Title: *Determining the effects of past gold mining using a sediment palaeotoxicity model*

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Abstract

Ore processing techniques used in Yellowknife's largest mining operation, Giant Mine, is responsible for the atmospheric release of approximately 20,000 tonnes of particulate arsenic trioxide and other heavy metal(loids). This rapid deposition of heavy metal(loids) may have caused ecological disturbances to aquatic food webs. Here we use ^{210}Pb and ^{137}Cs dated lake sediment cores from 20 lakes within a 40km radius of Yellowknife to examine the spatial-temporal distribution of arsenic, antimony and lead. Further, we model the toxicity of the sediment to aquatic biota pre-, during, and post-mining using palaeotoxicity modelling, enrichment factor assessment, and comparisons to national sediment quality guidelines. We found that metal(loid) profiles in sediment peaked during the height of mining operations. These peak metal(loid) concentrations were highest in lakes near the mine's roaster stack, and decreased with distance from the historic mine. Palaeotoxicity modelling of lake sediment archives indicate that there is no significant difference in the mean predicted toxicity of pre- and post-mining samples ($p=0.14$), however mining activities in the region significantly increased the predicted toxicity of sediments to aquatic organisms during mining operations ($p<0.001$). In the years since roasting processes ceased, the mean palaeotoxicity of all lakes has decreased significantly ($p<0.05$), indicating a projected pattern of biological recovery. Importantly, some lakes remain at an elevated risk, indicating that aquatic ecosystems in Yellowknife may continue to have lingering effects on aquatic biota despite the closure of the mine two decades ago.

Keywords
lake sediments, palaeotoxicity, spatial analysis, mining emissions, aquatic ecosystems

Abbreviations

FeAsS	Arsenopyrite
CCME	Canadian Council for the Ministers of the Environment
PEC	Probable Effect Concentration
PEC-Q	Probable Effect Concentration Quotient
CRS	Constant Rate of Supply
CALA	Canadian Association for Laboratory Accreditation Inc.
ICP-MS	Inductively Coupled Plasma-Mass Spectroscopy
EF	Enrichment Factor
C_x	The concentration of the metal(loid) of interest
Ti_{Ref}	The concentration of titanium
n	The number of values used in the calculation
ANOVA	Analysis of Variance
ANCOVA	Analysis of Covariance
LOD	Limit of Detection
ISQG	Interim Sediment Quality Guideline
UET	Upper Effects Threshold
DoF	Degrees of Freedom
Adj. R^2	Adjusted R^2

1. Introduction

Global aquatic landscapes have been altered by natural resource extraction for centuries. Aerial industrial emissions have left a legacy of heavy metal contamination that has inspired scientists to reconstruct sedimentary geochemical signals to estimate the historic risk posed by these emissions on the historic aquatic biota (de Castro-Català et al., 2016; Kihlman and Kauppila, 2010; Machado et al., 2017; Salonen et al., 2006; Tipping et al., 2006). Sediments can be both a contaminant sink (Arsic et al., 2018; Aurilio et al., 1994; Vignet et al., 2014) or source to the overlying water, depending on the physical and biological characteristics of the environment (Tiquio et al., 2017). Following the deposition of a contaminant to the surface of a lake, the contaminants sink and become buried in the sediment, where they are preserved in natural sedimentary archives as fresh sediment layers collect above older layers. Several environmental conditions including organic matter content, redox potential, and pH, regulate the sequestration and release of these contaminant mixtures into overlying water bodies, which subsequently influences the toxicity (Lari et al., 2017; Linnik and Zubenko, 2000). At sites of legacy contamination, sites where contamination occurred before the onset of biomonitoring regulations, the absence of biomonitoring data makes it difficult to identify ecological changes attributed to contaminants from anthropogenic activity (Government of Canada, 1985). Fortunately, lake sediment cores can be used as natural historical archives to infer the legacy effect of historic mining to aquatic ecosystems (Doig et al., 2015; Korosi et al., 2017; Sprague and Vermaire, 2018).

Methods to assess historical effects of industrial emissions on aquatic biota are under development (Salonen et al., 2006). The emerging field of paleoecotoxicology aims to quantify sediment-bound contaminants and compare them to reconstructed historic biological responses

using lake sediment archives and preserved sedimentary micro-fossils (Korosi et al., 2017). Another method for examining mixture toxicity in lake sediments uses the Probable Effect Concentration (PEC) of multiple metals of concern to create a PEC-Quotient (PEC-Q) which is used to predict the overall toxicity of sediments (Ingersoll et al., 2001). Rippey et al. (2008) used the PEC-Q method to develop a Tier I Sediment Ecological Risk Assessment of lake sediments contaminated by metals and Persistent Organic Pollutants. Chapman et al. (1999) outlined a tiered risk assessment approach and provided risk assessors with an initial screening tool to identify sediment metal(loid) concentrations of biological concern. More recently, Rose et al. (2018) applied the PEC-Q technique to time-constrained lake sediment records from waterbodies across the UK to estimate the historic toxicity of lake sediment archives. This tiered approach to risk assessment using the PEC-Q of time constrained lake sediment intervals provides regional stakeholders with information on sediment quality and ecosystem health in lakes prior to, during, and after mining activities.

In Canada, there are 1,131 of sites of metal(loid) contamination in sediments under federal jurisdiction (Government of Canada, 2016). One of the largest remediation projects in Canadian history (~900 million CAD remediation estimate (Indigenous and Northern Affairs Canada, 2012)) focuses on Giant Mine, a legacy gold mining operation in Yellowknife, Northwest Territories, Canada. Yellowknife is home to approximately 20,000 people, which is 45 % of the Northwest Territories total population (Statistics Canada 2016). In Yellowknife, large scale gold mining operations began in the early 1930s with three gold mines established in the region. The largest operation was Giant Mine, which opened in 1948 (Amuno et al., 2018), and roasted arsenopyrite ore to liberate gold until 1999 (Andrade et al., 2010; Fawcett et al., 2015). The roasting process released over 20,000 tonnes of the highly toxic particulate arsenic trioxide, in

addition to other mining-related metal(loid) contaminants, into the region surrounding the mine (Jamieson, 2014). Emission control initiatives began in 1951, with the most effective control being the baghouse facility built in 1958, which significantly reduced the aerial emission of arsenic trioxide (Jamieson, 2014). Arsenic is known to be a human carcinogen (Mandal et al., 2003), and is also known to induce toxic effects in aquatic biota (Cott et al., 2016; He et al., 2009). The concern of human toxicity, coupled with the potential to impact aquatic biota, has resulted in arsenic being considered an element of community concern in Yellowknife (Galloway et al., 2015).

The legacy of gold mining in Yellowknife is evidenced on the landscape, as arsenic concentrations in surface waters within 11km of Giant Mine exceed the World Health Organization's guideline for safe levels in drinking water and exceed the Canadian Council for Ministers of the Environment (CCME) guidelines for the protection of aquatic life (Houben et al., 2016). A public health advisory is issued to the City of Yellowknife restricting the consumption of wild foods in areas close to the mine and advises against consuming water from impacted lakes (Government of the Northwest Territories, 2016). Several studies have characterized the legacy of mining in the Yellowknife region, with a focus on the distribution of arsenic in regional surface waters and sediments (Galloway et al., 2017; Schuh et al., 2019, 2017; Van Den Berghe et al., 2018). Recently, Sivarajah et al. (2019) examined surface sediments in the region to determine the influence of multiple stressors on diatom population structure. To date, no study has characterized the spatial extent of historic metal(loid) deposition in small regional lakes as a result of mining emissions in the region, and background geochemical and biological conditions have yet to be determined. Determining regional biological aquatic baseline

conditions was identified as an area of interest by the Northwest Territories Cumulative Impact Monitoring Program as an objective of future research in the region (Palmer et al., 2015).

Yellowknife is a region of high cultural and historical importance for the Yellowknives Dene First Nation, whose ancestors have a long history of occupation here. The lands surrounding Yellowknife were traditionally used for sustenance, and the people inhabiting this land today are affected by the legacy of mining contamination, often traveling long distances to access country food sources free of contamination from the mines (Sandlos and Keeling, 2016). There is little information available regarding the pre-mining concentrations of metal(loids) in regional lakes. Therefore, a thorough assessment of the geogenic concentration of mining-associated metal(loids) is needed to better understand the environmental impact of mining development in the region. This study aims to estimate the toxicity of sedimentary records in Yellowknife pre-, during, and post-mining by; (1) Investigating the temporal distribution of arsenic, lead and antimony along a spatial gradient from Giant Mine, and (2) Calculating the predicted toxicity of lake sediments influenced by historic mining activities in the region. This work will expand the current understanding of metal(loid) dispersal from roasting activities and will provide a more thorough understanding of the extent of mining-derived contamination of lake sediments in the region through time.

2. Methods

2.1 Field Methods

This study was conducted in Yellowknife, Northwest Territories during the summers of 2014-2017. During this time, 20 sediment cores were extracted from lakes within a 40km radius of Giant mine (Figure 1) using a Uwitec gravity corer (Mondsee, Austria). The lakes selected represent a variety of lake types in the region, with most being small, shallow lakes, while

several other lakes are larger and deeper. These lakes were chosen based on their proximity to, and direction from, Giant Mine. Based on the predominant wind direction, study lakes were assumed to be downwind of the roaster stack if they were between the westerly and north-northwesterly directions (112°-180°) (Galloway et al., 2017). Sampling was focused in the northwesterly direction, and lakes sampled east of the mining operations were to be used as unimpacted reference lakes.

Sites were accessed using a combination of helicopter and zodiac boat. A single core was then extracted from the central basin of each lake. During the summer of 2015, all cores were sectioned on site in 0.5 cm intervals using a modified Glew extruder (Glew, 1988). During the 2016 and 2017 sampling seasons, cores were sectioned under nitrogen-rich conditions at the Taiga Environmental Laboratory in Yellowknife. Sediment samples were shipped on ice to the laboratory where they were stored until analysis. Cores from the 2015 sampling season were stored in the freezer, while cores from the 2016 and 2017 sampling seasons were stored in the dark at 4ºC.

2.2 Laboratory Methods

Select sediment intervals were freeze-dried and prepared for ^{210}Pb analysis. Intervals were prepared in Sarstedt polypropylene 8mL tubes, capped with clear epoxy, and equilibrated for three weeks prior to analysis using an Ortec Gamma Spectrometer (Oak Ridge, TN, USA) at the University of Ottawa. The chronology of the sediment cores was determined by calculating the Constant Rate of Supply (CRS) model (Appleby and Oldfield, 1978) using supported ^{210}Pb concentrations. The CRS dates, obtained using ScienTissiMe (Barry's Bay, ON, Canada), were then validated using ^{137}Cs, a radionuclide indicative of large scale nuclear weapons testing in 1963 (Appleby, 2001). Across the 20 lakes sampled, a total of 259 sediment intervals were

analyzed using aqua regia extraction, followed by Inductively Coupled Plasma-Mass Spectroscopy (ICP-MS) analysis for total trace metal concentration by SGS Laboratories (Lakefield, ON, Canada), which is a CALA (Canadian Association for Laboratory Accreditation Inc.) accredited laboratory for measuring these elements in sediments (Method Detection Limits presented in Table S2). Due to the redox-sensitive nature of some of the elements including in this study, the less mobile element lead was used to assess the potential post-depositional mobility of redox-sensitive elements in the sedimentary deposition profiles (Chen et al., 2003; Nikolaidis et al., 2004; Town and Filella, 2002; Wang et al., 2012).

2.3 Statistical Methods

Based on both the dates produced by the CRS dating models, and estimations of timing based on metal(loid) profiles for undated intervals, we grouped each sediment core interval into three separate time treatment groups: pre (<1948), during (1948-1999), and post-mining (1999-present). All statistical analyses, and palaeotoxicity quotients were quantified based on the means calculated for these three time intervals. Individual metal(loid) concentrations were compared to the CCME interim sediment quality guidelines (ISQG) for arsenic and lead, and the Upper Effects Threshold (UET) for antimony. Arsenic, antimony and lead are known emission by-products from roasting activities.

Using the method outlined by Garcia-Ordiales et al. (2017), we calculated the arsenic, antimony, and lead enrichment factor (EF) for each sediment interval analyzed. Enrichment factors are often used in paleolimnological investigations to distinguish between anthropogenically derived, and catchment derived inputs for the compound of interest (Machado et al., 2017). The lithogenic reference metal titanium was used to normalize the influence of terrigenous catchment input on each sediment interval (Boës et al., 2011), as seen in Equation 1.

$$EF=(C_x/Ti_{Ref})_{Sample}/(C_x/Ti_{Ref})_{Background} \quad (1)$$

Here the corrected enrichment factor for each metal is calculated based on the concentration of the metal(loid) (C_x) using the sampling and background intervals. The oldest analyzed sediment interval for each core was used as the background concentration in this equation. C_x is corrected by the concentration of titanium in the corresponding sample and background sediment interval (Ti_{Ref}). Enrichment factors are interpreted according to the five-category system proposed by Sutherland (2000); (1) EF < 2 no, or minimal pollution is present, (2) EF 2-5, moderate pollution is present, (3) EF 5-20, a significant pollution signal is present, (4) EF 20-40, A very strong pollution signal is present, and (5) EF>40, an extreme pollution signal is present.

Data were log-transformed prior to statistical analysis to meet the assumption of normality for parametric tests. The Levene test was used to assess the homogeneity of variance between groups prior to analysis. Then, an analysis of variance (ANOVA) was used to determine if the mean concentrations of arsenic, antimony and lead measured in the three treatment groups were statistically different. The ANOVA was followed by the Tukey post-hoc test. In cases where the Levene test was violated, the ANOVA test was replaced by the non-parametric Kruskal-Wallis test, followed by the Dunn post-hoc test.

An analysis of covariance (ANCOVA) was used to determine if there was a relationship between the measured metal concentrations (arsenic, antimony, and lead) in each group and the distance or wind direction from the roaster stack to the sampling site. Interaction between the two independent variables was also tested. The distance and angle between the roaster stack and the core sample were calculated in ESRI's ArcGIS 10.6.0. In the analysis, lakes were separated into two discrete groups, in the predominant wind direction (112-180°) and not in the predominant wind direction. The model residuals were assessed for normality, linearity, and

homoscedasticity using the Shapiro-Wilk test, the Breusch-Pagan test, and the reset test respectively.

The risk of lake sediments pre, during, and post-mining to aquatic biota was calculated using the palaeotoxicity method outlined by Rose et al. (2018). This method calculates the Probable Effect Concentration Quotient (PEC-Q) for contaminated sediments according to Equation 2.

$$\text{PEC-Q} = \frac{\Sigma \frac{[M_S]}{PEC_M}}{n} \qquad (2)$$

Here $[M_s]$ is the metal(loid) concentration in the interval of interest, PEC_M is the PEC of the metal, and *n* is the number of PEC's included in the calculation. PEC's are derived using experimental evidence following spiked sediment toxicity tests of benthic and pelagic organisms (Rose et al., 2018). This method allows for the quantitative assessment of total metal(loid) concentration in the sediment sample, without further analyzing the sample with methods of bioavailable fractionation. When evaluating the toxicity of a mixture, the higher the mean palaeotoxicity quotient, the more likely it becomes that the concentration of contaminants present in the sample would induce negative biological effects (Rippey et al., 2008). Results were categorized into; "no biological effects predicted" for palaeotoxicity quotients less than 0.5, "biological effects possible" when the mean palaeotoxicity quotient is between 0.5 and 2.0, and "biological effects probable" when the mean palaeotoxicity quotient is greater than 2.0 (Rose et al., 2018). ANOVA was used to assess the significance of the relationship between palaeotoxicity quotient and time period, and ANCOVA was used to determine the influence of direction from the roaster stack as well as the predominant wind direction. The PEC's used in

this analysis are the consensus based guidelines proposed by Macdonald et al. (2000), and are provided in Table S1.

All statistical analyses were completed in R 3.5.2 (R Core Development Team, 2017) using the packages *lmtest* (Hothorn et al., 2018), *car* (Fox et al., 2018), and *lmperm* (Marco Torchiano, 2016). Plots were created using *ggplot2* (Wickham et al., 2019). All mapping was completed in ESRI's ArcGIS 10.6.0 (ESRI ArcGIS Desktop, 2011).

3. Results

The majority of the sediment cores date back 100 years or more, with the exception of YKW-1 and BC-24, which are both limited to the past 85 years (Figure S1). Summary statistics for arsenic, antimony, and lead in each lake pre, during and post-mining are presented in Table 1. With the exception of two lakes, YK-60 and BC-18, the concentration of arsenic in all lakes examined shows an increase in concentration that coincides with the CRS modelled date of mining operations when compared to background arsenic concentrations (peak arsenic concentration: 6.3 ug g^{-1} dw to 15000 µg g^{-1} dw). A similar trend is seen in both antimony and lead, where peak concentrations range from below the Method Detection Limit (MDL) to 350 ug g^{-1} dw and 4.1 to 64 ug g^{-1} dw respectively. In YK-60 and BC-18, the highest arsenic concentration occurs at a time corresponding to before mining operations began in the region, according to the CRS dating model. Individual profiles of arsenic, lead, and antimony deposition through time can be found for each lake in Figures S5-S7.

With the exception of three lakes, BC-36, YKE-1, and Small Lake, all lakes sampled were above the arsenic interim sediment quality guidelines (ISQG) of 5.9 µg $^{-1}$g dw (Canadian Council of Ministers of the Environment, 2001) prior to the onset of mining operations. During

mining, all lakes sampled exceeded the arsenic ISQG. Following the cessation of mining activities, sediments from BC-36 and YKE-1 returned to concentrations below the arsenic ISQG; however, the arsenic concentration of Small Lake remained elevated above the CCME ISQG for arsenic (Figure S2). All lakes were below the lead ISQG prior to mining while two lakes exceeded the lead sediment quality ISQG guideline of 35 $\mu g\ g^{-1}$ dw during mining (YK-42 and YK-11). The lead guideline was exceeded in one post-mining sample at David Lake, and one at YK-42 (Figure S3). Before mining, 13 lakes contained at least one sediment interval that was above the Upper Effects Threshold (UET) of 3 $\mu g\ g^{-1}$ dw for antimony (Buchman, 2008). The UET for antimony was exceeded in 14 of the lakes during mining. After mining, the same lakes that were above the UET for antimony remained elevated, with the exception of Duckfish Lake, whose antimony sedimentary concentration was at the UET of 3 $\mu g\ g^{-1}$ dw (Figure S4).

All the lakes are enriched in arsenic, lead, and antimony; however, the degree of enrichment varies between lakes (titanium corrected enrichment profiles of arsenic, lead and antimony through time can be found for each lake in Figures S8-S10). Lakes closer to the mine, as well as lakes in the predominant wind direction have higher titanium corrected enrichment factors than lakes further from the mine in the opposing wind direction. Peaks of enrichment also generally coincide with the time of uncontrolled emissions at Giant Mine (1948-1951) except for lakes BC-18 and Alexie, where arsenic enrichment peaks occur in the sediment interval analyzed prior to the predicted CRS date corresponding to peak emissions (Figure S8). The arsenic enrichment peak for Fiddlers peaks in the uppermost sediment interval (Figure S8). Lead enrichment peaks during mining activities in all lakes sampled, except Vital and YKE1, where lead enrichment peaks in the interval prior to the during mining CRS modelled dates. In some lakes, there is evidence of some lead enrichment occurring before the onset of mining in the

region (Figure S9). Antimony is enriched in all lakes, and the peak of enrichment corresponds to the increase in mining activity in the region (Figure S10). In BC-36, titanium corrected antimony enrichment peaks in the uppermost layer of the sediment core (Figure S10). The maximum enrichment factor for each metal is displayed in Figure 3 as a percentage of the total number of lakes sampled. Extreme pollution is indicated by enrichment levels in 5 of the lakes for arsenic (25%), and 4 of the lakes for antimony (20%). Extreme pollution is not indicated by the enrichment of lead in any of the sampled lakes, however, 7 lakes (35%) indicate significant enrichment of lead.

The ANOVA, and Kruskal-Wallis test, results indicate that there is a significant difference between the mean arsenic ($F_{2,256}$=11.16, p-value <0.001), lead (Chi square=61.62, p-value <0.001, df=2), and antimony (Chi square=25.25, p-value <0.001, df=2) concentrations in the three time periods (Figure 2). The Tukey post-hoc test indicates that the mean arsenic concentration in the sediment is 4.22 ug g^{-1} dw lower pre-mining when compared with during mining (adj. p<0.001)) and the mean arsenic concentration in the sediment is 2.40 ug g^{-1} dw lower post-mining when compared with during mining (adj. p-value=0.014). There was no difference between the average arsenic concentration in pre-mine and post-mine samples (adj. p= 0.16). The Dunn post-hoc test indicates that the concentration of lead deposited in the sediment pre-mining was 1.95 ug g^{-1} dw lower than lead deposited in the sediment during mining (adj. p<0.001) and the mean lead concentration in the sediment is 1.54 ug g^{-1} dw lower post-mining when compared with during mining (adj. p-value<0.05). While the mean concentration of lead in current sediments is lower than peak mining concentrations, it is still 1.73 ug g^{-1} dw higher than pre-mining concentrations (adj. p-value<0.001). The Dunn post-hoc test indicates that the antimony concentrations in the pre-mining sediment were 1.76 ug g^{-1} dw lower than during

mining sediments (adj. $p<0.001$). The difference in the antimony sediment concentration post-mining and during-mining was marginally statistically different (adj. $p=0.08$), where the concentration post-mining is 1.40 ug g^{-1} dw lower than during mining. Similar to lead, the concentration of antimony in current sediments has not returned to pre-mining concentrations and is currently 1.50 ug g^{-1} dw higher than pre-mining values (adj. $p= 0.02$).

ANCOVA results show the interaction between the treatment group and log distance was approaching significance at an $\alpha = 0.05$ ($F_{2, 2534}=2.34$, $p=0.098$) when predicting total arsenic. Similarly, there is also an interaction between the treatment group and the predominant wind direction, which approached significance ($F_{(2, 253)}=2.85$, $p=0.059$). Consequently, both wind direction and distance from the roaster stack influence the concentration of total arsenic measured. The degree of influence depends on whether the concentration was measured pre-, during, or post-mining. The interaction between the mining group and the predominant wind direction was significant for total lead ($F_{(2, 253)}=1.03$, $p<0.001$) but is insignificant for total antimony ($F_{(2, 253)}=1.89$, $p=0.15$). The non-homogeneity of the slopes can be seen in Figure 4.

The main effect of the ANCOVA for total arsenic is presented in Table 2. All variables and groups are significant in this model. The slope is steepest during mining, followed by post mining, and then pre-mining. The log distance from the roaster stack is inversely related to total arsenic concentration. Lakes sampled in the predominant wind direction had higher concentrations of total arsenic than lakes sampled in the non-predominant wind direction. Overall, these variables explain 70% of the variance. Of this variance explained, distance explained the most variance (partial-$R^2=0.60$), followed by predominant wind direction (partial-$R^2=0.24$), and time group (partial-$R^2=0.18$).

The main effect of the ANCOVA for total lead is shown in Table 3 and antimony is shown in Table 4. Similar to arsenic, all variables and groups are significant in these models. The slope estimate is smallest pre-mining, highest during mining, and the slope post mining is between that of pre and during mining. The log distance from the roaster stack is inversely related to total antimony and to a lesser extent total lead concentration. Lakes sampled in the predominant wind direction also had higher concentrations of total arsenic than lakes sampled in the non-predominant wind direction. These variables explained 40% of the variance in total lead, and 68% of the variance in total antimony. The time group explained most of the variance (partial-R^2=0.27), followed by distance (partial-R^2=0.14), and wind (partial-R^2=0.08) in the variance of total lead. The distance explained most of the variance (partial-R^2=0. 54), followed by predominant wind direction (partial-R^2=0. 27), and time group (partial-R^2=0. 20) in the variance of total antimony.

The predicted biological effect that the emissions mixture may have on biota in the lakes, derived from the calculated mean PEC-Q pre, during, and post-mining for each sample lake is shown in Figure 5. Prior to the onset of mining operations, the mixture of metal(loid) concentrations measured in this study shows that 20% of the lakes sampled were at risk of probable biological effects, and an additional 40% of the lakes indicate that biological effects are possible. During mining operations, the number of lakes in which biological effects are probable increases to 55%, with a further 15% of lakes indicating biological effects were possible. In the post-mine period 30% of the total number of lakes studied indicate that biological effects are probable, and an additional 35% indicate that biological effects are possible. Further, all of the lakes in which biological effects are possible or probable pre, during, and post-mining are within 20km of the Giant Mine roaster stack.

The PEC-Q decreases as the distance from the roaster stack increases (Figure S11). ANOVA analysis of the log palaeotoxicity quotient between the three time periods indicates that the mean log palaeotoxicity quotient in sediments deposited during mining is significantly higher than sediments deposited pre-mining (p-value <0.001) and post-mining (p <0.05) ($F_{(2,256)}$=11.66, p-value <0.001) (Figure S11). The Tukey post-hoc testindicates the palaeotoxicity quotient of sediments deposited during mining are 3.2 and 2.2 times higher than those deposited pre- and post-mining, respectively. There is no statistically significant difference in the log palaeotoxicity quotient between sediments deposited pre and post-mining (p=0.14) (Figure S11). ANCOVA analysis indicates time period, distance from the stack, and wind direction account for 17%, 53%, and 21% of the variance respectively.

4. Discussion

4.1 Metal Deposition in lakes surrounding Giant Mine

The results of this study indicate that the concentration of arsenic increased from background levels in all regional lakes sampled during mining operations (Figure S5). The concentrations of lead and antimony increased substantially in all lakes except Small Lake and YKE1 (Figures S6-7); these lakes do not lie in the predominant wind direction and therefore were not as influenced by mining operations. Further, despite the flaws often cited in the use of enrichment factors (Reimann and De Caritat, 2005), analysis of enrichment factors suggests that metal(loid) inputs substantially influenced the potential sediment toxicity in our study lakes during mining operations (Figure 3). These findings are supported by the PEC-Q of sediments deposited during mining, which was significantly higher than in pre-mining sediments, indicating mining had a significant impact on the potential toxic influence of sediments deposited into the sampled lakes (Figure S11). Although previous investigations have reported

that arsenic concentrations in surface sediments are significantly higher within 11km of the Giant Mine's roaster stack (Galloway et al., 2017), our study shows that all lakes examined within the 40 km study radius show a measurable increase in the concentration of arsenic, antimony and lead during mining operations. Thus the radius of impact from gold mining operations during the peak emission interval was much larger than is currently indicated by surface water and surface sediment analyses (Galloway et al., 2012).

There is a sharp decline in arsenic, antimony, and lead concentrations at each of the lakes following the introduction of strict emission controls (1959) at Giant Mine, and metal(loid) concentrations continue to decline inrecent sediments (Figures S5-S7). Current arsenic concentrations in the surface sediments of regional lakes are not significantly different from background values, while the concentrations of both antimony and lead in post-mining sediments are still significantly higher than pre-mining values (Figure 2). The historic trends of legacy metal(loid) sedimentary deposition we report in this study (Figures S5-S7) are consistent with other lake sediment cores reflecting historic metal(loid) deposition in the region (Andrade et al., 2010; Chételat et al., 2018; Schuh et al., 2017; Thienpont et al., 2016). Additionally, our findings are consistent with other studies examining the anthropogenic impact of mining emissions in lake sediment profiles worldwide (Doig et al., 2015; Leppänen et al., 2017; Punning et al., 2007). The cores from David Lake and Fiddlers Lake do not follow this increasing then decreasing metal(loid) concentration trend. The David Lake core shows multiple peaks of arsenic, antimony, and lead concentrations throughout the depth of the lake sediment core (Figures S5-S7). Examining the enrichment factors of antimony (1.01 ± 0.22) and lead (2.68 ± 1.04) at David Lake (Figures S9-S10), reveals that the peaks are substantially less pronounced, and suggest minimal enrichment (Sutherland, 2000). The enrichment of arsenic, however, continues to

increase in two main peaks and one sub-peak, suggesting possible post-depositional arsenic mobility (Figure S8). Further analysis of arsenic speciation in sediment and porewaters is required to confirm this hypothesis. At Fiddlers Lake, a sub-surface peak in arsenic concentration was observed (Figure S5). Interestingly when the arsenic profile is compared to lead (Figure S6) and antimony (Figure S7), which both peak during mining operations, we observe that arsenic in this lake may be experiencing upwards post-depositional migration. Similar sediment core trends with sub-surface arsenic peaks were observed by Schuh et al. (2017) in shallow regions of larger lakes. Although the Fiddlers Lake sediment core was taken from the centre of the lake, in the presumed deepest region, the bathymetry of the lake may have been such that the centre of the lake was shallower than near-shore regions. Resultantly, the arsenic depth profile reflects that of a shallow area within other large lakes of the region (Figure S5).

According to CRS dating models, some lakes increase in arsenic concentration prior to the onset of mining operations at Giant Mine in 1948 (Figure S5). This discrepancy may be due several factors including; (1) The vertical diffusion and subsequent sequestration of arsenic within sediment porewaters; (2) The physical mixing of sediments due to freeze-thaw cycles in the region; (3) The biological mixing of metal(loids) throughout the core due to the activity of benthic organisms; or (4) The error associated with CRS modelled dates (Boudreau, 1999). Previous analysis of the geochemical movement of arsenic in regional sediment cores indicate that post-depositional mobility of arsenic occurs, suggesting that the shifting arsenic peaks observed by this study may be influenced by post-depositional arsenic mobility (Schuh et al., 2017; Van Den Berghe et al., 2018). Analysis of arsenic diffusion in lake sediment porewaters, and arsenic mineral hosting phases, on a spatial scale would be needed to draw further

conclusions about arsenic mobility in lakes within the region. Additionally, as lead is less mobile in lake sediments than arsenic, due to its strong binding affinity to natural organic matter, it can be used to more accurately trace the temporal deposition of mining-related contaminants in the region (Town and Filella, 2002). Our results indicate that the concentration of lead increased in all lakes during mining operations, and pre-mining lead concentration increases in regional lakes were negligible (Figure S6). Modelling of the historic roaster emission plume, in conjunction with determining the depth profiles of isotopic lead ratios in each lake would help to draw more firm conclusions about historic spatial distribution of emissions from Giant Mine (Pelletier et al., 2020).

4.2 Palaeotoxicity of deposited metals

As summarized in Table 1, prior to the onset of mining in the region, 90% of lakes naturally exhibited mean arsenic concentrations greater than the CCME ISQG for freshwater sediments, and 50% were above the site-specific regional guideline of 150 μg g^{-1}. Further, the mean antimony concentration exceeded the UEL in 55% of lakes studied pre-mining. Lead did not exceed ISQG in any of the lakes sampled prior to the onset of mining operations.The elevated mean pre-mining arsenic concentrations at many of the sites is indicative of natural background arsenic concentrations in the region, which is within the range of 2-100 μg g^{-1} (Galloway et al., 2012). Specific arsenic concentrations for the regional bedrock types for lakes in our study are; granitoid (2-90 mg kg^{-1}), sedimentary (2-64 mg kg^{-1}), and volcanic (1-33 mg kg^{-1}) (Figure 5) (Galloway et al., 2015). Consequently, naturally elevated geogenic arsenic concentrations in the region may have resulted in the natural adaptation of native aquatic biota to be more tolerant to the toxic effects of arsenic, which would have served as a biological advantage during the time of mining operations. Theinpont et al. (2016) reported a range of

multi-trophic biological responses in a lake heavily influenced by emissions from the Giant Mine roaster stack. The study reported a functional loss of a group of primary consumers, the Cladocera (Branchiopoda, Crustacea), following the onset of mining operations. However, more pollution tolerant species of chironomid thrived during the time of mining, when high concentrations of mining-associated metal(loids) entered the lake. Our study provides an initial large-scale risk assessment of the spatial impact of historic gold mining on freshwater ecosystems in Yellowknife, and estimates that other lakes in the region would have experienced a shift in freshwater biotic populations historically, possibly similar to those experienced by aquatic species reported in the Thienpont et al. (2016) study.

Sediment quality values, such as PEC-Q, have been used as a first-tier approach to ecological risk assessment (Chapman et al., 1999; Rand and Schuler, 2009; Rippey et al., 2008). Algae, the base of food webs in aquatic ecosystems, are keenly sensitive to metal pollution in river ecosystems (Kuzmanović et al., 2016), suggesting that cascading negative food web effects could be seen in sites predicted to have major biological effects possible/probable, such as those reported in this study. The predicted palaeotoxicity of lake sediments increased during the time of mining, with PEC values in 90% of the lakes within 5km of the Giant Mine roaster stack indicating that significant biological effects were probable (Figure 5). Prior to mining, 40% of these lakes indicated significant biological effects were probable. The biological effect also decreases as the distance from the mine increases (Figure S11). Although biomonitoring data are not available prior to mining, several Yellowknife lake surveys completed during the height of mining operations in the 1970's indicated a decrease in water quality in lakes near Giant and Con Mines. A survey of the biological effects of Giant Mine tailings waste entering Yellowknife Bay, completed in 1973, indicates that the mining waste induced acute toxicity in both fish and benthos, however, aerial

emissions to far-field lakes were not inspected in this study (Falk et al., 1973). Following this investigation, Wagemann et al. (1978) observed that there was an absence of Pelecypoda, Ephemeroptera nymphs, Amphipoda, and Hirundinea in two lakes directly influenced by Con Mine. These observations are consistent with the predicted negative biological effects in lakes sampled in the present study (Figures 5 and S11) and support the prediction that the biota of freshwater ecosystems was negatively influenced by contaminants deposited during mining operations.

Mean metal(loid) concentrations naturally above ISQG in the region indicate that lake sediments were historically predicted to cause some biological effect to aquatic organisms even before mining (Figure 5). When compared to regional geogenic baseline metal(loid) concentrations reported in the literature (Galloway et al. 2015), baseline PEC-Q values for the bedrock types examined in this study vary from 0.06-2.9. Although the bioavailability of the metal(loids) used to calculate the PEC-Q is unknown, some lakes in our study may be naturally above the biological effects probable threshold, and therefore natural regional adaptations to metal(loid) toxicity may have evolved in some lakes. It is important to note that contaminants deposited by regional gold mining did exacerbate this trend, and substantially increased the estimated toxicity to aquatic biota in the region surrounding Giant Mine (Figure S11). Additionally, our results do not address the issue of arsenic mobility, and therefore the mean metal(loid) concentrations of redox-sensitive elements deposited during mining may be influencing the pre-mining concentration used in this study, providing an inflated estimation of pre-mining toxicological risk. However, the magnitude of the increase (Figure S11) should be considered by regional stakeholders when interpreting the historical risk of lake sediments deposited during mining. The toxic effect of mining modelled in this study extends beyond the

boundaries of the mine lease territory, with the greatestincrease in estimated biological effect observed in lakes lying in the predominant wind direction, and close to the mine. Current remediation efforts focus solely on the mine lease boundaries, however, the assessment of the recovery of lakes outside the mine lease boundaries should be considered when assessing regional ecosystem recovery from legacy mining emissions. Recovery in the predicted toxicity is evident as time progresses, with several lakes being downgraded from probable effects in sediments deposited during mining to possible effects in current sediments. However, a return to baseline biotic conditions is not observed in all lakes sampled (Figure 5). The influence of confounding variables, such as climate change, will also need to be considered during the recovery assessment. For example, Sivarajah et al. (2019) examined regional surface sediment diatom populations and concluded that complex factors, including climate change and to a lesser extent, mining influence, were causing shifts in diatom population structure. These confounding variables will affect lake ecosystem recovery, and may prevent the full recovery of regional freshwater systems to pre-mining biological conditions.

One limitation of the PEC-Q method is that it does not consider the bioavailability of metal(loid) mixtures to aquatic biota. However, the PEC's themselves are derived from laboratory exposures experiments and chemical datasets and are therefore arguably reflective of environmental biological response (Macdonald et al., 2000). Without regional bio-monitoring data prior to the onset of mining, biological response must be inferred from historical archives by comparing the concentration of a contaminant, determined through chemical analysis, to established benchmark values that are known to induce toxicity in aquatic biota. Developing real-time toxicity tests using historic sediments as exposure media will strengthen the conclusions

derived from palaeotoxicity methods, such as PEC-Q's, and have the potential to accommodate the confounding variables of mixture effects and bioavailability (Korosi et al., 2017).

5. Conclusion

Our study provides the most extensive assessment of the impact of legacy of gold mining operations on historic regional sediments in the Yellowknife region to date. We examined the impact of historical gold mining operations on regional lake sediments, which has important implications for assessing the legacy of gold-mining contamination in the region, and the recovery of impacted lakes. Our results indicate that uncontrolled roaster emission releases at Giant Mine resulted in the deposition of mining-related metal(loid) contaminants to aquatic ecosystems in all lakes sampled, as far as 40 km from the mine. This radius is much greater than previously indicated by surface sediment and water analyses. The implementation of emission controls effectively reduced contaminant inputs to aquatic systems and resulted in a marked decrease in total metal(loid) sedimentary concentrations. If bioavailable, the naturally elevated sedimentary metal(loid) concentrations in several lakes in the region closest to the Giant Mine lease territory may have impacted biota prior to the onset of mining. The bioavailability of these metal(loids), and the subsequent biological effect should be explored in future paleolimnological studies to differentiate the biological impact of legacymining operations from those of natural fluxes. Assessing the recovery of regional aquatic ecosystems impacted by historic mine emissions is of both cultural and economic significance. Information from this study can help inform policy makers about the recovery of regional aquatic ecosystems to pre-impact biological conditions, resulting in the promotion of positive human and environmental health outcomes in the future as the continued access to and safetyof traditional foods is critical for the health and cultural well-being of Indigenous People.

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References

Amuno, S., Al Kaissi, A., Jamwal, A., Niyogi, S., Quenneville, C.E., 2018. Chronic arsenicosis and cadmium exposure in wild snowshoe hares (Lepus americanus) breeding near Yellowknife, Northwest Territories (Canada), part 2: Manifestation of bone abnormalities and osteoporosis. Sci. Total Environ. 612, 1559–1567. https://doi.org/10.1016/j.scitotenv.2017.08.280

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

Appleby, P.G., 2001. Chronostratigraphic Techniques in Recent Sediments, in: Last, W.M., Smol, J.P. (Eds.), Tracking Environmental Change, and Chronological Techniques. Kluwer Academic Publishers, Dordrecht, The Netherlands, pp. 171–204. https://doi.org/https://doi.org/10.1007/0-306-47669-X

Arsic, M., Teasdale, P.R., Welsh, D.T., Johnston, S.G., Burton, E.D., Hockmann, K., Bennett, W.W., 2018. Diffusive gradients in thin films (DGT) reveals antimony and arsenic mobility differs in a contaminated wetland sediment during an oxic-anoxic transition. Environ. Sci. Technol. acs.est.7b03882. https://doi.org/10.1021/acs.est.7b03882

Aurilio, A.C., Mason, R.P., Hemond, H.F., 1994. Speciation and Fate of Arsenic in Three Lakes of the Aberjona Watershed. Environ. Sci. Technol. 28, 577–585. https://doi.org/10.1021/es00053a008

Boës, X., Rydberg, J., Martinez-Cortizas, A., Bindler, R., Renberg, I., 2011. Evaluation of conservative lithogenic elements (Ti, Zr, Al, and Rb) to study anthropogenic element enrichments in lake sediments. J. Paleolimnol. 46, 75–87. https://doi.org/10.1007/s10933-011-9515-z

Boudreau, B.P., 1999. Metals and models: Diagenetic modelling in freshwater lacustrine sediments. J. Paleolimnol. 22, 227–251. https://doi.org/10.1023/A:1008144029134

Buchman, M.F., 2008. NOAA Screening Quick Reference Tables. National Oceanic and Atmospheric Administration, Seattle, Washington, pp. 1–34.

Canadian Council of Ministers of the Environment, 2001. Canadian Sediment Quality Guidelines for the Protection of Aquatic Life. Environ. Prot. 1–3.

Chapman, P.M., Wang, F., Adams, W.J., Green, A., 1999. Appropriate Applications of Sediment Quality Values for Metals and Metalloids. Env. Sci Technol 33, 3937–3941. https://doi.org/10.1021/es990083n

Chen, Y., Deng, T., Filella, M., Belzile, N., 2003. Distribution and Early Diagenesis of Antimony Species in Sediments and Porewaters of Freshwater Lakes. Environ. Sci. Technol. 37, 1163–1168. https://doi.org/10.1021/es025931k

Chételat, J., Amyot, M., Muir, D., Black, J., Richardson, M., Evans, M., Palmer, M., 2018. Arsenic, antimony, and metal concentrations in water and sediment of Yellowknife Bay, Northwest Territories Geological Survey, NWT Open File 2017-05.

Cott, P.A., Zajdlik, B.A., Palmer, M.J., McPherson, M.D., 2016. Arsenic and mercury in lake whitefish and burbot near the abandoned Giant Mine on Great Slave Lake. J. Great Lakes Res. 42, 223–232. https://doi.org/10.1016/j.jglr.2015.11.004

de Castro-Català, N., Kuzmanovic, M., Roig, N., Sierra, J., Ginebreda, A., Barceló, D., Pérez, S., Petrovic, M., Picó, Y., Schuhmacher, M., Muñoz, I., 2016. Ecotoxicity of sediments in rivers: Invertebrate community, toxicity bioassays and the toxic unit approach as complementary assessment tools. Sci. Total Environ. 540, 297–306. https://doi.org/10.1016/j.scitotenv.2015.06.071

Doig, L.E., Schiffer, S.T., Liber, K., 2015. Reconstructing the ecological impacts of eight decades of mining, metallurgical, and municipal activities on a small boreal lake in northern Canada. Integr. Environ. Assess. Manag. 11, 490–501. https://doi.org/10.1002/ieam.1616

ESRI ArcGIS Desktop, 2011. Release 10. Redlands, CA Environ. Syst. Res. Inst.

Falk, M.R., Miller, M.D., Kostiuk, S.J.M., 1973. Biological Effects of Mining Wastes in the Northwest Territories.

Fawcett, S.E., Jamieson, H.E., Kirk Nordstrom, D., Blaine McCleskey, R., 2015. Arsenic and antimony geochemistry of mine wastes, associated waters and sediments at the Giant Mine, Yellowknife, Northwest Territories, Canada. Appl. Geochemistry 62, 3–17. https://doi.org/10.1016/j.apgeochem.2014.12.012

Fox, J., Weisberg, S., Price, B., Adler, D., Bates, D., Baud-Bovy, G., Bolker, ben, Ellison, S., Firth, D., Friendly, M., Gorjanc, G., Graves, S., Heiberger, R., Laboissiere, R., Maechler, M., Monette, G., Murdoch, D., Nilsson, H., Ogle, D., Ripley, B., Venables, W., Walker, S., Winsemius, D., Zeileis, A., R-Core, 2018. Companion to Applied Regression.

Galloway, J.M., Palmer, M., Jamieson, H.E., Patterson, R.T., Nasser, N., Falck, H., Macumber, A.L., Goldsmith, S.A., Sanei, H., Normandeau, P., Hadlari, T., Roe, H.M., Neville, L.A., Lemay, D., 2015. Geochemistry of lakes across ecozones in the Northwest Territories and implications for the distribution of arsenic in the Yellowknife region. Part 1: Sediments. https://doi.org/10.4095/296954

Galloway, J.M., Sanei, H., Patterson, R.T., Mosstajiri, T., Hadlari, T., Falck, H., 2012. Total arsenic concentrations of lake sediments near the City of Yellowknife , Northwest Territories 1–47. https://doi.org/10.4095/xxxxxx

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

Garcia-Ordiales, E., Loredo, J., Covelli, S., Esbrí, J.M., Millán, R., Higueras, P., 2017. Trace metal pollution in freshwater sediments of the world's largest mercury mining district: sources, spatial distribution, and environmental implications. J. Soils Sediments 17, 1893–1904. https://doi.org/10.1007/s11368-016-1503-5

Glew, J.R., 1988. A portable extruding device for close interval sectioning of unconsolidated core samples. J. Paleolimnol. 1, 235–239. https://doi.org/10.1007/BF00177769

Government of Canada, 2016. About Contaminated Sites [WWW Document]. Gov. Canada. URL https://www.canada.ca/en/environment-climate-change/services/federal-contaminated-sites/about.html (accessed 1.29.18).

Government of Canada, 1985. Canada Water Act.

Government of the Northwest Territories, 2016. Arsenic in Lake Water Around Yellowknife.

He, W., Megharaj, M., Naidu, R., 2009. Toxicity of tri- and penta-valent arsenic, alone and in combination, to the cladoceran Daphnia carinata: the influence of microbial transformation in natural waters. Environ. Geochem. Health 31 Suppl 1, 133–41. https://doi.org/10.1007/s10653-008-9239-9

Hothorn, T., Zeileis, A., Farebrother, R.W., Cummins, C., Millo, G., Mitchell, D., 2018. Testing Linear Regression Models.

Houben, A.J., D'Onofrio, R., Kokelj, S. V, Blais, J.M., 2016. Factors Affecting Elevated Arsenic and Methyl Mercury Concentrations in Small Shield Lakes Surrounding Gold Mines near the Yellowknife, NT, (Canada) Region. PLoS One 11, e0150960. https://doi.org/10.1371/journal.pone.0150960

Indigenous and Northern Affairs Canada, 2012. Internal Audit Report: Value for Money Audit of the Giant Mine Remediation Project, Audit and Assurances Survey Branch Project 12-32.

Ingersoll, C.G., MacDonald, D.D., Wang, N., Crane, J.L., Field, L.J., Haverland, P.S., Kemble, N.E., Lindskoog, R.A., Severn, C., Smorong, D.E., 2001. Predictions of sediment toxicity using consensus-based freshwater sediment quality guidelines. Arch. Environ. Contam. Toxicol. 41, 8–21. https://doi.org/10.1007/s002440010216

Jamieson, H.E., 2014. The Legacy of Arsenic Contamination from Mining and Processing Refractory Gold Ore at Giant Mine, Yellowknife, Northwest Territories, Canada. Rev. Mineral. Geochemistry 79, 533–551. https://doi.org/10.2138/rmg.2014.79.12

Kihlman, S., Kauppila, T., 2010. Tracking the Aquatic Impacts of a Historical Metal Mine Using Lacustrine Protists and Diatom Algae. Mine Water Environ. 29, 116–134. https://doi.org/10.1007/s10230-009-0096-2

Korosi, J.B., Thienpont, J.R., Smol, J.P., Blais, J.M., 2017. Paleo-ecotoxicology: What Can Lake Sediments Tell Us about Ecosystem Responses to Environmental Pollutants? Environ. Sci. Technol. acs.est.7b02375. https://doi.org/10.1021/acs.est.7b02375

Kuzmanović, M., López-Doval, J.C., De Castro-Català, N., Guasch, H., Petrović, M., Muñoz, I., Ginebreda, A., Barceló, D., 2016. Ecotoxicological risk assessment of chemical pollution in four Iberian river basins and its relationship with the aquatic macroinvertebrate community status. Sci. Total Environ. 540, 324–333. https://doi.org/10.1016/j.scitotenv.2015.06.112

Lari, E., Gauthier, P., Mohaddes, E., Pyle, G.G., 2017. Interactive toxicity of Ni , Zn , Cu , and Cd on Daphnia magna at lethal and sub-lethal concentrations. J. Hazard. Mater. 334, 21–28. https://doi.org/10.1016/j.jhazmat.2017.03.060

Leppänen, J.J., Weckström, J., Korhola, A., 2017. Multiple mining impacts induce widespread changes in ecosystem dynamics in a boreal lake. Sci. Rep. 7, 1–11.

https://doi.org/10.1038/s41598-017-11421-8

Linnik, P.M., Zubenko, I.B., 2000. Role of bottom sediments in the secondary pollution of aquatic environments by heavy-metal compounds. Lakes Reserv. Res. Manag. 5, 11–21. https://doi.org/10.1046/j.1440-1770.2000.00094.x

Macdonald, D.D., Ingersoll, C.G., Berger, T.A., 2000. Development and Evaluation of Consensus-Based Sediment Quality Guidelines for Freshwater Ecosystems. Arch. Environ. Contam. Toxicol. 39, 20–31. https://doi.org/10.1007/s002440010075

Machado, K.S., Ferreira, P.A., Rizzi, J., Figueira, R., Froehner, S., 2017. Spatial and Temporal Variation of Heavy Metals Contamination in Recent Sediments from Barigui River Basin, South Brazil. Environ. Pollut. Clim. Chang. 01, 1–9. https://doi.org/10.4172/2573-458X.1000108

Mandal, B.K., Ogra, Y., Suzuki, K.T., 2003. Speciation of arsenic in human nail and hair from arsenic-affected area by HPLC-inductively coupled argon plasma mass spectrometry. Toxicol. Appl. Pharmacol. 189, 73–83. https://doi.org/10.1016/S0041-008X(03)00088-7

Marco Torchiano, M., 2016. Permutation Tests for Linear Models.

Natural Resources Canada, 2015. CanVec.

Nikolaidis, N.P., Dobbs, G.M., Chen, J., Lackovic, J.A., 2004. Arsenic mobility in contaminated lake sediments. Environ. Pollut. 129, 479–487. https://doi.org/10.1016/j.envpol.2003.11.005

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

Pelletier, N., Chételat, J., Cousens, B., Zhang, S., Stepner, D., Muir, D.C.G., Vermaire, J.C., Pelletier, N., Cousens, J., Zhang, B., 2020. Lead contamination from gold mining in Yellowknife Bay (Northwest Territories), reconstructed using stable lead isotopes. Environ. Pollut. https://doi.org/10.1016/j.envpol.2019.113888

Punning, J.-M., Boyle, J.F., Terasmaa, J., Vaasma, T., Mikomägi, A., 2007. Changes in lake-sediment structure and composition caused by human impact: repeated studies of Lake Martiska, Estonia. The Holocene 17, 145–151. https://doi.org/10.1177/0959683607073297

R Core Development Team, 2017. R: A Language and Environment for Statistical Computing.

Rand, G.M., Schuler, L.J., 2009. Aquatic Risk Assessment of Metals in Sediment from South Florida Canals. Soil Sediment Contam. 18, 155–172. https://doi.org/10.1080/15320380802659919

Reimann, C., De Caritat, P., 2005. Distinguishing between natural and anthropogenic sources for elements in the environment: Regional geochemical surveys versus enrichment factors. Sci. Total Environ. 337, 91–107. https://doi.org/10.1016/j.scitotenv.2004.06.011

Rippey, B., Rose, N., Yang, H., Harrad, S., Robson, M., Travers, S., 2008. An assessment of toxicity in profundal lake sediment due to deposition of heavy metals and persistent organic pollutants from the atmosphere. Environ. Int. 34, 345–356.

https://doi.org/10.1016/j.envint.2007.03.006

Rose, N.L., Turner, S.D., Yang, H., Yang, C., Hall, C., Harrad, S., 2018. Palaeotoxicity : reconstructing the risk of multiple sedimentary pollutants to freshwater organisms. Environ. Geochem. Health 40, 1667–1682. https://doi.org/10.1007/s10653-018-0080-5

Salonen, V.-P., Tuovinen, N., Valpola, S., 2006. History of Mine Drainage Impact on Lake Orijärvi Algal Communities, SW Finland. J. Paleolimnol. 289–303. https://doi.org/10.1007/s10933-005-0483-z

Sandlos, J., Keeling, A., 2016. Toxic Legacies , Slow Violence , and Environmental Injustice at Giant Mine, Northwest Territories. North. Rev. 7–21.

Schuh, C.E., Jamieson, H.E., Palmer, M.J., Martin, A.J., 2017. Applied Geochemistry Solid-phase speciation and post-depositional mobility of arsenic in lake sediments impacted by ore roasting at legacy gold mines in the Yellowknife area , Northwest Territories , Canada. Appl. Geochemistry 0–1. https://doi.org/10.1016/j.apgeochem.2017.10.025

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

Sivarajah, B., Korosi, J.B., Blais, J.M., Smol, J.P., 2019. Multiple environmental variables influence diatom assemblages across an arsenic gradient in 33 subarctic lakes near abandoned gold mines. Hydrobiologia 1–19. https://doi.org/10.1007/s10750-019-04014-1

Sprague, D.D., Vermaire, J.C., 2018. Legacy Arsenic Pollution of Lakes Near Cobalt , Ontario , Canada : Arsenic in Lake Water and Sediment Remains Elevated Nearly a Century After Mining Activity Has Ceased. Water Air Soil Pollut 229.

Sutherland, R.A., 2000. Bed sediment-associated trace metals in an urban stream, Oahu, Hawaii. Environ. Geol. 39, 611–627. https://doi.org/10.1007/s002540050473

Thienpont, J.R., Korosi, J.B., Hargan, K.E., Williams, T., Eickmeyer, D.C., Kimpe, L.E., Palmer, M.J., Smol, J.P., Blais, J.M., 2016. Multi-trophic level response to extreme metal contamination from gold mining in a subarctic lake. R. Soc. Publ. Proc. B 283, 1–9. https://doi.org/10.1098/rspb.2016.1125

Tipping, E., Lawlor, A.J., Lofts, S., Shotbolt, L., 2006. Simulating the long-term chemistry of an upland UK catchment: Heavy metals. Environ. Pollut. 141, 139–150. https://doi.org/10.1016/j.envpol.2005.08.019

Tiquio, M.G.J., Hurel, C., Marmier, N., Taneez, M., Andral, B., Jordan, N., Francour, P., 2017. Sediment-bound trace metals in Golfe-Juan Bay, northwestern Mediterranean: Distribution, availability and toxicity. Mar. Pollut. Bull. 118, 427–436. https://doi.org/10.1016/j.marpolbul.2017.02.065

Town, R.M., Filella, M., 2002. Implications of natural organic matter binding heterogeneity on understanding lead(II) complexation in aquatic systems, The Science of the Total Environment.

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

Vignet, C., Devier, M.H., Le Menach, K., Lyphout, L., Potier, J., Cachot, J., Budzinski, H., Bégout, M.L., Cousin, X., 2014. Long-term disruption of growth, reproduction, and behavior after embryonic exposure of zebrafish to PAH-spiked sediment. Environ. Sci. Pollut. Res. 21, 13877–13887. https://doi.org/10.1007/s11356-014-2585-5

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

Wang, S.L., Lin, C.Y., Cao, X.Z., Zhong, X., 2012. Arsenic content, fractionation, and ecological risk in the surface sediments of lake. Int. J. Environ. Sci. Technol 9, 31–40. https://doi.org/10.1007/s13762-011-0015-5

Wickham, H., Chang, W., Henry, L., Pedersen, T.L., Takahashi, K., Wilke, C., Woo, K., RStudio, 2019. Create Elegant Data Visualisations Using the Grammar of Graphics.

Table 1. Summary statistics for arsenic, antimony, and lead concentration pre-, during and post-mining for each sample lake. Samples in which the mean metal concentration is above the Interim Sediment Quality Guideline (arsenic and lead), or the Upper Effects Threshold (antimony) are highlighted in green. Samples that are above the Probable Effect Concentration are in bold.

		Pre-Mining *n=88*						During Mining *n=85*						Post-Mining *n=86*					
			Arsenic		Antimony		Lead		Arsenic		Antimony		Lead		Arsenic		Antimony		Lead	
Study Lake	D_R (km)	*n*	Mean	SD	Mean	SD	Mean	SD	*n*	Mean	SD	Mean	SD	Mean	SD	*n*	Mean	SD	Mean	SD	Mean	SD
Alexie	23	4	16	7	1	0	9	2	5	**34**	7	2	1	12	2	3	13	6	1	0	7	4
BC-17	3	6	**246**	247	10	4	3	1	3	**3500**	102 6	39	13	17	4	2	**2000**	113 1	35	15	14	1
BC-18	3	5	**3044**	2536	65	42	10	8	3	**2400**	813	39	29	12	4	4	**370**	118	7	0	6	1
BC-24	22	2	**290**	141	7	4	4	1	3	**730**	67	9	2	6	0	4	**453**	46	5	1	5	0
BC-36	24	4	13	9	1	0	2	1	3	**37**	6	1	0	7	1	4	9	7	1	1	3	1
BCR-07a	4	5	**288**	155	2	1	6	1	5	**4500**	187 1	17	15	13	5	2	**325**	120	5	0	7	1
YKC-1	19	5	25	17	1	1	5	0	3	**58**	5	2	0	4	0	2	**42**	1	2	1	5	1
David	4	3	**537**	159	21	4	8	2	8	**5100**	173 6	26	8	24	8	1 0	**784**	395	29	8	24	7
Duckfish	4	3	**81**	46	4	2	5	1	5	**200**	38	6	2	9	1	7	**63**	20	2	1	5	1
Fiddlers	9	6	**111**	36	2	1	5	1	3	**320**	75	13	6	10	4	5	**872**	303	14	2	12	2
L. Martin	24	3	**513**	438	12	10	8	6	5	**2000**	553	18	11	23	4	5	**530**	27	11	1	16	1
Small	29	5	4	0	1	0	7	0	3	9	1	1	0	6	1	2	7	1	1	0	6	1
U. Martin	5	6	**125**	118	4	5	5	1	6	**720**	170	26	5	12	1	7	**260**	130	14	4	10	1
Vee	6	3	**82**	34	1	0	7	0	6	**3500**	120 4	20	11	15	5	3	**377**	83	10	3	15	3
Vital	12	6	**183**	290	4	7	11	4	3	**1500**	713	21	13	18	3	5	**198**	43	9	1	10	2

YK-11	4	4	**2230**	2095	84	60	11	7	5	**8000**	2376	166	57	41	7	4	**975**	391	34	11	14	4
YK-42	2	5	**1332**	1398	41	38	8	5	6	**15000**	5	250	98	53	8	3	**2700**	110	64	32	29	8
YK-60	5	5	**3120**	1139	101	51	16	11	4	**3500**	656	130	34	30	4	5	**1154**	482	74	28	20	6
YKE-1	54	6	5	2	1	0	5	1	4	10	1	1	0	6	0	4	6	1	1	0	6	1
YKW1	39	2	13	1	1	0	7	0	2	24	2	2	0	7	0	5	17	3	1	0	7	0

Table 2. Summary of the slope estimate, standard error (Std. Error), and p-value for the arsenic regression. The overall model p-value, degrees of freedom (DoF), and adjusted R^2 (Adj. R^2) are indicated.

	Slope Estimate	Std. Error	P-value
Pre-mining (Intercept)	3.22	0.10	< 2e-16
During mining	0.56	0.08	2.32e-12
Post-mining	0.21	0.08	0.007
Log(Distance)	-1.51	0.08	< 2e-16
Wind	0.57	0.06	< 2e-16
P-value	< 2.2e-16		
DoF	254		
Adj. R^2	0.70		

Table 3. Summary of the slope estimate, standard error (Std. Error), and p-value for the lead regression coefficients. The overall model p-value, degrees of freedom (DoF), and adjusted R^2 (Adj. R^2) are indicated.

	Slope Estimate	Std. Error	P-value
Pre mining (Intercept)	0.95	0.05	< 2e-16
During Mining	0.36	0.04	< 2e-16
Post Mining	0.20	0.04	1.81e-07
Log Distance	-0.24	0.04	5.48-10
Wind	0.15	0.03	2.86e-06
P-value	< 2.2e-16		
DoF	254		
Adj. R^2	0.40		

Table 4. Summary of the slope estimate, standard error (Std. Error), and p-value for the antimony regression coefficients. The overall model p-value, degrees of freedom (DoF), and adjusted R^2 (Adj. R^2) are indicated.

	Slope Estimate	Std. Error	P-value
Pre mining (Intercept)	1.44	0.09	< 2e-16
During Mining	0.53	0.07	3.2e-14
Post Mining	0.27	0.07	0.000115
Log Distance	-1.19	0.07	< 2e-16
Wind	0.54	0.06	< 2e-16
P-value	< 2.2e-16		
DoF	254		
Adj. R^2	0.67		

2-column image

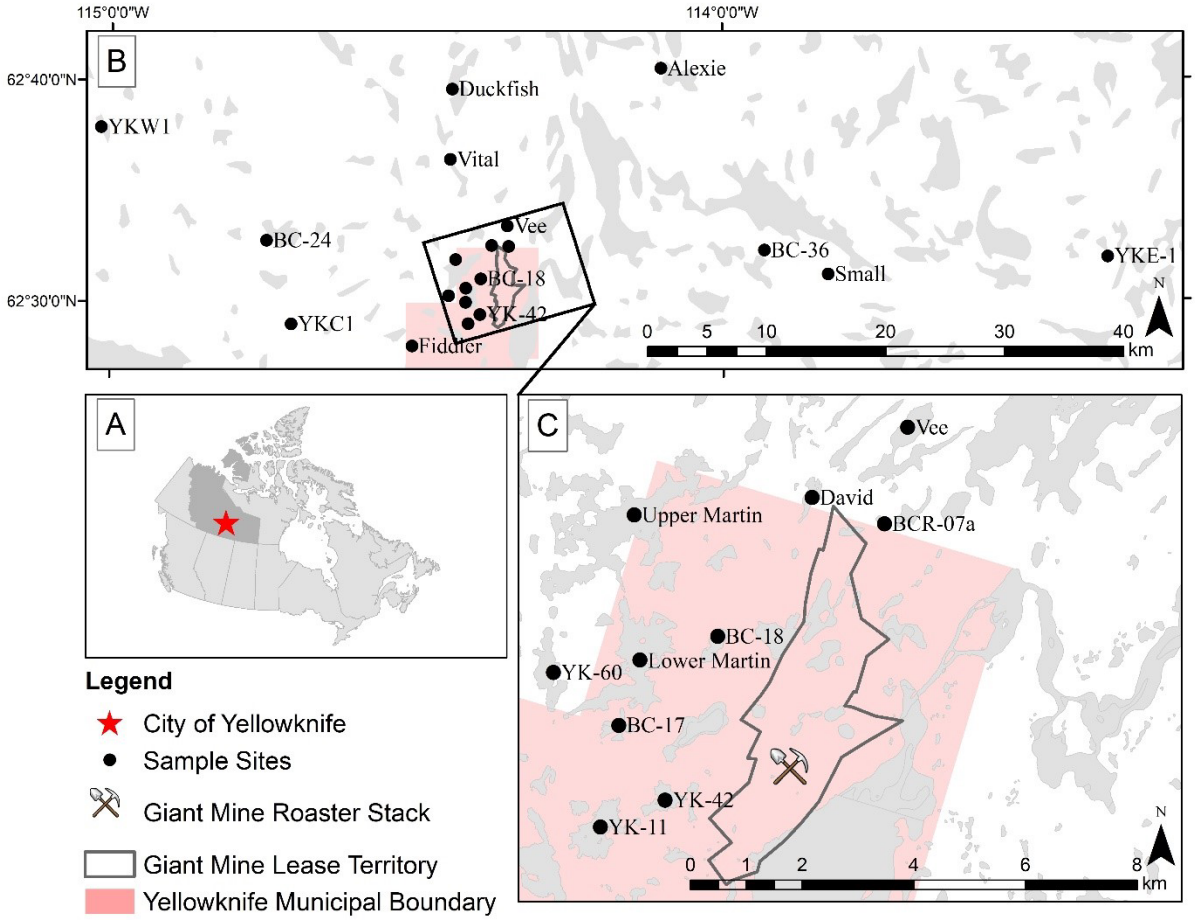

Figure 1. Map of study sites (B) relative to its location within Canada (A). The extent of the Yellowknife municipal boundary is indicated by the red shaded region. Sites close to the mine have been highlighted in the inset map for ease of identification (C). The base layer for these maps is Natural Resources Canada CanVec hydrological layer (2015). Lake names used are from the Cumulative Impact Monitoring Program water quality survey, with the exception of YKC1, YKW1 and YKE-1, which were un-named prior to this study (Palmer et al., 2015).

1.5 column image

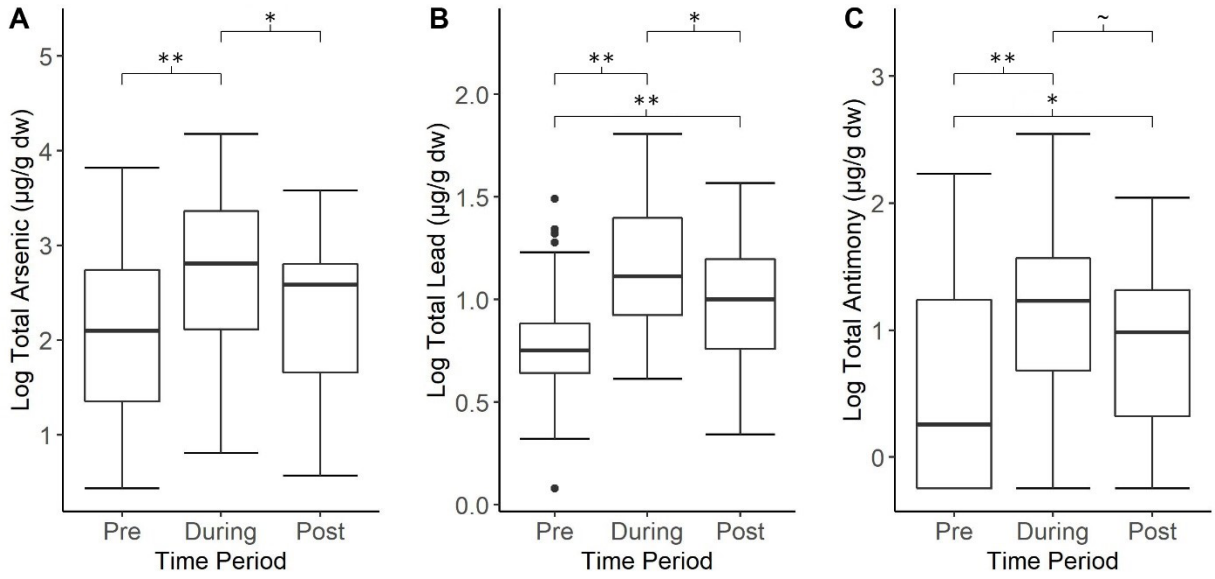

Figure 2. ANOVA and Kruskal-Wallis analysis of the $\log_{10}$ of total arsenic (A), total lead (B), and total antimony (C) respectively in each of the time-periods examined. Relationships determined by Tukey and Dunn's post-hoc analyses ($p<0.1$ (~), $p<0.05$ (*), and$p<0.001$ (**)) are indicated.

Single column image

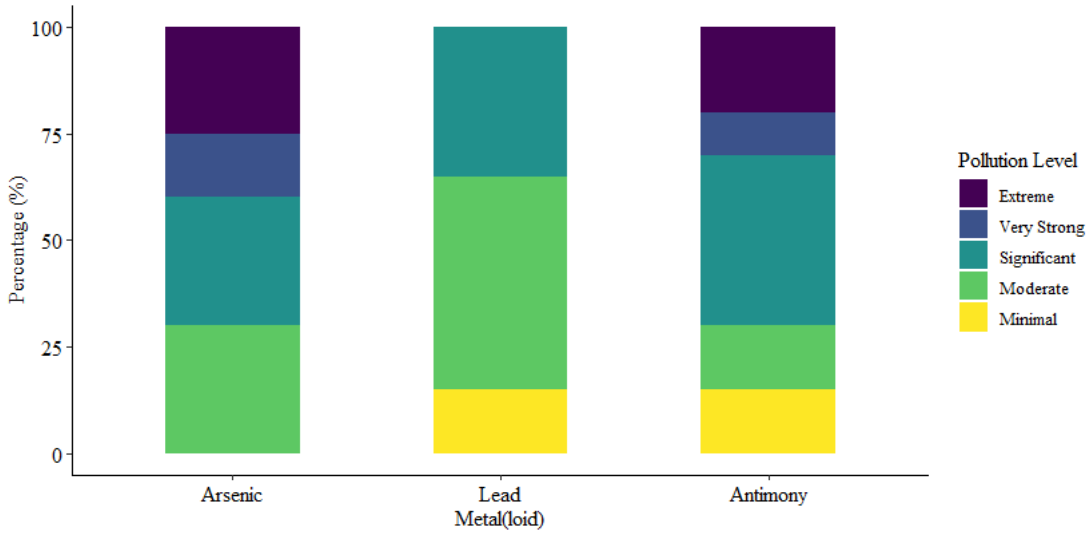

Figure 3. The pollution level derived from the maximum enrichment factor in each lake for arsenic, lead, and antimony is displayed as a fraction of the total number of lakes examined. The percentage of lakes indicating extreme pollution signal are shown in dark purple, lakes with a very strong pollution signal are in light blue, lakes with a significant pollution level are in turquoise, lakes with a moderate pollution signal are indicated by a light green colour, and lakes which show a minimal pollution signal are shown in yellow.
single column image

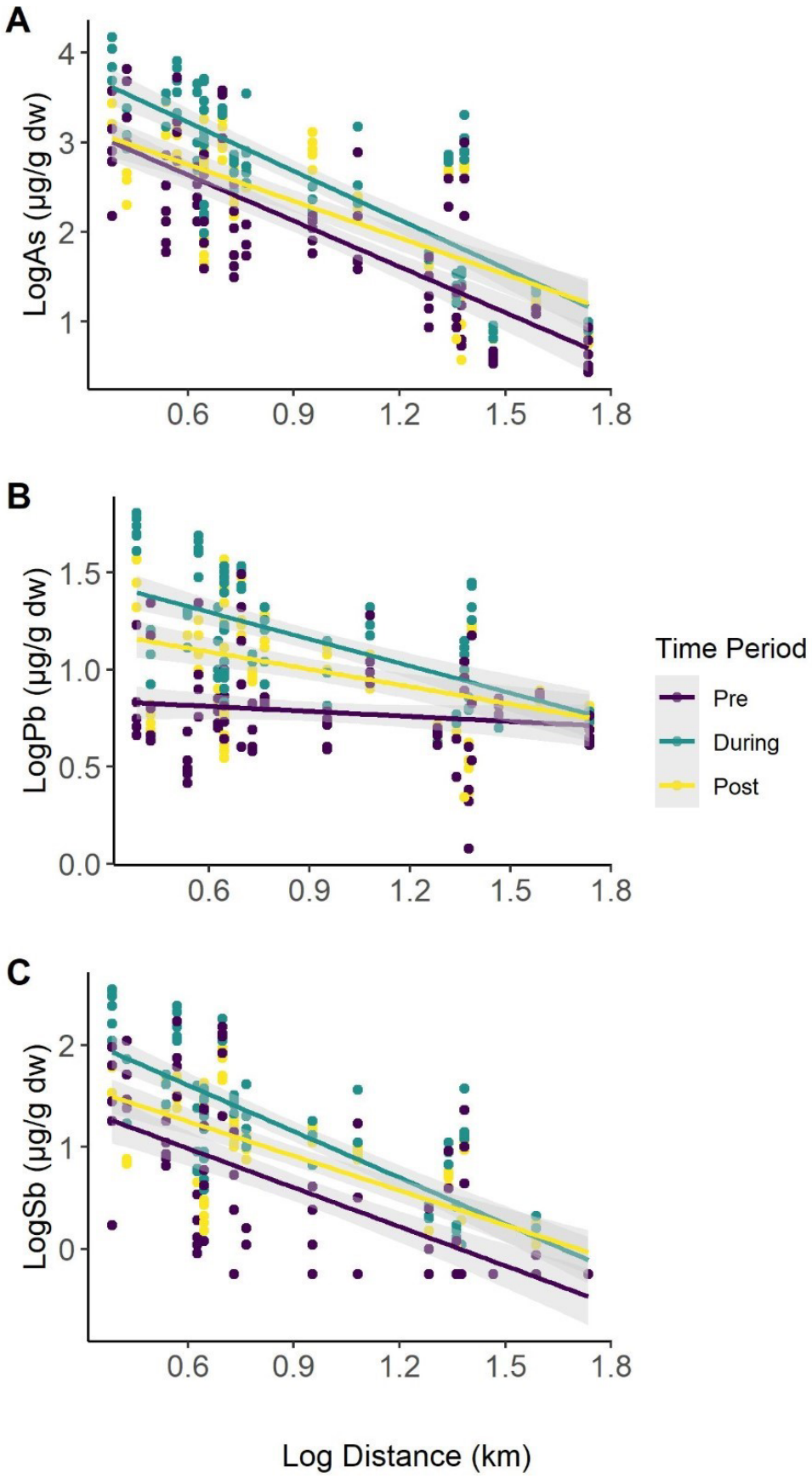
A
LogAs (µg/g dw)
4
3
2
1
0.6
0.9
1.2
1.5
1.8
B
LogPb (µg/g dw)
1.5
1.0
0.5
0.0
0.6
0.9
1.2
1.5
1.8
Time Period
Pre
During
Post
C
LogSb (µg/g dw)
2
1
0
0.6
0.9
1.2
1.5
1.8
Log Distance (km)

Figure 4. The slopes from the linear regression of $\log_{10}$(Arsenic) (A), $\log_{10}$(Lead) (B) and $\log_{10}$(Antimony) (C) concentrations for the sampled lakes as a function of $\log_{10}$(Distance). Samples correlating to the time period of pre-mining are shown in purple, samples deposited during mining are in green, and samples deposited post-mining in yellow.

1.5 column image

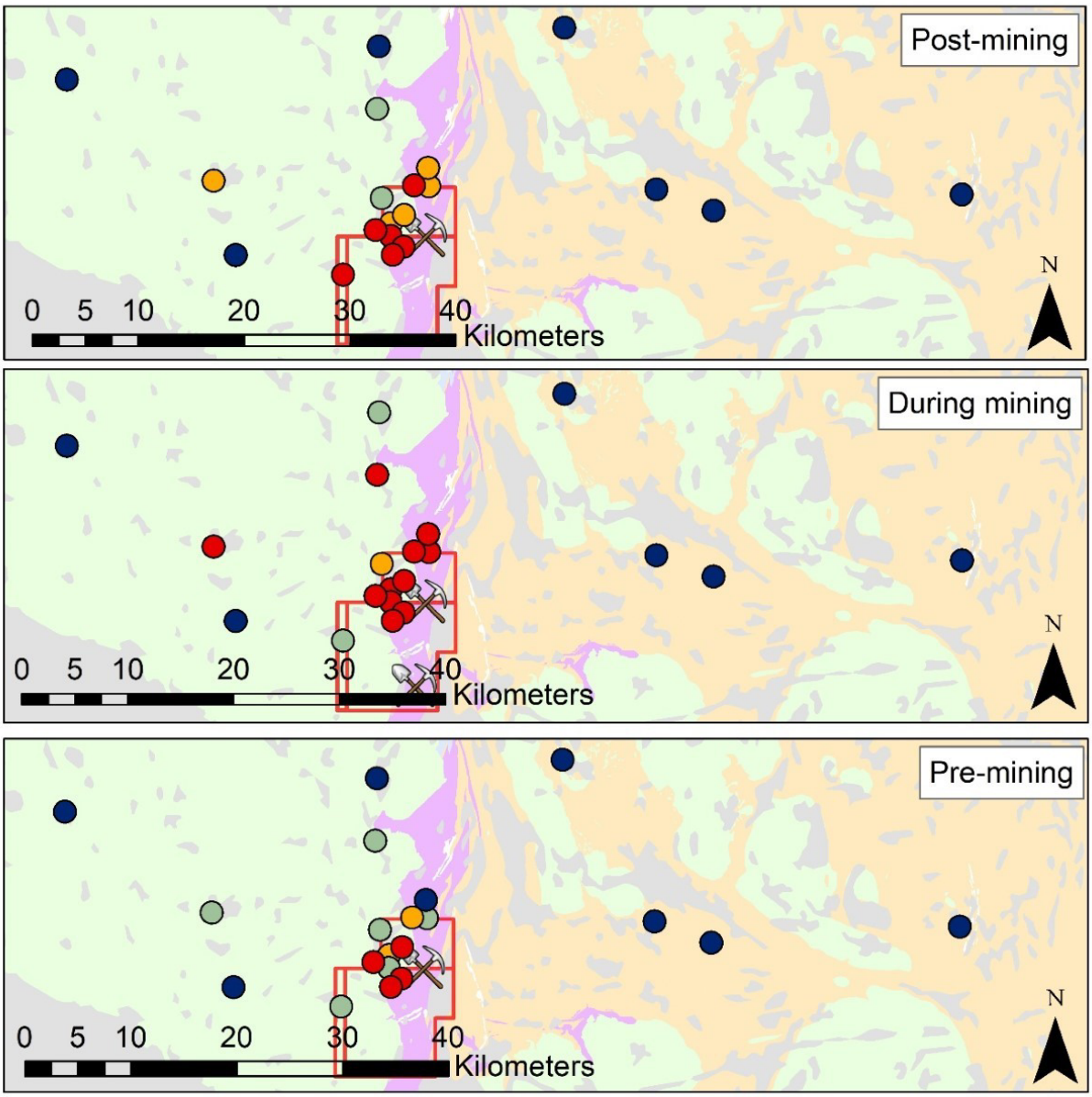

Figure 5**.** The calculated mean palaeotoxicity of sampled lake sediment post- (A) , during (B), and pre-mining (C) operations at Giant Mine. Sediments with no expected biological effect are indicated in dark blue circles, sediments with biological effects possible are indicated in light blue, yellow and orange circles, and sediments with biological effects probable are indicated with red circles. The underlying regional bedrock is indicated, with granitoid bedrock indicated by light green, sedimentary bedrock displayed with amber, and volcanic bedrock displayed as light purple.