_3). This phase is most abundant in the mining-impacted sediment of Powder Mag Lake, accounting for up to 50% of the total As (Figs. 4 and 5).

Arsenic-bearing framboidal pyrite was identified in all sediments studied. Electron microprobe analysis of 26 particles (27 spots) demonstrates an average of 0.20 wt % As. In lakes of the Tundra mine region, this phase accounts for 0.10–25% of total As in the near-surface sediment (Fig. 5).

Iron-bearing phyllosilicates (illite, biotite, and chlorite) with intercalated mineralization along cleavage planes were also detected through SEM-based automated mineralogy in all samples (Fig. 4). Electron microprobe analysis demonstrates that in lakes proximal to the former mine site, this phase contains elevated S and As. Sulfur content of this phase ranges from 0.1–4.2 wt % (mean = 1.6 wt %). The presence of trace S associated with phase suggests that traces of sulphide minerals may be forming between the phyllosilicate sheets, leading to the sequestration of As through the formation of discrete precipitates and/or adsorption at the layer edges. EDS analysis of selected mineral grains suggest that the composition of this discrete mineral phase is FeS; however, a more comprehensive investigation would be required to draw conclusions regarding the average chemical composition of this phase (Supplemental Data SF2). In the near-surface sediment of Powder Mag, Bulldog, and Hambone lakes the As content of this phase ranges from < D.L. to 0.20 wt % (mean = 0.10 wt %; $n = 46$), accounting for 1–5% of total As (Fig. 5).

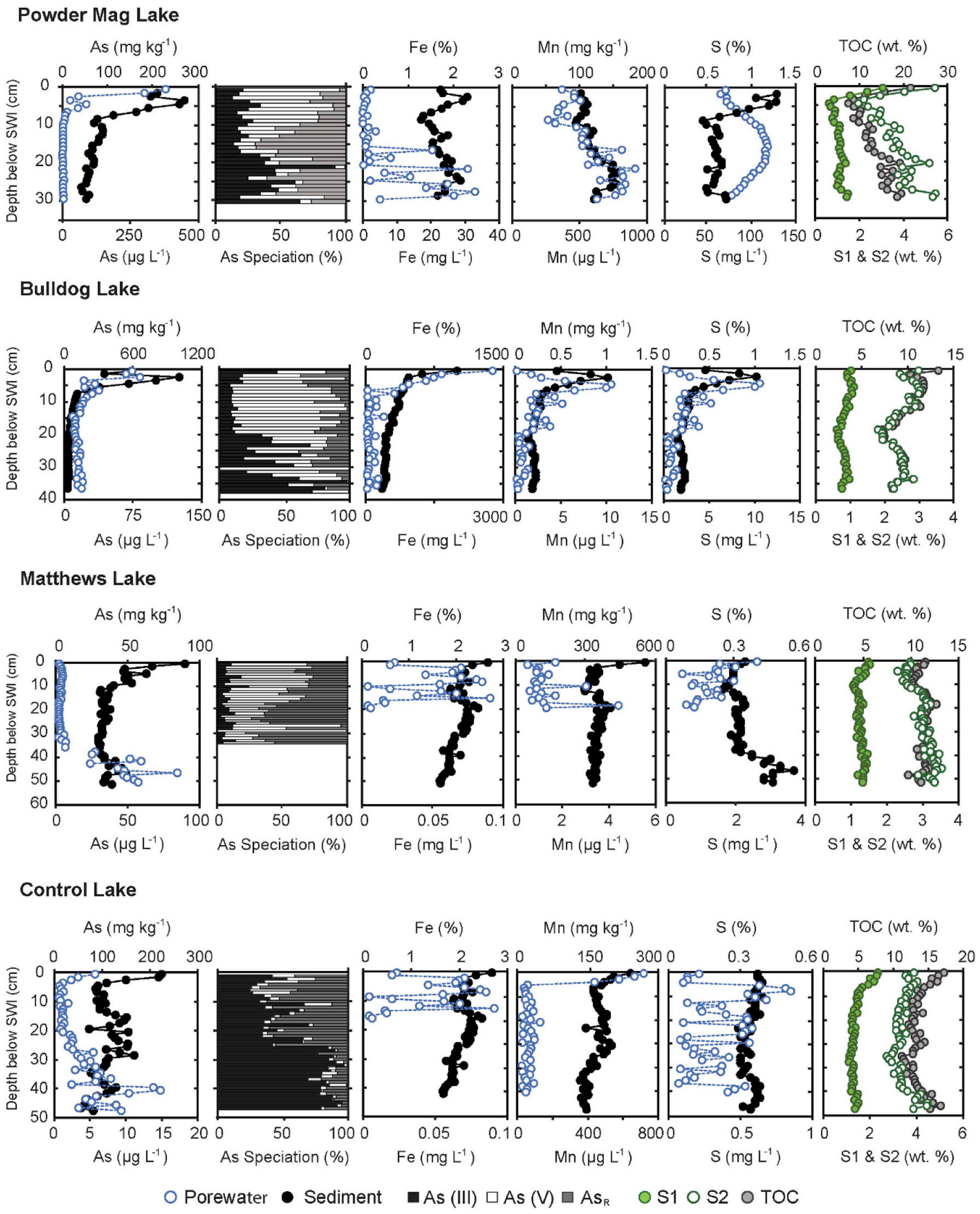


Fig. 3. Depth profiles of sediment and dissolved porewater As, Fe, Mn, and S concentrations, porewater As speciation, TOC, and organic matter fractions S1 and S2 in Powder Mag Lake, Bulldog Lake, Matthews Lake, and Control Lake. Concentrations for each element are plotted on different scales and scales are different for each lake.

4.7. Sediment textural and organic characteristics

All lake sediment samples are dominated by silt (< 63 µm) sized particles (median: 71%; range: 52%–78%; *n* = 160) (Fig. 2). In all lakes, with the exception of Matthews Lake, an increase in particle size is observed near the sediment surface (Fig. 2). Particle size in the sediments of Powder Mag Lake and Bulldog Lake is highly variable throughout the sediment column, demonstrating short intervals of increased sand content (Fig. 2). Total organic carbon content of the sediment ranges from 7.17–21.5% (median = 11.6%; *n* = 173) (Fig. 3). In shallow, impacted sediment, TOC concentrations are highest in Control Lake (17.2 wt %), Hambone Lake (15.5 wt %) and Powder Mag Lake (21.5 wt %). The majority of organic matter in all sediment samples is S2 (median = 3.17 wt %; range 1.80–5.44 wt %; *n* = 172), however, concentrations are different between lakes studied (Supplemental Data ST2 to ST6). Increases in organic matter concentrations are observed at the SWI of most lakes sampled, with the exception of Matthews Lake, which has lower sediment organic matter in near-surface sediment (Fig. 3).

Table 2
Sediment concentrations of selected elements in grab samples collected from Hambone Lake; the highest concentrations are bolded for each element. Sampling locations presented on Fig. 1.

Sample ID	Units	HAM1	HAM2	HAM3	HAM4	HAM5	HAM6
Distance from Discharge	m	540	515	310	230	125	250
Water Depth	m	0.70	0.90	1.80	1.90	1.70	1.00
As	mg·kg^{-1}	**622**	576	304	195	302	79.6
Ag	mg·kg^{-1}	469	**497**	247	138	373	69.0
Au	μg·kg^{-1}	**3,750**	3,730	2,400	210	2,381	380
Cu	mg·kg^{-1}	85.9	**96.5**	72.3	57.5	83.0	29.5
Hg	μg·kg^{-1}	**104**	87.0	86.0	50.0	84.0	18.0
Mn	mg·kg^{-1}	122	**133**	105	110	112	96
Ni	mg·kg^{-1}	97.3	**123**	85.1	73.2	83.7	53.1
Pb	mg·kg^{-1}	8.12	**8.56**	5.03	3.42	5.81	2.74
S	%	1.20	**1.80**	0.99	0.97	1.02	0.21
Sb	mg·kg^{-1}	0.90	**1.25**	1.02	0.38	0.7	0.34
W	mg·kg^{-1}	**4.60**	4.30	2.30	1.30	2.40	0.80
Zn	mg·kg^{-1}	143	**165**	96.0	80.5	108	75.7

4.8. Statistical analysis of controls on As distribution

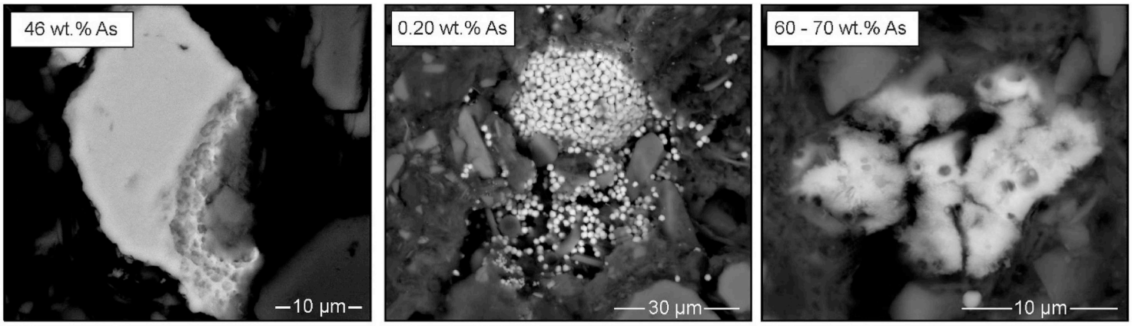
Spearman's Rank Correlation analysis shows that the associations between As and other elements, sedimentary particle size, and organic matter are different in the near-surface sediment of each of the study lakes (Fig. 6). Sample size for the near-surface sediment (P–MI) of Powder Mag Lake was not large enough ($n < 4$) to perform this analysis. In Hambone Lake, As is highly positively ($r_s \geq 0.70$) and significantly ($p \leq 0.05$; $n = 6$) correlated to other elements enriched in the ore or used in processing at Tundra Mine (Au, Sb, W) (Fig. 6). Although also proximal to the former Tundra Mine site, these relationships are not observed in the near-surface sediment of Bulldog Lake (Fig. 6). Positive ($r_s \geq 0.80$) and significant ($p \leq 0.05$) correlations between As and redox-sensitive elements (Fe, Mn, S) are observed in the near-surface sediments of Matthews Lake ($n = 13$) and Control Lake ($n = 14$).

Correlations in concentrations of As and S1 organic matter are evident in the mining-impacted sediment of Matthews Lake and Hambone Lake but the relationship between As and S1 organic matter is non-significant ($p \geq 0.05$) in near-surface sediment of Control Lake ($n = 14$) and Bulldog Lake ($n = 7$) (Fig. 6). The relationships between TOC and organic matter fractions (S1, S2, S3) are different in the near-surface sediment of all lakes studied (Fig. 6). The association (r_s) between variables is stronger when lakes are assessed as individual populations. This increase in statistical significance may be indicative of differing natural processes contributing to the mobility of As in each of these systems and highlights the importance of examining distinct geochemical populations to determine relevant associations. Significant correlations between As and grain size exist in certain geochemical populations in Powder Mag, Matthews and Control lakes; however, no consistent relationship was observed.

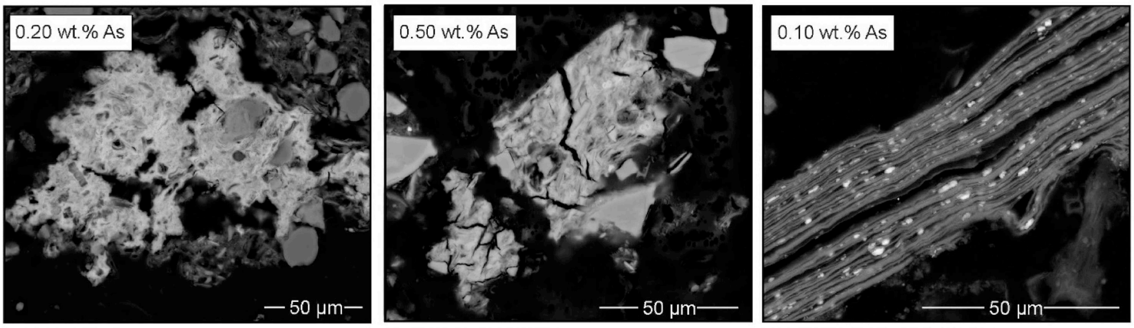
5. Discussion

5.1. Delineating mining impacts in lake sediment

Dating of modern sediments suggests that increases in solid phase As concentrations in the shallow sediment of each lake (Fig. 2a and b) correspond approximately to the initiation of exploration and mine development activities in 1946 (Silke, 2009). The sediment geochemistry of lakes near the former Tundra and Salmita mines has been altered through disposal of waste rock and its use in mine site construction, tailings overtopping and seepage, deposition of airborne dust, and/or disposal of mine water and treated tailings effluent. However, mining impacts extend to different depths in the sediment of lakes in the Tundra Mine region (Fig. 2a and b). Cluster analysis and radiometric dating shows distinct changes in the loading of elements enriched in the mined ore and waste rock in the upper 4–14 cm of



a) Arsenopyrite b) Frambodial pyrite c) As-sulphide



d) FeS_x/FeO e) Fe-(oxy)hydroxide f) Fe-bearing phyllosilicates

Fig. 4. Backscattered electron (BSE) images and mean As content (wt. %), determined by EPMA, of the predominant As-hosting solid phases identified in the near-surface sediment of lakes of the Tundra Mine region. a) Arsenopyrite (Bulldog Lake 0–1 cm); b) framboidal pyrite (Powder Mag 4–5 cm); c) As-sulphide (Powder Mag 3–4 cm); d) FeS_x/FeO (Powder Mag 3–4 cm); e) Fe-(oxy)hydroxide (Matthews Lake 4–5 cm); f) Fe-bearing phyllosilicate with intercalated minerals along cleavage planes (HAM1). Representative EDS spectra for each phase are presented in Supplemental Data SF2.

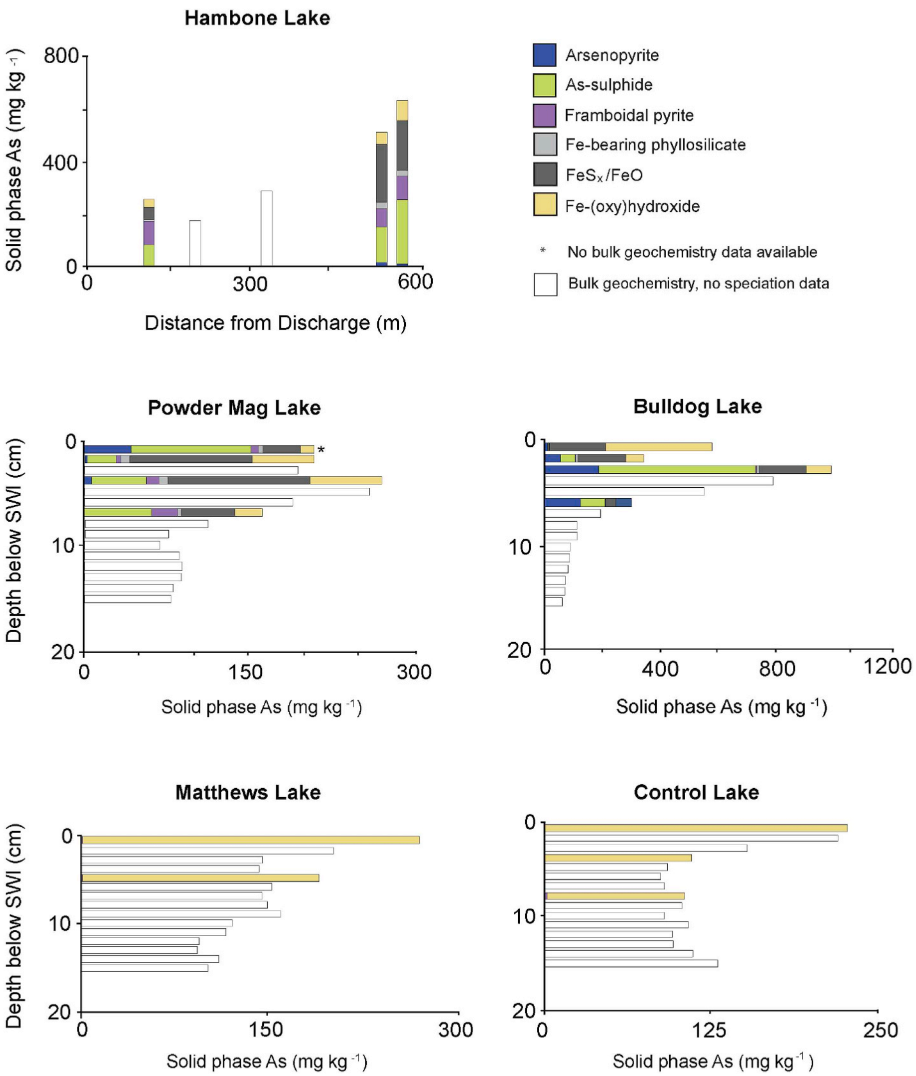


Fig. 5. Relative contribution of each As-hosting solid phase to total As concentrations in the top 15 cm of sediment samples from Hambone, Powder Mag, Bulldog, Matthews and Control lakes. Sediment grab samples collected from Hambone Lake are plotted as distance from effluent discharge location and not relative to depth in the sediment column.

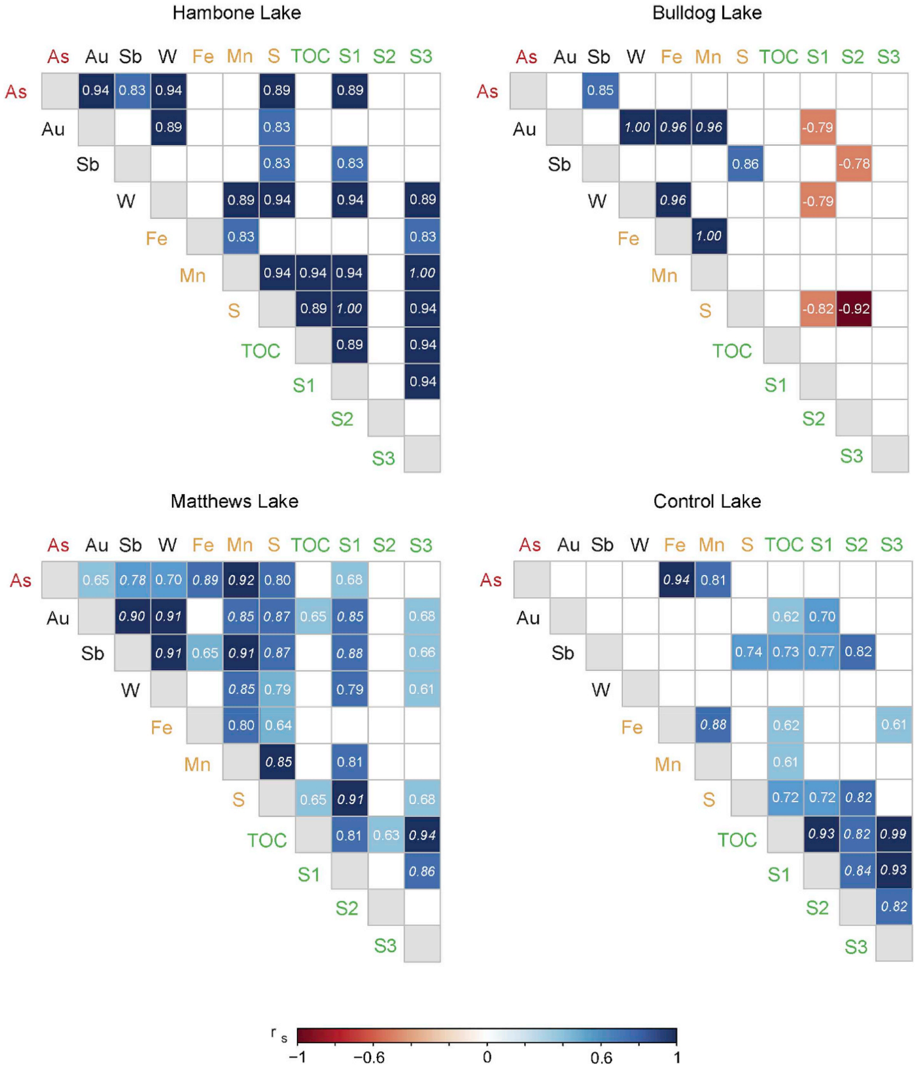
sediment cores from all lakes studied (Fig. 2a and b).

5.2. *Sources of As in near-surface sediment*

Increased concentrations of As in surficial sediments of lakes of the former Tundra and Salmita mines region are attributed to the increased natural input of arsenopyrite and secondary As-bearing hosts released during weathering of bedrock and surficial material and to anthropogenic activities associated with mining and mineral processing. Five sources of As to lakes of the Tundra Mine region have been identified including: direct disposal and weathering of waste rock, tailings overtopping and seepage, discharge of treated tailings effluent, weathering and airborne deposition of tailings and waste rock, and natural weathering of mineralized bedrock (Fig. 7).

5.2.1. *Hambone Lake*

Seepage and overtopping of tailings effluent (winter historic average (2007–2010): 2,830 $\mu g\,L^{-1}$ As), and the disposal of treated tailings effluent (average (2009–2013): 79 $\mu g\,L^{-1}$ As) have provided the primary sources of As to the sediment and surface water of Hambone Lake. Arsenopyrite-bearing waste rock used in construction of the original tailings dam and mine facilities and windblown tailings are the most likely sources of trace arsenopyrite observed in the near-surface sediment of Hambone Lake (Fig. 7). A positive ($r_s \geq 0.8$) and significant ($p \leq 0.05$) relationship between sediment As concentrations and W, Au (Fig. 6) and Zn ($r_s = 0.9$; $p \leq 0.05$; $n = 6$) also suggest that waste rock and tailings provide the primary sources of As to this lake. In mineralized veins of the Tundra Mine region, there is a strong correlation between As and Sb in Au-bearing arsenopyrite (Fig. 6; Adam, 2016). A significant ($r_s \geq 0.8$; $p \leq 0.05$) relationship between solid-phase As and Sb concentrations is evident in Hambone Lake, suggesting that arsenopyrite provides a primary source of As to this lake. However, the abundance of As-bearing authigenic sulphides indicate that diagenetic remobilization and active sequestration of As is occurring in the near-surface sediment (Figs. 5 and 7). Concentrations of As, Zn, Ag, and Cu are highest in sediment at the northeastern end of the lake, farthest from the treated effluent discharge location (Fig. 1; Table 2). The increased concentration of elements, which have historically exceeded CCME guidelines in effluent discharge, suggest that this area may provide an ongoing source of downstream contamination (Table 2; AECOM, 2015). Relatively oxidized effluent water may have oxidized authigenic As-bearing sulphides, or an increase in pH may have decreased the sorption of arsenate on Fe-(oxy)hydroxides due to competitive sorption (Jeong et al., 2010; Campbell and Nordstrom, 2014; Desbarats et al., 2015; Golder Associates Ltd., 2017). In addition, the overtopping and seepage of alkaline tailings waters (pH = 8.22) and



Hambone Lake

	As	Au	Sb	W	Fe	Mn	S	TOC	S1	S2	S3
As		0.94	0.83	0.94			0.89		0.89		
Au				0.89			0.83				
Sb							0.83		0.83		
W						0.89	0.94		0.94		0.89
Fe						0.83					0.83
Mn							0.94	0.94	0.94		*1.00*
S								0.89	*1.00*		0.94
TOC									0.89		0.94
S1											0.94
S2											
S3											

Bulldog Lake

	As	Au	Sb	W	Fe	Mn	S	TOC	S1	S2	S3
As			0.85								
Au				*1.00*	*0.96*	*0.96*			-0.79		
Sb							0.86			-0.78	
W					*0.96*				-0.79		
Fe						*1.00*					
Mn											
S									-0.82	-0.92	
TOC											
S1											
S2											
S3											

Matthews Lake

	As	Au	Sb	W	Fe	Mn	S	TOC	S1	S2	S3
As		0.65	*0.78*	0.70	*0.89*	*0.92*	0.80		0.68		
Au			*0.90*	*0.91*		*0.85*	*0.87*	0.65	*0.85*		0.68
Sb				*0.91*	0.65	*0.91*	*0.87*		*0.88*		0.66
W						*0.85*	0.79		0.79		0.61
Fe						0.80	0.64				
Mn							*0.85*		0.81		
S								0.65	*0.91*		0.68
TOC									0.81	0.63	*0.94*
S1											*0.86*
S2											
S3											

Control Lake

	As	Au	Sb	W	Fe	Mn	S	TOC	S1	S2	S3
As					*0.94*	0.81					
Au								0.62	0.70		
Sb							0.74	0.73	0.77	0.82	
W											
Fe						*0.88*		0.62			0.61
Mn								0.61			
S								0.72	0.72	*0.82*	
TOC									*0.93*	*0.82*	*0.99*
S1										*0.84*	*0.93*
S2											*0.82*
S3											

Fig. 6. Spearman's Rank correlations of inorganic and organic geochemical parameters for the near-surface sediment of Bulldog Lake (B-MI) ($n = 7$), Hambone Lake (HL-MI) ($n = 6$), Matthews Lake (ML-MI) ($n = 13$) and Control Lake (CL-I) ($n = 14$) sediment cores. Organic fractions include TOC, S1, S2, and S3. Data shown as Spearman's Rank (r_s) correlation coefficients. Italicized r_s values represent $p \leq 0.001$, non-italicized values represent $p \leq 0.05$; only correlations with $r_s \geq 0.6$ are included. For the colour version of this figure the reader is referred to the online version of this article.

disposal of treated effluent (pH = 8.4–8.5) into Hambone Lake has increased the pH of surface waters in this lake (average pH = 7.35–7.92; AANDC, 2014; AECOM, 2015). As the post-depositional mobility of As is governed by redox conditions and pH of sediment porewaters, any change in geochemistry resulting from tailings seepage and discharge of treated tailings effluent may influence the long-term stability of legacy contaminants (Smedley and Kinniburgh, 2002).

5.2.2. Powder Mag Lake

Surface water and porewater As concentrations in Powder Mag Lake are an order of magnitude higher than the other lakes studied, reflecting the transport of dissolved and particulate-bound As species from the TCA through Hambone Lake to the downstream environment (Table 1; Figs. 1 and 2a). The oxidation and dissolution of secondary As-minerals due to the disposal of treated tailings effluent may also have contributed to increased dissolved As concentrations in Powder Mag Lake. Trace arsenopyrite occurs in sediment deposited after the onset of mining activities, but is much less abundant than observed in Bulldog Lake sediments. Within Powder Mag Lake, the main As-hosts are authigenic Fe-(oxy)hydroxides and Fe-sulphides (Figs. 5 and 7). The relative absence of arsenopyrite, abundance of secondary As minerals, and prevalence of oxidized aqueous As species in the near-surface sediment of Powder Mag Lake (Figs. 3 and 5) are attributed to tailings seepage and discharge of treated effluent into this drainage pathway. Oxidation of arsenopyrite in the tailings necessitated treatment with ferric sulphate to precipitate As-bearing Fe-(oxy)hydroxides during remediation activities (WESA Technologies Inc., 2014). This precipitate was separated by dewatering using Geotubes ®; however, the formation of suspended or colloidal As-bearing Fe-(oxy)hydroxides in the effluent discharge has contributed to the transport of As along this drainage pathway. Anoxic wetlands have been demonstrated to be an effective trap of As (Langner et al., 2011); therefore, the peatland between Hambone and Powder Mag Lake may also provide and long-term sink and/or source of mining-derived As and influence its mobility to the downstream environment. In sediment pre-dating mining activities, As concentrations exceed CCME Probable Effects Level (PEL) of 17 μg kg^{-1} and interim sediment quality guideline (ISQG) of 5.9 mg kg^{-1} (range: 42–70 mg kg^{-1}; median = 60 mg kg^{-1}; $n = 12$); however, fall within the global average range for greywacke and slate which surround Powder Mag Lake (0.5–143 mg kg^{-1}; Fig. 1; Boyle and Jonasson, 1973; Smedley and Kinniburgh, 2002).

5.2.3. Bulldog Lake

The greatest abundance of arsenopyrite identified in sediment of the

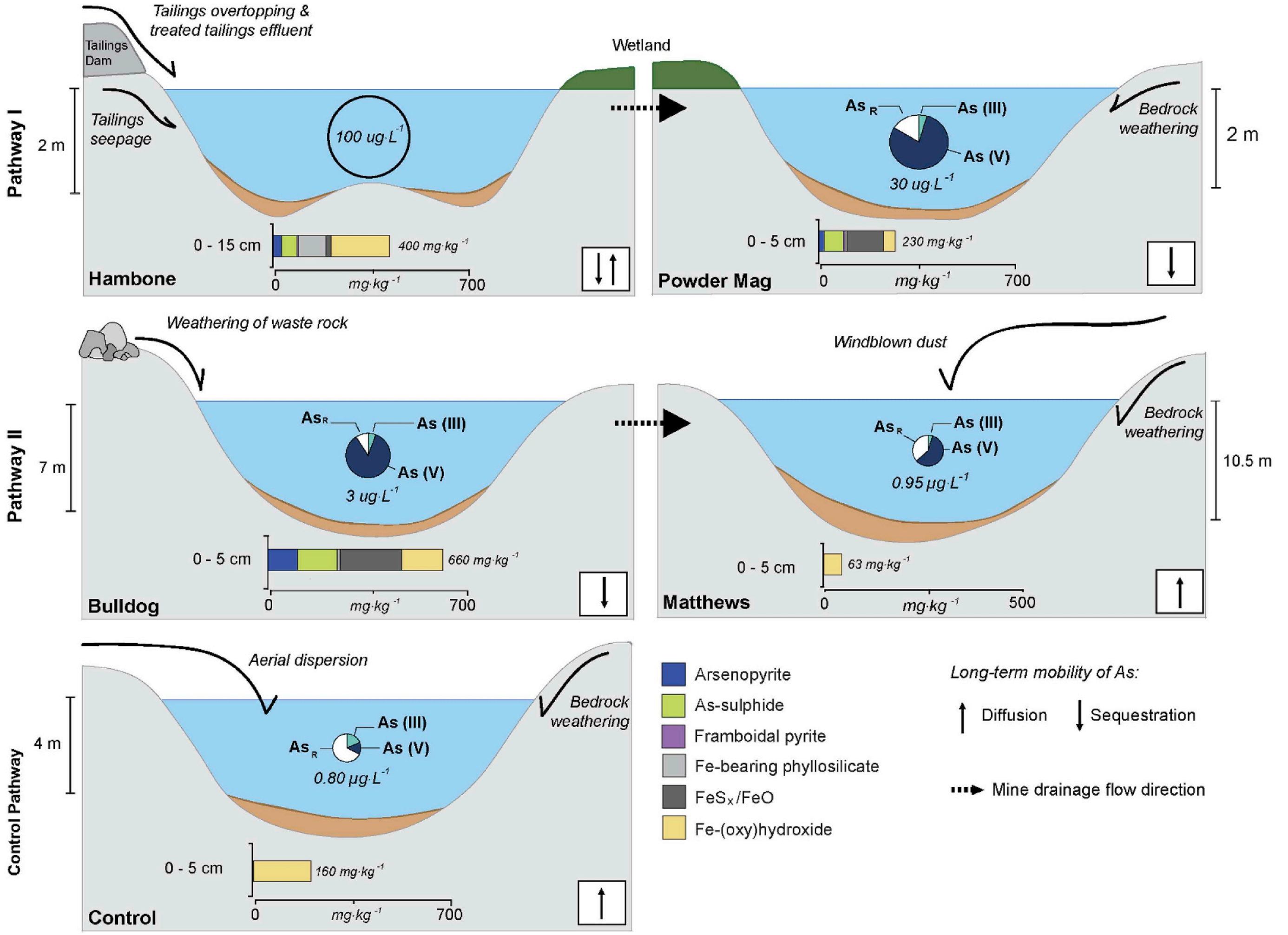


Fig. 7. Schematic diagrams showing the predominant As sources, relative concentration of aqueous As species, and relative contribution of each As-hosting solid phase to total As concentrations in near-surface sediment samples from lakes of the Tundra Mine region. Arrows in the bottom-right corner of each diagram denote the predicted influence of increased organic matter on As mobility in each lake. Vertical scales are not meant to be representative of the actual bathymetric features of each lake.

Tundra Mine region is in Bulldog Lake, accounting for 1–40% of total As in these shallow sediments (Fig. 5). The largest and most abundant grains are present at 5–6 cm depth in the Bulldog Lake sediment column, and this depth coincides temporally with the onset of surface exploration activities in 1946 at the former Tundra Mine. The presence of arsenopyrite grains, ranging in size from 1–25 µm, suggests the disposal and/or weathering of As-bearing waste rock is the primary source of As to this lake. Bulldog Lake is adjacent to the former mill pad (Fig. 1), which was constructed using waste rock (Hatfield Consulting, 1982; Lorax Environmental, 2007). The higher sedimentation rates observed at the surface of Bulldog Lake (0.16 cm yr^{-1}) are attributed to the increased activity and associated terrain disturbance on-site during recent remediation activities. In the early days of mining, water pumped from the underground workings was discharged into Bulldog Lake (Hatfield Consulting, 1982) and may have provided an additional source of dissolved As, which has since become incorporated into the lake sediment in secondary As-bearing minerals. Dissolution and surface oxidation of arsenopyrite grains is apparent in the shallow Bulldog Lake sediment, providing a source of dissolved As to the porewaters (Fig. 3). A significant ($r_s \geq 0.8$; $p \leq 0.05$) relationship between solid-phase As and Sb concentrations is also evident in the mining-impacted sediment of Bulldog Lake, suggesting that arsenopyrite is a source of both of these elements. Low concentrations of As in pre-mining sediment (median = 34 mg kg^{-1}; $n = 17$) suggest that the adjacent volcanic lithologies and mineralized shear vein have had little influence on As loading and mobility in this lake (Fig. 1).

5.2.4. Matthews Lake and Control Lake

Arsenic concentrations in the near-surface sediment of both Matthews and Control lakes exceed both the CCME PEL and ISQG (CCME, 2001a). No arsenopyrite was identified in the near-surface sediments of these lakes. Arsenic concentrations in the shallow sediments of both lakes are similar to those observed in sediment pre-dating mining activities. Elevated As concentration at the SWI in both of these lakes is attributed primarily to reductive dissolution of naturally-occurring, As-bearing Fe-(oxy)hydroxides during burial, and re-precipitation near the SWI (Fig. 2b; Martin and Pedersen, 2002). Increasing concentrations of As, Au, Sb, and W in the sediment cores of Matthews and Control lakes correspond to the onset of advanced exploration activities around 1946, indicating that runoff and dust from the former waste rock and ore piles from both Salmita and Tundra mine sites may have provided sources of mining-related contamination to these lakes (Hatfield Consulting, 1982). Higher sedimentation rates (1.75 yr cm^{-1}) and an increase in grain size in sediments of Control Lake coincide temporally with runway construction and increased development activity at the Tundra Mine site at ca. 1946 (Fig. 2b). An increase in grain size is not observed in the other lake sediment cores and therefore may be the result of erosion from the nearby airstrip and roadways (Fig. 1) or natural changes within the catchment of Control Lake (Fig. 2b). Grain size of particles in the near-surface sediment of Control Lake ranges from 27–173 μm (arithmetic mean), suggesting that some of this coarser grained material may be derived from the mine site, mine roads, and/or the airstrip and transported short distances by aerial suspension (Livingstone and Warren, 1996; Petavratzi et al., 2005).

In both of these lakes, authigenic As-bearing Fe-(oxy)hydroxide is the most abundant As host suggesting that the weathering and oxidation of As-bearing iron sulphides in mine wastes or mineralized bedrock may contribute dissolved Fe, Mn and As to these lakes (Figs. 5 and 7; Corkhill and Vaughan, 2009). Matthews Lake is primarily bound by felsic volcanics (rhyolite and dacite) whereas Control Lake is bound by metasedimentary (greywacke and slate) lithologies; global average As content for these bedrock types ranges from 3.2–13.4 mg kg^{-1} and 0.5–143 mg kg^{-1}, respectively (Smedley and Kinniburgh, 2002). Higher than global crustal average concentrations of As in pre-mining sediment of Matthews Lake may be attributed to As associated with Au-mineralization along the eastern shore of this lake or to the weathering of other bedrock types and derived surficial materials in the region. The presence of trace arsenopyrite in pre-mining sediment of both Control and Matthews Lakes also confirms the presence of a geogenic source of As and suggests local-scale variability in geochemical baselines in sediments of lakes in the CLGB.

5.3. Intra-lake variance in As mobility and implications of climate warming on the long-term stability of As

The source of As, distance from the mine site, sedimentation rates, and sediment geochemistry (organic and inorganic) control the depth and magnitude of impacts in lake sediments of the Tundra Mine region. These and other parameters also influence the speciation and post-depositional mobility of As in sediment. These factors vary for each lake studied, demonstrating that the mechanisms influencing the distribution of As can be highly variable, even on the scale of a single mining district. As a result, the effects of past and future climate change on the long-term stability of mining-related As contamination is expected to differ for each lake.

Post-depositional mobility of As in most lacustrine environments is largely governed by dissolution of Fe-(oxy)hydroxides and the synchronous co-precipitation with poorly crystalline Fe-(oxy)hydroxides and sulphides (Moore et al., 1988; Rickard and Luther, 1997; Nickson et al., 2000; O'Day et al., 2004). An influx of reactive, labile organic carbon (S1 and S2) to lake sediments, expected as a result of climate warming (Smol et al., 2005; Frey and McClelland, 2009; Prowse et al., 2011; Stern et al., 2012), may influence these redox-mediated mechanisms and thus the long-term stability of As in lake systems. The source of As and type of organic material are likely to be important in determining the magnitude of As mobility associated with organic loading (Nickson et al., 2000; Redman et al., 2002; Bauer and Blodau, 2006; Sharma et al., 2010; Galloway et al., 2017). Due to the association of As with metal oxides and sulphides in near-surface sediment, changes to redox conditions may significantly influence the distribution and mobility of As in lakes of the Tundra Mine region (Fig. 7; Martin and Pedersen, 2002; Couture et al., 2010).

The highest concentrations of As in surface waters and sediments are observed in lakes proximal to the mine site and impacted by the direct disposal of mine wastes (Hambone, Powder Mag, and Bulldog lakes); however, As concentrations and solid-phase speciation vary between these three lakes. The highest sediment As concentrations are observed in sediments of Bulldog Lake, whereas surface water and mean porewater concentrations in Powder Mag Lake and Hambone Lake (surface water average (summer 2016): 98.7 μg L^{-1}) are higher than in Bulldog Lake (Table 1; Fig. 2a; AANDC, 2014). Powder Mag Lake and Bulldog Lake both demonstrate multiple peaks in porewater As concentrations in the near-surface sediment. One peak occurs at the SWI with subsequent increases just below this boundary, suggesting remobilization of As is occurring in both of these lakes (Fig. 2a). However, increased porewater concentrations in the near-surface sediment of Powder Mag Lake suggest that As is being actively remobilized in sediment to a larger degree than observed in Bulldog Lake.

Total surface water concentration of As in Powder Mag Lake is lower than total As concentrations in treated effluent (average As (2009–2014): 75.3 μg L^{-1}) and surface waters of Hambone Lake (average As: 35–40 μg L^{-1}), suggesting that As is being removed from overlying surface water and settling into the bottom sediments (AANDC, 2013; AECOM, 2015). Additionally, the low As concentrations in surface water and sediment of lakes further downstream of Powder Mag Lake indicate that As is being sequestered in the sediment of this lake (AECOM, 2015). Colloidal and suspended As-bearing Fe-(oxy)hydroxides are deposited to the surface sediment of Powder Mag Lake where they are reductively dissolved; As is then sequestered through the precipitation of authigenic sulphides (Fig. 7). The rapid onset of reducing conditions in the sediment column of Powder Mag Lake likely results from the accumulation of labile organic matter derived from the peatland connecting Powder Mag to Hambone Lake (Figs. 1 and 2a). In general, reducing conditions are thought to increase the mobility of As due to the reductive dissolution of Fe-(oxy)hydroxides and the transformation of As (V) to As (III) (Smedley and Kinniburgh, 2002; Martin and Pedersen, 2002; Dixit and Hering, 2003; Andrade et al., 2010). However, a positive relationship between labile organic matter (S1) and sediment As concentrations in modern sediment impacted by mining activities in sub-Arctic Canada was recently observed by Galloway et al. (2017), who suggested that increased labile organic matter may provide a substrate for microbial growth that in turn mediates the precipitation of As-bearing secondary minerals (*i.e.* framboidal pyrite, As-sulphides).

Organic matter concentrations in surface water (DOC) and near-surface sediment (TOC, S1, S2) of Powder Mag Lake are higher than other lakes studied (Table 1, Supplemental Data ST2). This is attributed to the influence of seasonal effluent discharge to Hambone Lake (mean = 254,500 m^3 yr^{-1}; median: 180,000 m^3 yr^{-1}; $n = 7$) that increased the flow of water through the peatland area into Powder Mag Lake and mobilized organic material (Fig. 1) (INAC, 2005, 2008; AANDC, 2010, 2012, 2013, 2014). The abundance of As-bearing sulphides in the near-surface sediment of Powder Mag Lake suggest that sediments enriched in S, Fe and NOM may be efficient geochemical traps for As and support the mechanisms of As attenuation observed by Drahota et al. (2009) in organic-rich groundwaters, and Langner et al. (2011) in wetlands. Burton et al. (2013) demonstrated that microbial sulfate reduction can result in changes in As speciation and highlighted the important role of thioarsenate species on the mobility of As in mining-impacted environments. The presence of these complexes may account for the abundance of As_R species in the porewaters of Powder Mag Lake (Fig. 3) and contribute to the mobility of As; however, further porewater speciation analyses would be required to test this hypothesis (Couture et al., 2013).

A positive (r_s) relationship between S1 and sediment As concentrations occurs in two of the five lakes studied (Hambone Lake ($r_s = 0.88$; $p \leq 0.05$; $n = 6$) and Matthews Lake ($r_s = 0.68$; $p \leq 0.05$; $n = 13$) (Fig. 6); however, no relationship between As_{sed} and labile organic matter is observed in Bulldog Lake or Control Lake. Increases in reactive organic matter input to lakes may lead to higher rates of sulfide production and promote the onset of reducing conditions by increasing sediment oxygen demand (Wilkin and Barnes, 1997; Toevs et al., 2006). The influx of organic matter facilitates the microbially mediated reduction of both Fe (III) and SO_4^{-2}, leading to the formation of As-bearing sulphide minerals in the near-surface sediment (Wilkin and Barnes, 1997; Thamdrup, 2000; Kirk et al., 2004; Lowers et al., 2007). As a result, the influx of organic matter may facilitate the formation of microbially mediated As-bearing sulphide minerals in the near-surface sediment (Nordstrom and Archer, 2003). In lakes proximal to the former mine site, As is primarily hosted in sulphides or authigenic agglomerations of authigenic Fe-(oxy)hydroxide and iron monosulphide, possibly amorphous mackinawite (FeS_{1-x}). It has been demonstrated that amorphous mackinawite may provide an effective mechanism of As attenuation under changing redox conditions in lake sediment (An et al., 2017; Vega et al., 2017). Increased organic matter loading to these lakes may, therefore, facilitate the precipitation of As-bearing sulfides and increase the stability of As in sediment; however, the relationships between As, S, and organic matter are not consistent (Fig. 6). Previous studies show that organic matter influences the speciation and mobility of As in peatlands, lake sediment, and soils, through various mechanisms, including competition with As for sorption on mineral surfaces (Redman et al., 2002; Bauer and Blodau, 2006; Wang and Mulligan, 2006; Stuckey et al., 2016; Galloway et al., 2017; Wang et al., 2018). However, the interaction of organic matter with elements is influenced by its characteristics and composition (Grafe et al., 2002; Ritter et al., 2006; Langner et al., 2011; Burton et al., 2013). In the near-surface sediment of lakes proximal to the former mine site, the relationship between TOC and labile organic matter fractions (S1, S2, S3) is different (Fig. 6). This reflects the natural heterogeneity of sediment organic matter and suggests that the varied sources of both As and organic matter influence the speciation and mobility of As in mining-impacted lake sediments of the Tundra Mine region.

In lakes more distal to the former mine site, weathering and dust transport of exposed waste rock used for construction of mine facilities may have influenced As concentrations in the near-surface sediment; however, the predominant source of As to these lakes is likely natural weathering of As-rich bedrock (Fig. 7). In the near-surface sediment of Matthews and Control lakes, median As concentrations are lower than lakes closer to Tundra Mine and As in the near-surface sediment is primarily hosted by Fe-(oxy)hydroxides (Figs. 5 and 7). In sediment cores from both Matthews Lake and Control Lake, a significant relationship between sediment As, Fe, and Mn indicates the important role of Fe-(oxy)hydroxides in the sequestration of As at the SWI (Fig. 6). Increased organic matter input to these lakes may result in enhanced diffusion of As from sediment to surface waters by promoting reducing conditions and thus drive reductive dissolution of As-bearing Fe-(oxy) hydroxides (Nickson et al., 2000; Harvey et al., 2002; Islam et al., 2004). However, the presence of As-bearing framboids in the near-surface sediment of both Matthews Lake and Control Lake suggests that the precipitation of authigenic pyrite may also sequester As released from reductive dissolution of As-bearing Fe-(oxy)hydroxides (Fig. 7). A significant correlation between labile organic matter (S1), S ($r_s = 0.91$; $p \leq 0.001$; $n = 13$) and As ($r_s = 0.67$; $p \leq 0.05$; $n = 13$) in near-surface sediments of Matthews Lake may represent this mechanism of As attenuation (Fig. 6; Galloway et al., 2017).

The results of this study support Galloway et al. (2017), who suggested that in lakes impacted by As from legacy gold mining in sub-Arctic Canada, organic matter may facilitate the precipitation of As-bearing sulfides and increase the stability of As in sediment. In contrast, this study highlights that in lakes where As is hosted mainly by Fe-(oxy) hydroxides, increasing organic matter may enhance the diffusion of As from sediment to surface water.

6. Conclusions

The sediment geochemistry of lakes near a former gold mine site in sub-Arctic Canada has been altered due to the influence of historical mining, mineral processing, and subsequent terrain disturbance associated with remediation. Five main sources have contributed As to lakes around the former Tundra Mine: disposal of waste rock, tailings overtopping and seepage, weathering and airborne deposition of waste rock and tailings, discharge of treated tailings effluent, and natural weathering of mineralized bedrock. Impacts were observed in each of the lakes studied through analysis of sediment, surface water, and porewaters. The depth of impacts in the sediment column and primary controls on the post-depositional mobility of mining-derived As contamination are highly variable between lakes.

The findings of this study suggest that benthic grab samples, commonly collected during environmental site assessments, may not provide an accurate assessment of mining impacts as changes in geochemistry occur on a sub-centimeter scale and deposition rates vary between lakes. As a result, interpretation of sediment geochemistry and mining impact based only on grab samples with uncertain depth control complicates the accurate determination of geochemical baselines. Sediment gravity cores can more precisely capture the uppermost sediments so that they may be sub-sampled at higher resolution (*e.g.* 0.5–1.0 cm). This study highlights that sampling depth control is essential for the interpretation of sediment geochemistry and differentiation of mining impact in lacustrine systems. This is especially important in sub-Arctic lakes where sedimentation rates are low.

The distribution of As in these lakes is influenced by lake-specific variables including: the source of As, Fe and S concentrations in sediment, depth of the lake, sedimentation rate, and organic matter type. This study also demonstrates variability in pre-mining background As concentrations in sediment cores and provides evidence for the influence of bedrock weathering on the natural loading of As to lakes in this region.

Labile organic matter (S1 as determined by Rock Eval pyrolysis) demonstrated significant positive relationships to sedimentary As and S concentrations in two of the five lakes studied. The relationship between S1, As, and S, in addition to the abundance of As-bearing framboidal pyrite in mining-impacted sediment, suggests that S1 may mediate the authigenic precipitation of As-bearing sulphides. Differing relationships between near-surface sediment As concentrations and organic matter in lakes of the Tundra Mine region may be explained by the natural heterogeneity of sediment organic matter. The findings of this study suggest that increasing organic matter loading to lakes expected with continued climate warming will have varying effects on As mobility and fate in mining-impacted lakes and that these effects depend on the main hosts of As in lake sediments. In lakes where As is hosted in reduced sulphide form, increasing organic matter input may increase the stability of As in sediment, whereas in lakes where the primary host of As is Fe-(oxy)hydroxides, increasing organic matter to these lakes may enhance the diffusion of As from sediment to surface waters. These results have implications for long-term monitoring of lakes impacted by legacy contamination. Knowledge from this study can aid in the development of robust geochemical baselines and be used to improve environmental monitoring and remediation strategies at future northern metal mines.

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Appendix A. Supplementary data

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References

AANDC, 2010. Tundra Mine, NWT Remediation Environmental Monitoring Program: Water Quality Part H: 2009 and Historic Results. Available online: http://registry.mvlwb.ca/Documents/MV2009L8-0008/MV2009L8-0008%20-%202010%20Annual%20Report%20-%20Mar31-11.pdf.

AANDC, 2012. Water Surveillance Network Program (SNP) Report for Type 'A' Water Licence MV2009L8-0008 (Tundra Mine Remediation) June 2012 Water Quality Results. AANDC. http://registry.mvlwb.ca/Documents/MV2009L8-0008/MV2009L8-0008%20-%20AANDC-CARD%20-%20Tundra%20Mine%20Remediation%20-%20June%202012%20SNP%20Report%20-%20Jul30-12.pdf.

AANDC, 2013. Water Balance Monitoring at the Tundra Mine Site: 2012 Update. AANDC Available from: http://registry.mvlwb.ca/Documents/MV2009L8-0008/MV2009L8-0008 AANDC CARD 20Tundra Minesite 2012 WL Annual Report - Mar28-13.pdf.

AANDC, 2014. Tundra Mine, NWT Remediation Environmental Monitoring Program: Water Quality Part L: 2013 and Historic Results. AANDC. http://registry.mvlwb.ca/Documents/MV2009L8-0008/MV2009L8-0008%20-%20AANDC-CARD%20-%202013%20Annual%20Report%20for%20Tundra%20Mine%20Site%20-%20Mar27-14.pdf.

Adam, M.A., 2016. Gold Mineralisation at the FAT Deposit, Courageous Lake Greenstone Belt, Northwest Territories, Canada, Masters Thesis. University of Western Ontario. https://ir.lib.uwo.ca/cgi/viewcontent.cgi?article=5245&context=etd.

AECOM, 2015. Tundra Mine, NWT Remediation Environmental Monitoring Program: Water Quality Part L: 2014 and Historical Results. AECOM. http://registry.mvlwb.ca/Documents/MV2009L8-0008/MV2009L8-0008%20-%20AANDC-CARD%20-%20Tundra%20Mine%202014%20Annual%20WL%20Report%20-%20May5-15.pdf.

AECOM, 2018. Tundra Mine Adaptive Management Plan. AECOM Available from: http://registry.mvlwb.ca/Documents/MV2016L8-0003/MV2016L8-0003 INAC CARD – Adaptive Management Plan – Revision from May 24-18 - Oct26-18.pdf.

An, X.L., Huang, F.G., Ren, H.T., Wang, Y.F., Chen, Y., Liu, Z.M., Zhang, H.W., Han, X., 2017. Oxidative dissolution of amorphous FeS and speciation of secondary Fe minerals: effects of pH and As(III) concentration. Chem. Geol. 462, 44–54. https://doi.org/10.1016/j.chemgeo.2017.04.025.

Andrade, C.F., Jamieson, H.E., Kyser, T.K., Praharaj, T., Fortin, D., 2010. Biogeochemical redox cycling of arsenic in mine-impacted lake sediments and co-existing pore waters near Giant Mine, Yellowknife Bay, Canada. Appl. Geochem. 25, 199–211. https://doi.org/10.1016/j.apgeochem.2009.11.005.

Appleby, P.G., 2001. Chronostratigraphic techniques in recent sediments. In: Last, W.M., Smol, J.P. (Eds.), Tracking Environmental Change Using Lake Sediments Volume 1: Basin Analysis, Coring, and Chronological Techniques. Kluwer, Dordrecht, pp. 171–203.

Ardakani, O.H., Sanei, H., Snowdon, L.R., Outridge, P.M., Obermajer, M., Stewart, R., Vandenberg, R., Boyce, K., 2016. The Accepted Values for the Internal Geological Survey of Canada (GSC) 9107 Rock-Eval 6 Standard (Upper Cretaceous Second White Speckled Shale, Colorado Group), Western Canada Open File 8043. https://doi.org/10.4095/298729.

Azcue, J.M., Mudroch, A., Rosa, F., Hall, G., 1994. Effects of abandoned gold mine tailings on the arsenic concentrations in water and sediments of Jack of Clubs Lake, B.C. Environ. Technol. 15, 669–678. https://doi.org/10.1080/09593339409385472.

Barrett, P.M., Hull, E.A., Burkart, K., Hargrave, O., Mclean, J., Taylor, V.F., Jackson, B.P., Gawel, J.E., Neumann, R.B., 2019. Contrasting Arsenic Cycling in Strongly and Weakly Stratified Contaminated Lakes : Evidence for Temperature Control on Sediment – Water Arsenic Fluxes. https://doi.org/10.1002/lno.11119.

Bauer, M., Blodau, C., 2006. Mobilization of arsenic by dissolved organic matter from iron oxides, soils and sediments. Sci. Total Environ. 354, 179–190. https://doi.org/10.1016/j.scitotenv.2005.01.027.

Blais, J.M., Kalff, J., 1995. The influence of lake morphometry on sediment focusing. Limnol. Oceanogr. 40, 582–588. https://doi.org/10.4319/lo.1995.40.3.0582.

Bleeker, W., Ketchum, J.W.F., Jackson, V.A., Villeneuve, M.E., 1999. The Central Slave Basement Complex, Part I: its structural topology and autochthonous cover. Can. J. Earth Sci. 36, 1083–1109. https://doi.org/10.1139/e98-102.

Blott, S.J., Pye, K., 2001. Gradistat: a grain size distribution and statistics package for the analysis of unconsolidated sediments. Earth Surf. Process. Landforms 26, 1237–1248. https://doi.org/10.1002/esp.261.

Boyle, R.W., Jonasson, I.R., 1973. The geochemistry of as and its use as an indicator element in geochemical prospecting. J. Geochem. Explor. 2, 251–296. http://doi.org/10.1016/0375-6742(73)90003-4.

Bright, D.A., Coedy, B., Dushenko, W.T., Reimer, K.J., 1994. Arsenic transport in a watershed receiving gold mine effluent near Yellowknife, Northwest Territories, Canada. Sci. Total Environ. 155, 237–252. https://doi.org/10.1016/0048-9697(94)90503-7.

Bright, D.A., Dodd, M., Reimer, K.J., 1996. Arsenic in subarctic lakes influenced by gold mine effluent: the occurrence of organoarsenicals and 'hidden' arsenic. Sci. Total Environ. 180, 165–182. https://doi.org/10.1016/0048-9697(95)04940-1.

Buckwalter-Davis, M., 2013. Automated Mineral Analysis of Mine Waste, Masters Thesis. Queen's University. https://qspace.library.queensu.ca/bitstream/handle/1974/8200/Buckwalter-Davis_Martha_J_201308_MSc.pdf?sequence=1&isAllowed=y.

Burton, E.D., Johnston, S.G., Planer-Friedrich, B., 2013. Coupling of arsenic mobility to sulfur transformations during microbial sulfate reduction in the presence and absence of humic acid. Chem. Geol. 343, 12–24. https://doi.org/10.1016/j.chemgeo.2013.02.005.

Campbell, K.M., Nordstrom, D.K., 2014. Arsenic speciation and sorption in natural environments. Rev. Mineral. Geochem. 79, 185–216. https://doi.org/10.2138/rmg.2014.79.3.

Carrie, J., Sanei, H., Stern, G., 2012. Standardisation of Rock-Eval pyrolysis for the analysis of recent sediments and soils. Org. Geochem. 46, 38–53. https://doi.org/10.1016/j.orggeochem.2012.01.011.

CCME, 2001. Canadian Sediment Quality Guidelines for the Protection of Aquatic Life, Environmental Protection. CCME Available from: https://ccme.ca/en/resources/canadian_environmental_quality_guidelines/.

CCME, 2001. CCME Water Quality Guidelines for the Protection of Aquatic Life. CCME Available from: https://ccme.ca/en/resources/canadian_environmental_quality_guidelines/.

Corkhill, C.L., Vaughan, D.J., 2009. Arsenopyrite oxidation - a review. Appl. Geochem. 24, 2342–2361. https://doi.org/10.1016/j.apgeochem.2009.09.008.

Couture, R.M., Gobeil, C., Tessier, A., 2010. Arsenic, iron and sulfur co-diagenesis in lake sediments. Geochim. Cosmochim. Acta 74, 1238–1255. https://doi.org/10.1016/j.gca.2009.11.028.

Couture, R.M., Rose, J., Kumar, N., Mitchell, K., Wallschläger, D., Van Cappellen, P., 2013. Sorption of arsenite, arsenate, and thioarsenates to iron oxides and iron sulfides: a kinetic and spectroscopic investigation. Environ. Sci. Technol. 47, 5652–5659. https://doi.org/10.1021/es3049724.

Crann, C.A., Patterson, R.T., Macumber, A.L., Galloway, J.M., Roe, H.M., Blaauw, M., Swindles, G.T., Falck, H., 2015. Sediment accumulation rates in subarctic lakes: insights into age-depth modeling from 22 dated lake records from the Northwest Territories, Canada. Quat. Geochronol. 27, 131–144. https://doi.org/10.1016/j.quageo.2015.02.001.

Davis, J., 2011. In: Statistics and Data Analysis in Geology, Third ed. John Wiley & Sons, Ltd.

Desbarats, A.J., Parsons, M.B., Percival, J.B., 2015. Arsenic mobility in mildly alkaline drainage from an orogenic lode gold deposit, Bralorne mine, British Columbia. Appl. Geochem. 57, 45–54. https://doi.org/10.1016/j.apgeochem.2014.11.015.

Dillion-Leitch, H.C., 1981. Volcanic Stratigraphy, Structure and Metamorphism in the Courageous-Mackay Lake Greenstone Belt, Slave Province, Northwest Territories. University of Ottawa. https://doi.org/10.20381/ruor-13514.

Dixit, S., Hering, J.G., 2003. Comparison of arsenic (V) and arsenic (III) sorption onto iron oxide minerals: implications for arsenic mobility. Environ. Sci. Technol. 37, 4182–4189. https://doi.org/10.1021/es030309t.

Donato, S.V., Reinhardt, E.G., Boyce, J.I., Pilarczyk, J.E., Jupp, B.P., 2009. Particle-size distribution of inferred tsunami deposits in Sur Lagoon, Sultanate of Oman. Mar. Geol. 257, 54–64. https://doi.org/10.1016/j.margeo.2008.10.012.

Drahota, P., Rohovec, J., Filippi, M., Mihaljevic, M., Rychlovsky, P., Cerveny, V., Pertold, Z., 2009. Mineralogical and geochemical controls of arsenic speciation and mobility under different redox conditions in soil, sediment and water at the Mokrsko-West gold deposit, Czech Republic. Sci. Total Environ. 407, 3372–3384. http://doi.org/10.1016/j.scitotenv.2009.01.009.

Environment Canada, 2012. Metal Mining Technical Guidance for EEM. Environment Canada Available from: http://ec.gc.ca/esee-eem/AEC7C481-D66F-4B9B-BA08-A5DC960CDE5E/COM-1434 Tec-Guide-for-Metal-Mining-Env-Effects-Monitoring_En_02[1].pdf.

Fandrich, R., Gu, Y., Burrows, D., Moeller, K., 2007. Modern SEM-based mineral liberation analysis. Int. J. Miner. Process. 84, 310–320. https://doi.org/10.1016/j.minpro.2006.07.018.

Folinsbee, R.E., Moore, J.C.G., 1950. Matthews Lake, Northwest Territories. Paper 50-2. https://doi.org/10.4095/108448.

Folinsbee, R.E., Moore, J.C.G., 1955. Matthews Lake Bedrock Geology Map 1024A. Obtained from NTGO Library.

Frey, K.E., McClelland, J.W., 2009. Impacts of permafrost degradation on arctic river biochemistry. J. Glaciol. 23, 169–182. https://doi.org/10.1002/hyp.

Galloway, J.M., Sanei, H., Patterson, R.T., Mosstajiri, T., Hadlari, T., Falck, H., 2012. Total arsenic concentrations of lake sediments near the City of Yellowknife, Northwest Territories. Geol. Surv. Can. Open File 7037, 1–47.

Galloway, J.M., Swindles, G.T., Jamieson, H.E., Palmer, M., Parsons, M.B., Sanei, H., Macumber, A.L., Timothy Patterson, R., Falck, H., 2017. Organic matter control on the distribution of arsenic in lake sediments impacted by ~ 65 years of gold ore processing in subarctic Canada. Sci. Total Environ. 622 (623), 1668–1679. https://doi.org/10.1016/j.scitotenv.2017.10.048.

Gasiorowski, M., 2008. Deposition rate of lake sediments under different alternative stable states. Geochronometria 32, 29–35. https://doi.org/10.2478/v10003-008-0020-y.

Golder Associates Ltd., 2005. Terrestrial and Aquatic Field Surveys and Ecological Risk Assessment of the Tundra Gold Mine. Golder Associates Ltd.. http://www.mvlwb.ca/Registry.aspx?a=MV2009L8-0008.

Golder Associates Ltd, 2008. Phase II Remedial Action Plan: Tundra Mine Site. Golder Associates Ltd Available from: http://www.mvlwb.ca/Registry.aspx?a=MV2009L8-0008.

Golder Associates Ltd., 2016. Public Works and Government Services Canada Tundra Mine, NWT Remediation Environmental Monitoring Program: Water Quality: 2015 and Historical Results. Golder Associates Ltd.

Golder Associates Ltd., 2017. Public Works and Government Services Canada Tundra Mine, NWT Remediation Environmental Monitoring Program: 2016 and Historical Water Quality Results. Golder Associates Ltd.

Goldfarb, R.J., Berger, B.R., Klein, T.L., Pickthorn, W.J., Klein, D.P., 1995. Low-sulfide Au quartz veins. Denver CO In: du Bray, E.A. (Ed.), Preliminary Compilation of Descriptive Geoenvironmental Mineral Deposit Models. U.S. Geol. Surv. Open-File

Report 95–831, pp. 261–267 (Chapter 34).

Government of the Northwest Territories, Executive and Indigenous Affairs, 2007. Interim Land Withdrawal - Akaitcho Dene First Nations. Government of the Northwest Territories Available from: https://www.eia.gov.nt.ca/sites/eia/files/adfn_interim_land_withdrawal_map_crownland.pdf.

Grafe, M., Eick, M.J., Grossl, P.R., Saunders, A.M., 2002. Adsorption of arsenate and arsenite on ferrihydrite in the presence and absence of dissolved organic carbon. J. Environ. Qual. 31, 1115. https://doi.org/10.2134/jeq2002.1115.

Groves, D.I., Goldfarb, R.J., Gebre-Mariam, M., Hagemann, S.G., Robert, F., 1998. Orogenic gold deposits—a proposed classification in the context of their crustal distribution and relationship to other gold deposit types. Ore Geol. Rev. 13, 7–27. https://doi.org/10.1016/S0169-1368(97)00012-7.

Gu, Y., 2003. Automated scanning electron microscope based mineral liberation analysis an introduction to JKMRC/FEI Mineral Liberation Analyser. J. Miner. Mater. Charact. Eng. 02, 33–41. https://doi.org/10.4236/jmmce.2003.21003.

Guo, L., Ping, C.L., Macdonald, R.W., 2007. Mobilization pathways of organic carbon from permafrost to arctic rivers in a changing climate. Geophys. Res. Lett. 34, 1–5. https://doi.org/10.1029/2007GL030689.

Harvey, C.F., Swartz, C.H., Badruzaman, A.B.M., Keon-Blute, N., Yu, W., Ali, M.A., Jay, J., Bechie, R., Niedan, V., Brabander, D., Oates, P.M., Ashfaque, K.N., Islam, S., Hemond, H.F., Ahmed, M.F., 2002. Arsenic mobility and groundwater extraction in Bangladesh. Science 298, 1602–1606.

Hasegawa, H., Rahman, M.A., Kitahara, K., Itaya, Y., Maki, T., Ueda, K., 2010. Seasonal changes of arsenic speciation in lake waters in relation to eutrophication. Sci. Total Environ. 408, 1684–1690. https://doi.org/10.1016/j.scitotenv.2009.11.062.

Hatfield Consulting, 1982. Initial Environmental Evaluation for Giant Yellowknife Mines - Salmita Project. Unpublished report prepared for Giant Yellowknife Mines Ltd., Yellowknife, NT, pp. 1–24.

Henderson, J., 1970. Stratigraphy of the Yellowknife Supergroup, Yellowknife Bay - Prosperous Lake Area, District of MacKenzie. https://doi.org/10.4095/100647.

Hollibaugh, J.T., Carini, S., Gürleyük, H., Jellison, R., Joye, S.B., LeCleir, G., Meile, C., Vasquez, L., Wallschläger, D., 2005. Arsenic speciation in Mono Lake, California: response to seasonal stratification and anoxia. Geochim. Cosmochim. Acta 69, 1925–1937. https://doi.org/10.1016/j.gca.2004.10.011.

Houben, A.J., D'Onofrio, R., Kokelj, S.V., Blais, J.M., 2016. Factors affecting elevated arsenic and methyl mercury concentrations in small shield lakes surrounding gold mines near the Yellowknife, NT, (Canada) Region. PLoS One 11. https://doi.org/10.1371/journal.pone.0150960.

INAC, 2005. Tundra Mine, NWT Environmental Monitoring Program: Water Quality Part D: 2005 Results. Prepared for: Contaminants and Remediation Directorate. Indian and Northern Affairs Canada. http://registry.mvlwb.ca/Documents/MV2005X0031/PartD-WaterQualityMon-Nov05.pdf.

INAC, 2008. Tundra Mine, NWT Environmental Monitoring Program: Water Quality Part F: 2007 Results. Contaminants and Remediation Directorate. Indian and Northern Affairs Canada. http://registry.mvlwb.ca/Documents/MV2005L8-0014/2007- Part F - Water Quality Monitoring Program (Mar_08).pdf.

Islam, F.S., Gault, A.G., Boothman, C., Polya, D.A., Charnock, J.M., Chatterjee, D., Lloyd, J., 2004. Role of metal-reducing bacteria in arsenic release from Bengal Delta sediments. Nature 430, 68–71.

Jamieson, H.E., Maitland, K.M., Oliver, J.T., Palmer, M.J., 2017. Regional Distribution of Arsenic in Near-Surface Soils in the Yellowknife Area. NWT Open File 2017-03.

Jeong, H.Y., Han, Y.S., Park, S.W., Hayes, K.F., 2010. Aerobic oxidation of mackinawite (FeS) and its environmental implication for arsenic mobilization. Geochim. Cosmochim. Acta 74, 3182–3198. https://doi.org/10.1016/j.gca.2010.03.012.

Jiang, S., Liu, X., Chen, Q., 2011. Distribution of total mercury and methylmercury in lake sediments in Arctic Ny-Ålesund. Chemosphere 83, 1108–1116. https://doi.org/10.1016/j.chemosphere.2011.01.031.

Juggins, S., 2017. Analysis of Quaternary Science Data, Package ' Rioja. http://cran.r-project.org/package= rioja.

Kirk, M.F., Holm, T.R., Park, J., Jin, Q., Sanford, R.A., Fouke, B.W., Bethke, C.M., 2004. Bacterial sulfate reduction limits natural arsenic contamination in groundwater. Geology 32, 953–956.

Langner, P., Mikutta, C., Kretzschmar, R., 2011. Arsenic sequestration by organic sulphur in peat. Nat. Geosci. 5, 66–73. https://doi.org/10.1038/ngeo1329.

Livingstone, I., Warren, A., 1996. Aeolian Geomorphology: an Introduction. Longman, Harlow, pp. 1–63.

Lorax Environmental, 2007. Tundra Mine Geochemical Assessment. Pp. 1 – 105. (Internal report).

Lowers, H.A., Breit, G.N., Foster, A.L., Whitney, J., Yount, J., Uddin, Md N., Muneem, Ad A., 2007. Arsenic incorporation into authigenic pyrite, Bengal Basin sediment, Bangladesh. Geochim. Cosmochim. Acto 71 (11), 2699–2717. https://doi.org/10.1016/j.gca.2007.03.022.

Lynch, J., 1990. Provisional elemental values for eight new lake sediment and stream sediment reference materials LKSD-1, LKSD-2, LKSD-3, LKSD-4, STSD-1, STSD-2, STSD-3 and STSD-4. Geostand. Newsl. 14, 153–167. https://doi.org/10.1111/j.1751-908X.1990.tb00070.x.

Macdonald, R., Harner, T., Fyfe, J., 2005. Recent climate change in the Arctic and its impact on contaminant pathways and interpretation of temporal trend data. Sci. Total Environ. 342, 5–86. https://doi.org/10.1016/j.scitotenv.2004.12.059.

Macumber, A.L., Patterson, R.T., Neville, L.A., Falck, H., 2011. A sledge microtome for high resolution subsampling of freeze cores. J. Paleolimnol. 45, 307–310. https://doi.org/10.1007/s10933-010-9487-4.

Macumber, A.L., 2015. Grain-size Analysis and Arcellinida as Tools for Inferring Paleoclimatological Variability : a Case Study from Holocene Canadian Subarctic Lake Sediments. PhD. Thesis. Carleton University. https://curve.carleton.ca/system/files/etd/622aaee1-0a90-4077-bdf7-838298d14c0e/etd_pdf/083ece3a2a5ee991a0e74ef0fa67858e/macumber-grainsizeanalysisandarcellinidaastoolsfor.pdf.

Martin, A.J., Pedersen, T.F., 2002. Seasonal and interannual mobility of arsenic in a lake impacted by metal mining. Environ. Sci. Technol. 36, 1516–1523. https://doi.org/10.1021/es0108537.

McGlynn, J., Henderson, J., 1970. Archean volcanism and sedimentation in the Slave structural Province. In: Symposium on Basins and Geosynclines of the Canadian Shield. Geological Survey of Canada, pp. 31–44. https://doi.org/10.4095/119840.

McGuire, A.D., Anderson, L.G., Christensen, T.R., Dallimore, S., Guo, L., Hayes, D.J., Heimann, M., Lorenson, T.D., Macdonald, R.W., Roulet, N., 2009. Sensitivity of the carbon cycle in the Arctic to climate change. Ecol. Monogr. 79, 523–555. https://doi.org/10.1890/08-2025.1.

Moore, J.C.G., 1951. Courageous Lake; Geological Survey of Canada Paper 51-14. Available from: https://doi.org/10.4095/108378.

Moore, J.W., 1978. Biological and Water Quality Surveys at Potential Mines in the Northwest Territories. III. Salmita Gold Property, Mathews Lake. Environment Canada, Environmental Protection Service, Manuscr. Obtained from DFO Library, Yellowknife, NT Rep. NW-78-7: 24 p. + Appendices.

Moore, J.N., Ficklin, W.H., Johns, C., 1988. Partitioning of arsenic and metals in reducing sulfidic sediments. Environ. Sci. Technol. 22, 432–437. https://doi.org/10.1021/es00169a011.

Mudroch, A., Joshi, S.R., Sutherland, D., Mudroch, P., Dickson, K.M., 1989. Geochemistry of sediments in the back bay and Yellowknife Bay of the Great Slave lake. Environ. Geol. Water Sci. 14, 35–42. https://doi.org/10.1007/BF01740583.

Murray, M., 2002. Is laser particle size determination possible for carbonate rich lake sediments? J. Paleolimnol. 27, 173–183.

Nickson, R.T., Mcarthur, J.M., Ravenscroft, P., Burgess, W.G., Ahmed, K.M., 2000. Mechanism of arsenic release to groundwater, Bangladesh and West Bengal. Appl. Geochem. 15, 403–413. https://doi.org/10.1016/S0883-2927(99)00086-4.

Nordstrom, D.K., Archer, D.G., 2003. In: Welch, A.H., Stollenwerk, K.G. (Eds.), Arsenic in Goundwater, pp. 1–25 Kluwer, Boston.

O'Day, P.A., Vlassopoulos, D., Root, R., Rivera, N., 2004. The influence of sulfur and iron on dissolved arsenic concentrations in the shallow subsurface under changing redox conditions. Proc. Natl. Acad. Sci. U. S. A. 101, 13703–13708. https://doi.org/10.1073/pnas.0402775101.

Outridge, P., Sanei, H., Goodarzi, F., 2007. Evidence for control of mercury accumulation rates in Canadian high arctic lake sediments by variations of aquatic primary productivity. Environ. Sci. Technol. 41, 5259–5265. https://doi.org/10.1021/es070408x.

Outridge, P.M., Sanei, H., Stern, G.A., Goodsite, M., Hamilton, P.B., Carrie, J., Goodarzi, F., Macdonald, R.W., 2011. Response to comment on climate change and mercury accumulation in Canadian high and subarctic lakes. Environ. Sci. Technol. 45, 6705–6706. https://doi.org/10.1007/s10533-010-9543-1.(8.

Outridge, P.M., Sanei, H., Courtney Mustaphi, C.J., Gajewski, K., 2017. Holocene climate change influences on trace metal and organic matter geochemistry in the sediments of an Arctic lake over 7,000 years. Appl. Geochem. 78, 35–48. https://doi.org/10.1016/j.apgeochem.2016.11.018.

Palmer, M.J., Galloway, J.M., Jamieson, H.E., Patterson, R.T., Falck, H., Kokelj, S.V., 2015. The concentration of arsenic in lake waters of the Yellowknife area. NWT Open File 2015-06 29. Available from: https://doi.org/10.13140/RG.2.1.2582.5041.

Palmer, M.J., Chételat, J., Richardson, M., Jamieson, H.E., Galloway, J.M., 2019. Seasonal variation of arsenic and antimony in surface waters of small subarctic lakes impacted by legacy mining pollution near Yellowknife, NT, Canada. Sci. Total Environ. 684, 326–339. https://doi.org/10.1016/j.scitotenv.2019.05.258.

Parsons, M.B., LeBlanc, K.W.G., Hall, G.E.M., Sangster, A.L., Vaive, J.,E., Pelchat, P., 2012. Environmental Geochemistry of Tailings, Sediments and Surface Waters Collected from 14 Historical Gold Mining Districts in Nova Scotia. Geological Survey of Canada Open File 7150. https://doi.org/10.4095/291923.

Parsons, M.B., Jamieson, H.E., Miller, C.B., Galloway, J.M., 2019. Choosing an appropriate digestion protocol for environmental risk assessments of mineralized earth materials. Geol. Surv. Can. Sci. Present. 97, 1. https://doi.org/10.4095/314499.

Petavratzi, E., Kingman, S., Lowndes, I., 2005. Particulates from mining operations: a review of sources, effects and regulations. Miner. Eng. 18, 1183–1199. https://doi.org/10.1016/j.mineng.2005.06.017.

Planer-Friedrich, B., Wallschläger, D., 2009. A critical investigation of hydride generation-based arsenic speciation in sulfidic waters. Environ. Sci. Technol. 43, 5007–5013. https://doi.org/10.1021/es900111z.

Prowse, T., Alfredsen, K., Beltaos, S., Bonsal, B., Duguay, C., Korhola, A., McNamara, J., Pienitz, R., Vincent, W.F., Vuglinsky, V., Weyhenmeyer, G.A., 2011. Past and future changes in arctic lake and river ice. Ambio 40, 53–62. https://doi.org/10.1007/s13280-011-0216-7.

PS Analytical, 2018. Available from: https://www.psanalytical.com/.

R Core Team, 2014. R: A Language and Environment for Statistical Computing. Available from: http://www.r-project.org.

Ransom, A., Robb, M., 1986. The Salmita gold deposit, Courageous Lake, Northwest Territories. In: In: Clark, L.A., Francis, D.R. (Eds.), Gold in the Western Shield, vol 38. Can. Inst. Min. Met., pp. 285–305.

Redman, A.D., Macalady, D.L., Ahmann, D., 2002. Natural organic matter affects Arsenic speciation and sorption onto hematite. Environ. Sci. Technol. 36, 2889–2896. https://doi.org/10.1021/es0112801.

Reimann, C., Filzmoser, P., Garrett, R., Dutter, R., 2008. Statistical Data Analysis Explained: Applied Environmental Statistics with R. John Wiley & Sons, Ltd.

Rickard, D., Luther, G.W., 1997. Kinetics of pyrite formation by the H_2S oxidation of iron (II) monosulfide in aqueous solutions between 25 and 125 degrees C: the mechanism. Geochim. Cosmochim. Acta 61, 135–147. https://doi.org/10.1016/S0016-7037(96)00321-3.

Ritter, K., Aiken, G.R., Ranville, J.F., Bauer, M., Macalady, D.L., 2006. Evidence for the aquatic binding of arsenate by natural organic matter-suspended Fe(III). Environ. Sci. Technol. 40, 5380–5387. https://doi.org/10.1021/es0519334.

Rydberg, J., Klaminder, J., Rosén, P., Bindler, R., 2010. Climate driven release of carbon and mercury from permafrost mires increases mercury loading to sub-arctic lakes. Sci. Total Environ. 408, 4778–4783. https://doi.org/10.1016/j.scitotenv.2010.06.056.

Salminen, R., Tarvainen, T., 1997. The problem of defining geochemical baselines. A case study of selected elements and geological materials in Finland. J. Geochem. Explor. 60, 91–98. https://doi.org/10.1016/S0375-6742(97)00028-9.

Sanei, H., Stasiuk, L.D., Goodarzi, F., 2005. Petrological changes occurring in organic matter from recent lacustrine sediments during thermal alteration by Rock-Eval pyrolysis. Org. Geochem. 36, 1190–1203. http://doi.org/10.1016/j.orggeochem.2005.02.009.

Sanei, H., Goodarzi, F., 2006. Relationship between organic matter and mercury in recent lake sediment: the physical–geochemical aspects. Appl. Geochem. 21, 1900–1912. http://10.1016/j.apgeochem.2006.08.015.

Sanei, H., Outridge, P.M., Dallimore, A., Hamilton, P.B., 2012. Mercury-organic matter relationships in pre-pollution sediments of thermokarst lakes from the Mackenzie River Delta, Canada: the role of depositional environment. Biogeochemistry 107, 149–164. https://doi.org/10.1007/s10533-010-9543-1.

Schelske, C.L., Peplow, A., Brenner, M., Spencer, C.N., 1994. Low-background gamma counting: applications for ^{210}Pb dating of sediments. J. Paleolimnol. 10, 115–128. https://doi.org/10.1007/BF00682508.

Schuh, C.E., Jamieson, H.E., Palmer, M.J., Martin, A.J., 2018. Solid-phase speciation and post-depositional mobility of arsenic in lake sediments impacted by ore roasting at legacy gold mines in the Yellowknife area, Northwest Territories, Canada. Appl. Geochem. 91, 208–220. https://doi.org/10.1016/j.apgeochem.2017.10.025.

Schuh, C.E., Jamieson, H.E., Palmer, M.J., Martin, A.J., Blais, J.M., 2019. Controls governing the spatial distribution of sediment arsenic concentrations and solid-phase speciation in a lake impacted by legacy mining pollution. Sci. Total Environ. 654, 563–575. https://doi.org/10.1016/j.scitotenv.2018.11.065.

Seabridge Gold Inc., 2010. Courageous Lake Project Description in Support of a Class " A " Land Use Permit (Former Permit MV2003C0050). Seabridge Gold Inc. http://registry.mvlwb.ca/Documents/MV2010C0046/MV2010C0046%20-%20Project%20Description%20-%20Oct06-10.pdf.

SENES Consultants Ltd., 2006. Tundra Mine Site Ecological Risk Assessment of Water Management. SENES Consultants Ltd Available from: http://www.mvlwb.ca/Registry.aspx?a = MV2009L8-0008.

SENES Consultants Ltd., 2008. Remediation Completion Report for Tundra Mine Phase I (2007) Restoration Program Tundra Mine, NT. SENES Consultants Ltd. http://www.mvlwb.ca/Registry.aspx?a = MV2009L8-0008.

SENES Consultants Ltd., 2011. Development of Tundra Mine construction monitoring, long-term monitoring, and status of the environment programs. SENES Consultants Ltd Available from: http://www.mvlwb.ca/Registry.aspx?a = MV2009L8-0008.

Sharma, P., Rolle, M., Kocar, B.D., Fendorf, S., Kappler, A., 2010. Influence of natural organic matter on as transport and retention. Environ. Sci. Technol. 45, 546–553. https://doi.org/10.2134/jeq2003.1393.

Silke, R., 2009. The Operational History of Mines in the Northwest Territories, Canada. Northwest Territories Geoscience Office, pp. 487–500. http://miningnorth.com/_rsc/site-content/library/NWT_Mines_History_RSilke2009.pdf.

Smedley, P.L., Kinniburgh, D.G., 2002. A review of the source, behaviour and distribution of arsenic in natural waters. Appl. Geochem. 17, 517–568. https://doi.org/10.1016/S0883-2927(02)00018-5.

Smol, J.P., Wolfe, A.P., Birks, H.J.B., Douglas, M.S.V., Jones, V.J., Korhola, A., Pienitz, R., Ruhland, K., Sorvari, S., Antoniades, D., Brooks, S.J., Fallu, M.-A., Hughes, M., Keatley, B.E., Laing, T.E., Michelutti, N., Nazarova, L., Nyman, M., Paterson, A.M., Perren, B., Quinlan, R., Rautio, M., Saulnier-Talbot, E., Siitonen, S., Solovieva, N., Weckstrom, J., 2005. Climate-driven regime shifts in the biological communities of arctic lakes. Proc. Natl. Acad. Sci. 102, 4397–4402. https://doi.org/10.1073/pnas.0500245102.

Stern, G.A., Macdonald, R.W., Outridge, P.M., Wilson, S., Chételat, J., Cole, A., Hintelmann, H., Loseto, L.L., Steffen, A., Wang, F., Zdanowicz, C., 2012. How does climate change influence arctic mercury? Sci. Total Environ. 414, 22–42. https://doi.org/10.1016/j.scitotenv.2011.10.039.

Stuckey, J.W., Schaefer, M.V., Kocar, B.D., Benner, S.G., Fendorf, S., 2016. Arsenic release metabolically limited to permanently water-saturated soil in Mekong Delta. Nat. Geosci. 9, 70–76. https://doi.org/10.1038/ngeo2589.

Tetra Tech Wardrop, 2012. Courageous Lake Prefeasibility Study. Tetra Tech Wardrop Available from: https://secure.kaiserresearch.com/i/jk/tr16/TRSEA20120905.pdf.

Thamdrup, B., 2000. Bacterial manganese and iron reduction in aquatic sediments. In: In: Schink, B. (Ed.), Advances in Microbial Ecology. Advances in Microbial Ecology, vol 16 Springer, Boston, MA.

Thompson, P.H., Kerswill, J.A., 1994. Preliminary Geology of the Winter Lake - Lac de Gras Area, District of MacKenzie, Northwest Territories, Open File 2740 (revised), scale 1:250000. Geological Survey of Canada. https://geoscan.nrcan.gc.ca/starweb/geoscan/servlet.starweb?path = geoscan/downloade.web&search1 = R = 194794.

Thornton, I., 1996. Sources and pathways of arsenic in the geochemical environment: health implications. In: Fuge, J.D., McCall, R. (Eds.), Environmental Geochemistry and Health. Geological Society Special Publication No 113, pp. 153–161.

Toevs, G.R., Morra, M.J., Polizzotto, M.L., Strawn, D.G., Bostick, B.C., Fendorf, S., 2006. Metal(loid) diagenesis in mine-impacted sediments of lake Coeur d'Alene, Idaho. Environ. Sci. Technol. 40, 2537–2543. https://doi.org/10.1021/es051781c.

URS, 2005. Geochemical Assessment of Acid Rock Drainage and Metal Leaching Potential of Tailings and Waste Rock, Tundra Mine, NWT. Internal Report.

Van Den Berghe, M.D., Jamieson, H.E., Palmer, M.J., 2018. Arsenic mobility and characterization in lakes impacted by gold ore roasting, Yellowknife, NWT, Canada. Environ. Pollut. 234, 630–641. https://doi.org/10.1016/j.envpol.2017.11.062.

van Hengstum, P.J., Reinhardt, E.G., Boyce, J.I., Clark, C., 2007. Changing sedimentation patterns due to historical land-use change in Frenchman's Bay, Pickering, Canada: evidence from high-resolution textural analysis. J. Paleolimnol. 37, 603–618. https://doi.org/10.1007/s10933-006-9057-y.

Vega, A.S., Planer-Friedrich, B., Pastén, P.A., 2017. Arsenite and arsenate immobilization by preformed and concurrently formed disordered mackinawite (FeS). Chem. Geol. 475, 62–75. https://doi.org/10.1016/j.chemgeo.2017.10.032.

WESA Technologies Inc, 2014. Water Treatment Monitoring and Discharge Plan 2014 (Monitoring Plan: MV2009L8-0008).

Wagemann, R., Snow, N.B., Rosenberg, D.M., Lutz, A., 1978. Arsenic in sediments, water and aquatic biota from lakes in the vicinity of Yellowknife, Northwest Territories, Canada. Arch. Environ. Contam. Toxicol. 7, 169–191. https://doi.org/10.1007/BF02332047.

Wang, S., Mulligan, C.N., 2006. Effect of natural organic matter on arsenic release from soils and sediments into groundwater. Environ. Geochem. Health 28, 197–214. https://doi.org/10.1007/s10653-005-9032-y.

Wang, Y., Le Pape, P., Morin, G., Asta, M.P., King, G., Bártová, B., Suvorova, E., Frutschi, M., Ikogou, M., Pham, V.H.C., Vo, P. Le, Herman, F., Charlet, L., Bernier-Latmani, R., 2018. Arsenic speciation in mekong Delta sediments depends on their depositional environment. Environ. Sci. Technol. 52, 3431–3439. https://doi.org/10.1021/acs.est.7b05177.

Wilkin, R.T., Barnes, H.L., 1997. Formation processes of framboidal pyrite. Geochim. Cosmochim. Acta 61, 323–339. https://doi.org/10.1016/S0016-7037(96)00320-1.