

Temporal trends of pollution Pb and other metals in east-central Baffin Island inferred from lake sediment geochemistry

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ABSTRACT

Concentrations and stable isotope ratios of lead (Pb) from lake sediments were used to quantify temporal patterns of anthropogenic Pb pollution in the Clyde River region of Baffin Island, Arctic Canada. Surface sediments from eight lakes on eastern Baffin Island and one from northern-most Greenland, spanning a gradient of 20° latitude, showed great variability with respect to Pb concentration and stable isotopic Pb ratios, with little apparent latitudinal trend. To constrain the temporal evolution of regional Pb pollution, a well-dated core from one of the sites, Lake CF8 on east-central Baffin Island, was analyzed geochemically at high stratigraphic resolution. A pronounced decrease in the $^{206}\text{Pb}/^{207}\text{Pb}$ ratio occurs in sediments deposited between 1923 and the mid-1970s, likely reflecting alkyl-Pb additives derived from the combustion of fossil fuels at a global scale. A two-component mixing model indicates that 17–26% of the Pb in the labile fraction of sediments deposited in Lake CF8 between 2001 and 2005 is from anthropogenic input. A Pb–Pb co-isotopic plot ($^{206}\text{Pb}/^{207}\text{Pb}$ vs. $^{208}\text{Pb}/^{206}\text{Pb}$ ratios) of the Lake CF8 time series data indicates multiple possible sources of industrial Pb pollution. Despite widespread reductions in industrial Pb emissions since the 1970s, there is no evidence for attendant reductions of pollution Pb at Lake CF8. Enhanced scavenging from increased primary production as well as changing precipitation rates as climate warms may represent important factors that modulate Pb deposition to Lake CF8, and Arctic lakes elsewhere.

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1. Introduction

Global Pb production is steadily rising and the potential for further increases looms as China and India, which possess massive and largely unexploited Pb deposits continue to industrialize at unprecedented rates (EPA, 2000). The elimination of leaded gasoline in North America and other developed countries since the 1970s has led to significant reductions in atmospheric Pb emissions. Despite the restrictions on leaded gasoline usage, aerosols in remote regions of the Canadian Arctic are still highly contaminated with anthropogenic Pb suggesting an increase in pollution Pb from sources other than gasoline additives (Shotyk et al. 2005). Increased Pb emissions have serious implications for the Arctic, which is predicted to become a more efficient trap for Pb, as increased precipitation, and thus greater atmospheric scavenging, continues apace with recent warming (Zhang et al., 2007; Macdonald et al., 2005). The ecological

repercussions of Pb, and other metals, on Arctic freshwater systems remain poorly understood, especially within the context of potential synergies with climate change (Köck et al., 2001).

Natural environmental archives, such as lake sediments, offer a means of obtaining long-term histories of atmospheric Pb pollution (Brännvall et al., 2001). In addition, stable isotopes of Pb can be used to fingerprint pollution sources because ore bodies from disparate regions have detectable differences in isotopic composition (Sangster et al., 2000). In the Canadian High Arctic, studies of Pb deposition and source attribution are rare. Outridge et al. (2002) examined lake sediment cores from four different High Arctic regions and found no detectable changes in either isotopic shifts or concentration increases that could be attributable to anthropogenic Pb pollution. However, shorter duration studies based on aerosol and snowpack samples have detected the presence of anthropogenic Pb in the Canadian High Arctic. For example, Sturges and Barrie (1989) showed that mean $^{206}\text{Pb}/^{207}\text{Pb}$ ratios in aerosol samples from two locations in the Canadian Arctic (Mould Bay, Prince Patrick Island and Alert, Ellesmere Island) were very close to ratios recorded at Spitsbergen during air flow from the former U.S.S.R., suggesting a Eurasian origin of pollution Pb. More recent work by Shotyk et al. (2005) on snowpack samples

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from Devon Island also confirmed a Eurasian origin of pollution Pb and concluded that Pb inputs to this region of the Arctic are still overwhelmingly dominated by anthropogenic sources. Clearly, further studies are needed to more completely understand geographical and temporal variations of Pb pollution across the vast Canadian High Arctic.

In this study, we use a lake sediment record to document the temporal trends of atmospheric Pb pollution in east-central Baffin Island near the hamlet of Clyde River (Fig. 1). Although lake sediments have been used to document the history of atmospheric Pb contamination on the Greenland side of Baffin Bay (Bindler et al., 2001; Lindeberg et al., 2006), there are no similar studies on the Canadian side of the bay. In fact, there are no studies of Pb contamination and source attribution from Baffin Island, which is the fifth largest island in the world. Here, we use Pb concentration and flux data to evaluate the relative contribution of this metal from natural versus anthropogenic sources, as well as stable isotope data to trace the provenance of the emissions and make inferences concerning transport pathways (Bollhöfer and Rosman, 2001). The atmospheric trajectories suggested by Pb geochemistry are likely relevant for other contaminants that are readily incorporated into terrestrial and lacustrine ecosystems, including highly-chlorinated and high-molecular weight organic compounds (Macdonald et al., 2005). In addition to the sediment core from Clyde River, we also analyze modern sediments from seven sites spanning the eastern coastline of Baffin Island and one site from northern-most Greenland to explore the spatial variability of Pb concentrations and isotopic values along a north-south transect.

2. Materials and methods

2.1. Site descriptions

The analyzed sediments include eight sites on eastern Baffin Island, and one from northern-most Greenland (Fig. 1). These sites range from polar desert ecosystems in the north, to mid- and low-shrub tundra in the south. The lakes on Baffin Island occur mainly on Precambrian crystalline bedrock composed of granite and gneiss and are situated above the limit of Holocene marine emergence, whereas the north Greenland lake occupies a coastal strand flat. The latter site represents the northern-most permanent lake in the world. These lakes are all dilute, highly oligotrophic, and circumneutral to slightly acidic. Locations and additional limnological features of the investigated sites are given in Table 1.

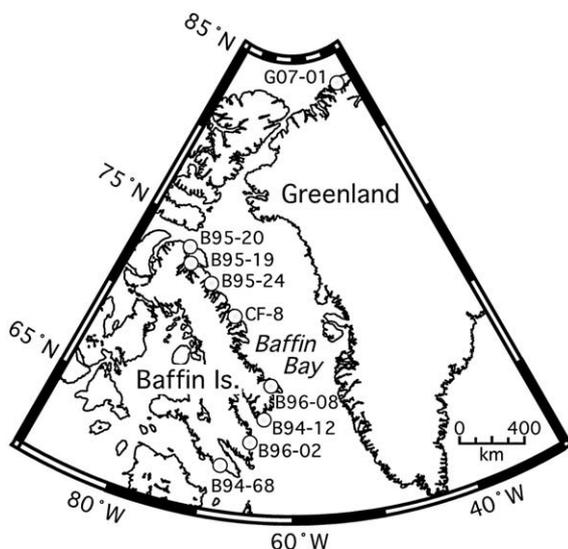


Fig. 1. Map of the Baffin Bay region showing locations of the study lakes on eastern Baffin Island and northern Greenland.

The sediment core used to reconstruct temporal trends in metal pollution is from Lake CF8 (70°33' N, 68°57' W), located near the hamlet of Clyde River, Nunavut (Fig. 1). Meteorological data from Clyde River (1971–2000) indicate mean annual and mean July temperatures of $-12.83\text{ }^{\circ}\text{C}$ and $+4.43\text{ }^{\circ}\text{C}$, respectively, and mean annual precipitation of 233 mm yr^{-1} , of which over 80% falls as snow. Accordingly, the open-water period is limited to approximately three months (July–September) in typical years.

2.2. Sample collection

All sediments were collected with a gravity corer that preserves an intact mud–water interface (Glew, 1989). With the exceptions of Lake CF8 and G07-01, which were collected in 2005 and 2007, respectively, the samples originate from materials already considered by Joynt and Wolfe (2001) in the context of diatom studies, which were collected between 1994 and 1996.

2.3. Sediment core chronology

The 26 cm long core from Lake CF8 was sectioned on-site into consecutive 0.25 cm increments, and kept cool and dark until lyophilization prior to analysis. The chronology of the core is based on excess ^{210}Pb activities determined by α -spectroscopy and the constant-rate-of-supply (CRS) model, augmented by accelerator mass spectrometric (AMS) ^{14}C ages derived from aquatic macrofossils from depths beneath the unsupported ^{210}Pb inventory (Fig. 2). ^{14}C ages were calibrated to years before present (cal yr BP) using CALIB 5.0.1 (Stuiver and Reimer, 1993). In order to match the timescale of the ^{210}Pb dates, all ^{14}C dates were adjusted to zero age for 2005 AD. All dates are reported in calendar years AD or BC. A composite age model was developed by applying linear fits to the ^{14}C ages below the base of the ^{210}Pb chronology (Fig. 2C).

2.4. Trace metal and Pb isotope analyses

For each sediment interval, approximately 100 mg of freeze-dried sediment was placed in pre-cleaned Teflon Savillex[®] beakers (15 ml volume) with 10 ml of 1 M HNO_3 ultrapure Seastar[®] acid at room temperature overnight ($\sim 12\text{ h}$). The supernate was extracted from the sediment and diluted with ultrapure MilliQ H_2O by a factor of 10. The same aliquot of supernate was used for both trace element and Pb isotope analysis on the quadrupole ICP-MS, with the exception of CF8 lake sediment samples. For the latter, a separate aliquot of sediment from the same depth interval was also leached prior to Pb separation using HBr-HNO_3 anion exchange chromatography modified from Lugmair and Galer (1992); these were subsequently analyzed by solution mode MC-ICP-MS for their Pb isotope composition.

Trace element concentrations were determined on a Perkin-Elmer Sciex Elan 6000 quadrupole ICP-MS. Instrumental conditions were as follows: RF power of 1200 W; dual detector mode; blank subtraction applied subsequent internal standard correction; measurement units cps (counts per second); auto lens on; 4 points calibration curve (0, 0.025, 0.050, and 0.100 ppm for Na; 0, 0.25, 0.50, and 1.00 ppm for Ca, Mg, Fe, K; 0, 0.005, 0.010, and 0.020 ppm for the remaining elements); typical count rate for a 10 ppb Pb solution is 150,000 to 200,000 cps. The sample uptake rate was approximately 1 mL min^{-1} with 35 sweeps per reading, 1 reading per replicate and 3 replicates. Dwell times were 10 to 20 ms for all elements with the exception of As (100 ms each). The relative standard deviation (2σ level) for As, Ni, Pb, and Zn are between 5 and 10%. The accuracy of the ICP-MS analytical protocol was periodically evaluated via the analysis of certified reference standard materials (whole rock powders) BE-N and DR-N available from the SARM laboratory at the CRPG (Centre de Recherches Pétrographiques et Géologiques), Nancy (France), and BCR-1 from the United States Geological Survey. For the trace elements investigated here, measured concentrations agree within 0 to 5% of the certified values.

Table 1
Selected; limnological characteristics and Pb geochemistry of surficial sediments for all study sites.

Location	Lake ID	Lat. (°N)	Long. (°W)	Elev. (m a.s.l.)	Depth (Z_{\max} , m)	Area (km ²)	Cond. ($\mu\text{S cm}^{-1}$)	pH	Surface sediments	
									$^{206}\text{Pb}/^{207}\text{Pb}$	Pb (ppm)
Pearyland, Greenland	G07-01	83.39	37.50	45	14.2	0.05	95.7	7.60	1.157	31.50
Bylot Island, Nunavut	B95-20	73.67	80.57	229	6.2	1.06	18.8	7.23	1.203	5.36
Baffin Island, Nunavut	B95-19	73.00	79.33	366	6.6	0.05	14.9	7.10	1.096	5.59
Baffin Island, Nunavut	B95-24	72.06	74.33	165	2.9	0.08	10.9	7.10	1.432	8.39
Baffin Island, Nunavut	CF-8	70.55	68.95	195	10.0	0.30	18.8	5.34	1.408	5.02
Baffin Island, Nunavut	B96-08	66.95	62.90	201	14.7	0.18	1.2	7.08	1.704	8.88
Baffin Island, Nunavut	B94-12	64.95	63.60	10	25.6	0.29	12.6	6.94	1.253	15.87
Baffin Island, Nunavut	B96-02	63.60	65.52	597	17.9	0.65	1.0	7.06	1.194	6.66
Baffin Island, Nunavut	B94-68	62.51	68.24	328	17.2	0.17	10.4	6.94	1.239	14.41

Pb isotope measurements were also conducted on the Perkin-Elmer Sciex Elan 6000 quadrupole ICP-MS following the procedure outlined in Erel et al. (2001). The sensitivity of the ICP-MS was

approximately 2×10^7 counts per second (cps) per $\mu\text{g g}^{-1}$ for ^{208}Pb with a detection limit of 0.03 ppb. The dwell time was 25 ms with an integration time of 5.5 s (corresponding to 221 sweeps). Pb isotope analysis of the leachates was bracketed by intermittent measurement of a 50 ppb solution of the NIST SRM 981 Pb isotope standard to monitor the instrumental drift. The typical %RSD (relative standard deviation) associated with an individual $^{206}\text{Pb}/^{207}\text{Pb}$ measurement is 0.3%, whereas the %RSD related to the repeated measurements of the NIST SRM 981 Pb standard (i.e. short-term instrumental drift) was also 0.3% or better. Mass discrimination values were calculated by comparing the average 'bracketed' Pb isotope measurements for the NIST SRM 981 standard to the accepted values obtained by ID-TIMS (Todt et al., 1996). The mass discrimination values for the $^{206}\text{Pb}/^{207}\text{Pb}$ varied between ~ 1.003 and ~ 1.007 .

The Pb isotopic composition of leachates from CF8 lake sediments was also determined by solution mode MC-ICP-MS following the procedure outlined in Simonetti et al. (2004). Pb isotope measurements were conducted on a NuPlasma MC-ICP-MS instrument (Nu Instruments, UK). Following chemical separation of the Pb, evaporated samples were taken into the solution with 1.5 ml of 2% HNO_3 spiked with the NIST SRM 997 Thallium isotope standard (10 ppb solution). Samples were aspirated ($\sim 100 \mu\text{L min}^{-1}$) into the ICP source using a DSN-100 (desolvating nebuliser from Nu Instruments, UK). All of the Pb and Tl isotopes and ^{202}Hg were simultaneously measured using 7 Faraday collectors. The $^{205}\text{Tl}/^{203}\text{Tl}$ ratio (accepted value of 2.3871) was measured to correct for instrumental mass bias using the exponential law. Data acquisition consisted of 3 blocks with 10 s baseline measurements at half-mass position, and 20 integrations (10 s each). The isobaric interference of ^{204}Hg on ^{204}Pb was monitored using ^{202}Hg . At the beginning of the analytical session, a 50 ppb solution (2% HNO_3) of the NIST SRM 981 Pb isotope standard also spiked with the NIST SRM 997 Tl isotope standard (10 ppb) was analyzed. The long-term external reproducibility (2σ) based on repeated measurements of this standard solution is better than 0.04% for the $^{206}\text{Pb}/^{207}\text{Pb}$ ratio. Of importance, a comparison of the $^{206}\text{Pb}/^{207}\text{Pb}$ values for the CF8 leachates obtained by both quadrupole and MC-ICP-MS instruments yields an excellent corroboration as values agree within 0 to 0.5%.

2.5. Data analysis

To assess the relative contributions of natural versus anthropogenic sources of Pb and other metals in the Lake CF8 and Greenland sediment cores, metal concentrations were expressed as enrichment factors (EFs, Fig. 3). Here, we define EF as the recent [metal]/[Al] ratio of any particular sample divided by the pre-industrial [metal]/[Al] ratio, which we calculated by averaging values from the two bottom-most sediment intervals from Lake CF8 (i.e., 10.125 and 15.125 cm core depths), and likewise for the Greenland site (i.e., 30.5 cm core depth). Pristine sediment, unimpacted by anthropogenic pollution, will therefore produce an EF approximating 1. All concentration, flux, EF and isotope values for Pb and other metals refer to the acid-leachable

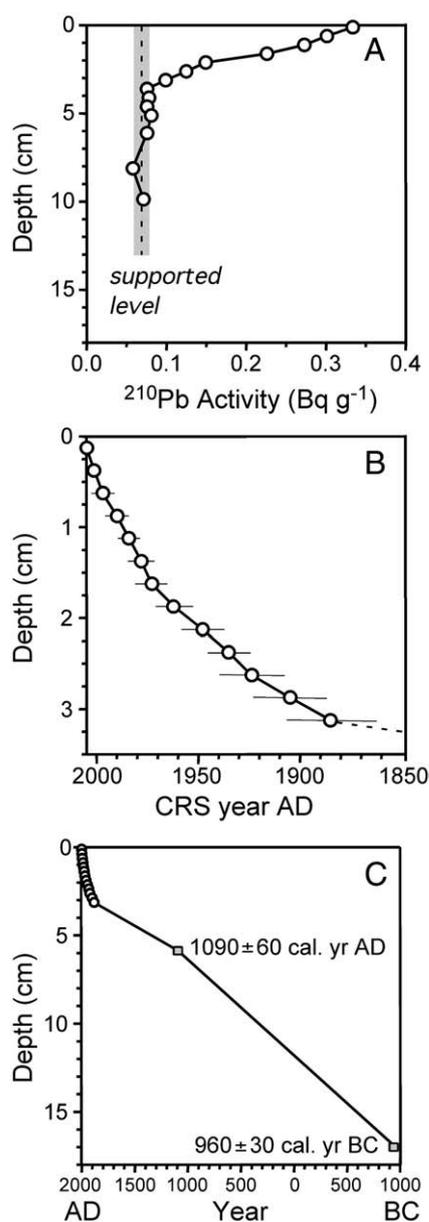


Fig. 2. Total ^{210}Pb activities (A) and the corresponding CRS-derived age-depth profile for the near surface sediments (B) from Lake CF8. A master chronology was developed by splicing the ^{210}Pb dates with two ^{14}C ages derived from aquatic macrofossils at deeper depths (C).

(labile) fraction of the sediments, given that metals not released during acid extraction are deemed unavailable for biogeochemical cycling.

For down-core samples from Lake CF8, Pb and the other metals considered (i.e. As, Cu, Ni, and Zn) are presented successively as concentrations, fluxes, and enrichment factors (EFs) determined by normalization to [Al] in the manner described above. The history of anthropogenic Pb pollution was also assessed using Pb stable isotope data and the following two-component mixing model:

$$^{206}\text{Pb}/^{207}\text{Pb}_{\text{sample}} = (f\text{Pb}_{\text{anthro}} * ^{206}\text{Pb}/^{207}\text{Pb}_{\text{pollution}}) + (1 - ^{206}\text{Pb}/^{207}\text{Pb}_{\text{pollution}}) * ^{206}\text{Pb}/^{207}\text{Pb}_{\text{background}}$$

where $^{206}\text{Pb}/^{207}\text{Pb}_{\text{sample}}$ is the isotopic ratio of a given sample, $f\text{Pb}_{\text{anthro}}$ is the fraction of anthropogenic Pb in any given sample, $^{206}\text{Pb}/^{207}\text{Pb}_{\text{pollution}}$ is the mean isotopic ratio of pollution Pb for a particular source region, and $^{206}\text{Pb}/^{207}\text{Pb}_{\text{background}}$ is the isotopic value calculated from pre-industrial sediments, represented by the mean value of the two lower-most sediment intervals. Published values of mean pollution $^{206}\text{Pb}/^{207}\text{Pb}$ ratios from four potential source regions (Sangster et al., 2000) including Canada (1.15), USA (1.21), Eurasia (1.14), and the UK (1.06) were run, in turn, as the fraction of anthropogenic Pb was varied until a $^{206}\text{Pb}/^{207}\text{Pb}$ ratio was attained that matched the value measured in the sediment. The concept of linear arrays depicting binary mixing on a Pb–Pb co-isotopic plot ($^{206}\text{Pb}/^{207}\text{Pb}$ vs. $^{208}\text{Pb}/^{206}\text{Pb}$ ratios) was used to make inferences

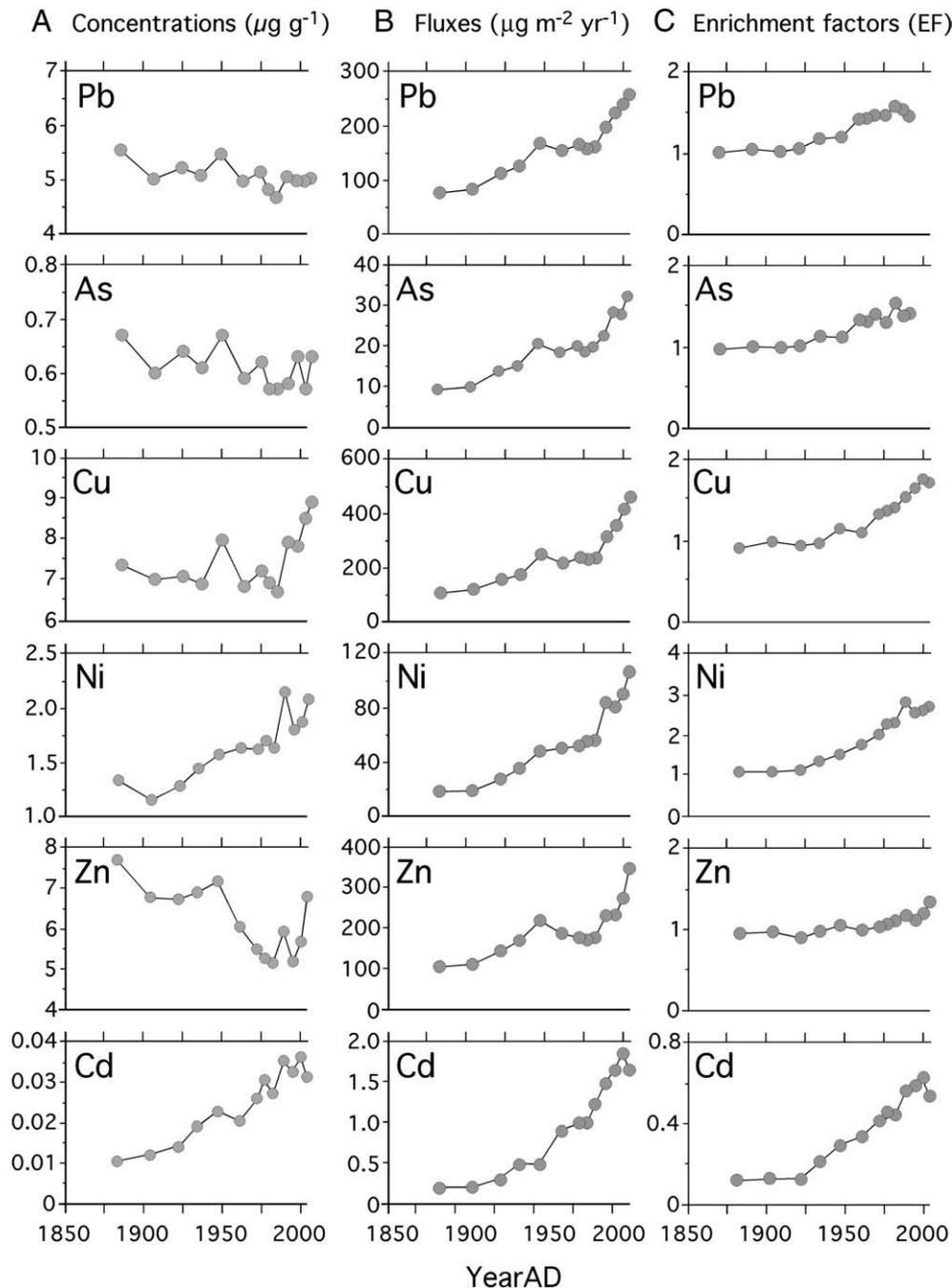


Fig. 3. Profiles of Pb, As, Cu, Ni, Zn and Cd over the past ~150 years plotted as (A) concentrations, (B) fluxes, and (C) enrichment factors.

regarding the most likely source of anthropogenic Pb impacting the region near Lake CF8.

3. Results and discussion

3.1. Spatial patterns of surface sediment Pb

The nine surface sediment samples showed great variability with respect to Pb concentration (range: 5.02 to 31.5 ppm) and Pb stable isotope ratios ($^{206}\text{Pb}/^{207}\text{Pb}$ range: 1.096–1.706), with little apparent latitudinal trend (Table 1). The range of $^{206}\text{Pb}/^{207}\text{Pb}$ ratios in lake sediments combines differences in anthropogenic Pb deposition coupled to the natural variability of Pb isotopes associated with local to regional-scale geological heterogeneity. In the Canadian High Arctic, where anthropogenic Pb pollution is known to be low (Outridge et al., 2002), geological differences are likely to account for most of the variability among Pb stable isotopes. For example, the surface sediment from our north Greenland site recorded the highest Pb concentration in our dataset (Table 1) and a $^{206}\text{Pb}/^{207}\text{Pb}$ ratio (1.16) characteristic of pollution Pb from Eurasia (~1.14–1.16). However, the surface sediment Pb concentration (31.5 ppm) and $^{206}\text{Pb}/^{207}\text{Pb}$ ratio (1.158) are nearly identical to those recorded in pre-industrial sediments from this core (31.5 ppm and 1.157, respectively). Based on this cursory top–bottom approach, we cautiously infer that this northern-most region of Greenland is relatively pristine with respect to anthropogenic Pb pollution. Clearly, resolving the amount of anthropogenic Pb from natural cycles requires a more complete understanding of background variability and pollution history, especially during the period of marked Pb emissions following the Industrial Revolution. The sediment core data from Lake CF8 provide a much-needed temporal perspective that allows for greater insight into the onset, magnitude, and source of Pb pollution in eastern Baffin Island.

3.2. Radiochronology of the Lake CF8 core

Typical of lacustrine sediments on Baffin Island (Michelutti et al., 2007; Michelutti et al., 2005; Wolfe et al., 2004), the ^{210}Pb flux was low ($13 \text{ Bq m}^{-2} \text{ yr}^{-1}$), but still sufficient for dating purposes. The inventory of excess ^{210}Pb is restricted to the upper 3.125 cm of the core, and indicates an undisturbed sedimentary sequence (Fig. 2A). The CRS-derived dates provide a detailed chronology for the upper 3.125 cm (last ~120 years), and indicate an average sediment accumulation rate of 0.026 cm yr^{-1} over this interval. Despite such a low accumulation rate, which is due to low primary production and minimal clastic input to the lake, we have obtained a well-resolved inventory of excess ^{210}Pb . The two ^{14}C ages at 5.9 and 17.0 cm depths form a near-linear fit to the base of the ^{210}Pb chronology, and indicate an even lower mean sediment accumulation rate of $0.0049 \text{ cm yr}^{-1}$ for the lower portion of this core (Fig. 2C). The lower accumulation rate in the bottom portion of the core reflects, in part, sediment compaction and organic matter remineralization. The basal ^{14}C age indicates that the 17 cm core section encompasses nearly 3000 years of lacustrine sedimentation. Despite such low sediment accumulation rates, the ^{210}Pb and ^{14}C results indicate that the core retains fully the stratigraphic integrity that is pre-requisite for the use of lake sediments to chronicle metal pollution. Although the thickness of the sediment capturing the industrial period in Lake CF8 is miniaturized by approximately an order of magnitude relative to mid-latitude lakes, we demonstrate that current sampling strategies nonetheless enable a detailed record of pollution to be resolved.

3.3. Temporal variations in metal concentrations and Pb isotopic ratios in Lake CF8

The concentration profiles for Pb and other metals in Lake CF8 show no temporal trends displaying only minor fluctuations that, with the possible exception of Ni and Cu, occur within the range of natural

variability over the past ~150 years (Fig. 3A). Additional samples of late-Holocene age (1650 and 2400 cal yr BP), yielding mean concentrations ($n = 2$) of 0.78, 0.110, 8.78, 1.27, 5.49, and 5.73 for As, Cd, Cu, Ni, Zn, and Pb, respectively, confirm that background pre-industrial metal concentrations have been sustained until present day. However, when plotted as either fluxes or EFs, all metals show coeval increases towards the surface starting around 1925 (Fig. 3B, C). These trends are corroborated by the coeval declines recorded in all stable Pb isotopic ratios from Lake CF8 sediments (Fig. 4; Table 2). While both the Pb stable isotopes and the metal EF and flux results clearly pinpoint the onset of atmospheric pollution, the metal concentration data, taken alone, do not. This indicates that metal concentrations have been diluted in recent decades, most likely by greater authigenic sedimentation from increased primary production (Michelutti et al., 2005).

The increase in Pb flux and Pb EFs is coincident with the steady decline in $^{206}\text{Pb}/^{207}\text{Pb}$ ratios (Figs. 3 and 4), which directly implicates an influx of pollution Pb. The near-synchronous shifts recorded in fluxes and EFs of As, Cd, Cu, Ni and Zn support the inference of

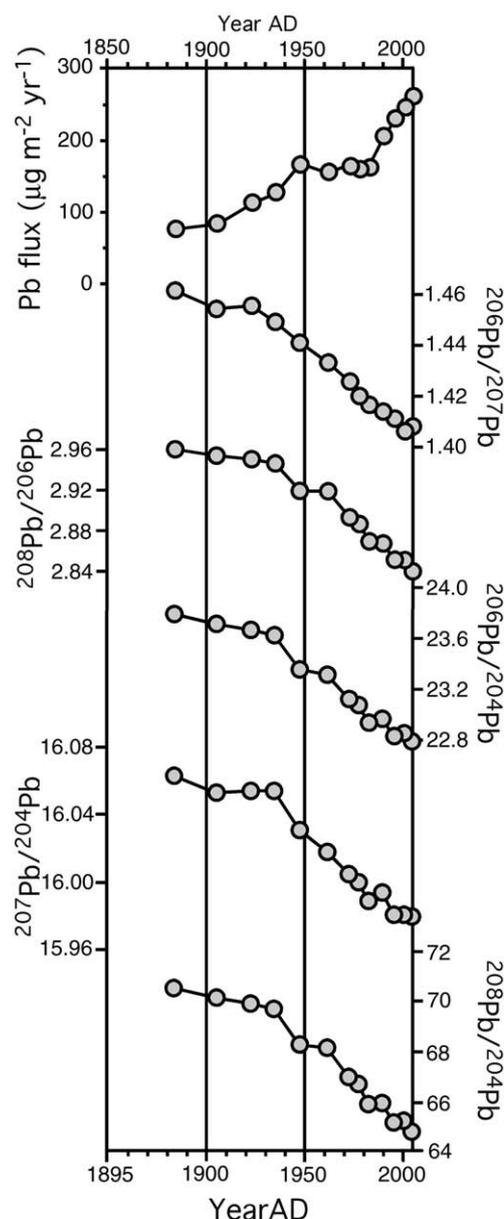


Fig. 4. Ratios of the four stable isotopes of Pb since ~1850 AD, shown in relationship to total Pb flux, in sediments from Lake CF8. Analytical uncertainties are within the size of the symbol.

Table 2
Pb stable isotope ratios from Lake CF8 sediments obtained by MC-ICP-MS.

Depth interval (cm)	$^{206}\text{Pb}/^{204}\text{Pb}$	$\pm 1\sigma$	$^{207}\text{Pb}/^{204}\text{Pb}$	$\pm 1\sigma$	$^{208}\text{Pb}/^{204}\text{Pb}$	$\pm 1\sigma$	$^{206}\text{Pb}/^{207}\text{Pb}$	$\pm 1\sigma$	$^{208}\text{Pb}/^{206}\text{Pb}$	$\pm 1\sigma$
0.0–0.25	22.791	0.0012	15.980	0.0009	64.739	0.004	1.4080	0.00002	2.8405	0.00005
0.5–0.75	22.833	0.0016	15.981	0.0012	65.114	0.005	1.4109	0.00018	2.8519	0.00005
1.0–1.25	22.939	0.0013	15.989	0.0010	65.836	0.005	1.4164	0.00001	2.8702	0.00005
1.5–1.75	23.125	0.0010	16.005	0.0008	66.917	0.004	1.4256	0.00003	2.8937	0.00004
2.0–2.25	23.359	0.0014	16.031	0.0011	68.200	0.004	1.4408	0.00003	2.9197	0.00005
2.5–2.75	23.668	0.0023	16.054	0.0017	69.842	0.009	1.4554	0.00003	2.9512	0.00006
3.0–3.25	23.795	0.0012	16.063	0.0007	70.452	0.003	1.4613	0.00003	2.9608	0.00005
10.0–10.25	24.036	0.0010	16.085	0.0007	71.990	0.003	1.4758	0.00003	2.9951	0.00005
15.0–15.25	24.207	0.0011	16.103	0.0008	72.102	0.004	1.4798	0.00004	2.9785	0.00005

anthropogenic inputs. The onset of the increased Pb flux is consistent with the history of accelerated atmospheric Pb emissions following the introduction of alkyl-Pb additives to gasoline in 1923. Moreover, the subsequent declines of Pb isotopic ratios are consistent with anthropogenic emissions that combine source regions (Bollhöfer and Rosman, 2001) including Canada ($^{206}\text{Pb}/^{207}\text{Pb}$ range: 1.094–1.177), the United States ($^{206}\text{Pb}/^{207}\text{Pb}$ range: 1.173–1.231), and Western Europe ($^{206}\text{Pb}/^{207}\text{Pb}$ range: 1.097–1.165).

The large range recorded in $^{206}\text{Pb}/^{207}\text{Pb}$ ratios from surface sediments (1.10–1.70; Table 1) highlights the importance of local geology in determining Pb isotopic ratios in lake sediments. Natural edaphic factors, including aeolian activity, catchment soil development, and erosion, can produce fluctuations in sedimentary metal profiles similar in magnitude to those caused by anthropogenic emissions (e.g., Lindeberg et al., 2006; Wolfe and Härtling 1997). At Lake CF8, sediment from 10.125 and 15.125 cm depths, corresponding to ages of ~1650 and 2400 cal yr BP, respectively, provide some insight into the signature of natural Pb sources. These two pre-industrial sediment samples recorded nearly identical $^{206}\text{Pb}/^{207}\text{Pb}$ ratios of 1.48. Although only a few samples characterize the pre-industrial period at Lake CF8, the relatively minor fluctuations record in Pb flux and stable isotope ratios prior to the 20th century deem natural factors unlikely to be responsible for the unprecedented shifts recorded since ~1925. Similar to the $^{206}\text{Pb}/^{207}\text{Pb}$ ratios, Pb EFs at Lake CF8 did not fluctuate greatly from their theoretical background values of 1 in pre-1900's sediments. Only since ~1925, when global atmospheric Pb emissions started to increase markedly, did Pb fluxes and stable isotope ratios exceed their range of natural variability over the past ~3000 years.

We do not suspect that the recent increases in Pb and other metal fluxes are due to greater catchment erosion. This is because pollution Pb isotopic ratios from the most plausible source regions are depleted ($^{206}\text{Pb}/^{207}\text{Pb} < 1.3$; Bollhöfer and Rosman, 2001) relative to background Pb isotopic values recorded from Lake CF8 ($^{206}\text{Pb}/^{207}\text{Pb} \sim 1.48$). Thus, under the scenario of enhanced contributions of natural Pb and other metals from the surrounding bedrock, $^{206}\text{Pb}/^{207}\text{Pb}$ ratios in the Lake CF8 core should show a return to pre-industrial values. In contrast, we record a continued decline in $^{206}\text{Pb}/^{207}\text{Pb}$ ratios towards the surface of the core (Fig. 4).

3.4. Comparison to other Arctic regions

In Lake CF8, Pb flux and stable isotopes show a shift from background values beginning at ~1925, consistent with the upswing of global anthropogenic emissions. Elsewhere in the Canadian Arctic, Outridge et al. (2002) recorded only minor variability in $^{206}\text{Pb}/^{207}\text{Pb}$ ratios in pre-19th century sediments from four High Arctic lakes (Table 3). None of the four High Arctic cores (Amituk, Hazen, DV09, Ya-Ya) analyzed by Outridge et al. showed any consistent shift in $^{206}\text{Pb}/^{207}\text{Pb}$ ratios relative to pre-industrial sediments (Table 3), and any recent changes in Pb concentration or stable isotopes attributable to anthropogenic activities were considered negligible (Fig. 7). However, two sediment cores from the Canadian Low Arctic (Imitavik

and Far) showed noticeable declines in $^{206}\text{Pb}/^{207}\text{Pb}$ ratios in recent sediments relative to pre-industrial sediments (Table 3, Fig. 7), with the shift commencing around 1800. Outridge et al. (2002) attributed this distinct latitudinal difference to the much lower precipitation rates at higher latitudes, which limit scavenging of atmospheric Pb. Lake CF8 is one of the northern-most lakes in the Canadian Arctic to record signs of anthropogenic Pb pollution.

On the eastern side of Baffin Bay, Bindler et al. (2001) and Lindeberg et al. (2006) recorded large variations in $^{206}\text{Pb}/^{207}\text{Pb}$ ratios in pre-19th century sediments from lakes near Kangerlussuaq, West Greenland (Table 3). In some instances the fluctuations recorded prior to the 19th century were as large as the changes recorded in the uppermost sediments during the period of peak industrial activity. Despite such natural variability in pre-industrial sediments, Bindler et al. (2001) demonstrated that lakes in this region have been unequivocally impacted by modern anthropogenic Pb emissions, with pollution Pb signatures characteristic of Eurasian sources. In some instances, there were large differences in the total amount of pollutant Pb deposited in the West Greenland study lakes. For example, the cumulative inventory of pollutant Pb in Nunatak Lake was 14 mg m^{-2} , whereas in Lake 53 it was more than double at 33 mg m^{-2} . These differences were attributed to differences in rainfall, and hence scavenging efficiency, between the two sites.

Table 3
A comparison of $^{206}\text{Pb}/^{207}\text{Pb}$ ratios in recent and pre-1850 sediments in lake sediment cores from the Canadian Arctic and eastern Baffin Bay.

	$^{206}\text{Pb}/^{207}\text{Pb}$ pre-1850s	$^{206}\text{Pb}/^{207}\text{Pb}$ modern
<i>This study</i>		
CF8, Baffin Island	1.46–1.48	1.41
Baffin Island surface sediments	n/a	1.10–1.70
Pearyland, Greenland	1.16	1.16
<i>Canadian High Arctic</i>		
Amituk Lake, Cornwallis Is.	1.22–1.23	1.22
Lake Hazen, Ellesmere Is.	1.18–1.19	1.19
Lake DV-09, Devon Is.	1.23–1.27	1.25
Ya-Ya Lake, NWT	1.22–1.23	1.22
<i>Canadian Low Arctic</i>		
Imitavik Lake	1.29–1.31	1.19
Far Lake	1.31–1.34	1.17
<i>Kangerlussuaq, West Greenland</i>		
Lake B	1.29–1.45	1.24
Lake G	1.28–1.57	1.20
Lake SS16	1.24–1.40	1.20
<i>Nunatak Lake</i>		
Lake 16	1.28–1.47	1.23
Lake 53	1.339 ± 0.029	1.163
	1.267 ± 0.006	1.19

Note that “pre-1850” $^{206}\text{Pb}/^{207}\text{Pb}$ ratios represent different time periods for each core due to varying sediment core lengths. Sources for $^{206}\text{Pb}/^{207}\text{Pb}$ ratios are: Amituk, Hazen, DV-09, Ya-Ya, Far, Imitavik (Outridge et al. 2002); Lakes B, G and SS16, (Lindeberg et al. 2006); Nunatak, Lake 16, Lake 53 (Bindler et al. 2001).

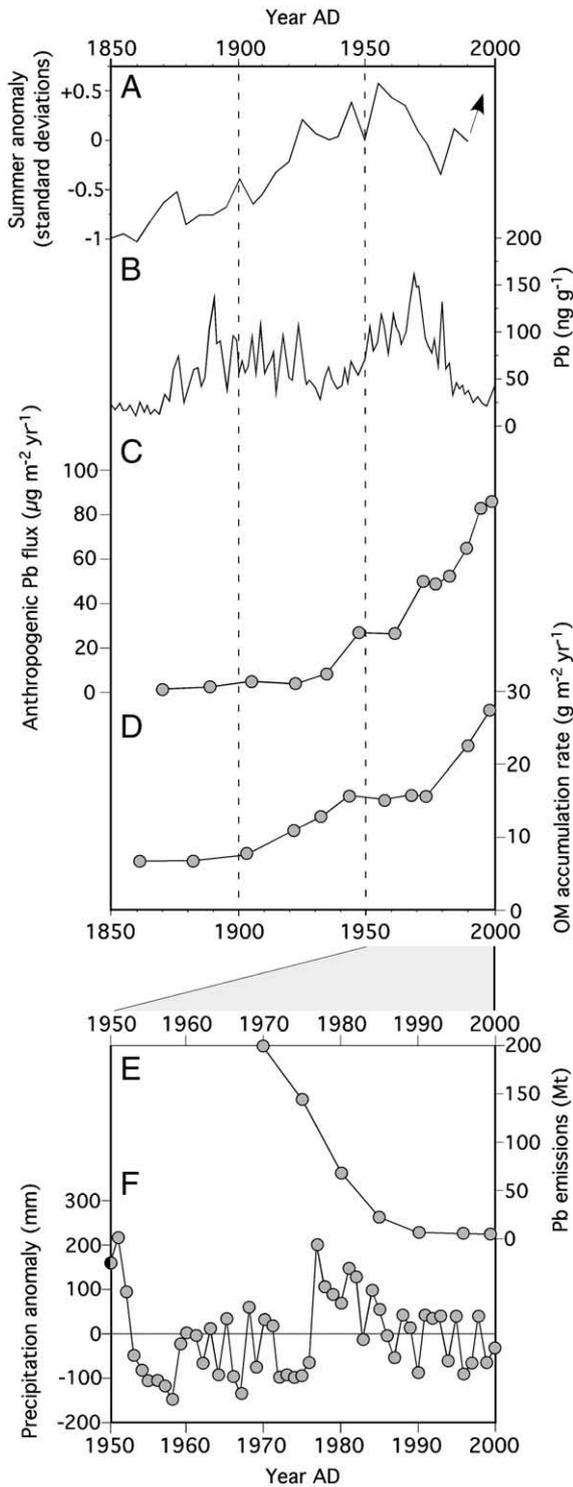


Fig. 5. Profiles of various circum-Arctic proxies, trends in US industrial Pb emissions, and precipitation anomalies from Clyde River, Baffin Island plotted in relation to fluxes of anthropogenic Pb and organic matter at Lake CF8. Plots include: (A) inferred circum-Arctic summer temperature anomalies (Overpeck et al. 1997); (B) yearly averaged Pb concentrations at Summit, Greenland (core ACT2 of McConnell and Edwards, 2008); (C, D) rates of organic matter accumulation and anthropogenic Pb flux at Lake CF8; (E) US Pb emissions since 1970 (EPA 2000); and (F) mean annual precipitation rates at Clyde River since 1950.

In Lake CF8, most of the metal profiles do not follow the history of atmospheric pollution, nor do they correspond to metal profiles recorded in Greenland snow and ice over the same time period (Boutron et al., 1991). Historically, global Pb emissions were greatest between the 1950s and 1970s with significant reductions occurring

after the placement of strict controls on leaded gasoline usage since the 1970s in North America, and the 1980s in Europe. This Pb ban is reflected in snow and ice samples at Summit Greenland that show maximum Pb concentrations during the late 1960s with gradual decreases to present day (Boutron et al., 1991, 1995). Likewise concentrations of Cd, Cu, and Zn have also decreased in Greenland snow samples since peaking in the late 1960s. In contrast, at Lake CF8 fluxes of Pb and other metals are greatest in the most recent sediments. Lake sediment profiles from Greenland show similar trends to the ice core records. For example, the anthropogenic Pb flux, calculated by multiplying anthropogenic Pb (total Pb minus mean Pb concentration in pre-industrial sediments) by sedimentation rate, for Nunatuk Lake and Lake 53 located near Kangerlussuaq peaked in the 1970s around 120 and 500 $\mu\text{g m}^{-2}\text{yr}^{-1}$, respectively (Bindler et al. 2001). By comparison, anthropogenic Pb flux at Lake CF8 peaked in the most recent sediments at a lower value of 85 $\mu\text{g m}^{-2}\text{yr}^{-1}$. Below we discuss two possible explanations for the lack of decline in pollution Pb in recent years at Lake CF8, namely (1) redox-associated metal remobilization, and (2) increased efficiency in the scavenging of metals to lake sediments.

Redox-related migrations can affect the sedimentary profiles of metals such that they do not reflect the history of atmospheric deposition. For example, Outridge et al. (2005) noted that peak concentrations of Cd, Cu, and Zn in a varved, Arctic lake sediment core did not agree with nearby archives of environmental metals or with emission trends. They attributed this discordance to post-depositional remobilization as corresponding subsurface maxima in Cd, Cu and Zn concentrations coincided with peaks in elements such as Fe, S, Co, U and Cr, which are known to be susceptible to redox-related migrations.

Although we cannot completely rule out redox-mediated post-burial alteration of sedimentary metals, there are a number of factors that indicate redox-related migration has not significantly altered the metal profiles at Lake CF8. First, the profiles of metal concentrations at Lake CF8 show no apparent similarities (Fig. 3A), such as the distinct subsurface peaks in Cd, Cu and Zn recorded by Outridge et al., (2005), which are characteristic of redox-mediated migration. Second, not all

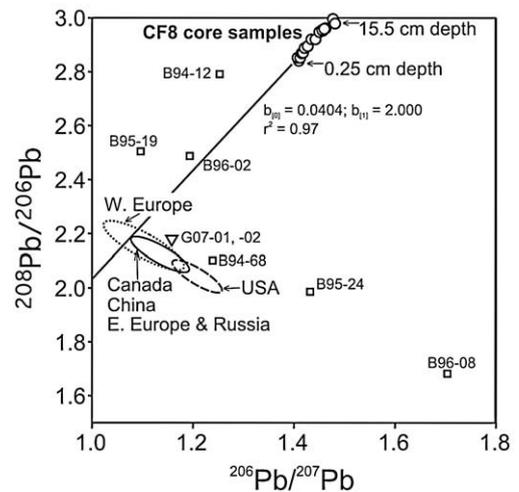


Fig. 6. Co-isotopic plots ($^{206}\text{Pb}/^{207}\text{Pb}$ vs. $^{208}\text{Pb}/^{206}\text{Pb}$) for CF8 sediment core samples (open circles), Baffin Island surface sediments (open squares), and north Greenland surface and pre-industrial sediment (open triangles). The solid line represents an extension of the slope of the line delineated by the CF8 sediment core data. Note that north Greenland surface (G07-01) and pre-industrial (G07-02) sediments yielded nearly identical values and thus overlap on this plot. Also shown are Pb pollution values for different source regions within the Northern Hemisphere (Bollhöfer and Rosman, 2001; Sangster et al., 2000; Rosman et al., 1998; Carignan and Gariépy, 1995; Rosman et al., 1994; Véron et al., 1992). Pb pollution ratios for Western Europe are delineated by the dotted ellipse, those for the USA by the dashed ellipse, and those for Canada, China, Eastern Europe and Russia by the solid ellipse.

of the metal profiles follow the expected pattern of redox-related remobilization in lake sediment cores. For example, the response of Cd to a fluctuating redox boundary is a downward migration to the lower limit of the redox excursion (Gobeil et al., 1997). At Lake CF8, Cd concentration and flux data show increases towards the surface of the core (Fig. 3) suggesting little if any redox-induced migration, at least for this element, as there is no upward transport of Cd in response to redox gradients.

One possible explanation for the absence of a marked decline in the flux of Pb and other metals at Lake CF8 following North American emission controls since the 1970s relates to changes in atmospheric delivery and the efficiency of metal scavenging to lake sediments. There are a number of potential climate factors that can influence the delivery of metallic aerosols to lake basins, of which wet and dry removal processes have the greatest capacity for change (Macdonald et al., 2005). The aridity that characterizes much of the Arctic limits scavenging of atmospheric contaminants by precipitation, preventing

as much as 90% of emissions from being deposited (Pacyna et al., 1995). Mean annual precipitation rates recorded at Clyde River were generally below the 1948–2002 mean during the period of maximum Pb emissions (~1950–1970) and slightly above average during the period of initial Pb reductions in North America (Fig. 5E, F). We posit that slight increases in regional precipitation may have contributed to sustaining pollution Pb fluxes despite reduced automotive emissions in recent decades.

The temperature increases experienced in the Arctic during the 20th century (Overpeck et al., 1997) may also have impacted the sequestration of Pb and other metals to sediments via a number of synergistic processes. The notion that warming in the first half of the 20th century was driven exclusively by natural factors at the termination of the Little Ice Age is now challenged (McConnell et al., 2007) by the realization that black carbon, which has a strongly positive radiative forcing, was consistently delivered to the Arctic shortly after the turn of the 19th century, in quantities that are

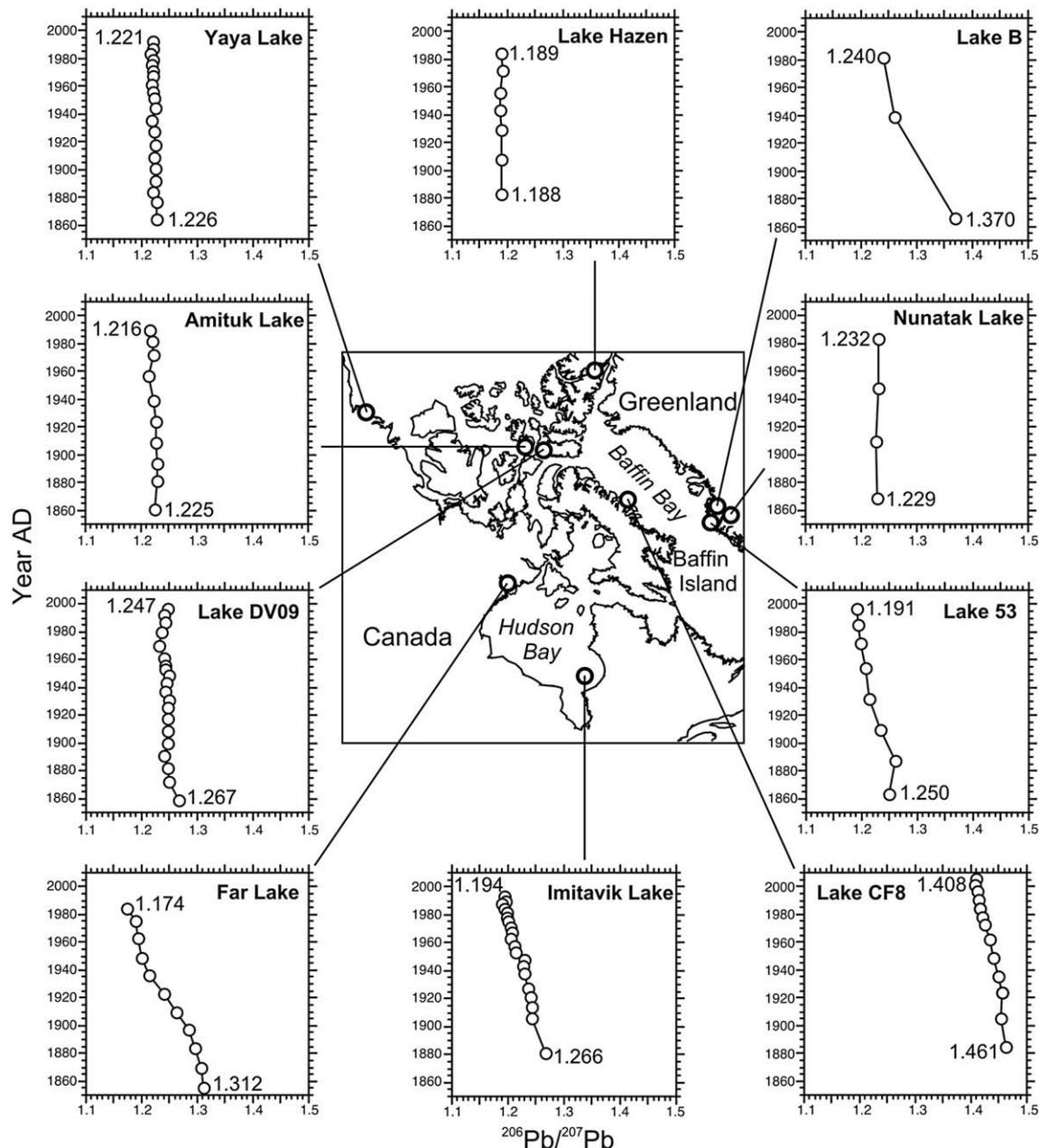


Fig. 7. Trends in $^{206}\text{Pb}/^{207}\text{Pb}$ ratios over the past ~150 years for lakes in the Canadian Arctic and Greenland. $^{206}\text{Pb}/^{207}\text{Pb}$ ratios are shown for the upper- and bottom-most data points for each site.

climatically-relevant. Although black carbon fluxes subsequently declined after ~1950, by this time climate forcing by anthropogenic greenhouse gases had largely supplanted its radiative influence, leading to further, and currently accelerating, warming of the Arctic.

Longer ice-free seasons drive increases in primary production in aquatic ecosystems, as documented in lakes on eastern Baffin Island (Michelutti et al. 2005) and elsewhere in the Arctic (Smol et al. 2005). In Lake CF8, the dry mass accumulation rate of organic matter closely parallels the total Pb flux (Fig. 5C, D) suggesting that Pb recruitment to sediments may be closely linked to climate-induced changes in aquatic production. The scavenging of Pb and other metals by algae and other reactive organic moieties is one potential mechanism linking primary production to lake sediment metal burdens in Baffin Island lakes (Wolfe and Härtling, 1997). The same mechanism has been advanced with respect to elevated halogenated organic contaminant (Stern et al., 2005) and pollution Hg (Outridge et al., 2007) fluxes to Arctic lake sediments. These findings have potential implications with respect to the interpretation of contaminant time series data from natural archives such as lake sediment cores (Macdonald et al., 2005).

3.5. Pollution sources and atmospheric trajectories

Most studies tracing the provenance of industrial Pb in the Canadian Arctic implicate Eurasian or western European sources (Shotyk et al., 2005; Akerdolu et al., 1994; Barrie et al., 1992). In Lake CF8, the fraction of the anthropogenic end member contributing to the Pb concentration in the labile fraction of the sediments, calculated using the two-component isotope mixing equation, varied from 17 to 26% depending on the Pb pollution ratio utilized (i.e., Canada, USA, UK, Eurasia). Although this percentage of Pb pollution is less than that recorded in lake sediments from more southerly regions (Outridge et al., 2002; Brännvall, 2001), it is enough to cause detectable shifts from background in both Pb flux and stable isotopes. We use a Pb–Pb co-isotopic plot (Fig. 6) to provide insight into the potential source(s) of anthropogenic Pb emissions to Lake CF8. Pb–Pb co-isotopic plots of the surface sediment data place the temporal range for Lake CF8 within the context of spatial variability of modern values within our entire sample population (Fig. 6).

In Pb–Pb co-isotopic plots, mixing between two components will always generate a straight line; a feature that is independent of the Pb concentrations characterizing each component. The Pb–Pb co-isotopic plot of the Lake CF8 sediments (Fig. 6) defines a well-constrained straight line, which is entirely consistent with the mixing of natural Pb with an anthropogenic component. The lack of a return to pre-industrial stable isotope values indicates that anthropogenic Pb continues to enter Lake CF8 sediments. An extension of the slope of the line delineated by the linear array of the CF8 time series data (dotted line, Fig. 6) does not intersect any particular field that defines a Pb isotopic composition characteristic of industrial emissions from Western and Eastern Europe, Canada, Russia or China. Thus, the Pb–Pb co-isotopic plot could not unequivocally identify or eliminate any one of these possible continental Pb source areas that might impact the study region. However, based on the plot in Fig. 6 it appears unlikely that the pollution Pb signal at CF8 originated from the USA.

As Lake CF8 is far removed from any industrialized activities, the source of Pb pollution impacting the lake likely reflects regional-scale patterns of atmospheric deposition (Outridge et al., 2002). Although attempts to attribute provenance of Pb pollution were equivocal, the sediment record reveals that anthropogenic inputs began after ~1925, and presently represent up to one quarter of the Pb burden in the labile fraction of the sediments. Despite recent reductions in industrial Pb emissions, there is no evidence for attendant reductions of anthropogenic Pb at Lake CF8. Local to regional-scale processes, in particular enhanced primary production and changing precipitation patterns as climate warms, may represent important factors that

modulate Pb deposition to Arctic lakes. This has direct relevance for other sorbible contaminants known to impact Arctic ecosystems including polychlorinated biphenyls (PCBs), polybrominated diphenyl ethers (PBDEs), and high-molecular weight polycyclic aromatic hydrocarbons (PAHs). This has potentially serious biogeochemical and ecological implications, given that Arctic regions are warming at faster rates than more southerly latitudes.

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