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Regional changes in Cladocera (Branchiopoda, Crustacea) assemblages in subarctic (Yellowknife, Northwest Territories, Canada) lakes impacted by historic gold mining activities

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Abstract In Yellowknife (Northwest Territories, Canada), roaster stack emissions from historic gold activities, particularly Giant mining Mine (1948-2004), have left a legacy of arsenic contamination in lakes. We examined Cladocera (Branchiopoda, Crustacea) subfossil remains in the recent and pre-industrial sediments of 23 lakes (arsenic gradient of 1.5-750 µg/l) within a 40 km radius of Giant Mine to provide a snapshot of regional change in Cladocera since pre-1850. We found that littoral and benthic taxa dominated the recent assemblages in high-[As] lakes (surface water [As] > 100 μ g/l), while pelagic Bosmina was dominant in lakes with lower [As]. Cladocera richness and diversity were positively correlated with [As] (P = 0.004, $R^2 = 0.39$; and P = 0.002, $R^2 = 0.46$, respectively), except for four lakes with $[As] > 100 \mu g/l$. The lakes that

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B. Sivarajah · J. P. Smol Paleoecological Environmental Assessment and Research Lab (PEARL), Department of Biology, Queen's University, Kingston, ON K7L 3N6, Canada showed the most pronounced changes in Cladocera since pre-1850 were those affected by both metal(loid) pollution and urban development, where complete shifts in the dominant taxa occurred. Lakes that were most heavily impacted by arsenic emissions did not experience notable shifts in Cladocera assemblages. Our study suggests that changes in Cladocera assemblages in mining-impacted subarctic lakes are modulated by local, lake-specific limnological conditions and the interaction of multiple stressors.

Keywords Arsenic · Limnology · Paleoecotoxicology · Zooplankton · Legacy contaminants · Arctic

Introduction

Cladocera are a superorder of small crustaceans (Class Branchiopoda) that are useful bioindicators of metal contamination, owing to their rapid responses to changing environmental conditions (Leppänen, 2018; Pociecha et al., 2019). Many cladoceran taxa are considered to be keystone species, and impacts to their communities have the potential to cascade through the aquatic food web (Wetzel, 2001). Furthermore, Cladocera leave identifiable subfossil remains (primarily post abdominal claws, headshields, antennules and carapaces) composed of chemically inert chitin that preserve in lake sediments over centuries to millennia (Korhola & Rautio, 2001). Cladocera are therefore useful paleoecological indicators to track aquatic ecosystem changes over timescales not otherwise feasible through contemporary sampling. Importantly, in mining regions where pre-impact ecological data are limited or unavailable, Cladocera subfossil remains provide an opportunity to assess the environmental impacts of mining on nearby aquatic ecosystems within a temporal context that includes an assessment of natural variability and baseline conditions (Saulnier-Talbot, 2016).

The response of Cladocera to metal pollution has been documented in paleolimnological studies globally. In the Canadian province of Québec, increases in the concentrations of iron, aluminium, copper, cobalt and nickel from wastewater inputs, and atmospheric deposition from local mining operations resulted in a decrease in Cladocera species diversity and richness (Winegardner et al., 2017). In southern Poland, Pociecha et al. (2019) found that sediment records from subsidence ponds downstream of mine discharge exhibited a negative correlation between copper concentration and the occurrence of the cladoceran taxa Alona (Baird, 1850), Alonella (G. O. Sars, 1862), Daphnia (O. F. Müller, 1785) and Graptoleberis (G. O. Sars, 1862). In addition, the subsidence ponds showed a negative correlation between sedimentary zinc and lead concentrations and the abundance of Alona species (Pociecha et al., 2019). Cladocera-based paleolimnological studies have also documented biological recovery from mining-associated metal pollution. In northwest Russia, Daphnia and Leptodora kindtii (Focke, 1844) were extirpated in Lake Imandra due in part to nickel and copper pollution; however, decreases in anthropogenic stressors in the region, and the introduction of stricter pollution control measures, led to the recolonization and recovery of these taxa (Moiseenko et al., 2009).

The long-term sensitivity of cladocerans to arsenic pollution has received less attention compared to copper, aluminum, cadmium, nickel and zinc pollution. Arsenic is a naturally occurring element in the environment that in some cases is a significant stressor on water quality from widespread urbanization and industrialization (Smedley & Kinniburgh, 2002). *Daphnia*, one of the most commonly used model organisms in ecotoxicology, are relatively tolerant of high arsenic, but can still experience high mortality in highly contaminated waters (Suhendrayatna et al., 1999; Okamoto et al., 2015). The smaller pelagic taxon, *Bosmina* (Baird, 1845), may be more sensitive than *Daphnia* to arsenic pollution (Passino & Novak, 1984), but despite this possibility, *Daphnia* are more commonly used in arsenic toxicity studies while *Bosmina* are rarely used in lab toxicity bioassays.

Paleolimnological studies of highly arsenic-contaminated lakes support the findings documented in lab bioassays on Daphnia and Bosmina. In two arsenic-contaminated lakes in China, a > 10-fold decline in the abundance of Daphnia and Bosmina subfossil remains occurred concurrent with an increase in sediment arsenic concentrations (Chen et al., 2015). Sedimentary arsenic peaked at 479 and 949 µg/g dry weight, compared to pre-industrial baseline levels of $34.4 \pm 5.1 \ (\pm 1 \text{ SD}) \ \mu\text{g/g}$ and $44.2 \pm 7.1 \ (\pm 1 \text{ SD}) \ \mu g/g \ dry \ weight, respectively$ (Chen et al., 2015). The reductions in daphniid and bosminid abundances occurred despite increases in nutrient concentrations that would otherwise be expected to increase cladoceran abundances (Chen et al., 2015).

In the subarctic City of Yellowknife (Northwest Territories, Canada), historic gold mining has resulted in substantial long-term contamination of freshwater ecosystems by arsenic and other metal(loid)s (Palmer et al., 2015). Several lakes within a ~ 15 km radius of Giant Mine (the largest gold mine in Yellowknife) currently have arsenic concentrations exceeding the 10 µg/l maximum acceptable concentration (MAC) for arsenic in drinking water established by Health Canada (Health Canada, 2017), and the Canadian Council of Ministers of the Environment (CCME) water quality guideline of 5.0 µg As/l (CCME, 1999). Analysis of fish tissues showed that burbot [Lota lota (Linnaeus, 1758)] and lake whitefish [Coregonus clupeaformis (Mitchill, 1818)] in lakes near Giant Mine (the source of arsenic trioxide emissions) had comparatively higher total arsenic concentrations than their counterparts 25 km away (Cott et al., 2016). The dominant species of arsenic in fishes collected from Yellowknife was arsenobetaine, a nontoxic arsenic compound, with toxic inorganic arsenic only accounting for 20% of the total arsenic (Tanamal et al., 2020). No evidence of enhanced arsenic bioaccumulation was apparent for slow growing, long-lived fish species (Chételat et al., 2019).

Sediment core reconstructions of the history of arsenic contamination of Yellowknife lakes showed that post-mining sediment enrichment of arsenic, antimony, and lead was highest in lakes closer to Giant Mine, and decreased with increasing distance from the roaster stack (Cheney et al., 2020). Paleotoxicity modelling based on dated sediment core intervals deposited at different periods in the history of the mine found that the predicted toxicity to aquatic organisms was highest during the height of mining, and decreased following the cessation of roasting, suggesting some potential for biological recovery for sediment-associated taxa (Cheney et al., 2020). For some lakes, however, legacy metal(loid) contamination of lake sediments may continue to have ecosystem effects, as arsenic concentrations exceed the CCME interim sediment quality guidelines (ISQG) (Cheney et al., 2020). Elevated pre-mining concentrations of arsenic have been noted in some lakes, indicating naturally elevated geogenic arsenic in Yellowknife lakes (Galloway et al., 2012; Cheney et al., 2020). Paleotoxicity modelling based on sediment arsenic concentrations suggested that some lakes may have been naturally above the biological effects probable threshold, defined as a mean paleotoxicity quotient of > 2.0 (Cheney et al., 2020).

Thienpont et al. (2016) examined the long-term biological effects of arsenic on lake biota in a paleolimnological study of Pocket Lake, located within a 1 km radius of the Giant Mine roaster stack. This study showed that despite the naturally elevated arsenic concentrations, the biological assemblages were stable prior to mining. However, a striking ecological shift from epiphytic and benthic taxa like Alona to pelagic Daphnia occurred following the onset of mining (Thienpont et al., 2016), supporting lab toxicity studies that indicate Daphnia are relatively tolerant of arsenic (Passino & Novak, 1984; Suhendrayatna et al., 1999). At the peak of arsenic emissions, when arsenic concentrations in the Pocket Lake sediments reached greater than 30,000 µg/g (more than 3% arsenic by dry weight), all Cladocera (including Daphnia) were functionally extirpated with no evidence of recovery since emissions were reduced in 1951 and mining operations ceased in 2004 (Thienpont et al., 2016). Similarly, planktonic diatom (siliceous algae) taxa disappeared from the sediment assemblage at the height of arsenic contamination and have not recovered (Thienpont et al., 2016).

In addition to mining contamination, Yellowknifearea lakes have also been influenced by climate

warming and municipal development. An examination of subfossil diatom assemblages in the surface sediments of thirty-three Yellowknife lakes spanning a gradient of arsenic concentrations found that diatom assemblages were primarily influenced by nutrients and ionic compounds while mining-related variables played a limited role in explaining the variation in species assemblages, richness, and diversity (Sivarajah et al., 2019). The combined stressors of urbanization, eutrophication, and climate warming are also related to shifts in subfossil diatom assemblages in paleolimnological studies of Yellowknife lakes (Sivarajah et al., 2020). In Niven Lake, a Yellowknife lake that received raw sewage inputs from 1948 to 1981, recent climate warming has exacerbated water quality issues associated with eutrophication (Stewart et al., 2018). Climate warming and eutrophication stressors are modulating factors that can influence arsenic cycling and toxicity in the environment. For example, mid-winter anoxia during freeze over contributes to the mobilization of arsenic in Yellowknife lakes, while during warmer periods, evapo-concentration of arsenic occurs (Palmer et al., 2019). Additionally, nutrient loading, especially phosphorous, has been reported in Yellowknife (Mackenzie Valley Land and Water Board, 2015), which can have a significant influence on arsenic toxicity (Awoyemi et al., 2020). Clearly, multiple stressors complicate efforts to understand the ecological legacy of arsenic pollution from historic gold mining activities on Yellowknife lakes.

The purpose of this study is to investigate the potential of subfossil Cladocera assemblages as bioindicators of arsenic pollution in Yellowknife lakes in a multi-stressor framework, expanding on the findings from Pocket Lake (Thienpont et al., 2016) to include lakes along a gradient of impact from mining activities. We used a "top-bottom" paleolimnological approach (Smol, 2008) to provide a snapshot of present-day (surface or "top" sediments) and preindustrial (sediment interval representative of the preindustrial period, ca. 1850, or "bottom" sediments) cladoceran assemblages in twenty-three Yellowknifearea lakes. The primary objectives of our study were to: (1) reconstruct regional changes in cladoceran assemblages since pre-industrial times; and (2) identify cladoceran taxa that appear to be sensitive or tolerant of arsenic, which can be explored as candidate ecological indicators of arsenic pollution in future

research. This study provides insights into ecological change in Yellowknife lakes influenced by historic gold mining, urban development, and climate warming, as well as the use of Cladocera as paleoecotoxicological indicators of arsenic contamination in freshwater ecosystems.

Methods

Study Site Description

The City of Yellowknife is located on the northern shore of Great Slave Lake (Fig. 1). It is the capital of the Northwest Territories (Canada), and has a population of 18,884 people (Statistics Canada, 2017). Yellowknife, and the surrounding area, is underlain by the Slave Structural Province of the Canadian Shield, and located within the Great Slave Uplands and Lowlands of Taiga Shield High Boreal ecoregions (Ecosystem Classification Group, 2008). The regional landscape is dominated by exposed bedrock plains, hilly bedrock uplands, and an abundance of lakes and streams (Ecosystem Classification Group, 2008). Vegetation is characterized by lichen woodlands and moss forests, which are comprised primarily of black spruce [Picea mariana (Mill.) Britton, Sterns & Poggenburg], white spruce [Picea glauca (Moench)] Voss], lichen on exposed bedrock, paper birch (Betula papyrifera Marshall), trembling aspen (Populus tremuloides Michx), and jack pine (Pinus banksiana Lambert). Variable-textured Brunisols, Organic Cryosols, Organic, and Gleysols are the dominant soil types in the region (Ecosystem Classification Group, 2008). Climate in the region is subarctic continental, and the permafrost is discontinuous (Wolfe, 1998). Mean annual temperature is - 4.38°C and mean annual precipitation is 289 mm, based on meteorological data



Fig. 1 Map of the study region (Yellowknife, Northwest Territories, Canada) showing the locations of the 23 study lakes and their present-day arsenic concentrations. The locations of Giant Mine (north of Yellowknife) and Con Mine (south of Yellowknife) are indicated by the black and brown pentagons,

and their respective footprints are shown. The shapes of the symbols for the study lakes represent the surface water arsenic concentrations. Inset map shows the study location in the context of Canada

recorded by Yellowknife Airport averaged over the period of 1981 to 2010 (Environment and Climate Change Canada, 2019). The Yellowknives Dene (Willideh) First Nation have a long history of habitation and traditional subsistence use of the land and surface water resources in the north Great Slave Lake region (Sandlos & Keeling, 2016).

Mining in Yellowknife began in 1938, with Giant Mine (1948–2004) being one of the most productive large-scale mines established since this period (Hutchinson et al., 1982). The gold deposits of Giant Mine were hosted in arsenopyrite ores (FeAsS), necessitating an extraction process that separated the gold and arsenopyrite through the oxidation of arsenic and sulphur, which was accomplished using roasters (Hutchinson et al., 1982; Canam, 2006). This process resulted in the production of arsenic trioxide (As₂O₃) dust, a highly toxic, bioavailable and water-soluble arsenic compound (Liu et al., 2008), which was freevented (unregulated emission) into the atmosphere in the early years of the mine (Wagemann et al., 1978). Emissions decreased after 1951 when an electrostatic precipitator and baghouses were used to reduce emissions following public pressure (Jamieson, 2014). From 1948 to the cessation of roasting in 1999, As₂O₃ emissions to the surrounding environment were estimated to be approximately 20,000 tonnes, with most emissions occurring prior to the implementation of emission controls more than 50 years ago (Bromstad, 2011; Bromstad et al., 2017).

The selection of the 23 study lakes (Fig. 1; Table 1) was based on multiple criteria. These included present-day arsenic concentrations in water and sediment, the distance from Giant Mine and Con Mine, and the position from the mine relative to the prevailing northwest wind direction (Tanamal et al., 2018). Distance from Giant Mine ranged from 1.52 km to as far as 42.2 km. The estimated zone of impact based on present-day surface [As] is within a 15 km radius of the mine (Palmer et al., 2015), and within a ~ 40 km radius based on historic arsenic concentrations inferred from lake sediment cores (Cheney et al., 2020). Sediment core profiles for arsenic and other metals have been published (Cheney et al., 2020) for the following study lakes: Alexie, BC 17, David, Duckfish, Lower Martin, Vee, and Vital (Table 2).

The selected lakes are underlain by either Archean metasedimentary bedrocks, volcanic rocks or

Precambrian granitoids (Kerr & Wilson, 2000; Houben et al., 2016), are generally shallow (median depth of 5.00 m with a range of 0.5 to 21 m) and small (median surface area of 0.52 km^2 , with a range of 0.02 to 6.28 km²; Table 1).

Apart from gold mining and arsenic trioxide deposition, other stressors acting on the lakes include municipal development in Yellowknife (Gavel et al., 2018) and climate warming (Sivarajah et al., 2020). In order to better explore the changes in Cladocera assemblages across different arsenic concentrations, our study lakes were sorted into four groups based on present-day lake-water [As]: $< 5 \ \mu g/l \ (n = 7), 5$ to 10 $\mu g/l \ (n = 3), 10$ to 100 $\mu g/l \ (n = 8)$ and 100 to 1000 $\mu g/l \ (n = 5).$

Field Methods

Sediment cores were collected from each of the study lakes using a UWITEC gravity corer (Mondsee, Austria) over numerous sampling seasons conducted during the period of March 2014 to July 2016. Lake bathymetries were unavailable for most of the study lakes, and as such sediment coring locations were selected from the centre of each of the lakes. The depths presented in Table 1 were measured at the coring locations. Water samples were collected from the surface waters at the coring locations. Water chemistry variables for YK 04 (4.00 m in depth), Batwing (8.00 m in depth) and Alexie (21.00 m in depth) were analyzed based on under-ice water samples and may therefore influenced by solute exclusion. However, it should be noted that solute exclusion in Yellowknife lakes may only be an issue in those with depths measuring < 4 m (Palmer et al., 2019). As such, of the three lakes, YK 04 may be the only lake in the subset where solute exclusion is a concern. Cores were sectioned into 0.5 cm intervals using a modified Glew (1988) vertical extruder and stored cold (4°C) or frozen until analysis at York University.

Laboratory Methods

Water chemistry variables were analyzed at the Taiga Environmental Laboratory located in Yellowknife, a Canadian Association for Laboratory Accreditation Inc. (CALA) certified institute, using Standard US Environmental Protection Agency methods.

Table 1 A summ.	ary of the lin	nological char ⁶	acteristics of the 25	3 study lakes									
Lake Name	Latitude	Longitude	Distance from Giant Mine	Elevation	Lake Area	Depth	Hq	DOC	SO_4	Ca	AI	As	Sb
	Decimal de	grees	km	ш	km^{2}	ш	Ι	mg/l	mg/l	mg/l	µg/l	hg/l	μg/l
BC 17*	62.49985	- 114.421	3.10	202.00	0.16	0.50	8.25	35.80	13.00	19.10	101.00	750.00	12.30
BC 20*	62.50542	-114.388	1.52	196.00	0.36	0.50	9.76	52.20	22.00	23.60	98.60	697.00	12.20
Frame* ²	62.45712	- 114.389	5.35	188.00	0.93	5	7.59	42.8	174	120	9.7	343	5.1
David*	62.54320	-114.378	4.55	199.00	0.13	2.00	8.25	37.20	67.00	42.20	54.20	184.00	5.60
$YK 04^{\$}$	62.43778	- 114.115	14.58	190.00	0.02	4.00	6.93	150.00	1.00	53.20	84.50	117.00	0.30
Jackfish	62.46703	-114.392	4.25	180.00	0.52	7.50	9.07	9.70	31.00	35.10	6.50	74.50	1.50
Lower Martin ¹ *	62.51312	-114.419	3.27	201.00	1.35	7.00	7.88	15.90	3.00	14.90	7.80	40.60	1.20
$Long^{1*}$	62.47439	-114.430	4.69	198.00	1.15	9	7.63	9.10	14.00	29.40	1.50	39.70	1.20
Vee*	62.55253	-114.348	5.79	179.00	0.77	5.20	8.00	20.60	14.00	42.40	41.70	34.20	1.00
YK 06	62.46120	- 114.558	12.10	191.00	0.03	06.0	7.41	29.90	2.00	8.50	97.00	32.30	0.60
DET 15	62.47524	-114.294	4.50	191.00	0.02	0.86	7.36	33.40	2.00	11.20	39.00	26.60	0.90
Martin*	62.53313	-114.436	5.49	199.00	3.05	3.50	7.83	14.30	5.00	14.90	14.20	25.80	1.00
BC 43	62.50851	-114.175	9.75	198.00	0.40	5.00	8.64	33.70	4.00	29.90	11.70	16.40	0.30
Grace ¹ *	62.42068	-114.431	10.23	171.00	0.63	16.00	7.49	15.30	14.00	18.50	3.30	9.70	0.40
Moose*	62.22893	- 113.796	42.20	160.00	3.68	1.00	7.36	130.00	1.00	96.60	34.20	7.40	0.20
Pontoon	62.54077	-114.003	18.95	199.00	3.17	5.70	8.45	24.20	4.00	32.50	5.20	5.70	0.20
Vital*	62.59334	-114.432	10.74	204.00	1.52	10.00	7.44	15.90	3.00	13.70	9.30	4.80	0.30
Tees*	62.55828	-114.041	17.69	198.00	0.17	6.00	7.52	16.70	6.00	18.80	9.20	2.90	0.10
Batwing* [§]	62.68025	-114.169	22.05	236.00	0.22	8.00	7.13	35.40	1.00	17.50	5.40	2.60	0.10
ING-28	62.56122	-114.005	18.50	227.00	0.18	2.10	8.23	12.60	1.00	10.10	20.00	2.50	0.10
Duckfish ¹ *	62.66088	-114.448	18.24	230.00	6.28	3.00	8.12	28.6	3.00	22.2	7.90	2.20	0.50
ING-27	62.56450	-114.014	18.30	228.00	0.12	11.50	7.94	8.60	3.00	9.00	20.00	2.00	0.20
Alexie* [§]	62.67648	-114.102	23.52	221.00	4.56	21.00	7.69	13.40	4.00	13.80	4.50	1.50	0.10
Lakes are arranged hetween 2014 and	1 in descendi 2016 Lakes	ng order based for which the c	on their arsenic (A vores were 210 Ph d	As) concentrat	ons (highest to ed bv"*"	o lowest).	Measurei	ments of w	ater chemis	stry parame	sters were t	taken in 20	10 and

[§]Lakes were sampled in the winter, and therefore water chemistry parameters will be influenced by solute exclusion during ice formation

¹Data from Palmer et al. (2015) ²Data from Sivarajah et al. (2019)

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Table 2 Results of the 210 Pb and 137 Cs sediment core dating for 15 of the 23 study lakes used to select "bottom" intervals deposited ~ 1850 or pre-1850

Lake name	Depth of sediment core (cm)	Bottom interval selected cm	Depth ²¹⁰ Pb background was reached cm	Earliest Date returned by CRS model (associated sediment core depth)	Error (CRS)	¹³⁷ Cs peak (where available)
BC 17 ¹	30.25	29.25	18.25	1891.40	70.9746	
BC 20	34.25	24.75	20.25	1936.77	19.0657	1885.01
Frame	24.25	20.25	6.25	1903.72	27.2059	1965.05
David ¹ *	40.25	20.25	40.00	1985.15	1.4972	
YK 04		19.75				
Jackfish		20.25				
Lower Martin ¹	24.50	25.25	18.50	1907.37	25.4952	
Long	24.25	20.25	12.25	1916.48	15.1332	1749.39
Vee ¹	29.50	20.25	20.50	1888.29	22.6196	
YK 06		39.00				
DET 15		41.00				
Martin ¹	34.50	20.25	22.50	1921.53	7.2882	
BC 43		18.25				
Grace	18.25	18.75	12.25	1920.35	19.4032	1908.60
Moose	17.25	17.25	12.25	1923.34	72.6105	1907.55
Pontoon		25.50				
Vital ¹	24.25	20.25	15.25	1903.02	7.2973	
Tees	24.25	20.25	15.25	1931.33	5.6134	
Batwing	24.25	20.25	12.25	1923.34	5.0648	
ING-28		33.00				
Duckfish ¹	35.25	20.25	20.50	1912.34	8.0423	
ING-27		21.00				
Alexie ¹	24.25	20.25	14.50	1899.96	11.6471	

CRS constant rate of supply dating model. Lakes are arranged in descending order based on their arsenic (As) concentrations (highest to lowest)

*Dating profiles are extremely variable possibly due to sediment mixing

¹Data from Cheney et al. (2020)

Elemental analysis was done by ICP-MS and water samples were filtered prior to analysis. Water chemistry variables taken in 2010 were analyzed for trace metals (EPA Method 208-1) at the Taiga Environmental Laboratory, with sulphates, calcium, and dissolved organic carbon analyses conducted at Environment Canada's National Laboratory for Environmental Testing (NLET, a CALA accredited institute) following standard operating procedures (SOP #s 1080, 1061, 1021) by Environment Canada, and pH was measured in situ with a Thermo Orion Model 106 m (Houben et al., 2016).

Chronologies have been established for sediment cores from 15 of the 23 study lakes (Table 1) using gamma spectroscopy techniques to measure ²¹⁰Pb and ¹³⁷Cs activities, and the constant rate of supply (CRS) model (Appleby, 2001), at the University of Ottawa. The results of ²¹⁰Pb dating were used to select bottom intervals that would represent sediments that were deposited at least 150 years ago, in the pre-industrial period prior to the onset of warming in the

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Yellowknife region in the late nineteenth century (Table 2). For the 8 lakes that were not ²¹⁰Pb-dated, bottom intervals were chosen based on a conservative estimate of regional sedimentation rates from similar lakes that had established ²¹⁰Pb chronologies. We chose a bottom interval of 20.5 cm for most lakes, which is a reliable estimate for the pre-1850 time period for lakes in the Yellowknife region (Table 2). Grace Lake and Moose Lake cores were shorter than 20.5 cm (18.5 and 17.5 cm, respectively), and so we used the deepest interval sectioned (i.e. second last interval, not the bottom sediment layer that was in contact with the core bung) instead. The sediment core collected from David Lake, one of our high-arsenic lakes, had evidence of sediment mixing and our bottom interval of 20.5 cm in David Lake may not be a reliable estimate of background conditions. For all other lakes, however, we have high confidence that our bottom intervals were deposited pre-1850 based on available ²¹⁰Pb chronologies, although the specific pre-1850 time period encompassed by our bottom intervals may vary within ~ 200 years among lakes. Diatom-based paleolimnological reconstructions of climate impacts on subarctic lakes in and near Yellowknife indicate that this pre-industrial time period represents a period of ecological stability prior to the onset of regional warming (Rühland & Smol, 2005; Thienpont et al., 2016; Sivarajah, 2020).

Cladoceran subfossils were isolated from the sediment matrix in the top 0.5 cm interval (representing modern conditions) and a bottom 0.5 cm interval (representing pre-industrial conditions) using the methods described in Korosi & Smol (2012a, b). Bottom intervals chosen for analysis ranged from 17.25 to 29.25 cm. Approximately 1 g of wet sediment was deflocculated in 100 ml of a 10% potassium hydroxide (KOH) solution and heated to $\sim 70^{\circ}$ C for 30 min. The KOH-sediment mixture was then filtered through a 36 µm sieve to remove excess organic matter and rinsed with distilled water. The residue was transferred to a vial, with a few drops of 80% ethanol added as a preservative, and two drops safraninglycerol solution added to colour the remains. Next, 50 µl aliquots were transferred to microscope slides and allowed to dry until the water had evaporated, a process which was repeated to attain an optimal concentration of subfossil remains. Aliquots were doubled and tripled on slides for some lakes, where materials that can occlude cladoceran remains were not present. Slide covers were mounted using glycerin jelly and examined under an Amscope B690C-PL microscope to identify and count the cladoceran remains at ×200-400 magnification. Cladocera remains were identified to the genus level, and where possible the species level, using Korosi & Smol (2012a, b) as taxonomic guides. The most frequent body part identified for each cladoceran was used as a measure of the number of individuals (Korhola & Rautio, 2001). A minimum of 70 individuals was used for lakes where the concentration of Cladocera remains was high, and for lakes where the concentration of remains was lower, a minimum count of 50 individuals was used (Kurek et al., 2010). Lakes were considered to have a low concentration when the minimum count of 70 could not be achieved from the examination of 30 slides, representing 30 to 90 aliquots of 50 μ l.

Statistical Analyses

Variation in Cladocera assemblages across the 23 study lakes, and changes in Cladocera assemblages between the modern and pre-industrial samples, were summarized using a principal component analysis (PCA) in RStudio Version 1.2.5033 using the vegan package (Oksanen et al., 2019). Prior to undertaking the ordination, taxa that did not meet the criteria of $\geq 2\%$ relative abundance in at least five samples were excluded to reduce the influence of rare taxa on the PCA. The relative abundance data were also square root transformed to stabilize variance. Modern samples were plotted actively, and pre-industrial samples were plotted passively in the ordination. A PCA was also used to visualize variation in measured environmental variables across the study lakes. Prior to analysis, to meet the assumptions of normality, all environmental variables apart from pH were log (base 10)-transformed. A Pearson correlation matrix was also produced using the Hmisc package (Harrell, 2020) to assess correlations among the measured environmental variables. The variable antimony was excluded from the subsequent redundancy analysis (RDA) only because of its high positive correlation with arsenic.

The RDA with forward selection was performed using the rioja (Juggins, 2017) and vegan packages (Oksanen et al., 2019) to examine the relationships between modern cladoceran assemblages and the measured environmental variables. Data transformation for the RDA followed the same methods used for the PCAs. Significance of the RDA was tested using the vegan package's permutation test for redundancy analysis, 'anova.cca' (Oksanen et al., 2019). Forward selection was done using the 'adespatial package' (Dray et al., 2012). Rarefied species richness and Hill's N2 diversity, were calculated using the rioja and vegan packages in RStudio (Oksanen et al., 2019). Statistical differences in species diversity (N2) and rarefied species richness between modern and preindustrial samples among all lakes was tested using the Wilcoxon signed-rank test (also known as paired samples Wilcoxon test).

The relationship between rarefied species richness and arsenic, and Hill's N2 species diversity and arsenic, were also explored using linear regression. The regression models were run both with and without the major outliers (four most highly arsenic-contaminated lakes, BC 17, BC 20, Frame and David; [As] > 100 μ g/l). In addition, to determine whether the response was unimodal, statistical tests for unimodality based on the method proposed by Jamil & ter Braak (2013) were also run with and without the major outliers. To compare all Cladocera assemblages across four a priori defined arsenic classes, the ANOSIM test based on Bray–Curtis dissimilarity was performed using the vegan package (Oksanen et al., 2019).

An analysis of similarity (ANOSIM) test, based on Bray–Curtis dissimilarity, was used to test for significant differences in the Cladocera assemblages between modern and pre-industrial samples across all 23 lakes, using the vegan package for RStudio (Oksanen et al., 2019). The exclusion criteria and square-root-transformation used for the PCA were also used for this test. Differences in relative abundance of individual abundant taxa since pre-industrial times were also examined in the context of the four a priori defined arsenic classes. The Kruskal–Wallis nonparametric analysis of variance, using R Studio version 1.2.5033, was used to test whether differences in cladoceran taxa among arsenic categories were statistically significant.

Results

Differences in water chemistry variables amongst Yellowknife study lakes

Generally, the pH of the lakes was circumneutral to alkaline, with calcium concentrations ranging from 8.5 to 120 mg/l, [As] ranged from 1.5 to 750 μ g/l and dissolved organic carbon (DOC) concentrations from 8.6 to 150 mg/l (Table 1).

PCA axis 1 of the environmental variables was primarily influenced by water quality variables indicative of impact from mining emissions, including arsenic and antimony, and to a lesser extent sulphate. PCA axis 2 represented a gradient of lake area, aluminum, pH, and sulfates (Fig. 2a). Cumulatively, these two axes explained 74% of the variation in the limnological variables of the 23 lakes. Arsenic and antimony plotted in the opposite direction to lake depth and distance from Giant Mine (Fig. 2a). Not surprisingly, these variables were also negatively correlated (Pearson correlation coefficients < -0.52).

Cladocera assemblages in the surface sediments of the Yellowknife study lakes

We identified 28 Cladocera taxa, both littoral and pelagic, across our 23-lake dataset. The dominant taxa were *Bosmina* spp., *Chydorus brevilabris* (Frey, 1980)/*Chydorus biovatus* (Frey, 1985), and several taxa belonging to the genus *Alona* [*A. circumfimbriata* (Megard, 1967), *A. guttata* (Sars, 1862), *A. affinis* (Leydig, 1860), *A. quadrangularis* (O.F. Müller, 1776) and *A. barbulata* (Megard, 1967)]. Subfossil remains were generally intact, with only some fragmentation noted for carapaces of *Alona*. In addition, subfossils were clearly visible in most cases, even for the most contaminated lake in the dataset. The exception was Frame Lake, where visibility of the remains in the bottom interval was hindered by a high concentration of clastic material in the sediments.

Bosmina were present in 15 of the 23 study lakes, ranging in relative abundance from ~ 2 to 91%, with an average relative abundance of ~ 27% across all lakes (Fig. 3, Table 3). C. brevilabris/biovatus was found in 22 of the 23 lakes at ~ 2 to 49%, and an average relative abundance of 12.3% (Fig. 3, Table 3). At comparatively lower relative abundances



Fig. 2 Principal component analysis (PCA) showing (a) the distribution of the study lakes along the gradients of the measured environmental variables; (b) variation in cladoceran species assemblages in the surface sediments of Yellowknife lakes; (c) direction of change in cladoceran species assemblages

in Yellowknife lakes between present-day (surface sediments) and the pre-industrial (bottom sediments) periods. Cladocera assemblages in the bottom sediment interval are plotted passively. The shapes of the symbols represent the present-day surface water arsenic concentrations



Fig. 3 Simplified Cladocera relative frequency diagram comparing the percentage relative abundances of the most common cladoceran taxa in surface (black bars) and pre-industrial (gray bars) sediments for twenty-three lakes in Yellowknife,

Northwest Territories. Lake sites are arranged in order of increasing arsenic (As) concentrations, as shown on the right. The number of individuals for each interval is shown on the far right

were the littoral taxa *Acroperus harpae* (Baird, 1834) which was present in 18 lakes at an average of $\sim 3\%$, *Eurycercus* (Baird, 1843) in 10 lakes at an average of

~ 1.5%, *Pleuroxus* (Baird, 1843) in 11 lakes at an average of ~ 1.6%, and the predatory cladoceran taxon *Polyphemus* (O. F. Müller, 1785) in 9 lakes at an

 Table 3
 List of the most common cladoceran taxa encountered in the 23 study lakes, a summary of their distribution (abundance and number of lakes) and basic ecology

Cladocera taxa	Number of Lakes	Average relative abundance	Basic ecology
Acroperus harpae (Baird, 1834)	18	3.07	Commonly found in littoral zones of lakes and exhibits high habitat heterogeneity
			Species is indifferent to pH (Walseng et al., 2001, 2003)
Alona affinis (Leydig, 1860)	16	6.43	Epiphytic taxon that shows habitat specificity, being associated with vegetation beds (Tremel et al., 2000). Taxon is indifferent to pH (Walseng et al., 2008)
Alona barbulata (Megard, 1967)	15	6.82	Associated with soft water lakes in northeastern North America (Megard, 1967)
Alona circumfimbriata (Megard, 1967)	16	9.50	Eurybiontic species (Megard, 1967) not frequently found in soft water lakes
Alona guttata (Sars, 1862)	7	4.67	Occurring more in lakes with a circumneutral pH (Walseng et al., 2001, 2008). Adapted to both mud-vegetation and sandy-rocky habitats (Chengalath, 1982)
Alona quadrangularis (O.F. Müller, 1776)	9	4.07	Large mud dwelling taxon abundant in muddy areas with vegetation (Evans, 1984; Tremel et al., 2000). Observed over a broad pH range (Walseng et al., 2008)
Alonella nana (Baird, 1843)		8.01	Small taxon commonly found in the littoral zones of lakes in Canada (Chengalath, 1982). Found to be uncommon at $pH < 5.0$ (Walseng et al., 2008)
Bosmina (Baird, 1845)	15	27.19	A planktonic taxon often found in the epilimnion of lakes. It is ubiquitous, with its subfossil remains being the most commonly recovered among all cladocerans.
Chydorus brevilabris (Frey, 1980)/ Chydorus biovatus (Frey, 1985)	22	12.12	<i>C. brevilabris</i> and <i>C. biovatus</i> are the two branches of the <i>C. sphaericus</i> complex. The former dominates in southeastern Canada and northeastern USA (Chengalath, 1982) and the latter is more abundant in northern North America (Frey, 1980)
Daphnia longispina (O.F. Müller, 1776)	4	4.69	Planktonic, filter feeding taxa observed in both ephemeral rock pools and lakes (Pajunen & Pajunen, 2007)
Daphnia pulex (Leydig, 1860)	10	3.68	Relatively large, planktonic filter feeding taxa. High variability between populations in response to toxins from cyanobacteria (Laurén-Määttä et al., 1997)
Eurycercus (Baird, 1843)	10	1.62	Largest of the chydorid family (Frey, 1971). Widely found in northeastern North America (Hann, 1982; Bekker et al., 2012)
Graptolebris testudinaria (Fischer 1848)	8	0.78	Epiphytic taxon commonly observed in water bodies with dense vegetation (Chengalath, 1982; Walseng et al., 2008)
Pleuroxus (Baird, 1843)	11	1.51	Consistent but not abundant species comprising the chydorid assemblage of soft water lakes
Polyphemus pediculus (Linnaeus, 1761)	9	0.87	Commonly littoral, raptorial, omnivorous taxon that feeds on <i>Daphnia</i> and <i>Bosmina</i> . One species, <i>Polyphemus pediculus</i> exhibits high ecological plasticity (Xu et al., 2009)
Sida crystallina (O.F. Müller, 1776)	7	1.63	Filter feeder commonly found in the littoral zones of lakes attached to plant surfaces
			abilities (Fairchild, 1981). Found to be common at $pH > 5.0$ (Walseng et al., 2003)

Information on basic ecology was adapted from Korosi & Smol, (2012a, b)

average of ~ 1%. *Daphnia pulex* (Leydig, 1860) and *Daphnia longispina* (O.F. Müller, 1776) occurred sporadically across the lake set but were often the dominant taxa when present (Fig. 3).

PCA of the cladoceran data showed that the variation in the assemblages across the study lakes was driven mainly by Bosmina, Daphnia (both the D. pulex and D. longispina complex), Sida crystallina (O. F. Müller, 1776), Alonella nana (Baird, 1850), and Alona species (Fig. 2b, c). Cumulatively, PCA axis 1 and PCA axis 2 explained 49% of the variance in the modern Cladocera assemblages ($\lambda_{axis1} = 0.36$, λ_{axis2} -= 0.13; Fig. 2b). The lakes with the highest arsenic concentrations (100-1000 µg/l) plotted in the lower left quadrant of the ordination (Fig. 2b), which was primarily driven by the littoral species Alona circumfimbriata, A. affinis, and A. guttata. The exception to this trend was YK 04, for which the modern sample scores plotted in the top left quadrant of the ordination. YK 04 had the lowest surface water arsenic concentration of the five lakes in the 100 to 1000 μ g/l arsenic group with a concentration of 117 μ g/l. This value is likely an overestimation of open-water arsenic concentrations since it is measured on a water sample collected in winter under the ice. Arsenic and other solutes are excluded during ice formation and due to mid-winter anoxia, being most substantial in Yellowknife lakes with depths < 4 m (Palmer et al., 2019). *Bosmina* were absent or rare in both the preindustrial and modern time periods in the four lakes with the highest arsenic concentrations (Fig. 2b). The RDA with forward selection only identified one variable, namely arsenic, as explaining the variation in assemblages, and given the lack of dimensionality in the cladoceran assemblages, the RDA was not pursued further.

Cladoceran species diversity (Hill's N2) and rarefied species richness in the surface sediments showed a significant positive relationship with lake-water [As] (Hill's N2: P = 0.002, $R^2 = 0.46$, F-statistic: 14.31 on 1 and 17 DF; richness: P = 0.004, $R^2 = 0.39$, Fstatistic: 11.04 on 1 and 17 DF) when the four lakes with the highest [As] (BC 20, BC 17, Frame and David) were removed (Fig. 4a, c). However, the



Fig. 4 Regression plots showing the relationship between: (a) cladoceran species diversity (Hill's N2, surface sediments) and lake-water arsenic concentrations for 19 of the 23 study lakes (4 lakes with the highest arsenic concentrations removed); (b) species diversity (Hill's N2) regression plot with all 23 study lakes included; c) rarefied species richness (surface sediments)

and lake-water arsenic concentrations for 19 of the 23 study lakes (4 lakes with the highest arsenic concentrations removed); d) rarefied species richness regression plot with all 23 study lakes included. The shapes of the symbols represent the presentday surface water arsenic concentrations

inclusion of BC 20, BC 17, Frame and David Lake resulted in trends not being statistically significant (Fig. 4b, d). For lakes with [As] < 5 µg/l, Hill's N2 and rarefied species richness ranged from 1.3 to 7.1, and 4.0 to 11.0, respectively. Lakes within the [As] 10 to 100 µg/l category had values that ranged from 1.7 to 6.0 (N2) and 7.9 to 12.0 (richness). Lake YK 04 ([As] > 100 µg/l) had the highest Hill's N2 and richness values at 8.8 and 12.8, respectively. David, BC 20, and BC 17 have Hill's N2 values ranging from 2.6 to 4.9, and similar species richness values of 6.9. Frame Lake has a species richness value of ~ 4 and a Hill's N2 value of 3.1. Unimodal response was significant in both cases, i.e. with and without the major outliers (P < 0.001).

Regional changes in Cladocera assemblages since pre-industrial times

There were no substantial differences in regional cladoceran assemblage between the present-day and pre-industrial sediment intervals (one-way ANOSIM, R = -0.047, P = 0.982, n = 999 permutations). Cladoceran species richness and Hill's N2 diversity were similarly not significantly different (paired Wilcoxon signed-rank, species richness – P = 0.67; Hill's N2—P = 0.92) between the top and bottom intervals (Fig. 5). Although no significant regional differences in cladoceran assemblages and diversity

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indices were observed, many individual lakes exhibited notable changes in cladoceran assemblages since pre-industrial times (Figs. 3, 6). The lakes that had the greatest dissimilarity between top and bottom assemblages (based on Bray-Curtis Dissimilarity) were Grace Lake ([As] = 9.7 μ g/l), ING-27 ([As] = 2.0 μ g/l) and Frame Lake ([As] = 343 μ g/l). In Frame Lake, Chydorus brevilabris/biovatus increased from 12.1% relative abundance in the bottom sediments to 49.0% in the surface sediments while many Alona guttata, A. affinis and A. quadrangularis, which were present in the bottom sediments, were absent in the surface sediments abundance. In Grace Lake, Daphnia longispina decreased by 59.6% relative abundance from the bottom sediments to the surface sediments. with a corresponding 68.2% increase in Bosmina by (Figs. 3, 6). In contrast, *Bosmina* decreased by 41.4% relative abundance in Lake ING 27, while Alonella nana increased by 16.4% relative abundance (Fig. 3, 6). Jackfish Lake ([As] = 74.5 μ g/l) and Tees Lake $([As] = 2.9 \mu g/l)$ also exhibited notable declines in Bosmina relative abundance, with corresponding increases in D. longispina (Figs. 2b, 3, 6). The lakes with the least dissimilarity between top and bottom cladoceran assemblages were BC 17 (the lake with the highest surface water arsenic concentration) and Lower Martin Lake.

The Kruskal–Wallis nonparametric analysis of variance for the four a priori defined arsenic lake



Fig. 5 Scatterplots showing cladoceran rarefied species richness and species diversity (Hill's N2) in present-day and preindustrial sediment intervals. Samples that plot above the 1:1 line have higher rarefied species richness and Hill's N2

diversity in the surface interval compared to the bottom interval. Significance values are based on the Wilcoxon tests. The shapes of the symbols represent the present-day surface water arsenic concentrations



Fig. 6 Changes in the relative abundance of the most abundant cladoceran taxa between present-day and pre-industrial times for the 23 study lakes arranged by measured surface water arsenic concentrations. Kruskal–Wallis nonparametric analysis

categories showed no significant regional differences for the common cladoceran taxonomic groups between present-day and pre-industrial sediments in any of the categories (Fig. 6). Additionally, while the ANOSIM indicated differences between the presentday Cladocera assemblages across the four arsenic groups (one-way ANOSIM, P = 0.003, n = 999 permutations), a low *R* statistic value of 0.28 suggests that these differences were not pronounced. Of the 6 lakes with [As] < 5 µg/l in which *Bosmina* was present, the taxa increased in 3 lakes since pre-industrial times, but also decreased in 3 lakes. *Alona circumfimbriata* and *Alona affinis* increased in 3 of the 4 lakes with [As] > 100 µg/l (Fig. 6).

of variance for all arsenic classes: $< 5 \ \mu g/l \ (n = 7)$; 5 to 10 $\mu g/l \ (n = 3)$; 10 to 100 $\mu g/l \ (n = 8)$; and 100 to 1000 $\mu g/l \ (n = 5)$ are provided in each plot

Discussion

Our study aimed to provide a regional snapshot of Cladocera assemblage changes from the pre-industrial period to the modern day and identify possible bioindicators for arsenic contamination in Yellowknife lakes. Our findings showed that cladoceran species richness and diversity increased along an arsenic gradient until a critical threshold (> 100 μ g/l) was reached, after which both diversity and richness decreased. Littoral/benthic taxa dominated the assemblages in the highly contaminated lakes, while the pelagic *Bosmina* dominated in lakes with lower [As]. Overall, no consistent regional trends in cladoceran assemblage shifts were detected between present-day

and pre-1850 sediments, and instead cladoceran changes were lake-specific.

Differences in Cladocera species richness and diversity along a gradient of arsenic

We found that arsenic was positively correlated with rarefied species richness and alpha diversity across our study lakes that spanned an arsenic gradient of 1.5 to 117 µg/l, when the four most heavily contaminated lakes were removed from the analysis. This differs from the findings of Winegardner et al. (2017) for mining-impacted lakes in Québec (Canada) and Leppänen et al. (2018) for mining-impacted lakes in Finland, where Cladocera species richness and diversity decreased with metal pollution. In their study, the primary metals of concern were copper, nickel, and zinc, which are well known to have deleterious impacts on cladoceran communities (Yan et al., 2004; Labaj et al., 2015). In Yellowknife, the main metal(loid) pollutants released from mine emissions were arsenic and antimony, while copper, nickel, and zinc are not a concern in this region.

Our findings indicate that lake ecosystem responses to arsenic pollution may result in increases in cladoceran species richness and diversity below a certain threshold, following a unimodal response. This increase contrasts with other metals more commonly studied in the aquatic environment. The four most arsenic-contaminated lakes in our dataset (BC 17, BC 20, Frame and David; [As] > 180 μ g/l) clearly deviated from the trend of increasing richness and diversity with [As], and may indicate a negative influence of arsenic on Cladocera once a threshold in arsenic is reached.

The increase in diversity may be attributed to hormesis, i.e. a biphasic response where there is a stimulating effect at low concentrations, but an inhibitory effect at high concentrations (Mattson, 2008). While not well researched for Cladocera, a stimulating effect from low arsenic concentrations has been observed for cyanobacteria like *Microcystis aeruginosa* [(Kützing) Kützing, 1846] exposed to inorganic arsenite (Gong et al., 2011). The presence of biofilms in the benthic zone may serve to buffer or reduce the concentration of arsenic (Roeselers et al., 2008; Thienpont et al., 2016), stimulating higher benthic production and thereby resulting in higher benthic Cladocera diversity. However, the positive relationship between cladoceran richness and diversity with arsenic concentrations may also be a spurious correlation, instead tracking the influence of lake depth on Cladocera. A clear relationship was evident between lake depth and [As] in our dataset, where shallower lakes were more likely to have elevated surface water [As]. Lakes with low water levels have higher Cladocera richness and diversity relative to lakes with higher water levels (Ghidini & Santos-Silva, 2018), and shallow lakes are often dominated by diverse littoral/benthic assemblages (Nevalainen, 2011; Gałka et al., 2014).

If the positive relationship between species richness/diversity and [As] is direct (i.e. driven by [As] and not an indirect association with depth or other related environmental variable), we might expect increases in species richness and diversity since preindustrial times for lakes that have received arsenic deposition, with the exception of the most heavily contaminated lakes where [As] exceeded a threshold where toxic effects become evident (somewhere between 115 μ g/l to 180 μ g/l based on our data). We observed no significant differences in species richness and alpha diversity (Hill's N2) between the preindustrial and modern time periods across all lakes, although many lakes with [As] between 10 and 100 µg/l did exhibit increases in species diversity and richness since the pre-industrial time period. Of the four lakes with $[As] > 100 \mu g/l$, David Lake and Lake YK 04 exhibited increases in Hills N2 diversity and rarefied species richness, while BC 17 and BC 20 decreased. In YK 04 [As] is based on measurements in water samples taken under the ice, and solute exclusion during ice formation likely resulted in higher [As] than would be measured if the water sample had been collected in the open-water season. David Lake had an unreliable ²¹⁰Pb dating record, and the "bottom" sample may not truly be representative of pre-industrial assemblages. Additionally, as a minimum count of 50 was used for some lakes, including the most contaminated lakes, it is possible that very rare species may not have been identified, lowering the calculated diversity value. However, Hill's N2 measures the number of equally common species, or figuratively the number of very abundant species, and is not significantly affected by rare species (Alatalo, 1981). As such, while rarer species could have been missed, using a reasonable counting effort and following the standard methods, it would not significantly affect our findings.

Subfossil Cladocera species assemblages as paleoecological indicators of arsenic contamination

In a detailed paleolimnological analysis of Pocket Lake (Thienpont et al., 2016), Daphnia appeared and then increased in relative abundance at the onset of arsenic contamination, but were then extirpated at the height of arsenic emissions, indicating that they are relatively tolerant of arsenic until a threshold is reached. Lab bioassays support this, with EC50 values of 49.6 \pm 9.0 mg arsenate/l documented for *Daphnia* pulex (Passino & Novak, 1984), and for Daphnia similis (Claus, 1876) 0.54 mg arsenate/l (de Sales et al., 2016). The one lab bioassay study available for Bosmina recorded a 96 h EC₅₀ of 0.85 \pm 0.12 mg arsenate/l for Bosmina longisrostris (O.F. Müller, 1785), lower than what was documented for Daphnia (Passino & Novak, 1984). These effects concentrations are much higher than the values we report for the most contaminated lakes in our study; however, EC_{50} and other similar metrics are functions of time, and may not necessarily capture the responses of Cladocera to long-term exposure (years), as is the case for Yellowknife lakes.

Although we did not document similarly strong associations between cladoceran assemblages and [As] in our study, some patterns were evident in the presence and absence of certain taxa in lakes with high surface water arsenic concentrations. The most heavily [As]-contaminated lakes were dominated by *Alona* taxa, particularly *A. circumfimbriata* and *A. guttata*, while *C. brevilabris/bioavatus* were also common. *Chydorus brevilabris* has been observed at a surface water arsenic concentration of 1110 μ g/l in Cart Lake, in northeastern Ontario (Little et al., 2020), and has also been shown to increase with copper and nickel contamination in lakes near Wawa and Sudbury in Ontario, Canada (Jeziorski et al., 2013; Labaj et al., 2015).

Arsenic contamination appears to have a disproportionate effect on pelagic organisms relative to littoral/benthic ones, and benthic algal/microbial mats may be protecting benthic taxa by binding or detoxifying arsenic and other contaminants (Bender et al., 1994; Roeselers et al., 2008; Thienpont et al., 2016). In Yellowknife lakes, pelagic feeding fish tended to have higher arsenic concentrations relative to littoral feeding taxa (Chételat et al. 2019). Yellowknife lakes with [As] > 5 μ g/l also had higher abundances of opportunistic benthic diatoms (small fragilarioid taxa and *Achnanthidium minutissimum*) (Sivarajah et al., 2019). *Daphnia* species, which increased with the onset of arsenic contamination in Pocket Lake (Thienpont et al. 2016), were not an important part of the assemblage in our high [As] lakes.

Bosmina were dominant across many of the lakes in our dataset, including shallow lakes (e.g. Moose Lake, depth = 1 m, *Bosmina* relative abundance $\sim 60\%$), but were absent in the highly contaminated lakes $([As] < 100 \mu g/l)$ in both the surface and pre-industrial sediments. Several lakes within 40 km of Giant Mine's roaster stack had naturally high geogenic arsenic (Cheney et al., 2020), which may explain the absence of Bosmina in both surface and pre-industrial sediments. A paleolimnological study documented decreases in the abundance of bosminids in Yangzong Lake and Datun Lake, China, coincident with high arsenic enrichment (Chen et al. 2015). Toxicity bioassays have shown that Bosmina longirostris are more sensitive to arsenic than Daphnia magna (Straus, 1820) and Daphnia pulex (Passino & Novak, 1984); however, in Cobalt (Ontario), Bosmina were reported in lakes with surface water arsenic concentrations as high as 1110 µg/l (Little et al., 2020). Geographic variation in genetic background (Burge et al., 2018; Radzikowski et al., 2018), the bioavailability and form of arsenic to which the taxa is exposed, and the influence of other water quality variables such as calcium and phosphorus on arsenic toxicity (Awoyemi et al., 2020) can act collectively to influence species ecotoxicological responses to arsenic concentration across different regions.

Notably, highly contaminated lakes in our dataset showed only muted changes in cladoceran assemblages since pre-industrial time, indicating that Giant Mine emissions played a limited role in Cladocera assemblages changes at the regional scale. Most of our study lakes are situated in organic-rich catchments, in contrast to Pocket Lake which is situated in a granite basin and experienced an apparent extirpation of all Cladocera as a result of arsenic pollution (Thienpont et al., 2016). Organic matter facilitates the microbially-mediated conversion of highly toxic arsenic trioxide released from Giant Mine into less toxic arsenic sulphides, as it acts as a substrate for microbial growth (Galloway et al., 2017). In contrast, arsenic trioxide particulate matter persists in granitic outcrops (Palmer et al., 2015). This suggests that lakes with high organic matter may be more protected from arsenic toxicity than those in predominantly granitic basins (such as Pocket Lake, Thienpont et al., 2016).

Subfossil Cladocera assemblage and diversity changes in Yellowknife lakes since pre-industrial times

Several of our study lakes showed notable changes in cladoceran assemblages between present-day and preindustrial times, but we did not detect any regional patterns of directional changes in Cladocera assemblages and diversity indices. From this, we infer that site-specific limnological characteristics are important drivers of Cladocera assemblage changes in Yellowknife lakes, perhaps modulating lake responses to regional stressors like climate warming and metal contamination. Grace Lake, Frame Lake, and Jackfish Lake, all located within the City of Yellowknife, exhibited the greatest dissimilarity in cladoceran assemblages between present-day and pre-industrial times, although species-specific changes differed between the three lakes. For example, Grace Lake experienced a decline in Daphnia longispina coincident with increases in Bosmina, while Jackfish Lake showed the opposite trend.

In Grace Lake, nutrient enrichment from increased urbanization has been inferred from subfossil diatom assemblages analyzed in a sediment core (Sivarajah et al., 2020). Gianuca et al. (2018) examined taxonomic, functional and phylogenetic metacommunity ecology of Cladocera across an urbanization gradient and found that species of the Daphniidae family are negatively associated with urbanization, but positively associated with phosphorus. Jackfish Lake has experienced water quality problems associated with algal blooms in recent years possibly linked to high phosphorus concentrations (Mackenzie Valley Land & Water Board, 2015). An ecological shift from Daphnia to Bosmina has been linked to the combined stressors of eutrophication, climate warming, and increases in cyanobacteria blooms that can negatively impact Daphnia (Li et al., 2016); however, despite documented algal blooms, Daphnia have increased in Jackfish Lake while Bosmina have decreased. This

shift from *Bosmina* to *Daphnia* occurred at the onset of mining, and it is therefore possible that it was driven by metal(loid) pollution (Sivarajah, 2020).

Frame Lake has also been subjected to multiple stressors associated with urbanization, including nutrient enrichment from urban runoff and sewage seepage, compounded by high arsenic concentrations in the sediments linked to Giant Mine emissions (Dirszowsky & Wilson, 2016; Gavel et al., 2018). Winter fish kills in Frame Lake are becoming more common as a result of high biological oxygen demand in the sediments, which contributes to dysoxic conditions under the ice when the lake is sealed off from atmospheric oxygen inputs (Gavel et al., 2018). In our study, we observed an increase in C. brevilabris/ biovatus in Frame Lake since pre-industrial times, with corresponding decreases in A. circumfimbriata, A. guttata and A. affinis. Bosmina were absent in both the surface and pre-industrial sediments. Chydorus (Leach, 1816) are known to be tolerant of eutrophication, as well as urbanization and pollution more generally (Bartoli et al., 2018; Gianuca et al., 2018).

Subarctic freshwater ecosystems, such as those in Yellowknife, are particularly susceptible to limnological changes associated with climate warming (Vincent et al., 2012). In the northern hemisphere, widespread shifts in diatom assemblages towards assemblages dominated by the planktonic, cylotelloid taxa of the Discostella stelligera (Cleve & Grunow)/ Discotella pseudostelligera [(Hustedt) Houk and Klee, 1939] complex have been attributed to stronger lake thermal stratification and a longer ice-free season (Rühland et al., 2003, 2008; Rühland & Smol, 2005; Rühland et al., 2015). In Yellowknife, high resolution examination of the diatom record from Grace and Alexie lakes by Sivarajah et al. (2020) found increases in D. stelligera coincident with the warmest years noted for the region, despite metalloid pollution from mining. The authors posited that this may have occurred due to stronger thermal stratification and the increase in the ice-free period giving a competitive advantage to taxa like D. stelligera.

The responses of Cladocera to climate warming are comparatively less understood and characterized. Increases in *Bosmina* in subarctic lakes of northwest Finland have been attributed to regional climate warming (Leppänen et al., 2017), while Thienpont et al. (2015) suggested that climate warming in western Arctic lakes triggered shifts from generalist taxa (e.g. *C. brevilabris*, *A. circumfimbriata*) to specialized planktonic (*Bosmina*), and littoral/benthic taxa such as the mud-dwelling *Leydigia leydigi* (Leydig, 1860). In our Yellowknife lakes, we did not observe significant regional, directional changes in Cladocera assemblages that would suggest that climate warming on its own is a strong driver of Cladocera changes since pre-industrial times. These relatively muted changes in cladoceran assemblages compared to diatom changes are consistent with findings from other Arctic and subarctic regions within Canada (Sweetman et al., 2008; Rühland et al., 2014; Jeziorski et al., 2015).

Conclusions and Future Directions

Our top-bottom paleolimnological analyses provided evidence of Cladocera assemblage changes in several lakes, but we observed no regional, directional changes. As such, assemblages in Yellowknife did not appear to show consistent responses to the regional external forcing factors of climate change, urbanization and mining, despite significant changes noted for diatom taxa in similar regions. Lake-specific limnological factors and the influence of multiple stressors likely underlay the lack of consistent regional response. It is notable that the lakes that experienced the greatest magnitude of change in Cladocera assemblages are not those most impacted by mining emissions, but those located directly within the City of Yellowknife that are impacted by multiple stressors.

The most notable trend in Cladocera assemblages associated with lake [As] was a positive correlation between species richness and diversity along an arsenic gradient of 1.5 to 117 µg/l. This correlation was driven mainly by littoral/benthic taxa, potentially attributed to conditions in the benthic/littoral zone that buffer the effects of arsenic contamination on these taxa, and the fact that shallow lakes typically have higher arsenic concentrations. Traditional laboratory bioassays focus on arsenic effects to one or a few model organisms, and littoral and benthic taxa are often underrepresented. Furthermore, littoral and benthic taxa are also underrepresented in contemporary surveys of zooplankton assemblages. As such, subfossil remains in sediments, which integrate bioindicators from all lake habitats, are highly effective for investigations on littoral and benthic cladoceran communities because key taxonomic diagnostic features (e.g., headpores) are readily visible on subfossil remains (Frey, 1960), and sediments collected from the centre of a lake integrate the remains of organisms that live throughout the lake in different habitats through sediment focusing (Korhola & Rautio, 2001). Sediment focusing is a process in which lake sediments are moved from shallower zones of a lake to deeper zones by water turbulence (Blais & Kalff, 1995). Therefore, paleo-ecotoxicological approaches (Korosi et al. 2017a, b) are well designed to identify patterns of potential ecotoxicological significance in these underrepresented groups that can be examined in subsequent studies using diverse methodologies.

Bosmina was absent in highly contaminated lakes, but dominant in many others with lower [As], even very shallow systems. The apparent sensitivity of Bosmina to arsenic has been noted in one traditional lab bioassay but the long-term toxicological responses and sensitivity of Bosmina to arsenic are still poorly understood. The application of modern ecological techniques, such as resurrection ecology studies (Jeppesen et al., 2001) may serve to provide important insights. Additionally, a potential confounding factor to the changes in Yellowknife could be antimony, which increased during the period of mining (Palmer et al., 2015; Cheney et al., 2020) and was highly correlated with arsenic in our PCA. There is a general knowledge gap on the ecotoxicological effects of antimony on Cladocera assemblages, apart from toxicity assays involving Daphnia magna (Kimball, 1978; Waaijers et al., 2013). As such, the extent to which antimony is influencing the assemblages in Yellowknife remains unclear. The relationship between the diversity of lake taxa and arsenic should also be explored in future studies to determine if the positive relationship is limited to Cladocera or extends to other plankton groups.

Top-bottom paleolimnological studies such as ours are effective for providing a snapshot of ecological change across a region, allowing a larger number of lakes to be examined across broader spatial and environmental gradients. To further disentangle the influence of multiple stressors, high-resolution downcore paleolimnological studies in a subset of lakes are required to constrain the timing of notable ecological changes in Frame and Grace Lake. Moreover, at a higher resolution, the change in biological productivity through the calculation of cladoceran fluxes can be achieved. This would provide important information on the impact of metal contamination in the region on zooplankton biomass. Future high-resolution paleolimnological reconstructions of the most heavily arsenic-contaminated lakes outside of the City of Yellowknife (e.g. BC 17 and BC 20) are also needed to confirm our initial assessment of minimal response of cladoceran taxa to arsenic pollution, particularly as some ecological recovery is possible following the implementation of emission restrictions 50 years ago.

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