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LEAD ISOTOPIC CHRONOLOGIES FROM INLAND LAKES: WATERSHED VS. REGIONAL SCALE SOURCES OF LEAD IN THE GREAT LAKES REGION

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The Department of Geological Sciences

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LEAD ISOTOPIC CHRONOLOGIES FROM INLAND LAKES: WATERSHED VS. REGIONAL SCALE SOURCES OF LEAD IN THE GREAT LAKES REGION

By

Meredith Lee Benedict

A THESIS

Submitted to Michigan State University in partial fulfillment of the requirements for the degree of

MASTER OF SCIENCE

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ABSTRACT

LEAD ISOTOPIC CHRONOLOGIES FROM INLAND LAKES: WATERSHED VS. REGIONAL SCALE SOURCES OF LEAD IN THE GREAT LAKES REGION

By

Meredith Lee Benedict

Environmental regulations have greatly reduced anthropogenic Pb input to the environment from the mid 1970's to the present. However, Pb concentration profiles from inland lake sediment cores in Michigan show that the rates of decrease to natural background concentrations of Pb differ among lakes. This disparity may be due to the dominance of watershed scale sources of Pb over the past three decades following a reduction in the major regional sources of Pb in the 1970's. In the 1970's and 1930's regional sources may have provided the dominant contribution of Pb to inland lakes. For this study, sediment Pb isotopic chronologies from six inland lakes across Michigan were compared to determine temporal and spatial trends. These chronologies were also examined to determine the possible sources of current and historical Pb input to inland lakes. Results show that watershed scale sources of Pb such as deforestation were dominant before 1900. From 1900 to the mid 1970's the regional scale sources of coal combustion, ore smelting, and leaded gasoline combustion were dominant. However, watershed scale sources of Pb also impacted inland lakes during this time period. From the 1970's to 2000 the major sources of Pb were watershed scale sources such as industrial emissions or municipal waste water discharges. This study may have future implications for the control and environmental monitoring of Pb and other metal pollutants.

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Images in this thesis are presented in color.

1. Introduction

Anthropogenic lead emissions to the environment have been observed on a global scale throughout the 20th century (Brannvall et al., 2001; Dunlap et al., 2000; Jackson et al., 2004). The major source of atmospheric Pb loading during this period was from the combustion of leaded gasoline, especially from the 1930's to the 1980's (Jackson et al., 2004; Graney et al., 1995). Environmental legislation in the U.S., such as the Clean Air Act and Clean Water Act has done much to reduce the output of Pb to the environment over the past three decades. In the early 1970's the U.S. Environmental Protection Agency called for the gradual phasing out of Pb additives from gasoline due to increasing knowledge of the adverse health effects of Pb to humans (Nriagu, 1990). Removal of Pb from gasoline led to a steep decline in atmospheric Pb outputs after the early 1970's. A corresponding decline in Pb concentrations is shown in many lake sediments in the U.S. (e.g., Yohn et al., 2004; Graney et al., 1995). Environmental regulations have shown great success in reducing a major source of Pb to the environment. However, Pb concentration profiles from inland lake sediment cores in Michigan show that the rates of decrease to natural background concentrations of Pb differ among lakes (Yohn et al., 2002). This leads to the questions: 1) Is the dominant contribution of Pb to inland lakes from regional scale influences or watershed scale influences?, and 2) What are the current and historical sources that contribute Pb to inland lakes?

An overall hypothesis for this study is that regional sources were the dominant contributor of Pb to the environment from the 1930's to the 1970's; however, within the past three decades the major regional source of Pb to the atmosphere (i.e., leaded gasoline

emissions) has been greatly reduced and consequently watershed scale sources have become more important.

Regional scale influences on the distribution of Pb are dominated by sources with an atmospheric pathway that allow for the pollutant to move outside of the local watershed. Lead that is influenced on the watershed scale is affected by local sources within the watershed (Yohn et al., 2004). This study investigates spatial and temporal patterns of Pb isotopic ratios and concentration data from six inland lakes in Michigan to determine the relative contribution of watershed, as opposed to regional scale influences on Pb inputs. Lead isotopic ratios, in conjunction with lead concentration data, can be used to determine different sources of lead because lead isotopic ratios have distinctive signatures that depend on the geochemistry of the original ore deposit from which they were derived (Outridge et al., 2002). The analysis of data from six lakes that span a large geographic area across Michigan allows for the examination of Pb inputs to the environment at both the local and the regional scale (Yohn et al., 2004; Outridge et al., 2002). This assessment is important to determine on what level further environmental regulations are needed. Also, determining the relative importance of watershed vs. regional sources of Pb input will give insight into the processes involved in the transport and fate of Pb and other metals at local, regional, and perhaps even global scales.

The approach to determine if Pb inputs are influenced by regional sources or sources within the watershed is to examine the temporal sediment Pb isotopic profiles from multiple lakes across Michigan. If the data reveal a correlation between temporal isotopic profiles among lakes across the region, then a regional source is the dominant input of Pb to inland lakes. If, however, the data indicate no correlation among the lakes,

or if the profiles of adjacent lakes show no correlation, then watershed-scale sources are the dominant input of Pb to inland lakes. It may also be possible that the data show an overall regional influence with smaller watershed scale influences imprinted on it. Finally, if the data show that the recent isotopic signature has significantly shifted toward the isotopic signature of the natural background sediments, then it is possible that with the decline of large anthropogenic Pb inputs (i.e. leaded gasoline emissions) the lake may show recovery towards the natural background composition. This research shows that isotopic studies from inland lakes provide an important complement to previous research done in the Great Lakes region.

2. Background

2.1 U-Th-Pb

The lead isotopes used for this study are ²⁰⁴Pb, which is non-radiogenic, and ²⁰⁸Pb, ²⁰⁷Pb, and ²⁰⁶Pb which are formed from the radioactive decay of ²³²Th, ²³⁵U, and 238 U, respectively. There are also radioactive isotopes of Pb including 210 Pb, which is distributed to sediments by atmospheric deposition from nuclear fallout (Appleby et al., 1997). The ²¹⁰Pb isotope has a half-life of 22.26 y. and is used for radiometric dating purposes (e.g., Appleby et al., 1979; Smith et al., 1993; Yohn, 2004). The Pb isotopic composition of a sample is dependent upon the varying amounts of ²⁰⁸Pb, ²⁰⁷Pb, and ²⁰⁶Pb within the sample (Heyl et al., 1974). The ²⁰⁴Pb isotope is found in fixed quantities within a sample because it is not derived from a radioactive parent (Lima et al., 2005). The parents of the radiogenic isotopes each have a different decay rate with half lives of 235 U = 0.7038 x 10⁹y, 238 U = 4.468 x 10⁹y, and 232 Th = 14.010 x 10⁹y (Lima et al., 2005; Hurst, 2002). Therefore, the rate of increase of radiogenic Pb isotopes in rocks and sediments throughout geologic time depends on the decay rate of the parent U and Th isotopes (Eby, 2004). The crustal abundances of Th and U are 3.5 mg/kg and 0.91 mg/kg respectively (Eby, 2004). Thus, the abundance of ²⁰⁸Pb should be greater than ²⁰⁷Pb and 206 Pb in the crust. Furthermore, the abundance of 238 U in Earth's crust is much greater than ²³⁵U which means that there should be a greater proportion of ²⁰⁶Pb than ²⁰⁷Pb in the crust (Eby, 2004). Uranium and Thorium tend to occur in higher concentrations in specific rock types such as in granites, quartz conglomerate metamorphics, organic shales, sandstones, carbonates, and phosphorites (Cowart and Burnett, 1994). In granites, shales, and sandstones the abundance of Th tends to be greater than U, thus these rock

types tend to be enriched in ²⁰⁸Pb over ²⁰⁷Pb and ²⁰⁶Pb (Cowart and Burnett, 1994). In carbonates, the abundance of U is generally equal to or greater than the abundance of Th so ²⁰⁷Pb and ²⁰⁶Pb should be greater than or equal to ²⁰⁸Pb in these rock types (Eby, 2004). However, in all of these cases the rate of decay of the parent isotope must be taken into account.

Uranium and Thorium are large radii elements, with atomic radii of 156 pm and 179 pm respectively, that do not fit well in the mineral structure of most lead ore minerals like galena (PbS) (Cowart and Burnett, 1994). Thus, when lead ore minerals and coal deposits are formed the daughter Pb isotope is isolated from the parent U and Th isotopes and the Pb isotopic composition of the deposit becomes "locked in" throughout time (Eby, 2004). Therefore, different coal and ore deposits can be distinguished from one another by their unique isotopic composition that depends on the age of formation of the deposit, the original U, Th, and Pb concentrations in the source rock, and the geological history of the source material (Heyl et al., 1974). Most of the major Pb ore deposits have ${}^{207}\text{Pb} / {}^{206}\text{Pb}$ ratios ranging from 0.83 to 1.09 (Erel et al., 1997). Mississippi Valley Type lead ores have anomalously low ${}^{207}\text{Pb} / {}^{206}\text{Pb}$ ratios that range from 0.75 to 0.78 (Shirahata et al., 1980).

The isotopic composition of Pb will change over time when its parent isotopes are present due to the continued radioactive decay of the uranium and thorium parent isotopes (Lima et al., 2005). For example, Pb found in soils, sediments, and the continental crust tends to be more enriched in radiogenic isotopes (207 Pb / 206 Pb ranges from 0.806 to 0.833 for sediments) than Pb in ore bodies. As a result, natural Pb can generally be differentiated from anthropogenic Pb (Marcantonio et al., 2002; Chow and

Earl, 1972). Natural Pb refers to Pb found in rocks, sediments, and soils (Lima et al., 2005). Anthropogenic sources of Pb are those that have been mined from Pb ore bodies beneath the earth's surface by humans, processed into useful substances (i.e., coal and leaded gasoline), and then reemitted to the surface of the earth through human consumption (Hansmann and Koppel, 2000).

In the Great Lakes region the major natural sources of Pb to lakes are the erosion of glacial deposits and bed rock that make up shoreline bluffs, as well as inputs from fluvial and aeolian particles (Ritson et al., 1994). Erosional events can cause changes in the isotopic composition of Pb incorporated into lake sediments (Brannvall et al., 2001). These isotopic changes are affected by the rate and type of erosion that the source material undergoes (Graney et al., 1995). When a rock or glacial deposit undergoes total dissolution, Pb will be released that reflects the concentration of U and Th and the geological history of the source material. Total rock dissolution will also release Pb produced by the further radioactive decay of U and Th (Graney et al., 1995; Lima et al., 2005). Partial dissolution of a rock or glacial deposit may preferentially release radiogenic Pb from crystal sites in U and Th rich minerals that have been damaged from alpha particle decay (Cowart and Burnett, 1994; Graney et al., 1995). Also, U and Th tend to accumulate more in soils than in the underlying bedrock due to rock weathering and soil formation processes (Hansen and Stout, 1967). These processes have implications for the relative proportions of the radiogenic Pb isotopes in soil vs. bedrock materials. Overall, sediments are more radiogenic than the source rocks which they were eroded from (Graney et al., 1995; Lima et al., 2005).

2.2 Lead isotopic ratios

Lead isotopic ratios have been used in many studies to determine the dominant sources for Pb in the environment throughout time (e.g., Graney et al., 1995; Hansmann and Koppel, 2000; Chiaradia et al., 1997; Outridge et al., 2002). Anthropogenic outputs of Pb to the environment have been recorded using Pb isotopes in ice cores from Antarctica and Greenland (Vallelonga et al., 2002; Rosman et al., 1993), soils (Hansmann and Koppel, 2000; Erel et al., 1997), peat bogs (Shotyk et al., 1998; Jackson et al., 2004; Monna et al., 2004), and estuarine and marine sediments (Marcantonio et al., 2002; Gobeil et al., 1995; Ritson et al., 1999). Lead isotopes in lake sediments have also been used to provide a temporal record of anthropogenic lead input to lakes and the surrounding regions (e.g., Outridge et al., 2002; Renburg et al., 2002; Graney et al., 1995; Ritson et al., 1994; Chiaradia et al., 1997; Ndzangou et al., 2005). The stratification of lake sediment reflects the chronological sequence of deposited sediment and of elements or compounds that are adsorbed to the sediment at the time of deposition. Therefore, sediment cores can provide a record of geochemical changes in the environment through time. Lead is adsorbed easily and quickly from the water column to lake bottom sediments; as a result, isotopic ratios and concentrations of lead found in sediment cores can be used to determine sources of lead to the environment at a particular time.

Lead isotopic ratios, in conjunction with lead concentration data, can provide a better indicator of sources of lead than studying concentration data alone because lead isotopic ratios reflect the unique signatures of the source(s) of lead (Outridge et al., 2002). Lead isotopic ratios are effective indicators of source(s) of lead because they do not show measurable fractionation during industrial processing or biological

consumption, and therefore reflect the isotopic composition of the original source(s) (Chiaradia et al., 1997; Bollhofer and Rosman, 2001). In addition, to differentiate anthropogenic Pb from natural Pb inputs, anthropogenic inputs must show unique isotopic signatures that differ from those of naturally occurring Pb (Graney et al., 1995). In the Great Lakes region, the isotopic composition of Pb derived from natural sources, such as weathering of rocks and sediment, has been shown to differ from the isotopic signature of anthropogenic inputs such as emissions from leaded gasoline and the burning of coal (Graney et al., 1995); therefore, anthropogenic inputs to the environment can be identified.

2.2.1 Natural and Anthropogenic Sources of Pb

Natural sources of Pb include the dissolution of Pb-bearing minerals from rocks and soil. Pb can also be transported naturally through the atmosphere by dust particles or volcanic emissions (Graney et al., 1995). Anthropogenic sources of Pb are largely responsible for most recent changes in Pb isotopic and concentration profiles in lake sediments. A major pathway of anthropogenic Pb to the environment involves atmospheric deposition of particulate matter containing adsorbed Pb (Chiaradia et al., 1997; Ritson et al., 1999; Jackson et al., 2004; Edgington and Robbins, 1976). Regional anthropogenic sources of Pb include combustion of fuels such as wood, coal, peat and oil, smelting of Pb and metal ores, mining of Pb ores, and combustion of leaded gasoline. More localized sources of Pb include municipal and industrial Pb-containing waste effluents (Callender and Rice, 2000). Global sources of Pb to the atmosphere within the past decade include industrial processing (41%) and automobile emissions (28%), which are especially important in urban areas of high population and traffic density. It is also

possible that dust particles containing Pb, once settled, will be recycled back into the atmosphere and may become a significant source of Pb input (Bollhofer and Rosman, 2001). It is important to remember that Pb emissions can undergo long-range transport in which the isotopic signatures of many sources will be mixed, and that the resulting isotopic ratios in lake sediments will reflect the isotopic ratios from all contributing sources (Hansmann and Koppel, 2000).

2.3 Previous Work

Yohn et al. (2004) have documented the temporal and spatial patterns of Pb concentrations in lakes within the proposed study area of the state of Michigan. Results from this study show that the Pb concentration profiles of several inland lakes that span the state of Michigan are well correlated from the mid -1800's until approximately 1972-1981, the period when Pb was phased out of gasoline. This indicates a regional source of Pb until ~1981. From ~1981 to the present the Pb concentration profiles of these lakes show differing rates of decrease toward the background concentration characteristic of each lake. One proposed explanation is that watershed scale sources have provided the dominant Pb input in recent decades as regional Pb sources, such as leaded gasoline and coal emissions, have declined. The goals of this study are to expand upon that work by examining isotopic evidence to determine possible sources of Pb to inland lakes.

Studies from the Great Lakes suggest that the major sources of Pb to the environment from the mid to late 1800's were the burning of wood associated with deforestation and forest fires and the combustion of coal. From the late 1800's to 1930 coal and ore smelting provided the main source of Pb to the region (Graney et al., 1995;

Ritson et al., 1994). From the 1930's to ~1980 the combustion of leaded gasoline was the major source of atmospheric Pb in the U.S. Shifts in Pb isotopic ratios due to leaded gasoline emissions during this period are recorded across the U.S. in Great Lakes sediments (Graney et al., 1995; Ritson et al., 1994), Chesapeake Bay sediments (Marcantonio et al., 2000), Rhode Island river sediments (Lima et al., 2005), and California pond sediments (Shirahata et al., 1980). Although Pb from gasoline dominates isotopic ratios across the U.S. from the 1930's to ~1980, the isotopic signature of Pb in gasoline varied spatially and temporally worldwide during this time period due to the use of different sources of Pb ore in the production of leaded gasoline (Marcantonio et al., 2002; Shirahata et al., 1980). For example, it is well documented that Mississippi Valley type ores from Missouri were used increasingly in the production of leaded gasoline in the U.S. from the late 1960's to the mid 1970's (Shirahata et al., 1980; Hurst, 2002; Ritson et al., 1994). These ores have anomalously low ²⁰⁷Pb/²⁰⁶Pb values, which make them easily distinguishable from other anthropogenic Pb sources (Shirahata et al., 1980). After the removal of Pb from gasoline in the 1970's, the relative influence of Pb from other sources may be more important (Bollhofer and Rosman, 2002). For example, isotopic ratios from Lake Erie after the 1970's reflect increases in Pb from a homogenous source possibly related to industrial and municipal emissions (Graney et al., 1995). Ritson et al. (1994) shows that municipal and industrial waste water discharge has also contributed significant amounts of Pb to sediments in the West Basin of Lake Erie. Isotopic signatures from the Chesapeake Bay and Rhode Island river sediments also reflect a homogenous source of Pb from 1982 to 1996. This source is most likely industrial outputs (Lima et al., 2005). After the removal of lead from gasoline in the U.S.

and Canada, isotopic ratios from Lake Clair, Quebec sediments still had not reached background isotopic ratios. It is suggested that this may be due to continued emissions of industrial Pb from ore smelting (Ndzangou et al., 2005).

3. Methodology

3.1 Sample selection

Sediment cores were collected as part of the Inland Lakes Project (Michigan Department of Environmental Quality) from 33 inland lakes in Michigan from 1999 to 2005. The lakes were chosen for sampling based on their depth, location, and accessibility. Lead and other trace-metal concentrations were previously determined for these lake sediments (Yohn et al., 2004). The lakes have a variety of watershed characteristics and are distributed over a large area of Michigan. From these lakes, six lakes were chosen for Pb isotopic analysis for this study: Gull Lake, Lake Cadillac, Houghton Lake, Higgins Lake, Avalon Lake, and Round Lake (Fig. 1). These lakes were chosen such that they were distributed over a north to south transect of Michigan to represent a large area with varying amounts of anthropogenic disturbance. Only lake sediments for which background Pb concentrations were known were chosen for analysis. Michigan is an ideal location for this study because of its numerous lakes and large geographical area covering 58,527 square miles (Encyclopedia Britannica, 2005). Lakes located in the Southern Peninsula of Michigan overlie Pleistocene glacial deposits. Round Lake, which is located in the Upper Peninsula of Michigan, also overlies Pleistocene glacial deposits.

Round

Avalon • Higgins Cadillac - Houghton

Gull

Fig. 1. Location of inland lakes analyzed for Pb isotopic composition in Michigan, USA.

3.2 Field Methods

Four sediment cores were taken from the deepest portion of each lake, determined by bathymetry maps and an electronic depth finder. In each lake a modified MC-400 Lake/ Shelf Multi-corer (Ocean Instruments, San Diego, CA) was used to take the cores simultaneously to a depth of 40-58 cm. The monitoring vessel Nibi (Michigan Department of Environmental Quality), designed specifically for access to inland lakes, was used for deployment of the multi-corer. Cores were examined for evidence of disturbance, and if any disturbance was detected new cores were collected. Cores were immediately brought to shore and described for color, texture, and zoobenthos. They were then extruded at 0.5 cm increments for the top 8.0 cm, and then at 1.0 cm increments for the remainder of the core.

3.3 ²¹⁰Pb analysis

One of the sample cores from each lake was used to measure ²¹⁰Pb to determine sedimentation rates, sediment ages, and sediment focusing factors (Freshwater Institute in Winnipeg, Manitoba, Canada). Sediment ages and accumulation rates were determined by Yohn (2004) using four models: constant flux: constant sedimentation (CF: CS), segmented CF: CS (SCF: CS), rapid steady state mixing (RSSM), and constant rate of supply (CRS). ²¹⁰Pb dating results were verified using ¹³⁷Cs, resulting from the testing of nuclear weapons with a peak in 1967, and stable Pb accumulation profiles, which peak around 1972.

Sediment focusing is the tendency of fine-grained sediments to move towards the deepest portion of a lake. In order to compare total Pb concentrations and sediment chronologies among lakes this effect must be accounted for by using a focusing factor (Yohn et al., 2004). The focusing factor is the actual ²¹⁰Pb inventory in each lake divided by the theoretical ²¹⁰Pb inventory.

Focusing Factor = $\frac{\text{actual}^{210}\text{Pb inventory}}{\text{theoretical}^{210}\text{Pb inventory}}$

Focusing factors for lakes in the study area were calculated previously by Yohn (2004).

3.4 Analytical Methods

Sediments for chemical analyses were transported on ice to the laboratory, where they were frozen for storage, freeze-dried and microwave digested with a 2% HNO₃ solution in a CEM-MDS-81D microwave (CEM, Matthews, NC; EPA Method 3051). Sediments were then filtered through an acid-washed, 0.40 μ m polycarbonate filter (Nuclepore), rinsed with distilled-deionized water (DDW). The samples were then frozen for future analysis. The reference material NIST 8701 Buffalo River Sediment and procedural blanks were also digested using the same procedure as for sediment samples. Three replicate digestions were performed on two randomly chosen samples from each lake.

Pb concentration analyses were completed by Yohn (2004) from 1999 to 2003 using a Micromass Platform inductively coupled plasma mass spectrometer with hexapole technology (ICP-MS-HEX). Reproducibility of the reference material was better than 15% relative standard deviation, and recovery of Pb was greater than 90%.

Samples from each lake sediment core were selected to represent a time sequence of geochemical events, based on available ²¹⁰Pb and Pb concentration data (Yohn, 2004). Pb isotopic analyses were performed on these samples so that a temporal Pb isotopic profile could be constructed for each lake. Samples were analyzed for ²⁰⁴Pb, ²⁰⁶Pb, ²⁰⁷Pb, and ²⁰⁸Pb isotopes using the ICP-MS-HEX. Sample solutions, prepared by Yohn (2004), were diluted 1:10 (one part sample and nine parts 2% HNO₃). The final solution for isotopic analysis was then made by mixing 6 ml of the 1:10 diluted sample with 6 ml of the Tl internal standard (20 ppb Tl solution). Six replicate measurements were taken for each sample on the ICP-MS-HEX and the response of integrated counts for replicates 2 to

6 were averaged. The first replicate was not included in the average because it was used as a conditioning measurement to stabilize the sample introduction system and the detectors. Operating parameters for analysis are shown in table 1. The peristaltic pump was not used for sample acquisition because precision was found to increase when the pump was not used. Acquisition times of up to three minutes have been shown to increase precision (Encinar et al., 2001); this increase in precision was validated in this study during protocol development for the isotopic analysis.

Acquisition Mode	Selected Ion Recording
Acquisition Time	3 minutes
Dwell Time for isotopes ²⁰³ Tl, ²⁰⁵ Tl, ²⁰⁶ Pb, ²⁰⁷ Pb, and ²⁰⁸ Pb	0.5 s
Dwell Time for ²⁰⁴ Pb	1.0 s
Inter-channel delay time	0.05 s

Table 1 Operating parameters for ICP-MS

Thallium (Tl) was used as an internal standard to correct for mass bias effects (Longerich et al., 1987; Ketterer et al., 1991). Tl has been used for this purpose because its isotopes are similar in atomic mass to Pb isotopes and the isotopic ratio of 205 Tl / 203 Tl is known and constant in natural samples (Encinar et al., 2001; Ketterer et al., 1991). Accuracy was checked using NIST 981 Pb isotopic standard, analyzed at the beginning and end of each run. Relative standard deviations for the isotopic ratios of the Pb isotopic standard within the five measurements is as follows (excluding Lake Cadillac): 0.1575% - 0.3151% for 207 Pb / 206 Pb, 0.2664% - 0.6328% for 208 Pb / 204 Pb, and 0.2558% -0.5631% for 206 Pb / 204 Pb. Lake Cadillac was not included because the NIST 981 Pb isotopic standard was not acquired at the time of analysis; however, it is not expected that the relative standard deviations from Lake Cadillac would vary significantly from those of the other lakes. The analytical precision of the lead isotopic ratios is comparable to

those of other studies (e.g., Jackson et al., 2004; Ketterer et al., 1991; Outridge et al.,

2002; Weiss et al., 2003).

3.5 Mass Bias Correction Calculations

Pb isotopic ratios were corrected for mass bias using Tl as an internal standard. This was done using a power law as described in Longerich et al. (1987) and Ketterer et al. (1991). The equations used are shown below.

 $\binom{206 \text{Pb}}{204 \text{Pb}}_{c} = \binom{206 \text{Pb}}{204 \text{Pb}}_{m} [2.3871/(\binom{205 \text{Tl}}{203 \text{Tl}}_{m}] \\ \binom{208 \text{Pb}}{204 \text{Pb}}_{c} = \binom{208 \text{Pb}}{204 \text{Pb}}_{m} [2.3871/(\binom{205 \text{Tl}}{203 \text{Tl}}_{m}]^{2} \\ \binom{208 \text{Pb}}{206 \text{Pb}}_{c} = \binom{208 \text{Pb}}{206 \text{Pb}}_{m} [2.3871/(\binom{205 \text{Tl}}{203 \text{Tl}}_{m}] \\ \binom{207 \text{Pb}}{206 \text{Pb}}_{c} = \binom{207 \text{Pb}}{206 \text{Pb}}_{m} [2.3871/(\binom{205 \text{Tl}}{203 \text{Tl}}_{m}]$

The terms $({}^{206}\text{Pb}/{}^{204}\text{Pb})_{c}$, etc., are the isotopic ratios corrected for mass discrimination effects. The terms $({}^{206}\text{Pb}/{}^{204}\text{Pb})_{m}$, etc., are the measured isotopic ratios. The accepted value for ${}^{205}\text{T1}/{}^{203}\text{T1}$ is 2.3871, and the term $({}^{205}\text{T1}/{}^{203}\text{T1})_{m}$ is the measured isotopic ratio.

3.6 Calculating the Anthropogenic Pb component

The anthropogenic Pb concentration and isotopic composition was calculated by subtracting the natural background component from the total Pb in the sample as described by Graney et al. (1995). The natural background concentrations and isotopic ratios are represented by the portion of the Pb concentration and isotopic profile that remains relatively constant through time. The background component does not need to occur over the same time period in each lake nor do the lakes need to have similar background Pb isotopic ratios in order for the anthropogenic component of each lake to be determined (Graney et al., 1995). The background Pb component was determined by

averaging the Pb concentrations and isotopic ratios that occur in the years prior to any anthropogenic additions. The equation used was as follows, using 207 Pb / 206 Pb as an example:

 207 Pb / 206 Pb Anthropogenic = [(207 Pb/ 206 Pb)_T (Pb_T) - (207 Pb/ 206 Pb)_B (Pb_B)] / (Pb_T - Pb_B), where $(^{207}\text{Pb}/^{206}\text{Pb})_{T}$ represents the mass bias corrected total lead isotopic ratio, $(^{207}\text{Pb}/^{206}\text{Pb})_{B}$ represents the mass bias corrected background lead isotopic ratio, (Pb_T) represents the total Pb concentration in the sample, and Pb_B represents the background lead concentration. The calculated anthropogenic isotopic ratios of Pb are sensitive to the measured concentrations, particularly when the total Pb and background Pb concentrations are very similar (Graney et al., 1995; Lima et al., 2005). Therefore, the error associated with the calculated anthropogenic isotopic ratio will generally be larger in samples that have concentrations nearer to the background component (at the bottom of the core) than those that have concentrations much greater than the background component (samples closer to the top of the core) (Marcantonio et al., 2002). The total Pb isotopic composition reflects contributions from both anthropogenic Pb sources and natural background Pb. It is necessary to distinguish the anthropogenic Pb component of the sample from the total Pb component in a sample so that the anthropogenic Pb isotopic composition of the sample can then be matched to the Pb isotopic composition of possible anthropogenic Pb sources. This is done in order to more accurately constrain anthropogenic sources of Pb to the lakes.

4. Results

4.1 Comparison of ²⁰⁷Pb / ²⁰⁶Pb profiles among lakes

The ²⁰⁷Pb / ²⁰⁶Pb ratios from the six inland lakes all seem to follow a general trend (Fig. 2). The background isotopic ratios in all lakes are represented by the bottom portion of the Pb isotopic profile where the isotopic ratios remain relatively constant through time. All lakes show large increases from background ²⁰⁷Pb / ²⁰⁶Pb ratios beginning in the period from ~1800 to 1860 until their peak isotopic ratios, which occur from 1962 to 1974 in the lakes. After this period, ²⁰⁷Pb / ²⁰⁶Pb decreases from the peak isotopic ratio until 1973-1990 in most of the lakes. Houghton Lake differs from the other lakes in that its isotopic ratios remain relatively constant from 1962 to the top of the core. Following the period from 1973 to1990, isotopic trends differ among the lakes. The ²⁰⁷Pb / ²⁰⁶Pb ratios remain constant in some lakes until ~2000 while other lakes show increases in the isotopic ratio. It is important to note that even though ²⁰⁷Pb / ²⁰⁶Pb declined among lakes after the period from 1962 to 1974, isotopic ratios have not reached natural background levels in any of the lakes as of 2000.



Fig. 2. Temporal changes in total ²⁰⁷Pb / ²⁰⁶Pb for six Michigan lakes. The orange circles represent background isotopic ratios for each lake. The isotopic ratio for Gull Lake in 1545 is not included on this graph. Trend lines have been smoothed.

The anthropogenic ²⁰⁷Pb / ²⁰⁶ Pb profiles for Gull, Higgins, and Avalon lakes follows the same trend as the total 207 Pb / 206 Pb profiles for these lakes (Fig. 2 & 3). The anthropogenic isotopic profile for Houghton Lake differs from the isotopic profile of the total Pb isotopic ratio before 1900. The total Pb ²⁰⁷Pb / ²⁰⁶Pb profile for Houghton Lake increases from 1800 to 1860 (207 Pb / 206 Pb ratios of 0.792 - 0.809), whereas, the anthropogenic ²⁰⁷Pb / ²⁰⁶Pb profile increases from 1800 to 1837 (²⁰⁷Pb / ²⁰⁶ Pb ratios of 0.792 – 0.843), then decreases until 1900. The total Pb isotopic profile for Round Lake increases from 1850 to 1900, while the anthropogenic Pb isotopic profile increases from 1850 to 1860, then decreases until 1900. After 1900, the total Pb isotopic profile and anthropogenic Pb isotopic profile follow the same trend for both Houghton Lake and Round Lake. Lake Cadillac also shows differences in the isotopic profiles of total and anthropogenic ²⁰⁷Pb / ²⁰⁶Pb ratios towards the bottom of the core, but similar trends between the two profiles after 1886. After 1900, the anthropogenic ²⁰⁷Pb / ²⁰⁶Pb profiles of all the lakes (Fig. 3.) follow the same general trend observed for the total Pb isotopic profiles (Fig. 2.).



Fig. 3. Temporal changes in the calculated anthropogenic ²⁰⁷Pb / ²⁰⁶Pb component. The orange circles represent background isotopic ratios for each lake. The isotopic ratio for Gull Lake in 1545 is not included on this graph. Trend lines have been smoothed.

4.2 Similar observations among lakes

All of the lakes follow a general trend as described above. Many of the lakes also exhibit other similarities among their Pb concentration and Pb isotopic profiles (Fig. 2-9). These similarities are outlined below and occur in many, but not necessarily all of the lakes. In many of the lakes:

- The ²⁰⁸Pb / ²⁰⁴Pb profile is the inverse of the ²⁰⁷Pb / ²⁰⁶Pb profile. Examples of this are shown in Round Lake, Avalon Lake, and Gull Lake (Figs. 4, 5, 9).
- There is an offset between the peak in concentration and the peak isotopic ratio.
 This occurs in Round Lake, Avalon Lake, Higgins Lake, and Cadillac Lake (Figs. 4, 5, 7, 8)
- A small change in Pb concentration is accompanied by a larger change in the isotopic Pb signature.
- The anthropogenic Pb isotopic profile tends to diverge from the total Pb isotopic profile towards the bottom of the core, but the anthropogenic isotopic profile tends to follow the total Pb isotopic profile towards the top of the core. Examples of this are shown in the isotopic profiles of Round Lake, Houghton Lake, and Cadillac Lake (Figs. 4b, 6b, 8b).

Although there are many similarities among the concentration and isotopic profiles of the inland lakes, there are also noticeable differences between lake profiles. Therefore, it is necessary to discuss the isotopic and concentration profiles of each lake in more detail (Fig. 4 - 9). 4.3 Pb concentration and isotopic profiles of inland lakes

4.3.1 Round Lake

Lead concentrations in Round Lake sediments remain relatively constant from 1850 to 1870 (Fig. 4). There is an increase in concentration from 1870 to 1900. Concentration values then remain relatively constant from 1900 to 1925. After 1925, there is a large increase in concentration values until the peak concentration in 1971 (102 ppm), followed by decreasing concentrations to 2002.

Although concentration values remain relatively constant from 1850 to 1860, there is an increase in anthropogenic 207 Pb/ 206 Pb. After 1860, the isotopic ratio decreases until 1901, and then increases with concentration values to the peak isotopic value in 1967. Then, 207 Pb/ 206 Pb decreases until 1982. From 1982 to 2000 207 Pb / 206 Pb remains relatively constant. The trend of the 208 Pb/ 204 Pb isotopic profile is the inverse of the trend shown in the 207 Pb / 206 Pb profile for this lake.



Fig. 4. Round Lake data showing temporal variations in: (a) Pb concentration (b) ²⁰⁷Pb / ²⁰⁶Pb isotopic ratios, and (c) ²⁰⁸Pb / ²⁰⁴Pb isotopic ratios. (a) Pink dots in the concentration profile represent samples for which isotopic ratios were measured. In graphs (b) and (c) the pink diamonds represent the total Pb isotopic ratio. The black diamonds represent the anthropogenic Pb isotopic ratios calculated using the average isotopic ratio and concentration of the bottom two points. The blue squares represent the anthropogenic Pb isotopic ratio used to calculate the isotopic ratios for the samples represented blue squares.
4.3.2 Avalon Lake

Avalon Lake lead concentrations remain constant from ~ 1730 to1850 (Fig. 5a). After 1850, concentrations increase rapidly until the peak concentration in 1974. During the period 1850 –1974 there are repetitive intervals of increasing concentrations followed by concentrations leveling off and then increasing again. For example, concentrations increase from 1850 until 1868 then level off until 1878 and increase again after 1878. Increases in concentration occur during the periods ~1900-1930 and 1950-1960. After 1974, concentrations decrease until 1986 and then remain constant until 2003.

The ²⁰⁷Pb/ ²⁰⁶Pb ratio remains relatively constant from 1800 to 1838 and then decreases to 1863 (Fig. 5b). After 1863, the isotopic profile increases to 1930, levels off from 1930 to1951, and then increases again to its peak in 1967. Changes in isotopic ratios coincide relatively well with changes in the concentration profile. From 1967 to1982 the isotopic ratio decreases then increases from 1982 to 1992. The isotopic ratio then remains constant to 2003. The trend of the ²⁰⁸Pb / ²⁰⁴Pb isotopic profile is the inverse of the ²⁰⁷Pb / ²⁰⁶Pb profile for most of the core with a few exceptions (Fig. 5c). The isotopic shift shown in the ²⁰⁷Pb / ²⁰⁶Pb profile from decreasing ratios before 1863 to increasing ratios after 1863 can not be seen as clearly on the ²⁰⁸Pb / ²⁰⁴Pb profile. Before 1863, ²⁰⁸Pb / ²⁰⁴Pb isotopic ratios remain relatively constant and then begin to decrease after 1863. Also, the ²⁰⁷Pb / ²⁰⁶Pb profile shows a shift towards lower isotopic ratios after 1967, then towards higher ratios from 1982 to 1992. The ²⁰⁸Pb / ²⁰⁴Pb ratios remain relatively constant from 1974 to 2003 and do not show a shift from 1982 to 1992. Avalon Lake and Round Lake show similar profiles after 1860 (Fig. 4 & 5). Both lakes display increases in concentration and 207 Pb / 206 Pb and decreases in 208 Pb / 204 Pb after ~1860. The peak isotopic ratio occurs in 1967 in both lakes, and both lakes show decreases in 207 Pb / 206 Pb from 1967 to 1982 followed by relatively constant values (of ~0.83) to ~2000.



Fig. 5. Avalon Lake data showing temporal variations in: (a) Pb concentration (b) ²⁰⁷Pb/ ²⁰⁶Pb isotopic ratios, and (c) ²⁰⁸Pb/ ²⁰⁴Pb isotopic ratios. (a) Dark blue dots in the concentration profile represent samples for which isotopic ratios were measured. In graphs (b) and (c) the blue diamonds represent the total Pb isotopic ratios. The red squares represent the anthropogenic Pb isotopic ratios. The orange triangles show the isotopic ratios of the background component.

4.3.3 Houghton Lake

Pb concentrations in Houghton lake sediments are constant from 1720 to1825 (Fig. 6a). From 1825 to1900 the concentration increases with a gently sloping trend. Pb concentrations increase rapidly starting in 1900 until the peak concentration in 1969. After 1969, there is a large decrease in Pb concentration to 2001.

²⁰⁷Pb/ ²⁰⁶Pb values increase from 1800 to 1837, decrease from 1837 to 1900, and then increase until 1928 (Fig. 6b). The ²⁰⁷Pb / ²⁰⁶Pb ratio increases after 1928 to 1962/1969 and then remains constant to 2001. The ²⁰⁸Pb / ²⁰⁴Pb isotopic profile for Houghton Lake is not the inverse of the ²⁰⁷Pb/ ²⁰⁶Pb isotopic profile (Fig. 6c). This is different from Avalon and Round Lake which do have ²⁰⁷Pb/ ²⁰⁶Pb and ²⁰⁸Pb / ²⁰⁴Pb profiles which closely mirror each other (Fig. 4 & 5). The ²⁰⁸Pb / ²⁰⁴Pb ratio decreases from 1800 until 1969 and increases to higher values from 1969 to 1983, then decreases again to 1992, and finally increase rapidly to 2001. A shift towards background levels from the early 1990's to 2001 can be seen in both the Pb concentration profile and the ²⁰⁸Pb / ²⁰⁴Pb isotopic profile.

Houghton Lake Pb isotopic profiles are somewhat similar to those of Avalon Lake and Round Lake; however, there are significant differences in isotopic shifts in Houghton Lake from Avalon Lake and Round Lake (Fig. 4-6). These differences are especially noticeable in the ²⁰⁸Pb / ²⁰⁴Pb profile after the peak in 1969.



Fig. 6. Houghton Lake isotopic and concentration data showing temporal variations in: (a) Pb concentration (b) 207 Pb / 206 Pb isotopic ratios, and (c) 208 Pb / 204 Pb isotopic ratios. (a) Dark green dots in the concentration profile represent samples for which isotopic ratios were measured. In graphs (b) and (c) the dark green diamonds represent the total Pb isotopic ratios. The black squares represent the anthropogenic Pb isotopic ratios. The orange triangles show the isotopic ratios of the background component.

4.3.4 Higgins Lake

Higgins Lake Pb concentration values are constant from 1729 to1839, then increase to 1863 (Fig. 7a). From 1863 to 1977 Pb concentrations increase rapidly, Pb concentrations then increase gradually from 1977 to the peak value in 1984. After this period, Pb concentrations decrease until 1996 then increase gradually towards the surface sediments in 1999.

Higgins Lake 207 Pb / 206 Pb isotopic ratios remain relatively constant from 1750 to 1839 then increase to the peak isotopic ratio in 1966 (Fig. 7b). Next, 207 Pb / 206 Pb values decrease to 1990 and then remain at a constant ratio until 1999. Changes in the 208 Pb / 204 Pb profile are the inverse of shifts in the 207 Pb / 206 Pb profile during the same time periods (Fig. 7c). However, the 208 Pb / 204 Pb profile illustrates an isotopic shift in ratios in 1863 more clearly than the 207 Pb / 206 Pb profile. 208 Pb / 204 Pb ratios decrease from 1839 to 1863 then increase after 1863. From 1863 to 1904 there are increases in 208 Pb / 204 Pb profile then increases again to 1946 and remains constant until 1966. The 208 Pb / 204 Pb profile then increases gradually from 1966 to 1977 and then remains constant until 1999.

Temporal isotopic profiles from Higgins Lake and Houghton Lake are different from each other. Higgins Lake does not show as much variation in the ²⁰⁷Pb / ²⁰⁶Pb or ²⁰⁸Pb / ²⁰⁴Pb isotopic profiles as Houghton Lake. The ²⁰⁸Pb / ²⁰⁴Pb isotopic profile of Higgins Lake is especially different from those of all of the previously mentioned lakes. The ²⁰⁸Pb / ²⁰⁴Pb values for Higgins Lake fall in a much lower range than all of the other lakes before the 1950's to 1960's. Houghton Lake, Avalon Lake, and Round Lake do not reach ²⁰⁸Pb / ²⁰⁴Pb values \leq 40 until the 1950's to 1960's, whereas all ²⁰⁸Pb / ²⁰⁴Pb values

from Higgins Lake fall below 40. Additionally, background 208 Pb / 204 Pb values from the other three lakes are much higher and range from 48.6 to 49.7.



Fig. 7. Higgins Lake isotopic and concentration data showing temporal variations in: (a) Pb concentration (b) 207 Pb / 206 Pb isotopic ratios, and (c) 208 Pb / 204 Pb isotopic ratios. (a) Dark green dots in the concentration profile represent samples for which isotopic ratios were measured. In graphs (b) and (c) the green diamonds represent the total Pb isotopic ratios. The black squares represent the anthropogenic Pb isotopic ratios. The orange triangles show the isotopic ratios of the background component.

4.3.5 Lake Cadillac

Lead concentrations in Lake Cadillac are constant from 1834 to ~1860 (Fig. 8). Concentrations increase from 1860 to the peak concentration in 1972, then decrease to 1996 and remain constant until 1999.

The ²⁰⁷Pb / ²⁰⁶Pb and ²⁰⁸Pb / ²⁰⁴Pb isotopic ratios vary the least in the Lake Cadillac core out of all lake cores that were studied (Fig. 8 b & c). The general isotopic trends can still be deduced even though the isotopic ratios vary little. The ²⁰⁷Pb / ²⁰⁶Pb ratio increases from 1841 to 1862, then decreases from 1862 to 1886 (Fig. 8b). The ²⁰⁷Pb / ²⁰⁶Pb ratio then increases to 1950 and remains constant until 1963 when it begins to decrease gradually until 1973. From this point, the ²⁰⁷Pb/ ²⁰⁶Pb ratio remains constant until 2000. The ²⁰⁸Pb/ ²⁰⁴ Pb isotopic profile follows the same trend as the ²⁰⁷Pb/ ²⁰⁶Pb before 1886 (Fig. 8c). After 1886, the ²⁰⁸Pb/ ²⁰⁴ Pb isotopic profile is the inverse of the ²⁰⁷Pb/ ²⁰⁶Pb profile.

The background ²⁰⁸Pb / ²⁰⁴Pb value from the Lake Cadillac profile is lower than the values from the rest of the core. This is different from the profiles of the other lakes that have ratios which decrease from the high background values. Lake Cadillac has an even lower background ²⁰⁸Pb / ²⁰⁴Pb value than Higgins Lake. Lake Cadillac has a background ²⁰⁸Pb / ²⁰⁴Pb value of 35.9 in 1841 whereas Higgins Lake has a ²⁰⁸Pb / ²⁰⁴Pb value of ~ 38.8 in 1839 and Avalon, Houghton, and Round Lakes have values ranging from 48.9 to 49.7 during the late 1830's to early 1850's.



Fig. 8. Lake Cadillac isotopic and concentration data showing temporal variations in: (a) Pb concentration (b) 207 Pb / 206 Pb isotopic ratios, and (c) 208 Pb / 204 Pb isotopic ratios. (a) Dark red dots in the concentration profile represent samples for which isotopic ratios were measured. In graphs (b) and (c) the red diamonds represent the total Pb isotopic ratio. The black squares represent the anthropogenic Pb isotopic ratio. The orange triangles show the isotopic ratios of the background component.

4.3.6 Gull Lake

Gull Lake Pb concentration values are constant from 1545 to 1800 (Fig. 9a). Concentrations increase gradually from 1800 to 1900 and then increase rapidly from 1900 to 1974. The peak Pb concentration occurs in 1977. After 1977, lead concentrations decrease to 1999. The Gull Lake core spans the longest time period out of all of the lakes studied (1545-1999) and may provide insight into sources of pre-industrial Pb.

The 207 Pb / 206 Pb isotopic profile begins in 1545 showing constant isotopic ratios until 1700 (Fig. 9b). The 207 Pb/ 206 Pb ratio of these background sediments is very high (~0.841). The isotopic ratio decreases from 1700 to 1837 from 0.841 to 0.771 followed by an increase from 1837 to 1920 of 0.771 to 0.818. From 1920 to 1950 207 Pb / 206 Pb levels off then increases again to the peak isotopic ratio in 1974. The Pb isotopic ratio was not measured for the sample with peak concentration which occurred in 1977; however, the concentration in 1974 and 1977 only differed by 1 ppm. After 1974, the isotopic ratio decreases to 1989 and then increases to 1989.

The ²⁰⁸Pb / ²⁰⁴Pb isotopic profile shows the inverse of the isotopic shifts in the ²⁰⁷Pb / ²⁰⁶Pb profile before 1837 (Fig. 9c). After 1837, there is less variance in the ²⁰⁸Pb / ²⁰⁴Pb profile than in the ²⁰⁷Pb / ²⁰⁶Pb profile. For example, from 1837 to 1974 ²⁰⁷Pb / ²⁰⁶Pb values increase rapidly, while ²⁰⁸Pb / ²⁰⁴Pb values decrease gradually. After 1974, ²⁰⁷Pb / ²⁰⁶Pb values decrease until 1989 then begin to increase to 1999, while ²⁰⁸Pb / ²⁰⁴Pb values continue to increase from 1974 to 1999.

The background isotopic ratios of Gull Lake are unique from the other lakes in that the background ratios are different from those recorded in the other lakes. However, the Gull Lake isotopic record extends to 1545 and the next longest record from Higgins

Lake extends to only 1747. Gull Lake also contains the lowest 207 Pb / 206 Pb value recorded in any of the cores. This value occurs in the 1837 sample.



Fig. 9. Gull Lake isotopic and concentration data showing temporal variations in: (a) Pb concentration (b) 207 Pb / 206 Pb isotopic ratios, and (c) 208 Pb / 204 Pb isotopic ratios. (a) Purple dots in the concentration profile represent samples for which isotopic ratios were measured. In graphs (b) and (c) the purple diamonds represent the total Pb isotopic ratios. The black line represents the anthropogenic Pb isotopic ratios. The orange triangles show the isotopic ratios of the background component.

4.4 208 Pb / 204 Pb vs. 207 Pb / 206 Pb inland lake profiles

Many studies have used graphs that plot two isotopic ratios against each other to better discern sources of anthropogenic Pb to the environment (e.g., Graney et al., 1995; Outridge et al., 2002; Ritson et al., 1994). Any two isotopic ratios can be plotted against each other to determine sources of Pb. In this study, the ratios ²⁰⁸Pb / ²⁰⁴Pb vs. ²⁰⁷Pb / ²⁰⁶Pb were chosen because the isotopic signature of the source could be determined using all four stable isotopes of Pb. Changes in the ratio ²⁰⁸Pb / ²⁰⁴Pb are caused by changes in ²⁰⁸Pb, a radiogenic isotope derived from ²³²Th. These changes in ²⁰⁸Pb in the ²⁰⁸Pb / ²⁰⁴Pb ratio are compared to ²⁰⁴Pb, which is non-radiogenic and remains fixed throughout time. Conversely, the ratio ²⁰⁷Pb / ²⁰⁶Pb compares changes in two radiogenic isotopes against each other. Therefore, using all four ratios on one graph allows for a comprehensive examination of changes in anthropogenic sources of Pb.

Figure 10 shows the ranges in Pb isotopic ratios of both domestic and imported coal and Pb ore sources. The isotopic ratios of these anthropogenic sources lie within a general trend line with isotopic ratios of 208 Pb / 204 Pb ranging from 35.7 to 41.7 and 207 Pb / 206 Pb ratios ranging from 0.96 to 0.71.

The temporal anthropogenic Pb isotopic profiles from the six study lakes are superimposed over the general trend line made by the isotopic ratios of coal and sources of Pb ore in Figure 10. Round, Avalon, and Houghton Lakes all have background isotopic ratios that are above the trend of coal and Pb ore sources and with ²⁰⁸Pb/²⁰⁴Pb ratios, ranging from 48.7 to 49.7. The ²⁰⁸Pb / ²⁰⁴Pb ratios from these three lakes decrease with time to become closer in value to the ²⁰⁸Pb / ²⁰⁴Pb ratios of the coal and Pb ore sources. Gull Lake, Lake Cadillac, and Higgins Lake have background ²⁰⁸Pb / ²⁰⁴Pb ratios

that either lie within or below the trend line of the coal and ore Pb sources. Gull Lake and Lake Cadillac ²⁰⁸Pb/ ²⁰⁴Pb ratios increase with time from their background isotopic ratios to become closer in value to the ratios of ²⁰⁸Pb / ²⁰⁴Pb from the coal and ore lead trend line. The background isotopic ratios from Higgins Lake lie within the trend line of the coal and ore lead sources. The ²⁰⁸Pb / ²⁰⁴Pb ratios from Higgins Lake do not change as much with time from background sediments to recent sediments as do the other study lakes.

The most recent sediment isotopic ratios from all six lakes have ²⁰⁷Pb / ²⁰⁶Pb ratios ranging from 0.81 to 0.84 and with the exception of Houghton Lake have ²⁰⁸Pb/ ²⁰⁴Pb ratios ranging from ~ 37 to 40 (Fig. 10- 16) . These most recent lake sediments have isotopic ratios that are close to those of a number of coal and ore sources including coals from Pennsylvania and Appalachia as well as other sources of U.S. coal and lead ores including those from Mexico, Peru, Utah, and British Columbia. The anthropogenic isotopic profile of each lake superimposed over isotopic ratios from anthropogenic Pb sources is shown in figures 11-16; the graphs are enlarged so that more details can be seen in the profiles.



Fig. 10. Lead isotopic profiles of the anthropogenic Pb component from all lakes superimposed over the Pb isotopic ratios of coal (Chow and Earl, 1972) and sources of lead ore (Andrew et al., 1984; Cumming and Richards, 1975; Cumming et al., 1979; Cumming and Krstic, 1987; Doe and Delevaux, 1972; Gunnesch et al., 1990; Heyl et al., 1974; Stacey et al., 1968; Sverjensky, 1981). Data labels indicate the age of the oldest sediment sample from each lake. The open circle, square, diamond, and triangle symbols represent the samples that make up the background Pb component from each lake.

4.4.1 Round Lake

Background sediments from Round Lake fall above the trend line of anthropogenic sources (Fig. 11). Background sediments have ²⁰⁸Pb/ ²⁰⁴Pb ratios that are higher than samples from the rest of the core and ²⁰⁷Pb/ ²⁰⁶ Pb ratios that are lower than sediments from the rest of the core. The ²⁰⁸Pb / ²⁰⁴Pb ratio decreases from 1860 to 1967, while the ²⁰⁷Pb/ ²⁰⁶ Pb increases from 1852 to 1860, decreases to 1901, and then increases to 1967. In 1967, the isotopic ratios lie on the trend line of isotopic ratios from coal and ore lead sources. The isotopic trend shifts towards lower ²⁰⁷Pb / ²⁰⁶Pb ratios in 1967 until 1982, and then moves towards higher ²⁰⁸Pb / ²⁰⁴Pb and ²⁰⁷Pb / ²⁰⁶Pb ratios in 1992. From 1992 to 2002 the isotopic ratios cluster together.



Fig. 11. Round Lake isotopic ratios superimposed over isotopic ratios of coal and lead ores. The blue square represents natural background Pb. Black diamonds represent the isotopic ratios of total Pb. The Round Lake anthropogenic profile is made up of green squares and the data points are labeled with the age of sediment deposition. In cases where multiple data points lie close to each other sediment ages for all data points are included in one label and separated by commas.

4.4.2 Avalon Lake

Avalon Lake background sediments also lie above the trend line of anthropogenic sources (Fig. 12). The ²⁰⁸Pb/ ²⁰⁴ Pb ratios of background sediments are higher than sediments from the rest of the core. The ²⁰⁷Pb/ ²⁰⁶ Pb ratio decreases from the background to 1863. After 1863, isotopic ratios shift towards higher ²⁰⁷Pb / ²⁰⁶Pb and lower ²⁰⁸Pb / ²⁰⁴Pb ratios until 1951. Then, ²⁰⁷Pb / ²⁰⁶Pb shifts towards higher ²⁰⁷Pb / ²⁰⁶Pb and ²⁰⁸Pb / ²⁰⁴Pb ratios until 1967. In 1967, isotopic ratios from Avalon Lake are close to the trend line of isotopic ratios of coal and ore Pb sources. From 1967, the isotopic profile shifts back towards higher ²⁰⁸Pb/ ²⁰⁴Pb ratios. The isotopic ratios cluster from 1992 to 2003. Avalon Lake and Round Lake both show similar isotopic shifts towards lower ²⁰⁷Pb/ ²⁰⁶Pb in 1967 and higher ²⁰⁷Pb / ²⁰⁶Pb and ²⁰⁸Pb/ ²⁰⁴Pb in 1982. Isotopic ratios from both lakes also seem to remain relatively constant after the early 1990's.



Fig. 12. Avalon Lake isotopic ratios superimposed over isotopic ratios of coal and lead ores. The blue diamonds represent natural background Pb. The Avalon Lake anthropogenic profile is represented by green diamonds and the data points are labeled with the age of sediment deposition. In cases where multiple data points lie close to each other sediment ages for all data points are included in one label and separated by commas.

4.4.3 Houghton Lake

The ²⁰⁸Pb / ²⁰⁴Pb background isotopic ratios of Houghton Lake (Fig. 13), like those of Avalon Lake and Round Lake (Fig. 12 & 11), have greater values than the rest of the samples from the lake core. All three lakes have background ²⁰⁸Pb / ²⁰⁴Pb ratios that are greater than 49. Houghton Lake ²⁰⁸Pb / ²⁰⁴Pb ratios, also like Avalon Lake and Round Lake isotopic ratios, decrease from background ratios to become closer to the isotopic ratios of the anthropogenic sources trend line with time. The ²⁰⁷Pb/ ²⁰⁶ Pb ratio increases from background ratios to 1837 then shifts towards lower ²⁰⁷Pb/ ²⁰⁶ Pb until 1902. From 1902 to 1928 ²⁰⁷Pb / ²⁰⁶Pb ratios increase. After 1928, ²⁰⁷Pb / ²⁰⁶Pb ratios show no change; however, ²⁰⁸Pb / ²⁰⁴Pb ratios do show changes. The isotopic trend decreases in ²⁰⁸Pb / ²⁰⁴ Pb from 1837 to 1992 crossing over the range of isotopic values from coal and ore leads from 1954 to 1983. In 1992, ²⁰⁸Pb/ ²⁰⁴Pb ratios shift back towards higher isotopic ratios reaching 44 (²⁰⁸Pb/ ²⁰⁴Pb) by 2001.



Fig. 13. Houghton Lake isotopic ratios superimposed over isotopic ratios of coal and lead ores. The blue square represent natural background Pb isotopic ratios. The Houghton Lake anthropogenic profile is represented by green squares and the data points are labeled with the age of sediment deposition. In cases where multiple data points lie close to each other sediment ages for all data points are included in one label and separated by commas.

4.4.4 Higgins Lake

The background isotopic ratios from Higgins Lake (Fig. 14) are different from Round Lake, Avalon Lake, and Houghton Lake (Fig. 11, 12, 13). Higgins background isotopic ²⁰⁸Pb / ²⁰⁴Pb ratios range from 38.8 to 39.3 whereas Round, Avalon, and Houghton Lakes all had ²⁰⁸Pb / ²⁰⁴Pb background isotopic ratios greater than 48.7. The background isotopic ratios of Higgins Lake lie within the range of isotopic ratios of the anthropogenic coal and ore Pb trend line; whereas, the background isotopic ratios of Round, Avalon and Houghton Lakes were all above the anthropogenic sources trend line. Higgins Lake isotopic profile shifts from background ratios towards lower ²⁰⁸Pb / ²⁰⁴Pb ratios in 1863. From 1863 to 1904 208 Pb / 204 Pb and 207 Pb / 206 Pb ratios increase to just below the trend line for coal and ore leads. After 1904, ²⁰⁸Pb / ²⁰⁴Pb ratios decrease while 207 Pb / 206 Pb ratios increase until 1946. From 1946 to 1966 207 Pb / 206 Pb increases with little change in ²⁰⁸Pb / ²⁰⁴Pb. This is followed by a shift in isotopic ratios in 1966 with an increase in ²⁰⁸Pb / ²⁰⁴Pb and a decrease in ²⁰⁷Pb / ²⁰⁶Pb from 1966 to 1977. Isotopic ratios then remain relatively constant to 1999. The recent sediments from Higgins Lake have isotopic ratios which cluster in one area of the graph. The recent sediments from Avalon Lake and Round Lake also had isotopic ratios which clustered together. The recent sediments from all three lakes have isotopic ratios which remain relatively constant; however, the cluster of ratios from each lake is offset from the other lakes.



Fig. 14. Higgins Lake isotopic ratios superimposed over isotopic ratios of coal and lead ores. The blue diamonds represent natural background Pb ratios. The Higgins Lake anthropogenic profile is represented by green diamonds and data points are labeled with the age of sediment deposition. In cases where multiple data points lie close to each other sediment ages for all data points are included in one label and separated by commas.

4.4.5 Lake Cadillac

Lake Cadillac background isotopic ²⁰⁸Pb / ²⁰⁴Pb ratios lie below the isotopic trend line for coal and ore leads (Fig. 15). The isotopic ratios from Cadillac Lake vary the least out of all the study lakes. Isotopic ratios increase from below the trend line of anthropogenic sources in 1841 to above the trend line in 1862. After 1862, ²⁰⁸Pb / ²⁰⁴Pb and ²⁰⁷Pb / ²⁰⁶Pb ratios decrease until 1886. The isotopic profile shifts towards lower ²⁰⁸Pb / ²⁰⁴Pb and higher ²⁰⁷Pb / ²⁰⁶Pb from 1886 to 1912. Isotopic ratios do not show much variance from 1912 to 1930. There is a decrease in ²⁰⁸Pb / ²⁰⁴Pb and an increase in ²⁰⁷Pb / ²⁰⁶Pb from 1930 to 1950. After 1950, isotopic ratios cluster together; however, there is a shift towards higher ²⁰⁷Pb / ²⁰⁶Pb in 2000. The isotopic ratios from Lake Cadillac after 1950 and Higgins Lake after 1977 both cluster in the same area on the graph.



Fig. 15. Lake Cadillac isotopic ratios superimposed over isotopic ratios of coal and lead ores. The blue square represents natural background Pb ratios. The Lake Cadillac anthropogenic profile is represented by green squares and data points are labeled with the age of sediment deposition. In cases where multiple data points lie close to each other sediment ages for all data points are included in one label and separated by commas.

4.4.6 Gull Lake

Background isotopic ratios from Gull lake sediments lie the farthest below the trend line of isotopic ratios from anthropogenic sources out of all the lakes (Fig. 16). The background isotopic ratios from Gull Lake have ²⁰⁸Pb / ²⁰⁴Pb values that range from 27.7 to 30.4. This sediment core also records isotopic ratios over the longest time period out of all the lakes. From 1701 to 1837 there are increases in ²⁰⁸Pb / ²⁰⁴Pb ratios and decreases in ²⁰⁷Pb / ²⁰⁶Pb ratios. After 1837, ²⁰⁷Pb / ²⁰⁶Pb ratios increase until 1920 and sediment isotopic values are close to those for U.S. coals and Appalachian coal. Following 1920, ²⁰⁷Pb / ²⁰⁶Pb ratios shift towards lower values with relatively constant ²⁰⁸Pb / ²⁰⁴Pb ratios then after 1980, ratios shift towards lower values with relatively constant lower ²⁰⁷Pb / ²⁰⁶Pb values. From 1989 to 1999 both isotopic ratios increase. Gull Lake exhibits an isotopic shift after 1974 that is similar to isotopic shifts that occur in Avalon and Round Lake in 1967. The isotopic profiles of these lakes shift towards lower ²⁰⁷Pb / ²⁰⁶Pb / ²



Fig. 16. Gull Lake isotopic ratios superimposed over isotopic ratios of coal and lead ores. The blue squares represent natural background Pb ratios. Black squares represent the Gull Lake total Pb isotopic profile. The Gull Lake anthropogenic profile is represented by green diamonds and data points are labeled with the age of sediment deposition. In cases where multiple data points lie close to each other sediment ages for all data points are included in one label and separated by commas.

5. Discussion

5.1 General Isotopic Trends

Changes in Pb isotopic ratios accompanied by changes in Pb concentration reflect a change in sources of Pb to the environment. A correlation between temporal isotopic profiles from inland lakes across Michigan would indicate that regional sources of Pb may be more relatively important as a contributor of Pb to inland lakes. Conversely, if there is no correlation between isotopic profiles among the lakes, or if the profiles from two adjacent lakes show no correlation, then watershed scale sources of Pb may be relatively more important as a contributor of Pb.

There is an overall trend among all of the 207 Pb / 206 Pb profiles from the inland lakes. Total 207 Pb / 206 Pb profiles of the inland lakes begin to increase from background ratios beginning in the mid 1700's to mid 1800's. Peak isotopic ratios occur during a period from 1963 to 1974 then isotopic ratios decrease until the period from 1973 to 1990 for all lakes except for Houghton Lake, which has isotopic ratios that remain constant from the peak isotopic ratio until ~2000 (Fig. 2). Also, all lakes have not reached background ratios as of 2000. Anthropogenic 207 Pb / 206 Pb profiles from all of the inland lakes (Fig. 3) follow the general trend of the total Pb profiles after 1900. This general isotopic trend among all of the lakes reflects dominant regional sources have contributed Pb to the Great Lakes region from at least 1900 until the period from 1963 to 1974. Pb concentration profiles from inland lakes follow a similar general temporal trend to that of the Pb isotopic profiles (Figs. 4 – 9). Pb concentrations increase from the early to mid 1800's, peak between 1969 and 1984, then start to decrease towards background

concentrations. This provides further support that regional sources of Pb have influenced lakes in Michigan from at least the turn of the century until the 1960's to 1970's.

Many of the inland lakes have general similarities among their temporal concentration and isotopic profiles (Figs. 2 - 9). One observation is that 208 Pb / 204 Pb profiles are the inverse of ²⁰⁷Pb / ²⁰⁶Pb profiles in many, but not all of the lakes. The relative amounts of the radiogenic Pb isotopes in the sources of Pb to inland lakes are controlled by the relative amounts of their parent isotopes in the original Pb source. For example, changes in the 208 Pb / 204 Pb ratio are controlled by the amount of 232 Th that has decayed to 208 Pb in a particular ore body. Changes in 208 Pb in the 208 Pb / 204 Pb ratio are compared to ²⁰⁴Pb, which is non-radiogenic and remains fixed throughout time. Changes in the 207 Pb / 206 Pb ratio are controlled by the amounts of 235 U and 238 U in the source that have decayed to ²⁰⁷Pb and ²⁰⁶Pb respectively. Therefore, if one ore body is enriched only in ²³²Th and one ore body is enriched only in ²³⁵U and ²³⁸U and these ore sources are used in gasoline emissions at different times changes in the ²⁰⁸Pb/²⁰⁴Pb profiles of inland lakes will be distinct from changes in the 207 Pb / 206 Pb profiles. If 232 Th and 235 U and / or 238 U are enriched in an ore body that is used to make an anthropogenic source then simultaneous changes in the 208 Pb / 204 Pb ratio and the 207 Pb / 206 Pb may occur.

Another consistent observation among concentration and isotopic profiles from the inland lakes was that the concentration peak does not necessarily occur in the same year as the Pb isotopic peak in some of the lakes. This is because changes in Pb isotopic ratios reflect changes in anthropogenic sources of Pb; whereas changes in concentration can only show a change in the amount of Pb input into the lakes. This also explains how there can be a relatively small change in Pb concentration while there is a relatively large change in the Pb isotopic ratios.

The anthropogenic Pb isotopic profiles tend to follow the total Pb isotopic profiles of the lakes closely after 1900. This indicates that anthropogenic Pb sources have dominated the input of Pb to inland lakes since at least 1900. Also, anthropogenic Pb isotopic ratios from sediments towards the bottom of the core consistently have larger error than anthropogenic isotopic ratios from sediments closer to the top of the core. This is due to the sensitivity of the calculation used for determining anthropogenic isotopic ratios to Pb concentration. At the bottom of the core, Pb concentrations are close to background Pb concentrations, and the Pb anthropogenic ratios are most sensitive to the calculation. At the top of the core, Pb concentrations are much larger than background Pb concentrations, and the Pb anthropogenic ratios are least sensitive to the calculations used. The sensitivity of the anthropogenic isotopic ratio calculation to Pb concentrations has been documented (Graney et al., 1995; Marcantonio et al., 2002; Lima et al., 2005). Although some error is introduced into the anthropogenic isotopic ratios by using this calculation it is considered to be an acceptable approach, necessary to determine the anthropogenic Pb isotopic signature (Graney et al., 1995; Marcantonio et al., 2002).

Finally, there may be discrepancies between the exact years in which isotopic changes occur among lakes and between changes in concentration profiles and isotopic profiles. This is because only selected samples from the concentration profile were analyzed for isotopic composition whereas the concentration profile consists of samples analyzed for the entire core. In some cases it was not possible to analyze samples from the same year in every lake for their isotopic composition; however, comparisons of Pb

isotopic changes among lakes in samples that are close in age allows for interpretations within a general time period to be made.

Although there are many similarities among the Pb isotopic profiles of the inland lakes, there are also distinct differences among the isotopic and concentration profiles of the lakes indicating that both regional and watershed sources influence Pb input to Great Lakes region. Higgins Lake and Houghton Lake are of particular interest because their watersheds are in close proximity yet their isotopic profiles and concentration profiles differ. Watershed scale processes most likely account for these differences in Pb sources between the two lakes (This is discussed in further detail in section 5.3).

5.2 Comparison of Pb isotopic profiles among lakes

5.2.1 Background isotopic ratios

Round Lake, Avalon Lake, and Houghton Lake all have background ²⁰⁸Pb / ²⁰⁴Pb ratios ranging from 48.7 to 49.7 (Fig. 10). These ratios are greater than those of the coal and ore Pb sources, which have ²⁰⁸Pb / ²⁰⁴Pb ratios ranging from 35.7 to 41.7. The background sediments of these lakes must be enriched in ²³²Th which would radioactively decay to produce increased amounts of ²⁰⁸Pb. ²⁰⁴Pb is non radiogenic and therefore remains fixed throughout time. Ratios of ²⁰⁸Pb / ²⁰⁴Pb up to 61.0 have been measured in soils that were developed on glacial moraines in the Wind River Mountains of Wyoming (Harlavan et al., 1998). Outridge et al. (2002) also reports ²⁰⁸Pb / ²⁰⁴Pb ratios of up to 48.22 measured in Far Lake sediments in Canada. Background ²⁰⁸Pb / ²⁰⁴Pb isotopic values from Higgins Lake lie within the range of isotopic values of the anthropogenic Pb sources trend line. Gull Lake and Lake Cadillac have background

²¹⁸Pb / ²⁰⁴Pb ratios which lie below those of the trend line produced by anthropogenic sources (Fig. 10). The background sediments of these lakes are depleted in ²⁰⁸Pb compared to the other lakes because there is less ²³²Th present in the sediments to decay and produce ²⁰⁸Pb. Gull Lake has the lowest ²⁰⁸Pb / ²⁰⁴Pb background isotopic ratios out of all of the lakes with values ranging from 27.7 to 30.4. These ²⁰⁸Pb / ²⁰⁴Pb ratios are lower than many of the values for sediments found in the literature. Still, ²⁰⁸Pb / ²⁰⁴Pb values as low as 36.67 were measured in Lake Erie sediments (Ritson et al., 1994) and, ²⁰⁸Pb / ²⁰⁴Pb values as low as 32.58 have been documented in Pb mine ores from South Africa (Vermillion et al., 2005). The isotopic ratios of all of the lakes change through time from their background isotopic ratios to become closer in value to the isotopic ratios of the coal and ore Pb sources. This shows the increasing dominance of anthropogenic Pb sources to all of the lakes throughout time.

5.2.2 From Background to isotopic peaks in profiles

Avalon Lake and Round Lake show similar trends in their isotopic profiles after approximately the turn of the 20th century (Fig. 4, 5, 11, 12). In 1860, the anthropogenic Pb isotopic component of Round Lake is hard to determine with certainty because the concentration value is very close to background concentration levels (Fig. 4 & 11). By 1863, Avalon Lake Pb concentrations have increased from background values and the anthropogenic ²⁰⁷Pb / ²⁰⁶Pb isotopic ratio has decreased from background values (Fig. 5). This is during the time when wood burning associated with deforestation was the dominant source of Pb emissions to the atmosphere and is the most likely explanation for a decrease in the isotopic ratio (Fig. 17) (Graney et al., 1995).



Fig. 17. From Graney et al. (1995): Emissions of lead to the atmosphere from different sources through time.

Lima et al. (2005) suggest that another possible explanation for changes in Pb isotopic ratios during the mid 1800's was the regional atmospheric transport of Pb from Pb ore smelters in the Upper Mississippi Valley to the Northeastern United States. During the period from 1830 to 1870, the Upper Mississippi Valley was the major producer of Pb in the U.S. These ores had a ²⁰⁷Pb / ²⁰⁶Pb isotopic ratio that was distinctly lower than other coal and Pb ores that were produced at the same time; therefore, the input of Pb from this source into lake sediments could possibly account for the lowering of isotopic ratios in 1863 (Lima et al. 2005). However, this source is not as likely to have caused the change in isotopic ratios in the inland lakes studied because if it was a regional source, then it would have affected many of the inland lakes, but this is not the case. Not all of the lakes show isotopic departures during this time period; therefore, it is more likely that a Pb

source located within the watershed of Avalon Lake, such as the combustion of wood associated with deforestation, could have caused the departure of isotopic ratios in 1863.

Round and Avalon Lakes have similar isotopic profiles from approximately 1900 until 2000. Both lakes have increasing ²⁰⁷Pb / ²⁰⁶Pb and decreasing ²⁰⁸Pb / ²⁰⁴Pb after approximately 1900 (Fig. 11 & 12). The isotopic ratios of both lakes change over time from their background isotopic ratios to become closer in value to the coal and ore Pb sources. The increase in ²⁰⁷Pb / ²⁰⁶Pb ratios from 1900 until 1930 is most likely due to anthropogenic additions from coal and ore smelting, which were the dominant sources of Pb to the atmosphere from the late 1800's to ~1930 (Graney et al. 1995; Ritson et al., 1994). West Virginia and Pennsylvania were the major coal sources used in the region during the time period from 1900 until 1930 with ²⁰⁷Pb / ²⁰⁶Pb ratios ranging from about 0.818 to 0.841(Ritson et al., 1994; Chow and Earl, 1972). The isotopic ratios from Round Lake and Avalon Lake sediments during this time period are within the range of ²⁰⁷Pb / ²⁰⁶Pb ratios of coal from West Virginia and Pennsylvania; however, the ²⁰⁸Pb / ²⁰⁴Pb isotopic ratios do not match the range of coal ratios therefore the smelting of Pb ore is suggested as another possible source of Pb to these lakes as it was the second major source of Pb emitted in the region at that time (Graney et al., 1995). From 1930 to the peak isotopic ratio in 1967, both lakes show further decreases in 208 Pb / 204 Pb and increases in ²⁰⁷Pb / ²⁰⁶Pb. These isotopic changes are similar to those that are attributed to leaded gasoline emissions in sediments across North America (e.g., Marcantonio et al. 2002; Ndzangou et al., 2005; Ritson et al. 1994). The combustion of leaded gasoline was the dominant source of Pb to the atmosphere from ~1930 until the mid 1970's (Graney et al., 1995). The overall increase in Pb concentration in both of these lakes during this

time period is also consistent with the increased combustion of leaded gasoline additives in the U.S. The similarities in the temporal Pb isotopic profiles of Round Lake and Avalon Lake indicate that common sources of Pb existed for both of the lakes. Round Lake and Avalon Lake are located the furthest north in the state of Michigan out of all six lakes studied, and the population in Michigan generally decreases towards the north producing a population gradient from south to north (Yohn et al., 2004). Population can be used as a proxy measurement for the amount of anthropogenic disturbance within a watershed (i.e., leaded gasoline emissions); therefore, these two lakes should not have large amounts of anthropogenic Pb inputs within their watersheds. The similarity in the isotopic profiles of these two lakes signifies that regional atmospheric sources of Pb are the dominant contributor of Pb to both of these lakes after 1900.

The anthropogenic isotopic ratios of Houghton Lake in 1837 may be uncertain because the concentration is very close to background concentration levels (Fig. 6). In 1860 concentrations have increased above background values and isotopic ratios decrease from 1860 to 1900 (Fig. 6, 13). This trend is different from that of Avalon Lake during the same time period. After 1900, ²⁰⁷Pb / ²⁰⁶Pb ratios in the Houghton Lake profile increase until 1928. The isotopic profiles of Avalon Lake and Round Lake both exhibit similar isotopic trends during this time period. The isotopic changes in all three lake cores are most likely due to Pb inputs from coal emissions and Pb ore smelting. After ~1930, ²⁰⁸Pb / ²⁰⁴Pb ratios continue to decrease until 1992. The peak isotopic ratio in Houghton Lake occurs in 1969, which is similar to the peak isotopic occurrences in Avalon and Round Lake, but the isotopic profile differs from those of Avalon Lake and Round Lake in that there is little variation in ²⁰⁷Pb / ²⁰⁶Pb after 1930. This might reflect

that after 1930 watershed scale processes and sources of Pb are of more importance in Houghton Lake than in Avalon Lake or Round Lake.

The Higgins Lake anthropogenic isotopic ratio in 1863 may be sensitive to the calculations used because of the small increase in concentration between the background sediments and sediment deposited in 1863. Still, isotopic ratios do show a shift in Higgins Lake sediments in 1863 (Fig. 7, 14). This shift occurs during the time period when Pb emissions from the combustion of wood were the major source of Pb to the atmosphere and localized forest fires may be one explanation for the source of Pb to the lake during this time period. From 1904 to 1946 ²⁰⁷Pb / ²⁰⁶Pb ratios increase while ²⁰⁸Pb / ²⁰⁴Pb ratios decrease. Avalon Lake, Round Lake, and Houghton Lake exhibit similar trends from 1900 to ~1930; however, the isotopic ratios from Higgins Lake are offset from the ratios of the other lakes. Therefore, it is likely that watershed scale sources of either an additional source of Pb used within the watershed or a different source of Pb (i.e. the use of coal from another region) are needed to explain the Pb input to Higgins Lake during this time period. Increases in ²⁰⁷Pb / ²⁰⁶Pb from 1946 to 1966 are consistent with the combustion of Pb additives in gasoline. The ²⁰⁷Pb / ²⁰⁶Pb profile of Higgins Lake shows some similarities to the isotopic profiles of Avalon and Round Lakes. However, the ²⁰⁸Pb / ²⁰⁴Pb profile of Higgins Lake is different than the profiles of Houghton, Avalon, and Round Lakes. Higgins Lake ²⁰⁸Pb / ²⁰⁴Pb profile varies the least over time out of all of the previously discussed lakes. Furthermore, the isotopic profiles of Higgins Lake and Houghton Lake are different from each other even though the two lakes are very close in proximity to each other. The peak Pb concentration also occurs at different times in the two lakes. Watershed scale processes in Higgins Lake and

Houghton Lake may explain the dissimilarities in Pb isotopic profiles between the two lakes. This will be discussed in further detail in section 5.3.

The profile of Lake Cadillac is different from all of the previously discussed lakes because its isotopic profile varies the least out of all of the lakes. In 1862, the Pb concentration of Lake Cadillac is very close to the background concentration making the anthropogenic isotopic ratio hard to determine (Fig. 8, 15). By 1886, Pb concentrations have increased above background levels. The isotopic profile crosses close to the range of isotopic values for U.S. and Appalachian coals in 1886 suggesting that the burning of coal may have been a source of Pb to Lake Cadillac at that time. The ²⁰⁷Pb / ²⁰⁶Pb ratios increase from 1886 to 1930 with decreasing ²⁰⁸Pb / ²⁰⁴Pb ratios. Higgins Lake exhibits a similar trend in its isotopic profiles from 1904 to 1946 indicating that the lakes may have had a common source of Pb during that time period. One possibility for the source of Pb to the lakes during that time period is coal emissions. There is a decrease in 208 Pb / 204 Pb and an increase in ²⁰⁷Pb / ²⁰⁶Pb from 1930 to 1950. These changes are most likely due to the increased use of leaded gasoline in that time period. After 1950, there is little variance in the ratios of Lake Cadillac until 1997; therefore, it is hard to distinguish if there were any changes in the sources of Pb to the lake during this time period.

The Gull Lake isotopic profile is different from the other lakes profiles. From 1701 to 1837 there are increases in ²⁰⁸Pb / ²⁰⁴Pb ratios and decreases in ²⁰⁷Pb / ²⁰⁶Pb ratios (Fig. 9, 16). The low ²⁰⁷Pb / ²⁰⁶Pb ratios in 1837 may be due to forest fires associated with deforestation. After 1837, ²⁰⁷Pb / ²⁰⁶Pb ratios increase until 1920 and sediment isotopic values are close to those for U.S. coals and Appalachian coal. A similar isotopic trend from 1863 to 1910 exists in a southeastern Lake Michigan core that is located in

close proximity to Gull Lake (Graney et al., 1995). It is possible that both sediment cores could have been influenced by a period of deforestation in the mid 1800's and then by the burning of coal from the mid 1800's to the early 1900's. Increases in 207 Pb / 206 Pb ratios from 1920 to 1974 are associated with the combustion of leaded gasoline.

5.2.3 Pb isotopic profiles after peak ratios (late 1960's to 1970's)

The isotopic profiles of Round Lake, Avalon Lake, Higgins Lake, and Gull Lake all exhibit a shift toward lower ²⁰⁷Pb / ²⁰⁶Pb values during a period from the late 1960's to the mid 1970's (Fig. 4, 5, 7, 9, 11, 12, 14, 16). This change in ratios is most likely due to the increased use of Mississippi Valley Type (MVT) Pb ores from Missouri in the production of leaded gasoline beginning in the late 1960's. These ores have anomalously low ²⁰⁷Pb/ ²⁰⁶Pb ratios, between 0.752 and 0.781, which make them easily distinguishable from other anthropogenic Pb sources (Shirahata et al., 1980). The shift towards lower ²⁰⁷Pb / ²⁰⁶Pb ratios in Avalon, Round, Higgins, and Gull Lakes mimics the shift in gasoline Pb isotopic ratios from the late 1960's to the late 1970's. The use of MVT ores as Pb additives in gasoline caused the ²⁰⁷Pb / ²⁰⁶Pb isotopic ratio of U.S. gasoline to change from ~ 0.870 before 1967 to ~ 0.833 by 1974 and eventually reach ~0.813 by 1977 (Ritson et al., 1994). Similar shifts towards lower ²⁰⁷Pb / ²⁰⁶Pb isotopic ratios have been documented in Lake Erie in 1972, Lake Michigan in 1971, Rhode Island river sediments in 1970, and California marine sediments in the late 1960's. All of these shifts have been attributed to the increased use of MVT Pb ores in the production of leaded gasoline (Shirahata et al., 1980; Ritson et al., 1994, Graney et al., 1995; Lima et al., 2005). The shift towards lower ²⁰⁷Pb / ²⁰⁶Pb values in the late 1960's to mid 1970's that is documented in numerous lake and sediment cores across the U.S. indicates that
perhaps a regional or even national scale shift in the source of gasoline affected four of the inland lakes from this study. However, this shift is not clearly observed in Houghton Lake or Lake Cadillac; therefore, these two lakes most likely had dominant watershed scale Pb sources that masked the shift in isotopic ratios due to the use of MVT ores in gasoline. In the Lake Cadillac isotopic profile, the isotopic ratios vary little over time so it is more difficult to determine when changes in sources of Pb occurred.

5.2.4 1980's ratios

After 1982, there is another shift in the isotopic trends of both Avalon Lake and Round Lake. This shift is toward higher ²⁰⁸Pb / ²⁰⁴Pb ratios. Sediment profiles from Gull Lake also exhibit a shift in isotopic ratios after 1980. Shifts in isotopic ratios in the early-mid 1980's have also been observed in a study in Lake Quebec, Canada (Ndzangou et al., 2005). This shift may be attributed to the phasing out of Pb in gasoline in the U.S. and Canada during that time period (Ndzangou et al., 2005). It is unclear whether the isotopic shift in Gull Lake in 1980 and the isotopic shifts of Round Lake and Avalon Lake are due to the same change in source of Pb.

5.2.5 Clustering of Isotopic ratios in recent sediments

Many of the inland lakes have isotopic ratios from sediment deposited in varying years after the isotopic peak that remain relatively constant through time. Round Lake has isotopic ratios which cluster together from 1992 to 2002 (Fig. 4, 11). Likewise, Avalon Lake has isotopic ratios which cluster together from 1992 to 2003 (Fig. 5, 12). Avalon Lake and Round Lake both have isotopic ratios with relatively constant ²⁰⁷Pb / ²⁰⁶Pb values of ~ 0.83 from 1992 to after 2000. However, the ²⁰⁸Pb / ²⁰⁴Pb ratios from the two lakes are offset from one another.

The Higgins Lake isotopic profile remains relatively constant from 1977 to 1999 (Fig. 7, 14). Also, Lake Cadillac sediments have isotopic ratios which cluster together from 1950 to 1997, but there is a shift towards higher ²⁰⁷Pb / ²⁰⁶Pb in 2000 suggesting that a new source of Pb was introduced to the watershed (Fig. 8, 15). Higgins Lake sediments from 1977 to 1999 have similar isotopic ratios to those of Lake Cadillac sediments from 1950 to 1997. This is indicative that the same source of Pb was used in both watersheds during the time period from the late 1970's to the late 1990's. By this time, the use of leaded gasoline had drastically declined and some of the major sources of Pb included industrial Pb emissions and recycled Pb, which is old scrap Pb that is reused by industry (Hurst, 2002; Ndzangou et al., 2005). It is possible that this common source of Pb was later introduced to the Higgins Lake watershed, although there is no historical evidence readily available.

The clustering of Pb isotopic ratios from these recent lake sediments suggests that the source of Pb to each of these lakes has remained the same in recent decades. Recycled industrial Pb, which is composed of a mixture of domestic and imported ores, has become a major source of Pb since the phasing out of leaded gasoline (Graney et al., 1995). Graney et al. (1995) suggested that the increased use of these recycled Pb ores by industry after the 1970's has led to a constant Pb isotopic signal in the recent lake sediments from some of the Great Lakes. Sediments from the Pettaquamscutt River in Rhode Island and from the Chesapeake Bay also show a homogeneous Pb isotopic signature from 1982 to 1996 that is attributed to industrial Pb emissions (Lima et al., 2005). The average ²⁰⁷Pb / ²⁰⁶Pb isotopic ratio of urban U.S. atmospheric Pb is ~0.819

while the range of urban atmospheric Pb measured in Canada during the 1980's is ~0.863 - ~0.876 (Sturges and Barrie, 1987; Gobeil et al., 1995). Although the relative contribution of these and other sources of Pb to the inland lake sediments has not been calculated, the isotopic ratios from the inland lake sediments after the mid 1970's are much closer to those from U.S. atmospheric sources than from Canadian sources indicating that there was a greater contribution from U.S. industrial sources than Canadian sources to the Michigan inland lakes. Furthermore, the isotopic ratios from inland lake sediments are close to the U.S. industrial Pb signal after the mid 1970's $(^{207}\text{Pb} / ^{206}\text{Pb} < 0.842)$ (Gobeil et al., 1995). The use of recycled industrial Pb sources could help explain the constant isotopic ratios in some of the Michigan inland lakes. Although there is a homogenous isotopic signature in recent sediments from individual lake sediment cores, the isotopic signatures among lakes are offset from one another. Lake Cadillac and Higgins Lake sediments have similar isotopic ratios, but these differ from the isotopic ratios in recent sediments from Avalon Lake and Round Lake. Therefore, the source of recent Pb inputs cannot be explained completely by a regional source of recycled industrial Pb. One possibility to explain the variation in isotopic ratios among the lakes is that different sources of Pb were used by industry in different parts of the state of Michigan. Also, municipal and industrial sources of Pb within the watershed may account for the offset in isotopic ratios among the lakes.

Gull Lake does not show relatively constant isotopic ratios in sediments deposited after 1980 (Fig. 9, 16). Rather, in 1989 there is a shift in the isotopic profile towards higher ²⁰⁸Pb / ²⁰⁴Pb and lower ²⁰⁷Pb / ²⁰⁶Pb ratios. The difference in the recent isotopic

profile of Gull Lake and the profiles of the other inland lakes indicates that a change in source of Pb within only the Gull Lake watershed occurred in 1989.

The recent isotopic profile from Houghton Lake differs from those of the other lakes. Instead of having isotopic ratios that remain relatively constant through recent time, the isotopic profile of Houghton Lake shows distinct changes in ²⁰⁸Pb / ²⁰⁴Pb from 1928 until 2001. From 1928 to 1992, there is a decrease in ²⁰⁸Pb / ²⁰⁴Pb from 42 to 37.18, then, the isotopic ratio increases to 44.01 in 2001. The ²⁰⁷Pb / ²⁰⁶Pb ratio does not show much variance during this time period. The increase of ²⁰⁸Pb / ²⁰⁴Pb from 1992 until 2001 towards background ratios may signify the recovery of Houghton Lake from leaded gasoline inputs. This is further supported by the rapid decrease in Pb concentration from the 1990's to 2001 that was most likely due to the major decline in leaded gasoline emissions to the atmosphere.

5.3 Higgins Lake and Houghton Lake

Higgins Lake and Houghton Lake are of particular interest because the two watersheds are in close proximity to each other yet their temporal Pb isotopic profiles and Pb concentration profiles are different from each other (Fig. 6, 7, 13, 14). Differences in watershed scale processes among the two lakes may explain the dissimilarities in their Pb isotopic profiles. In order to better understand the watershed scale processes that affect Pb input to each lake the Al concentration profiles for each lake were examined. Aluminum is found in natural sources within the watershed such as clay minerals within soils and it is a relatively conservative element. Periods of large anthropogenic disturbances within a watershed, such as logging, will cause terrestrial inputs, such as soils containing Al, to run off of the watershed and into the lakes, resulting in periods of

increased Al concentration in lake sediments. Therefore, Al concentration profiles from lake sediments have been used as an indicator of anthropogenic disturbances within a watershed (Ndzangou et al., 2005; Yohn et al., 2004). The Al concentration profiles of Higgins Lake and Houghton Lake are shown in figure 18. Overall, the aluminum concentrations in Houghton Lake fluctuate much more widely and frequently through time than the aluminum concentrations in Higgins Lake. There does not seem to be a correlation between the years that the Al concentration peaks occur between the two lakes.

The aluminum concentration profiles did indicate that there were differences in when anthropogenic disturbances occurred between the two lakes; however, this evidence alone was not conclusive. Uranium, like aluminum, may also be an effective indicator of terrestrial inputs (Yohn, 2004). Therefore, uranium concentration profiles from Yohn (2004) were examined as an additional indicator of anthropogenic disturbances. The uranium concentration profiles of Higgins Lake and Houghton Lake are shown below in Figure 19. Temporal variations in uranium concentrations for Higgins Lake and Houghton Lake seem to correlate well until 1800. From 1800 to 1880, the uranium concentrations in Higgins Lake increase to a peak concentration in ~1880. After 1880, uranium concentrations show an overall decrease until 1950, at which point they increase to another peak in 1966. From 1966 to 2000, uranium concentrations in Higgins Lake decrease. In contrast, Houghton Lake shows an overall decrease in uranium concentrations from 1800 to 2000. During this period, uranium concentrations in Houghton Lake fluctuate between higher and lower concentrations. In the mid-late 1990's uranium concentrations in both lakes converge to lower values. The differences

in the Al and U concentration profiles between Higgins Lake and Houghton Lake indicate that anthropogenic disturbances have occurred at different time periods in the two watersheds. Also, during the same time period, the watersheds of Higgins Lake and Houghton Lake may have undergone different anthropogenic disturbances that contributed local sources of Pb to the lakes. The differences in the Al concentration profiles, U concentration profiles, and the Pb isotopic and concentration profiles between Higgins Lake and Houghton Lake suggests that watershed scale processes are the most important contributor of Pb to these lakes.



Fig. 18. Temporal variations in aluminum concentrations (mg/kg) for Higgins Lake and Houghton Lake (From Yohn, 2004).



Fig. 19. Temporal variations in uranium concentrations (mg/kg) for Higgins Lake and Houghton Lake (From Yohn, 2004).

5.4 Regional and watershed scale Pb sources

Before 1900, the isotopic profiles of the inland lakes differ. The profiles of Avalon Lake, Higgins Lake, and Gull Lake all show isotopic shifts in the mid 1800's that are attributed to forest fires and deforestation that occurred within the watershed of each individual lake. An overall trend among the anthropogenic ²⁰⁷Pb / ²⁰⁶Pb profiles of the six inland lakes in this study from 1900 until the period from 1963 to 1974 signifies that regional sources of Pb influenced the inland lakes during this time period. The burning of coal and smelting of Pb ore were most likely the dominant sources of Pb to the inland lakes from 1900 to ~1930. After ~1930, automobile gasoline emissions containing Pb additives were the predominant source of Pb to inland lakes until the mid 1970's to 1980's.

Although the trend of the Pb isotopic profiles during this time period are similar among lakes, differences in the Pb isotopic signature among lakes indicate that both regional and watershed scale sources influenced Pb input to inland lakes in the Great Lakes region. Differences in the source of Pb ore used in gasoline or other industries have been shown to produce spatial differences in atmospheric Pb isotopic compositions (e.g., Marcantonio et al., 2002; Sturges and Barrie, 1987; Bollhofer and Rosman, 2001). Therefore, differing sources of Pb used in gasoline from one watershed to another may account for the dissimilarity of isotopic profiles among lakes. It is also possible that sources of Pb from within the watershed such as Pb emissions from local industries or municipal waste water discharges could account for some of the differences in isotopic profiles between lakes.

In the late 1960's, the increased use of Mississippi Valley Type ores from Missouri in the production of leaded gasoline caused a regional or perhaps even national scale shift in the isotopic ratios recorded in lake sediments (Shirahata et al., 1980; Ritson et al., 1994, Graney et al., 1995; Lima et al., 2005; Hurst, 2002). Sediments from Avalon Lake, Round Lake, Higgins Lake, and Gull Lake all exhibit a shift in isotopic ratios in the late 1960's to mid 1970's that is consistent with the national scale change in the source of Pb used in gasoline. The isotopic profiles of Houghton Lake and Lake Cadillac do not display a shift in isotopic ratios during this time period. Therefore, it is likely that watershed scale sources of Pb, such as Pb emissions from local industries or municipal waste water discharges, masked the regional change in isotopic ratios due to the increased use of MVT ores in the production of leaded gasoline in Houghton Lake and Lake Cadillac.

After the period from the late 1960's to mid 1970's, the isotopic profiles of the inland lakes vary from one another. Avalon Lake and Round Lake exhibit similar trends in recent sediments however, the isotopic ratios from the two lakes are offset from one another. Lake Cadillac and Higgins Lake sediments have similar isotopic ratios, but these differ from the other lakes. With the decline of leaded gasoline in the U.S. and Canada in the mid 1970's to 1980's the relative importance of other sources of Pb has increased (Bollhofer and Rosman, 2000). Industrial emissions from the production of recycled Pb have become a major source of atmospheric Pb since after the 1970's (Graney et al., 1995). The use of recycled industrial Pb sources could help explain the constant isotopic ratios displayed in recent sediments from some of the Michigan inland lakes; however, the isotopic signatures among lakes are offset from one another. Therefore, it is suggested that varying sources of Pb have been used by industries throughout the different watersheds of Michigan. It is also possible that watershed scale sources of Pb other than industrial emissions could account for the differences in the isotopic composition of recent sediments between lakes.

The isotopic profile of Houghton Lake is unique from the other lakes and it is suggested that watershed scale Pb sources are the dominant contributor of Pb to Higgins Lake and Houghton Lake. Furthermore, the shift in the isotopic profile of Houghton Lake from 1992 until 2001 towards background isotopic ratios along with the rapid decrease in Pb concentrations from the 1990's to 2001 may indicate that Pb deposited on sediments within the watershed are now being transported off of the landscape and into the lake bottom sediments. This may signify the recovery of Houghton Lake from the major anthropogenic loadings of Pb, such as leaded gasoline inputs, that have occurred

since the early 1900's. The results of this study are in accordance with those of Graney et al. (1995) that both regional and watershed scale sources of Pb were predominant in the Great Lakes Region throughout the 19th and 20th centuries.

6. Conclusion

Sediment Pb isotopic chronologies from six inland lakes across Michigan record the temporal and spatial trends produced by differing sources of Pb to the lakes. The approach of using Pb isotopic chronologies in addition to Pb concentration profiles from multiple lakes that span a large geographic area provided insight into the influence of regional versus watershed scale sources of Pb on the input of Pb to lakes in the region. Lead isotopic chronologies also provided evidence of possible sources of current and historical Pb pollution to inland lakes.

The results of this study support the hypothesis that regional sources were the dominant contributor of Pb to the environment from the 1930's to the 1970's, and that within the past three decades watershed scale sources of Pb have become more important. However, differences in Pb isotopic profiles among inland lakes from 1900 to the mid 1970's show that watershed scale sources in addition to regional scale sources of Pb had an important impact on Michigan lakes.

Before 1900, watershed scale sources of Pb, most likely from forest fires and deforestation associated with the logging industry, were the dominant source of Pb to inland lakes. Regional scale sources of Pb influenced the inland lakes from 1900 until the period from 1963 to 1974, with coal burning and ore smelting being the dominant sources of Pb from 1900 to ~1930, and the combustion of leaded gasoline being the predominant source of Pb until the mid 1970's to 1980's. Emissions of leaded gasoline provided the dominant source of Pb to lakes in the region from ~1930 until the 1980's; however, the offset in isotopic profiles among lakes during this time period provides evidence that varying sources of Pb may have been used in the production of gasoline from one watershed to another. It is also possible that sources of Pb from within the

watershed such as Pb emissions from local industries or municipal waste water discharges provided additional sources of Pb to the lakes. In the late 1960's to mid 1970's some of the inland lakes record a regional scale shift in isotopic ratios due to the increased use of Mississippi Valley Type ores from Missouri in the production of leaded gasoline in the U.S. after the late 1960's. The isotopic profiles of Houghton Lake and Lake Cadillac do not exhibit a shift in isotopic ratios during this time period; therefore, it is likely that watershed scale sources of Pb to these lakes masked the regional change in isotopic ratios. With the decline of leaded gasoline in the U.S. and Canada from the mid 1970's to 1980's the major source of Pb to the atmosphere was drastically reduced and as a result the relative importance of other local sources of Pb may have increased (Bollhofer and Rosman, 2000). The use of recycled industrial Pb sources could help explain the constant isotopic ratios displayed in sediments from some of the Michigan inland lakes during the period from the 1970's to ~2000; however, the isotopic signatures among lakes are offset from one another. Therefore, it is suggested that varying sources of Pb have been used by industries throughout the different watersheds of lakes in Michigan. It is also possible that watershed scale sources of Pb other than industrial emissions could have been a major contributor of Pb to lakes over the past three decades. It is important to note that in 2000, nearly three decades after the decline of leaded gasoline, none of the inland lakes had recovered to their natural background isotopic signature or background Pb concentration indicating that the lakes have not fully recovered from anthropogenic loadings of Pb over the past two centuries. The recent isotopic profile of Houghton Lake is unique from the other lakes and it may show that the lake is recovering from the major anthropogenic loadings of Pb since the early 1900's.

The results of this study provide insight into the contributions of regional and watershed scale sources of Pb and other metals to inland lakes. This research also provides an important complement to previous studies from the Great Lakes Region that show that both regional and watershed scale sources of Pb have been predominant throughout the 19th and 20th centuries (Graney et al., 1995; Yohn et al., 2004). This study along with other studies on regional and local variations of metal emissions can hopefully assist environmental monitoring programs and help to determine what future regulations on Pb and other metal pollutants may be needed.



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APPENDIX

		Total Pb isotopic ratios and					Anthropogenic Pb		
		000	CON				209-150		200
	year of	²⁰⁸ Pb	²⁰⁷ Pb	²⁰⁸ Pb	Pb		²⁰⁰ Pb	²⁰ ′Pb	²⁰⁰ Pb
	sediment	201	206 - 1	206	concentration		204-1	206-1	206-
core	deposition	²º⁴Pb	²⁰⁰ Pb	²⁰⁰ Pb			²⁰⁴ Pb	200Pb	200Pb
Round	1852	49.71	0.7824	2.166	3.7		49.71	0.7824	2.166
	1860	49.05	0.7962	2.018	5.2		46.77	0.8434	1.514
	1901	44.64	0.8107	2.025	29.7		43.84	0.8151	2.002
	1932	42.83	0.8226	2.023	34.5		41.92	0.8279	2.005
	1948	41.56	0.8278	2.035	40.6		40.65	0.8329	2.020
	1960	40.03	0.8338	2.042	67.0		39.41	0.8371	2.034
	1967	39.15	0.8368	2.050	92.2		38.67	0.8393	2.044
	1971	38.75	0.8330	2.058	102.4		38.30	0.8351	2.054
	1982	38.85	0.8289	2.041	82.4		38.29	0.8313	2.034
	1992	39.54	0.8296	2.031	73.4		38.95	0.8324	2.023
	1997	39.67	0.8302	2.038	69.1		39.05	0.8332	2.030
	2000	39.51	0.8320	2.041	69.6		38.88	0.8351	2.033
	2002	39.77	0.8296	2.045	69.3		39.15	0.8325	2.037
Avaion	• 1804	48 69	0.8124	2.035	8.6		48.69	0.8124	2.035
	1838	49 18	0.8062	2.043	7.1		49.18	0.8062	2.043
	1863	48.74	0.7956	2 003	14.9		48.52	0.7811	1.963
	1890	46.18	0.8139	2.026	24.9		44.91	0.8160	2.021
	1930	42.51	0.8298	2.047	50.7		41.34	0.8336	2.049
	1951	41.84	0.8300	2.050	57.9	[40.73	0.8333	2.051
	1960	40.72	0.8336	2.052	77.4		39.80	0.8363	2.053
	1967	40.36	0.8341	2.054	78.0		39.41	0.8369	2.056
	1974	40.68	0.8319	2.051	86.0		39.86	0.8341	2.052
	1982	40.82	0.8291	2.042	71.9		39.83	0.8315	2.042
	1992	41.05	0.8307	2.043	70.8		40.08	0.8334	2.044
	2000	41.09	0.8301	2.043	69.9		40.10	0.8327	2.043
	2003	41.07	0.8293	2.042	70.6		40.09	0.8317	2.042
Houghton	1000	40.00	0 7010	2010	70	1	49.22	0.7918	2.010
noughton	1800	49.22	0.7918	2.010	10.3		47.80	0.8430	2.063
	1837	48.87	0.8044	2.023	16.0	ŀ	45.09	0.8242	2.014
	1000	40.99	0.0093	2.012	35.6	ŀ	43.48	0.8127	2.011
	1902	44.73	0.0002	2.011	47.8	ł	42.00	0.8322	2.048
	1920	40.17	0.0200	2.041	85.1	ŀ	39.35	0.8312	2.040
	1060	40.20	0.0270	2.007	107.5	ľ	39.39	0.8317	2.047
	1060	30 11	0.0200	2.040	133.9		38.84	0.8304	2.042
	1070	30 17	0.0201	2 035	126.2		38.83	0.8289	2.037
	1082	40.36	0.0200	2 041	95.6	ľ	39.58	0.8312	2.043
	1002	38 30	0.0200	2 038	83.8		37.18	0.8313	2.041
	2000	41 12	0.8274	2.041	71.6	ľ	40.13	0.8317	2.045
	2001	44.75	0.8260	2.038	55.2		44.01	0.8316	2.043

Table 1: Total lead isotopic ratios and concentrations and the calculated anthropogenic lead isotopic ratios from inland lake sediments. The background lead isotopic ratios for each lake are shaded.

		²⁰⁸ Pb	²⁰⁷ Pb	²⁰⁸ Pb			²⁰⁸ Pb	²⁰⁷ Pb	²⁰⁸ Pb
	year of	1	1	1	Dh		1	1	1
core	deposition	204Ph	206Ph	206Ph	concentration		204Ph	206Ph	206Ph
Higgins	1747	39.33	0.8009	1.992	7.8		39.33	0.8009	1,992
	1801	38.94	0.8055	1.995	7.8		38.94	0.8055	1.995
	1839	38.78	0.8027	1 989	8.8		38.78	0.8027	1 989
	1863	37.26	0.8036	1.986	12.3	-	33.60	0.8049	1.000
	1904	39.04	0.8109	2 002	46.3		39.05	0.8126	2 005
	1946	37.60	0.8167	1.988	79.4		37.44	0.8182	1 988
	1966	37.60	0.8277	2 022	136.3		37.50	0.8293	2 024
	1977	37.84	0.8264	2.020	160.9		37.78	0.8277	2.021
	1984	37.77	0.8250	2.013	163.5		37.71	0.8262	2014
	1990	37.76	0.8235	2.012	130.1		37.67	0.8249	2.013
	1996	37.92	0.8236	2.013	105.6		37.82	0.8253	2.015
	1999	37.95	0.8243	2.015	106.2		37.86	0.8261	2.016
	1 1000	2.100			10012	-	2.100		
Cadillac	1841	35.89	0.8133	1.964	5.8		35.89	0.8133	1.964
	1862	37.05	0.8173	1.987	8.2		41.34	0.8321	2.074
	1886	37.96	0.8202	2.002	24.5		38.71	0.8227	2.016
	1912	37.75	0.8217	2.007	33.1		38.20	0.8238	2.017
	1930	37.82	0.8233	2.011	52.4		38.10	0.8247	2.018
	1950	37.52	0.8240	2.012	91.6		37.64	0.8248	2.016
	1956	37.52	0.8243	2.012	129.9	1	37.60	0.8248	2.015
	1963	37.51	0.8240	2.016	193.4		37.57	0.8244	2.018
	1968	37.57	0.8230	2.012	252.3		37.61	0.8233	2.014
	1973	37.58	0.8221	2.010	272.7	1	37.62	0.8223	2.011
	1980	37.64	0.8217	2.012	236.1		37.68	0.8219	2.014
	1992	37.51	0.8216	2.008	210.9		37.56	0.8218	2.009
	1997	37.55	0.8218	2.011	191.8		37.61	0.8221	2.013
	2000	37.53	0.8211	2.008	199.7		37.58	0.8287	2.010
Gull	1545	30.45	0.8422	2.002	0.23		30.45	0.8422	2.002
	1701	27.67	0.8403	2.000	0.18		27.67	0.8403	2.000
	1800	34.10	0.8079	1.965	1.0		35.27	0.8001	1.965
	1837	38.15	0.7744	1.942	4.0		38.59	0.7712	1.942
	1887	38.57	0.8047	1.989	10.0		38.74	0.8040	1.989
	1920	38.26	0.8184	2.002	29.0		38.32	0.8182	2.002
	1952	37.76	0.8206	2.002	75.2		37.78	0.8206	2.002
	1961	37.46	0.8232	2.006	109.0		37.48	0.8232	2.006
	1968	37.39	0.8244	2.007	131.5		37.40	0.8243	2.007
	1974	37.25	0.8300	2.018	145.6		37.26	0.8300	2.018
	1980	37.46	0.8127	1.985	142.0		37.47	0.8127	1.985
	1989	37.89	0.8103	1.977	68.8		37.91	0.8102	1.977
	1997	38.17	0.8160	1.992	36.7		38.21	0.8159	1.992
	1999	38.26	0.8192	2.001	23.9		38.33	0.8190	2.001

