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

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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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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