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Multi-trophic level response to extreme metal contamination from gold mining in a subarctic lake

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Giant Mine, located in the city of Yellowknife (Northwest Territories, Canada), is a dramatic example of subarctic legacy contamination from mining activities, with remediation costs projected to exceed $1 billion. Operational between 1948 and 2004, gold extraction at Giant Mine released large quantities of arsenic and metals from the roasting of arsenopyrite ore. We examined the long-term ecological effects of roaster emissions on Pocket Lake, a small lake at the edge of the Giant Mine lease boundary, using a spectrum of palaeoenvironmental approaches. A dated sedimentary profile tracked striking increases (approx. 1700%) in arsenic concentrations coeval with the initiation of Giant Mine operations. Large increases in mercury, antimony and lead also occurred. Synchronous changes in biological indicator assemblages from multiple aquatic trophic levels, in both benthic and pelagic habitats, indicate dramatic ecological responses to extreme metal(loid) contamination. At the peak of contamination, all Cladocera, a keystone group of primary consumers, as well as all planktonic diatoms, were functionally lost from the sediment record. No biological recovery has been inferred, despite the fact that the bulk of metal(loid) emissions occurred more than 50 years ago, and the cessation of all ore-roasting activities in Yellowknife in 1999.

1. Introduction

Anthropogenic metal contamination can be a detrimental and intense stressor on ecosystems. The repercussions are particularly evident in remote northern regions, which often lack other direct contamination sources due to limited population pressures. Historical metal contamination of northern aquatic ecosystems have been recorded globally in relation to mining and smelting activities, including in northern China [1,2], Finland [3,4], Sweden [5], Norway [6], and the Kola Peninsula [7] and Siberia [8] in Russia. In Canada, the legacy of metal(loid) contamination includes numerous examples of the release of arsenic to the environment [9], known to be a metalloid of great concern when elevated in natural systems owing to its toxicity [10].

The primary anthropogenic sources of arsenic to the environment include release from base metal smelting and refining, thermal and power generation (particularly coal combustion) and historic gold mining [9]. Large quantities of arsenic (among other metal(loid)s) were released as emissions and tailings from smelting and refining in Flin Flon, Manitoba [11,12] and Sudbury, Ontario [13]. In Canada, historic gold mining represents one of the major sources of arsenic contamination to the environment because many recoverable gold

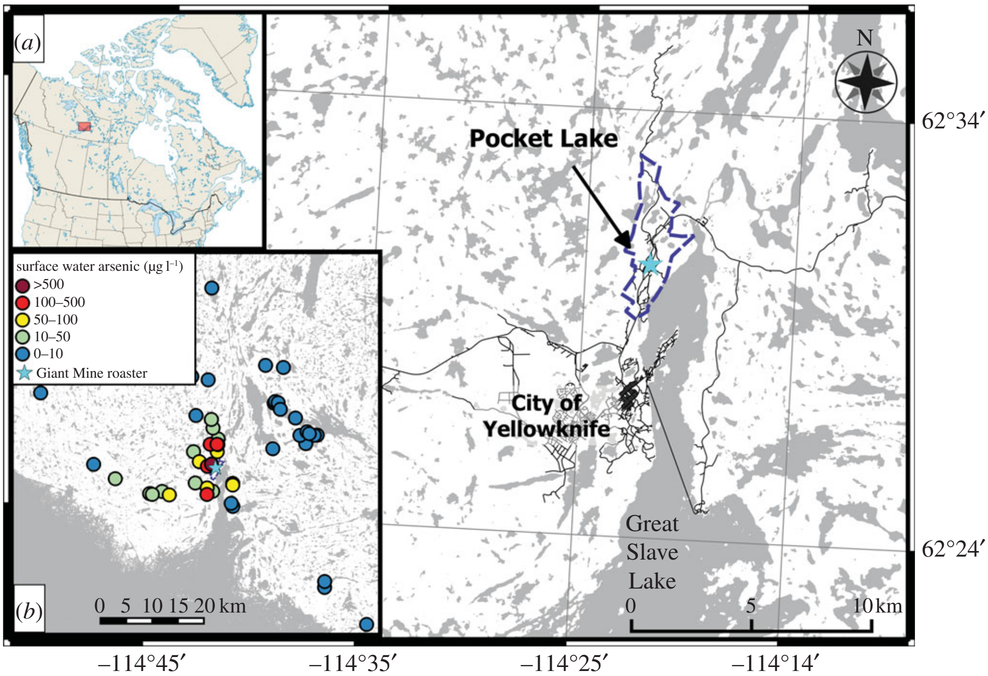

Figure 1. Map of the city of Yellowknife (Northwest Territories, Canada), with the location of Pocket Lake identified, Giant Mine lease area indicated with a dashed line, and the Giant Mine roaster indicated with a star. Inset (*a*) The study location (red transparent box) in the context of Canada. Inset (*b*) Surface water arsenic concentrations ($\mu g\ l^{-1}$) in the region based on 45 samples collected in 2011, 2014 and 2015, showing continued elevation of arsenic concentrations in lake water within approximately 15 km of the Giant Mine emission source.

deposits are found in arsenic bearing sulfide deposits [9]. Elevated arsenic and metal concentrations have been linked to mine drainage and emissions from gold mining in Ontario [14], Nova Scotia [15,16], British Columbia [17] and the Northwest Territories [18,19]. Despite the widespread documentation of arsenic contamination in aquatic environments, relatively little is known about the long-term ecological impacts of arsenic exposure.

In Canada's Northwest Territories, mining and resource extraction are key contributors to overall economic development [20]. The capital city of Yellowknife has a long history of gold mining, with three mines that operated within the city limits between 1938 and 2004: Con Mine (1938–2003) and Negus Mine (1939–1952) in the south and Giant Mine (1948–2004) in the north (figure 1). These mines were the major economic drivers of the region [21], but early operations undertaken prior to effective emissions and waste management controls resulted in substantial contamination to the local environment [22]. In particular, the roasting of arsenopyrite ore to facilitate gold extraction resulted in the creation and emission of large quantities of arsenic trioxide (As_2O_3) as a by-product [23], a form of arsenic known to be the most toxic, water-soluble and bioavailable of solid arsenic compounds [24].

During the early operational history of the Yellowknife gold mines, large amounts of As_2O_3 were released to the surrounding landscapes via roaster stacks, estimated at 7.3 tonnes per day from 1949 to 1951 for Giant Mine alone [22,25]. Most of the atmospheric As_2O_3 emissions were released from Giant Mine, where gold was predominately hosted in the refractory phase, which required roasting of the ore prior to cyanidation. Mitigation practices were ordered following the death of a local Dene boy from acute arsenic poisoning in the spring of 1951 [26]. The first attempts at capturing As_2O_3 occurred with the installation of an electrostatic precipitator in 1951 (emissions decreased to an estimated 5.5 tonnes per day for 1952–1953; [25]), followed by a baghouse in 1958. Emissions from 1959 to 1999 (when roasting ceased) were decreased substantially to approximately 0.01–0.4 tonnes per day [25]. During the full operational history of Giant Mine, an estimated 20 million kg of As_2O_3 were released to the environment [25], and thus the legacy of contamination during the course of the Giant Mine operation is substantial. Increases in arsenic concentrations in sediment core profiles from Yellowknife Bay (Great Slave Lake), adjacent to the Giant Mine lease, have been reported consistent with the opening years of the mine in approximately 1950 [27,28], and arsenic remains elevated in surface waters within approximately 15 km of the mine (figure 1) [18,19].

The remediation of the Giant Mine site, currently being undertaken by the Government of Canada, is expected to exceed one billion dollars [29], making it one of the most expensive mine reclamation projects ever planned in Canada. While most research has focused on quantifying arsenic contamination in surrounding ecosystems, other pollutants, including polycyclic aromatic hydrocarbons (PAHs), associated with roasting activities, and mercury may also be of concern. Mercury amalgamation was used at Giant Mine for gold recovery from 1948 until 1958 [23,30], and elevated PAH concentrations have been recorded as a result of smelting operations in other locations [31,32], though the potential for the roasting of arsenopyrite at Giant Mine as a source of PAHs to the environment has not previously been explored. Owing to the lack of direct monitoring data, the historical inputs of these toxicants and their ecological impacts remain largely unknown. Understanding the magnitude of ecosystem responses and the potential for recovery following metal(loid) and hydrocarbon contamination from mining operations is critical for understanding the impact of historic resource development in sensitive northern ecosystems.

In this study, we address this key knowledge gap by analysing proxy records preserved in a dated lake sediment core to characterize both the legacy of metal(loid) and PAH contamination from gold mining, and the response of aquatic biota to these legacy contaminants at multiple trophic levels in a small, high-closure, headwater lake (Pocket Lake) located approximately 1 km from the Giant Mine roaster stack (figure 1). We used a 'palaeo-ecotoxicological approach', where the sedimentary record of contaminant deposition is directly compared to the timing, magnitude and nature of changes in biological subfossil indicators of interest, including those organisms commonly used as model organisms in ecotoxicology (e.g. *Daphnia*, diatoms and chironomids). We hypothesized that, given the close proximity of Pocket Lake to the point emission source at Giant Mine, significant inputs of metal(loid)s and other toxicants have occurred historically, and resulted in substantial changes in the assemblage of biological organisms known to be sensitive to metal(loid) contamination. Importantly, Pocket Lake is not believed to have ever received inputs of tailings or other mine wastes, and thus any contaminants entering this ecosystem probably did so solely via airborne deposition, either onto the lake surface or onto the small catchment. As such, these findings can be used to place ecological changes in other lakes proximate to Giant Mine, as well as other mining-impacted regions globally, in the context of an ecosystem highly impacted by metal(loid) exposure.

2. Material and methods

Pocket Lake (62°30′32.3″ N, 114°22′25.6″ W) is a small (4.8 ha) headwater lake (sampling depth 2.0 m) located in the southern portion of the Baker Creek watershed (137 km^2), approximately 4 km north of the city of Yellowknife [33,34]. The small (less than 5 ha) catchment of Pocket Lake includes an exposed bedrock upland and a soil-filled valley to the south that drains the exposed outcrop into Pocket Lake. The bedrock upland occupies approximately 78% of the basin, and the valley approximately 22% [33]. Vegetation is absent from the bedrock outcrop, though lichen cover is common. Black spruce (*Picea mariana*) grow at the edge of the valley, where it borders the outcrop. Understory vegetation (especially dwarf willow—*Salix* spp.), mosses, sedges and grasses dominate the soil-filled valley [33]. Prior to the development of Giant Mine, the area around Pocket Lake (including the lower reaches of Baker Creek) was used heavily by members of the Yellowknives Dene First Nation for the collection of berries and traditional medicines (E. Sikyea, F. Sangris and M.-R. Sundberg 2015, personal communication). Permafrost is discontinuous in the region, and generally associated with peat plateaus [33]. The Yellowknife region experiences a subarctic continental climate, with long cold winters and short mild summers. The mean annual air temperature is −4.3°C, with a July mean of 17.0°C and a January mean of −25.6°C (1981–2010 average). Mean annual precipitation is 289 mm, approximately 40% of which falls as snow (Environment Canada, Climate Normals Online).

A single sediment core was obtained from Pocket Lake through the early spring ice (ice thickness 0.9 m) on 28 March 2014, and sectioned at 0.5 cm intervals using a Glew extruder [35]. Water and surficial sediment samples were collected for chemistry analyses at the Taiga Environmental Laboratory (Yellowknife, NT, Canada; electronic supplementary material, table S1). Sediment age determination for the last approximately 150 years was conducted using ^{210}Pb and ^{137}Cs radiometric dating techniques, with radioisotopic activity measured using an Ortec high-purity germanium gamma spectrometer (Oak Ridge, TN, USA) [36]. Certified reference materials obtained from the International Atomic Energy Association (Vienna, Austria) were used for efficiency corrections, and a chronology was developed using ScienTissiME (Barry's Bay, ON, Canada; electronic supplementary material, figure S1). Selected intervals were analysed for total metal(loid) concentrations (SGS Environmental Services, Lakefield, ON, Canada) via inductively coupled plasma–mass spectrometry. SGS is a Canadian Association for Laboratory Accreditation Inc. (CALA) accredited facility, and all metal(loid) data reported here fall under this accreditation.

Biological subfossil indicators were prepared and identified using standard techniques (diatoms [37], cladocerans [38], chironomids and chaoborids [39]). In order to minimize the potential for bias, samples were analysed using a blind method, where the analyst was not aware of which sediment interval was being examined. Estimates of overall primary production were determined using visible reflectance spectroscopy, conducted on a FOSS NIRSystems Model 6500 Rapid Content Analyzer, a technique that estimates both chlorophyll *a* and its degradative products [40]. Total mercury was measured by thermal decomposition with gold trap amalgamation and cold vapour atomic absorption spectrometry using a Nippon Instruments SP-3D mercury analyser with a theoretical detection limit of 0.01 ng g^{-1}, dry weight. Measurement accuracy was estimated by running blanks and calibrated with MESS-3 (certified: 91 ± 9 ng g^{-1}, measured: 113 ± 0.5 ng g^{-1}; National Research Council of Canada) and SRM2704 (certified: 1440 ± 70 ng g^{-1}, measured: 1662 ± 348 ng g^{-1}; National Institute of Standards & Technology (NIST), Gaithersburg, MD, USA) as certified, standard reference materials, every 10 samples. Total organic carbon (TOC) analysis was conducted at the G.G. Hatch Stable Isotope Laboratory (University of Ottawa), and ranged from 31 to 37%.

For PAH analysis, wet sediments were mixed with Hydromatrix™ (Agilent Technologies, Santa Clara, CA, USA) and elemental copper to remove sulfur (US EPA Method 3660B). Samples were also spiked with known concentrations of ^{13}C-labelled PAHs (Cambridge Isotope Laboratories, Tewksbury, MA, USA) prior to extraction. Analytes were extracted using US EPA Method 3540C modified for accelerated solvent extraction. Clean up with US EPA Method 3630C was adapted for use on 6 ml (1 g) Supelclean™ LC-Si solid-phase extraction cartridges and reduced to 1 ml. Method blanks of Hydromatrix™ and replicates ($n = 3$) of SRM1941b (NIST) were extracted following the same procedures. The PAH fraction was spiked with *p*-terphenyl-d14 (Cambridge Isotope Laboratories, Tewksbury, MA, USA) as an internal standard and analysed following methods outlined in [41]. Analytes were recovery corrected using the ^{13}C-labelled PAHs with mean recovery rates ranging from 11 to 198%. The concentrations of PAHs were also calculated per gram organic carbon, but owing to limited variability in TOC, the trends were virtually identical to those per gram dry weight, and as such only the latter were explored further. The detection limits for the 16 EPA priority PAHs are included as supplementary information (electronic supplementary material, table S2).

Linear, indirect ordinations (principal components analysis, PCA) were used to summarize the variation in the independent palaeoenvironmental proxies and facilitate the comparison of the timing of changes. PCA was conducted on square root-transformed assemblages for the biological indicators, and correlation matrices for the metal(loid)s and PAHs using vegan v2.3–0 [42] for the R statistical computing environment. Relative frequency diagrams were generated using Tilia v. 1.7.16.

3. Results and discussion

(a) Historical trends in contaminant deposition to Pocket Lake

Concentrations of metal(loid)s associated with roaster emissions (including arsenic, antimony, lead, iron and mercury)

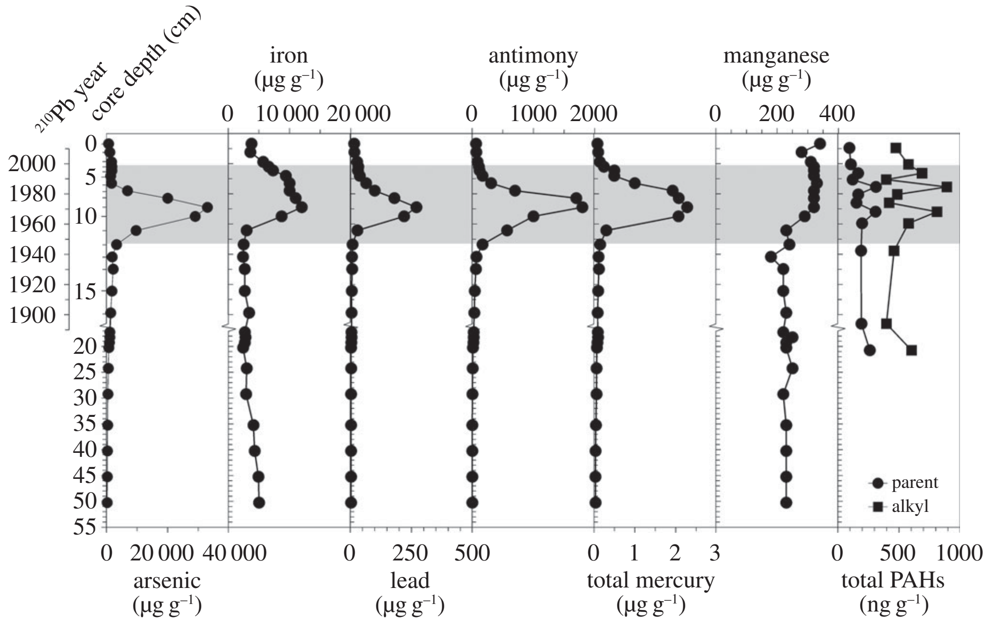

Figure 2. Metal, total parent and alkylated PAH concentrations (all units per gram dry weight) in the sediment core from Pocket Lake, near Yellowknife, Northwest Territories, Canada. The grey box represents the period during which roasting operations were occurring at nearby Giant Mine (1948–1999). ^{210}Pb dates are shown to the left.

exhibited substantial increases from pre-mining background levels in the ^{210}Pb-dated sediment core from Pocket Lake beginning in the early 1950s, exactly at the timing of the onset of operations at Giant Mine, when roaster emissions were vented freely to the atmosphere (figure 2). Of particular note, total arsenic increased approximately 1700% to greater than 30 000 $\mu g\ g^{-1}$ (i.e. more than 3% arsenic by dry weight), and total mercury increased approximately 2000% to greater than 2.0 $\mu g\ g^{-1}$, in comparison to concentrations in the sediments deposited prior to the onset of mining activities (figure 2). Daily arsenic (and other metal(loid)) emissions at Giant Mine peaked in the late 1940s and early 1950s, after which the implementation of emission abatement measures (e.g. the installation of a baghouse in 1958) drastically reduced roaster emissions [25]. By contrast, arsenic and metal concentrations in the sediment core from Pocket Lake peaked later, in approximately 1970, after which concentrations declined and returned to pre-impact conditions. Sedimentary arsenic profiles from Yellowknife Bay, an embayment of Great Slave Lake at Yellowknife, more closely followed the emission history of Giant Mine, exhibiting increases in arsenic concentrations consistent with the initiation of mining operations at Giant Mine and peaking in approximately 1960 [27,28]. There are two competing hypotheses to explain the delayed peak in metal(loid)s in Pocket Lake: (i) post-depositional remobilization of metal(loid)s in the sediments interfere with the use of the sediment core from Pocket Lake as a historical archive of Giant Mine emissions; and (ii) the delayed peak in metal(loid) concentrations in Pocket Lake is related to retention in the catchment, providing a source of continued influx of metal (loid)s into Pocket Lake after atmospheric emission reductions.

Both arsenic and antimony are known to undergo complex post-depositional sedimentary processes, including remobilization, changes in speciation and the formation of new As/Sb-oxide, As/Sb-sulfide and Fe–Mn oxide compounds, with pH, flow velocity, the presence of vegetation, and redox conditions as important controls on these processes [43–45]. Enhanced fixation of arsenic in the sediments has been linked to adsorption onto iron oxide compounds (known to have been produced by roasting at Giant Mine [46]), with decreased leaching to the water column exhibited when arsenic and iron co-precipitate [44,47]. Sediment records from nearby Yellowknife Bay, while recording a distinct peak in arsenic associated with the height of mining operations, also exhibit surficial enrichment attributed to post-depositional remobilization via reductive dissolution and re-precipitation in the oxic layer near the sediment–water interface [28]. In Pocket Lake, sedimentary arsenic concentrations slightly downcore to the timing of the onset of mining in 1948 are somewhat elevated compared to those below a core depth of 24 cm, suggesting some downward migration may occur; however, we observe no surficial enrichment of arsenic. Instead, the total arsenic and antimony trends are consistent with those of lead and mercury, which are not known to undergo substantial post-depositional mobility in lake sediments [48,49]. This similarity strongly suggests that sedimentary trends in arsenic and antimony are primarily a reflection of historic inputs of these metal(loid)s into Pocket Lake. Collectively, the evidence summarized above does not support a hypothesis that the delayed metal(loid)s peak in Pocket Lake is being driven by post-depositional sedimentary processes.

During the period of high emissions from Giant Mine in the first decade of its operations, large quantities of metal(loid)s would have accumulated in catchment soils in close proximity to the mine. Previous studies have shown that outcrop soils (such as those found in the catchment of Pocket Lake) contain high concentrations of legacy arsenic (56–5760 ppm, average 1546 ppm), and that the bulk of roaster-derived arsenic found in outcrop soils near Giant Mine was deposited over 45 years ago [25,50]. It has also been suggested that the solubility of As_2O_3 generated at Giant Mine, and now present in local soils, is lower than expected and may be owing to antimony impurities [50]. Presently in the Yellowknife region, the highest arsenic concentrations are recorded in small, high-closure lakes like Pocket Lake [19], and we expected that Pocket Lake would exhibit delayed chemical recovery compared with Yellowknife Bay (Great Slave Lake), which drains a larger catchment, and where hydrological and sedimentary inputs from the Yellowknife River would more quickly dilute legacy metal(loid)s.

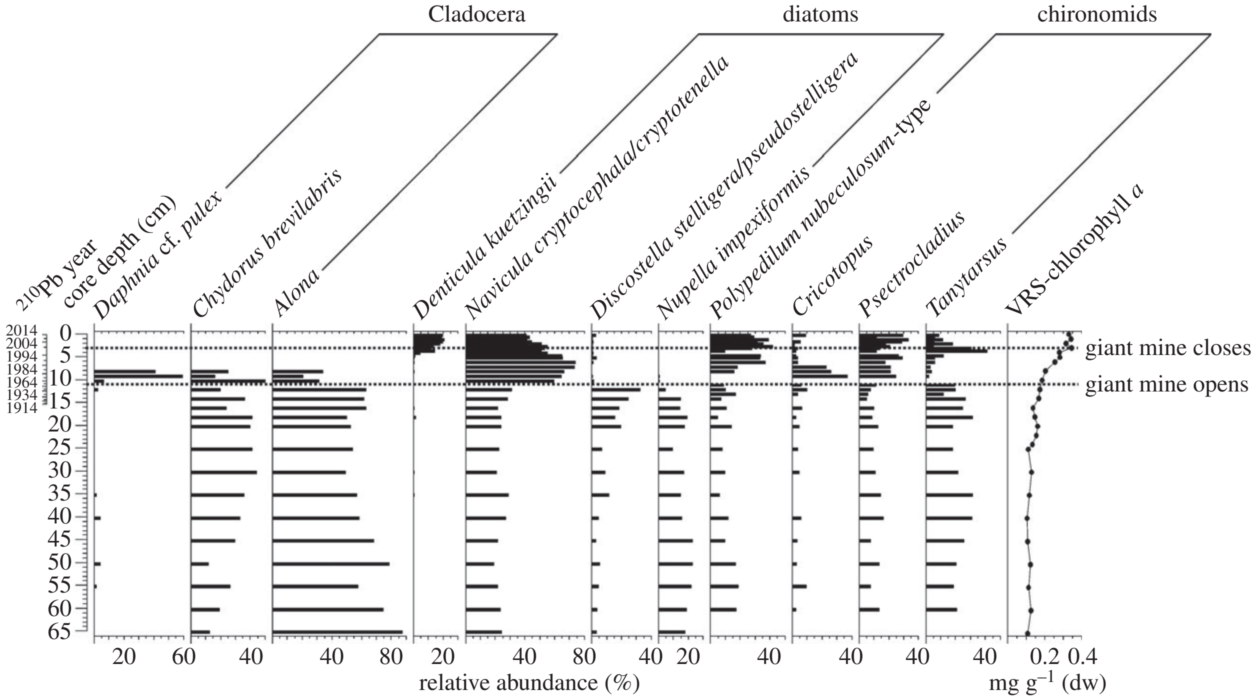

Figure 3. Summary diagram of the most common subfossil cladoceran, diatom and chironomid indicator taxa (relative abundances as %) from Pocket Lake, near Yellowknife, Northwest Territories, Canada. Overall lake primary production (chlorophyll *a*) is inferred using visible reflectance spectroscopy (VRS; mg g^{-1}, dry weight). The period of roasting operations at Giant Mine is indicated by dashed lines.

Delayed peaks following emission reductions have also been reported in lake sediment cores from other mining regions in Canada, including copper and zinc mining in Flin Flon, Manitoba [51] and nickel mining in Sudbury, Ontario [52]. In Sudbury, legacy concentrations of metals in terrestrial soils have been shown to delay recovery up to several decades after emission reductions, and even increase aquatic metal concentrations in some cases during drought [52,53]. Like Pocket Lake, it is the small, shallow, perched, closed-basin Sudbury lakes that exhibited the most delayed response to emission reductions [52]. Therefore, we conclude that the catchment was a critical source of metal(loid)s to Pocket Lake for more than a decade following the installation of the baghouse and decrease in roaster emissions at Giant Mine.

To date, investigations into legacy contaminants in the environment near Giant Mine have focused exclusively on metal(loid)s, but roaster emissions may also be an important source of PAHs [31,32]. PAHs represent a diverse group of organic contaminants formed during the combustion of biomass, either at high temperatures (pyrogenic), or at low temperatures over long geological timespans (petrogenic—naturally occurring in petroleum products). Although PAHs can be produced during natural processes (e.g. during forest fires), human activities are dramatically increasing the environmental burdens of these contaminants globally [54]. Because PAHs can be toxic [55], it is important to assess whether roaster emissions from Giant Mine also released PAHs to the surrounding environment, in addition to arsenic and other metal(loid)s. We observed increases in the total concentration of alkylated PAHs after the onset of mining operations at Giant Mine, though unlike the metal(loid)s, the magnitude of the increase was subtle (figure 2). Diagnostic ratios of select PAH compounds commonly used to identify the sources of complex PAH mixtures in the environment [56] indicate a greater contribution from petroleum combustion sources since the mid-twentieth century (electronic supplementary material, figure S2). This shift in PAH source could potentially be related to the roasting of ore deposits at nearby Giant Mine, and/or the urbanization of the city of Yellowknife occurring at the same time. However, the observed decrease in PAH concentrations (figure 2), coinciding with decreases in sedimentary metal (loid)s, suggest that roasting operations were the dominant anthropogenic source of PAHs to Pocket Lake, not urban development, which accelerated throughout the twentieth century. Metal(loid)s remain the primary group of contaminants of ecotoxicological concern related to Giant Mine emissions.

(b) Ecological impacts of metal contamination at multiple trophic levels

We examined the ecological impacts of metal(loid) exposure in three different groups of aquatic biota (diatoms (algae), Cladocera (zooplankton), Chironomidae and Chaoboridae (macroinvertebrates)) at different trophic levels by analysing subfossil remains preserved in the sedimentary record of Pocket Lake. Striking changes in all three groups of biological indicators were observed coincident with the opening of the mine in 1948 and the corresponding metal(loid) loading that followed (figures 3 and 4).

Following the opening of Giant Mine and the rapid increase in arsenic and other metal(loid)s, the epiphytic diatom taxon *Nupella impexiformis* and planktonic diatom species *Discostella stelligera/pseudostelligera* were rapidly lost from the assemblage. These taxa are known to be sensitive to mining-induced contamination [57,58]. The loss of *Discostella stelligera/pseudostelligera* is particularly notable, as these taxa had been increasing in abundance prior to around 1948 (figure 3). An overall decrease in planktonic taxa following metal contamination has been documented previously in other metal-contaminated lakes [58–60]. Plankters may be more susceptible to metal contamination, while benthic taxa may gain some protection from exposure in thick biofilms,

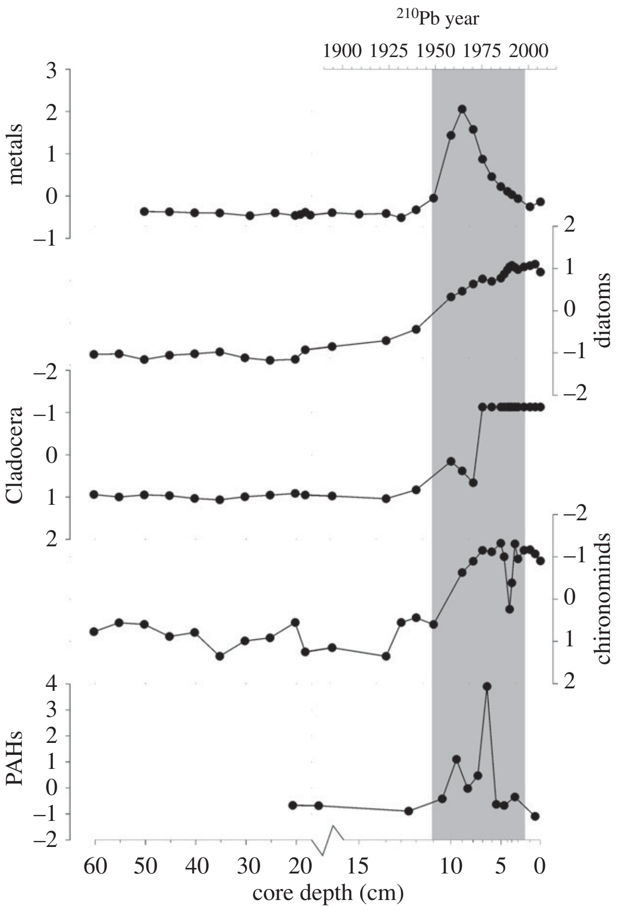

Figure 4. PCA axis one site scores for the five independent palaeoenvironmental indicators from Pocket Lake, near Yellowknife, Northwest Territories, Canada. The grey box corresponds to the period of roasting operations at Giant Mine (1948–1999). The proportion of variation explained by the first PCA axis for each indicator was: metals, 0.81; diatoms, 0.58; cladocerans, 0.66; chironomids, 0.35; PAHs, 0.37.

as algae and bacteria present in the benthic matrix may act to bind or detoxify toxicants [61,62]. In Pocket Lake, an increase in *Navicula cryptocephala* and *Navicula cryptotenella* occurred following the opening of Giant Mine, with the relative abundances of these taxa clearly following the trajectory of metal(loid)s in the sediments. *Navicula cryptocephala* was shown to be the dominant diatom taxon in both periphytic and planktonic samples in a lake that received tailings from a lead–zinc–copper mine in British Columbia, Canada [63], and thus it appears this taxon is tolerant of high metal concentrations. *Achnanthidium minutissimum*, another taxon previously reported as tolerant of high levels of metals [58,59], though not previously associated with high arsenic concentrations, increased in abundance coincident with metal(loid) contamination (electronic supplementary material, figure S4). While diatom teratogeny has been associated with metal contamination from mining in previous studies [57,60], no teratological forms were observed in Pocket Lake. Despite the major change in the diatom assemblages, which we infer to be closely linked to metal(loid) contamination, overall primary production (as measured by sedimentary chlorophyll *a* and its diagenetic products) was not related to the history of mining impacts (figure 3). Whether or not more metal(loid)-tolerant algal groups, such as green algae and/or cyanobacteria [64], replaced planktonic diatoms in the algal community of Pocket Lake is an important avenue for future research.

The Cladocera are a keystone group of primary consumers occupying both pelagic and benthic habitats and are an important component of the zooplankton community in lakes. In Pocket Lake, the cladoceran assemblage exhibited a shift from dominance by benthic taxa, including *Alona* spp. and *Chydorus brevilabris*, to the pelagic *Daphnia* cf. *pulex* complex immediately following the onset of metal(loid) contamination in Pocket Lake (figure 3; electronic supplementary material, figure S3). *Daphnia* are commonly used as model organisms in ecotoxicological studies [65], with some taxa known to be relatively tolerant of aqueous arsenic concentrations above 1–1.5 mg l^{-1} [66]. The cladoceran assemblage shift to arsenic-tolerant *Daphnia* as arsenic was increasing in the ecosystem suggests that the resident zooplankton taxa in the pre-mining era probably included organisms that are comparatively more sensitive to arsenic, such as copepods [67], which do not leave identifiable subfossil remains. *Daphnia* would have had a competitive advantage in a arsenic-contaminated environment, allowing them to exploit a newly available niche as resident zooplankton are out-competed. Coincident with the peak in sedimentary metal(loid)s and extreme arsenic contamination in the mid-1970s, *Daphnia* and other cladoceran remains were no longer recovered in the sediments of Pocket Lake, suggesting that Cladocera were functionally lost from this ecosystem and have not recovered. Dramatic, negative effects of arsenic contamination on Cladocera have also been observed in China [68] and Flin Flon, Manitoba [69].

Larval stages of the phantom midge genus *Chaoborus* are an important predator on *Daphnia* that also leave identifiable remains (mandibles) preserved in lake sediments. In Pocket Lake, *Chaoborus* mandibles were recovered in low abundances (less than 10 per interval) throughout the sediment core, including both the pre-, peak and post-mining periods, and no notable changes in biomass or productivity of these macroinvertebrate predators on *Daphnia* can be inferred in response to metal(loid) contamination. Furthermore, the large-bodied species *Chaoborus americanus* and *Chaoborus trivattatus* were recovered throughout, suggesting Pocket Lake has probably always been fishless, as *C. americanus* is a well-known indicator of fishless (or very low planktivorous fish) conditions, and *C. trivattatus*, which often coexists with *C. americanus*, generally dominates in lakes with minimal fish community [70]. The recovery of remains of these taxa at low, but consistent, abundances throughout the sediment core suggests that Pocket Lake has not undergone changes in fish community, and has most probably been fishless over the recent past, including the period of intense contamination from mining operations. As planktivorous fishes represent another important predator on *Daphnia*, the down-core trends we report for *Chaoborus* allow us to exclude with some confidence the potential influence of changes in predator abundance/composition as a primary driver of historical *Daphnia* trends in Pocket Lake. The identification of *Chaoborus* remains throughout the sediment record in Pocket Lake shows they were able to tolerate the metal(loid) exposure following contamination, including obtaining sufficient food despite the collapse of the cladoceran community, which would have probably represented an important food source. Future sampling should focus on characterizing the modern zooplankton and microinvertebrate communities of Pocket Lake.

Chironomids, an important group of benthic organisms in most freshwater ecosystems, are considered to be generally tolerant of metal(loid)s such as arsenic, lead and zinc [71]. Nonetheless, the chironomid assemblage in Pocket Lake also exhibited changes coincident with the timing of the onset of mining operations and contamination (figure 3; electronic supplementary material, figure S5). Immediately following the onset of mining operations, a decrease in *Tanytarsus* and a marked increase in *Cricotopus* and *Psectrocladius* were observed. After around 1970, decreased abundances of *Cricotopus* strongly tracked decreasing sedimentary metal concentrations, though *Psectrocladius* abundance did not change. Species of *Cricotopus* have been shown to be highly tolerant of metals and a useful indicator of contamination [72]. After the decrease in metal(loid)s, *Polypedilum nubeculosum*-type increased in abundance. A similar trend of decreasing abundance of species of the tribe Tanytarsini and increases in Chironomini have been observed in lakes receiving metal-rich effluent from mining operations in northern Siberia [7] and Manitoba, Canada [69]. Arsenic exposure has been shown to lead to chironomid mouthpart deformities [73], but similar to teratalogical diatom forms, none were observed in the subfossils from Pocket Lake.

Despite more than 50 years since the onset of arsenic emission reductions at Giant Mine, and more than a decade since the cessation of all gold processing activities in the Yellowknife area, we did not observe any evidence of recovery in the diatoms or Cladocera. Although the sedimentary profile of arsenic in Pocket Lake showed a return towards pre-impact concentrations, the water and surface sediments of Pocket Lake continue to exhibit remarkably high levels of arsenic (As_{aq}: 2070 $\mu g\,l^{-1}$; total $As_{sediment}$: 806 $\mu g\,g^{-1}$; electronic supplementary material, table S1). These concentrations are well above both the probable effects level for toxicity set out in the Canadian sediment quality guideline (17 $\mu g\,g^{-1}$; [74]) and the federal drinking water quality guideline (10.0 $\mu g\,l^{-1}$; [75]). Therefore, concentrations of legacy metal(loid)s from gold mining in Pocket Lake may still be too toxic to support biological recovery.

Similarly, elevated surface water total arsenic has been observed in small lakes within approximately 15 km of Giant Mine (figure 1) [19], indicating the potential for our observations of ecological change at multiple trophic levels in Pocket Lake to be applicable to a wider range of freshwater ecosystems in the proximity of Giant Mine. Several small lakes located west–northwest of Giant Mine, downwind of the prevailing wind direction, currently have arsenic concentrations more than 100 $\mu g\,l^{-1}$, and even up to 650 $\mu g\,l^{-1}$ in one instance, while arsenic concentrations in lakes more than 15 km from Giant Mine are typically below 10 $\mu g\,l^{-1}$ [18,19]. We expect, however, that given its close proximity to Giant Mine, Pocket Lake is among the most heavily impacted lakes in the region that has not received direct mine waste inputs, such as tailings. Although zooplankton communities in other arsenic-contaminated Yellowknife lakes have almost certainly undergone ecological changes related to legacy effects from mining activities, it is unlikely that *all* cladocerans were eliminated from other contaminated lakes in the region. For example, *Daphnia* are still abundant in Kam Lake, which was historically contaminated with arsenic from Con Mine [76]. Because several larger lakes in the area are used for fishing and recreational activities, including by the local First Nations community, studies such as this one are critical for understanding the potential consequences of legacy contaminants from mining for both ecosystem and human health.

4. Conclusion

We document extensive ecological effects at multiple trophic levels in response to extreme arsenic contamination (and other metals) at the precise time of the onset of gold mining operations at Giant Mine in 1948. The peak concentrations of arsenic observed in the sediments of Pocket Lake represent, to our knowledge, the highest reported in the sediments of non-tailings lakes that are impacted solely by anthropogenic emissions. The Cladocera and planktonic diatoms were the most heavily impacted of the biological organisms examined in this study, but even chironomids, which are relatively tolerant of pollution, exhibited shifts in species assemblage consistent with metal contamination. At the height of metal loading, all Cladocera were lost from the sediment record, and thus we conclude that this keystone group of primary consumers was functionally extirpated from Pocket Lake. The magnitude of impact at the study site was large enough that, despite decreased concentrations of heavy metals in the sediment record, biological assemblages have exhibited little to no recovery.

Data accessibility. Data associated with this manuscript are available through the NWT Discovery Portal http://sdw.enr.gov.nt.ca/nwtdp_upload/PocketLake_Core01Apr2014_Data.zip.

Authors' contributions. J.R.T., J.B.K., M.J.P., J.P.S. and J.M.B. conceived of and designed the study; J.R.T., J.B.K. and D.C.E. collected field samples; J.R.T., J.B.K., K.E.H., T.W., D.C.E. and L.E.K. carried out the analyses; J.R.T. and J.B.K. analysed the data, J.R.T. and J.B.K. drafted the initial manuscript and wrote the paper along with K.E.H., D.C.E., M.J.P., J.P.S. and J.M.B. All authors commented on the manuscript and gave final approval for publication.

Competing interests. We declare we have no competing interests.

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