Tracking the history of 20th century cultural eutrophication in High Arctic waterbodies

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Abstract

Human activities can greatly affect the chemical and biological composition of High Arctic lakes that otherwise receive only sparse inputs from their watersheds and airsheds. Here we present a study of three High Arctic waterbodies in which wastewater from an airport was released over the span of several decades. Using sediment cores from these waterbodies, we reconstructed the history of wastewater inputs using a multiproxy approach consisting of sterols, stanols, metals, and stable isotopes of carbon and nitrogen. This multi-proxy approach showed good concordance between $\delta^{15}N$, coprostanol (a stanol specific to human fecal sources), cholesterol, and cholestanol, which tracked the known history of human wastewater deposition to this High Arctic environment. Concentrations of plant derived sterols, such as campesterol and sitosterol, increased at the time of wastewater input, presumably due to increased plant growth stimulated by wastewater nutrients. Metal(loid)s normalized to titanium showed copper and lead tracked the input of wastewater into R-12, while arsenic, cadmium, chromium, nickel, and zinc increased more than 15 years after the onset of wastewater input. These results demonstrated the ability of sterols and stanols to reconstruct the historical presence of humans in High Arctic locations within the last 80 years and provided compelling evidence that these paleolimnological approaches may be used to track occupation of Arctic peoples beyond the last century.

Keywords: paleolimnology, sterols, metals, sewage, isotopes

1. Introduction

Eutrophication of waterbodies occurs from the presence of excess nutrients and can be the result of both natural and anthropogenic activity. The addition of untreated wastewater to inland lakes often results in signs of eutrophication and can lead to elevated concentrations of phosphorus in Arctic lake sediments (Dauvalter and Kashulin, 2018). Northern communities often lack sewage treatment facilities and thus wastewater is more commonly discharged directly into nearby waterbodies. Signs of eutrophication may not be evident due to short growing seasons; however, chemical and biological changes have been observed in water and sediments. For example, sewage waste can increase the concentration of heavy metals such as cadmium, lead, mercury, and thallium in Arctic lake sediments (Antoniades et al., 2011; Michelutti et al., 2007), increase nutrient availability as evidenced by increases in carbon and nitrogen in lake water (Schindler et al., 1974), and can lead to increased primary productivity (Schindler et al., 1974), which alters chironomid and diatom communities (Schindler et al., 1974; Stewart et al., 2018). Cadmium, chromium, copper, lead, and zinc peaked in lake sediments from Antarctica as a result of sewage input (Bueno et al., 2018b; Santos et al., 2005). The flux of lead, cadmium, and mercury to sediments also increased in Annak Lake, Belcher Island, Nunavut, Canada, coeval with sewage input (Michelutti et al., 2007).

In Resolute Bay, Cornwallis Island, Nunavut, Canada, there is a series of waterbodies that received sewage for decades: R-12 and R-13 (both ponds), and Meretta Lake. In 1949, the Department of Transport Airport Base was established, housing an average of 150 permanent

residents. From 1949 to 1979, raw sewage was released from the base through two utilidors into nearby waterbodies. A main utilidor ran 1.6 km, depositing sewage into several waterbodies, including R-12 and R-13, with a final destination of Meretta Lake. A second utilidor ran through a series of waterbodies, also ending its route in Meretta Lake. In the 1970s, the permanent population at the Airport Base more than halved (averaging 65 people), at which time the major utilidor carrying sewage was dismantled, leaving only one utilidor that deposited sewage directly into Meretta Lake. In 1998, the remaining utilidor was closed owing to the construction of a new airport.

The limnology of these waterbodies was studied as part of the International Biological Program (IBP) (Antoniades et al., 2011; Douglas and Smol, 2000); providing the unique opportunity to examine human impacts on waterbodies in the High Arctic. Meretta Lake was historically defined as an oligotrophic lake owing to low nutrient availability and few ice-free days (Antoniades et al., 2011; Smol and Douglas, 2007). However, following the addition of sewage wastewater in 1949, the lake quickly became eutrophic as evidenced by increased phytoplankton and chlorophyll *a* (chl *a*) concentrations (Kalff and Welch, 1974; Schindler et al., 1974). Biological changes have also been documented in sediment cores from these wastewater-receiving waterbodies. For example, shifts in the bacterial composition in Meretta Lake sediments (Antoniades et al., 2011) and changes in the diatom assemblages in Meretta Lake, R-12, and R-13 (Douglas and Smol, 2000; Stewart et al., 2014) have been shown to track the history of wastewater inputs.

There is some evidence that High Arctic lakes are able to recover from human-induced eutrophication. For example, the diatom assemblage in Meretta Lake recovered to pre-wastewater conditions as indicated by a decrease in the concentration of diatoms following a

reduction in wastewater input; sewage-associated metals, such as cadmium, also decreased as a result of a reduction in wastewater input (Antoniades et al., 2011). Furthermore, the diatom assemblage in Meretta Lake sediments deposited post-1990 is returning to pre-impact sediment assemblages (Michelutti et al., 2002) and total phosphorus and chl *a* concentrations in lake sediments in the 1990s are lower than those recorded for the IBP in 1968 (Douglas and Smol, 2000).

Sterols and stanols are a powerful and source-specific proxy that can be used to track the onset and termination of human wastewater input in this High Arctic environment. There is a growing interest in sterols and stanols for paleolimnological studies as they can offer more detail in reconstructing historical conditions. Sterols and stanols are a subgroup of steroids, present in varying concentrations and proportions in all eukaryotes. Sterols and stanols can be divided into two categories: phytosterol (naturally occurring sterols and stanols in plant cell membranes) and zoosterols (naturally occurring sterols and stanols in animals). Sterols and stanols are relatively stable within cold aquatic environments, and thus any change in their composition or abundance in a lake system, should be preserved within lake sediments (Leeming et al., 2015, 1997). Consequently, sterols and stanols can function as biomarkers of human presence as the specificity of the sterol composition in vegetation and animals can be used to reconstruct long-term trends in waterbody sediments.

Zoosterols, such as coprostanol, cholesterol, and cholestanol, are more source specific than stable isotopes and thus are frequently used to track sewage in lake sediments (e.g. Bull et al. 2003; Walker et al. 1982; Zocatelli et al. 2017). For example, coprostanol is produced in the gut of higher mammals and is typically ten-times more concentrated in humans relative to other animals (Leeming et al., 1996; Shah et al., 2007). As a result, coprostanol has been effectively

used to track the presence of human sewage in the New York Bight (Hatcher and McGillivary, 1979), Arctic lake sediments (Stewart et al., 2018), and Antarctic lake sediments (Tort et al., 2017). While coprostanol is the major component of human faeces (57 % of total sterols), cholesterol is also present in elevated concentrations; this differs from other omnivores and carnivores, where concentrations of cholesterol exceed those of coprostanol (Leeming et al., 1996; Prost et al., 2017). Cholestanol is formed from the microbial reduction of cholesterol (Leeming et al., 1996) and low, but detectable concentrations of cholestanol are also found in human faeces: 70 μg g^{-1} dry weight (dw); 1.4 % of total sterols (Leeming et al., 1996; Sánez et al., 2017). Thus, higher concentrations of cholestanol are commonly found in lake sediments as a result of sewage input (Nishimura, 1978; Sánez et al., 2017).

Common phytosterols include campesterol, sitosterol, and stigmastanol. Vegetation is typically abundant in sitosterol (Behmer and Nes, 2003; Cheng et al., 2016; Pereira et al., 2017); for example, sitosterol makes up ~40 – 70 % of the sterol composition in High Arctic plants and mosses (Cheng et al., 2016). Stigmastanol is produced by the microbial reduction of sitosterol in high trophic level mammals; as a result, stigmastanol is found in herbivore faeces (Leeming et al., 1996). When combined, sitosterols and stigmastanols account for 64 – 89 % of all sterols in herbivore faeces, with sitosterol being the dominant of the two sterols (Leeming et al., 1996; Prost et al., 2017). Stigmastanol concentrations in lake sediments have been correlated to manure inputs from herbivorous animals such as cows and sheep (Vane et al., 2010), and an increase in the concentration of sitosterol was observed in Niven Lake (Yellowknife, Northwest Territories, Canada) in response to sewage dumping (Stewart et al., 2018). Campesterol is also commonly found in higher plants as well as in small concentrations in algae, relative to sitosterol and stigmastanol (Patterson, 1994; Pereira et al., 2017). Consequently, campesterol has been used as

an indicator of terrestrial organic matter deposition in estuarine mangrove sediments (Ranjan et al., 2015).

The objective of this study was to reconstruct the history of sewage dumping using sterols and stanols in three High Arctic waterbodies (Meretta Lake, R-12, and R-13, Fig 1) and determine the extent to which these proxies persisted following the cessation of wastewater input. We compared the chemical profiles in sewage-influenced waterbodies to a nearby reference pond (Little Char) in order to differentiate between sewage impacted and unimpacted systems. Dated sediment cores from ponds with a known history of sewage dumping provided the opportunity to test explicit hypotheses about the ability of sterols and stanols to track human fecal contamination of surface waters. We thus aimed to answer the following research questions: (1) Is the sterol and stanol composition in wastewater-influenced sediments different from uninfluenced sediments? We hypothesized that sterols and stanols would be more concentrated in sediments receiving wastewater discharge than in uninfluenced sediments. (2) Does the sterol and stanol composition in sediments change during the period of wastewater discharge? We hypothesized that sterols and stanols would increase during the known period of wastewater input based on ^{210}Pb dating. (3) Are stanols (coprostanol and epicoprostanol) specific to human waste and thus do they track wastewater discharge in sediments? We hypothesized that coprostanol and epicoprostanol would increase in wastewater-influenced sediments and this increase would be absent in the reference pond, which did not receive wastewater. This project aimed to better understand historical changes in the chemistry of remote Arctic waterbodies and to relate those changes to human activity.

2. Methods

2.1 Site description

Little Char (located in Resolute Bay, Cornwallis Island, Nunavut, Canada) is so named as it is a small offshoot of nearby Char Lake (Fig 1, Table S1). While there are no records of sewage dumping into Little Char, sediments from the catchment of the inflow stream of Char Lake were used to construct an airstrip into the drainage basin from 1969 – 1972 (Michelutti et al., 2003). Beginning in 1975, Char Lake was used as a source of drinking water. Meretta Lake, R-12, and R-13 (Fig 1, Table S1) were selected as the wastewater-influenced sites as their chemistry and biology are already well-documented, thus allowing for a more in depth paleolimnological analysis. All field sample collections were performed in July 2017, under the Nunavut Research Institute Scientific Research License # 02 025 17N-A issued to JMB.

2.2 Water, periphyton, and zooplankton sampling

We compared the chemical composition of near-shore surface water samples in wastewater-influenced waterbodies to the chemical composition of a water sample from a reference pond to determine if influenced waterbodies recovered following the cessation of wastewater input. Electrical conductivity and pH were measured using a YSI meter (model 85, YSI Incorporated). Water bottles were pre-rinsed using 10 % HNO_3 for total metal concentrations. We used 10 % H_2SO_4 to pre-rinse Nalgene bottles for total phosphorus (TP), total dissolved phosphorus (TDP), total dissolved nitrogen (TDN), dissolved organic carbon (DOC), and dissolved inorganic carbon (DIC). Water samples for DOC were filtered through a Sartorious acetate filter (47 mm, 0.45 µm) and stored at 4°C. Water samples for particulate organic carbon (POC) were filtered through a Whatman glass microfiber filter (GF/F) (47 mm,

0.45 µm); the filter was frozen until analysis. All water chemistry data were analyzed by the National Laboratory for Environmental Testing (Burlington, Ontario, Canada).

We also examined the sterol and stanol profiles in zooplankton and periphyton to determine how these potential sources may have affected the sediment sterol and stanol composition. Near-shore periphyton was collected and stored at 4°C until they were sieved (125 µm) and filtered through a pre-heated (3 hours at 400°C) 110 mm Whatman GF/F (42.5 mm, 0.7 µm). Periphyton samples were air-dried and then homogenized. Near-shore zooplankton samples were collected using a 200 µm net; zooplankton samples were stored frozen and ultimately freeze-dried for analysis.

2.3 Sediment core collection

We collected a sediment core from the centre of each waterbody to determine if sterols, stanols, stable isotopes, and metal profiles in waterbody sediments tracked the introduction and cessation of wastewater input into High Arctic waterbodies. The maximum depth of Meretta Lake was determined by bathymetric map while the maximum depth of the remaining ponds was determined visually upon arrival at the site. Sediment cores were collected from the deepest part of each lake, either using a UWITEC© gravity corer (Uwitec, Mondsee, Austria) or a push corer in the shallower ponds (R-12, R-13, and Little Char) (Glew and Smol, 2016). We sectioned sediments into 0.5 cm intervals using a Glew extruder (Glew, 1988) and froze the sediments at -4°C.

Sedimentation rates and ^{210}Pb activity can be low in Arctic lakes, which can affect the accuracy and precision of ^{210}Pb dating (Douglas and Smol, 2000). Therefore, we explored two methods of ^{210}Pb dating (alpha and gamma counting). Alpha counting offers the advantage of

better sensitivity, accuracy, and precision in ^{210}Pb measurements; however, it is a destructive method, meaning extracted sediments cannot be recovered for other analyses. ^{210}Pb measurements by gamma counting are non-destructive. Consequently, we selected a single core (Meretta Lake) to ^{210}Pb date by alpha counting to determine whether there was sufficient ^{210}Pb activity to use gamma counting on the remaining ponds. Alpha counting was conducted at MyCore Scientific using a ^{209}Po tracer (0.839 Bq g^{-1}); background ^{210}Pb was set to 0.030 Bq g^{-1}. Sufficient excess ^{210}Pb activity was present for gamma counting, so cores from the remaining three ponds were dated using an Ortec High Purity Germanium Gamma Spectrometer (Oak Ridge, TN, USA) at the University of Ottawa. Efficiency corrections were made using Certified Reference Materials from International Atomic Energy Association (Vienna, Austria). Sediment chronologies were calculated from ^{210}Pb and ^{137}Cs profiles with the Constant Rate of Supply (CRS) model using ScienTissiMe (Barry's Bay, Ontario, Canada).

Freeze-dried sediments were analyzed for percent carbon and nitrogen using a Micro Cube elemental analyzer at the Ján Veizer Stable Isotope Laboratory (formerly G.G. Hatch SIL Laboratory), located at the University of Ottawa, Ontario, Canada. A subsample of sediments was acidified by repeatedly adding 6N HCl to the sample and oven-heating the sample for 20 minutes until no effervescence was observed for two consecutive acid additions. The volume of acid added increased from 10 – 50 µL and the oven temperature increased from 40 – 60°C over the course of the repetitions. Acidified samples were analyzed for organic δ^{13}C (‰ V-PDB), hereafter, referred to as δ^{13}C, and unacidified samples were analyzed for δ^{15}N (‰ air). The analyses were run separately using an elemental analyzer interfaced to an isotope ratio mass spectrometer at the Ján Veizer Stable Isotope Laboratory. Values were normalized to several internal standards: C-51 Nicotiamide (δ^{15}N: 0.07 ‰, δ^{13}C: -22.95 ‰), C-52 ammonium sulphate

and sucrose ($\delta^{15}N$: 16.58 ‰, $\delta^{13}C$: -11.94 ‰), and C-54 caffeine ($\delta^{15}N$: -16.61 ‰, $\delta^{13}C$: -34.46 ‰); the blind standard was C-55 glutamic acid ($\delta^{15}N$: -3.98 ‰, $\delta^{13}C$: -28.53 ‰). Results were reported in delta notation (δ), where δ = ((Rx-Rstd))/Rstd)*1000; R = ratio of the abundance of the heavy to light isotope, x = sample, and std = standard. $\delta^{15}N$ values were calibrated to the following international standards: IAEA-N1 (0.4 ‰), IAEA-N2 (20.3 ‰), USGS-40 (-4.52 ‰), and USGS-41 (47.57 ‰). $\delta^{13}C$ were calibrated to the following international standards: IAEA-CH-6 (-10.4 ‰), NBS-22 (-29.91 ‰), USGS-40 (-26.24 ‰), and USGS-41 (37.76 ‰). Analytical precision was ± 0.2 ‰ using glutamic acid. Zooplankton and periphyton samples were analyzed following the same protocol, except zooplankton samples were not acidified owing to low sample weight and the absence of carbonates.

We analyzed the sediment cores from R-12 and Little Char for total metals using approximately 0.5 g dw from each interval. Samples were submitted to SGS Minerals Services, Lakefield ON, Canada for analysis. Metal concentrations were determined using an aqua regia digestion and analyzed using inductively coupled plasma mass spectrometry. Concentrations below the method detection limit (MDL) were replaced with $MDL/\sqrt{2}$. The concentration of each metal was then normalized to the concentration of titanium in order to account for natural weathering (Boës et al., 2011; Last and Smol, 2001).

Sterol and stanol concentrations were determined in the periphyton and sediment cores using methods modified from Birk et al. (2011) and Cheng et al. (2016). 10 mL of dichloromethane (DCM) (high-grade Optima® brand) was added to 0.1 g of copper (Fisher C434-500, laboratory grade copper powder; CAS 7440-50-8) in a glass scintillation vial, sonicated for 10 minutes, and subsequently removed. This process was repeated twice more; the copper then air-dried. 0.1 g of freeze-dried material and 50 µL of 10,000 ng mL^{-1} deuterated

cholesterol (d6 cholesterol) was added to the copper. For blanks, d6 cholesterol was spiked directly into the copper. The samples were left for 12 hours at 4°C. To extract the sterols from the sediments, 10 mL of DCM was added, and the samples were sonicated for 10 minutes, and the DCM pipetted into pre-solvent washed Turbovap tubes. This process was repeated twice more to improve extraction efficiency. Samples were then evaporated to 1 mL at 23°C under a gentle stream of nitrogen. 1 g LC-Si SPE columns (Sigma-Aldrich, Oakville, ON, Canada), were conditioned with 6 mL of DCM; this DCM was discarded. The 1 mL sample was transferred to the SPE column and the Turbovap tube was rinsed three times using 0.4 mL DCM. The sample and an additional 20 mL of DCM was eluted into a pre-solvent washed Turbovap tube. The sample was again evaporated to 1 mL at 23°C under a gentle stream of nitrogen and transferred to a gas chromatography (GC) vial. The sample was then evaporated to dryness under nitrogen and reconstituted in 1 mL of DCM. A 10x dilution was created by transferring 100 µL of the stock sample to a new GC vial and evaporating to dryness. 100 µL of 99 % N,O-bis(trimethylsilyl)trifluoroacetamide) + 1 % trimethylchlorosilane was added and the sample was heated for two hours at 60°C. 0.9 mL of toluene (high-grade (Optima® brand)) and 10 µL, 10,000 ng mL^{-1} of p-terphenyl-d_{14} (Cambridge Isotope Laboratories, Tewksbury, MA, USA) were added to the sample. Samples were analyzed using an Agilent 6890 gas chromatograph – 5973 mass selective detector in electron impact, selected ion monitoring mode (Agilent 19091J-433 HP-5 5 % phenyl methyl siloxane 29.8 m x 250 µm x 0.25 µm column). Analytical conditions include: a pulsed splitless injection at 250°C at 16.26 psi, DB-5MS (Agilent, Santa Clara, CA, USA), oven start at 150°C, ramp 1 at 8°C $minute^{-1}$ to 250°C, ramp 2 at 12°C $minute^{-1}$ to 300°C held for 12 minutes. Mass selective conditions as follows: transfer line 280°C, source 230°C, quad 150°C. Sterol and stanol concentrations were volume corrected to p-terphenyl-d_{14}

using MSD ChemStation D.02.00.275. Samples were analyzed using additional dilutions, as required. Zooplankton sterols were extracted following the same protocol, except no d6 cholesterol was added.

Eleven sterols and stanols were measured: coprostanol (5β-cholestan-3β-ol), epicoprostanol (5β-cholestan-3α-ol), coprostanone (5β-cholestan-3-one), cholesterol (cholest-5-en-3β-ol), cholestanol (5α-cholestan-3β-ol), cholestanone (5α-cholestan-3-one), campesterol (campest-5-en-3β-ol), desmosterol (3β-cholesta-5,24-dien-3-ol), fucosterol (stigmasta-5,24-dien-3β-ol), sitosterol (β-sitosterol), and stigmastanol (5α-stigmastano-3β-ol). Concentrations were interpreted using a limit of quantification set to a signal to noise ratio of three. The sterol and stanol concentrations in each sample were recovery corrected to the concentration of d6 cholesterol (Table S2). Sterol and stanol concentrations below the MDL were corrected to the MDL divided by root two (Table S3). MDLs were calculated using a five-point calibration curve in triplicate. Sitosterol and stigmastanol are larger compounds that do not ionize as well as smaller compounds, and thus their MDLs were greater. The sterol and stanol concentrations in the blank were subtracted from the sterol and stanol concentrations in the sample. All concentrations were normalized to the dry sample weight. Concentrations were normalized to the percent organic carbon, when applicable. All data handling was conducted using R statistical computing environment (v3.5.2).

3. Results

3.1 Dating profiles

Meretta Lake was dated to the year 1873 (at 7.25 cm) using alpha counting with the majority of excess ^{210}Pb lost by 5 cm below the sediment surface. Excess ^{210}Pb activity in R-12

reached background (based on ^{214}Pb activity) at 8.75 cm, which was dated to an age of 1909 CE (Fig S1). Peak ^{137}Cs activity, representing the year 1963 in accordance with the height of above-ground nuclear weapons testing, closely corroborated the CRS dates. Excess ^{210}Pb activity in R-13 reached background by 3.75 cm (2.75 cm = 1956 CE); peak ^{137}Cs activity was recorded at 1.75 cm and thus closely matched the ^{210}Pb dating profile. In Little Char, ^{210}Pb activity reached background by 5.75 cm (4.75 cm = 1949 CE); ^{137}Cs corroborates this dating profile, as peak activity occurred at 4.75 cm.

3.2 Sterols in sediments, periphyton, and zooplankton

Sterol and stanol profiles in the sediment cores are presented in Figs 2 and 3, and summary concentrations are presented in Table S4 (μg g^{-1} organic carbon (OC) dw) and Table S5 (μg g^{-1} dw). The maximum cholesterol concentration was observed in R-12 at the CRS date of 1998 (416 μg g^{-1} OC dw), coincident with peaks in δ^{15}N and δ^{13}C values (Fig 2). Concentrations of coprostanol, cholestanol, campesterol, and sitosterol also increased during the period of sewage dumping, though appeared to lag beyond the time that effluents were released to this environment. In R-12, percent organic carbon increased after wastewater input stopped (Fig 2). The sterol, stanol, and percent organic carbon profiles in R-13 were similar to those observed in R-12, although to a lesser magnitude (Fig 3). Sterol and stanol concentrations and percent organic carbon in Meretta Lake sediments increased in 1949 at the onset of sewage dumping, but unlike R-12 and R-13, the sterol and stanol concentrations did not decrease in more recently deposited lake sediments. Sterol and stanol concentrations in R-12 generally exceeded those found in R-13 and Meretta Lake. δ^{15}N increased coeval with wastewater inputs in R-12 but were relatively constant in R-13 and Meretta Lake (Figs 2 and 3). In both R-13 and Meretta Lake,

$\delta^{15}N$ values did not increase at the time of wastewater inputs and $\delta^{15}N$ values in R-13 were more variable (2.3 – 5.0 ‰) than the $\delta^{15}N$ values observed in Meretta Lake (4.0 – 5.6 ‰) (Table S6). $\delta^{13}C$ values increased slightly over the timing of wastewater inputs in R-12 and Meretta Lake, increasing by 2 ‰ and 1 ‰, respectively. Conversely, $\delta^{13}C$ did not increase at the time of wastewater emissions to R-13.

Sterol and stanol concentrations in sediments from the reference pond, Little Char, were always lower than the concentrations recorded in the wastewater-influenced waterbodies (Figs 2 and 3). For example, the maximum concentration of any sterol and stanol observed in sediments from Little Char was stigmastanol at 14.0 μg g^{-1} OC dw versus a maximum of 253 μg g^{-1} OC dw cholesterol in Meretta Lake, 416 μg g^{-1} OC dw cholesterol in R-12, and 36.6 μg g^{-1} OC dw cholesterol in R-13 (Table S4). Percent organic carbon increased in more recently deposited sediments (2.2 – 5.2 %), but the increase was much lower than that observed in wastewater-influenced waterbodies (e.g. 18 – 41.9 % in R-12) (Table S7).

The principle component analyses (PCAs) presented in Figs 4 and S2 show the inter-relatedness of sterols and stanols in sediment through time. In R-12, 89 % of the total variance in the sterol and stanol concentrations in sediment was explained by the first two axes. Coprostanol and epicoprostanol drove the shift in the sterol and stanol composition starting in 1949, corresponding to the onset of wastewater emissions in R-12 (Fig 4). Cholesterol, campesterol, and sitosterol also contributed to the change in the sterol and stanol composition. Recently deposited sediments appeared to return to a composition similar to pre-impact sediments, as evidenced by the reversal in direction along the x axis. The PCA for R-13 was very similar to that of R-12, with 78 % of the variation explained by the first two axes (Fig S2). In Meretta Lake sediments, coprostanol, cholesterol, campesterol, and sitosterol also drove much of the variation

along the first two axes (96.6 % variance explained) (Fig S2). There was a clear shift from the pre-wastewater sterol and stanol composition to the present-day sterol and stanol composition. Unlike R-12 and R-13, sterol and stanol concentrations in Meretta Lake continued to increase even after wastewater input stopped. In Little Char, campesterol, sitosterol, and cholesterol explained little of the variation in the sterol and stanol composition down-core, and while coprostanol drove the composition in more recently deposited sediments, coprostanol only explained 9.5 % of the variation along axis 2 (which represented sediments deposited in the 20th century).

We also looked at the concentration of sterols and stanols in periphyton and zooplankton in order to determine if primary producers and consumers had higher concentrations of sterols and stanols relative to those in uninfluenced waterbodies. We were unable to collect sufficient zooplankton biomass to analyze for sterols and stanols in the reference pond, Little Char, and as a result, we only presented the sterol and stanol concentrations in zooplankton from the wastewater-influenced waterbodies. The concentration of sterols and stanols in zooplankton and sediments were generally similar (Table S5 and Fig S3) with a few exceptions: the concentration of cholesterol was approximately three and five-fold greater in zooplankton than in sediments from Meretta Lake and R-13, respectively. Similarly, the concentration of sitosterol was three to five-fold greater in zooplankton than in sediments from wastewater-influenced waterbodies. Stigmastanol was also more concentrated in zooplankton than in sediments from R-12 and R-13. The maximum concentration of any sterol and stanol in zooplankton was always greater than that in periphyton, with the exception of coprostanol in Meretta Lake. The sterol and stanol concentrations in periphyton from the sewage water receiving waterbodies was generally greater than the sterols and stanol concentrations in periphyton from the reference pond, Little Char,

with the following exceptions: the concentration of campesterol, cholesterol, and sitosterol in Little Char exceeded the concentration in R-13 and the concentration of coprostanol in Little Char exceeded the concentration in Meretta Lake (Fig S3). Periphyton was largely composed of cholesterol and sitosterol, followed by campesterol and stigmastanol; periphyton were very low in coprostanol and cholestanol.

3.3 Metal profiles in sediment cores

The proportion of copper and lead increased in R-12 sediments in 1949, the start of wastewater input; the remaining metals, (with the exception of vanadium, which was constant through time), increased more than a decade after the onset of wastewater input (Fig 5). The proportion of zinc and copper were approximately four and eight-fold, respectively, greater following wastewater input. The proportion of all metals were relatively low and stable throughout sediments in Little Char; for example, the maximum ratio of all the examined metals was 0.12 for zinc (Table S8). The concentration of metals in sediments from Little Char were also low, with maximum values ranging from 0.26 μg g^{-1} dw of cadmium to 33 μg g^{-1} dw for zinc (Table S9). Conversely, metal concentrations were generally greater in R-12, with maximum values ranging from 0.72 to μg g^{-1} dw of cadmium to 340 μg g^{-1} dw of copper.

4. Discussion

4.1 Using stable isotopes to reconstruct wastewater deposition in High Arctic waterbodies

$\delta^{15}N$ increased in R-12 coeval with sewage input, thus reflecting the elevated $\delta^{15}N$ signal commonly found in human faeces (Fig 2). Similar results were observed in sewage-receiving freshwater systems, were $\delta^{15}N$ increased to values of ~10 ‰ (Bueno et al., 2018a; Vane et al.,

2010). $\delta^{15}N$ remained relatively low and stable in both R-13 and Meretta Lake. The causes of low $\delta^{15}N$ values in sewage-affected lake sediments were well described by Vane et al. (2010). In short, $\delta^{15}N$ values varied widely depending on their source, for example: while higher trophic level mammals were enriched in $\delta^{15}N$, nitrogen-fixing algae can have $\delta^{15}N$ values closer to 0 ‰ (Cole et al., 2004). In fact, $\delta^{15}N$ values in raw sewage can be less than 3 ‰ (Cabral et al., 2019). While these factors may have contributed to the low and stable $\delta^{15}N$ values in sediments from R-13, the concentration of coprostanol was also low (relative to R-12), which suggests this pond may not have deposited as much of the sewage-derived suspended matter to its sediments as R-12. The very stable $\delta^{15}N$ profile in Meretta Lake was unexpected, as a previously constructed $\delta^{15}N$ profile in Meretta Lake sediments saw an increase in $\delta^{15}N$ over time of ~6 ‰ at the onset of sewage input (Antoniades et al., 2011). The difference in the $\delta^{15}N$ profiles may be attributed to differences in coring locations owing to Meretta Lake's large basin.

The range in $\delta^{13}C$ values were similar between waterbodies (Table S10). $\delta^{13}C$ values increased following wastewater input in R-12 to a maximum of -25.2 ‰ and then decreased to background values after sewage input stopped. Similarly, $\delta^{13}C$ values were relatively constant in Meretta Lake sediments and then increased to -24.21 ‰ during the period of wastewater input. This is in agreement with $\delta^{13}C$ profiles from other sewage-affected lake sediments, ranging from -26 ‰ to -22 ‰ (Andrews et al., 1999; Barros et al., 2010; Bueno et al., 2018a). In R-13, $\delta^{13}C$ values generally decreased in more recently deposited pond sediments, reaching a minimum value of -26.7 ‰. This is likely explained by a greater input of terrestrial Arctic vegetation, which typically has depleted $\delta^{13}C$ values relative to autochthonous primary producers (Choy et al., 2010; Skrzypek et al., 2008; Zibulski et al., 2017). Notably, there were two periods of increased $\delta^{13}C$, where $\delta^{13}C$ values increased by ~1 ‰ relative to the $\delta^{13}C$ values deposited before

and after. The variation in $\delta^{13}C$ values may be explained by the different $\delta^{13}C$ values reported for different Arctic vegetation; for example: sedges (-28.9 ‰), mosses (-22.5 to -37.0 ‰), lichen (-19.2 to -27.5 ‰), and saxifrage (-30.7 to -23.3 ‰) (Choy et al., 2010; Skrzypek et al., 2008; Zibulski et al., 2017). Consequently, the two small peaks in $\delta^{13}C$ values may reflect a greater input of low $\delta^{13}C$ mosses relative to sedges at that time. Similar trends were observed in sewage-influenced lake sediments from South America, where $\delta^{13}C$ values were variable over the period of sewage input (Cabral et al., 2019).

4.2 Reconstructing the history of wastewater discharge using zoosterols

Sterols and stanols are useful tools for reconstructing historical trends in lake sediments as they can often be linked to specific sources (Bull et al., 2002; Leeming et al., 1998, 1996; Pereira et al., 2017). Coprostanol has been used for sewage identification in environmental samples as far back as the 1980s and earlier (e.g. Vivian 1986 and references therein). In this study, we observed an increase in coprostanol coincident with wastewater input into the High Arctic waterbodies (Figs 2 and 3). The sediment concentrations at the study sites were at least two-fold lower than those observed in the other sewage-influenced sediments: for example, the concentration of coprostanol peaked at 252 μg g^{-1} OC in lake sediments from Manitoba, Ontario, Canada as a result of sewage input (Tse et al., 2014). Similarly, the concentration of coprostanol was 150 μg g^{-1} OC in surface sediments of an Antarctic stream as a result of sewage input (Tort et al., 2017). Coprostanol in sediments from Guanabara Bay, Brazil, reached 1,400 μg g^{-1} OC as a result of sewage input (Carreira et al., 2004). There was also a nearly 14-fold difference in coprostanol concentrations in R-12, relative to R-13 and Meretta Lake. The greater concentrations of coprostanol recorded in R-12 relative to Meretta Lake may be attributed to the

deposition of sewage *via* the two utilidors into R-12 (and other waterbodies) prior to Meretta Lake; sterols, bound to particulate matter, would be largely deposited before reaching Meretta Lake. Furthermore, Meretta Lake is ~82 times larger than R-12 and therefore the sterol and stanol signal would have been diluted to a much larger area in Meretta Lake. R-13, however, is nearly the same size as R-12, and was the first pond (examined in this study) to receive sewage. The difference in response to the wastewater biomarkers in R-12 and R-13 is likely the result of the higher dating resolution in R-12 (1953 is at 8 cm) relative to R-13 (1956 is at 3.5 cm). Consequently, R-13 likely has more intervals of diluted wastewater input than R-12. Stewart et al. (2014) found that diatoms in R-12 recorded a greater eutrophication impact than R-13, which they also attributed to differences in the dating resolution. The concentration of coprostanol in Little Char, the reference site, was very low throughout the sediment core. The small, but measurable coprostanol concentrations may be explained by *in situ* hydrogenation of cholesterol (Leeming et al., 1996; Nishimura and Koyama, 1977).

Cholesterol and cholestanol concentrations increased coeval with the onset of wastewater emissions into R-12, R-13, and Meretta Lake. As expected, the concentrations of cholesterol and cholestanol decreased in R-12 and R-13 in more recently deposited sediments, however neither the concentration of cholesterol nor cholestanol decreased in post-sewage sediments in Meretta Lake. Conversely, diatom assemblages did change immediately after sewage was stopped from flowing into Meretta Lake (Douglas and Smol, 2000; Michelutti et al., 2002). Although there was no apparent lag in diatom assemblage changes to Meretta Lake following the cessation of sewage inputs, a twenty-year lag in the response of diatoms to sewage input was observed in Annak Lake, Belcher Island, Nunavut, Canada (Michelutti et al., 2007). Similarly, cholesterol concentrations in sediments from Niven Lake, Yellowknife, Northwest Territories, Canada, did

not rise until ~25 years after sewage input had ceased (Stewart et al., 2018). There were no measurable concentrations of cholestanol in Little Char as we also did not measure any cholesterol in the sediments.

Epicoprostanol is a minor component in human faeces (Leeming et al., 1996) so the low, but detectable concentrations of epicoprostanol (maximum of 17.3 μg g^{-1} OC in R-12) in the wastewater-affected waterbodies may have been the result of the sewage itself. For example, sewage-affected lake sediments can be composed of up to 4 % epicoprostanol (compared to 2 % in pre-sewage sediments) (Stewart et al., 2018). Epicoprostanol may also be present in the pond sediments as a result of the aerobic bacterial degradation of coprostanol to epicoprostanol (Battistel et al., 2015). Low concentrations of epicoprostanol can also be indicative of raw sewage (relative to treated sewage) as the prolonged digestion of the sewage allows for greater microbial transformation of cholesterol to epicoprostanol (McCalley et al., 1981). For example, lake sediments from Brazil had low epicoprostanol concentrations (maximum: 2.24 μg g^{-1}), which reflected the input of untreated sewage (Carreira et al., 2004).

In the wastewater-influenced waterbodies, many sterols and stanols peaked after the cessation of wastewater input. Such a lag may have occurred from a slow release of contaminated sediments from the utilidor, or delayed particle settling due to currents or turbulence. This may be particularly true of R-12 and R-13, both small waterbodies, where any current created by wastewater input may have delayed the analytes from settling.

Faecal sterols appeared to be the main driver of the sterol and stanol composition in R-12 sediments from 1949 to 1990, as evidenced by the shift along axis 1 (Fig 4). Similar trends were observed in Meretta Lake and R-13 (Fig S2). The general absence of sterols in pre-sewage sediments was also evident within the PCAs: the sterol composition of pre-wastewater sediments

appeared in a separate quadrant from wastewater-input sediments and the sterol vectors travelled in the opposite direction of pre-wastewater sediments. The change in the sterol composition in R-12 following wastewater input was also traceable within the PCA: from 1990 to 2017, the sediment composition appeared in a separate quadrant from pre- and wastewater-input quadrants, and the sterol vectors extended in the opposite direction.

4.3 Phytosterols in waterbody sediments

In addition to faecal sterols, we examined an array of phytosterols, including campesterol, fucosterol, sitosterol, and stigmastanol. Campesterol is commonly found in vascular plants, as well as in phytoplankton and algae, although at lower concentrations (Pereira et al., 2017). In R-12, R-13, and Meretta Lake, campesterol concentrations increased in sediments at the onset of sewage input (Figs 2 and 3). Campesterol concentrations in this study are comparable to those found in sewage-affected sediments from a lake in northern Manitoba, Canada (peak of ~100 μg g^{-1} OC) (Tse et al., 2014). Fucosterol is abundant in algae (Mouritsen et al., 2017; Patterson, 1994; Pereira et al., 2017) and can be found in concentrations of up to 48.1 μg g^{-1}, more than double that of sitosterol and stigmastanol (Pereira et al., 2017). Accordingly, fucosterol in sediments also tracked sewage input, suggesting an increase in the abundance of algae as a result of the nutrients supplied by wastewater (Figs 2 and 3).

Sitosterol and stigmastanol are found in vegetation and have therefore been used to track the input of terrestrial vegetation in lake sediments (Nishimura, 1978). Sitosterol, in particular, makes up a large percentage of the sterol composition in plants; for example, ~30 – 70 % in High Arctic moss (Cheng et al., 2016). Consequently, sitosterol is also found in high concentrations in herbivore faeces (e.g. 497 μg g^{-1} in sheep) and human faeces (313 μg g^{-1}) (Prost et al., 2017).

Predictably, sitosterol concentrations increased in sediments at the time of wastewater input in R-13 and Meretta Lake (Fig 3), likely as a result of the increased plant growth associated with the presence of wastewater. Sitosterol increased later than the period of wastewater inputs in R-12, suggesting delayed plant growth in that location. Water from Meretta Lake has greater concentrations of several analytes, including TP, POC, DOC, and zinc, relative to Little Char (Table S11). Despite the elevated nutrients available in Meretta Lake, sitosterol was not measurable in periphyton, however sitosterol was present at concentrations in periphyton equal to ~50 % of that in surface sediments from R-12 (Fig S3). The generally low concentration of periphyton in Meretta Lake may be attributed to the low number of rocks located at this site and thus an absence of an adequate environment on which the periphyton can grow.

Stigmastanol, while also present in plants, is found in much lower concentrations than sitosterol; consequently, stigmastanol concentrations in human faeces are ~17 % of that of sitosterol (Prost et al., 2017). This is reflected within the sediments, as the concentration of stigmastanol is about half of that of sitosterol in Meretta Lake and very low in R-12 and R-13 (Table S4). The low, but detectable concentrations of stigmastanol before sewage dumping in Meretta Lake, may be the result of freshwater algae producing stigmastanol under low oxygen conditions (Fahrenfeld, 2008). The concentration of phytosterols in Little Char were consistently low, indicating that this pond was historically low in vegetation and algae. The absence of a nutrient source (such as sewage) would explain the low concentration of sterols, and this is further enforced by the water chemistry: Little Char had lower concentrations of many nutrients, including phosphorus, nitrogen, and OC, which are essential for vegetation growth (Table S11).

4.4 The effect of wastewater on the concentration of sterols in periphyton and zooplankton

We measured the concentration of sterols and stanols in periphyton and zooplankton in order to determine if periphyton and zooplankton from wastewater-influenced waterbodies had greater concentrations of sterols and stanols in primary producers and consumers, relative to unaffected waterbodies. Indeed, there was not enough zooplankton biomass to determine the sterol and stanol concentrations in zooplankton, and the concentration of sterols and stanols in periphyton was generally greater in wastewater-influenced waterbodies relative to the reference pond, Little Char. The only exceptions were the lower concentrations of campesterol, cholesterol, and sitosterol in periphyton from R-13 and the lower concentration of coprostanol in periphyton from Meretta Lake, relative to Little Char (Fig S3).

4.6 Metals show a delayed response to wastewater input

Wastewater can increase the concentration of certain biogenic metals in lake sediments. In particular, cadmium, chromium, lead, and zinc are commonly elevated in sewage-influenced lake sediments (Andrews et al., 1999; Antoniades et al., 2011; Bartkowska et al., 2019; Karthikeyan et al., 2018; Wang et al., 2016). With the exception of copper, metals decreased slightly and subsequently increased to baseline prior to wastewater input. In R-12, arsenic, cadmium, chromium, nickel, and zinc first surpassed background either ~15 years after wastewater input began or increased after wastewater input stopped (Fig 5). A delayed rise in these elements could be due in part to dissolution and diffusion in sediment porewaters (particularly for arsenic; (Pan et al., 2019)) or from sediment resuspension from turbulence or the wastewater discharge itself. Copper and lead increased slowly with wastewater input and peaked after wastewater input stopped. In R-12, cadmium and zinc increased by two and four-fold, respectively, after wastewater input stopped. Similarly, cadmium and zinc increased in sediments

previously collected from Meretta Lake (Antoniades et al., 2011), however the ratio of cadmium and zinc was at least four-times greater in R-12 than that previously observed in Meretta Lake. Similarly, chromium and lead were also more concentrated in wastewater-affected sediments from R-12; a similar rise in chromium and lead was observed in lake sediments from Antarctica (Bueno et al., 2018b). Conversely, metal ratios in the reference pond, Little Char, were generally low and were relatively constant through time. This is expected as there was no wastewater discharge into this pond. Similarly, low concentrations of cadmium and zinc were observed in a reference lake in a study of remote high Arctic lakes (Brimble et al., 2009), and pond sediments before impact by seabird guano (Evenset et al., 2007).

4.7 Tracking the return of lake sediments to pre-wastewater conditions

Sterol and stanol concentrations in sediments increased at the time of wastewater discharge, however unlike R-12 and R-13, sterol and stanol concentrations in Meretta Lake continued to rise in more recently deposited sediments. Wastewater discharge continued into Meretta Lake until 1998, 19 years longer than the discharge into R-12 and R-13, thus resulting in the elevated sterol and stanol concentrations. Furthermore, Meretta Lake is larger than both R-12 and R-13, and thus it may take more time for analytes to settle to the sediment-water interface. This is not the first instance that a delay in the response of a proxy has been observed in Meretta Lake: Michelutti et al. (2007) reported a lag of several decades before diatom assemblages responded to wastewater inputs in Meretta Lake. In this case, these authors attributed this delay to prolonged periods of ice cover, which would have prevented the establishment of new diatom species.

5. Conclusions

We presented a case study that examined sterols, stanols, metals, $\delta^{15}N$, and $\delta^{13}C$ in a multiproxy analysis to reconstruct wastewater input in High Arctic waterbodies. First, this study demonstrated that wastewater-receiving sediments had greater sterol and stanol concentrations than uninfluenced sediments. Second, sterol and stanol profiles in waterbody sediments tracked the introduction and cessation (in the case of R-12 and R-13) of wastewater input whereas sterols and stanols in reference pond sediments remained stable through time. This study found that sterol and stanol concentrations in R-12 and R-13 pond sediments approached pre-wastewater concentrations following the cessation of wastewater input, whereas elevated sterol and stanol concentrations persisted in Meretta Lake, likely due to its larger volume and longer period of wastewater input. Lastly, this study found that coprostanol and epicoprostanol were sensitive wastewater tracers as evidenced by the low to undetectable concentrations in sediments prior to wastewater input and greater concentrations in wastewater-influenced sediments.

This study highlighted the importance of using multiple proxies when studying paleo-archives. We demonstrated that in addition to stable isotopes and metals, sterols and stanols also tracked historical wastewater discharge. Sterols and stanols have the added advantage of being more source specific than stable isotopes and metals, and as such, they provide additional certainty when reconstructing historical environmental conditions. Furthermore, proxies can be influenced by several factors and thus examining multiple proxies allows for a more accurate reconstruction of historical events.

The authors declare no competing interests.

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Figures for

Tracking the history of 20th century cultural eutrophication in High Arctic waterbodies

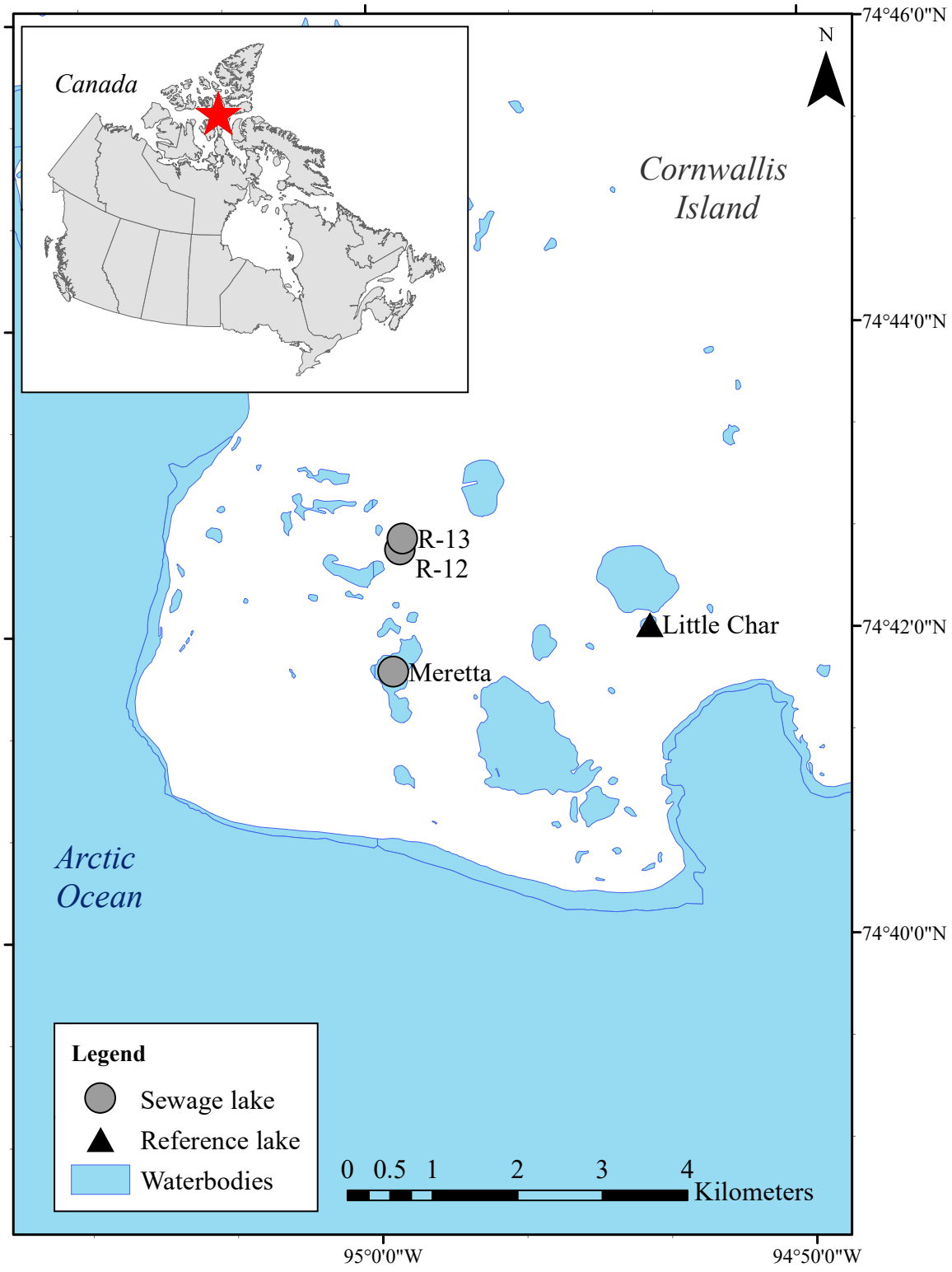

Figure 1: Map of study sites in Resolute Bay, Nunavut, Canada.

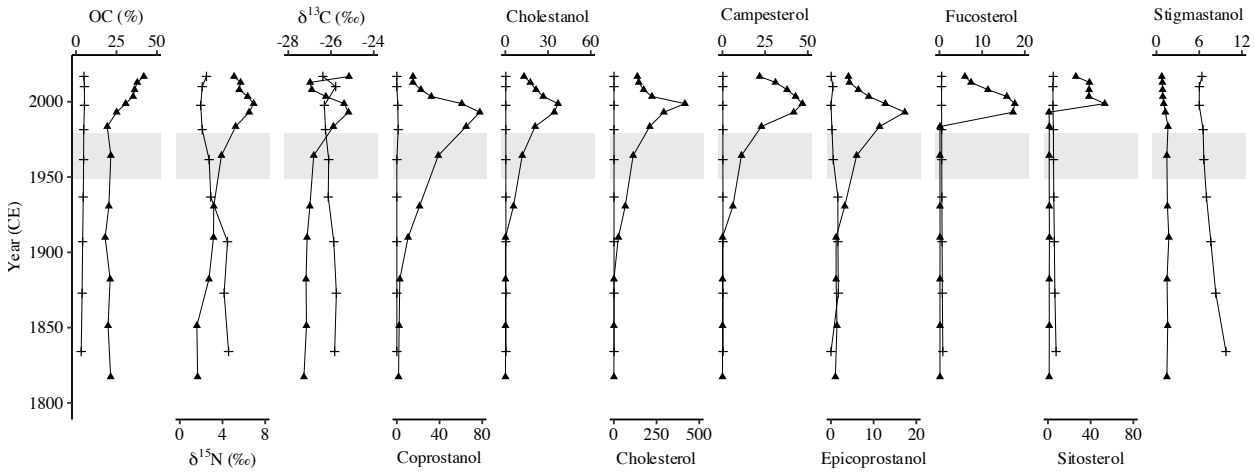

Figure 2: Percent organic carbon (OC), stable isotopes, and sterol and stanol concentrations (µg g^{-1} OC dw) in the sewage-water receiving pond, R-12 (▲), and the reference pond Little Char (+). The shaded area indicates the period of sewage input into R-12.

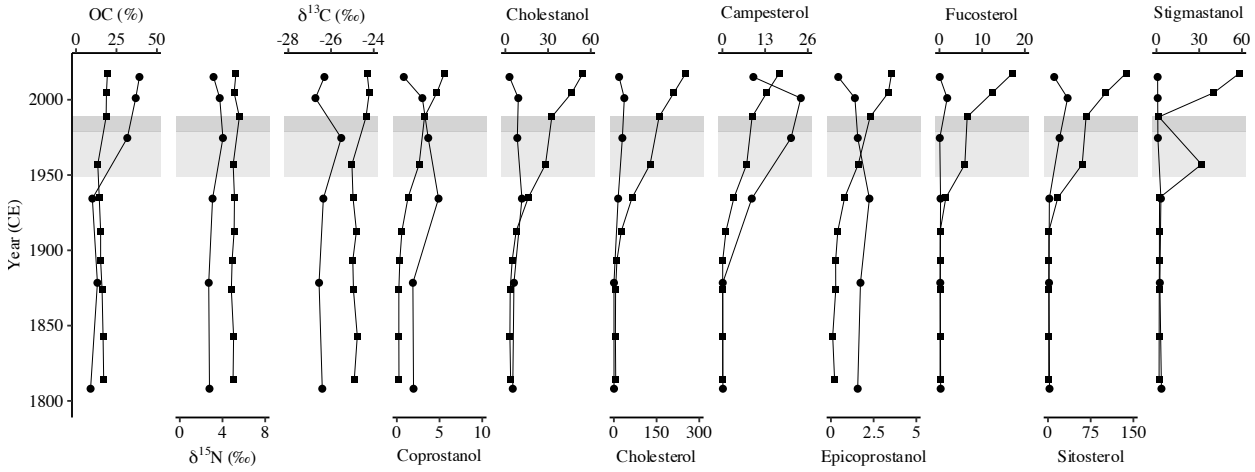

Figure 3: Percent organic carbon (OC), stable isotopes, and sterol and stanol concentrations (µg g^{-1} OC dw) in R-13 (●) and Meretta Lake (■), both sewage-receiving waterbodies. The light gray shaded area indicates the period of sewage input from 1949 to 1979; the dark gray shaded area indicates the additional 10 years of sewage input into Meretta Lake, from 1979 to 1989.

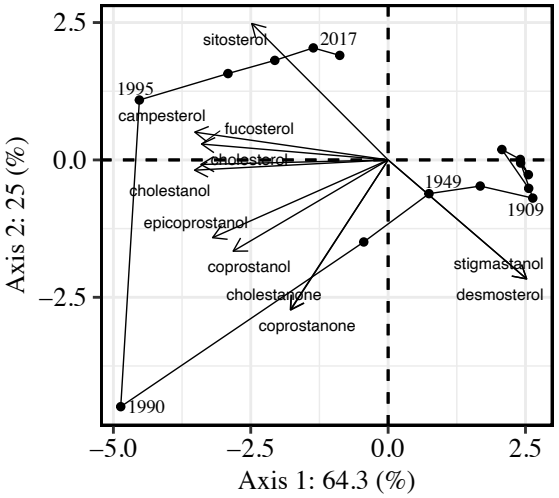

Figure 4: Principle Component Analysis (PCA) of the downcore sterol and stanol concentrations (μg g^{-1} OC dw) in R-12 (a sewage-influenced pond). Select ^{210}Pb dates are indicated adjacent to their corresponding depth. Principle component axis 1 and axis 2 explain a cumulative 89.3 % of the variation in the sterol and stanol composition of the pond sediments in R-12.

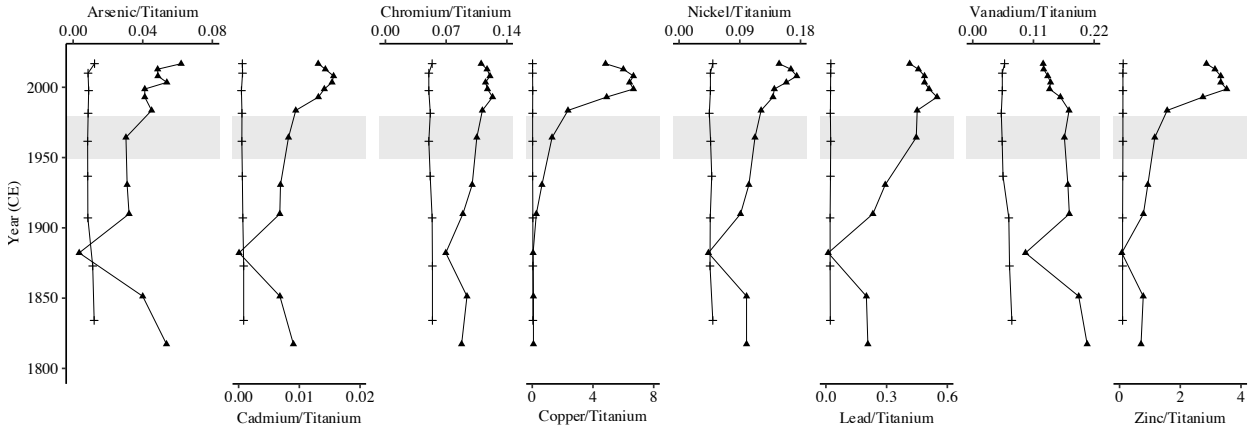

Figure 5: Metal ratios (metal concentration normalized to the titanium concentration to account for natural deposition) in the sewage-water receiving pond, R-12 (▲), and the reference pond, Little Char (+). The shaded area indicates the period of sewage input into R-12.