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Lead contamination from gold mining in Yellowknife Bay (Northwest Territories), reconstructed using stable lead isotopes^{\star}



POLLUTION

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ABSTRACT

The contributions of contaminant sources are difficult to resolve in the sediment record using concentration gradients and flux reconstruction alone. In this study, we demonstrate that source partitioning using lead isotopes provide complementary and unique information to concentration gradients to evaluate point-source releases, transport, and recovery of metal mining pollution in the environment. We analyzed eight sediment cores, collected within 24 km of two gold mines, for Pb stable isotopes, Pb concentration, and sediment chronology. Stable Pb isotope ratios (²⁰⁶Pb/²⁰⁷Pb, ²⁰⁸Pb/²⁰⁴Pb) of mining ore were different from those of background (pre-disturbance) sediment, allowing the use of a quantitative mixing model. As previously reported for some Arctic lakes, Pb isotope ratios indicated negligible aerosol inputs to sediment from regional or long-range pollution sources, possibly related to low annual precipitation. Maximum recorded Pb flux at each site reached up to 63 mg m⁻² yr⁻¹ in the period corresponding to early years of mining when pollution mitigation measures were at a minimum (1950s -1960s). The maximum contribution of mining-derived Pb to these fluxes declined with distance from the mines from $92 \pm 8\%$ to $8 \pm 4\%$ at the farthest site. Mining-derived Pb was still present at the sediment surface within 9 km of Giant Mine more than ten years after mine closure (5-26 km, 95% confidence interval) and model estimates suggest it could be present for another ~50-100 years. These results highlight the persistence of Pb pollution in freshwater sediment and the usefulness of Pb stable isotopes to quantify spatial and temporal trends of contamination from mining pollution, particularly as concentrations approach background.

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1. Introduction

The characterization of mining-related contamination of freshwater ecosystems is important to assess hazards from exposure and develop effective and realistic remediation plans. Paleoenvironmental methods have been established to detect and quantify mining-related metal pollution, and novel approaches are being developed to predict future ecosystem recovery (Kirk and Gleason, 2015). Gradients of metal fluxes and concentrations or comparison

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between control and contaminated sites can give good approximations of environmental baseline conditions (Kurek et al., 2013; Sprague and Vermaire, 2018a, 2018b; Wiklund et al., 2014). However, source attribution, whereby the relative contribution of observed metal fluxes in sediments are partitioned among anthropogenic and natural sources, remains challenging. Anthropogenic contaminants that are recirculated in the environment from various biological and geochemical processes are hard to distinguish from newly released contaminants or variation in background flux. Since a wide variety of environmental changes have occurred concurrently during the Anthropocene (Waters et al., 2016), the interactive effects of multiple disturbances (e.g. pollution, legacy contamination, land-use change, and climate) may confound interpretation of sediment records (Guilizzoni et al.,



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2012; Hawryshyn et al., 2012; Smol, 2010).

Lead isotope ratios are useful tracers of metal pollution sources because there are four stable isotopes (²⁰⁴Pb, ²⁰⁶Pb, ²⁰⁷Pb and ²⁰⁸Pb), and they have been widely used in paleolimnology (Komárek et al., 2008; Cheng and Hu, 2010) due to the stability of Pb in sediments (Outridge and Wang, 2015). One of the most common applications of Pb isotope ratios in sediment is for identification of atmospheric sources of Pb deposition from local, regional and long-range transport, typically measured on one sediment core to reconstruct the lake's contamination history (Babos et al., 2019; Liu et al., 2012; Gallon et al., 2006; Outridge et al., 2002). Isotope mixing models can resolve the relative contributions of different Pb sources if the source isotope ratios are known and distinct (Bird et al., 2010; Mariet et al., 2018), although precise quantification of source attribution is often not possible in lake sediment studies because isotopic information is not available for all sources (Cheng and Hu, 2010). This study presents a novel application of Pb stable isotopes involving quantitative source apportionment to reconstruct within-lake transport and burial of point-source mining pollution, which had a distinct and welldefined isotopic signature. Lead contamination from gold mining was investigated in Yellowknife Bay (Great Slave Lake, Northwest Territories, Canada) by measurement of Pb concentrations and isotope profiles in multiple sediment cores to characterize the within-lake accumulation rates, dispersion and burial of miningderived Pb in sediment and to predict the future recovery rate of Pb contamination in the bay. The application of Pb isotopes was particularly useful for resolving Pb of mining origin when Pb concentrations approached background and provided insights into the persistence of Pb contamination in surface sediment following mine closure. The findings are relevant for assessment of pointsource contamination of lakes from metal mining around the world.

2. Methods

2.1. Study area

Yellowknife Bay is located on the north shore of Great Slave Lake, near the City of Yellowknife, Northwest Territories, Canada (Fig. 1). The surface area of the bay covers approximately 20 km² out the 27,200 km² surface of Great Slave Lake. Maximum water depth in the bay varies from 15 m at the north end to 30 m at the south end (Canadian Hydrographic Service, 2005).

Gold production in Yellowknife spanned six decades during the 20th century (Silke, 2009), principally at the Giant and Con Mines, resulting in large releases of arsenic, antimony and metals (including Pb) to Yellowknife Bay via effluent, tailings dumps and atmospheric deposition of ore roasting emissions (Chételat et al., 2017). Gold production officially ceased in Yellowknife in 2004, but legacy contaminants are still present in the surface layer of lake sediments, which are enriched for some elements by orders of magnitude compared to background conditions (Chételat et al., 2017; Galloway et al., 2015).

The dust emitted during the ore roasting process at Con Mine until 1970 and at Giant mine until 1999 was a major source of metal(loid) contamination (mainly arsenic, antimony and to a lesser extent metals such as lead) to lake water, sediment, and catchment soils (Bromstad et al., 2017; Fawcett et al., 2015; Thienpont et al., 2016). The greatest emissions of metal(loid)s occurred during the earliest years of operation when few pollution control measures were in place and no environmental monitoring was being conducted. An estimated 86% (or 17,800 tonnes) of the total arsenic emissions at the Giant Mine occurred in the first 15 years of production (Jamieson, 2014). Estimates of metal(loid) pollution release, based on arsenic trioxide emissions, are 6.6 times greater for Giant Mine than Con Mine (Hocking et al., 1978; INAC, 2013). Arsenic and antimony concentrations in lake water and surficial sediment currently provide the best estimates of the footprint of stack emissions (Houben et al., 2016; Palmer et al., 2015). Non-atmospheric sources of anthropogenic metal(loid)s released to Yellowknife Bay from Giant Mine included the dumping of metal(loid)-rich tailings directly into the bay between 1948 and 1951 (INAC, 2013) and effluent flowing into the bay from Baker Creek (Chételat et al., 2017).

2.2. Sample collection

A total of nine sediment cores were collected from the study area during the summers of 2013-2015 by boat using an 8.6 cm diameter UWITEC gravity corer (Fig. 1). Eight of the cores were collected in offshore depositional areas along a transect from Yellowknife Bay into the main body of Great Slave Lake with increasing distance from the mines to determine the historical input of Pb to the sediments. The ninth sediment core was collected from a small unnamed lake on Ruth Island (referred to as Ruth Lake). Ruth Lake is disconnected from Great Slave Lake waters and is located outside of Yellowknife Bay. It offered an opportunity to compare sediments affected by the transport of metal(loid)s within Great Slave Lake to lake sediment only (potentially) affected by atmospheric deposition such as from roaster emissions or aerosol Pb from long-range transport. The cores ranged from 13 to 40 cm in length and were collected between 1 and 24 km from the location of the now decommissioned Giant Mine roaster stack (Fig. 1 and supplementary information).

Sediment cores were sliced every 0.5 cm in the top 10 or 15 cm and every centimeter below that depth. Sediment slices were packed in plastic bags, freeze dried, weighed and homogenized prior to chemical analysis. All measurements are reported on a dry weight basis. Surficial bedrock was sampled from nine locations in the Yellowknife Bay catchment to obtain an estimate of Pb isotope values for potential natural weathering sources of Pb. The samples include lavas and intrusions from the Kam and Banting Groups of the Yellowknife greenstone belt and two granitoid intrusions (Cousens, 2000; Cousens et al., 2002; Cousens et al., 2006a). All samples were collected using INAC geological maps of the region. Lichen samples were collected on young branches of trees, mainly Piceamariana, to estimate the Pb isotopic composition of local aerosol deposition (Carignan and Gariépy, 1995; Simonetti et al., 2003). Locations of sediment, bedrock and lichen samples were determined using a hand-held GPS unit (Fig. 1).

2.3. Chronology

Five of the sediment cores were dated using radiogenic lead (²¹⁰Pb) and cesium (¹³⁷Cs) measurements. Radioisotopes were measured at one of three labs in Canada over the three-year study: the Canada Centre for Inland Waters (Burlington, Ontario), Flett Research Ltd. (Winnipeg, Manitoba) or MyCore Scientific Inc. (Dunrobin, Ontario). Disintegrations per minute of the radioisotopes were counted using gamma or alpha spectrometry. Supported radiogenic lead activity was estimated by measuring the activity of the ²²⁶Ra isotope in the sediments (Appleby and Oldfield, 1978). Radiogenic lead dates were calculated using the constant rate of supply (CRS) model (Appleby and Oldfield, 1978), and age uncertainties were estimated by Bayesian statistics using the Sanchez-Cabeza et al. (2014) iterative calculation sheets implemented in Microsoft® Excel. The calculated ages and uncertainties



Fig. 1. Location of the study area within Canada (A) and on the north shore of Great Slave Lake in the Northwest Territories (B). View of Yellowknife Bay and the main body of Great Slave Lake (C) including locations of the two gold mines and sampling sites for sediment cores, bedrock samples, and lichen samples, with a close-up view of the north end of the bay (D).

were interpolated using the *Bacon* package (Blaauw and Christen, 2011) implemented in *R* (R Development Core Team, 2018). The age of sediment slices is reported here as the median of 2000 stored Markov Chain Monte Carlo iterations for that slice. Age-depth models were compared to the 137 Cs activity profile for independent validation. The age-depth models for the cores are provided in Chételat et al. (2017).

2.4. Metals concentrations

Sediments from cores S1, S2, S4, S7 and Ruth Lake were analyzed for 30 elements by inductively coupled plasma mass spectrometry (ICP-MS) at RPC Laboratories in Fredericton, New Brunswick, Canada. Sediments from three other cores (S3, S5, S8) were analyzed for 46 elements by ICP-MS at the Canada Centre for Inland Waters (Burlington, Canada). Sediments were digested with aqua regia at the Canada Centre for Inland Waters while samples at RPC Laboratories were digested with hydrochloric acid and hydrogen peroxide. Both methods do not completely decompose siliceous materials; therefore, the Pb analytical results represent leachable concentrations. Recoveries of leachable lead represented $65 \pm 2\%$ (n = 14) of the total Pb concentration in the certified reference material San Juaquin soil (Mackey et al., 2010). Relative standard deviations of duplicate samples from RPC Laboratories were $1 \pm 2\%$ for bulk concentrations of Pb (n = 7). Several sediment samples were analyzed for Pb concentration at both the Canada Centre for Inland Waters and RPC Laboratories for comparison, and relative standard deviations of these results were $4 \pm 2\%$ (n = 5). Measured concentrations of Pb for procedural blanks at both laboratories were below detection limit (<0.01 mg kg⁻¹, n = 14). All ICP-MS measurements along with QA/QC data are presented in Chételat et al. (2017).

2.5. Isotope analysis

Five to 18 sediment layers from each core along with lichen and bedrock samples were analyzed for Pb stable isotopes ratios on a Thermo-Finnigan TRITON mass spectrometer at the Isotope Geochemistry and Geochronology Research Centre at Carleton University (Ottawa, Canada). Approximately 100 mg of each sediment sample was weighed into a Teflon screw-cap vial and dissolved in a mix of 75% HF and 25% 15N HNO₃. Samples were left on a hotplate at 145 °C for two days, after which caps were removed and the HF/HNO₃ was evaporated to form a moist paste. The residue was then treated with 7N HNO₃, dried down, then 2 ml of 6N HCl was added to each sample, the beaker was capped and left on a hotplate for 24 h. After drying down the HCl, the residue was then dissolved in 1N HBr for column chemistry. For the bedrock samples, a weighed aliquot of the HBr was removed for Pb concentration determinations by isotope dilution. A weighed amount of ²⁰⁸Pb spike was added to the aliquot and returned to the hotplate for several hours to ensure complete mixing of the dissolved sample and the spike. All reagents were ultrapure, with Pb blanks <1 pg/g.

Lead was isolated in Bio-Rad 10-ml polyethylene columns and

Dowex AG1-8X anion resin, using 1N HBr to elute other elements and 6N HCl to elute Pb. The collected Pb solution was dried, dissolved in 1N HBr, and the above procedure was repeated with a small volume resin bed. After final drying, the residue was treated with 7N HNO₃ to eliminate bromides and residual organic matter in the Pb solution.

Total procedural blanks for Pb were <150 pg and were insignificant relative to the Pb content of samples (\ll 1% of total Pb). The samples were loaded onto single Re filaments with H₃PO₄ and silica gel and were run manually at a filament temperature of 1275 °C in a Thermo-Finnigan TRITON mass spectrometer. Lead isotope ratios were corrected for fractionation using the NBS 981 standard values of Todt et al. (1996). The total ranges measured for NBS 981 in a 2year period bracketing the analyses are (2σ errors) ± 0.017 for ²⁰⁶Pb/²⁰⁴Pb (0.05% RSD), ± 0.021 for ²⁰⁷Pb/²⁰⁴Pb (0.07% RSD), ± 0.038 for ²⁰⁸Pb/²⁰⁴Pb (0.05% RSD), ± 0.0021 for ²⁰⁸Pb/²⁰⁶Pb (0.05% RSD), ± 0.00038 for ²⁰⁷Pb/²⁰⁶Pb (0.02% RSD). The precision of the Pb concentration values in the bedrock samples is estimated at less than 1%. Within-run errors on the reference material isotopic ratios (n = 7) were below the aforementioned values for each ratio.

2.6. Isotope mixing model

Isotopic data expressed as ${}^{208}\text{Pb}/{}^{204}\text{Pb}$ vs. ${}^{206}\text{Pb}/{}^{207}\text{Pb}$ ratios were well described using a linear regression fit (R² = 0.98, p < 0.001) between the isotopic values of mining ore used at Giant Mine and Con Mine, lichen, bedrock and sediment samples (Fig. 2).

We used a well-established Bayesian mixing model to resolve the source partitioning in our sediment samples. We used the *Simmr* package implemented in R (Parnell, 2016), which was initially conceived to resolve mixing equations for quantifying the diet of an organism using an isometric log-ratio transformation (Egozcue et al., 2003; Parnell et al., 2013). However, the model can be implemented for geochemical studies by assuming a null trophic enrichment factor for each source. Source portioning uncertainty is estimated with a classical bootstrapping method (>10,000 iterations). Source attribution is reported as the average contribution from the Bayesian distribution and 2- σ uncertainties are reported.

We modelled the contribution of two sources to the Pb in the sediment using a linear mixing model relying on two isotope ratios $(^{206}\text{Pb}/^{207}\text{Pb} \text{ and } ^{208}\text{Pb}/^{204}\text{Pb})$. The two sources included in this



Fig. 2. Biplot of stable Pb isotope ratios (²⁰⁸Pb)²⁰⁴Pb and ²⁰⁶Pb)²⁰⁷Pb) for sediment layers (baseline pre-1938, and since the start of mining in Yellowknife in 1938), lichen, bedrock and ore from two gold mines. The Pb isotope data for ore are from Cousens et al. (2006b) and Cumming and Tsong (1975).

model were (1) background Pb occurring from stream sediment and watershed erosion, (2) mining-derived Pb released by the local gold mining industry. The isotope ratio of background Pb was estimated from the mean and standard deviation of Pb isotope values in the sediment layers dated prior to mining in the area (<A.D. 1938, 95% CI). The ratio of mining-derived Pb corresponded to the mean and standard deviation of isotopic values for pyrite, chalcopyrite and sphalerite processed at Giant Mine as measured by Cousens et al. (2006b) and galena processed at Con Mine as measured by Cumming and Tsong (1975).

As a separate analysis, source partitioning in samples from the sediment-water interface and sediment layers dated 1995 onward (last ~20 years) were modelled using the two previously mentioned sources and an additional source representing aerosol input to the sediment. The isotope value of aerosol input was determined from the isotopic composition of lichen samples. We used this model to assess the sensitivity of sediment Pb source portioning to the inclusion of aerosols as a source. We evaluated the relevance of the three-source model vs. the two-source model based on a comparison among sampling sites and geochemical profiles of Sb, Cu and Zn, which were emitted along with Pb during the mining operations (Chételat et al., 2017).

2.7. Flux calculation

Total Pb flux was calculated using equation (1) and the Pb flux contribution from mining pollution (Pb_m) was estimated from equation (2).

$$Pb_f = \frac{\rho Pb_c}{A_r} \tag{1}$$

$$Pb_m = Pb_f \times f_m \tag{2}$$

Where Pb_f is the Pb flux for a sediment slice (mg cm⁻² yr⁻¹), ρ is the dry density of the sediment slice (g cm⁻³), Pb_c is the Pb concentration in the sediment slice (mg g⁻¹), A_r is the average estimated accumulation rate for that depth (yr cm⁻¹) and f_m is the ratio of mining-derived Pb in the sediment according to the isotope mixing model (fraction varying between 0 and 1).

2.8. Spatial distribution of Pb contamination and recovery models

The past and current extent of mining-derived contamination in the sediment was estimated by extrapolating the log-linear trend in the relative contribution of mining-derived Pb versus distance from the Giant Mine at maximum impact and in surface sediment. Similarly, a recovery model was generated by extrapolating the loglinear trend in relative contribution of mining-derived Pb over time at each site. The sediment layers dated after 1958 were used for the recovery model since >85% of Giant Mine roaster emissions occurred before that date (Bromstad et al., 2017). The intercept of this log-linear trend provides a timeline for mining-derived Pb to be completely buried in the surface layer at each site. We also generated a three-dimensional gaussian spline based on the sediment core distance from Giant Mine (km), the average age of the sediment layers according to the age-depth models and the estimated contribution of mining Pb (f_m) for that age and location. The gaussian spline was modelled using Sigmaplot 14.0 software. This model provides a spatially smoothed estimation of recovery time over the studied area similar to a kernel density estimation.

3. Results

3.1. Chronologies

Chronologies for the five dated sediment cores showed that the sediment records extended back to pre-mining conditions (pre-1938). In each core, the modelled age of the peak in radiogenic cesium, which occurs in A.D. 1963 ± 2 (Pennington et al., 1973), was consistent with the 95% confidence interval of our age-depth model for that slice. The cores showed a linear decrease in unsupported ²¹⁰Pb activity with sediment cumulative dry weight down to a depth varying between 6 and 28.5 cm.

There was a clear trend of higher sedimentation rate with increasing distance from the Giant Mine (supplementary material, Fig. S2). Dry sedimentation rate in the shallow Ruth Lake was 73 ± 17 g m⁻² year⁻¹ (average and standard deviation), which was lower than anywhere in Yellowknife Bay, where it varied between 795 \pm 351 and 1138 \pm 505 g m⁻² year⁻¹.

3.2. Isotope ratios of Pb sources

The Pb isotope values of sediment dated prior to the opening of (²⁰⁸Pb/²⁰⁴Pb the mines = 40.161 ± 0.185 and 206 Pb/ 207 Pb = 1.2914 ± 0.0142) were significantly different from mining-derived Pb $(^{208}\text{Pb}/^{204}\text{Pb} = 34.071 \pm 0.545 \text{ and}$ 206 Pb/ 207 Pb = 0.9450 ± 0.0299) (Mann–Whitney U test, p < 0.001) (Fig. 2). Bedrock samples showed a large variability in Pb isotope ratios. Bedrock samples had significantly lower ²⁰⁶Pb/²⁰⁷Pb ratios (1.1776 ± 0.0970) but no difference in ²⁰⁸Pb/²⁰⁴Pb ratios (38.594 ± 2.388) compared to baseline sediments (Mann–Whitney U test, p = 0.018 and p = 0.157 respectively). One outlier, collected at a further distance from Yellowknife Bay than other bedrock samples, was present among our bedrock samples (DL-3, $^{208}\text{Pb}/^{204}\text{Pb}=58.737$ and $^{206}\text{Pb}/^{207}\text{Pb}=1.7983$). Lichen samples had Pb isotope values comprised between mining ore and baseline sediments in the biplot space $(^{208}Pb/^{204}Pb = 37.758 \pm 0.388$ and 206 Pb/ 207 Pb = 1.1657 ± 0.0276). There was no significant trend predicting isotope values of lichen samples with respect to the distance from the city or either of the mines (supplementary information, Fig. S1).

3.3. Sediment Pb concentrations

The mean background Pb concentration in sediments (pre-1938) was 14 ± 3.7 mg kg⁻¹ (mean and standard deviation, n = 15) in all cores from Great Slave Lake while Ruth Lake sediment had a lower background concentration at 7 \pm 0.2 mg kg⁻¹. Sediment Pb concentrations in cores from the north end of Yellowknife Bay exhibited sharp sub-surface peaks followed by a rapid decrease and a slower attenuation near the sediment-water interface (Fig. 3a). The maximum recorded Pb concentration in each core decreased with distance from Giant Mine (Fig. 3a). Core S1, located closest to the mine (1.4 km), had a maximum Pb concentration of $351 \pm 14 \text{ mg kg}^{-1}$, while core S4, located 3.5 km away, reached a maximum Pb concentration of 71 \pm 3 mg kg⁻¹. The sub-surface peaks in sediment concentration exceeded the Canadian sediment quality guideline within 3.5 km of Giant Mine (Interim Sediment Quality Guideline for $Pb = 35 \text{ mg kg}^{-1}$, probable effect level = 91 mg kg⁻¹) (CCME, 1998).

Although all sites recorded a simultaneous increase in Pb concentration during the 1950s, the timing of the maximum recorded concentration was slightly different among sites. Sites closer to the mines recorded a maximum impact slightly before far-field sites. In cores S3 and S4, Pb concentrations reached a maximum of 101 \pm 4 and 71 \pm 3 mg kg⁻¹ respectively between 1955 and 1965. Site S5 peaked at 27.5 \pm 1.1 mg Pb kg⁻¹ between 1960 and 1975 and site S8 peaked at 26.3 \pm 1.1 mg Pb kg⁻¹ between 1973 and 1985.

The Pb concentrations of the sediment surface layers (0–1 cm depth) varied between 16 ± 0.6 and 35 ± 1.4 mg Pb kg⁻¹ in all cores (enrichment factor of 1–2.2), following a log-linear relationship with the distance from the mines. Surface sediments had slightly elevated Pb concentrations compared to the background in cores S3 and S4 (+4 ± 1 mg kg⁻¹ and +10 ± 0.6 mg kg⁻¹; enrichment factors of 1.9 and 1.3, respectively) but comparable to the background in cores S5 and S8. The Pb concentrations in the sediment were directly correlated to concentrations of other mining-released elements (Sb, Zn and Cu) in all cores except Ruth Lake (Fig. 3b, supplementary material Fig. S3,Pearson coefficients = 0.67–0.90, p < 0.001).

3.4. Pb stable isotopes in sediment and source partitioning

There were clear changes in the isotopic ratios of Pb that



Fig. 3. Lead (a) and antimony (Sb) concentrations in sediment (b), Pb stable isotope ratios (²⁰⁶Pb/²⁰⁷Pb) (c), and modelled mining-derived Pb contribution (two-source model) for each sediment core (d). Note the log10 axis for concentrations in (a) and (b).

accumulated in sediments over time at sites located closer to the mines (Fig. 3c). The timing of isotopic changes was consistent with increases in Pb and Sb concentrations at these sites (Fig. 3) and dated back to the early years of mining operations (1945-1955). Sediment from the nearest sites to the mines had the largest changes in Pb isotope ratios throughout the core profiles. The furthest site from the mines (S8) in the main body of Great Slave Lake recorded limited change in Pb isotope ratios (Fig. 3c). Ruth lake, at the same distance as S8 but disconnected from the main water body, had no change in isotope ratio throughout the core (Fig. 3c). Isotope values closest to mining ore were found in sediment dating between 1955 and 1978. Partitioning the sediment Pb using a two-source mixing model suggested that at its peak, mining pollution represented 92 \pm 8% of all Pb deposited at the study site closest to the Giant Mine roaster (core S1, 6 cm depth, undated) and $8 \pm 4\%$ at the furthest study site (core S8, 17 cm depth, c.a. 1965) (Fig. S6). The estimated contribution of mining-related Pb for sediment deposited prior to the initiation of mining activity was close to but not zero $(2 \pm 2\%)$ due to uncertainties for both sources included in the model (background Pb and mining ore).

Including aerosols as a possible Pb source for recent surface sediment resulted in large uncertainties for the source attribution because of multiple possible solutions for the isotopic mixture. The Bayesian estimations from the three-source model diverged by as much as 85% (positive and negative) from the two-source model estimate for certain samples. The latter model suggested that mining-derived Pb at the sediment-water interface was <5% at all sites except S1 ($30 \pm 16\%$) and S4 ($11 \pm 10\%$). However, when using a three-source model, the spatial relationship between mining-derived Pb in surface sediment and distance to the mines was non-linear (supplementary material).

3.5. Sedimentary Pb fluxes

Background Pb fluxes (pre-1938) in cores S3, S4, S5 and S8 were 5.6 mg m⁻² yr⁻¹, 12.2 mg m⁻² yr⁻¹, 3.5 mg m⁻² yr⁻¹ and 7.4 mg m⁻² yr⁻¹, respectively. Ruth Lake had a lower background flux at 0.6 mg m⁻² yr⁻¹. A trend of increasing Pb flux started between 1940 and 1952 at all locations in Yellowknife Bay (Fig. 4b), concurrent with the opening of Con and Giant mines. Ruth Lake did not show a trend in Pb accumulation rate over time but only the top 5 cm of this core was datable, corresponding to sediment accumulated since *c.a.* 1944. Annual Pb fluxes in Yellowknife Bay reached their

maximum between 1955 and 1978 depending on the location, which is consistent with the rise in Pb concentration and Pb isotope ratios approaching values for mining ore. Sites that were located closer to the mines reached their maximum recorded Pb flux earlier (S3 and S4, 1960 and 1955, respectively) than further sites (S5 and S8, 1970 and 1978, respectively). The maximum recorded Pb flux at each site varied between 0.7 mg m⁻² yr⁻¹ [Ruth] and 63 mg m⁻² yr⁻¹ [S4] (Fig. 4b).

Over the years of operation, fluxes of Pb attributed to gold mining in the Yellowknife Bay area varied between 0 and 47 mg m⁻² yr⁻¹. At the time cores were collected (nine to eleven years after mines closure), surface Pb fluxes were higher than premining fluxes at each site except at Ruth Lake (Fig. 4)b. Higher fluxes were due to the ongoing accumulation of mining-derived Pb within at least 3.5 km of the mine (sites S1 to S4, Fig. 4c) and an increase in background Pb accumulation rate (mainly driven by increasing sedimentation rate) at sites within the main body of Great Slave Lake (Fig. 4d). Lead fluxes attributed to gold mining in the surface sediments were 4.5 and 4.7 mg m⁻² yr⁻¹ at sites S3 and S4, respectively, and approached zero at far-field sites S5 and S8 (0.2 and 0.4 mg m⁻² yr⁻¹, respectively).

3.6. Gold mining Pb contamination footprint over time

Using a linear regression model between the maximum inferred contribution of mining ore Pb and log distance to the Giant mine roaster (supplementary information, Fig. S6), we estimated that mining pollution extended 27 km south of Giant Mine at the time of maximum loading to the bay (18–45 km, 95% confidence interval, $R^2 = 0.96$, p < 0.001). A linear regression of mining ore contribution of Pb in surface sediment against log-distance had an intercept at nine km (5–23 km, 95% confidence interval, $R^2 = 0.92$, p < 0.001), indicating the presence of mining ore in surface sediment within 9 km of the mine more than forty years after the initiation of pollution reduction measures at the mine and ten years after complete mine closure. Mining-derived Pb was below 1.5% throughout the Ruth Lake core, which was not different from premining sediment in the main body of Great Slave Lake.

It took one to six years after the closure of Giant Mine before mining-derived Pb was absent from surface sediment >9 km away from the source (linear regression, 95% CI, supplementary material Fig. S6). Extrapolating the recovery rates since 1958 suggested that mining-derived Pb will be absent of surface sediment 23–56 years



Fig. 4. Sedimentation rate estimates from CRS modelling (a), modelled Pb flux (b), modelled mining-derived Pb flux (two-source model) (c), and modelled background Pb flux (d) against sediment age for five dated sediment cores.

after mine closure at 3.5 km and 46–97 years after mine closure at 1.9 km (95% CI). The distribution of mining ore contribution of Pb against space and time was well described by a Gaussian regression centered around the source and the period of maximum contribution from the mine (ca. 1970) (adj $R^2 = 0.85$; all parameters p < 0.0001, supplementary material Fig. S7). However, this model underestimated the most recent contribution of mining-derived Pb in cores within 3.5 km from the source and predicted a more rapid recovery than the linear regression approach. The Gaussian spline intercept for the absence of mining-derived Pb was 11 years beyond 10 km of the source and 34 years within 3 km of the mine.

4. Discussion

4.1. Sources of Pb to Yellowknife Bay

Background weathering of Pb from bedrock and mining-derived Pb were found to be the dominant sources of Pb to Yellowknife Bay sediments. Several lines of evidence indicated that aerosol inputs were a minor source of Pb to the lake sediment in the study area. First, the lack of change in the Pb isotope composition of sediment from Ruth Lake (a "control" site) and the return of Pb isotope ratios of surface sediment to pre-disturbance values at the far-field sites (cores S5, S7 and S8) indicated that regional aerosol deposition from anthropogenic sources during the mid-to-late twentieth century were not likely significant (Fig. 3c). Second, the enrichment of Sb and metals in addition to Pb at affected sites provided a geochemical signature of mining pollution that is unrelated to inputs from leaded gasoline, aviation fuel (avgas) or Pb contained in long-range aerosols (Fig. 3b and supplementary material). Third, estimates of regional Pb aerosol deposition in northwestern Canada, based on peat and ice cores, are very low at <1.5 mg m⁻² yr⁻¹ (Shotyk et al., 2017 Gross et al., 2012). That magnitude of aerosol deposition represents <5% of the total sediment Pb flux in the cores post-1960. Negligible anthropogenic Pb enrichment from longrange atmospheric transport was observed in lakes of the Canadian high Arctic, which was attributed to low precipitation with increasing latitude (Outridge et al., 2002). Yellowknife has a dry continental climate which could also result in low aerosol deposition. Nevertheless, our three-source mixing model could not adequately resolve the contribution of Pb aerosols, and it is possible that inputs from other anthropogenic sources of Pb (regional or local) may have also had a minor contribution to excess Pb in the surface layers of sediments, which could have influenced our assessment of recovery from mining-derived Pb. However, even the model that included Pb aerosols as a third source estimated that mining-derived Pb was present in surface sediment at nearfield sites S1 and S4.

4.2. *Pb stable isotopes as a tool for the identification of mining pollution in sediment*

The source attribution modelling using Pb isotopes highlights the persistence of Pb pollution within lakes. The presence of mining-derived Pb in surface sediments within 9 km of the source, ten years after the closure of the gold mines, suggests an ongoing input of legacy pollution in the lake. Sources of legacy metal(loid) pollution specific to Yellowknife Bay may include a combination of effluent release from Baker Creek, sediment focusing from tailings dumped in the early years of mining, and/or catchment erosion of mining-derived Pb from the surrounding terrestrial environment. However, our model estimates indicated that higher background Pb fluxes in recent years also contributed to Pb enrichment in surface sediment. Using a Pb concentration gradient alone would have overestimated the pollution contribution by up to 26% (see supplementary material). This information is relevant for assessing the fate of other metal(loid) pollutants emitted from the mines such as arsenic, which does not have multiple stable isotopes and is subject to remobilisation upon change in redox conditions. It should be noted that in this study, metal concentrations from the sediments were determined following an acid-labile digestion method, whereas a total dissolution technique was used to liberate the Pb from sediment for isotopic analysis. The total dissolution method included inert Pb bound within silicate minerals, which would not have been included in the acid-labile measurements of Pb concentrations. Therefore, our measurements of Pb concentration and Pb flux are conservative estimates of mining impact (due to partial digestion). However, we assume that the largest part of Pb in the Giant Mine ore was in sulfide minerals such as galena and various sulfosalts which would have been digested in the partial dissolution method (Jamieson, 2014; Walker et al., 2015). We nevertheless recommend that future investigation of sediment Pb isotopes use a consistent digestion method for both the measurement of Pb isotope ratios and concentrations.

4.3. Evidence for different metal transport processes with distance from the mines

The timing between mining activities and sediment flux records suggest different pathways for the transport of Pb at various locations in Yellowknife Bay. In lakes near a copper smelter in Eastern Canada where Pb pollution was atmospherically deposited, there was a 1-4 year delay between peak emissions and the peak flux in nearby lake sediment (Couillard et al., 2008). A similar short delay between the opening of Giant Mine and increases in sediment metal(loid) concentrations was evident in a smaller lake close to the mine (Thienpont et al., 2016). An onset of Pb accumulation in sediment coeval with the time of Giant Mine opening was only visible at coring sites closer than 3.5 km from the mine, suggesting that the deposition of roaster emissions may have had limited impact on far-field sites. Peak metal(loid) emissions from the Giant Mine roaster occurred around 1950 (Hocking et al., 1978) whereas peak flux in our sediment occurred only in 1970 at 9 km (1968-1971, 95% confidence) and in 1979 at 24 km (1978-1981, 95% confidence). This large delay is likely due to particle focusing rather than direct atmospheric deposition. The mining-derived Pb did not reach the isolated Ruth Lake but a small amount reached an equal distance on the main water body, suggesting that sediment migration transported mining-derived Pb over a longer distance than atmospheric deposition along this southward transect. Mining-derived Pb was deposited at the north end of the bay from atmospheric deposition, solid tailings or effluent flowing down Baker Creek, and a small fraction of this pollution then likely moved slowly southward over time by sediment migration.

4.4. Mining-derived Pb contamination footprint

We measured sediment Pb concentration gradients comparable to those reported for lakes near Canadian gold mines but well below the reported values for sediment in tailing ponds for the same mines (Mudroch et al., 1989; Azcue et al., 1995; Wong et al., 1999). The maximum mining-derived Pb flux reported in this study (63 mg m⁻² yr⁻¹) was comparable to the maximum recorded Pb fluxes from lakes located between 6 and 36 km from copper smelter of the Rouyn-Noranda mining area (27–58 mg m⁻² yr⁻¹) (Couillard et al., 2008; Gallon et al., 2006).

Our estimation of the mining pollution footprint at its peak (~27 km) is consistent with previous investigation of the Giant Mine footprint relying on arsenic concentrations in sediment and soils (Hocking et al., 1978; Kerr, 2006; Palmer et al., 2015; Galloway

et al., 2018). This footprint is site-specific since factors such as stack height and wind speed influence the distance that contaminants are dispersed. As a comparison, the footprint of copper smelters in Rouyn-Noranda, Québec, is 30–40 km (Zdanowicz et al., 2006), but their stacks are taller at 82 m and 116 m compared to now decommissioned roaster stack at Giant Mine (46 m).

4.5. Lake ecosystem recovery from Pb contamination

The recovery trends for mining-derived Pb in sediment differed with distance from the Giant Mine. A decrease in mining-derived Pb flux following the implementation of pollution mitigation measures in the first two decades of operations (e.g., reductions in roaster emissions and tailings management) is evident in the sediment records near Giant Mine. Sites further from the mines had lower recovery rates from Pb pollution, but also a lower impact magnitude. Similarly, closer to the source, the recovery rate gradually decreased, suggesting rates more typical of catchment retention and effluents (e.g., Wong et al., 1999; Ek and Renberg, 2001) than atmospheric deposition (e.g., Renberg et al., 2002).

Abandoned mine sites such as at Yellowknife provide useful data to predict recovery from point-source metal pollution. Our estimation of recovery time for Pb contamination of Yellowknife Bay was 1–97 years after mine closure, depending on the distance from the source, which is slightly lower than the 54-128 years estimated for the recovery from Pb pollution of a lake near a gold mine in Brotherswater, northeast England (Schillereff et al., 2016). Mining activity went on for 250 years in Brotherswater compared to the ~65 years gold mining and ore processing history at Yellowknife. The surface sediment from Yellowknife Bay could have received recent anthropogenic contributions from additional modern point-sources of Pb pollution from the City of Yellowknife, such as from the local aviation industry (which still uses leaded aviation fuel in piston engines) or household wastes. Such new sources of Pb would dampen the recovery rates of Pb in sediment. Comparing paleolimnological data from a greater number of decommissioned mining sites would improve our understanding of the factors involved in Pb pollution recovery (e.g., catchment retention, sediment burial, lateral transport, sediment mixing).

5. Conclusions

This study demonstrated that mining-derived Pb and background Pb were the two main sources of Pb in Yellowknife Bay sediments. Aerosol inputs were a negligible source of Pb to the lake sediment, probably due to low precipitation. Mining-derived Pb was still accumulating at the sediment-water interface in Yellowknife Bay more than ten years after the mine closure and that pollution is predicted be an on-going source of Pb to the sediment for up to a century after mine closure. Remobilisation processes may include a combination of effluent loading from tailings ponds, sediment focusing from tailings dumped directly into the bay in the early years of mining, and erosion of mining-derived Pb retained in catchment soils.

The use of Pb stable isotopes provided insights into the impact of mining pollution that concentration gradient methods could not provide, namely, (1) the distinction between changes in background Pb, mining pollution and aerosol inputs affecting Pb deposition, and (2) a more precise estimation of the distance reached by mining pollution from a point-source at different times during mining operations. Further, Pb stable isotopes were used to quantitatively estimate a timeline for return to baseline condition. At low concentrations, it can be challenging to distinguish changes in pollution Pb flux from natural variability. Concentration factors are a more common and less expensive way of determining metal pollution impact in paleolimnological studies, but our results indicate that using concentration enrichment factors alone would have resulted in an overestimation of the impact of mining pollution at the highest concentrations by not accounting for changes in background Pb contribution over time. This study demonstrates the potential for Pb isotopes to inform the remediation of metal mining pollution. Assessments of sediment recovery from metal mining pollution in a large water body are rare, and natural isotopic tracers have the potential to improve the accuracy of dispersion modeling and recovery prediction through further process research.

CRediT authorship contribution statement

Nicolas Pelletier: Formal analysis, Writing - original draft. John Chételat: Conceptualization, Funding acquisition, Investigation, Writing - review & editing, Supervision. Brian Cousens: Investigation, Writing - review & editing, Supervision. Shuangquang Zhang: Investigation. Dan Stepner: Investigation. Derek C.G. Muir: Investigation, Supervision. Jesse C. Vermaire: Writing - review & editing, Supervision.

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Appendix A. Supplementary data

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