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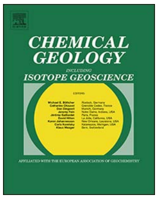

Lead isotopes as particulate contaminant tracers and chronostratigraphic markers in lake sediments in northeastern North America

Carol A.L. Cheyne[a,1], Alyson M. Thibodeau[a,2], Gregory F. Slater[b], Bridget A. Bergquist[a,*]

[a] *Department of Earth Sciences, University of Toronto, 22 Russell Street, Toronto, Ontario M5S 3B1, Canada*
[b] *School of Geography and Earth Sciences, McMaster University, General Sciences Building Room 306, 1280 Main Street West, Hamilton, Ontario L8S 4K1, Canada*

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ABSTRACT

The utility of lead (Pb) isotopes as tracers of particulate contamination and as chronostratigraphic markers was assessed in five lake sediment cores from the Great Lakes and southern Ontario region. The marker for smelting of highly radiogenic ores in the Upper Mississippi Valley in the mid-19th century was seen in the Pb isotopes in four lakes expanding the geographic range of this established marker into southern and central Ontario. This marker is useful for age-dating sediments deposited in the 1800s in archives where it is present. The estimated dates for this ~1850 marker using other dating methods span a range of 57 years, emphasizing the importance of the marker as a tie-point for extrapolated dates in the 19th century. Lead isotopes identified leaded gasoline as an important source only in one lake in the second half of the 20th century; its signal was not identified in all other lakes because the lakes were more affected by local and regional inputs. Lead isotopes combined with trace metal fluxes identified a potential marker for coal combustion or urban sources in the second half of the 20th century in southern Ontario, where these sources were significant enough to outweigh leaded gasoline input. The effects of Canadian mining and smelting activities were seen in the trace metal flux profiles of central Ontario lakes; however, these activities were not visible in the Pb isotopes, likely due to mixing of several sources with similar Pb isotopic signatures. This study demonstrates the usefulness of combining lead isotopes and trace metal flux profiles for identifying markers of historical and modern particulate contamination sources, especially in regions where several pollution sources exist.

1. Introduction

Lead (Pb) isotopes are useful tools for solving a wide range of problems in environmental geochemistry due to the highly varied natural abundances and half-lives of the radionuclides that decay to different Pb isotopes. Lead isotopes in the environment are particularly useful for determining the source of Pb-containing particulates to the environment, and more recently their utility for refining age-dating of lake sediments has been shown (Lima et al., 2005; Kelly et al., 2009; Gobeil et al., 2013). In this study, we used Pb isotopes as tracers of atmospheric particulate contaminants to lake sediments in the Great Lakes region and southern Ontario. The two main goals of this study were: (1) to assess the geographic range of the ~1850 Upper Mississippi Valley Pb isotope chronostratigraphic marker identified in recent studies and (2) to use Pb isotope and trace metal flux profiles to determine the atmospheric sources of trace metals to the Great Lakes and southern Ontario region over the past two centuries.

In the 1800s, ore smelting and coal combustion were primary sources of trace metals to the atmosphere (Graney et al., 1995; Nriagu, 1979). Over time, sources of trace metals diversified to also include oil combustion, the production of iron, steel, non-ferrous metal, and cement, and waste incineration (Pacyna and Pacyna, 2001). Between 1923 and the mid-1970s, Pb-bearing particulates were particularly important atmospheric contaminants due to the use of tetra-ethyl Pb as an anti-knocking agent in combustion engines (Nriagu, 1990; Patterson, 1965). Regulation of leaded gasoline began in the 1970s after studies showed elevated blood Pb levels in United States residents (Patterson, 1965) and Pb contamination in remote ecosystems (Murozumi et al., 1969). In addition, the passage of the Clean Air Act in the United States in 1963 and similar regulations in other developed countries have also led to measurable reductions in global anthropogenic emissions of Pb and several other trace metals in recent decades (Pacyna and Pacyna, 2001; Shen and Boyle, 1987).

Lead isotopes record the shifting sources of Pb to the atmosphere in

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* Corresponding author.
E-mail address: bergquist@es.utoronto.ca (B.A. Bergquist).
[1] Present address: Geosyntec Consultants, 130 Stone Road West, Guelph, Ontario, N1G 3Z2.
[2] Present address: Department of Earth Sciences, Dickinson College, Carlisle, Pennsylvania 17013, USA.

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lake sediments. Lead isotope ratios vary widely in nature because three of the stable Pb isotopes (^{206}Pb, ^{207}Pb, and ^{208}Pb) are formed from the radioactive decay of long-lived isotopes of U and Th, which have different half-lives (^{238}U half-life = 4.5 b.y., ^{235}U half-life = 0.7 m.y., ^{232}Th half-life = 14 b.y. for ^{206}Pb, ^{207}Pb, and ^{208}Pb respectively; Dickin, 2005) and differing concentrations in natural materials. ^{204}Pb is the only Pb isotope with a fixed abundance. The wide range of parent isotope half-lives along with the variable initial abundances of the U, Th, and Pb in different minerals results in a large and often unique range of Pb isotopes in different geological ore bodies. Furthermore, upon formation of Pb ore (e.g. galena), U and Th are largely excluded from the crystal lattice resulting in Pb isotope ratios that remain fixed over time. Stable Pb isotope fractionation during physico-chemical processes is minimal compared to the variation in isotope composition between Pb sources, such that Pb deposited in the environment has the same isotopic signature as the source in which it was originally formed (Doe, 1970) and can often be traced back to its source (e.g. Graney and Landis, 2013; Lee et al., 2007; Lima et al., 2005; Graney et al., 1995). Pb isotopes may also provide insights into the sources of other trace metals to the environment, because trace metals are often transported by the same mechanism and can come from similar sources. Thus, coupling Pb isotopes with trace metal abundances allows sources of particulate metals to be more clearly discerned (e.g. Chillrud et al., 2003; Couillard et al., 2008; Graney and Landis, 2013).

In this study, we use lake sediments as archives of regional Pb isotope signatures and trace metal abundances. Lake sediments provide a relatively easily obtained, high resolution record of past local, regional, or global atmospheric metal deposition since sediments are the dominant sink for suspended particulates in the lacustrine water column (Semkin and Kramer, 1976). However, for lake sediments to provide accurate historical reconstructions of metal fluxes and sources, their dates of deposition must be accurately known. ^{210}Pb-dating is often considered the most accurate method for dating sediments in the past 100 years, but requires extrapolation for older sediments due to the short half-life of ^{210}Pb (Appleby and Oldfield, 1978). ^{14}C-dating can reconstruct environmental changes over several millennia, but can be inaccurate for sediments from the past few centuries due to contamination by old carbon (Oldfield et al., 1997) and also because ^{14}C signatures in recent sediments can be difficult to distinguish from modern values. Varve counting is useful in lakes with clear annual lamination (Oldfield et al., 1997); however, varve counts can underestimate ages due to unclear sediment layers. Overall, these methods are problematic for determinations on sediments deposited 100–200 years ago.

Lead isotope signatures may provide suitable chronostratigraphic markers for sediment deposited in the past few centuries. Known changes in historical Pb sources translate to changes in Pb isotopic signatures in downwind lakes, which can be used to accurately date sediments in lakes where they are present. One such important marker for the mid-19th century was discovered in northeastern North America by Lima et al. (2005). The researchers observed a large shift in the isotopic composition of Pb (reported as a peak in the ^{206}Pb/^{207}Pb ratio) around ~1850 in a Rhode Island river basin sediment core (Fig. S1 in the Supplemental information [SI]) despite no large corresponding peak in Pb concentration. This isotopic excursion was attributed to a dominance of ore smelting in the Upper Mississippi Valley (UMV) between 1830 and 1870, where Pb ores are unusually radiogenic (Brown, 1962; Heyl et al., 1959; Lima et al., 2005). Lima et al. (2005) argued that this isotope peak could be used to determine the deposition dates of sediments from 100 to 200 years ago in watersheds where it exists. Since then, similar excursions have been measured in Bermuda oceanic corals (Kelly et al., 2009), a New Jersey salt marsh (Kemp et al., 2012), and several lakes throughout eastern Quebec (Gobeil et al., 2013). Lima et al. (2005) also found evidence for the marker in previously published sediment profiles from Chesapeake Bay (Marcantonio et al., 2002) and Lake Erie (Graney et al., 1995), and less well-defined markers in Lake Michigan and Lake Ontario sediment cores (Graney et al., 1995). The ^{206}Pb/^{207}Pb peak has been most accurately dated to ~1850–1854 using X-ray density counting and Sr/Ca cycle counting in Bermuda corals (Kelly et al., 2009).

In this paper, we expand the range of the Pb isotope UMV chronostratigraphic marker into central and southern Ontario and as far north as Thunder Bay, enhancing the utility of the marker as a tie-point for extrapolated dates or other dating techniques in the 19th century. We also identify markers of several 20th century pollution sources using Pb isotopes and trace metal fluxes, identifying important differences in dominant regional pollution sources over the past century in central and southern Ontario.

2. Methods

2.1. Study areas and sediment core collection

Five lakes located in the Great Lakes region were chosen for analysis. Locations and descriptions for each lake are provided in Table S1 (SI), and a map showing the locations of the studied lakes is provided in Fig. 1. All lakes are deep enough to have completely or seasonally anoxic benthic regions with minimal bioturbation. In addition, they all have minimally developed shorelines and are far from local runoff. Given these conditions, we assume the primary metal particulate input to these lakes is atmospheric deposition.

A gravity corer was used to collect cores from four of the lakes (Solitaire Lake, Fairbanks Lake, Big McDougal Lake, and Siskiwit Lake). 40–60 cm cores were collected using a 6.7 cm inner diameter corer from the deepest portion of each lake. Cores were sectioned into 1 cm intervals on shore, bagged, and frozen at −20 °C until analysis. The Crawford Lake core was obtained from the deepest portion of the lake using a freeze corer filled with dry ice. 0.5–1 cm sections were cut using a tile saw with a 2 mm thick blade. Solitaire Lake, Fairbanks Lake, and Big McDougal Lake cores were collected in 2014. Siskiwit Lake and Crawford Lake cores were collected in 2005 and 2006 respectively.

2.2. Sediment dating

All lake cores except Crawford Lake were dated using the ^{210}Pb dating method (Appleby and Oldfield, 1978). Briefly, dried and acid treated sediment was prepared using a ^{210}Po enrichment method. ^{210}Po was plated on Ag discs and sample activity was measured using an alpha counting device. Sediment age was determined using at least one of the following models: the Constant Initial Concentration model (CIC1 and CIC2) and the Constant Rate of Supply model (CRS) (Appleby and Oldfield, 1978; Yang, 2006). The CIC2 model was chosen to date all ^{210}Pb-dated lake cores. CIC2 calculates sediment age using directly measured cumulative dry weight, which involves fewer inaccuracies than modelled uncompacted mid-point depths used in the CIC1 model (Yang, 2006). CIC2 also provided sediment dates in Siskiwit Lake that corresponded better with previously reported contaminant peaks than the CRS model (Slater et al., 2013). The Crawford Lake core was dated using varve counting combined with ^{14}C dating of goose dung pellets (McAndrews and Turton, 2007). Varve counted sediment deposition dates for 1867–2000 were combined with dates spanning 910–1867 determined by ^{14}C analysis using accelerator mass spectrometry. All dating model results are available in Table S2 (SI). Table S3 (SI) includes the dating method and model used in reporting depth profiles for each lake, and the mass sedimentation rate for each lake.

2.3. Trace metal flux analysis

Cu, Zn, Cd, and Pb concentrations were determined using a dilute acid leach modified from Graney et al. (1995). Trace metal clean techniques were employed throughout trace metal sample preparation, including the use of acid-cleaned vials and ultra-pure acids. Frozen

Fig. 1. Map showing the locations of the 5 lakes sampled in this study, indicated with red stars. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

samples were weighed and freeze dried prior to analysis. 100 mg sediment samples were weighed into pre-cleaned 1.5 mL polypropylene centrifuge tubes and 1 mL of Optima grade 1.69 N HCl - 0.98 N HNO_3 was added. Samples were vortexed briefly, sonicated for 90 min at 44 °C, and allowed to digest and degas for 24 h. Leachates were separated by centrifugation, and an aliquot of each sample was diluted with 2% Optima HNO_3 for trace metal concentration analysis. The focus of this study is the anthropogenic component of metals within lake sediments, which is why the dilute HCl/HNO_3 method from Graney et al. (1995) was chosen. This method does not use hydrofluoric acid (HF) or concentrated acids to digest sediments, because these release the non-anthropogenic metal fraction contained within the mineral silicate structure (Graney et al., 1995).

Cu, Zn, Cd, and Pb concentrations were determined using a Thermo Scientific X Series II Quadrupole-ICP-MS located in the Department of Earth Sciences, University of Toronto. In order to monitor instrumental drift, samples, standards, and blanks were spiked with a constant concentration of indium (In) and bismuth (Bi) and all samples were normalized to the average counts per second of In and Bi in the calibration blanks. Raw concentration data was corrected for procedural blank concentrations before calculating dry sediment concentrations. Precision and accuracy of the measurements were determined through repeated analysis of the external standard NIST1944 (New York/New Jersey waterway sediment). Typical uncertainty (2RSD) for concentrations of the trace metals analyzed by quadrupole-ICP-MS was 12–18%. Details on the accuracy and precision on the analysis of Cu, Zn, Cd, and Pb in NIST1944 relative to their certified or reference values are outlined in Table S4 (SI).

Hg concentrations were determined by combustion atomic absorption spectrometry (AAS) of dried sediment samples. Freeze dried sediment samples were weighed into nickel boats between layers of sodium bicarbonate and aluminum hydroxide. Samples were analyzed for Hg concentration using a Teledyne Hydra-C combustion AAS. Precision and accuracy of the measurements were determined through repeated analysis of NIST1646a standard (Estuarine Sediment). Typical uncertainty (2RSD) for Hg concentration was 16%. Details on the accuracy and precision obtained in the analysis of Hg in NIST1646a relative to the reference value are outlined in Table S4 (SI). Sediment cores from Siskiwit Lake were also analyzed for Hg in Drevnick et al., 2007, and the analyses are in good agreement.

Trace metal concentrations were converted to trace metal flux ($\mu g\ cm^{-2}\ yr^{-1}$) by multiplying trace metal concentration ($\mu g\ g^{-1}$) by mass sedimentation rate ($g\ cm^{-2}\ yr^{-1}$). Flux captures the rate of trace metal input to a lake per sediment area over time. This quantity allows for trace metal input to be compared across multiple lakes, since it accounts for the differences in sedimentation rate for each lake.

2.4. Lead isotope analysis

Trace metal clean laboratory procedures were used throughout sample preparation for Pb isotope analysis and all reagents and matrix solutions were made using Optima™-grade HCl, HBr, or HNO_3. Leachates were prepared for isotopic analysis by a method modified from Reuer et al. (2003). An aliquot of each HCl-HNO_3 leachate was transferred to a 5 mL Savillex™ PTFE vial, brought to dryness, brought up in 900 μL HNO_3–100 μL HCl, and refluxed for 24 h to break down organic matter, which may interfere with isotopic analysis. The refluxed samples were brought to dryness and brought up in 2.1 N HBr. Lead was separated from the matrix using polypropylene microcolumns loaded with AG 1 × 8 (chloride form, 200–400 mesh) anion exchange resin. Samples were loaded into the pre-cleaned resin in 2.1 N HBr and eluted into clean 5 mL Savillex PTFE vials with 6 N HCl. Eluted samples were dried and prepared for isotopic analysis by dissolving in 1 mL of 2% HNO_3.

All samples were analyzed for Pb isotope ratios using a Thermo Scientific Neptune Plus Multi-Collector-ICP-MS located in the Department of Earth Sciences, University of Toronto. All samples and standards were spiked with a lead-free thallium solution to achieve a 2:1 Pb:Tl ratio. Samples, standards, and blanks were introduced into the mass spectrometer through an Apex nebulizer (ESI). The NIST981 standard was analyzed twice per three samples, and blanks were analyzed between each standard and sample. Faraday cups were configured to simultaneously measure Pb (mass 204, 206, 207, and 208) along with Tl (mass 203 and 205) and Hg (mass 202). All measurements were blank corrected and the isobaric interference on ^{204}Pb was corrected for ^{204}Hg, which was negligible. Instrumental mass bias was accounted for both by correcting with the Tl internal standard and by normalizing Pb isotopic measurements to the bracketing NIST981 standards.

Aliquots of NIST981 and USGS basalt standard BCR-2 were used as external standards and processed through the same procedure as samples. Typical uncertainty (2SD) on ^{206}Pb/^{207}Pb in analysis of NIST981 external standards was 200 ppm. Our NIST981 results are in excellent agreement with triple spike values reported by Galer and Abouchami (1998) and double spike values reported by Todt et al. (1996). Our BCR-2 results are similarly in agreement with the double spike values reported by Woodhead and Hergt (2000) and static multicollection values reported by Weis et al. (2006). Further details on error ranges for the analysis of the external standards compared to previously reported values are outlined in Tables S5 and S6 (SI). Details on the error ranges for the analysis of NIST981 as an instrumental standard are outlined in Table S7 (SI).

3. Results

There is wide regional and chronological variation in the measured Pb isotope and trace metal flux profiles of the five lakes in this study. Figs. 2 and 3 show the combined downcore ^{206}Pb/^{207}Pb and ^{208}Pb/^{207}Pb profiles of total leachable Pb in all lakes as a function of time. Figs. 4 and 5 show the total trace metal flux profiles for all the lakes combined and individually, respectively. Pb isotope ratios and trace metal concentration values for all lakes are presented in tabular format in the Supplemental information (Table S8). In the sections that follow, we describe the most important features of these profiles.

3.1. Lead isotope results

Sediment cores from Big McDougal, Crawford, Siskiwit, and Solitaire have maximum ^{206}Pb/^{207}Pb and ^{208}Pb/^{207}Pb in the mid-19th century. In the profile for Fairbanks Lake ^{208}Pb/^{207}Pb also peaks in the 19th century, but this maximum occurs significantly later than in the other lakes and the corresponding ^{206}Pb/^{207}Pb peak is not distinct from isotopic signatures deeper in the core. Siskiwit Lake exhibits a minimum in ^{206}Pb/^{207}Pb at ~1970 that is not present in the other lakes. Both Crawford Lake and Solitaire Lake contain small peaks in ^{206}Pb/^{207}Pb ~1970–1980, however it is more pronounced in Crawford Lake than Solitaire Lake. The ^{206}Pb/^{207}Pb profiles for Big McDougal Lake and Fairbanks Lake show uninterrupted declines towards the surface in the 20th century.

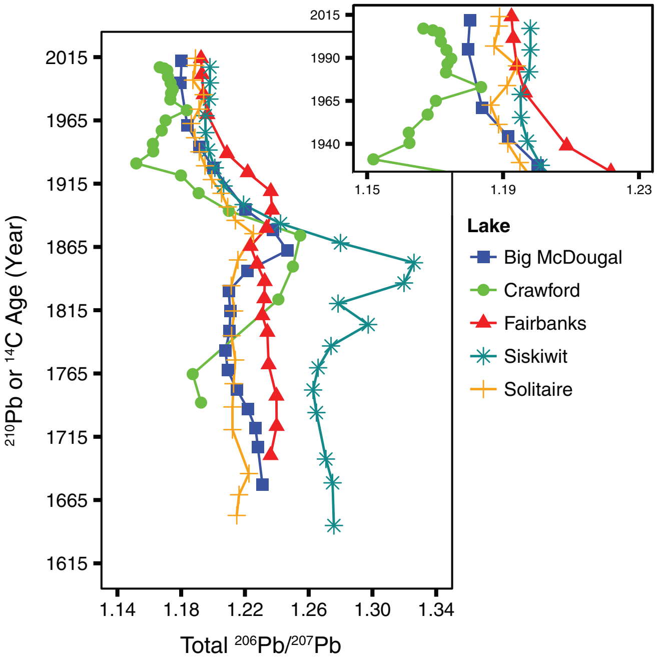

Fig. 2. Combined downcore profiles of leachable ^{206}Pb/^{207}Pb as a function of ^{210}Pb or ^{14}C age in all lakes from this study. The pop out shows a close up of the profiles in the 20th century. Error bars are 2SD for multiple analyses of the NIST981 external standard; however, they are smaller than the data symbols.

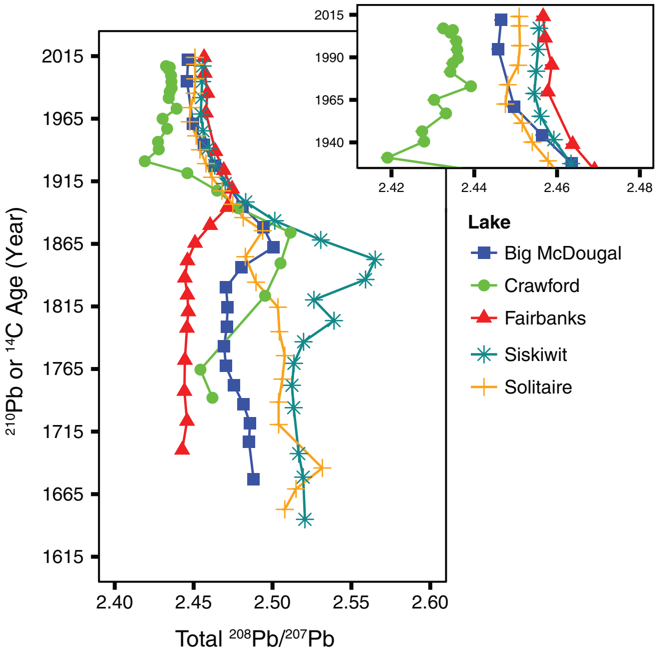

Fig. 3. Combined downcore profiles of leachable ^{208}Pb/^{207}Pb as a function of ^{210}Pb or ^{14}C age in all lakes from this study. The pop out shows a close up of the profiles in the 20th century for clarity. Error bars are 2SD for multiple analyses of the NIST981 external standard, however they are smaller than the points on the plot.

3.2. Trace metal flux results

Siskiwit Lake contains a peak in Pb flux at ~1970 that is uncoupled from all other measured trace metals (this study; Muir et al., 2009;

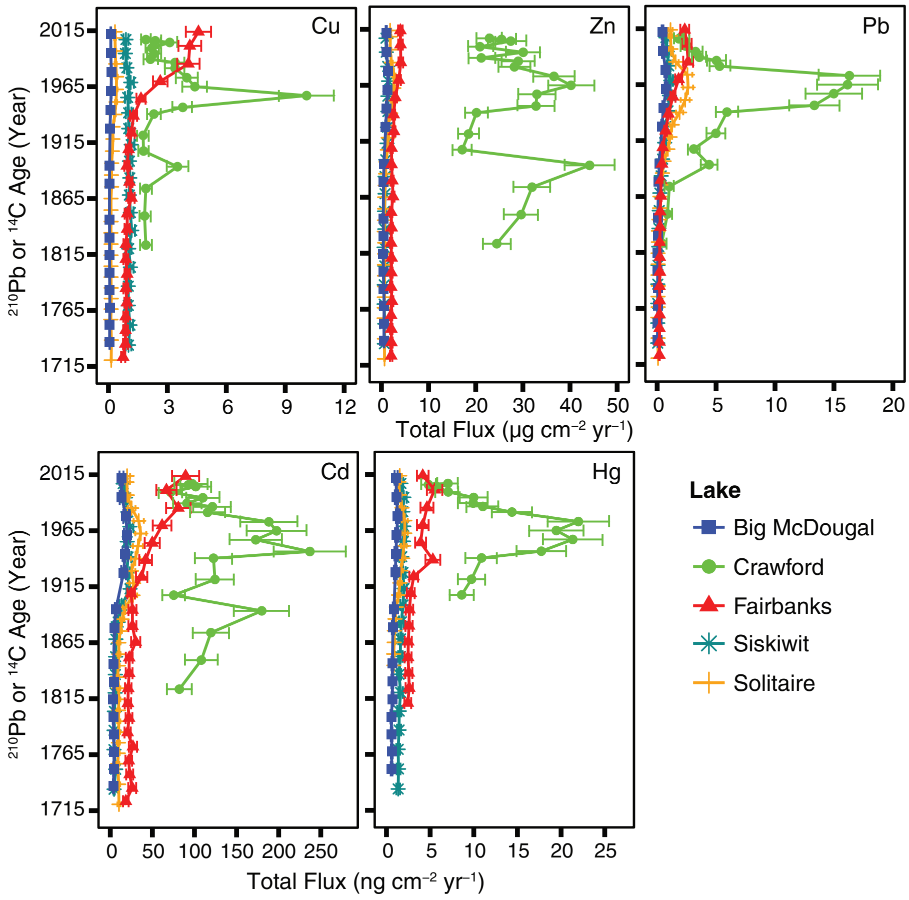

Fig. 4. Leachable trace metal flux as a function of ^{210}Pb or ^{14}C age for Cu, Zn, Pb, Cd, and Hg in the studied lakes. Error bars are 2RSD for multiple analyses of standard reference materials.

Drevnick et al., 2007; Drevnick et al., 2012). In the Crawford Lake profiles, there is clear covariance seen in the Pb, Cd, and Hg profiles, where they all exhibit flux peaks that span several decades in the late 20th century. Both Solitaire Lake and Big McDougal Lake exhibit co-varying late-20th century peaks in all the measured trace metals, with larger peaks in Solitaire Lake than in Big McDougal Lake. In Fairbanks Lake, Cu and Cd show co-varying increases in flux towards the surface.

4. Discussion

4.1. Upper Mississippi Valley chronostratigraphic marker

The observed variation in Pb isotopes and trace metal fluxes indicate several distinct sources of trace metals to each lake over time, suggesting regional and local patterns in the sources of trace metals to the atmosphere. We interpret the 19th century peaks in ^{206}Pb/^{207}Pb in four of the lakes as atmospheric contamination derived from the smelting of Pb-Zn ores in the Upper Mississippi Valley (UMV) during the mid-19th century. The peak exists for Big McDougal Lake, Crawford Lake, Siskiwit Lake, and Solitaire Lake (Fig. 2), though for Solitaire Lake the peak is less certain as it is only made up of one data point. Because the sediment cores for several of the studied lakes were not deep enough to establish a consistent natural background Pb isotope signature (particularly for Crawford Lake), the contribution from the UMV smelting region to the mid-19th century peaks was not quantified relative to a natural background. UMV (and UMV-type) ores tend to have relatively radiogenic Pb isotopic signatures relative to other ores and other sources of particulate contamination to the atmosphere (e.g. Sangster et al., 2000). In northeastern North American, smelting of UMV ores was a dominant Pb source to the atmosphere between 1830 and 1870 (Heyl et al., 1959) and peaks in ^{206}Pb/^{207}Pb are observed in several other archives downwind of the UMV mining district including a Rhode Island River Basin (Lima et al., 2005), Chesapeake Bay (Marcantonio et al., 2002), Lake Erie, Lake Michigan, and Lake Ontario (Graney et al., 1995), Bermuda oceanic corals (Kelly et al., 2009), a New Jersey salt marsh (Kemp et al., 2012), and several small lakes in eastern Quebec (Gobeil et al., 2013). The timing of the isotopic excursion related to UMV ore production is well constrained to ~1850–1854 based on its presence in well-dated Bermuda corals (Kelly et al., 2009). Thus, where present, isotopic excursions consistent with UMV ores may be used to anchor extrapolated ^{210}Pb dates or dates from other techniques in lake sediments. It is important to note that the marker is unique to the Pb isotope profiles and is not observed in the Pb flux profiles (Fig. 5).

In the four lakes where the UMV marker is most likely present in this study, it occurs between 1852 and 1875 based on other dating methods (Fig. 6). These dates were derived from ^{210}Pb or ^{14}C dating combined with varve counting, and the offset timings for the marker in these lakes are likely artefacts of dating errors or evidence of imprecision of the dating method. In Solitaire Lake, the marker at 1875 is only made of one data point more radiogenic than the shallower and deeper data points. For this reason, identification of the marker is less certain for Solitaire than for the other three lakes. However, based on the timing of the small peak and the location of Solitaire Lake among other archives that contain the marker, and the small uncertainty associated with the Pb isotope data, it is still highly likely that the small peak is caused by input from the UMV smelting region. The other North American archives where the UMV peak is present also demonstrate a wide range of estimated dates based on other dating techniques for the marker (Table 1), spanning from 1838 in Chesapeake Bay (Marcantonio et al., 2002) to 1895 in Lake Ontario (Graney et al., 1995). Several of the calculated dates for the marker in this study and in Graney et al. (1995) occur several decades after 1850–1854. This may be due to sediment focusing, which has been documented in other Ontario lakes

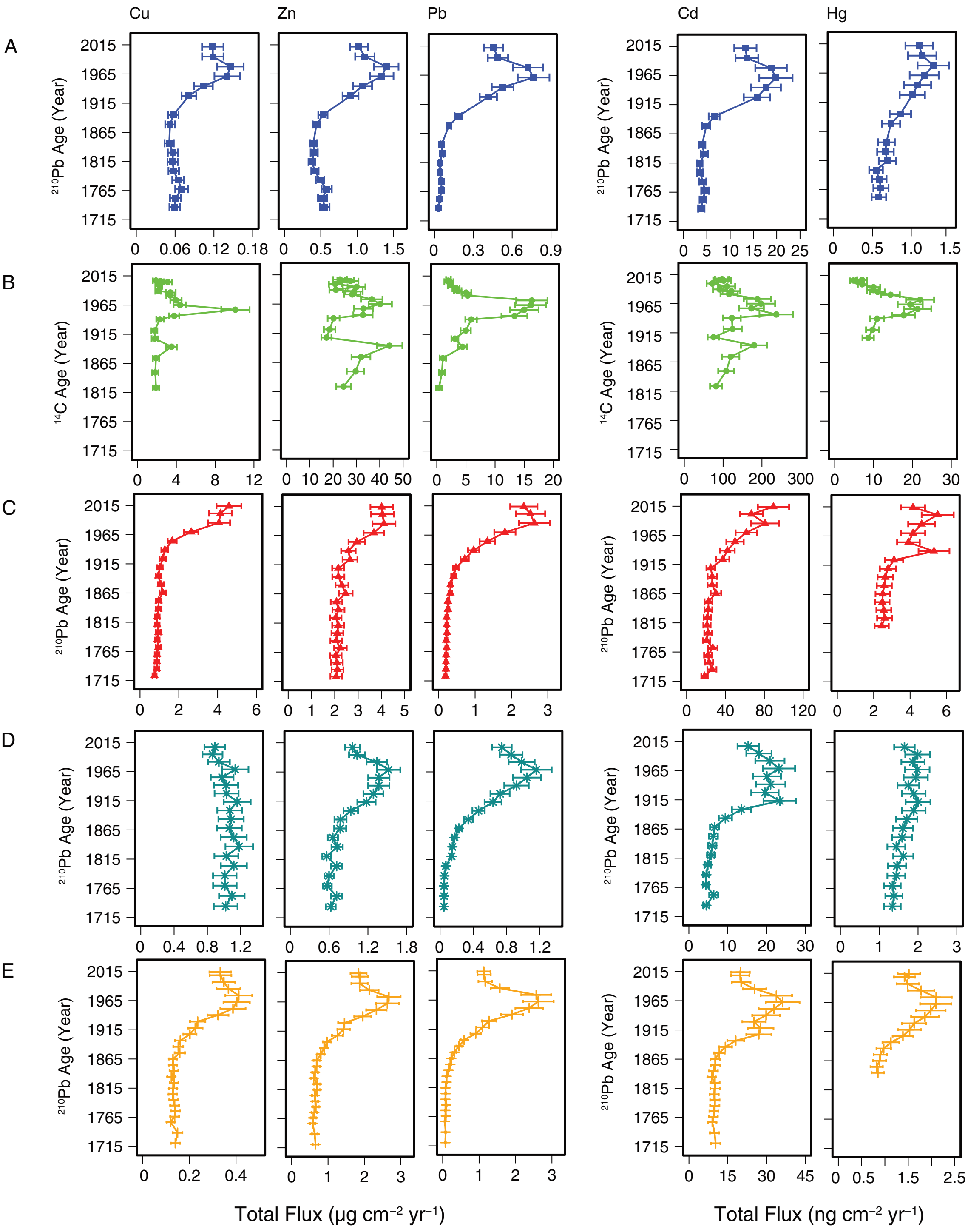

Fig. 5. Total trace metal flux as a function of ^{210}Pb or ^{14}C age for Cu, Zn, Pb, Cd, and Hg in Big McDougal Lake (A), Crawford Lake (B), Fairbanks Lake (C), Siskiwit Lake (D), and Solitaire Lake (E). Error bars are 2RSD for multiple analyses of standard reference materials.

(Anderson et al., 1987). The range of dates seen for this marker from other dating methods serves to emphasize the importance of the UMV chronostratigraphic marker as a tie-point for extrapolated dates or other dating techniques such as varve counting in the 19th century.

This study identifies the likely presence of the UMV marker in southern Ontario (Crawford lake), central Ontario (Solitaire Lake and Big McDougal Lake), and as far north as Siskiwit Lake in Lake Superior. However, although there is a small peak in ^{206}Pb/^{207}Pb at ~1893 (Fig. 2) in Fairbanks Lake, it is likely that this peak is not due to UMV smelting. Not only is the small peak unusually late for the UMV smelting marker, its isotopic composition is also very similar to the Pb isotope signature for deeper sediment in the lake. In addition, there is a decoupling of the ^{206}Pb/^{207}Pb and ^{208}Pb/^{207}Pb for this peak in Fairbanks Lake unlike the other lakes (Fig. 7), suggesting that this excursion is due to a unique Pb source to Fairbanks Lake. The Pb isotopic signature of this excursion is more consistent with the Pb isotopic signatures of certain ores in the south range of the Sudbury Basin, ~18 km from Fairbanks Lake (Dickin et al., 1996). Mining practices in Sudbury were far more localized at the turn of the 20th century than they were during and after World War One (LeBourdais, 1953). Thus it is likely

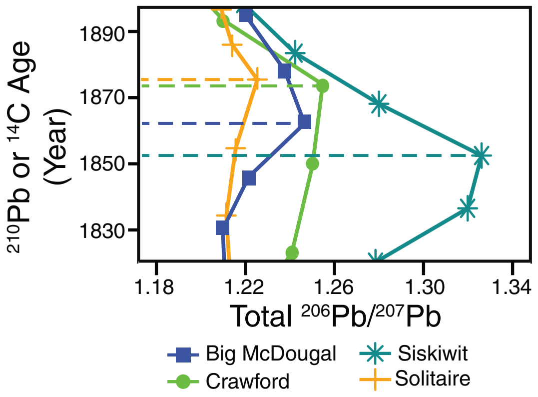

Fig. 6. Downcore profiles of leachable ^{206}Pb/^{207}Pb as a function of ^{210}Pb or ^{14}C age in the 19th century. The lakes reported here all exhibit peaks in ^{206}Pb/^{207}Pb that are likely due to UMV ore smelting. Dashed lines indicate the year of peak input from UMV ore smelting estimated from the dating methods used in this study. The UMV peak is well dated to 1850–1854 (Kelly et al., 2009).

the mining of the south range Sudbury ores did not affect more distant lakes. In Lake Andrus, a lake relatively close to Fairbanks Lake, there is similarly no evidence for the UMV marker (Graney et al., 1995). While this lake is outside the Sudbury mining region, the authors indicate the importance of other local to regional pollution sources to this lake, including a forest fire in the early 20th century. Big McDougal Lake, despite being within the Sudbury mining region, may have been too isolated to be affected by local to regional mining practices at this time. Longer range sources such as the UMV smelting region appear to be more important for this lake.

Fig. 8 summarizes the environmental archives where the UMV marker is present, absent, and contested in northeastern North America based on this study and previously reported archives. At this time, the northern extent of the marker is uncertain. In western Quebec the UMV marker is reportedly present in Lake Desperiers (Gobeil et al., 2013), but this may not be the case because it is absent in nearby Lac Caron, Lac Vaudray, and Lac Dufault (Couillard et al., 2008). There is a copper smelter (Rouyn Noranda) located in the centre of the four lakes, but copper was not discovered in the region until 1917 and particulate contamination from smelting would not have impacted the downwind lakes prior to this time. Gobeil et al. (2013) found that the sediment deposition dates for Lake Desperiers were highly inaccurate compared to lakes in eastern Quebec and suggested that low-pH emissions from the smelter affected the rate of ^{210}Pb supply to the sediment and thus impacted calculated sediment ages (Gobeil et al., 2013). Thus the age dating of this lake may be wrong. Based on the inconsistencies in lakes in this area and inconclusive dating of this core, we suggest it is doubtful that the UMV marker is truly present in this lake and that western Quebec may be beyond the northern extent of the UMV marker.

An Algonquin Park ombrotrophic peat bog also appears to be lacking the UMV marker, but lies within the geographic range where we expect it to be present. The peat bog record contains a peak in ^{206}Pb/^{207}Pb at ~1920 (Shotyk and Krachler, 2010). We suggest that in this case, the peak is not actually at ~1920 and is instead the UMV peak at ~1850, again highlighting the difficulty in dating archives. The Pb isotope profiles for the Algonquin Park peat core and for nearby Solitaire Lake are very similar with estimated timings of their ^{206}Pb/^{207}Pb peaks at ~1920 for the peat bog and at ~1875 for Solitaire Lake. Since the mid-19th century peak exists throughout a much wider region of central Ontario (Fig. 8), it is likely that both of the ^{206}Pb/^{207}Pb peaks in these lakes also occurred at the expected time (~1850).

4.2. Leaded gasoline marker

Widespread use of leaded gasoline in combustion engines began in the early 1930s in North America, and most leaded gasoline used in North America until 1968 was sourced from Canadian and Mexican ores with ^{206}Pb/^{207}Pb ranging from 1.15 to 1.19. After 1968, the United States began using more radiogenic Missouri lead in combustion engines (Chow et al., 1975). Therefore, if leaded gasoline is the dominant source of Pb to a lake, its effects should show up as a "trough" in the Pb isotope record, where ^{206}Pb/^{207}Pb reaches a minimum around 1970 before increasing again. Only one lake in this study exhibits this pattern in the 20th century. The Siskiwit Lake profile includes a small trough in ^{206}Pb/^{207}Pb throughout the 1960s (Fig. 2 pop out) that is consistent with US leaded gasoline as the primary source of Pb at this time. The marker has previously been found in Lake Michigan and Lake Erie (Graney et al., 1995), Chesapeake Bay (Marcantonio et al., 2002), a Rhode Island river basin (Lima et al., 2005), Bermuda oceanic corals (Kelly et al., 2009), a New Jersey Salt Marsh (Kemp et al., 2012), and seven lakes in eastern Quebec (Gobeil et al., 2013).

Unlike the UMV ore smelting marker, the effects of leaded gasoline use can also be seen in Pb flux profiles in environmental archives since the timing of the shift to more radiogenic Pb ore sources for leaded gasoline is approximately coincident with the beginning of the phase out of leaded gasoline use (Nriagu, 1990). There is a clear peak in Pb flux circa 1970 in Siskiwit Lake that is not coupled to any of the other trace metals (Fig. 5D). This is supporting evidence for dominant input due to leaded gasoline in the second half of the 20th century because leaded gasoline emissions were reduced around the time of peak Pb flux and because no other trace metals are present in significant quantities in leaded gasoline.

However, Pb flux profiles alone cannot identify leaded gasoline input to a lake in regions such as Ontario where ore smelting and coal combustion were also prevalent in the 20th century. Since these other pollutant sources also reduced emissions around 1970 in northeastern North America, a peak in Pb flux around 1970 cannot be uniquely attributed to leaded gasoline. In order to confirm leaded gasoline input, the isotopic minimum due to shifting ore sources around 1970 must be present. This issue is highlighted in the cores from Crawford Lake,

Table 1
Summary of calculated dates for the proposed Upper Mississippi Valley ore smelting chronostratigraphic marker in this study and in previous work, sorted by date.

Location	Archive	Date	Dating method	Author
Chesapeake Bay, USA	Estuary sediment core	1838–1841	^{210}Pb (CIC method), ^{137}Cs, pollen dating	Marcantonio et al. (2002)
Eastern Quebec, Canada	Lake sediment cores	1841–1855	^{210}Pb (CRS method)	Gobeil et al. (2013)
Rhode Island, USA	River basin sediment core	1842	Economic data, varve counting, ^{210}Pb (CRS method)	Lima et al. (2005)
Bermuda	Oceanic coral	1850	Sr/Ca cycle counting, X-ray density counting	Kelly et al. (2009)
Siskiwit Lake	Lake sediment core	1852	^{210}Pb (CIC2 method)	This study
New Jersey, USA	Salt marsh sediment core	1857	^{210}Pb (CRS and CIC methods)	Kemp et al. (2012)
Big McDougal Lake	Lake sediment core	1862	^{210}Pb (CIC2 method)	This study
Lake Michigan	Lake sediment core	1863	^{210}Pb (CRS method), ^{137}Cs	Graney et al. (1995)
Lake Erie	Lake sediment core	1873	^{210}Pb (CRS method), ^{137}Cs	Graney et al. (1995)
Crawford Lake	Lake sediment core	1874	^{14}C, varve counting	This study
Solitaire Lake	Lake sediment core	1875	^{210}Pb (CIC2 method)	This study
Lake Ontario	Lake sediment core	1895	^{210}Pb (CRS method), ^{137}Cs	Graney et al. (1995)

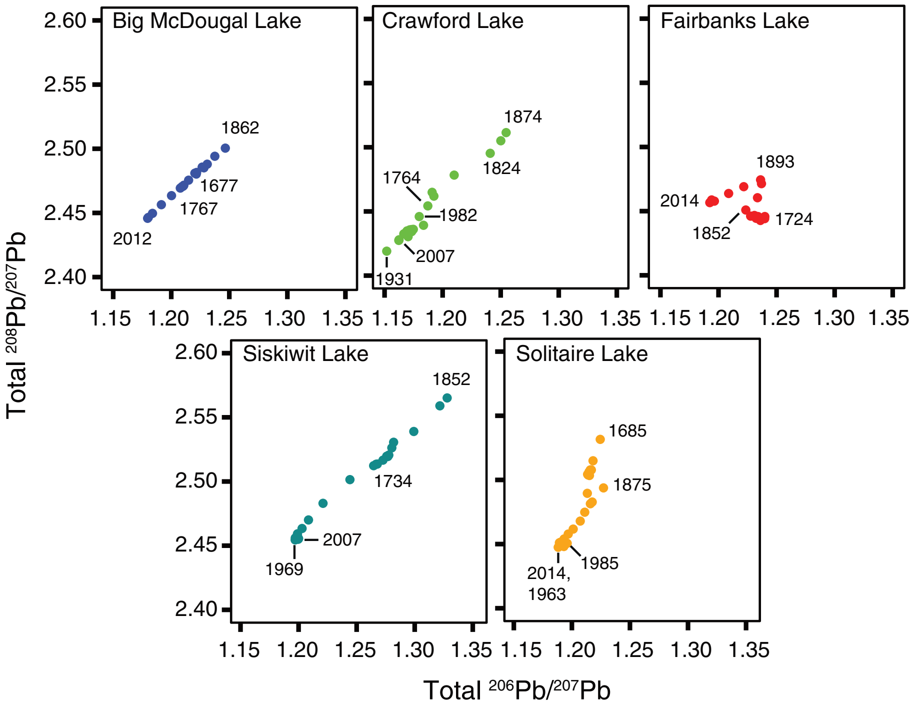

Fig. 7. Leachable ^{206}Pb/^{207}Pb vs leachable ^{208}Pb/^{207}Pb for all sampled lakes. The two isotope ratios are often linearly correlated, as is the case in Siskiwit Lake, Crawford Lake, and Big McDougal Lake. They are decoupled in Fairbanks Lake for the late 19th century peak suggesting a different source than UMV smelting.

Solitaire Lake, and Big McDougal Lake (discussed in detail in Section 4.3) where peaks in Pb circa 1970 are not associated with the characteristic Pb isotope trough, and the Pb fluxes in these lakes co-vary with other trace metals not present in gasoline. Together the Pb isotopes and other metals suggest that local and regional industrial sources were more important sources of Pb and other trace metals than leaded gasoline in the late 20th century.

4.3. Local/regional industrial and urban sources in the 20th century

In less industrialized regions, it is likely that a peak in Pb input around 1970 can be safely assumed to be from global leaded gasoline use rather than regional industry. However, in an industrialized region like southern and central Ontario, the effects of leaded gasoline may be overprinted by local and regional industrial and urban sources. In these cases, the Pb isotope and trace metal signatures are useful for identifying possible sources. However, they do not serve as broadly applicable time markers since they exist on local to regional scales.

4.3.1. Coal and urban sources

The Pb isotope profile for Crawford Lake includes an unusual peak in the late 20th century. After a ^{206}Pb/^{207}Pb minimum at 1931 the Pb isotopes increase to the mid-1970s before decreasing again towards the surface (Fig. 2 pop out). This unusual profile has not been identified for other North American archives in the literature so far. However, the Crawford Lake isotope profile is similar to records from Bermuda oceanic corals. In the case of the Bermuda corals, the Pb isotope pattern has been attributed to a shift from American leaded gasoline to less radiogenic European sources once phase out of leaded gasoline began in North America (Kelly et al., 2009). Although the isotope patterns are similar, it is unlikely that Crawford Lake would be affected significantly by European Pb sources, particularly because several large urban and industrial sources of Pb exist regionally surrounding Crawford Lake. This is also supported by the very high Pb and other trace metal concentrations in Crawford Lake. The rise from less radiogenic to more radiogenic Pb peaking in 1973 may reflect a rise in dominance of inputs from more local coal combustion or urban sources in southern Ontario. Lead isotope signatures for aerosols from nearby Toronto range from 1.15 to 1.17 (Bollhöfer and Rosman, 2001) and lead isotope signatures for coals used in North America range from 1.18 to 1.22 (Chow and Earl, 1972). Both signatures are similar to the Pb isotope values seen in Crawford Lake in the late 20th century.

Crawford Lake is located downwind of several industrial regions where coal combustion grew in prevalence in the late 20th century, primarily in electric power generation and steel production. A significant proportion of the electric power produced in the United States is generated through coal combustion (Baird and Cann, 2008), and a large number of the coal-fired power plants in the United States are located in the Ohio Valley, southwest of Crawford Lake. More proximal to Crawford Lake was Nanticoke Generating Station in southwest Ontario, which was the largest coal-fired power plant in North America that closed in 2013, and also the city of Hamilton, Ontario, where coal-powered steel production makes up the largest industry. The peak and following decline in ^{206}Pb/^{207}Pb in Crawford Lake coincides with further restrictions on stationary sources under the Clean Air Act, when coal-related emissions of pollutants in both the United States and Canada were reduced through implementation of cleaner technology. Pollution of most metals, sulfur species (SO_x), and nitrogen species (NO_x) from coal combustion fell by ~40% between 1973 and 2000 in North America (Baird and Cann, 2008). Regional urban sources also likely contribute to the Pb isotope profile in Crawford Lake. Large nearby cities such as Toronto and Hamilton include numerous sources of metal particulates such as cement production, waste incineration, and metal fabricating in addition to coal sources within the urban areas. In a study comparing Pb isotopes in aerosols in regions across the northern hemisphere, aerosols collected from Toronto contained more radiogenic Pb than any other sampled location in Canada with a maximum ^{206}Pb/^{207}Pb of 1.171 (Bollhöfer and Rosman, 2001), which may have contributed to the peak in Crawford Lake's Pb isotope profile before urban sources were subject to emissions reductions similar to coal facilities.

The trace metal flux profiles of Cd, Hg, and Pb support coal and urban sources as the dominant trace metal sources to Crawford Lake in the late 20th century (Fig. 5B). Strongly co-varying peaks in these three metals suggest a common source that caused long-term input of these metals over multiple decades before subsiding in recent decades.

Fig. 8. Map of northeastern North America showing environmental archives where the isotopic excursion due to smelting in the Upper Mississippi Valley has been documented as present, absent, or contested (this study; Graney et al., 1995; Marcantonio et al., 2002; Outridge et al., 2002; Lima et al., 2005; Couillard et al., 2008; Kelly et al., 2009; Shotyk and Krachler, 2010; Kemp et al., 2012; Gobeil et al., 2013). This study argues that the marker is present in the Algonquin Park peat bog (Shotyk and Krachler, 2010) and absent west of the Rouyn Noranda smelter in Quebec (Gobeil et al., 2013).

Because Cd, Hg, and Pb are common contaminants in coal and urban sources (Pacyna and Pacyna, 2001) and the region is home to several urban centres and coal combustion facilities, these metal profiles are likely due to a mixture of coal combustion and urban sources. Cd and Hg are not found in significant quantities in leaded gasoline, so primary input due to leaded gasoline should not also cause such a strong co-variance in Cd and Hg. In addition, the fluxes for all the trace metals to Crawford Lake are significantly larger than in any other lake, most likely due to Crawford Lake's proximity to industrial and urban regions.

Also in support of coal and urban sources being the cause of the late 20th century peak in ^{206}Pb/^{207}Pb in Crawford Lake, there is evidence that aerosols in the Midwestern United States still show significant Pb input from coal combustion and urban centres. In a study of aerosols in Bondville, Illinois, Graney and Landis (2013) determined that ~18% of the Pb in aerosols reaching the region was from coal combustion, ~56% from urban sources and ~26% from Missouri smelters. By modelling wind trajectories for representative air parcels reaching the site, they found that the coal Pb isotope signatures were primarily from the region southeast of their sampling site in the Ohio Valley (Graney and Landis, 2013). The Ohio Valley is also in close proximity to Crawford Lake, so that wind traveling through the Ohio Valley may also contribute aerosols to Crawford Lake. As coal combustion was far more prevalent before emissions control programs than in the Graney and Landis (2013) study, it is reasonable that coal from the Ohio Valley could have contributed to Crawford Lake to impart a unique signature on the Pb isotopes in the 1970s. However, the large trace metal peaks in Crawford Lake compared to other lakes (Fig. 4) also suggest that more local sources may also be important, like the nearby urban centres, the Nanticoke Generating Station and the Hamilton, Ontario steel production region. An earlier study by Graney et al. (1995) analyzed Pb isotopes in cores taken from Lake Erie, Lake Michigan, and Lake Ontario. While the Pb isotope profiles of the 20th century for Lake Erie and Lake Michigan reflect leaded gasoline use, the Lake Ontario profile did not (Graney et al., 1995). In Lake Ontario, ^{206}Pb/^{207}Pb stays nearly constant between 1945 and 1970 before declining to the surface. Input from coal combustion or urban sources combined with leaded gasoline could be the cause of this profile, and would explain why there is no clear leaded gasoline signature in Lake Ontario.

Solitaire Lake also contains a small peak in ^{206}Pb/^{207}Pb in the late 20th century (Fig. 2 pop out), as does the nearby peat bog in Algonquin Park previously discussed in Section 4.1 (Shotyk and Krachler, 2010). These peaks may reflect coal input to the Huntsville region. They are less likely caused by urban sources, since Solitaire Lake is 200 km north of the Greater Toronto Area. In addition, the peaks are less well-defined than the peak in Crawford Lake. The trace metal flux profiles all co-vary in Solitaire Lake, with peak input around the time of enhanced restrictions in the Clean Air Act (Fig. 5E). This could indicate coal input, however the trace metal flux profiles are significantly smaller than those of Crawford Lake (Fig. 4). It is also possible that the patterns in the Solitaire Lake trace metals are instead due to emissions from smelting sources such as those in Sudbury, Ontario to the northwest (discussed further in Section 4.3.2).

4.3.2. *Smelting source*

Big McDougal Lake, Fairbanks Lake, and Solitaire Lake are all in close proximity with the Sudbury, Ontario mining region, where mining and smelting activities grew until ~1970, after which emissions controls were put in place. The effects of the nearby mining and smelting region are evident in each lake's trace metal flux profiles. In Solitaire Lake and Big McDougal Lake, there are co-varying peaks in Cu, Zn, Cd, Hg, and Pb flux in the late 20th century, with peak input around 1970 (Fig. 5E and A) indicating a common source for all these metals. Since Big McDougal Lake is highly isolated from the major coal combustion region (> 300 km north of Toronto/Hamilton, ON and further from the Ohio Valley), but is relatively close to the Sudbury smelting region, the trace metal input to Big McDougal Lake is likely to be primarily from smelting sources. The trace metal profiles in Solitaire Lake could be due to coal combustion or smelting or both since Solitaire Lake is roughly equidistant between the Sudbury mining region to the north and the coal region to the south. Both sources emit all these metals as by-products and both sources reduced emissions in the 1970s (Pacyna and Pacyna, 2001).

The co-varying patterns for Cu and Cd in Fairbanks Lake are dissimilar to any other lakes (Fig. 5C). Fairbanks Lake is ~20 km south of Levack, Ontario, where several copper-nickel mines exist. The profiles for Cu and Cd correlate very well with the recent production record of a major mine in the area, which closed in 1999 and reopened in 2006. Ores extracted from this mine are crushed and sampled on site, then shipped to western Sudbury for processing and refining (Canadian Mining Journal, 2006). Since Fairbanks Lake is within 30 km of both the mine and processing plant, the metal profiles in Fairbanks Lake are likely due to local mining practices.

The effects of local and/or regional smelting are seen in the trace metal profiles for three central Ontario lakes (Big McDougal Lake, Fairbanks Lake, and Solitaire Lake) in the 20th century, yet there is no clear evidence of these effects in the Pb isotope profiles. The Solitaire Lake $^{206}Pb/^{207}Pb$ profile indicates possible coal input, while the Pb isotope profiles for Big McDougal Lake and Fairbanks Lake only show less radiogenic input over time (Fig. 2). Since the smelting source to all these lakes is most likely to be within the Sudbury mining region, which began emissions reductions in the 1970s and whose ores are distinctly non-radiogenic (Dickin et al., 1996), it is surprising that there is no isotope signature at ~1970 reflecting this in any of the lakes. Currently, there is also no evidence in the literature of smelting emissions reductions in Sudbury appearing in the Pb isotope profiles of other regional archives. It seems, since Pb isotopes in each lake do not reach the isotopic signature of Sudbury-type ores ($^{206}Pb/^{207}Pb \sim 1.05$), that there is enough mixing of Pb sources into these lakes such that no unique smelting signatures appear in the Pb isotope profiles. Fig. 9 shows the Pb isotope signatures of the most common Pb sources relevant in North America. The figure shows that most typical Pb sources are more radiogenic than most Sudbury, Ontario ores, so that if there is mixing of multiple sources, the unique Sudbury Pb isotope signature may not appear in an environmental archive. This would explain the gradual uninterrupted decline in $^{206}Pb/^{207}Pb$ in Fairbanks Lake and Big McDougal Lake, while presence of the mixed coal and urban signature in the Pb isotopes in Solitaire Lake means that these sources had a greater impact on Pb in Solitaire Lake than Sudbury smelting. The Pb isotopes in these three lakes serve to emphasize the limits of Pb isotopes in the case where mixing of multiple sources results in an ambiguous record, but highlights the usefulness of having multiple trace metal flux profiles for source apportionment.

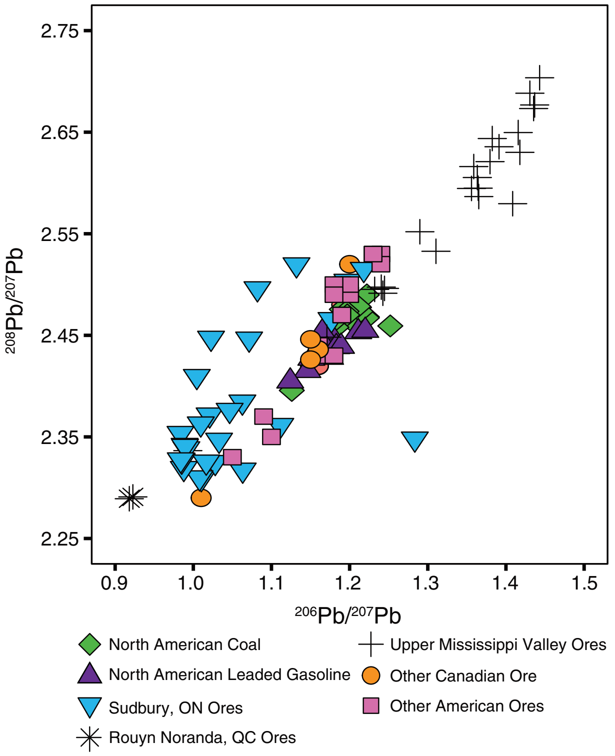

Fig. 9. Isotopic composition of sources of Pb relevant in North America; Brown (1962); Chow and Earl (1972); Chow et al. (1975); Couillard et al. (2008); Dickin et al. (1996); Franklin et al. (1983); Millen et al. (1995).

5. Conclusions

Lead isotopes and trace metal profiles from five lakes in the Great Lakes region and southern Ontario demonstrate the utility of Pb isotopes in two areas: (1) age-dating lake sediments downwind of UMV ore smelting, improving results from age-dating models of lake sediments using the isotopic signature from UMV and (2) elucidating regionally important atmospheric metal sources in the 20th century in a region where numerous pollution sources exist. This work expands the geographical range of the UMV ore smelting chronostratigraphic marker, which is useful for assisting with adjusting age-dated sediments from 100 to 200 years ago in archives where it exists. This is especially important due to the challenges involved in dating sediment cores by other means. Since the timing of the UMV smelting peak is well constrained and the peak exists over a wide geographical range in the Great Lakes region and other parts of northeastern North America, the marker can serve as an anchor for estimated dates from other dating techniques. Lead isotopes and trace metal fluxes also identified several important 20th century contaminant sources to the lakes in this study. Leaded gasoline from US emission sources was only the dominant source to Siskiwit Lake in the Thunder Bay region. Coal combustion and urban sources were identified as important sources in southern Ontario, while trace metals indicated that Sudbury ore smelting was an important source to central Ontario. In a region such as northeastern North America where several important historical and modern pollution sources exist, Pb isotopes coupled with trace metal profiles prove highly valuable for delineating sources of particulate contamination from the atmosphere.

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Appendix A. Supplementary data

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