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Organic matter control on the distribution of arsenic in lake sediments impacted by ~65 years of gold ore processing in subarctic Canada

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Abstract

Climate change is profoundly affecting seasonality, biological productivity, and hydrology in high northern latitudes. In sensitive subarctic environments exploitation of mineral resources led to contamination and it is not known how cumulative effects of resource extraction and climate warming will impact ecosystems. Gold mines near Yellowknife, Northwest Territories, subarctic Canada, operated from 1938 to 2004 and released more than 20,000 tonnes of arsenic trioxide (As_2O_3) to the environment through stack emissions. This release resulted in elevated arsenic concentrations in lake surface waters and sediments relative to Canadian drinking water standards and guidelines for the protection of aquatic life. A meta-analytical approach is used to better understand controls on As distribution in lake sediments within a 30-km radius of historic mineral processing activities. Arsenic concentrations in the near-surface sediments range from 5 $mg{\cdot}kg^{-1}$ to over 10,000 $mg{\cdot}kg^{-1}$ (median 81 $mg{\cdot}kg^{-1}$; 5->10,000 $mg{\cdot}kg^{-1}$; n=105). Distance and direction from the historic roaster stack are significantly ($p<0.05$) related to sedimentary As concentration, with highest As concentrations in sediments within 11 km and lakes located downwind. Synchrotron-based µXRF and µXRD confirm the persistence of As_2O_3 in near surface sediments of two lakes. Labile organic matter (S1) is significantly ($p<0.05$) related to As and S concentrations in sediments and this relationship is greatest in lakes within 11 km from the mine. These relations are interpreted to reflect labile organic matter acting as a substrate for microbial growth and mediation of authigenic precipitation of As-sulphides in lakes close to the historic mine where As concentrations are highest. Continued climate warming is expected to lead to increased biological productivity and changes in organic geochemistry of lake sediments that are likely to play an important role in the mobility and fate of As in aquatic ecosystems.

Keywords

Lake sediments, Subarctic, Arsenic, Organic matter, Climate change, Mining

1.0 Introduction

Lakes and wetlands play an important role in the storage and mobilization of arsenic (As) (La Force et al., 2000; Gurung et al., 2005; MacDonald et al., 2005; Du Laing et al., 2009). The mobility and bioavailability of As in the environment is strongly controlled by Fe and Mn oxides and (oxy)hydroxides, sulphides, and organic matter (OM) (La Force et al., 2000; Du Laing et al., 2009; Langner et al., 2012). Interactions between As and these solid phases are in turn mediated by pH and redox conditions (Smedley and Kinniburgh, 2000; Du Laing et al., 2009). Redox conditions in lacustrine settings are influenced by basin morphometry, temperature, OM production and decomposition, and microbial-mediated redox processes within the sediment column (Toevs et al., 2006). Twentieth and twenty-first century global warming has, and is predicted to, result in profound changes to the biogeochemical environment in high northern latitudes through changing hydrology, permafrost, and the length of the ice free season (MacDonald et al., 2005; Spence et al., 2015). These changes may result in increased biological productivity and OM transport to aquatic environments and influence loading, cycling, and stability of metal(loids) (Schindler et al., 1997; Hejzlar et al., 2003; Vonk et al., 2013). The complexity of potential biogeochemical interactions warrants detailed evaluation of the interaction between As and OM in lacustrine settings. Organic matter is a heterogeneous mixture of organic compounds with varying structural and functional properties that influence reactivity in natural environments (Gu et al., 1995; Chen et al., 2002, 2003). These compounds are redox reactive and can mediate the release and redox transformation of solid-phase As(V) at depth in the sediment column to As(III), which can diffuse upward to be released to overlying waters or re-precipitate in oxic sediments (Lovley et al., 1996; Redman et al., 2002; van Geen et al., 2004) and result in substantial surface sediment enrichment of As (Martin and Pedersen, 2002). Interactions between As and OM also include competitive adsorption (Grafe et al., 2001; Redman et al., 2002), stabilization and physical coating of As-bearing colloids (Neubauer et al., 2013), OM and dissolved OM-Fe complexation with As (Langner et al., 2012, 2014) and carbon-limited microbial-mediated precipitation of As-bearing minerals (Kirk et al., 2004). Dissolved OM (e.g., OM<0.45 or 0.22 µm) plays a critical role in controlling As mobility in soils (Kalbitz and Wennrich, 1998; Grafe et al., 2001; Redman et al., 2002; Arai et al., 2006; Dobran and Zagury, 2006), aquifer sediments (Lawson et al., 2016), and stream and wetland sediments (La Force et al., 2000; Beauchemim et al., 2006; Langner et al., 2012, 2014; Al-Sid-Cheikh et al., 2015) but comparatively little is known about the role of kerogen (sedimentary OM>0.45 or 0.22 µm that is solvent-insoluble; Durand, 1980) in element mobility in general (Langner et al., 2012) and in lake sediments in particular (Sanei and Goodarzi, 2006).

The Yellowknife region in subarctic Northwest Territories, Canada, contains geogenic As from hydrothermal gold mineralization in Yellowknife Supergroup rocks and anthropogenic As from historic gold ore processing activities that resulted in a release of over 20,000 tonnes of arsenic trioxide (As_2O_3) to the environment (Suppl. 1; Hocking et al., 1978). Historical release of As_2O_3 caused elevated concentrations of As in lake waters and sediments within ~20 km of the largest historic mine in the area relative to lakes outside of this range (Galloway et al., 2015; Palmer et al., 2015; Houben et al., 2016). To provide insight into the physical and chemical parameters affecting the mobility of As and to better understand the cumulative effects of past anthropogenic activities and current and forecasted climate change possible physical (distance and direction from historic mining activity, lake connectivity, lake order, lake size) and chemical (organic matter, other elements) controls on the distribution of As in lake sediments within a 30 km radius of a historic mine roaster stack are assessed.

2.0 Study area

The City of Yellowknife and surrounding area is located in the southwestern Slave Geological Province, District of Mackenzie (Fig. 1). Elevation in the region rises gradually from 157 m above sea level (MASL) near Great Slave Lake to approximately 400 MASL north of 63° latitude. The Yellowknife River is the main drainage for the area and its southern outlet flows into Yellowknife Bay, Great Slave Lake. Many lakes east of Yellowknife lie within the Cameron River-Prelude Lake watershed. The study area lies south of the treeline and spans the Great Slave Lake Lowland and Great Slave Lake Upland ecoregions of the Taiga Shield Ecozone (Ecosystem Classification Group, 2007). The climate has a mean summer temperature of 11°C and a mean winter temperature of -21.5°C (mean annual temperature ranges from -3.5 to -9 °C). Mean annual precipitation ranges between 200 and 375 mm. Vegetation is composed of a mosaic of closed stands of trembling aspen, balsam poplar, paper birch, jack pine, and white and black spruce Poorly drained fens and bogs are common and often covered with open stands of larch and black spruce.

Detailed information on the main bedrock elements of the Slave Geological Province and their structural evolution are summarized in Villeneuve et al. (1997), Villeneuve and Relf (1998), Yamashita and Creaser (1999), Yamashita et al. (1999), Bleeker and Davis (1999), Cousens (2000), Kjarsgaard et al. (2002), and Cousens et al. (2002). Major gold deposits of the area are hosted in Yellowknife Supergroup rocks dominated by 2.71-2.65 Ga mafic meta-volcanics that trend north-south. East of the City of Yellowknife Archean meta-sedimentary rocks dominate and consist of greywacke, slate, schist, and phyllite. West of Yellowknife, granitoid intrusions, consisting of granite, granodiorite, and tonalite, compose the majority of the bedrock. The region is crosscut by early Proterozoic diabase and gabbro dykes and several major faults, such as the Kam Lake Fault and the West Bay Fault that run through the City of Yellowknife, separating the volcanic rocks from younger granitoids (Yamashita and Creaser, 1999; Yamashita et al., 1999; Cousens, 2000; Cousens et al., 2002). Arsenic concentrations in local bedrock are comparable to global crustal averages for granitoid, meta-sedimentary, and basic and ultrabasic igneous rocks (Turekian and Wedepohl, 1961; Koljonen, 1992; Smedley and Kinniburgh, 2002); ranging from ~2 $mg \cdot kg^{-1}$ for granitoids to 33 $mg \cdot kg^{-1}$ in meta-volcanics and up to 90 $mg \cdot kg^{-1}$ in mineralized rocks (Boyle, 1960; Yamashita and Creaser, 1999; Yamashita et al., 1999; Cousens, 2000; Cousens et al., 2002; Ootes, 2004; Ootes et al., 2006; Kerr and Wilson, 2006). The surficial geology of the Yellowknife region is dominated by a mosaic of Glacial Lake McConnell sediments and glacial tills that infill the topographic lows of the abundant bedrock outcrops (Dyke and Prest, 1987; Smith, 1994; Kerr and Wilson, 2000; Wolfe et al., 2014). Accumulations of Holocene-aged peat also occur in the study area (Kerr and Wilson, 2000). Tills in the Yellowknife region can contain As concentrations up to 1560 $mg \cdot kg^{-1}$ within in situ weathered material over mineralized zones, although typically As concentrations are between 5 to 30 $mg \cdot kg^{-1}$ (Kerr, 2006). The As concentrations in glaciofluvial, glaciolacustrine, and peat deposits in the region are not published.

3.0 Methods

To assess the spatial distribution of arsenic in near-surface lake sediments in the Yellowknife area 105 near-surface sediment samples were collected from 100 lakes within a 30 km radius of

Yellowknife (Fig. 1). Sites were accessed during summer and fall between 2009 and 2014 by canoe and helicopter. To test the influence of physical and hydrological properties of the lakes on near-surface sediment geochemistry, sampled lakes span a range of sizes and connectivity (Suppl. 2). Lake area and order were calculated using the digital 1:50,000 National Topographic Database (NTDB) in ArcMap (v.10). Lake connectivity was assessed using a combination of the 1:50,000 NTDB, Google Earth^{TM}, and field observations. Sixty-eight lakes occur in catchments predominantly underlain by granitoid bedrock, the majority of which belong to the Defeat Plutonic Suite undifferentiated granitoids that occur W and SE of the City of Yellowknife. Twenty-nine lakes occur on metasedimentary bedrock of the Burwash Formation that lies west of Yellowknife, and 8 lakes occur on volcanic bedrock (Suppl. 2).

Near-surface sediment samples were collected using an Ekman Grab sampler. The top 2 to 5 cm of sediment was sub-sampled for analyses. Samples were kept cool in the field and during shipping to Carleton University where they were kept cold at 4 °C until analyses. Surface water chemistry of 98 of the lakes sampled are published in Palmer et al. (2015).

3.1 Sediment textural, organic, and elemental geochemical characterization

Sedimentary grain size was determined using a Beckman Coulter LS 13 320 laser diffraction particle size analyzer fitted with a universal liquid module and a measurement range between 0.37 and 2000 μm. Hydrogen peroxide (30%) was added to sub-samples in an 80 ^{o}C water bath to oxidize organic matter prior to analysis (Murray, 2002; van Hengstum et al., 2007). The samples were loaded into the instrument until an obscuration level of 10 ± 3% was attained. Summary statistics were compiled using GRADISTAT (Version 8; Blott and Pye, 2001). Two reference materials were used: an accuracy standard provided by Beckman Coulter (Garnet15:

mean diameter 15 µm) run once per month and an in-house mud sample (Cushendun Mud) as a precision control run at the beginning of every session.

Rock-Eval® 6 pyrolysis was used to analyze organic constituents of the sediments (Vinci Technologies, Rueil-Malmaison, France; Lafargue et al., 1998). The Rock-Eval® 6 instrument pyrolyses organic matter under an inert (N_2) atmosphere and oxidizes organic matter by programmed temperature heating of bulk sediments (~20 mg; heating rate of 25 °C/min). Rock-Eval® 6 pyrolysis measures the quantity of labile, readily degradable hydrocarbon devolatilized at 300 °C (S1, mg hydrocarbon/g), the hydrogen-rich, higher molecular weight kerogen-derived hydrocarbon released by thermal cracking of organic matter at 650 °C (S2, mg hydrocarbon/g), the amount of carbon dioxide released during pyrolysis of kerogen (S3, mg hydrocarbon/g), and refractory, residual carbon (RC wt. %) measured by automated transferal to an oxidation oven and heated from 400 °C to 850 °C. Total Organic Carbon (TOC; wt.%) represents the quantity of all organic matter released during pyrolysis and oxidation heating. S1, S2, and S3 were converted to weight % by multiplying by 0.083 (Sanei and Goodarzi, 2006). Analyses of standard reference materials (IFP 160000, Institut Français du Pétrole and internal 9107 shale standard, Geological Survey of Canada, Calgary; Ardakani et al., 2016) was run every 5th sample and shows accuracy and precision to be better than 5% relative standard deviation.

In near-surface sediments, the S1 fraction mainly consists of readily degradable geolipids and pigments predominantly derived from autochthonous OM (e.g., algal-derived lipids; Carrie et al., 2012). Operational definition of organic lipids is the fraction of organic matter isolated from biological material by extraction with organic solvents (Meyers and Ishiwatari, 1993). Geolipids are diagenetically derived from biological lipids that undergo degradative alteration as the algae sinks to the bottom of lakes and after sedimentation when molecular composition is modified to various degrees depending on the composition of the parent lipid (Meyers and Ishiwatari, 1993).

S2 compounds in near-surface sediment are derived from the highly aliphatic biomacromolecule structure of algal cell walls and other aquatic biological matter (Sanei et al., 2005; Carrie et al., 2012). The S3 portion of organic matter is dominated by carbohydrates, lignins, and terrigenous plant materials (Carrie et al., 2012). Humic and fulvic acids are also represented in the S3 fraction (Albrecht et al., 2015).

Sediment sub-samples were submitted to Acme Analytical Laboratories (Bureau Veritas), Vancouver, for geochemical analyses. Sub-samples were freeze dried and screened to <180 µm (-80 mesh ASTM) at the laboratory. Concentrations of elements in sediment samples were determined by inductively coupled plasma-mass spectrometry (ICP-MS) (ICP-MS 1F/AQ250 package) following digestion by a modified aqua regia treatment (0.50 g of sample digested in a solution of 2.0 mL HCl, 2.0 mL HNO_3 and 2.0 mL H_2O at 95 ºC for one hour) with the exception of phosphorus, which was extracted using $NaHCO_3$. Partial digestion with aqua regia was used to extract metal(loid)s that could become bioavailable and because complete digestion methods that involve high-temperature fuming can volatilize As and Sb, both contaminants of potential concern in this study (Parsons et al., 2012). Three pulp duplicates were analyzed to assess analytical precision. Relative Percent Difference (RPD) ranges from 1.5% to 4.3% for As. Standard reference materials (STD OREAS45EA n=11; STD D10 n=2; STD DS9 n=9) were used assess analytical accuracy. For STD OREAS45EA mean measured As concentration is 9.7 $mg{\cdot}kg^{-1}$ ± 1.16 (n=11) vs. an expected concentration of 10.3 $mg{\cdot}kg^{-1}$ for As following aqua regia digestion. Mean RPD between As concentrations measured in STD OREAS45EA vs. the expected value is 6.9% ± 11.9. STD DS10 had a mean measured As concentration of 45.6 $mg{\cdot}kg^{-1}$ ± 0.1 (n=2) vs. an expected concentration of 46.2 $mg{\cdot}kg^{-1}$ (mean RPD of 1.3% ± 0.3). STD DS9 had a mean measured As concentration of 27.4 $mg{\cdot}kg^{-1}$ ± 1.42 (n=9) vs. an expected concentration of 25.5 $mg{\cdot}kg^{-1}$ (mean RPD of 7.8% ± 4.0). Eleven laboratory methods blanks were analyzed. Arsenic is undetectable

(<0.1 mg·kg^{-1}) in n=9 laboratory blanks. Two blanks had measured concentrations of As of 0.2 mg·kg^{-1} and 0.1 mg·kg^{-1}.

3.2 Arsenic mineralogy

Several mineral forms of As are expected to be present in near-surface lake sediments of the Yellowknife area. These are arsenopyrite (FeAsS) containing up to 46 wt.% As, arsenic sulphides (e.g., realgar (As_4S_4) and arsenian pyrite (FeS_2)) that contain up to 70 wt.% As, and iron oxyhydroxides (e.g., goethite, ferrihydrite) containing up to 4 wt.% As (Walker et al., 2005). These minerals are geogenic or authigenic in origin. Iron oxides (hematite, magnetite, maghemite) containing up to 7 wt.% As (Schuh et al., 2017) and As_2O_3 containing up to 76 wt.% As are anthropogenic in origin and emitted directly from the roaster stack (Bromstad et al., 2017). Arsenopyrite in sediments of lakes away from tailings and waste rock is expected to be geogenic and unrelated to mining and mineral processing. The iron oxyhydroxides, realgar, and some pyrite, particularly framboidal pyrite, likely form in situ in sediments and can be therefore described as authigenic although the As, and possibly S, may originate from the deposition of stack emissions of As_2O_3 and SO_x (Schuh et al., 2017).

Near-surface lake sediment samples (L14S3, L19S2, BC-2, BC-13, BC-17, BC-19, BC-32, BC-47) within ~20 km of the historic Giant Mine roaster were selected based on total As concentration (>100 mg·kg^{-1}) for identification of mineral forms of As using Scanning Electron Microscopy (SEM) (Galloway et al., 2012, 2015; Howell, 2014; Fig. 1; Suppl. 2). Three additional near-surface lake sediment samples were analyzed as controls; one from a lake 15.6 km west of the historic Giant Mine roaster (L16S3; 62.6905°N, -114.6642°W) and two from lakes located distal to Giant Mine along the Tibbitt to Contwoyto Winter Road (R11-14-11, 65.0642°N, -

109.9141°W, ~372.4 km NE of the historic roaster; R11-15-05, 63.1354°N, -113.2303°W, ~109.5 km NE of the historic roaster; Macumber et al., 2011; Galloway et al., 2012, 2015).

Sediment sub-samples were dried and doubly-polished thin sections, 35-50 µm thick, were prepared by Vancouver Petrographics. Samples were designed to be "liftable" so that synchrotron-based µXRD would be possible. Two samples with high As concentrations (BC-13 and BC-17; 740.7 ppm and 4778.2 ppm, respectively, Suppl. 2) and one sample with a lower concentration of As (L16S3; 155 pm by ICP-OES and aqua regia digestion; Galloway et al., 2012) were carbon coated for Mineral Liberation Analysis (MLA). Mineral Liberation Analysis allows for automated scanning of thousands of particles to more efficiently locate and analyze rare As-bearing minerals (Sylvester, 2012; Van Den Berghe, 2016). Thin sections were examined using the MLA 650 FEG ESEM (Environmental Scanning Electron Microscope) at Queen's University, Kingston, Ontario, to observe As-bearing minerals. Samples were analyzed using a voltage of 25 kV, chamber pressure of 0.6 Torr, and a spot size of 5.00-5.78 µm. Operating conditions used during MLA analysis were set to 25 kV for the accelerating voltage and 5.78 µm for the spot size. Mineral Liberation Analysis (MLA) was used to locate rare As-oxide phases in two of the samples (BC-13, BC-17; Howell, 2014).

Samples BC-13 and BC-32 were selected for synchrotron-based microanalysis due to the presence of As-oxide in BC-13 as determined using MLA, and because of relatively high As concentrations in sample BC-32 (955.1 ppm; Suppl. 2). The thin sections used for synchrotron-based microanalysis were soaked in HPLC-grade acetone to dissolve the cyanoacrylate holding the polished section to the glass slide. Once detached, the polished sections were placed on polyimide (Kapton) tape. Synchrotron-based µXRF and µXRD were performed at the X26-A beamline at the National Synchrotron Light Source, Brookhaven National Laboratories, New York. A beam energy of 13.5 KeV was used for µXRF to excite elements of interest (K- and L-edge emissions). Beam spot size was approximately 6 x 9 µm. µXRF maps were produced with a step (pixel) size of 3 to 7 µm and a dwell time of 0.1 seconds/pixel. µXRD analyses were done at 17.479 KeV to enable a suitable 2-theta range to identify most minerals. Background diffraction patterns from analyses of the polyimide tape were subtracted, significant bright spots from macro-crystallinity were masked out, and the final 2-D diffraction pattern of the targeted minerals was integrated and converted to 1-D spectra using the computer program Fit2D™ (Hammersley, 2004). The spectra were then compared to mineralogical phases using the peak-matching software X-Pert HighScore Plus (PANalytical). Five As oxide grains located in BC-13 and BC-32 were analyzed using synchrotron-based µXRF to produce an elemental map to identify targets for µXRD. Two grains, 1 from each sample, were suitable for synchrotron-based µXRD (Stavinga, 2014).

3.3 Statistical analyses

Elements with concentration below detection in 35% or more of the samples were removed from statistical analyses (B, Te, Ge, In, Re, Pd, Pt). One half of the method detection limit (MDL) was used for element concentrations below the MDL (W, Hg, Se, Hf, Sn had 5, 2, 2, 16, and 10 % non-detects, respectively). While substituting ½ of the MDL for non-detects can result in loss of information (e.g., Helsel, 2006), this effect is minimized if the proportion of non-detects is low (e.g., 10-15%; e.g., Lubin et al., 2004) and is thus a commonly used method (e.g., RCRA, 1992, 2002). Where element concentration exceeded MDL, we used the upper MDL in statistical analyses. This case only occurred for As in sample BC-19 (As MDL = 10,000 $mg{\cdot}kg^{-1}$).
Statistical analyses are conducted on raw data. Geochemical data are not normalized because grain size variation is low (e.g., CV_{silt}=7.87%; Reimann and de Caritat, 2005) and is not related to As concentration (e.g., clay; Suppl. 3).

Principal Components Analysis was used to explore the chemical and ordinal dataset following log-transformation of numerical data. Potential control variables (grain size, Rock Eval pyrolysis parameters, lake area, and distance from the historic roaster) were fitted to the solution post-hoc using the Envfit procedure with 999 permutations. Permutational Multivariate Analysis of Variance (PERMANOVA) was used to test the homogeneity of multivariate dispersions within groups and thus evaluate which possible controls are important for explaining differences in the multivariate dataset. Samples were tested for normality using the Anderson-Darling normality test alongside plotting on a normal probability plot. Arsenic concentrations are highly non-normally distributed. Spearman's rank correlation analysis was used to explore the relationship between sedimentary As concentration and other variables. Distance from the historic mine has one of the strongest relationships with sedimentary As concentration (r_s=-0.57, $p<0.05$, n=105) and was further evaluated using log-transformed linear regression modelling. To remove the influence of distance and explore the relationship of the other variables with As concentration, two sub-populations of samples were determined using distance-constrained paired group hierarchical cluster analysis based on sedimentary As concentration. The two sub-populations, those within 11 km from the historic roaster stack and those beyond this distance have non-identical As concentrations (Kruskal-Wallis test H=7.29, $p<0.05$, n=105). Spearman's rank correlation analysis was again performed on the two sub-populations to explore the relationship of chemical and other ordinal variables with sedimentary As concentration. Direction from the historic roaster stack (circular data) cannot be analyzed by standard statistical methods. These data were binned into eight categories (0-45, 46-90, 91-135, 136-180, 181-225, 226-270, 271-315, 316-360°). Median As concentrations in each category were compared using the Kruskal-Wallis test and box plots. All analyses were performed in R v.3.1.2 (R Core Team, 2014) and PAST v. 3.11 (Hammer et al., 2001). The vegan package in R was also used for multivariate analysis (Oksanen et al., 2013).

4.0 Results

The area of each of the 100 lakes sampled range between 0.3 to 3561.0 ha (median 30.3 ha, n=105). Median sample site distance from the historic Giant Mine roaster stack is 10.3 km (range, 1.0 to 31.4 km, n=105). Surface waters are circum-neutral (median pH = 7.9, range 6.6-9.0, n=104) and well oxygenated (median dissolved oxygen surface 11.2 mg/L, range 1.7-14.2 mg/L, n=103). Only one site had surface water oxygen <3.0 mg/L. Bottom waters range from dysoxic to oxic (median dissolved oxygen 10.4 mg/L, range 0.1-13.9 mg/L, n=73) and seven lakes are dysoxic (bottom water oxygen <3.0 mg/L) during the open water season. Surface water conductivity ranges from 31.3-626.0 µS/cm (median 124.8 µS/cm, n=103) and bottom water conductivity ranges from 31.3-626.0 µS/cm (median 91.1 µS/cm, n=73). Median water depth at sampling locations was 1.6 m (range 0.3-13.3 m, n=102; Suppl. 2).

4.1 Sediment characteristics

Lake sediment samples are dominated by silt sized particles (<63 µm; median 74.77%, range 4.92% to 90.32%, n=105). Median clay (<4 µm) content of samples is 13.13% (range 1.40% to 35.55%) and median sand (>63 µm) content of samples is 9.98% (range 0.00% to 93.68%) (Suppl. 2).

The samples have total organic carbon (TOC) content typical of lake sediments (median 24.86%, range 1.15% to 33.39%, n=105). The majority of organic matter in sediment samples is

S2 kerogen (median 7.38 wt.%, range 0.20-11.26 wt.%). S3 kerogen ranges from 0.17-4.68 wt.% (median 2.91 wt.%) and S1 kerogen ranges from 0.03-5.52 wt.% (median 2.33 wt.%) (Suppl. 2).

4.2 Arsenic concentration

Arsenic concentration in the lake sediment samples is highly variable, ranging from 5.0 $mg{\cdot}kg^{-1}$ to >10,000 $mg{\cdot}kg^{-1}$ (median 81.2 $mg{\cdot}kg^{-1}$, n=105; Suppl. 2). Median As concentration in the sediments is above the Canadian Council of the Ministers of the Environment (CCME) Probable Effects Level (PEL) of 17 $mg{\cdot}kg^{-1}$ (CCME, 2002) and regional background concentrations of ~25 $mg{\cdot}kg^{-1}$ for As in lake sediments of the Yellowknife area (Galloway et al., 2015).

4.4 Assessing controls on the distribution of arsenic in lake sediments

Principal Components Analysis reveals an association of As with both Au and Sb in the lake sediments (Fig. 2). PERMANOVA analysis shows that the lithology of the catchment bedrock is important for explaining differences in the overall multivariate chemical dataset ($p<0.04$).

The relationship of As to other elements, bedrock type, sedimentary particle size, organic matter, and physical characteristics (e.g., lake area, connectivity) was explored using Spearman's Rank correlation analysis to determine the association and potential influence of these variables on the concentration of As in the lake sediments. In order of decreasing importance, these are S1, bedrock type, S3, S2, silt, and TOC ($p<0.05$, n=105; Suppl. 3). Arsenic is highly positively ($r_s \geq 0.50$) and significantly ($p<0.05$) correlated to other elements enriched in the ore mined at Giant Mine, including Sb, Au, Cd, Mo, and S. The relationship between As and all of the other ordinal variables, including lake order, hydrology, area, connectivity, and Strahler stream order and catchment type are non-significant (Suppl. 3).

Ordinary least squares regression on log-transformed data was used to model the relationship between the concentrations of sedimentary As and distance from the historic Giant Mine roaster and S1, the two non-element geochemical variables with the highest relationship to sedimentary As concentration, for all lakes. Sedimentary As concentration is significantly negatively related to distance from the historic mine ($r^2=0.35$, $p<0.001$, $n=105$) and positively related to S1 ($r^2=0.25$, $p<0.001$, $n=105$; Suppl. 3, 4).

Sedimentary As concentrations decline with increasing distance from the historic mine (Suppl. 4). To remove the influence of distance on sedimentary As concentration and explore other relationships, distance-constrained paired group hierarchical cluster analysis was used to delineate two sub-populations of lakes based on sedimentary As concentration (Suppl. 5). We selected 11 km as a cut-off based on cluster analysis results and sample size consideration in sub-populations for further statistical analyses. Arsenic concentrations of sediment samples from lakes within 11 km of the historic mine are significantly greater (median 160.5 $mg{\cdot}kg^{-1}$, 5.0-10,000 $mg{\cdot}kg^{-1}$, $n=54$) than those in samples from lakes beyond this distance ($n=51$) (39.6 $mg{\cdot}kg^{-1}$, 5.0-5.2 $mg{\cdot}kg^{-1}$, $n=51$; Kruskal-Wallis test $H=7.29$, $p<0.05$, $n=105$; Fig. 3).

Spearman rank correlation analysis on the two sub-populations show that similar to the whole dataset, Au and Sb remain correlated ($p<0.05$) to As concentration in sediments from lakes within 11 km from the historic roaster and in lakes beyond this distance. S1 and As are also significantly ($p<0.05$) correlated in both sub-populations but the relationship is strongest in the within 11 km sub-population ($r_s=0.71$ vs. $r_s=0.38$; Suppl. 3).

Direction from the historic roaster also appears to be a control on sedimentary As concentrations because there is a significant difference between category medians (Kruskal-Wallis

H=42.78; $p<0.05$, n=105, 8 groups). Median As concentrations are higher in sediments of lakes to the N and NW of the historic roaster (Fig. 4).

4.3 Mineralogy

4.3.1 Scanning electron microscopy and mineral liberation analysis (SEM-MLA)

Iron-oxides, As-sulphides, As-oxides, rare arsenopyrite (FeAsS), and pyrite (FeS_2) were observed and identified using SEM and MLA analysis of sediments. Fe-oxides were observed in many of the samples and were common in samples R11-14-11 and BC-2, where Fe-oxides appeared to be Fe-Mn-oxides and did not exhibit the texture associated with roaster-generated Fe oxides. Pyrite was present in every sample except R11-14-11 and was particularly abundant in samples and L19S2, BC-32, and BC-47. Where present, pyrite was often framboidal and As was present in trace amounts. SEM-MLA was used to identify arsenopyrite, As-sulphides, and traces of As-oxides with a distinct spongy texture in BC-13 and BC-17.

4.3.2 Synchrotron-based µXRF and µXRD

Five As-bearing grains in two selected samples (BC-17, BC-32) were targeted for µXRF and µXRD analysis (BC-17, BC-32). Two grains (one from each sample) could be reliably located on µXRF images and subsequently provided adequate diffraction patterns for integration and identification. The grain from sample BC-32, which was obtained from sediments of a lake 9.2 km from the historic Giant Mine Roaster at 273° (NNW and down-wind from the roaster), gave the clearest diffraction pattern with the most distinct peaks (Suppl. 6). The mineral phase arsenolite (As_2O_3) provided the closest match to the sample's integrated diffraction spectra. The As-oxide grain from sample BC-17 (3.2 km and 249° (NW) from the historic Giant Mine roaster) had a less distinct pattern; however, the main peaks still provided a close match to arsenolite.

A single As- and S-rich grain on the MLA map from sample BC-17 was selected for µXRD. Diffraction from this grain proved to be relatively poor and there was difficulty in reliably matching the integrated spectra to a known mineral phase. Peaks matching both realgar and arsenolite suggest this may be a mixture.

5.0 Discussion

Basin bathymetry was not known for Yellowknife study lakes and Z_{max} could not be targeted. As a result, As and other element concentrations of Yellowknife area lakes reported here may, if zones of erosion or transportation (sensu Blais and Klaff, 1995) were sampled, be substantially lower than those in the zone of accumulation in the study lakes. A lack of grain size variation (CV silt = 7.87%) and lack of relationship between clay and As ($p<0.05$; Suppl. 3) suggests that sediment size, expected to be related to sample location, is not a dominant control on As concentration in Yellowknife area lake sediment samples. Approximately 86% of the As_2O_3 released as stack emissions from Giant Mine occurred prior to 1963 (Wrye, 2008). Consequently, maximum As concentration in some lake sediment profiles occurs below the sediment-water interface in sediments dating to the late 1940's (Schuh et al., 2017), but in other lakes maxima occur in younger sediments (Andrade et al., 2010) or sediments near the sediment-water interface (Schuh et al., 2017) likely controlled by post-depositional remobilization of arsenic via reductive dissolution and upward diffusion.

5.1 Legacy mineral processing released arsenic to surrounding environments

Arsenic concentrations in the Yellowknife area lake sediment samples are significantly negatively related to the distance from the historic Giant Mine roaster (r_s=-0.57, $p<0.05$, n=105, Suppl. 3; ordinary linear squares regression r=-0.60, r^2=0.35, $p<0.001$, n=105; Suppl. 4). Palmer et al. (2015) show that the concentration of As Yellowknife area lake surface water within a 17.5 km radius of Giant Mine and downwind from historic mining activity are elevated relative to more distal lakes and upwind sites. Houben et al. (2016), in their study of As concentration of surface waters of 25 small (median 2.9 ha) and shallow (median 1.2 m) lakes within a 25 km radius of Giant Mine, also show that As concentrations in surface waters are highest in lakes closest to the mine, a pattern they interpret to be the result of relatively proximal deposition of atmospherically emitted roaster stack combustion products. Roasting of gold ore associated with arsenopyrite released SO_2 along with metal(loid)s, including Sb, to the atmosphere (Hocking et al., 1978; Hutchinson et al., 1982). Stibnite (Sb_2S_3) and Sb-bearing sulfosalts were present in the ore roasted at Giant Mine, resulting in generation of a gaseous Sb-phase that was incorporated in the structure of As_2O_3 during its crystallization (Riveros et al., 2000; Fawcett and Jamieson, 2011) and Sb oxide was the third largest oxide concentration in baghouse dust collections from Giant Mine (SRK, 2002). Antimony also declines with distance from the roaster stack in Yellowknife area lake surface waters (Houben et al., 2016). Sedimentary Sb is highly correlated to As and Au in Yellowknife area lake sediments (r_s=0.92 and r_s=0.84, respectively, $p<0.05$, n=105) and declines with distance from the historic roaster stack (r_s=-0.58, $p<0.05$, n=105; Suppl. 3). While these spatial observations and high positive element correlations between As, Au, and Sb are suggestive of point source emission (e.g., Bonham-Carter, 2005; Houben et al., 2016), the Giant Mine is also located on mineralized bedrock elevated in these elements relative to average upper crustal composition (As=4.4-4.8 $mg \cdot kg^{-1}$; Au=1.2-1.8 $ng \cdot g^{-1}$; Sb=0.4 $mg \cdot kg^{-1}$; Rudnick and Gao, 2004).

This bedrock and locally derived surficial materials represent a geogenic source of As and other elements to lake sediments. Our analysis show that bedrock formation is related to the As concentration of lake sediments (r_s=-0.35, $p<0.05$, n=105, Suppl. 3; PERMANOVA p=0.04; Fig. 2). The concentration of metal(loid)s associated with gold ore and its mineral processing, including Au, Sb, and Hg are also significantly related to bedrock type (r_s=-0.35, r_s=-0.48, respectively, $p<0.05$, n=105), with highest concentrations in sediments of lakes occurring on granitoid bedrock, expected to provide little geogenic input of these elements (Suppl. 3). Sedimentary As concentrations are significantly related to direction from the historic roaster (Fig. 4). Higher concentrations occur in sediments of lakes to the N and NW underlain by granitoid bedrock occurs where prevailing winds would have dispersed emitted As_2O_3 and other roaster emissions (Figs. 1, 4; Galloway et al., 2012). We therefore interpret these element relations with bedrock to reflect emission from the historic roaster, transport to the NW with prevailing winds and airborne deposition into these lakes and their watersheds (Galloway et al., 2012). The meta-analysis of Houben et al. (2016) on a smaller number of sample lakes show that while bedrock composition has an influence on the As concentration of regional surface waters, geogenic sources are not an important factor controlling elevated As in waters of lakes near the mine.

To explore the hypothesis that mineral processing has influenced lake sediment geochemistry further, SEM and MLA analyses of selected sediment samples from lakes within 20 km of Giant Mine were used to demonstrate the presence of As oxide in sediments of two of the five lake sediment samples analyzed (BC-17, BC-32; Howell, 2014). Synchrotron-based µXRF was used to target two As oxide grains in sediment samples from lakes BC-13 and BC-32 and µXRD was used to identify the As oxide phases as arsenolite (As_2O_3). These lakes are located 3.2 km and 9.2 km away from the Giant Mine historic roaster, respectively, and both are located downwind of the historic roaster and underlain by granitoid bedrock (Suppl. 3). To our knowledge, arsenolite has never been found to naturally occur in lake sediments; its presence therefore provides convincing evidence that roasting of gold ore in the Yellowknife region resulted in atmospheric dispersion of this mineral to the landscape near the Giant Mine historic roaster stack. Previous studies demonstrated the persistence of As_2O_3 in the immediate environment surrounding the historic Giant Mine roaster in thin soils on rocky outcrops (Bromstad et al., 2017). Recent studies document As_2O_3 in the sediments of five other lakes within five km of the historic roaster (BC-20, Handle Lake/YK-42, Lower Martin Lake/BC-15, Long Lake, Martin Lake/BC-13; Van Den Berghe, 2016; Schuh et al. 2017).

5.2 Controls on sedimentary arsenic in Yellowknife area lakes

Several interrelated processes control As cycling in freshwater sediments. Arsenic that enters surface waters as detrital minerals may be directly deposited into lake sediments with little or no alteration of the original As-bearing phases. The ore roasting product As_2O_3 is present in Yellowknife area lake sediments, indicating that deposition and preservation of even this highly soluble mineral form is possible (Stavinga, 2014; Van Den Berghe, 2016; Schuh et al., 2017). In oxic and circum-neutral settings, oxidation and dissolution of As-bearing sulphide minerals may release As into waters where dissolved As(V) has a strong affinity for mineral surfaces, particularly Fe/Mn(hydr)oxides, and may be removed from solution through adsorption or co-precipitation (Bowell, 1994; Smedley and Kinniburgh, 2002). Arsenic sorbed to mineral surfaces may then be accumulated in the sediments and this can be an effective means of sequestration (Bowell, 1994; Smedley and Kinniburgh, 2002; Langner et al., 2013), so long as redox conditions remain consistent. In Yellowknife area lake sediments, As is negatively correlated to Al (Suppl. 3) although the partial digestion method used makes this difficult to interpret. Arsenic is nonsignificantly correlated to Mn, regardless of distance from the historic mine, and displays a significant relationship with Fe in samples from lakes beyond 11 km from the historic mine but not in those within 11 km, despite the fact that Fe and Mn are significantly related to each other (Fig. 5). These relationships suggest that in lakes close to the historic roaster stack, Fe/Mn(hydr)oxide sequestration of As is not a dominant process controlling elevated sedimentary As concentration.

Using X-ray Absorption Near Edge Spectroscopy (XANES), Van Den Berghe (2016) documents As(V) and As(III) associated with ferric oxides in the upper 4 cm of Handle Lake (YK-42), Lake BC-20, and Lower Martin Lake (BC-15), but not as a major host of As**.** Most of the As is hosted in As-sulphide minerals, and more As is hosted in As_2O_3 than in Fe oxides. Van Den Berghe (2016) hypothesizes that dissolution of As_2O_3 and reductive dissolution of Fe/Mn(hydr)oxides is releasing soluble As to porewaters, most of which diffuses upward in the sediment, while the remaining As is authigenically reprecipitated as As-sulphide. In Yellowknife study lakes, sediment As concentration is correlated with S (r_s=0.49, p<0.05, n=105) but negatively correlated with Fe (r_s=-0.22, p<0.05, n=105; Fig. 5), suggesting that formation of secondary As-sulphide minerals is an important process throughout the region. In deep water sediments from Long Lake enriched in As_2O_3, the presence of As-bearing sulphides suggests that partial dissolution of As_2O_3 in the presence of reduced S has attenuated more bioaccessible As_2O_3 from stack emissions to a less accessible sulphide phase (Schuh et al., 2017). Iron free As-sulphide is not associated with mineralization (Coleman, 1957) or any tails at Giant (Walker et al., 2015; Fawcett and Jamieson, 2011), and is therefore interpreted to be an authigenic amorphous, realgar-like preciptitate (Schuh et al., 2017). Authigenic precipitation of As-bearing sulphides is likely to be mediated by OM through its influence on pore water redox gradient and microbial activity. Precipitation of As-bearing sulphide minerals such as realgar, pararealgar, or orpiment is often microbial-mediated (Newman et al., 1997; Smedley and Kinniburgh, 2002; O'Day, 2004; Root et al., 2009; Drahota et al., 2013). Organic carbon is a substrate for microbial growth (Campbell and Nordstrom, 2014), and in particular, the labile geolipids that represent the S1 fraction of TOC, are readily biodegradable (Sanei et al., 2005). Promotion of microbial-mediated authigenic precipitation of As-sulphides by OM may explain the observed relationship between the highly bioavailable and labile form of OM (S1) and the concentration of As in Yellowknife area lake sediments (As:S $r_s=0.55$, $p<0.05$, $n=105$; Fig. 5). S1 and As are also both correlated to S ($r_s=0.63$, $p<0.05$; $r_s = 0.49$, $p<0.05$, respectively, $n=105$; Fig. 5).

In addition to promoting and mediating sulphide formation in sediments, OM, and in particular the S1 fraction, can also coat surface sediment particles providing an organic substrate with a large surface area for metal(loid)-OM complexation (Sanei et al., 2005; Campbell and Nordstrom, 2014). Organic carbon is also capable of directly storing adsorbed As (Sadiq, 1997; Wrye, 2008; Meunier et al., 2011). For example, As(III) can be sequestered through passive complexation with sulfhydryl groups on OM that appear to occur under conditions unfavorable for As-sulfide precipitation, such as where the quantity of dissolved S was too low to support precipitation of As-sulphide minerals (Langner et al., 2013). Breakdown of low molecular weight OM, such as sugars (related to the S1 fraction; Carrie et al., 2015), can release organic acids that comprise a portion of dissolved OM (DOM; Martínez et al., 2003). Dissolved OM can affect the mobility of As through direct complexation with aqueous As(III) and As(V) via positively charged amino groups in DOM (Saada et al., 2003), metal cation bridges (Redman et al., 2002), or through mediation of processes at mineral surfaces (precipitation, dissolution, ad- and de-sorption). Dissolved OM (e.g., fulvic and humic acids) can form stable complexes with mineral surfaces that block As adsorption (Kaiser et al., 1997; Grafe et al., 2001, 2002; Bauer and Blodau, 2006; Dobran and Zagury, 2006). Organic anions and DOM have been found to enhance As leaching from soil material (Lin et al., 2002; Dobran and Zagury, 2006) where As is associated with the metal oxide fraction (Lombi et al., 2000). Arsenic desorption from Fe oxides in the presence of DOM (Redman et al., 2002; Bauer and Blodau, 2006) and fulvic or humic acids (Grafe et al., 2001, 2002) may also be microbial-mediated whereby DOM serves as a labile substrate for microbial growth (Harvey and Swartz, 2002; Mladenov et al., 2009; Campbell and Nordstrom, 2014). Redox active functional groups associated with DOM can also act as an electron shuttle between micro-organisms and Fe and thus enhance microbial iron reduction and release of sorbed As (Schwarzenbach et al., 1990; Lovley et al., 1996; Mladenov et al., 2009).

The relationship between S1 and As in Yellowknife area lake sediments may reflect a complex set of mechanisms by which both kerogen and DOM can influence As mobility, and are likely to become more important under a warming climate with enhanced OM flux from thawing permafrost (e.g., Vonk et al., 2013) among other mechanisms, resulting in potential for increased As concentrations in the water column of Yellowknife area lakes over time. Additional research (e.g., Carrie et al., 2005) is required to better characterize solid organic matter fractions as determined by Rock-Eval pyrolysis to better understand the nature of S1 and As interaction. Additional research characterizing bacterial assemblages and their metabolic activities would be key for understanding OM and metal redox geochemistry in the lake sediments.

6.0 Conclusions

Lake sediment As concentrations are significantly related to distance and direction from the former Giant Mine, with increased concentrations in lakes close to and downwind from the historic roaster. Ordination shows that lakes with the highest concentration of As in sediments occur on granitoid bedrock; a bedrock type containing average As concentrations near 2 $mg{\cdot}kg^{-1}$.

We interpret this relationship to reflect aerial emission and transport direction of As predominantly to the NW by winds and deposition in lakes and catchments located on granitoid bedrock.Arsenic trioxide (As_2O_3) is documented in the sediments of two lakes studied using synchrotron-based μXRF and μXRD, providing direct evidence of historic roaster impacts and persistence of this mineral in lake sediments.

Labile organic matter (S1 as determined by Rock Eval pyrolysis) is significantly related to sedimentary As and S concentrations in Yellowknife area lake sediments. S1 may be a substrate for microbial growth and mediation of authigenic precipitation of As-sulphides. Other possibilities include physical coating of particles by S1, creating a large and reactive surface for As complexation, coating and encapsulation of pre-existing solid-phase As; and, soluble organic anion competition with As for sorption sites on mineral surfaces. Increased biological production, release of OM from melting permafrost, and changes in transportation pathways though changing hydrological regimes may thus lead to changes in As biogeochemical cycling. The type and source of OM is an important consideration for characterization of the mobility and fate of As and other elements.

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Figure captions

Figure 1: Map showing sample locations colour coded by sedimentary Arsenic concentration (bedrock geology modified after Falck, 2002)

Figure 2. Principal Components Analysis of log-transformed data. Potential control variables (grain size, Rock Eval parameters, lake area, and distance from the historic roaster) were fitted to the solution post-hoc using the Envfit procedure with 999 permutations

Figure 3: Box and whisker plot of sedimentary As concentration in samples from lakes within 11 km from the historic roaster and lakes beyond this distance

Figure 4: Top – wind rose diagram for the Yellowknife A climate station (62.46°N, 114.44°W 205.7 m asl) showing how many hours per year the wind blows in the indicated direction. Data from 1970-2010 available at http://climate.weather.gc.ca/climate_normals/results_e.html?stnID=1706; figure from https://www.meteoblue.com/en/weather/forecast/modelclimate/yellowknife-airport_canada_6296340). Bottom – Box and whisker plot of sedimentary log As concentration in samples from lakes at different directions (degrees) from the historic roaster

Figure 5: Log-log scatterplot of selected variables. Note changes in scale. Spearman rank correlation coefficients from Suppl. 3