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Arsenic, Antimony and Metal Concentrations in Water and Sediment of Yellowknife Bay

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Cover photo: View from the community of Ndilo on the shore of Yellowknife Bay, looking north towards Back Bay and the Giant Mine site in 2015. Source: John Chételat

ABSTRACT

An environmental study of Yellowknife Bay was conducted from 2013 to 2016 to investigate impacts of gold mining on arsenic, antimony and metals in sediment and water. Dated sediment cores were used to reconstruct historical loadings of metal(loid)s to Yellowknife Bay during the 20th century and with increasing distance from Giant Mine, located on the north shore of the bay. Of the 48 elements analyzed in sediment, 14 elements had maximum enrichment factors greater than 2, reflecting concentration increases relative to background sediment accumulated before 1930. The eight most enriched elements were arsenic, antimony, copper, lead, manganese, mercury, silver and zinc. Peak concentrations of arsenic and antimony in the nearfield zone were enriched by as much as 180 and 347 times, respectively, relative to pre-mining levels. In general, metal(loid) levels in sediment peaked during the early years of mining operations in the 1950s or 1960s, and then began to decline towards background. The peak enrichment of metal(loid)s in sediment declined exponentially with distance in a southerly direction from Giant Mine. The plume of metal(loid) pollution reached into the main body of Great Slave Lake, an estimated ~30 km south of Giant Mine.

Surface sediments of Yellowknife Bay showed positive recovery in recent decades with levels generally returning to near pre-mining conditions for metals. However, at the north end of Yellowknife Bay, levels of arsenic and antimony in surface sediments remained well above pre-mining levels (up to 37 fold higher). Thus, surface sediments in north Yellowknife Bay continue to accumulate metalloid pollution either from loadings from the Giant Mine site and/or internal recycling within the bay. The evaluation of several

sediment core profiles from Yellowknife Bay indicated high concentrations of solid-phase arsenic near the sediment-water interface suggesting that post-depositional movement of legacy pollution occurred by upward diffusion of dissolved arsenic. Consistent with this process, high concentrations of dissolved arsenic (168–1319 µg/L) were measured in layers of nearfield surface sediments, and this arsenic was predominately in a reduced form as arsenite (As^{3+}).

Surface water measured near Ndilo and Dettah showed that arsenic and antimony were 2–3 times higher at the north end of Yellowknife Bay, consistent with the closer proximity to pollution sources at Giant Mine. Water concentrations of total arsenic declined to approximately 1 µg/L or less at a distance of 10 km south from Giant Mine, at the mouth of Yellowknife Bay. Arsenic in surface water was predominately in the dissolved fraction as inorganic oxyanions, as arsenite (As^{3+}) and arsenate (As^{5+}). Although surface water arsenic was enriched at the north end of Yellowknife Bay, average concentrations were relatively low and below the Health Canada drinking water guideline of 10 µg/L.

Overall, there was evidence of ecosystem recovery from historical loadings of metal(loid)s to water and sediment of Yellowknife Bay. However, the long-term stability of legacy arsenic in the sediments remains an outstanding issue. Arsenic in sediments is not being buried efficiently over time. The highest solid-phase concentrations of arsenic are in the surface layer of sediments and porewater arsenic concentrations are elevated at the north end of the bay. Yellowknife Bay sediments are a large and potentially leaky reservoir of legacy arsenic pollution. Further research is recommended to evaluate the long-term stability of sediment arsenic in Yellowknife Bay during the 21st century.

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INTRODUCTION

Yellowknife Bay, on the north shore of Great Slave Lake, is a water body of cultural, subsistence and recreational importance for the Yellowknives Dene First Nation and the residents of Yellowknife. During the 20th century, this aquatic ecosystem was impacted by gold mining on its shores and the environmental legacy of those developments continues today (INAC 2010). Considerable environmental study has been conducted in Yellowknife Bay since the 1970s, and contamination of arsenic, antimony and metals has been documented in water and sediment at the north end of the bay adjacent to the Giant Mine site (Moore et al. 1978; HydroQual 1989; Jackson et al. 1996; Stantec 2014b).

Gold mining developments began in the mid-1930s with claims staked along the northwest and west shores of Yellowknife Bay. Gold production began shortly after at the Con-Rycon Mine in 1938 and the Negus Mine in 1939 (Sandlos and Keeling 2012). Giant Mine opened a decade later, beginning production in 1948 and, in 1953, Negus and Con mines merged (Sandlos and Keeling 2012). Over the next 5 decades, the Giant and Con mines together produced more than 12 million ounces of gold before closing in the early 2000s (Silke 2009). Remediation of both mine sites is on-going at the time of this report publication.

During the 20th century, mining pollution entered Yellowknife Bay via three main transport pathways. Over 200,000 tons of tailings (processed ore waste) from Giant Mine were released directly into Back Bay during the first 3 years of operation from 1948 to 1951 (Golder 2005; INAC 2010). Those tailings, which have a high metal(loid) content, are estimated to cover approximately 5 hectares on the bottom of Yellowknife Bay, although some dispersal and erosion of the deposited waste has occurred in subsequent decades (EBA 2001; Golder 2005). The second transport pathway was the release of effluent from Giant Mine into Baker Creek, which flows into Yellowknife Bay. The effluent was untreated until 1981 when a waste water treatment plant was constructed to improve water quality in Yellowknife Bay (Sandlos and Keeling 2012; Silke 2013). Effluent loadings of metal(loid)s from Baker Creek continue today, including an estimated 800 kg of arsenic per year entering the bay (INAC 2010). The third transport pathway was the aerial deposition of metal(loid)s from ore roasting emissions at Giant and Con Mines. Sulphide ores were roasted to facilitate the recovery of gold at Giant Mine from 1949 to 1999, at Con Mine in 1942 and 1948 to 1970, and briefly at Negus Mine in 1952 (Silke 2009). The greatest pollution emissions from ore roasting occurred at Giant Mine in the early years of operation from 1949 until 1958, at which time a baghouse dust collector was installed (Hocking et al. 1978). Direct surface runoff from the mine properties likely also transported lesser amounts of metal(loid) pollution into Yellowknife Bay (INAC 2010).

The chemical composition of mining wastes released into the receiving environment differed among transport pathways and varied over the period of mine operation. Ore roasting resulted in the formation of arsenic products, specifically arsenic trioxide (As_2O_3) and arsenic-bearing iron oxides (maghemite and hematite) (Jamieson 2014). Tailings deposited at Giant Mine were referred to as calcines and were predominately composed of iron oxides, which often host arsenic within their structure (Walker et al. 2015). Some of these tailings were transported to Yellowknife Bay via effluent and tailings releases (Walker et al. 2005; Jamieson 2014). Arsenic trioxide was the primary form of arsenic emitted from the roaster although it was likely also a component of the tailings waste stream (Jamieson 2014; Walker et al. 2015). Antimony and lead were also associated with roaster emission products and consequently have been deposited onto terrestrial and aquatic surfaces in the region (Thienpont et al. 2016; Bromstad et al. 2017). Tailings and effluent from Giant Mine were high in arsenic, antimony and metals including copper, lead, manganese and zinc (Golder 2005; 2013; Fawcett et al. 2015). The mineralogy of the arsenic products generated in the roaster and the geochemistry of metal(loid)s released from mining activities have implications for their long-term fate and stability in the receiving environment (Fawcett and Jamieson 2011; Jamieson 2014; Fawcett et al. 2015; Bromstad et al. 2017). Further, the volume and chemical composition of waste streams changed over the decades of operation as technologies were replaced and pollution controls improved (see Walker et al. 2015 for details).

Early environmental studies in the 1970s identified significant impacts of mining pollution on Yellowknife Bay including water concentrations of arsenic above drinking water guidelines (at that time the guideline was 50 µg/L), elevated levels of metal(loid)s in sediment, acute toxicity of effluent to fish, and impoverished benthic invertebrate communities in sediments close to Giant Mine (Falk et al. 1973; Moore et al. 1978). Subsequent studies in the 1980s and 1990s reported lower water arsenic concentrations in Yellowknife Bay (HydroQual 1989; Jackson et al. 1996), likely reflecting more stringent pollution controls that had been implemented at Giant Mine. However, sediment concentrations of arsenic have remained higher near Giant Mine with evidence of on-going impacts to the benthic invertebrate community (HydroQual 1989; Mudroch et al. 1989; Sutherland 1989; Golder 2005). Recent measurements of water and sediment metal(loid) levels were conducted in 2012 and 2013 throughout Yellowknife Bay to provide baseline information for remediation efforts at Giant Mine (Stantec 2014b).

Despite the considerable data collection from environmental studies since the 1970s, important questions remain regarding impacts of gold mining on Yellowknife Bay. Most study has focused on the nearfield area in Back Bay, adjacent to Giant Mine, and estimates of how far pollution dispersed throughout Yellowknife Bay are lacking. Recent investigations of lakes to the west of Yellowknife indicate that dispersal of metal(loid) pollution from roaster emissions reached approximately 20 km to the west of Giant Mine (Palmer et al. 2015; Houben et al. 2016). Similarly, a suite of elements have been analyzed in water and sediment of Yellowknife Bay over several decades, but the lack of information on background levels has made the interpretation of spatial and temporal trends challenging. It is well established that Yellowknife Bay received significant loadings of arsenic, antimony, zinc, copper and lead (Mudroch et al. 1989; Andrade et al. 2010) but contamination of other elements of potential concern such as cadmium, chromium, nickel and mercury has not been well characterized. Further, the chemical speciation of arsenic, which is one of the main pollutants in Yellowknife Bay, has received relatively little study. The phases of arsenic in water and sediment (particulate versus dissolved) and the speciation (e.g., arsenite, arsenate, organo-arsenic compounds) affect the transport, mobility and toxicity of this element (Cullen and Reimer 1989). Andrade et al. (2010) demonstrated that a substantial portion of dissolved arsenic in Yellowknife Bay sediments is as inorganic arsenite (considered more mobile and toxic that arsenate; Smedley and Kinniburgh 2002; Rahman et al. 2014), but comparable speciation measurements for the overlying water column are lacking.

This study builds on previous environmental research and monitoring in order to address some remaining knowledge gaps. Detailed sediment core profiles of metal(loid) concentrations were measured in Yellowknife Bay and the main body of Great Slave Lake to characterize historical impacts and recent recovery from mining pollution. Since sediments accumulate over time and can be dated with radioisotope methods, sediment core profiles are a valuable tool for reconstructing the timing and extent of contamination in aquatic ecosystems (Kirk and Gleason 2015). Although several earlier studies have examined sediment core profiles in Yellowknife Bay (Mudroch et al. 1989; Mace 1998; Andrade et al. 2010), this report presents greater spatial coverage and includes additional elements not previously reported. The sediment core profiles provided new information on background levels of metal(loid)s before the onset of mining developments at Yellowknife, identified key elements that were the most enriched in sediments during the early years of gold production, and allowed for an estimation of the spatial extent of pollution emissions in Yellowknife Bay and beyond. Water chemistry was also examined in this study, which provided complimentary information (to sediments) on the spatial extent of water-borne metal(loid)s in Yellowknife Bay and the nearby main body of Great Slave Lake. The water analyses included inorganic and organic speciation of arsenic, which were the first detailed speciation measurements to date for Yellowknife Bay. Together, the main findings of this study indicate significant recovery of Yellowknife Bay from mining pollution in the 20th century as well as on-going issues where further research and monitoring is recommended.

METHODS

Study area

The City of Yellowknife and two communities of the Yellowknives Dene First Nation (Ndilo and Dettah) are located on the shores of Yellowknife Bay (Figure 1). Yellowknife Bay has a surface area of approximately 20 km^2 between the mouth of the Yellowknife River at its north end to the community of Dettah at the south, where it meets the main body of Great Slave Lake. The maximum water depth is 15 m at the north end of Yellowknife Bay and approximately 30 m at the south end near Dettah (Canadian Hydrographic Service chart 6369). The section of Yellowknife Bay adjacent to the Giant Mine site and nestled behind Latham Island is referred to as Back Bay (Figure 1, inset A). The main water sources entering the bay are the Yellowknife River and Great Slave Lake, although there are additional small inflows including from Baker Creek (which receives effluent from the Giant Mine site) and storm water from the City of Yellowknife.

Field programs were conducted in September of 2013 and 2014 and in August of 2015 and 2016 to collect water and sediment from Yellowknife Bay and the nearby main body of Great Slave Lake. A subset of the data presented here were initially reported in technical documents (Chételat 2015; 2017) for the Giant Mine Remediation Project team.

Insert Figure 1.

Sediment

Two types of sampling were conducted in the study area from 2013 to 2016 to determine sediment concentrations of metal(loid)s. Surface sediments were collected at 12 nearshore sites adjacent to Ndilo, Dettah, and Old Town on Yellowknife Bay (Table 1, Figure 1). The sites often had shallow water depth (such as at beach areas) although some nearshore sites adjacent to steep bathymetric gradients were in deeper water (>10 m). Triplicate sediment cores were collected at each site with a gravity corer, and the top 10 cm of the cores were removed for analysis of bulk sediment. For two nearshore sites (BBS, CS, Figure 1), the cores were sliced into four depth intervals (0–5 cm, 5–10 cm, 10–15 cm, 15–25 cm) to investigate depth variation in the nearshore zone. In addition to nearshore sampling, a total of eight sediment cores were collected in offshore depositional areas to measure profiles of metal(loid) concentrations and determine historical changes in sediment accumulation of pollution deposited in Yellowknife Bay from anthropogenic activities since the early 20th century (Table 2, Figure 1). The offshore sites were in deeper areas where particles accumulate due to transport from sediment focusing (Blais et al. 1995). Cores were collected with varying distance from the Giant Mine (ranging from 1.4 to 23.7 km, using the location of the now decommissioned ore roaster as the reference point) to determine the spatial extent of metal(loid) pollution in a southerly direction from the mine. One sediment core was collected per site with a gravity corer and sliced into 0.5 cm intervals for the top 10 or 15 cm and subsequently sliced at 1 cm intervals for the remainder of the core. The cores varied in length from 13–40 cm, depending on the nature of sediment (Table 2).

Insert Table 1 & 2

Sediment samples were freeze-dried and homogenized prior to element analysis. Most sediments were analyzed for 30 elements by inductively coupled plasma mass spectrometry (ICP-MS) at RPC Laboratories in Fredericton, New Brunswick. Additionally, two nearshore sites (BBS, CS) were analyzed for 37 elements by ICP-MS at ACME Analytical Labs Ltd. in Vancouver, British Columbia, and three sediment cores (S3, S5, S8) were analyzed for 46 elements by ICP-MS at the Canada Centre for Inland Waters (CCIW) of Environment and Climate Change Canada in Burlington, Ontario. A list of elements analyzed in the sediments by ICP-MS in each laboratory is provided in Appendix 1. For offshore sediment cores (S1 to S8), slices were analyzed for element concentrations at regular intervals to obtain profiles, with the total number of analyses varying from 10–40 per core. Sediments analyzed at RPC were digested with hydrochloric acid and hydrogen peroxide while an aqua regia digest (nitric and hydrochloric acids) was used for digestion of sediment at CCIW and ACME. Neither of these acid digestions decompose siliceous materials; therefore, results represent leachable concentrations (NIST 2009). Several sediment samples (n=5) were analyzed at both CCIW and RPC laboratories for comparison, and the element concentrations were highly consistent. For the main solid-phase elements examined in this report (antimony, arsenic, copper, lead, manganese, zinc), the relative standard deviations of results from both laboratories were ≤10%. Silver concentrations were more variable between the two laboratories (~50% RSD) but in that case, the levels in the samples were very close to detection. Silver concentrations of the compared samples were within 0.2 μg/g between laboratories. Total mercury was measured in nearshore bulk sediment and in sediment core slices at the National Wildlife Research Centre (Environment and Climate Change Canada) in Ottawa, Ontario. Mercury concentration was determined by atomic absorption spectrometry with a Direct Mercury Analyzer (DMA). For two nearshore sites (BBS, CS), mercury was analyzed by ICP-MS at ACME Analytical Labs.

Solid-phase element concentrations in sediment are reported on a dry weight basis, and the raw data are presented in Appendix 1. Recoveries of elements from certified reference materials (NIST 2709a; MESS-3) for confirmation of accuracy and the precision of duplicate analyses are also provided in Appendix 1.

Four of the sediment cores were dated using radioisotope methods to estimate the timing of peak element concentrations in the sediment profiles. Sediment slices from three of the cores (S3, S5, S8) were analyzed for lead-210 and cesium-137 at the CCIW. Core slices from a fourth core (S4) were analyzed for lead-210, cesium-137 and radium-226 at Flett Research Ltd in Winnipeg, Manitoba. Ages of sediment depths were estimated using the constant rate of supply model and 95% confidence intervals for the dates were calculated with the package Bacon in R (Blaauw and Christin 2013; R Development Core Team 2013). There was agreement between model estimates and the peak level of cesium-137 in each core, assuming maximum atmospheric input of cesium-137 occurred in 1963. The age estimates of sediment layers in the four cores are presented in Appendix 2.

Porewater concentrations and speciation of inorganic arsenic were measured in sediment from three sites (S3, S4, S5) in Yellowknife Bay in August 2015, as reported previously in Chételat (2017). Duplicate sediment cores were collected from each site in modified core tubes with ports at 1 cm intervals along the length of the tubes to allow for insertion of Rhizon porewater samplers at multiple sediment depths, according to the method by Seeberg-Elverfeldt et al. (2005). Rhizon samplers are thin microporous tubes produced by Rhizosphere Research Products (Wageningen, Netherlands) that allow for extraction of porewater from sediment under vacuum pressure. For this study, the Rhizons had a 5 cm long porous section (0.15 µm mean pore size) of 2.5 mm diameter, reinforced with a glass fibre wire. Sediments collected in the modified core tubes were returned to the lab where Rhizons were inserted into ports at 8 or 9 depths (0–2 cm above and 1–6 cm below the sediment-water interface). Porewater was extracted by vacuum pressure created with acid-washed syringes. EDTA (ethylenediaminetetraacetic acid, 2.5 mM) was added into the syringes prior to extraction of 4–5 mL of porewater to preserve arsenic entering the syringe in its original oxidation state. Porewater samples were stored in trace-metal clean vials with glacial acetic acid (87 mM) and analyzed for total inorganic arsenic and trivalent arsenic (arsenite, As+3) by hydride generation atomic fluorescence spectrometry (HG-AFS) in the Laboratory of Environmental Biogeochemistry at the Université de Montréal (Montreal, Quebec). Pentavalent arsenic (arsenate, As+5) was estimated by difference between total inorganic arsenic and arsenite.

Water

Water was collected for chemical analysis from nearshore and offshore areas of Yellowknife Bay and the main body of Great Slave Lake. A total of 19 sites were sampled on one or two occasions between 2014 and 2016 (Table 3, Figure 2). In general, duplicate water samples were collected per site and sampling date. Water was collected in bottles using a Teflon line attached to a peristaltic pump, and trace metal protocols were employed, including the use of non-powdered disposable gloves, metal-clean sampling containers (double bagged in ziplock bags), daily acid-cleaning of the Teflon line and filter, and the “clean hands – dirty hands” technique. For two of the sites (BBS, CS), water was collected as surface grabs without the use of a Teflon line. Water samples for analysis of dissolved elements were filtered in the field using an acid-washed high capacity groundwater filter (0.45 µm) attached to the Teflon line. If the Teflon line system was used to sample multiple sites on one day, it was rinsed between sites for several minutes with ambient water. In nearshore areas (<2 m depth), water was only sampled near the surface (0.2–1 m depth) whereas offshore sites were sampled 1–2 m below the surface and 1 m above the lake bottom (Table 3). Field measurements of water pH, temperature, and dissolved oxygen were taken with a YSI water quality sonde at the time of water sampling.

Insert Figure 2 and Table 3

Water was analyzed for general chemistry (including major ions, dissolved organic carbon, hardness), total (unfiltered) and dissolved (filtered, 0.45 µm) concentrations of elements by ICP-MS, mercury (total), and arsenic speciation. In most cases, only a subset of the full suite of water analyses were conducted per sampling site (site-specific analyses are identified in Table 3). General chemistry was measured in water from nine sites at RPC Laboratories. Water from all sites was analyzed for total and/or dissolved concentrations of 30 elements by ICP-MS at RPC Laboratories, with the exception of sites BBS and CS, where water was analyzed for 25 elements by ICP-MS at Taiga Laboratories (Yellowknife, Northwest Territories). The samples were acidified with nitric acid but not digested, and therefore the results are estimates of soluble and acid-labile concentrations. Total mercury in water was measured by cold vapour atomic fluorescence spectrometry at the Laboratory of Environmental Biogeochemistry at the Université de Montréal using standard methods reported elsewhere (MacMillan et al. 2015). Water chemistry results from individual sites are presented in Appendix 3 along with analytical quality assurance and quality control information (spike recoveries and precision of analytical duplicates).

Arsenic speciation measurements in water were conducted at two separate laboratories (Brooks Rand Labs in Seattle, USA, and the Laboratory of Environmental Biogeochemistry at the Université de Montréal), which allowed for a comparison of analytical methods and inter-laboratory cross-validation of results. At nine sites, unfiltered water was analyzed for arsenic speciation at Brooks Rand Labs and preserved with nitric acid or hydrochloric acid for total recoverable arsenic and arsenic speciation, respectively. Total recoverable arsenic was measured by closed-vessel oven digestion with nitric acid followed by detection using an ICP-MS with dynamic reaction cell (DRC) technology to reduce potential polyatomic interferences and to achieve lower detection limits. Total inorganic arsenic, trivalent arsenic (arsenite, As^{+3}), and the organic arsenic species monomethylarsonic acids (MMAs) and dimethylarsinic acids (DMAs) were analyzed by hydride generation with $NaBH_4$ reduction and atomic absorption detection (HG-AAS). Pentavalent arsenic (arsenate, As^{+5}) was estimated by difference between total inorganic arsenic and arsenite. Water from ten sites was separately analyzed for arsenic speciation at the Laboratory of Environmental Biogeochemistry. Unfiltered water was preserved with 2% HCl and analyzed for total arsenic by HG-AFS following digestion with potassium persulfate. Filtered water was preserved with EDTA (1.25 mM) and glacial acetic acid (87 mM), and analyzed for total inorganic arsenic and trivalent arsenic (arsenite, As^{+3}) by HG-AFS. Pentavalent arsenic (arsenate, As^{+5}) was estimated by difference between total inorganic arsenic and arsenite.

In both 2014 and 2015, surface water samples from 4 sites were analyzed for arsenic at both Brooks Rand Labs and the Université de Montréal to compare methods. Total arsenic concentrations in unfiltered water determined by nitric acid digestion and ICP-MS detection were highly comparable to values obtained by persulfate digestion and HG-AFS detection (relative standard deviation = 10 ± 5%, n=16). Total inorganic arsenic concentrations were more variable between analytical laboratories (relative standard deviation = 24 ± 20%, n=16), perhaps in part due to differences in the methods used for processing the water samples (e.g., analysis of filtered vs unfiltered water). Nevertheless, absolute differences in total inorganic arsenic were low (0.3 ± 0.3 µg/L, n=16) between laboratories. Analyses of arsenite concentrations were also very similar between laboratories (relative standard deviation = 7 ± 4%, n=10). This laboratory intercalibration exercise indicated high comparability of surface water arsenic measurements, and therefore, the data from both laboratories were pooled together for this report. The results of this intercalibration exercise are provided in Appendix 3.

RESULTS

Enrichment of arsenic, antimony and metals in Yellowknife Bay sediments

Elements released from human activities into Yellowknife Bay during the 20th century were identified using the closest dated sediment core to the Giant Mine site (site S3; located 1.9 km from the roaster; Figure 1). Of the 48 elements analyzed in this core, 14 elements had maximum enrichment factors greater than 2, reflecting concentration increases relative to background sediment accumulated pre-1930 (Table 4). The remaining elements showed little to no enrichment (factor of 0.8–1.9) in the sediment profile or were at concentrations below analytical detection (palladium, platinum, rhodium, tellurium). The fourteen enriched elements were: arsenic, antimony, cadmium, copper, lead, manganese, mercury, molybdenum, phosphorus, silver, sulphur, tin, tungsten, and zinc. For this report, subsequent examination of spatial and temporal trends of metal(loid) pollution in Yellowknife Bay focused on eight elements with the greatest enrichment: arsenic, antimony, copper, lead, manganese, mercury, silver, and zinc. Concentration profiles of those elements in core S3 are presented in Figure 3.

Insert Figure 3 and Table 4

Tungsten was not examined further because limited data on that element were generated in this study (no measurements in water and only a subset of the sediment). Likewise, five other elements (cadmium, molybdenum, phosphorus, sulphur, and tin) were not examined further because of the relatively low maximum enrichment (a factor of 2–3 fold in core S3). Eleven of the 14 enriched elements had a concentration peak in the sediment layers dated to the early years of mining operations at Giant, the exceptions being molybdenum, tin and sulfur. For enriched redox sensitive elements (i.e. arsenic, manganese, molybdenum, phosphorus, tungsten), a second (higher) peak was observed in the top 3 cm surface layer (see Figure 3 for arsenic and manganese).

All eight sediment cores were examined to determine spatial variation of maximum enrichment factors for the eight most enriched elements identified in Table 4. The cores were categorized as nearfield sites (S1 to S4), for those located at the north end of Yellowknife Bay, or as farfield sites (S5 to S8), for those located 9 to 24 km from the location of the Giant Mine roaster. Maximum enrichment factors for the eight elements were determined by comparing the peak concentration for the core of interest to the average concentration in pre-mining sediment layers (before 1930) pooled from the four dated sediment cores. This approach, taking the average background levels of the four dated cores was used because pre-1930 sediment depths could not be confirmed in the undated cores. Arsenic and antimony were by far the most enriched elements in the Yellowknife Bay sediment profiles (Table 5). Peak concentrations of arsenic and antimony in the nearfield zone were enriched up to 180 and 347 times, respectively, relative to pre-mining levels. Copper, lead, manganese, mercury, silver and zinc were also substantially enriched relative to pre-mining levels in sediments at the north end of Yellowknife Bay (nearfield), although to a lesser degree (3 to 38 fold). Greater enrichment occurred at nearfield sites than farfield sites (Table 5).

Insert Table 5

The maximum enrichment of metal(loid)s in the sediment cores declined with distance from Giant Mine (Figure 4). The location of the now decommissioned roaster at Giant Mine was used as km 0 in this spatial analysis although effluent exiting Baker Creek into Yellowknife Bay and tailings released from the Giant Mine property at the beach site were also important transport pathways contributing to element enrichment. Ore roasting emissions from Con and Negus mines likely also contributed to metal(loid) loading in Yellowknife Bay. The maximum enrichment of elements declined exponentially with distance, and the greatest enrichment was found in the first 5 km south of the Giant Mine roaster in Yellowknife Bay (Figure 4). When the spatial trends were examined on a logarithmic scale, the linear regression lines relating element enrichment with distance were statistically significant (log-log linear regressions: $r^2 = 0.57$ to 0.92, $p < 0.03$, $n = 8$ per element) (Figure 5). The regression slopes suggest that the pollution plume of gold mining emissions reached approximately 30 km south of the Giant Mine roaster and into the main body of Great Slave Lake. One of the cores, S6, had very low organic matter content and high clay content, which may explain the lower enrichment of metal(loid)s relative to two other cores (S5, S7) collected nearby.

Insert Figure 4 and Figure 5

Historical timing of maximum enrichment and recovery of metal(loid)s in sediments

The four dated sediment cores showed relatively good agreement in historical timing of metal(loid) enrichment in Yellowknife Bay. The sediment profiles of antimony, as an example, indicated that concentrations began to increase during the early years of mining development in the 1940s, reached a peak in the 1950s or 1960s, and began to decline thereafter (Figure 6, Table 6). This trend was observed for antimony in the four cores although the changes in concentration varied because collection sites were located at different distances from mining operations. Error in the radioisotope chronologies of the sediment cores prevented a more precise characterization of the pollution history for Yellowknife Bay (±5–10 years; Table 6). These profiles indicate that metal(loid) pollution in Yellowknife Bay peaked during the early years of production at Giant Mine when few pollution control measures were in place (Silke 2013).

Insert Figure 6 and Table 6

The depths of concentration peaks in the sediment profiles were similar for copper, lead, mercury and zinc but differed for silver, manganese and arsenic (e.g, core S3 shown in Figure 3). For silver, the maximum enrichment peaked slightly later (data not shown, except core S3 in Figure 3). For arsenic, two concentration peaks were typically observed in the dated cores, with maximum concentrations observed in the youngest, surface layers of sediment (post 2000) (Figure 7). A secondary smaller peak was also often observed in deeper layers of the cores. These profiles indicate that there has been post-depositional movement of arsenic pollution in the sediments, a phenomenon that was previously reported in an earlier study of Yellowknife Bay (Andrade et al. 2010). A portion of arsenic particles deposited in the sediments likely underwent dissolution over time, and dissolved arsenic has subsequently diffused up or down within the sediment layers. The near-surface maxima of arsenic likely resulted from binding of dissolved arsenic to iron oxyhydroxides at the oxygen boundary near the sediment surface (Andrade et al. 2010). In general, the concentration of arsenic was correlated with iron and both elements had peaks in the near-surface layer for individual sediment core profiles (data not shown).

Insert Figure 7

Recovery of Yellowknife Bay sediments from legacy metal(loid) pollution was examined by comparing element concentrations in the surface layer (top 2.5 cm) with pre-mining concentrations (Table 7). Based on the four dated cores, the top 2.5 cm of sediment represented accumulation that occurred since around 2002 to 2010, depending on the sedimentation rate at the site. Farfield sites showed a return to pre-mining levels in surface sediments for antimony, copper, lead, mercury, silver, and zinc. Minor surface enrichment (2 or 3-fold) of the redox-sensitive elements arsenic and manganese was found at farfield sites (S5, S7, S8). At nearfield sites, surface sediments had levels approaching background (enrichment of ≤2) for copper, lead, mercury, and zinc. In contrast, arsenic and antimony, and to a lesser extent manganese and silver, remained considerably above pre-mining levels in nearfield surface sediments (up to 37 fold higher). Thus, nearfield sediments in Yellowknife Bay continued to accumulate metal(loid) pollution from Giant Mine following operational closure in 2004, possibly from on-going effluent release at the mouth of Baker Creek or lateral transport of contaminated sediments within Back Bay. Post-depositional dissolution of legacy arsenic and manganese in the sediments and upward diffusion to the sediment surface likely also contributed to the elevated levels of those elements in surface sediments.

Insert Table 7

Arsenic concentrations and speciation in sediment porewater

The solid-phase measurements of arsenic in sediments of Yellowknife Bay indicated there has been post-depositional movement, by upward diffusion of dissolved arsenic. Sediment porewater was measured for inorganic arsenic speciation at two nearfield sites (S3, S4) and a farfield site at the mouth of Yellowknife Bay (S5) in August 2015 (Table 8). A consistent pattern with depth was observed at all three sites, with the lowest dissolved arsenic concentrations measured just above the sediment-water interface and the highest concentrations measured in the deepest sediment layer examined (3–6 cm below the surface). Inorganic arsenic concentrations in the deeper layer were 1–2 orders of magnitude higher (168–1319 µg/L) at the nearfield sites (S3, S4) compared to the mouth of Yellowknife Bay (S5). This spatial variation reflects greater anthropogenic enrichment closer to the mine site. Dissolved arsenic was predominately as arsenate (As^{5+}) above the sediment-water interface and in the top 2 cm below the sediment in nearfield cores S3 and S4. Arsenite (As^{3+}) was the dominant inorganic form in the layer 3–6 cm below the sediment-water interface. In the farfield core (S5), approximately half of the arsenic measured in the overlying water was present as arsenite and the transition to predominately arsenite occurred 1–2 cm below the sediment interface. The general pattern of increasing concentrations and proportions of arsenite with depth in the sediment can be explained by a gradient in oxidation-reduction potential with depth in the sediments. Oxygen depletion in the sediment column with depth leads to reducing conditions, which favours the dissolution of solid-phase arsenic and increases concentrations in porewaters. Under reducing conditions, arsenic is typically stable as arsenite, which explains why arsenite is the dominant form of inorganic arsenic in deeper porewater.

Insert Table 8

Comparison of metal(loid)s levels in nearshore and offshore sediment

Levels of metal(loid)s in bulk sediment (top 10 cm) were investigated at shallow nearshore and deeper offshore sites close to the communities of Ndilo and Dettah in Yellowknife Bay (Figure 1). Two spatial patterns of metal(loid) concentrations were evident. First, deeper offshore sites close to Ndilo had higher metal(loid) concentrations than shallow nearshore sites (Figure 8). This pattern indicates that legacy pollution has accumulated more in offshore depositional areas rather than along shorelines. At Ndilo, total organic carbon concentrations of nearshore sediment (0.4 ± 0.2 %) were lower than at offshore sites (1.2 ± 0.2 %), which can be explained by the transport of organic matter to low-energy depositional areas via particle focusing (Blais et al. 1995). At Dettah, insufficient offshore sampling prevented a nearshore versus offshore comparison. The second spatial pattern observed was that nearshore bulk sediment at Ndilo had low and similar levels of metals compared to nearshore sites at Dettah, but arsenic and antimony levels were higher at Ndilo (Figure 8). This observation is consistent with the sediment core results that showed good recovery of metals in surface layers of sediments but on-going enrichment of arsenic and antimony.

Insert Figure 8

Sediment cores collected from two shoreline sites in Back Bay (CS, BBS) were sliced into four sections (0–5 cm, 5–10 cm, 10–15 cm, 10–25 cm) to examine depth variation of bulk sediment. There was little depth variation in metal concentrations and only modest declines in arsenic and antimony with depth (Figure 9). Further, metal(loid) concentrations were relatively low in all depth layers and similar to values of surface bulk sediment (top 10 cm) from other nearshore sites close to Ndilo (Figure 8, 9). Further, Nearshore areas are high energy environments where wave action continuously resuspends and moves sediment particles. Metal(loid)s bound to particles are transported over time to low energy environments in deep, offshore areas. These processes likely account for the lower concentrations and lack of stratigraphy in nearshore sediments.

Insert Figure 9

Surface water of Yellowknife Bay: General chemistry

Summer measurements in 2014 and 2015 indicated that Yellowknife Bay surface waters had an alkaline pH (7.9 ± 0.1; mean ± standard deviation; n=17, 9 sites in 2014 and 8 sites in 2015), low turbidity (2 ± 2 NTU), and low dissolved organic carbon (4.7 ± 0.1 µg/L). Surface waters had moderate ionic conductivity (184 ± 35 µS/cm), with slightly lower values near Ndilo (163 ± 33 µS/cm) compared with Dettah (208 ± 17 µS/cm). This spatial variation was likely due to the influence of low ion waters of the Yellowknife River entering the north end of the bay. Dissolved nutrients (nitrate + nitrite, phosphate) were below analytical detection.

Total and dissolved concentrations of arsenic, antimony and metals in surface waters were compared for a subset of sites, focusing on the nearfield area at Ndilo and Back Bay versus farfield at Dettah and Akaitcho Bay (Figure 10). Overall, concentrations of the eight key metal(loid)s were relatively low in water (including at depths near the sediment-water interface of offshore sites) and average values in Yellowknife Bay were below Canadian Drinking Water guidelines for the four elements with guidelines (antimony, arsenic, lead, mercury; Health Canada 2014). Arsenic and antimony were 2–3 times higher at the north end of Yellowknife Bay, consistent with the closer proximity of Back Bay and Ndilo to pollution sources at Giant Mine. Copper, lead and mercury concentrations were similar throughout Yellowknife Bay. Total zinc and manganese concentrations were approximately 2 times higher in the nearfield area but dissolved concentrations were not, suggesting the presence of more particulate zinc and manganese in surface waters near to Giant Mine. Lead and silver concentrations were very low and were close to analytical detection (total lead) or below detection (silver, dissolved lead) in surface waters of Yellowknife Bay.

Insert Figure 10

At offshore sites, variation in element concentrations through the water column was examined by comparing water collected 1 or 2 m from the lake surface with water collected 1 m above the lake bottom (see Table 3 for depths at specific sites). In general, there was little variability in metal(loid) concentration with depth. For example, the median difference in total arsenic concentration between surface and bottom depths at a site was 0.1 μg/L (n = 11 comparisons). However, on a few occasions greater variability with depth was found at sites in Back Bay. In August 2015, bottom water at sites W2 and W4 had 1.3-2.1 μg/L more arsenic than surface water. At site W3, the surface total arsenic concentration was 2.5 μg/L while the bottom water concentration was 14.0 μg/L. It is unclear why the bottom water concentration was considerably higher but thermal stratification at the time of sampling would have prevented mixing of the surface and bottom layers. The bottom water arsenic was primarily in the dissolved fraction so it was not due to resuspension of sediment. It could have diffused from contaminated sediments or originated from the effluent plume exiting nearby Baker Creek (500 m away from site W3).

Water concentrations of total arsenic declined with distance from the Giant Mine roaster (now decommissioned) (Figure 11). This relationship was statistically significant (linear regression $r^2 = 0.74$, $p<0.001$, n = 17 sites). The highest water arsenic concentrations (average > 2.5 μg/L) were observed within 3 km of the Giant Mine and higher temporal variability in the measurements was also observed at the closest sites (see error bars in Figure 11). Ten kilometres south of Giant Mine, at the mouth of Yellowknife Bay, total arsenic concentrations were approximately 1 μg/L or lower. One exception was site W16 (total arsenic = 1.6 μg/L), which was located near the Peg Lake outflow (Figure 2) and likely received arsenic from Con Mine effluent being discharged into Great Slave Lake. The total arsenic concentration at the farthest station (W17, 0.4 ± 0.1 μg/L) can be considered as the background level in summer for the main body of Great Slave Lake near Yellowknife Bay.

Insert Figure 11

Arsenic speciation in surface waters of Yellowknife Bay

The form and speciation of arsenic in water provides information on its mobility and fate in Yellowknife Bay. Arsenic in surface water was predominately in the dissolved form (i.e. passed through a 0.45 μm filter) and only a small portion was bound to particles (Figure 12). A comparison of dissolved arsenic and total (digested) arsenic measurements on the same water samples indicated that, on average, 88% of water arsenic was in the dissolved form (88±8%, n=55). Within the dissolved fraction, most of the arsenic was in the form of inorganic oxyanions, of either arsenite (As^{3+}) or arsenate (As^{5+}). On average, 77±19% of the dissolved arsenic in Yellowknife Bay surface waters was inorganic arsenic (n=52). The remaining portion of the dissolved arsenic was presumably in the form of organo-arsenic compounds. There are a large number of organo-arsenic compounds in the environment, with monomethylarsonic acids (MMAs) and dimethylarsinic acids (DMAs) being dominant in fresh waters (Cullen and Reimer 1989; Hasegawa et al. 2009). In Yellowknife Bay, MMAs were generally below analytical detection (<0.01 μg/L). Concentrations of DMAs were detected in most samples but at low levels (<0.3 μg/L). On average, DMAs represented 7±2% (n=32) of dissolved arsenic in surface waters of Yellowknife Bay.

Arsenic in surface waters of Yellowknife Bay (measured in late summer) was predominately as inorganic arsenic in both nearfield and farfield areas (Figure 12). Arsenate (As^{5+}) was typically found at higher concentrations than arsenite (As^{3+}), although arsenite was a significant component of the inorganic arsenic pool (38±15%, n=58). In a small number of water samples (n=6) from Yellowknife Bay, arsenite was found at a higher proportion that arsenate. The maximum arsenite concentration observed in Yellowknife Bay surface waters in this study was 2.1 μg/L. Arsenite was below analytical detection (<0.09 μg/L) at two sites on the main body of Great Slave Lake (W15, W17).

Insert Figure 12

DISCUSSION

This study generated several findings on the historical impact and present-day fate of metal(loid) pollution in Yellowknife Bay resulting from gold mining during the 20th century. Our analysis of the sediment record identified a suite of elements that were enriched during the early years of mining developments. Further, the dispersion of these elements extended a greater distance south into Great Slave Lake than previously recognized. We characterized the present-day recovery of elements enriched during the early years of mining operations and, overall, found relatively low levels of metals in surface sediment and water of Yellowknife Bay. In contrast, there was evidence of on-going inputs of arsenic and antimony to surface waters at the north end of Yellowknife Bay and high mobility of arsenic pollution in sediments. These main findings are discussed in more detail below.

20th Century enrichment of metal(loid)s in Yellowknife Bay from gold mining

Previous studies of environmental impacts of gold mining on Yellowknife Bay since the 1970s have focused on several elements including arsenic, antimony, lead and zinc, although the choice of elements was likely influenced, in part, by sampling and analytical considerations.

Recent and more thorough measurements have identified a suite of elements of potential concern in Baker Creek (Golder 2013) and in sediment of Back Bay (Golder 2005). Our study builds on that work by evaluating which specific elements were most enriched at the north end of Yellowknife Bay using the sediment record. We identified 14 elements that showed at least a two-fold enrichment in relation to background (pre-1930) levels. While high enrichment of arsenic, antimony, copper, lead and zinc in Yellowknife Bay has been previously reported (Sutherland 1989, Andrade et al. 2010), we identified additional elements, specifically manganese, mercury, silver and tungsten, which have received less attention. We identified lower enrichment (2–3 fold) above pre-1930 conditions for other elements, specifically cadmium, molybdenum, phosphorus, sulphur, and tin. Likewise, we found that cobalt, chromium and nickel were minimally enriched (1.1–1.6 fold) above pre-1930 concentrations in sediment. Of the 48 elements analyzed in sediment, antimony, arsenic, copper, lead, manganese, mercury, silver and zinc were the most highly deposited in Yellowknife Bay by historical mining releases during the 20th century.

Several caveats are important to consider with regard to our evaluation of historical element enrichment in north Yellowknife Bay. First, it is possible that sources of pollution other than mining could have contributed to the sediment accumulation, particularly for the suite of "less enriched" elements that had less defined profiles in the sediment (Table 4). For example, phosphorus loading to Back Bay occurred by release of sewage effluent from the 1950s to around 1980 (HydroQual 1989; Jackson et al. 1996), which may have contributed to the profile for that element. Nevertheless, the most highly enriched elements had depth profiles with peaks in sediment dated to the early years of mining activity (Figure 3), suggesting that gold mining releases were the dominant source. Second, some of the enriched elements are redox sensitive (arsenic, manganese, molybdenum, phosphorus, sulfur, and tungsten), and post-depositional movement in sediments could have resulted in surface peaks that positively biased the enrichment estimates. Finally, our evaluation of the main elements released into Yellowknife Bay was based on a core (S3) that was collected 1 km away from the mouth of Baker Creek and 1 km from the tailings beach on the north shore. There was likely considerable spatial variation in element enrichment within the receiving environment of Back Bay (particularly at the mouth of Baker Creek and near the tailings beach), and it is possible that some elements were more enriched within a localized area (e.g., such as cadmium near the beach area; Golder 2005).

Metal(loid) pollution generated on the Giant Mine property

The metal(loid)s that were most enriched in Yellowknife Bay sediments (arsenic, antimony, copper, lead, manganese, mercury, silver, and zinc) were also elevated in wastes generated on the Giant Mine property. An estimate 20,000 tonnes of arsenic trioxide were emitted from the roaster stack over the life of Giant Mine (Jamieson 2014), and large amounts of arsenic-bearing iron oxides were released in effluent and tailings (MVEIRB 2013; Fawcett et al. 2015; Walker et al. 2015). Antimony, copper, lead, silver, and zinc were also concentrated in dust particles generated during ore roasting (INAC 2010; Fawcett and Jamieson 2011). Mercury waste was generated during the amalgamation process used to extract gold during the earliest years of Giant Mine operations (Silke 2013). Calcine tailings contained elevated concentrations of arsenic and antimony, and to a lesser extent metals including cadmium, copper, cobalt, lead, manganese, nickel and zinc (INAC 2010). Those metals were enriched downstream in Baker Creek sediments, which received mining effluent since 1951 (Golder 2013). Interestingly, little enrichment of some of those metals (specifically nickel, cadmium, and cobalt) was found in sediment at site S3, located 1 km from the mouth of Baker Creek in Back Bay (Table 4). The low enrichment of those metals may be related to their geochemistry or lower total loadings exiting Baker Creek, which could have reduced the extent of dispersion.

Background concentrations of elements in Yellowknife Bay sediments

Background concentrations of the eight key elements in sediment were characterized using pre-1930 levels in four dated sediment cores from the study area (Table 4). Although not presented here, background concentrations of other elements could be determined using the raw data provided in Appendix 1 and 2. Previous evaluations of metal(loid) concentrations in Yellowknife Bay sediments have used the Canadian Council of Minister of the Environment (CCME) sediment quality guidelines to determine which elements are of potential concern (Golder 2005; Stantec 2014b). That approach is limited, however, when CCME guidelines do not exist for an element and when background concentrations are close to or exceed an established guideline. For example, the levels of chromium in Yellowknife Bay sediments have previously been highlighted because they exceeded the CCME interim sediment quality guideline of 37 µg/g (Golder 2005; Stantec 2014b). Our observations that chromium was minimally enriched in Yellowknife Bay sediment during the mid-20th century and that background sediment concentrations are slightly above the guideline (~40 µg/g) suggest that this element does not pose a significant issue in terms of historical loadings to the receiving environment from gold mining. Similarly, cadmium was previously highlighted because it slightly exceeded (0.7 µg/g) the CCME interim sediment quality guideline of 0.6 µg/g at some sites in Back Bay (Stantec 2014b). We observed background levels of 0.3 µg/g in Back Bay and 0.6–0.8 µg/g in Great Slave Lake, which were similar to the CCME guideline. Although higher cadmium concentrations (up to 3.2 µg/g) were observed in a localized area near the tailings beach by Golder (2005), their detailed spatial mapping of sediment cadmium concentrations in Back Bay showed that most of the nearfield area had levels near background (<0.6 μg/g). Those findings suggest that cadmium also does not pose a significant issue in terms of historical enrichment from gold mining on a broad spatial scale in north Yellowknife Bay. These two examples highlight the utility of using estimates of background levels of elements (instead of CCME sediment quality guidelines) to evaluate the spatial and temporal trends of sediments in Yellowknife Bay.

We estimated the background arsenic concentration in Yellowknife Bay sediments at 25±10 μg/g prior to the start of mining activities in the 1930s. This estimate is considerably lower than the 150 μg/g background value from RiskLogic (2002) that has been used recently to evaluate arsenic sediment concentrations in Yellowknife Bay (Stantec 2014b). The 150 μg/g estimate from RiskLogic (2002) is based on arsenic concentrations in terrestrial soils, and the application of that guideline to lake sediments is questionable because different environmental processes control arsenic levels in soils compared to sediments. Other Yellowknife studies have obtained similar estimates for background arsenic in lake sediments. Mace (1998) estimated background sediment arsenic of 7–25 μg/g for Yellowknife Bay, and Galloway et al. (2015) estimated background arsenic at 25 μg/g in lake sediments in the Yellowknife Area. We recommend the use of our lower background estimate of arsenic (25±10 μg/g) from this study rather than the 150 μg/g guideline for future evaluations of sediment arsenic levels in Yellowknife Bay. Note that 25 μg/g is above the CCME probable effects guideline of 17 μg/g for sediment although the CCME guideline is generic, and no information is available on the site-specific toxicity of background arsenic levels in Yellowknife Bay sediments.

Historic dispersion of metal(loid)s in Yellowknife Bay and the main body of Great Slave Lake

This study generated the first detailed measurements of metal(loid) dispersion from mining pollution in a southerly direction from Yellowknife into the main body of Great Slave Lake. Using evidence from sediment core profiles, we found enrichment of antimony in sediments dated to the mid-20th century as far as 24 km (site S8) to the south of the Giant Mine roaster (Figure 6). Arsenic was also slightly enriched at that site but the peak was near the sediment surface, likely due to post-depositional migration of arsenic in the sediment column (Figure 7). The regression models of metal(loid) maximum enrichment in sediment versus distance suggested that the dispersion of mine pollution extended approximately 30 km south of Giant Mine (Figure 5). This estimate is similar to that of Palmer et al. (2015) and Houben et al. (2016), who found that arsenic concentrations in lake water approached background at an approximate distance of 17 km to the west of the Giant Mine roaster.

It is likely that farfield sites at the mouth of Yellowknife Bay and the main body of Great Slave Lake were impacted from aerial deposition of roaster emissions, and our findings are consistent with previous studies of the Yellowknife area (Hocking et al. 1978; Galloway et al. 2015; Palmer et al. 2015; Houben et al. 2016; Thienpont et al. 2016). Similarly, studies of aerial dispersion from other industrial developments have shown that arsenic emissions from stacks can reach considerable distances. For example, particulate arsenic was found to deposit in snow within 50 km of upgrader facilities in the Oil Sands region of Alberta (Kelly et al. 2010). Lake sediments sampled up to 20 km away from the smelters at Sudbury indicated significant arsenic enrichment (Nriagu 1983). Snow surveys near Flin Flon showed that the zone of arsenic deposition of a base metal smelter with a super stack height of 250 m extended approximately 70 km from the site (Franzin et al. 1979). A more recent study of soils generated a larger estimate of 100 km for the zone of arsenic deposition (McMartin et al. 1999). The dispersion distance of arsenic released from a stack is determined by many factors including the stack height, the exit velocity of emissions, the atmospheric pressure and wind velocity (Smith 1977). The lower estimate of dispersion distance in our study (30 km) relative to other industrial sites described above may be due to relatively short height of the Giant Mine roaster stack (45 m). Historical records of roaster emissions indicate that most arsenic released into the air from ore roasting originated from Giant Mine although Con Mine also roasted ore until 1970 (Hocking et al. 1978).

It remains unclear to what extent effluent and tailings released from Giant Mine and Con Mine (via Peg Lake outlet) also reached the farfield sites (S5 to S8) in this study. The chemical composition of roaster emissions from Giant Mine during the initial years of operation was not well characterized, although arsenic trioxide was released from the stack and the sediment record of nearby Pocket Lake indicated elevated aerial deposition of arsenic, antimony, mercury and lead (Thienpont et al. 2016). Other enriched elements in Yellowknife Bay sediments such as copper, zinc and manganese may have originated primarily from effluent and tailings releases. Future mineralogical measurements of sediment particles could provide information on transport pathways and the relative importance of aerial versus effluent or tailings sources of arsenic and antimony at farfield sites of Yellowknife Bay and Great Slave Lake (Fawcett and Jamieson 2011; Jamieson 2014; Bromstad et al. 2017).

The dispersion of mining pollution extended farther south into Great Slave Lake than previously recognized. Horseshoe Island (south of Yellowknife Bay and Akaitcho Bay) has been widely used in previous environmental studies as a reference area to investigate mining impacts (Jackson et al. 1996; Andrade et al. 2010; Stantec 2014b; 2014a). Although metal(loid) concentrations are far lower in sediment near Horseshoe Island than the north end of Yellowknife Bay or the Peg Lake outflow, subsurface arsenic peaks in sediment from that area were above background in this study and in that of Andrade et al. (2010). Our findings also imply that the community of Dettah, located at the mouth of Yellowknife Bay, was exposed to metal(loid)s during the early years of mining operations, although to a lesser extent than Ndilo which was closer to the Giant and Con mines.

Recovery of metal(loid) levels in Yellowknife Bay

The sediment record of Yellowknife Bay indicated that the greatest inputs of mining contamination occurred during the early years of operation. Sediment concentrations of enriched elements began to decline in the 1960s, likely in response to improvements in the ore roasting process and infrastructure that reduced emissions at Giant Mine (Hocking et al. 1978; Silke 2013). Reductions of metal loadings following the installation of an effluent treatment plant in 1981 likely also contributed to recovery of nearfield sediment more recently. Metal concentrations in surface sediments (top 2.5 cm, dated to post 2002) have, in general, returned to near background conditions although localized enrichment may remain, particularly near the Baker Creek outlet and tailings beach. Similarly, surface water concentrations of metals were relatively low and generally showed little spatial variation in Yellowknife Bay, except for higher particulate fractions of zinc and manganese in the nearfield area. In contrast, arsenic and antimony remain enriched both in surface sediments and in water at the north end of the bay.

General recovery of metal levels in Yellowknife Bay sediments reflects the long-term process of burial of legacy pollution by younger sediment of low metal content. It implies that loadings of metals to Yellowknife Bay have declined dramatically in recent decades following pollution mitigation measures and are approaching background. On-going significant enrichment (5 to 37 fold) of arsenic and antimony in surface sediments of north Yellowknife Bay indicates there are continued loadings of those metalloids either from external sources, internal recycling or more likely from both. Arsenic from the Giant Mine site continues to enter Yellowknife Bay via Baker Creek (800 kg/year) and surface runoff (110 kg/year) (MVEIRB 2013). Although loadings for antimony have not been calculated, elevated concentrations in effluent and mine waste on the site (Fawcett et al. 2015) are likely transported to Yellowknife Bay in a similar manner to arsenic. Lateral migration of sediments has been observed along the north shore of Yellowknife Bay in the tailings beach area (Golder 2005), and sediment transport could also contribute to the enrichment in surface sediments of profundal areas. Finally, post-depositional mobility of arsenic in sediments and recycling between the water column and sediments are likely contributing to on-going enrichment of arsenic in the bay (Martin and Pedersen 2002; Andrade et al. 2010). The continued enrichment of manganese in surface sediments likely also reflects redox processes resulting in upward diffusion of reduced manganese to the sediment-water interface. The antimony profiles in Yellowknife Bay sediments showed limited diagenetic behaviour although little information exists on the potential for diffusion of porewater antimony into overlying water (Chen et al. 2003).

Estimate of background arsenic in surface waters of Yellowknife Bay

In contrast with sediments, it is not possible to determine the pre-mining concentration of arsenic in surface waters of Yellowknife Bay. However, arsenic concentrations from the two main water sources entering Yellowknife Bay, the Yellowknife River and the main body of Great Slave Lake, could be used to estimate pre-mining arsenic concentrations in the bay. This approach assumes that present-day arsenic concentrations in the two main water sources are similar to pre-mining conditions. Our measurements of total arsenic in the main body of Great Slave Lake (sites W15, W17) and the mouth of Yellowknife Bay near Dettah (site W14) were <0.6 µg/L. Similarly, recent measurements of total arsenic concentrations in the Yellowknife River from 2005 to 2013 were typically <1 µg/L (mean ± SE = 0.56 ± 0.03 µg/L, n = 92) (Environment and Natural Resources, GNWT, unpublished data). Together, these data suggest that total arsenic in Yellowknife Bay water may have been <1 µg/L before the onset of mining activities. In this study, the average concentration of total (digested) arsenic in water at the north end of Yellowknife Bay was 3.1 ± 0.5 µg/L (mean ± SE, n = 22; sites W2 to W4, W6 to W10, surface and bottom depths). Sampling was not conducted throughout the year, and those results reflect summer conditions. Seasonal sampling conducted by Stantec over the course of a year from 2012 to 2013 indicated that north Yellowknife Bay surface waters had an average total arsenic concentration of 1.90 ± 0.17 µg/L (mean ± SE, n = 48) (Stantec 2014b). We estimate that current levels of arsenic in surface waters at the north end of Yellowknife Bay remain enriched 3 to 5 times above background. Most of the arsenic was in the dissolved fraction as arsenate and to a lesser extent arsenite. Although surface water arsenic was above background, these levels were relatively low and below the Health Canada drinking water guideline of 10 µg/L (Health Canada 2014).

Post-depositional movement of arsenic

The long-term stability of arsenic in sediments remains a significant uncertainty in the recovery of the Yellowknife Bay environment following gold mining impacts from the 20th century. Arsenic pollution in Yellowknife Bay is not being buried deeper in sediments over time, in contrast with legacy metals (e.g., copper, lead, zinc). Solid-phase concentrations of arsenic in near surface sediments remain elevated (often > 1000 µg/g) and porewater arsenic concentrations were also elevated (> 100 µg/L). The water column of Yellowknife Bay is typically well oxygenated in both summer and winter (Stantec 2014b), and the maintenance of an oxygen rich-layer at the sediment-water interface is critical for arsenic retention in sediments. The onset of a reducing environment at the sediment-water interface, such as through increased microbial degradation of organic matter, would result in reductive dissolution of arsenic at that boundary and increase diffusion of arsenic into overlying water (Martin and Pedersen 2002; Andrade et al. 2010). Further research is recommended to conduct a process-focused investigation of arsenic diffusion from sediment to the water column of Yellowknife Bay in order to: 1) better constrain the environmental conditions (such as warmer temperatures or anoxia) that could stimulate diffusion of arsenic to overlying water; and 2), estimate how much levels of arsenic in overlying water could potentially increase with greater sediment diffusion.

In addition, there is evidence that current levels of sediment arsenic may be sufficiently elevated in Yellowknife Bay to impact aquatic invertebrate communities

(Moore et al. 1978; Sutherland 1989; Golder 2005). The total abundance and species richness of benthic invertebrates and the absence of sensitive species in sediment with >150 µg/g of arsenic (Golder 2005) suggest that additional research is warranted on the toxicological consequences of legacy arsenic on the benthic community in the bay. Slow recovery of sediment arsenic in Yellowknife Bay may have ecological consequences for resident benthic invertebrates.

CONCLUSION

Widespread dispersal of arsenic, antimony and metals occurred during the early years of gold mining from the 1940s to 1960s. Although the greatest loadings to Yellowknife Bay occurred in the nearfield area within a few kilometres of Giant Mine, evidence of the deposition plume was observed in the sediment record at a distance of 24 km to the south of the mine in the main body of Great Slave Lake. Improved pollution control measures were implemented over decades at Giant Mine and the mine's eventual closure have resulted in reduced loadings of metal(loid)s to Yellowknife Bay. There are positive signs of recovery for metals with levels returning to near background concentrations in surface sediment and relatively low levels were found in present-day surface waters. However, there is evidence of continued loadings and/or internal recycling of arsenic and antimony in the nearfield area adjacent to Giant Mine. Current levels of arsenic in surface waters at the north end of Yellowknife Bay remain an estimated 3 to 5 fold above background, although those levels are below the Health Canada drinking water guideline of 10 µg/L. Sediments of Yellowknife Bay are a large and potentially leaky reservoir of legacy arsenic pollution. Further research is recommended to evaluate the long-term stability of sediment arsenic in Yellowknife Bay during the 21st century.

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Table 1. Site information for bulk surface sediment (top 10 cm) collected in nearshore areas adjacent to Ndilo, Dettah and Old Town on Yellowknife Bay.

Site ID	Latitude (°N)	Longitude (°W)	Community	Collection Date	Water Depth (m)
ND1[a]	62°28.608'	114°20.325'	Ndilo	Sept 2014	0.5
ND2[a]	62°28.832'	114°19.746'	Ndilo	Sept 2014	1.2–10.3
ND3[a]	62°28.683'	114°19.890'	Ndilo	Sept 2014	0.8–4.5
ND4[a]	62°28.414'	114°19.971'	Ndilo	Sept 2014	11.5–12
ND6[b]	62°28.671'	114°19.708'	Ndilo	Aug 2015	7.4–14.5
ND7[b]	62°28.560'	114°19.880'	Ndilo	Aug 2015	11.8–16.8
DE1[a]	62°24.445'	114°18.463'	Dettah	Sept 2014	3.8–5.5
DE2[a]	62°24.849'	114°18.966'	Dettah	Sept 2014	3–4
DE3[a]	62°24.632'	114°16.644'	Dettah	Sept 2014	3
DE5[b]	62°24.745'	114°17.940'	Dettah	Aug 2015	0.8–1.7
BBS	62°27.804'	114°21.348'	Old Town	Aug 2016	0.5–1
CS	62°28.244'	114°20.885'	Old Town	Aug 2016	1–1.5

[a] Site reported in Chételat (2015)

[b] Site reported in Chételat (2017)

Table 2. Site information for eight sediment cores collected to characterize historical changes in element accumulation during the 20th century. The cores were collected in Yellowknife Bay and the north arm of Great Slave Lake, and are presented by increasing distance from Giant Mine.

Site ID	**Latitude (°N)**	**Longitude (°W)**	**Distance from Roaster[a] (km)**	**Collection Date**	**Water Depth (m)**	**Core Length (cm)**
S1	62°29.515'	114°20.502'	1.4	Aug 2015	8	19
S2	62°29.127'	114°21.067'	1.9	Aug 2015	9	13
S3	62°29.189'	114°20.409'	1.9	Sept 2014	11	40
S4[b]	62°28.375'	114°19.956'	3.5	Sept 2014	16	36
S5	62°25.181'	114°20.156'	9.2	Sept 2013	25	25
S6[b]	62°24.260'	114°17.292'	11.5	Sept 2014	~7	30
S7	62°22.532'	114°23.357'	14.2	Aug 2015	25	26
S8	62°17.461'	114°18.702'	23.7	Sept 2013	29	25

[a] Aerial distance to location of the Giant Mine roaster (prior to decommissioning)

[b] Site reported under a different ID in Chételat (2015)

Table 3. Site information for water chemistry measurements in Yellowknife (YK) Bay and the main body of Great Slave Lake (GSL) from 2014 to 2016.

Site ID	Location	Latitude (°N)	Longitude (°W)	Distance from Roaster[a] (km)	Collection Dates	Water Depth (m)	Collection Depths (m)	Analyses[c]
W1	Baker Creek	62°29.240'	114°21.779'	1.7	Sept 2014, Aug 2015	0.3	0.2	3–4
W2	Back Bay	62°29.603'	114°20.493'	1.3	Sept 2014, Aug 2015	9	2, 8	3–4
W3	Back Bay	62°29.127'	114°21.067'	1.9	Sept 2014, Aug 2015	9.5	2, 8.5	3–5
W4[b]	Back Bay	62°29.187'	114°20.250'	2.0	Sept 2014, Aug 2015	10	1, 2, 9	1–5
W5	Yellowknife River	62°31.096'	114°19.236'	2.6	Aug 2015	0.3	0.2	3–4
W6[b]	Back Bay, Ndilo shore	62°28.625'	114°20.219'	3.0	Sept 2014, Aug 2015	0.3-0.5	0.2	1–4
BBS	Back Bay, Old Town shore	62°27.804'	114°21.348'	4.3	Aug 2016	0.5-1	0.2	2
CS	Back Bay, Old Town shore	62°28.244'	114°20.885'	3.5	Aug 2016	1-1.5	0.2	2
W7[b]	YK Bay, Ndilo shore	62°28.824'	114°19.905'	2.8	Sept 2014	1	0.2	1–4
W8[b]	YK Bay, Ndilo shore	62°28.739'	114°19.888'	2.9	Sept 2014, Aug 2015	0.3	0.2	1–4
W9[b]	YK Bay, Ndilo shore	62°28.375'	114°19.957'	3.5	Sept 2014, Aug 2015	12-15.5	1	1–4
W10	YK Bay, Pumphouse No.1	62°27.047'	114°20.997'	5.7	Sept 2014	6	2	3–4
W11[b]	YK Bay, Dettah shore	62°24.652'	114°18.722'	10.4	Sept 2014, Aug 2015	0.3	0.2	1–4
W12[b]	YK Bay, Dettah shore	62°24.678'	114°18.786'	10.4	Sept 2014, Aug 2015	0.3	0.2	1–4
W13[b]	Akaitcho Bay	62°24.540'	114°16.828'	11.1	Sept 2014	3	1	1–4
W14[b]	YK Bay, near Dettah	62°24.553'	114°19.590'	10.4	Sept 2014, Aug 2015	12.6-14.2	1, 13	1–5
W15	GSL, near Kam Point	62°22.532'	114°23.357'	14.2	Aug 2015	25	1, 22	3–5
W16	GSL, Peg Lake outflow	62°22.273'	114°24.938'	14.9	Aug 2015	2.3	1	3–5
W17	GSL, near Ruth Island	62°17.929'	114°17.429'	22.9	Sept 2014, Aug 2015	14.5-20.3	1, 2, 11, 19	3–5

[a] Aerial distance to location of the Giant Mine roaster prior to deconstruction

[b] Site reported under a different ID in Chételat (2015, 2017)

[c] Chemical analyses: 1 – general chemistry, 2 – total (unfiltered) elements, 3 – dissolved (filtered) elements, 4 – arsenic speciation, 5 –mercury (total)

Table 4. Mean and maximum concentrations of elements, and their enrichment factors in north Yellowknife Bay sediment core S3 before and after the onset of gold mining activities. Fourteen elements with a maximum enrichment factor ≥2 are highlighted in green. Note that platinum, palladium, rhodium and tellurium were below analytical detection.

Element	**Sediment Concentration (µg/g)**			**Enrichment Factor**		**A peak in 1950s to 1970s?**
	Pre-1930[a] (Mean ± 1 SD)	**Post-1930[b] (Mean ± 1 SD)**	**Maximum**	**Mean**	**Maximum**	
Sb	0.5 ± 0.1	38.1 ± 40.1	128	74	248	Yes
Ag	0.12 ± 0.01	2.23 ± 1.97	5.67	19	49	Yes
As	38 ± 15	413 ± 397	1270	11	34	Yes
Cu	32.0 ± 1.2	261.5 ± 266.4	798	8	25	Yes
Mn	464 ± 8	1310 ± 1895	6930	3	15	Yes
Pb	11.8 ± 0.6	43.0 ± 29.0	101	4	9	Yes
Hg	0.022 ± 0.002	0.086 ± 0.046	0.172	4	8	Yes
Zn	91 ± 2	173 ± 100	419	1.9	5	Yes
W	0.15 ± 0.03	0.48 ± 0.13	0.75	3	5	Yes
Cd	0.3 ± 0.1	0.5 ± 0.2	1.0	1.4	3	Yes
P	605 ± 5	891 ± 393	1640	1.5	3	Yes
Mo	1.04 ± 0.06	1.02 ± 0.58	2.57	1.0	3	No
Sn	0.7 ± 0.1	0.9 ± 0.2	1.3	1.4	2	No
S	1283 ± 116	1140 ± 714	2520	0.9	2	No
Nb	0.26 ± 0.03	0.34 ± 0.07	0.48	1.3	1.8	---
Na	273 ± 7	319 ± 49	468	1.2	1.7	---
Co	13.7 ± 1.2	18.1 ± 2.4	21.2	1.3	1.6	---
Ni	38.7 ± 1.8	48.5 ± 8.3	62.2	1.3	1.6	---
Ba	243 ± 6	226 ± 35	332	0.9	1.4	---
Fe	30767 ± 551	35058 ± 3960	42800	1.1	1.4	---
Sr	32.4 ± 1.3	32.7 ± 4.9	43.8	1.0	1.4	---
Bi	0.323 ± 0.012	0.356 ± 0.036	0.425	1.1	1.3	---
Se	0.83 ± 0.03	0.84 ± 0.10	1.06	1.0	1.3	---
Ca	3977 ± 92	4013 ± 529	5060	1.0	1.3	---
B	6 ± 1	6 ± 1	7	1.0	1.2	---
Cs	1.52 ± 0.06	1.55 ± 0.08	1.64	1.0	1.1	---
Cr	45.4 ± 0.7	46.3 ± 1.6	48.5	1.0	1.1	---
Ti	500 ± 48	478 ± 69	562	1.0	1.1	---
V	49.8 ± 0.6	49.0 ± 1.5	52	1.0	1.1	---
Mg	9017 ± 117	9230 ± 256	9590	1.0	1.1	---
Zr	5.6 ± 0.2	4.6 ± 1.4	6.3	0.8	1.1	---
Ge	0.32 ± 0.02	0.31 ± 0.02	0.34	1.0	1.1	---
Be	0.846 ± 0.028	0.743 ± 0.035	0.813	0.9	1.0	---
Ce	63.7 ± 0.7	55.9 ± 2.6	61.8	0.9	1.0	---
Ga	7.33 ± 0.06	7.05 ± 0.18	7.37	1.0	1.0	---
La	31.0 ± 0.2	27.9 ± 1.1	29.7	0.9	1.0	---
Li	33.2 ± 0.2	32.0 ± 0.9	33.5	1.0	1.0	---
Rb	31.8 ± 0.5	29.1 ± 1.5	31.6	0.9	1.0	---
Tl	0.294 ± 0.005	0.254 ± 0.026	0.294	0.9	1.0	---
Al	18033 ± 252	17692 ± 571	18500	1.0	1.0	---
K	3463 ± 38	3260 ± 166	3590	0.9	1.0	---
Sc	5.76 ± 0.26	5.48 ± 0.35	5.99	1.0	1.0	---
Y	11.8 ± 0.3	10.1 ± 0.4	11.3	0.9	1.0	---
U	5.26 ± 0.19	4.12 ± 0.39	4.8	0.8	0.9	---

[a]n=3, [b]n=12

Table 5. Maximum and background concentrations (µg/g), and maximum enrichment factors of eight elements measured in sediment core profiles of nearfield and farfield sites in Yellowknife Bay and the main body of Great Slave Lake.

Element	**Peak Sediment Concentration**		**Background[c] Concentration**	**Maximum Enrichment Factor**	
	Nearfield[a]	**Farfield[b]**		**Nearfield[a]**	**Farfield[b]**
Antimony	77–249	1.6–8.7	0.7 ± 0.1	107–347	2–12
Arsenic	741–4560	29–126	25 ± 10	29–180	1.1–5
Copper	297–798	63–87	40 ± 9	7–20	1.6–2.2
Lead	71–351	15–29	16 ± 4	4–22	0.9–1.8
Manganese	2540–17200	520–1960	451 ± 59	6–38	1.2–4
Mercury	0.13–0.34	0.05–0.07	0.04 ± 0.01	4–10	1.3–2.1
Silver	1.6–5.7	0.1–0.9	0.2 ± 0.1	10–34	0.6–5
Zinc	343–520	93–190	109 ± 18	3–5	0.9–1.7

[a] Nearfield cores S1-S4; [b] Farfield cores S5-S8; [c] Average concentration (± 1 standard deviation) in pre-mining layers (before 1930) pooled over the four dated sediment cores (S3, S4, S5, S8); Samples sizes for background concentrations were n=15 for each element except mercury (n=34) and silver (n=8)

Table 6. Sediment depths and estimated dates (with 95% confidence intervals) for when antimony concentrations began to increase in sediment and when peak concentrations occurred in four cores from Yellowknife Bay and the main body of Great Slave Lake.

	Start of Concentration Increase			**Peak Concentration**		
Core	**Depth (cm)**	**Year**	**95% CI**	**Depth (cm)**	**Year**	**95% CI**
S3	12–13	1952	1938–1964	9–9.5	1965	1954–1974
S4	22–23	1940	1932–1947	16–17	1959	1954–1964
S5	21–22	1942	1938–1945	15–16	1969	1967–1970
S8	22–23	1936	1924–1948	18–20	1957	1948–1962

Table 7. Surface sediment concentrations (µg/g) and enrichment factors of eight elements measured in sediment core profiles of nearfield and farfield sites in Yellowknife Bay and the main body of Great Slave Lake.

Element	**Surface Concentration (0 – 2.5 cm)**		**Background[c] Concentration**	**Surface Enrichment Factor**	
	Nearfield[a]	**Farfield[b]**		**Nearfield[a]**	**Farfield[b]**
Antimony	3.9–17.5	0.7–1.2	0.7 ± 0.1	5–24	1.0–1.6
Arsenic	386–927	13–71	25 ± 10	15–37	0.5–3
Copper	38–83	43–49	40 ± 9	1.0–2	1.1–1.2
Lead	18–38	11–21	16 ± 4	1.2–2	0.7–1.3
Manganese	1975–3571	329–1447	451 ± 59	4–8	0.7–3
Mercury	0.04–0.06	0.03–0.05	0.04 ± 0.01	1.2–1.8	0.8–1.5
Silver	0.1–0.7	0.1–0.2	0.2 ± 0.1	0.6–4	0.6–1.3
Zinc	95–119	74–131	109 ± 18	0.9–1.1	0.7–1.2

[a] Nearfield cores S1-S4; [b] Farfield cores S5-S8; [c] Average concentration (± 1 standard deviation) in pre-mining layers (before 1930) pooled over the four dated sediment cores (S3, S4, S5, S8); Samples sizes for background concentrations were n=15 for each element except mercury (n=34) and silver (n=8)

Table 8. Total inorganic arsenic concentrations (mean ± standard deviation) and percent arsenite in sediment porewater and water just above the sediment-water interface (SWI) measured at three sites in Yellowknife in Bay in August 2015. Measurements are means of duplicate sediment cores from each site.

Site	**Depth (Layer)**	**Total Inorganic Arsenic (µg/L)**	**% Arsenite**
S3	1–2 cm above SWI	3.7 ± 1.0	33 ± 3
	0–2 cm below SWI	22.2 ± 26.4	21 ± 17
	3–6 cm below SWI	479 ± 195	92 ± 13
S4	1–2 cm above SWI	3.1 ± 0.4	25 ± 1
	0–2 cm below SWI	11.3 ± 10.9	22 ± 14
	3–6 cm below SWI	763 ± 398	89 ± 5
S5	1–2 cm above SWI	0.5 ± 0.2	55 ± 13
	0–2 cm below SWI	2.2 ± 1.7	75 ± 32
	3–6 cm below SWI	9.8 ± 6.2	94 ± 4

Figure 1. Locations of sites sampled for bulk sediment (brown circles) and sediment core profiles (green circles) from 2013 to 2016 in Yellowknife Bay and the main body of Great Slave Lake.

Figure 2. Locations of sites sampled for water chemistry on one or two occasions between 2014 and 2016 in Yellowknife Bay and the main body of Great Slave Lake.

Figure 3. Depth profiles of element concentrations in sediment core S3 collected near Giant Mine at the north end of Yellowknife Bay. Each of the metal(loid)s had maximum enrichment factors ≥5. The horizontal dashed line indicates the approximate sediment depth dated to the opening of Giant Mine in 1948 (with dotted lines for upper and lower 95% confidence intervals). Note the different concentration scales among the four panels.

Figure 4. Decline in maximum enrichment of antimony in sediment with increasing distance from the Giant Mine roaster (now decommissioned).

Figure 5. Declines in maximum enrichment of eight metal(loid)s in sediment with increasing distance from the Giant Mine roaster (now decommissioned). Note that both axes are presented on a logarithmic scale. A reference (dashed) line for no enrichment above background (enrichment factor = 1) is included. All regression models were statistically significant ($p<0.03$).

Figure 6. Historical changes in antimony concentration in four dated sediment cores collected in Yellowknife Bay and the main body of Great Slave Lake. Note the change in concentration scale between the two panels.

Figure 7. Arsenic concentration profiles in four dated sediment cores collected in Yellowknife Bay and the main body of Great Slave Lake. Note the change in concentration scale between the two panels.

Figure 8. Average metal(loid) concentrations (± 1 standard error) in bulk sediment (top 10 cm) collected nearshore at Ndilo (n=5 sites; BBS, CS, ND1, ND2a, ND3) and Dettah (n=4 sites; DE1, DE2, DE3, DE5) and offshore at Ndilo (n=4 sites; ND2b,c, ND4, ND6, ND7). One to three replicates were collected per site. Note that the concentrations are presented on a logarithmic scale. Silver concentrations were below analytical detection at nearshore sites and in those cases, the detection limit was used.

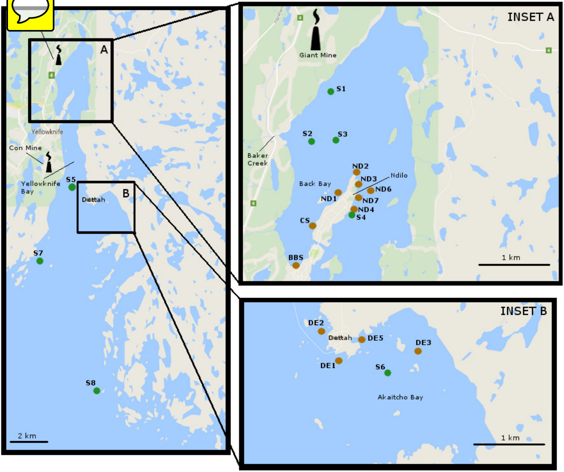
Figure 9. Average metal(loid) concentrations (± 1 standard error) in four bulk layers of sediment from three cores collected at a shoreline site (CS) in Back Bay. Note that concentrations are presented on a logarithmic scale.

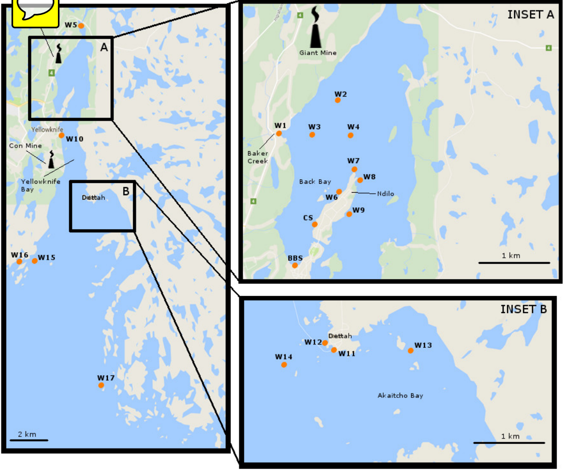
Figure 10. Surface water concentrations (mean ± standard error) of total (acid-leachable) and dissolved metal(loid)s in the nearfield area of Back Bay / Ndilo (n=10 sites; W2 to W4,

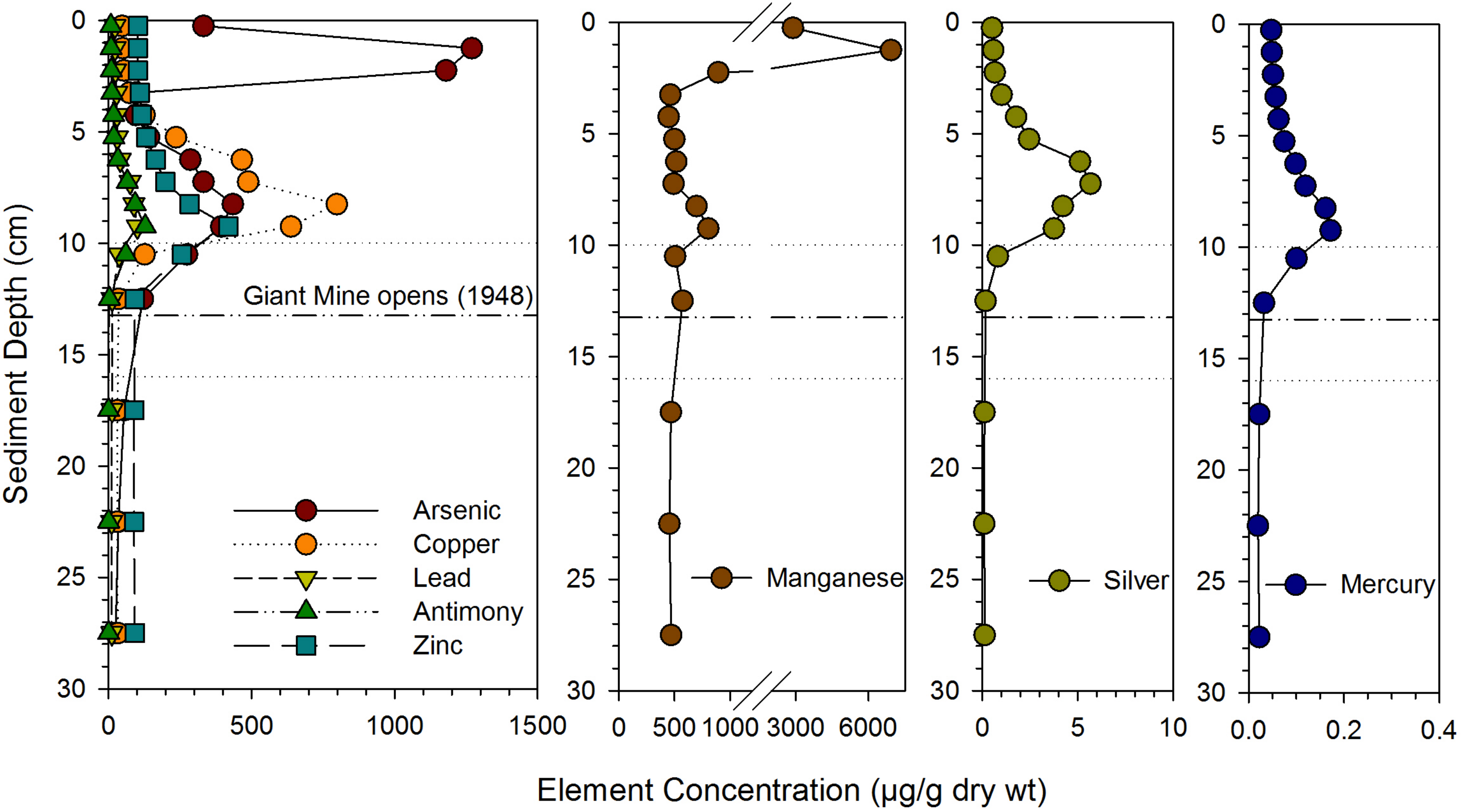
W6 to W10, BBS, CS) and in the farfield area of Dettah / Akaitcho Bay (n=4 sites; W11 to W14). Silver and dissolved lead are not presented because values were below analytical detection. Dissolved mercury was not measured. *Values are reported in µg/L except for mercury (ng/L).

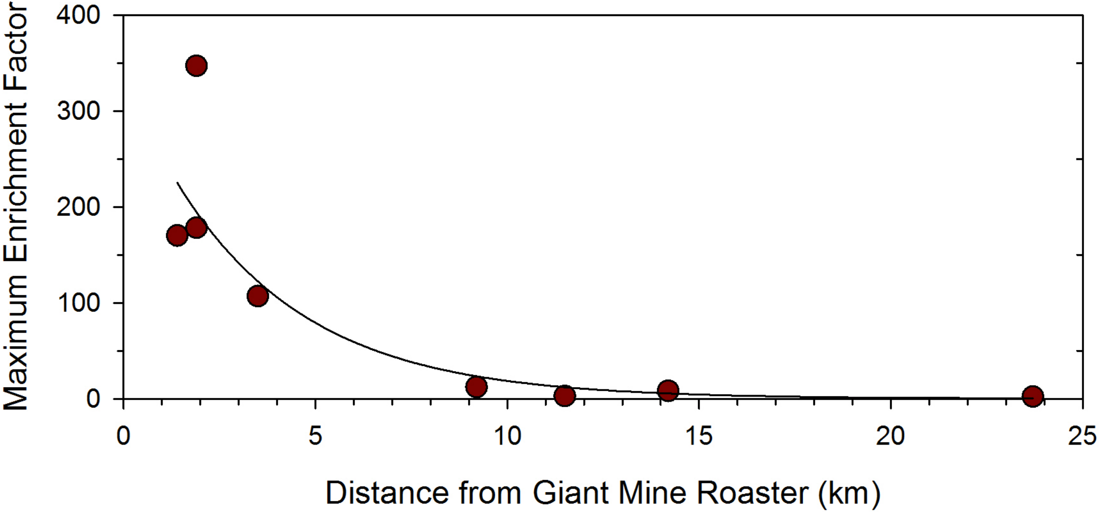
Figure 11. Decline in water total arsenic concentration with increasing distance from the Giant Mine roaster (now decommissioned). The data points are means (± standard deviation) for sites in Yellowknife Bay and the main body of Great Slave Lake. Note that distance is presented on a logarithmic scale. The site mean with large variation is W3, located 500 m from the mouth of Baker Creek.

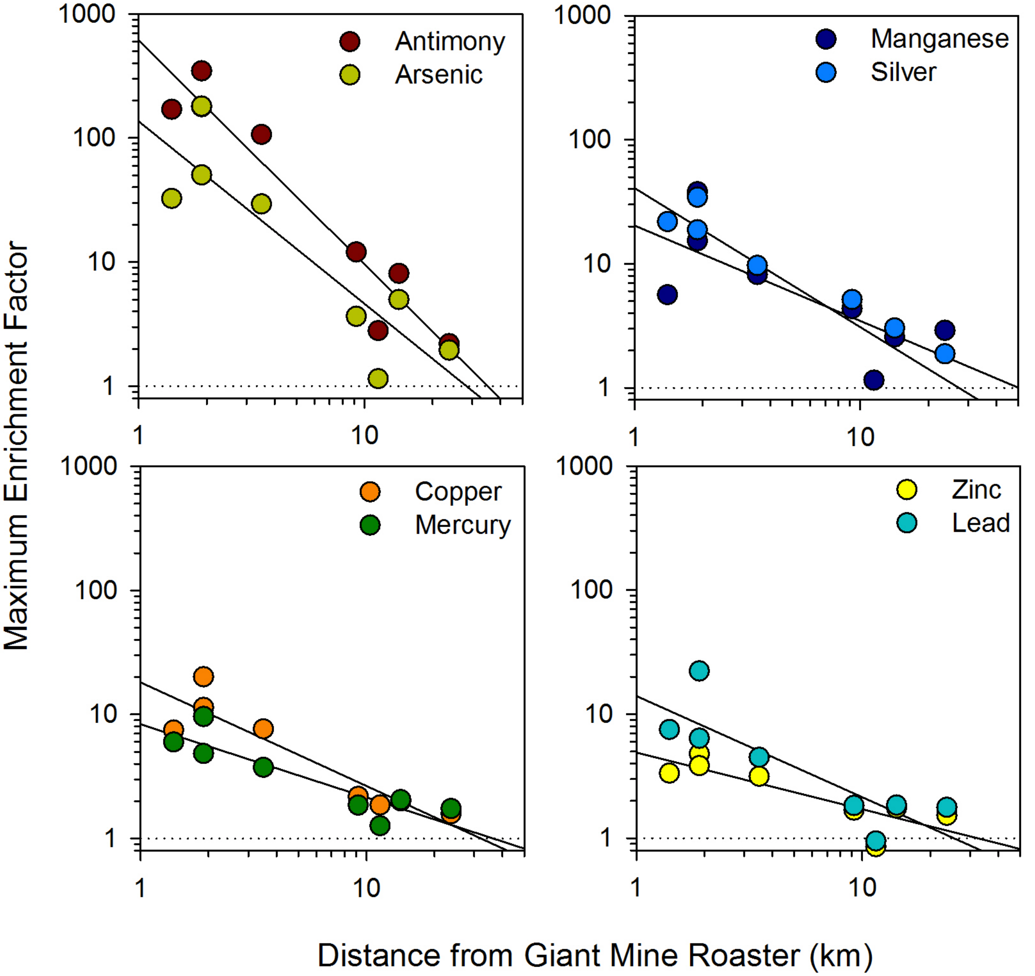
Figure 12. Surface water arsenic concentrations (total, dissolved, and inorganic speciation) measured throughout the study area in September 2014 and August 2015. Box plots identify the median (mid-line), 25th and 75th percentiles (box edges), minimums and maximums (error bars) and outliers (black points).

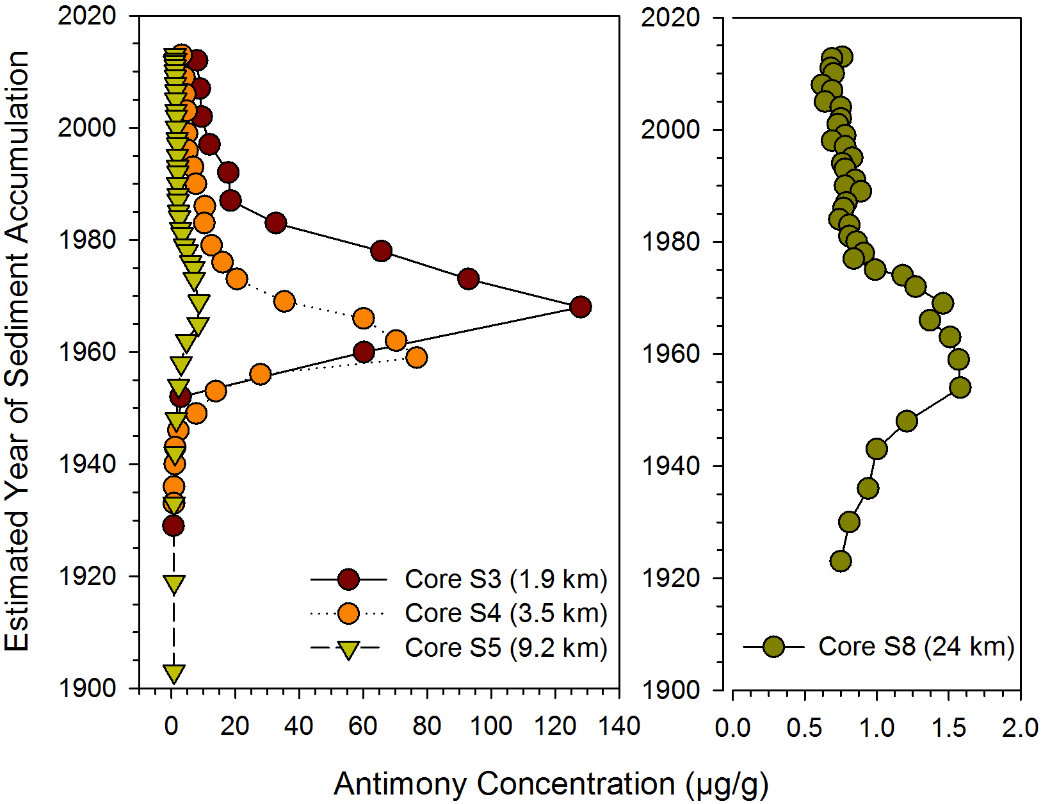

A
Yellowknife
Con Mine
Yellowknife Bay
S5
Dettah
B
S7
S8
2 km
INSET A
Giant Mine
S1
S2
S3
Baker Creek
ND2
Ndilo
ND3
ND6
Back Bay
ND1
ND7
ND4
S4
CS
BBS
1 km
INSET B
DE2
Dettah
DE5
DE3
DE1
S6
Akaitcho Bay
1 km

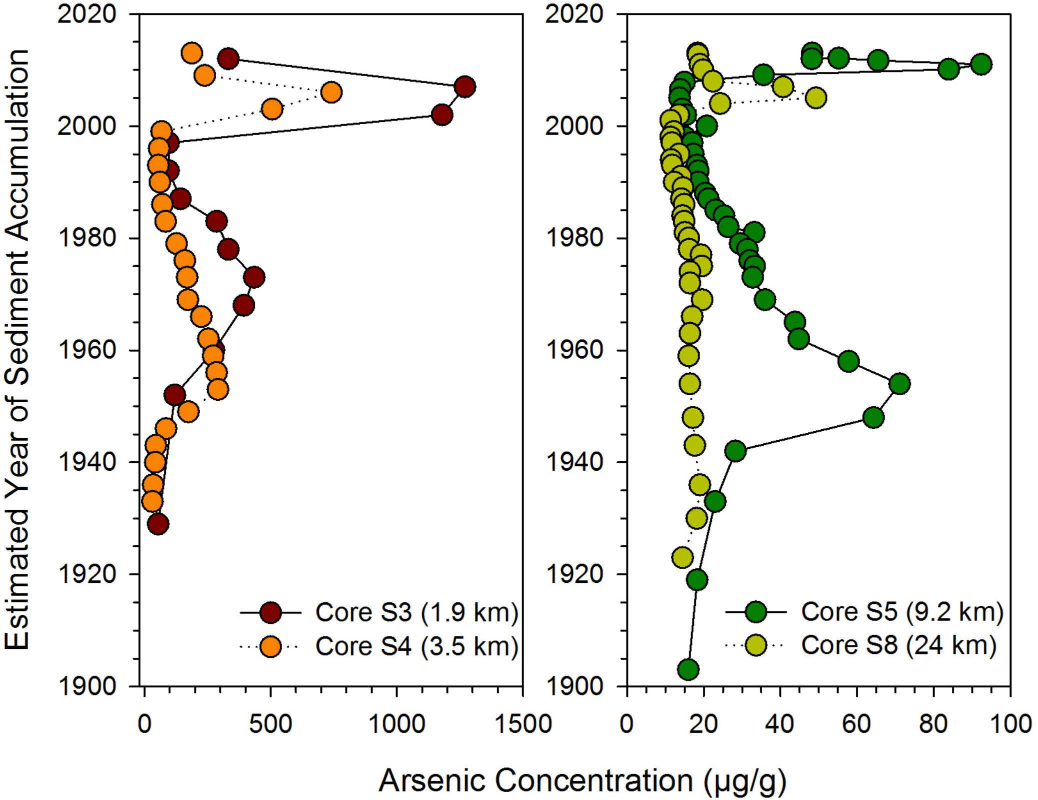

W5
A
4
Yellowknife
W10
Con Mine
Yellowknife Bay
B
Dettah
W16
W15
W17
2 km
INSET A
Giant Mine
4
W2
W1
W3
W4
Baker Creek
W7
W8
Back Bay
W6
Ndilo
CS
W9
BBS
1 km
INSET B
Dettah
W12
W11
W13
W14
Akaitcho Bay
1 km

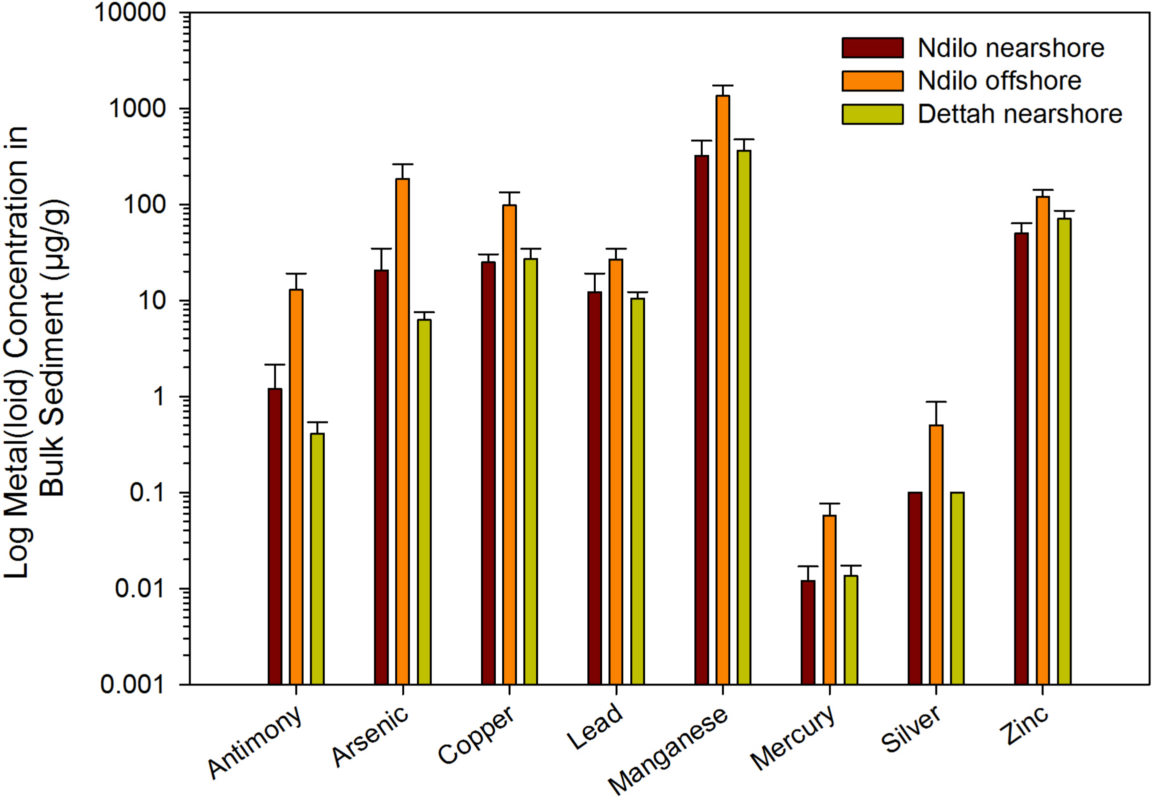

Sediment Depth (cm)
0
5
10
15
20
25
30
0
500
1000
1500
Giant Mine opens (1948)
Arsenic
Copper
Lead
Antimony
Zinc
0
500
1000
3000
6000
Manganese
0
5
10
Silver
0.0
0.2
0.4
Mercury
Element Concentration (µg/g dry wt)

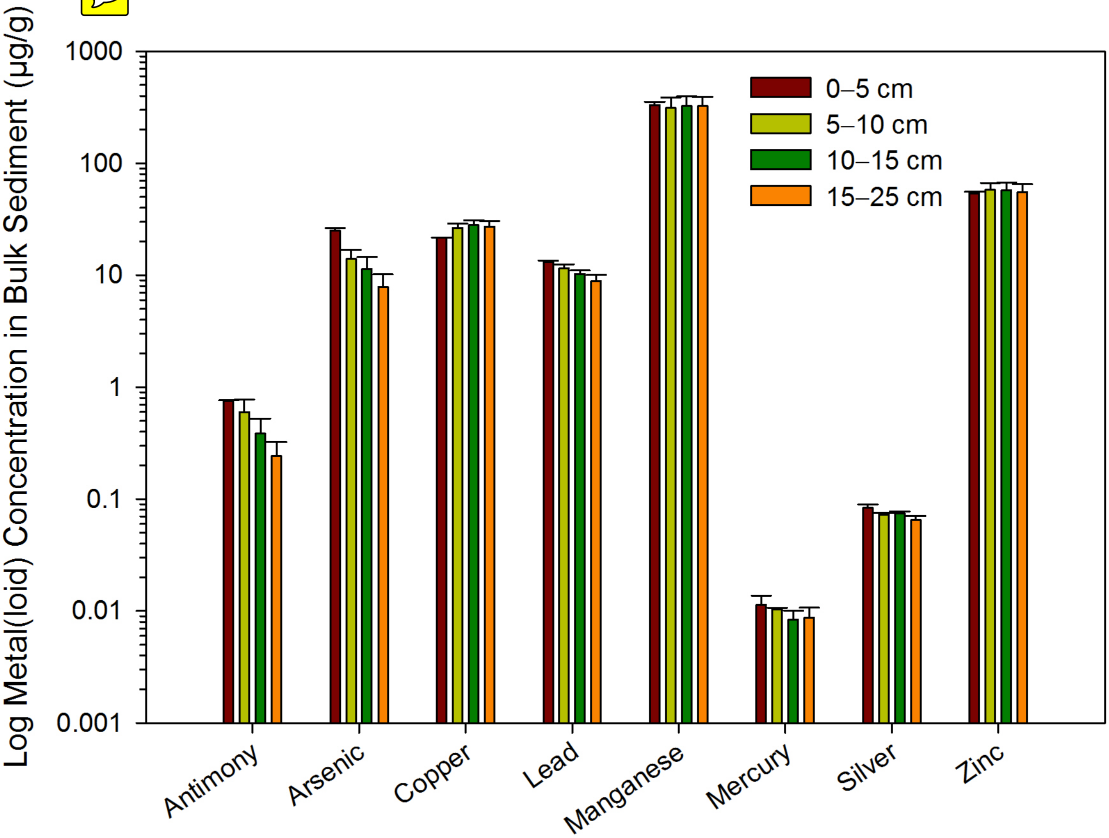

Maximum Enrichment Factor
400
300
200
100
0
0
5
10
15
20
25
Distance from Giant Mine Roaster (km)

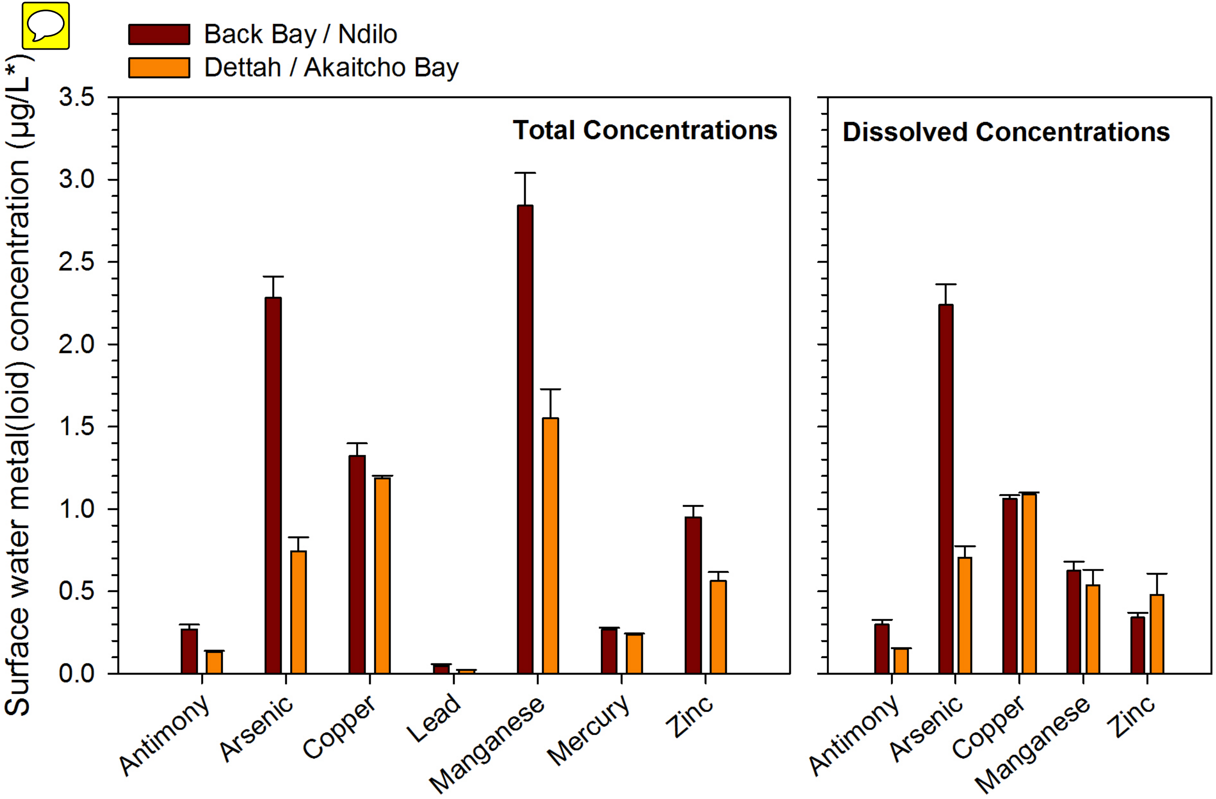

Antimony
Arsenic
Manganese
Silver
Copper
Mercury
Zinc
Lead
1000
100
10
1
1
10
Maximum Enrichment Factor
Distance from Giant Mine Roaster (km)

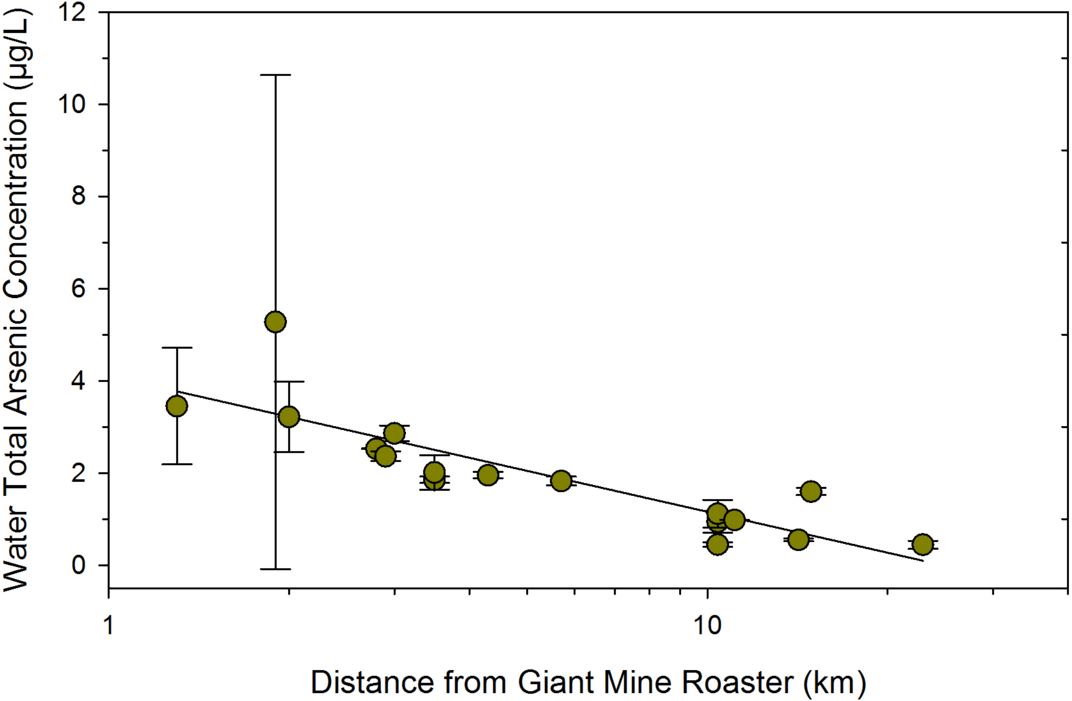

Estimated Year of Sediment Accumulation
2020
2000
1980
1960
1940
1920
1900
0
20
40
60
80
100
120
140
Core S3 (1.9 km)
Core S4 (3.5 km)
Core S5 (9.2 km)
2020
2000
1980
1960
1940
1920
1900
0.0
0.5
1.0
1.5
2.0
Core S8 (24 km)
Antimony Concentration (µg/g)

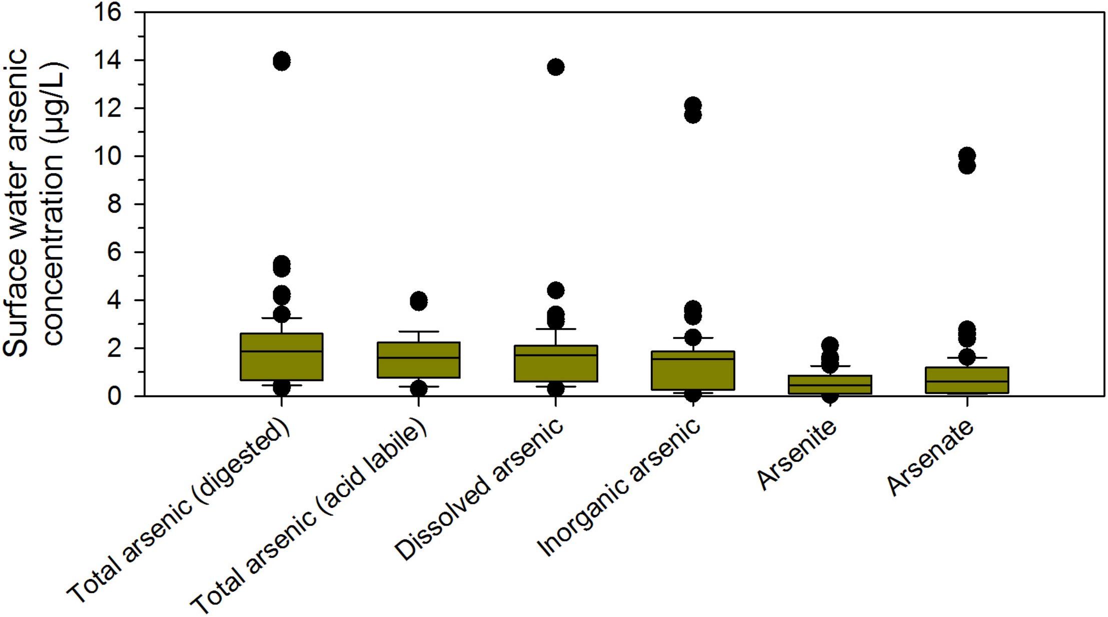

Estimated Year of Sediment Accumulation
2020
2000
1980
1960
1940
1920
1900
0
500
1000
1500
Core S3 (1.9 km)
Core S4 (3.5 km)
2020
2000
1980
1960
1940
1920
1900
0
20
40
60
80
100
Core S5 (9.2 km)
Core S8 (24 km)
Arsenic Concentration (µg/g)


Log Metal(loid) Concentration in Bulk Sediment (µg/g)
10000
1000
100
10
1
0.1
0.01
0.001
Ndilo nearshore
Ndilo offshore
Dettah nearshore
Antimony
Arsenic
Copper
Lead
Manganese
Mercury
Silver
Zinc


Log Metal(loid) Concentration in Bulk Sediment (µg/g)
1000
100
10
1
0.1
0.01
0.001
0–5 cm
5–10 cm
10–15 cm
15–25 cm
Antimony
Arsenic
Copper
Lead
Manganese
Mercury
Silver
Zinc


Back Bay / Ndilo
Dettah / Akaitcho Bay
Surface water metal(loid) concentration (μg/L*)
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
Total Concentrations
Dissolved Concentrations
Antimony
Arsenic
Copper
Lead
Manganese
Mercury
Zinc
Antimony
Arsenic
Copper
Manganese
Zinc


Water Total Arsenic Concentration (µg/L)
0
2
4
6
8
10
12
1
10
Distance from Giant Mine Roaster (km)


Surface water arsenic concentration (μg/L)
0
2
4
6
8
10
12
14
16
Total arsenic (digested)
Total arsenic (acid labile)
Dissolved arsenic
Inorganic arsenic
Arsenite
Arsenate