DEVELOPING RAPID METHODS FOR DATING SEDIMENTS

IN MISSISSIPPI USING ICPMS

Final Project Report

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ABSTRACT

Sediment cores from seasonal wetland and open water areas from Oxbow lakes [Beasley (BL), Hampton (HL), Washington (WL), Roundaway (RL), Sky (SL) and Wolf (WL)] in the Mississippi Delta, whose chronology was previously determined by conventional ^{210}Pb and ^{137}Cs age-dating, were analyzed, for the first time, for Pu isotopes (^{239}Pu and ^{240}Pu), and Pb isotopes (^{206}Pb, ^{207}Pb, ^{208}Pb and ^{210}Pb). The primarily purpose was to evaluate the feasibility of using ICPMS as an alternative to radiochemical analyses for fallout-Pu and ^{210}Pb.

For Pu, the mean ^{240}Pu/^{239}Pu atom ratio was ~0.177 indicating global fallout as the primary and likely source of the Pu. Analyses of an undisturbed sediment core yielded a Pu peak at a depth which is in good agreement with conventional ^{137}Cs and ^{210}Pb dating. Analysis of the Washington Lake sediment core yielded a Pu vs. depth profile that was broad and uncharacteristic of normal sedimentation patterns. It was later found out that the conventional dating technique also yielded data scatter indicative of sediment that was likely disturbed *in-situ*. Indeed, because sediment can be mixed by natural events after deposition, this demonstrates that ICPMS can serve as a useful tool to simultaneously identify (screen for) sediments that have been disturbed (eliminating costly ^{210}Pb analyses on such cores), and to provide a chronological marker for those that haven't (either alone or in conjunction with conventional dating).

For Pb, total concentrations varied from 1.5 ppm to 12 ppm, with peak levels generally occurring during the 1950's. Isotopic signature plots suggest "natural" Pb (from soil) as the primary source of the lead, with coal and gasoline as slight contributors; however, more study is needed to confirm this. Accurately measuring the ^{210}Pb isotope by ICPMS was problematic. The levels were low and subject to interference from stable isotopes of Pb, possibly by the tail of the large ^{208}Pb peak and/or from polyatomic interference such as ^{208}Pb^{1}H^{1}H. To overcome these barriers, it is recommended to boost the sensitivity, possibly with a jet-face interface, and/or remove the interference using collision cell technology.

Information transfer: Publications resulting from this work include a paper in the 2012 Mississippi Water Resource Conference Proceedings. This work also contributed toward a Master's thesis by Ms. Pragya Chakravarty titled "Elemental and Isotopic Analysis of Sediments from Oxbow Lakes in the Mississippi Delta" (University of Mississippi, 2012). The current report contains elements from each of those reports.

ACKNOWLEDGEMENTS

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BACKGROUND AND PURPOSE OF STUDY

Sediments are complex deposits of inorganic and organic matter that can serve as a natural storage system for metals and anthropogenic contaminants. Because sediment cores can go back decades and even centuries, they are useful as environmental proxies providing a window on the past. Chronology of recent sediments (<100 years since deposition) is traditionally determined using ^{210}Pb and/or "bomb-pulse" isotopes, such as ^{137}Cs and $^{239+240}$Pu. These isotopes are commonly determined by radiochemical techniques, a process that is tedious and requires long analysis (count) times.

Sediment cores were collected from seasonal wetland (W) and open water (OW) areas from Oxbow lakes [Beasley (BL), Hampton (HL), Washington (WL), Roundaway (RL), Sky (SL) and Wolf (WL)] in the Mississippi Delta as part of previous studies by Dr. Davidson (UM Geology Department) and Dr. Wren (National Sedimentation Laboratory) [1, 2]. The core chronology was determined by conventional ^{210}Pb and ^{137}Cs age-dating and a number of trace elements were determined. Subsequently the dried sediment samples were archived in plastic bags and stored in boxes at room temperature.

In this study, these well-characterized sediment samples were, for the first time, analyzed for Pu isotopes (^{239}Pu and ^{240}Pu), and Pb isotopes (^{206}Pb, ^{207}Pb, ^{208}Pb and ^{210}Pb). The purpose was to: 1) assess temporal and spatial patterns of metal deposition in the region, and 2) evaluate the feasibility of using ICPMS for dating recent sediment by measuring fallout-Pu and ^{210}Pb in sediment profiles and comparing with conventional radiochemical dating methods. Specific objectives for each part of the study are given in their respective chapters. I am very grateful to our collaborators to have been given these sediment samples for this study.

SAMPLE SITES, SAMPLING, SAMPLE PREPARATION AND SEDIMENT CHRONOLOGY

Sediment cores were collected as a part of previous investigations by Dr. Davidson (UM Geology Department) and Dr. Wren (National Sedimentation Laboratory) [1, 2]. Detailed information on sample sites, sampling, sample preparation and sediment chronology are available from prior reports [1,2]. Briefly, cores were sampled using a vibracorer from both open water and wetland areas within six different Oxbow Lakes (Roundaway, Washington, Beasley, Wolf, Sky and Hampton) in the Mississippi Delta (Figures 1-3). Core identity, total watershed area, surface area, GPS specifications, core locations and maximum depth of the cores from six Oxbow Lakes are presented in Table 1. Plastic core pipes were inserted in the vibracorer before sampling. To account for compaction core depths were normalized to mean water content by the NSL. All lakes were sampled in 2009, except Wolf Lake and Sky Lake which were sampled in 2010 and 2006, respectively. The cores were stored at 4oC until processing. Cores were extruded soon after collection (within weeks) (except Sky Lake, which

was extruded in Sept. 2011) and sliced (figure 4) into 1cm (approx.) thick intervals, dried at 60°C in the oven, crushed and sieved through mesh of 1mm pore size. Once sieved the cores were stored at room temperature in labeled plastic bags. The cores were dated using both ^{210}Pb and ^{137}Cs analyses using conventional radioanalytical techniques as described elsewhere.

Table 1. Sample Information

Lake	Latitude (N)	Longitude (W)	Surface Area (Ha)	Watershed Area (Ha)	Sample ID	Core Location	Maximum Depth (cm)
Beasley	33.2408°	90.4032°	25	915	BL1A	Open Water	97
					BL2	Wetland	58
Hampton	33.8436°	90.2353°	NA	NA	HL2A	Open Water	333
					HL9	Wetland	134
Washington	33.0253°	91.0246°	1260	10,995	LW1A	Open Water	126
					LW2	Wetland	211
Sky	33.2888°	90.4985°	NA	1860	SL5	Open Water	136
Wolf	32.5563°	90.2799°	450	11,750	WF1	Wetland	126
Roundaway	34.0125°	90.3574°	21	1254	RL1B	Wetland	71
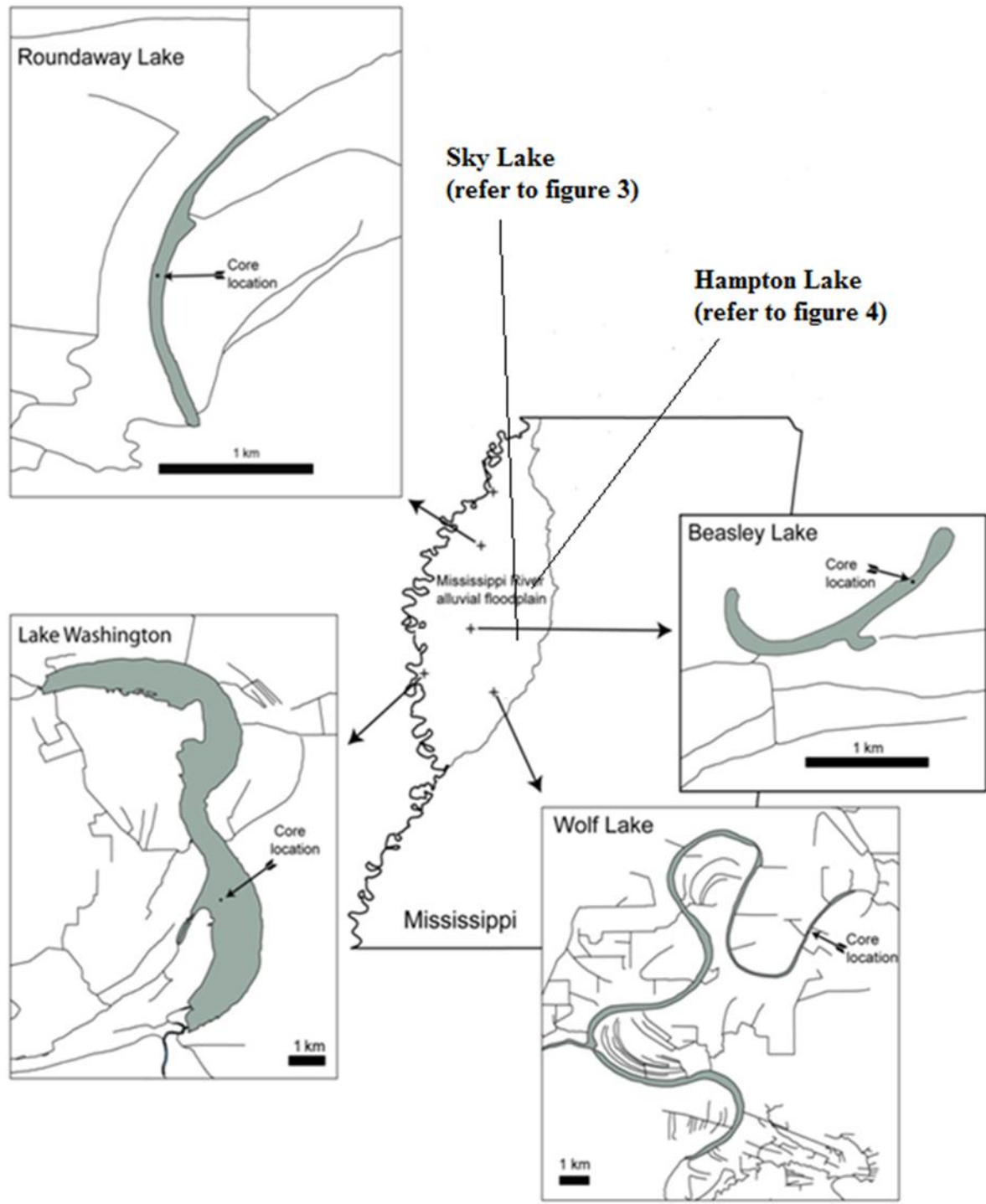
Figure 1. Locations of Oxbow Lakes in this study [adapted with permission from ref. 2]
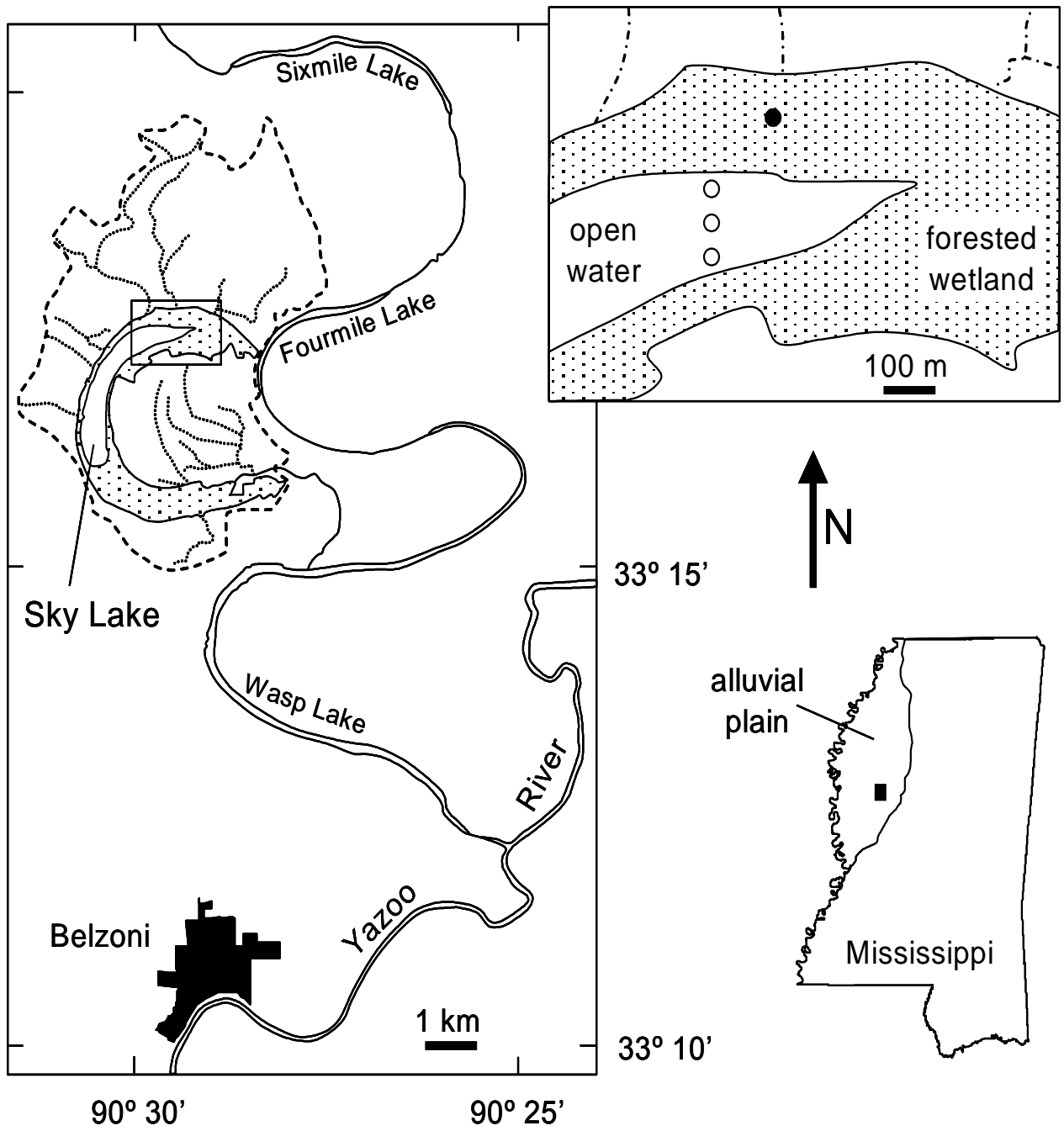
Figure 2. Sky Lake watershed shown in dashed lines. 1mm cores were sampled from middle circle [ref. 1].
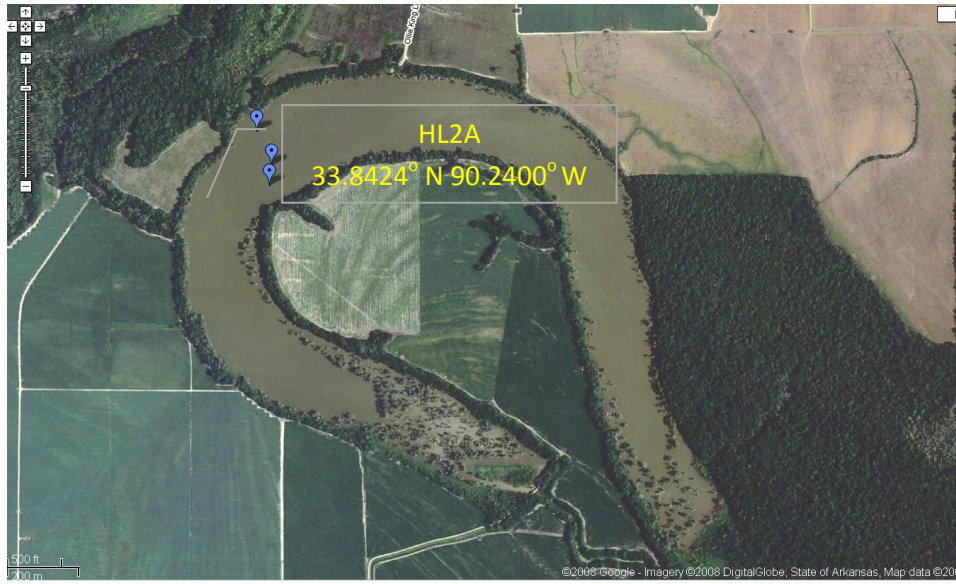
Figure 3. Core Location shown for Hampton Lake [3]

Figure 4. Sky Lake sediment core (SL5) being sliced into 1cm intervals at the National Sedimentation Laboratory.

PLUTONIUM

INTRODUCTION

Artificial radionuclides like ^{239}Pu and ^{240}Pu are introduced into the environment due to accidental releases from the nuclear power plants and testing of nuclear weapons. ^{239}Pu and ^{240}Pu are the most abundant isotopes of plutonium [4]. Their fallout records are preserved in the sediment and they are used to determine chronology for sediments; peak concentrations in sediments correspond to the year 1963 [5]. Years since 1963 divided by the depth yields average sedimentation rate (figure 5). The stratospheric fallout ratio is ^{240}Pu/^{239}Pu = 0.180 ± 0.014 and the Nevada Test Site fallout ratio is ^{240}Pu/^{239}Pu = 0.03 ± 0.07. Using these ratios one can decipher the source of fallout in a region.

Conventionally, radiometric analyses of ^{239}Pu and ^{240}Pu have been performed by alpha spectrometry. Alpha spectrometry is destructive, requires the use of large sample volumes and involves a lot of sample preparation. Further, alpha spectrometry cannot categorize ^{239}Pu and ^{240}Pu separately due to small difference in their alpha particle energies [6]. A potential alternative to using radiochemistry is the use of mass spectrometry. ICPMS has a number of advantages for long-lived radionuclides because it counts atoms instead of decays. It is suitable for routine analysis of large number of samples and can measure isotope ratios.
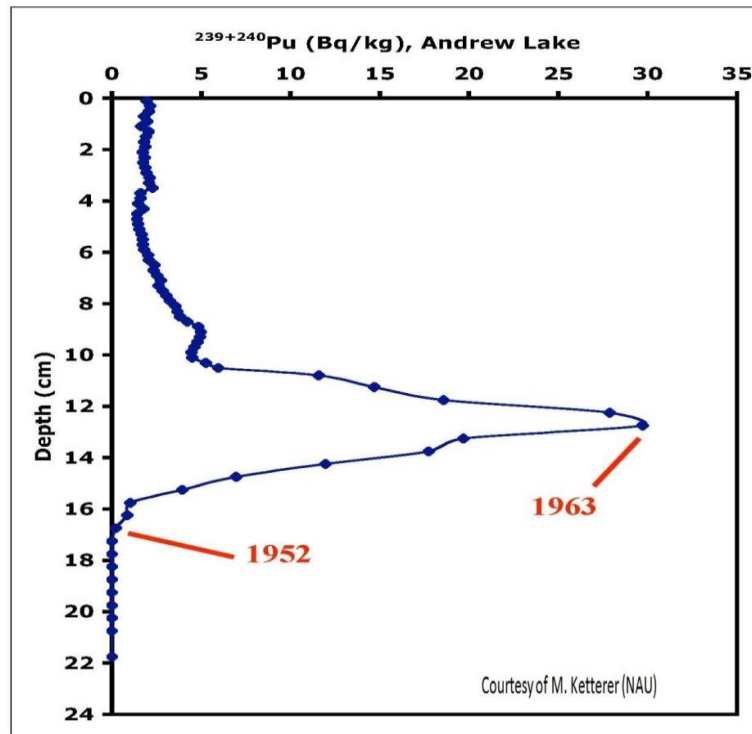
Figure 5. Example of use of Pu for age-dating sediments. Depth vs. $^{239+240}$Pu activity (Bq/g) in Andrew Lake sediments [7].

OBJECTIVES

- To transfer and optimize analytical protocols to measure "fallout" plutonium (Pu) in sediments using Sector Field ICPMS.
- Use ICPMS to measure Pu activity and atom ratios in sediment cores from Oxbow Lakes in the Mississippi Delta to age-date the sediment.
- Compare sediment core age-dating results for Pu with that for conventional radioanalytical analysis of ^{137}Cs and ^{210}Pb.
- Determine the source(s) of Pu in the sediment using Pu isotopic signatures.

METHODS

PLUTONIUM EXTRACTION, ISOLATION AND CONCENTRATION

Sediment core samples from Washington Lake (WL1A) and Beasley Lake (BL1A) were analyzed for ^{239}Pu, ^{240}Pu and ^{242}Pu isotopes. The sample weights used for BL1A and WL1A cores ranged from 1.7 to 2.5 grams and 4.5 to 5 grams respectively. The samples were weighed into a 20ml glass vial and dry ashed at 600°C for 6 hours to remove organic matter. 50 pg of ^{242}Pu (NIST 4334g) was added as a spike for isotope dilution analysis. Five milliliters of 16M HNO_3 was added and the mixture was leached at 80°C for 16 hours. The samples were filtered using vacuum filtration and filters of mesh size 0.45 microns. The filters were rinsed with 15ml of de - ionized water and the rinsing solution was combined with the filtrate. Twenty milligrams of ascorbic acid were added to the solution for the conversion of all the Pu (III) to Pu (IV). The solution is kept as such for 1 hour for the complete conversion of Pu (III) to Pu (IV). The molarity of this solution is 4. TEVA Resin columns were prepared using 5ml pipettes and TEVA Resin powder. The narrow end of the 5ml pipettes were clogged with glass wool and 0.1 – 0.2gm TEVA Resin powder was added. The columns were conditioned by passing 5ml of 4M HNO_3. 5ml of the sample solution were flushed through the column. During this step, Pu (IV) along with Np, Th and U is retained within the columns and other matrix elements are discarded. The columns were rinsed with 3ml of 4M HNO_3 and 5ml of 1M HNO_3. The left over sample solution was loaded into the column in 5ml aliquots each time followed by rinsing with 3ml of HNO_3 and 5ml of 1M HNO_3. The rinse step with 1M HNO_3 allows wash out of the majority of the U from the column. A final rinse of the column with 20 ml of 9M HCl was performed to wash out Th. Pu was eluted using 10ml of 0.02M HCl.

COLUMN CHEMISTRY

The functional group in the TEVA Resin that extracts Pu from sample solutions is a quarternary ammonium salt (figure 6) [8].

Trialkyl, methylammonium
nitrate (or chloride)
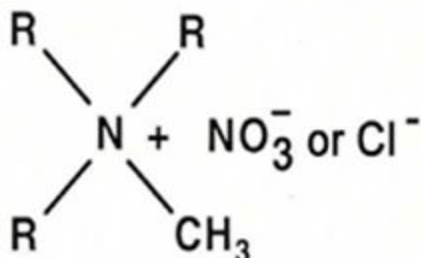
Figure 6. TEVA Resin Quarternary Ammonium Salt [8]

The assumed extraction equilibrium is as follows [8]:

$$Pu^{4+} + 4NO_3^- + 2\overline{E \cdot NO_3} \Leftrightarrow \overline{E_2^+ \cdot Pu(NO_3)_6^{2-}}$$
$$(Th^{4+}, Np^{4+})$$
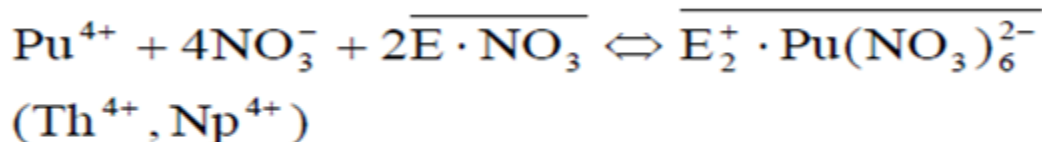
with E = extractant

In aqueous solutions, Pu can exist in Pu(III), Pu(IV), Pu(V), Pu(VI) and Pu(VII) oxidation states simultaneously [9]. Pu(III) and Pu(IV) are in general believed to be relatively insoluble in solutions compared to Pu(V) and Pu(VI) which are considered to be more soluble [9]. It has been reported that in 7M HNO_3 solution, Pu(IV) can exist as a complex mixture of $Pu(NO_3)_2^{2+}$, $Pu(NO_3)_4$, and $Pu(NO_3)_6^{2-}$ [9].

Figure 7 presents the elution profiles of different radionuclides in HNO_3 and HCl. Pu(IV) shows maximum retention within 2M-4M HNO_3. In this range U(VI) tends to elute. When the samples are loaded on the TEVA Resin from 4M HNO_3, Pu(IV) is retained. Th, which can interfere with Pu analysis, maybe eluted with 6M HCl [8].
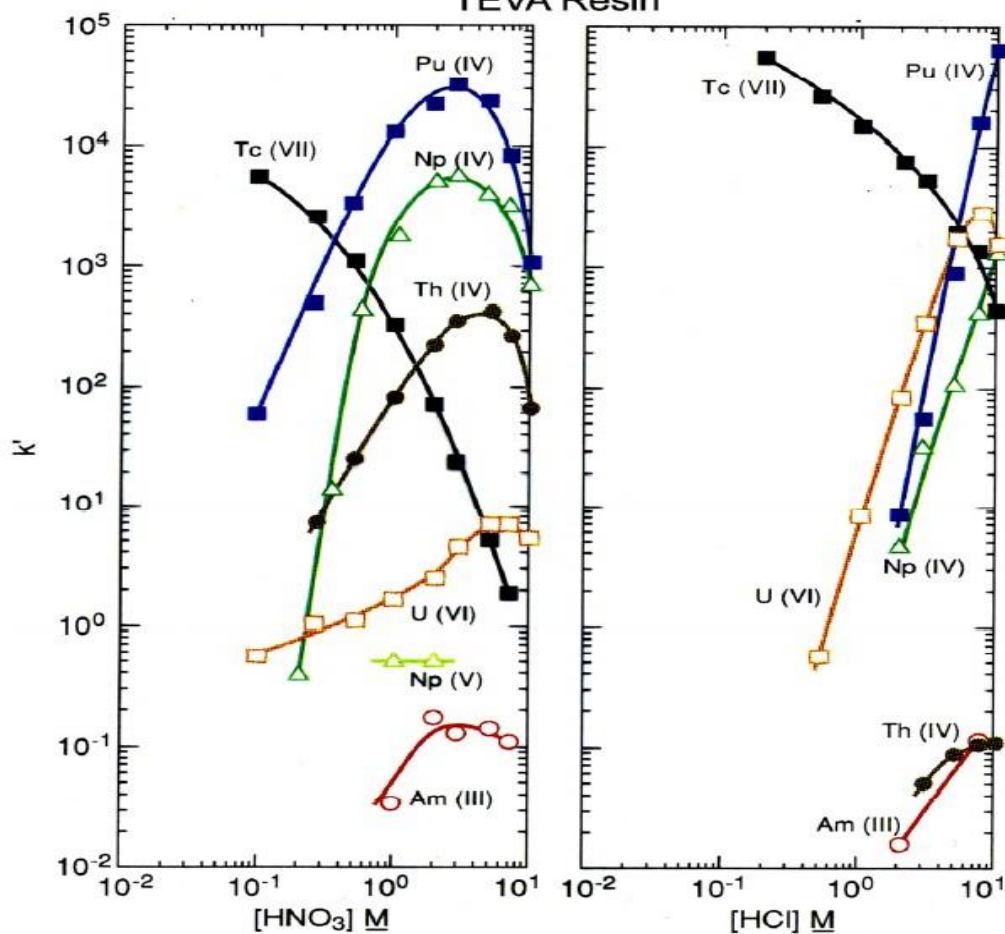
Figure 7. TEVA Resin Elution profiles in HNO₃ and HCl solutions [8].

Figure 8. Sample preparation for Pu analysis.


```
┌─────────────────────┐
│   5gm soil ashed at │
│  600°C for 6 hours. │
└─────────────────────┘
          │
          ▼
┌─────────────────────┐
│  50pg ²⁴²Pu tracer  │
│   (NIST 4334g) was  │
│  added to the       │
│  samples.           │
└─────────────────────┘
          │
          ▼
┌─────────────────────┐
│ Acid leached with 5ml│
│  conc. HNO₃ for 16  │
│ hours at 80°C in a hot│
│       block.        │
└─────────────────────┘
          │
          ▼
┌─────────────────────┐
│  Sample solution was│
│   filtered and residue│
│ was washed with 15ml│
│      DI water.      │
└─────────────────────┘
          │
          ▼
┌─────────────────────┐
│  Filtrate and residue│
│   wash solutions were│
│    combined. (4M    │
│     solution)       │
└─────────────────────┘
          │
          ▼
┌─────────────────────┐
│ Valence Adjustment: 20mg of│
│    Ascorbic acid    │
└─────────────────────┘
          │
          ▼
┌─────────────────────┐
│  Solutions heated at│
│   50°C for 1 hour.  │
│  Cooled for another1│
│        hour.        │
└─────────────────────┘
          │
          ▼
┌─────────────────────┐
│    Column Load      │
│     Solution        │
└─────────────────────┘
```

Figure 9. Column Chemistry for Pu isotope separation

TEVA resin column preconditioned with 5ml of 3M HNO_3

↓

Load solution of 5ml aliquot passed through the column.

↓

Column rinsed with: 3ml 4M HNO_3 ; 5ml 1M HNO3

↓

Rinses discarded.

↓

5ml of load solution passed through the column and rinsed with 3ml 4M HNO_3 and 1M HNO_3. Sample loading (5ml) and rinsing continued until entire sample is used up.

↓

Column rinsed with 20ml 9M HCL

↓

Pu eluted with 10ml of 0.02M HCl.

↓

Quantified by SF-ICP-MS.

MEASURING PLUTONIUM ISOTOPES BY ICPMS

Sample handling preparation of standards and reagents were performed in clean rooms under laminar flow clean air benches to minimize the risk of contamination. All ICP-MS measurements were carried out using an Element XR (Thermo Fisher), figure 10. For measuring Pu isotopes, a high efficiency sample introduction system APEX desolvation unit was utilized to minimize hydride formation. SF-ICP-MS operating conditions are summarized in table 2. Use of SF-ICP-MS provides good accuracy and precision and detection limits within femtogram levels. The main issues associated with the determination of Pu isotopes are the following:

a) Formation of $^{238}U^1H$, $^{238}U^1H^1H$ that cause interferences with ^{239}Pu and ^{240}Pu [5].
b) Tailing effect of ^{238}U on the ^{239}Pu signal [6].

Uranium ideally should be removed from the sample solutions during resin treatment and before analysis as resolution of $^{238}U^1H$ is not possible using SF-ICP-MS [5].
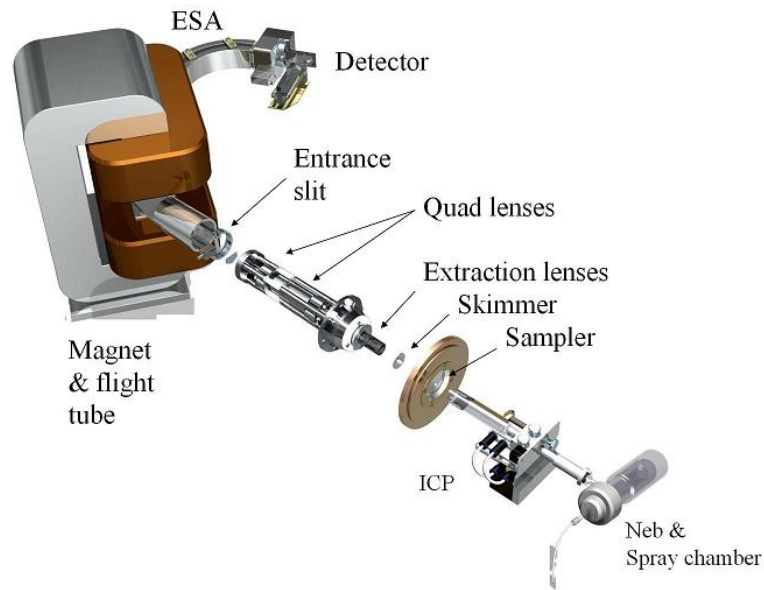
Figure 10. Schematic of Sector Field Inductively Coupled Plasma mass Spectrometry [10].

Table 2. Operating Conditions of the SF-ICP-MS.

Parameter		Operating Condition
Forward Power		1450
Cool gas flow rate		16 L/min
Auxiliury gas flow rate		1.0 L/min
Sample gas flow rate		1.2 L/min
Mass Window		20
Scan type		Escan
Integration window		80
Samples/peak	^{239}Pu	150
	^{240}Pu	150
	^{242}Pu	50
Dwell time	^{239}Pu	0.1s
	^{240}Pu	0.1s
	^{242}Pu	0.01s

RESULTS AND DISCUSSION

Table 3 shows the results for the determination of ^{239}Pu, ^{240}Pu concentration, $^{239+240}$Pu activity and ^{240}Pu/^{239}Pu atom ratio for Beasley lake open water core. ^{241}Pu was too low in concentration to accurately measure and will not be reported here. In some cases, concentrations of Pu determined by ICPMS were converted to activities using the specific activity of the isotope. The results for Washington and Roundaway lakes wetland core are presented in tables 8 and 9 (appendix). Of the cores analyzed the Beasley Lake open water core has the best defined chronology [1]. The lake was recently found to show a reduction in sediment accumulation rates due to erosion control and cropping practices [1]. We analyzed sediment samples using both batch (resin beads mixed with the solution) and column methods. Whereas Pu levels were found to be lower in the batch method, trends for both were similar (figure 11). The peak Pu depth was in agreement with peak ^{137}Cs depth. Usually these peaks correspond to 1963, the peak year for fallout, but the ^{210}Pb dating places them a few years later. It is possible that the recent changes in sedimentation rates affected that determination. In any case, the profiles show Pu peaks in general agreement with the conventional dating methods. A core a greater number of samples (from Sky Lake) was also prepared for analysis with the hope of demonstrating an even better resolved peak profile, however due to instrument repair the samples were not analyzed by the time this report was completed.

^{240}Pu/ ^{239}Pu atom ratios averaged 0.177, consistent with a global fallout source. The Pu activity profile for Washington and Roundaway Lakes are shown in figures 12 and 13. The data suggests that these sediments were, to some extent, mixed since deposition. This agrees with conventional dating results which also showed data scatter indicative of mixing [1]. Interestingly,

for Washington Lake the peak Pu level occurred at a depth of ~21 cm which is similar to the peak depth for ^{137}Cs (18 cm, not shown). In retrospect, these wetland cores were not the best choice for testing; but they do show that the method is useful for identifying cores that have uncharacteristic global fallout profiles, which in turn suggests that the core has been mixed and may not be the best choice for costly ^{210}Pb dating.

Table 3. Pu Summary for Beasley Lake.

Year	Depth(cm)	^{239}Pu(pg/g)		^{240}Pu(pg/g)		^{240}Pu/^{239}Pu		$^{239+240}$Pu(Bq/kg)	
		column	batch	column	batch	column	batch	column	batch
2003	6	0.94	0.10	0.18	0.02	0.19	0.21	3.65	0.39
1992	16	1.04	0.17	0.18	0.03	0.17	0.18	3.89	0.63
1982	23	1.51	0.13	0.24	0.03	0.16	0.20	5.49	0.50
1971	47	2.72	1.07	0.42	0.25	0.16	0.23	9.82	4.55
1966	60	2.41	0.31	0.46	0.06	0.19	0.21	9.43	1.25
1963	68	0.06	0.06	0.02	0.01	0.25	0.25	0.27	0.24
1953	90	1.69	0.43	0.30	0.09	0.18	0.21	6.43	1.74
Avg		1.48	0.32	0.26	0.07	0.19	0.21	5.57	1.33
SD		0.91	0.36	0.15	0.08	0.03	0.02	3.37	1.52

Figure 11. Depth vs. $^{239+240}$Pu activity for Beasley Lake

Beasley Lake (Open Water)

$^{239+240}$Pu (Bq/Kg)
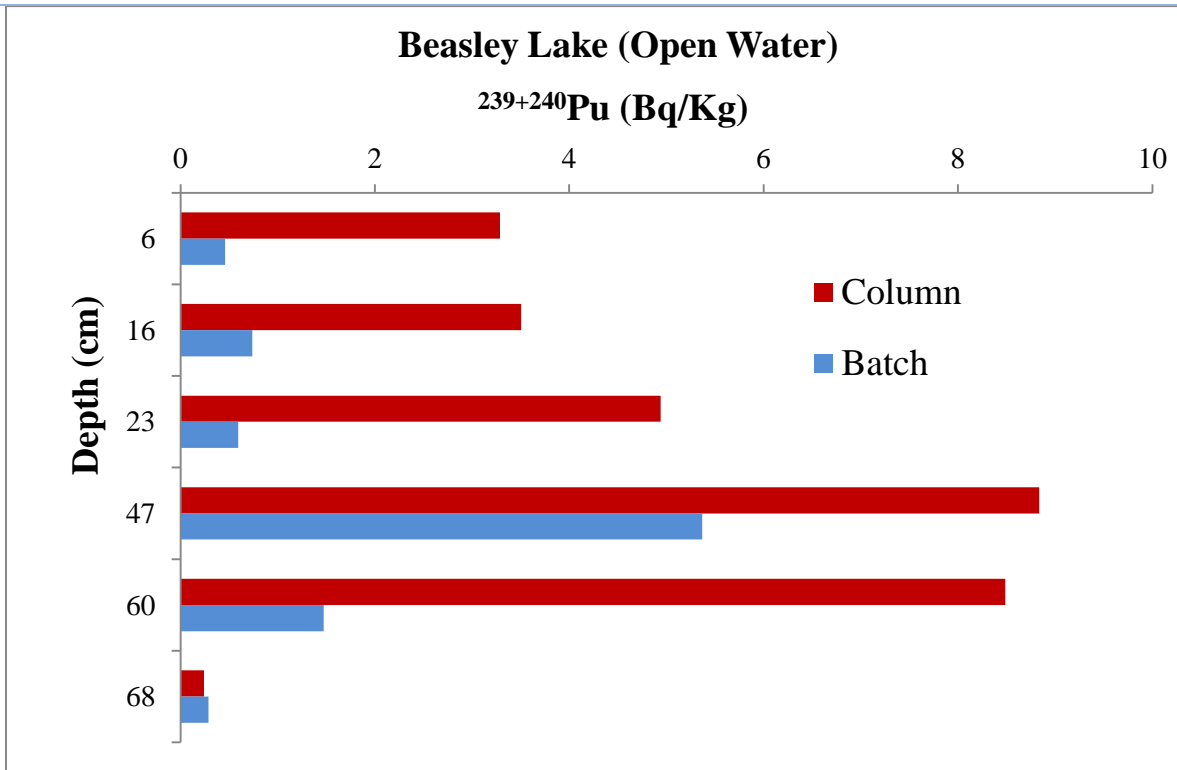
Column

Batch

Depth (cm)

Figure 11. Depth vs. $^{239+240}$Pu activity for Beasley Lake

Figure 12. Depth vs. $^{239+240}$Pu activity for Washington Lake
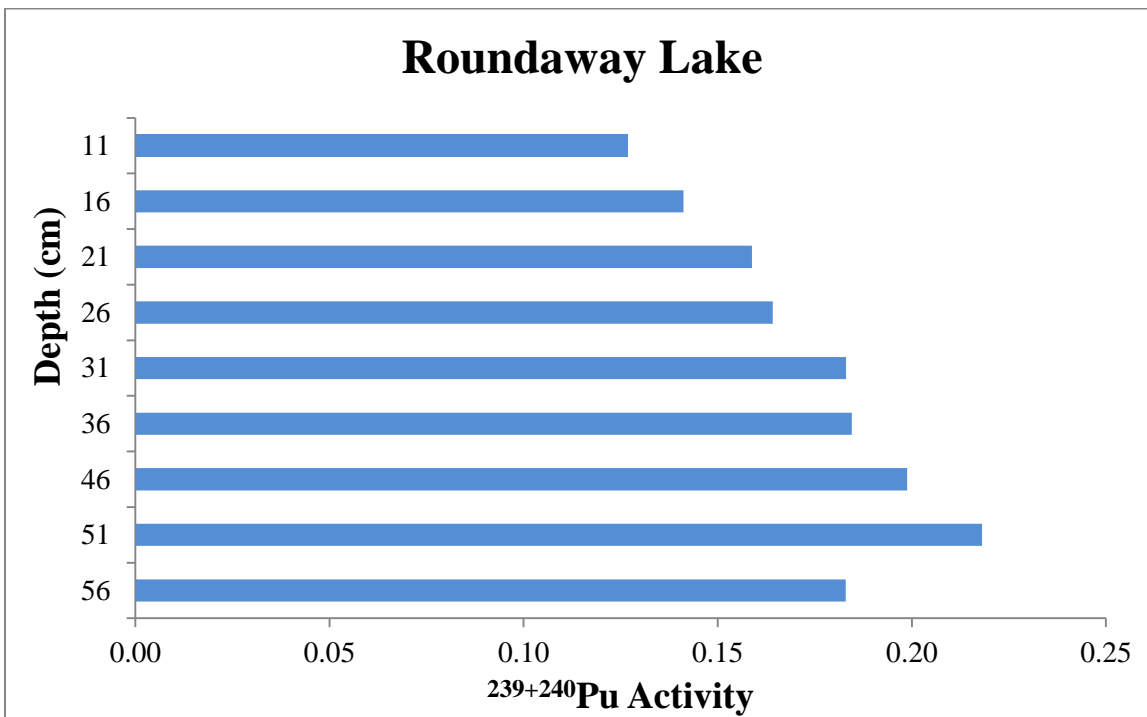
Figure 13. Depth vs. $^{239+240}$Pu activity (Bq/kg) for Roundaway Lake

16

<div align="center">

LEAD

</div>

INTRODUCTION

LEAD IN SEDIMENTS

Pb has been mined and used by humans for several thousand years [11]. Deposits of Pb have characteristic isotopic composition [11]. Analyzing stable Pb isotopes (^{206}Pb, ^{207}Pb and ^{208}Pb) and identifying the ratios (^{206}Pb/^{207}Pb and ^{208}Pb/^{207}Pb) can help in the determination of point sources of Pb contamination. Two well-known sources of Pb contamination are usage of leaded gasoline (~1924 – ~1960) and coal mining [11].

AGE-DATING OF SEDIMENTS USING ^{210}Pb

Sediments are dated to determine the spatial and temporal patterns of metal deposition in an area, to determine the effectiveness of erosion control methods (figure 14 and 15), to manage reservoirs more effectively and ultimately to calculate the rates of sediment accumulation. Dating of sediments is done by using natural radio nuclides like ^{210}Pb and ^{14}C and artificial radio nuclides like ^{137}Cs, ^{239}Pu and ^{240}Pu. ^{210}Pb is a member of the ^{238}U decay series. Half life of ^{210}Pb is 22 years. The content of 'supported' ^{210}Pb in soils is produced by the decay of ^{226}Ra. ^{222}Rn diffuses from the soil surface and decays in the atmosphere (figure 16). This results in the deposition of 'unsupported' or 'excess' ^{210}Pb combined with aerosol and moisture on the soil surface. ^{210}Pb dating method is based on measuring and comparing the quantities of supported and unsupported ^{210}Pb. However there are two major limitations in applying this method. Firstly, mixing or displacement of sediment particles gives erroneous dates and secondly this method does not hold good for sediments more than 100 years old as no excess ^{210}Pb can be detected beyond the background level. ^{210}Pb decays by emitting beta particles of energy 17 kev and 63.5 kev and gamma rays of energy 46.5kev [12]. The decay products are ^{210}Bi and ^{210}Po respectively.

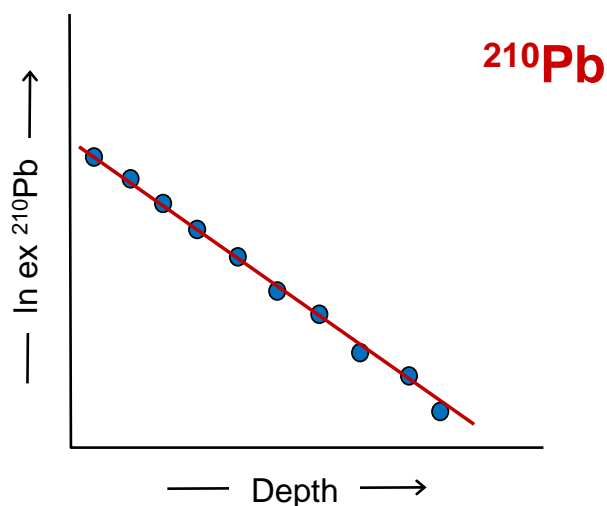**Figure 14. Plot of ^{210}Pb activity (dpm/g) vs. depth in absence of an erosion control measure. Higher activity is seen at lower depths meaning more sedimentation [13].**
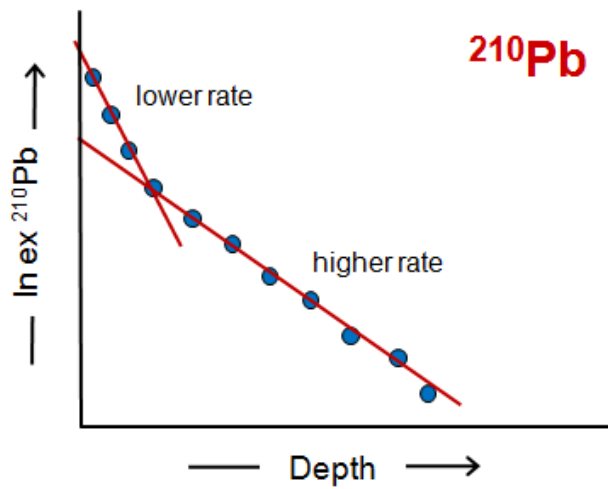
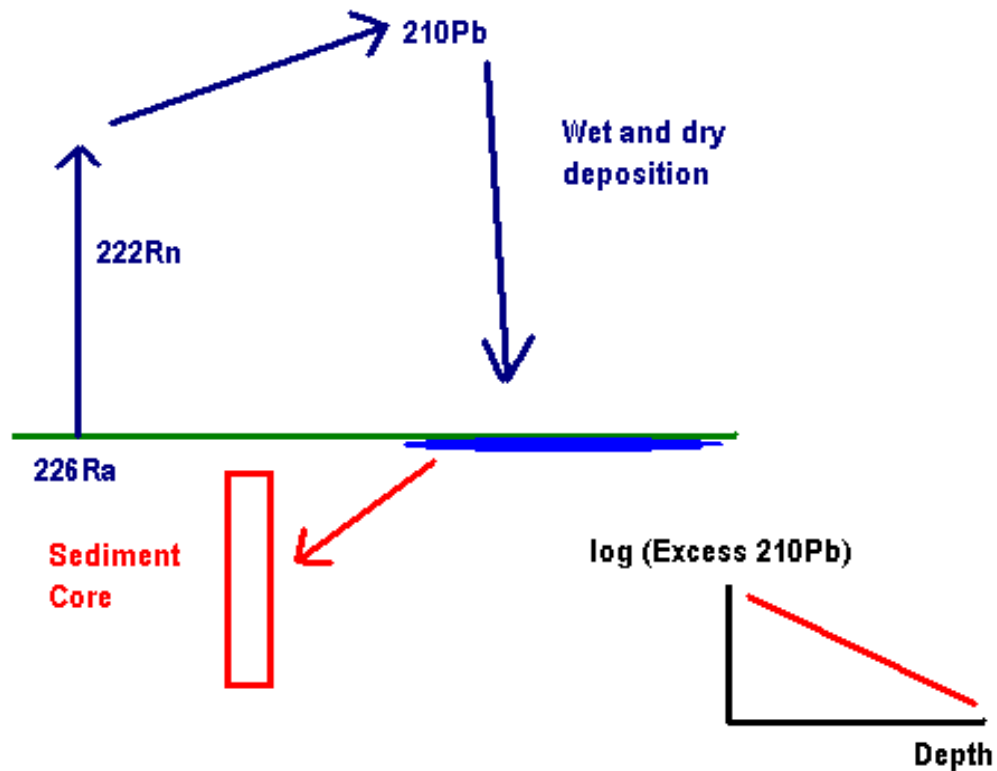**Figure 15. Plot of ^{210}Pb activity vs. depth after an erosion control structure is introduced [13].**

Figure 16. Upward diffusion of ^{222}Rn and subsequent deposition of ^{210}Pb (excess) on the sediment surface [7].

OBJECTIVES

- Determine the feasibility of using ICPMS for ^{210}Pb age-dating of sediments
- Analyze total-Pb in the sediment cores and determine changes with time (depth).
- Determine Pb isotopic ratios in open water and wetland cores to see if they can be used to determine the source(s) of lead in Hampton and Washington lakes.

METHODS

Wetland and open water sediment core samples from Lake Washington (WL1A and WL2 respectively) and open water sediment samples from Hampton Lake (HL2A) were subjected to total Pb and Pb isotopes (^{206}Pb, ^{207}Pb, ^{208}Pb and ^{210}Pb) analysis.

SAMPLE PREPARATION FOR TOTAL Pb ANALYSIS

Two grams of each sediment sample was weighed in a 20 ml glass vial and ashed in a muffle furnace at 600°C for 6 hours. The ashed samples were transferred to already cleaned 50ml tubes and leached with 20ml of concentrated HNO_3 for 8 hours in a hot block. The leached samples were filtered using filters of mesh size 0.45 microns and the leach-ate volume was made to 50ml with de-ionized water. 0.5ml liquid from the diluted leach-ate was transferred to 15ml clean centrifuge tubes and the volume was made up to 10ml with 2% HNO_3. Sample preparation process is summarized in figure 17.

SAMPLE PREPARATION FOR LEAD ISOTOPE (^{206}Pb, ^{207}Pb, ^{208}Pb, ^{210}Pb) ANALYSIS

Two grams of each sediment sample was weighed in a 20 ml glass vial and ashed in a muffle furnace at 600 °C for 6 hours. The ashed samples were transferred to already cleaned 50ml tubes and leached with 20ml of concentrated HNO_3 for 8 hours in a hot block. The leached samples were filtered using vacuum filtration with filters of mesh size 0.45 microns and the leach-ate volume was made to 50ml with de-ionized water. 0.5ml liquid from the diluted leach-ate was used for total Pb analysis. The remaining 49.5 ml liquid was heated to complete dryness in a hot block. The volumes of the samples were made up to 10ml using 1M HNO_3. Pb resin columns were prepared by clogging the narrow end of 5000µl pipette tips with glass wool and filling it up with 0.1 - 0.2gm of Pb resin powder (100 - 150µm). The columns were conditioned by passing 5ml of 1M HNO_3. The sample solutions were then loaded on to the columns and the eluent was discarded. The columns were washed using 20ml of 1M HNO_3. This wash is performed to remove Bi and Fe if present. The eluent was discarded. 10ml of 0.1M HNO_3 was added to the columns to remove any ^{210}Po if present. Following the last wash, 40ml of 0.1M citric acid monohydrate solution was added to the columns and the eluent was collected in 50 ml centrifuge tubes. The solutions were heated to complete dryness in a hot block and the volumes were raised to 10ml with 1% HNO_3. The sample solutions and two method blanks were then analyzed for ^{206}Pb, ^{207}Pb, ^{208}Pb and ^{210}Pb using Element XR. Sample preparation and column chemistry processes are summarized in figures 17 and 18. It should be noted that a Pb-isotope reference material (NIST 981) was included in the analyses.

Figure 17. Sample Preparation for Pb analysis

2.0g sediment sample ashed for 6 hours at 600°C

⬇

Acid leached with 20ml conc. HNO_3 for 16 hours at 80°C in a hot block.

⬇

Sample solution was filtered and residue was washed with 20ml DI water.

⬇

Filtrate and residue wash solutions were combined. Volume was made up to 50ml. (40% acid).

Total Pb

0.5ml of the 50ml solution was transferred to 15ml centrifuge tube.

⬇

The volume was raised to 10ml by 2% HNO_3.

⬇

Quantified by SF-ICP-MS.

Pb Isotope Analysis

49.5ml of the solution was transferred to 50ml digestion vessels.

⬇

Solution was evaporated to complete dryness.

⬇

Volume was made up to 10ml with 1M HNO_3.

⬇

Column load solution.

Figure 18. Column Chemistry for Pb isotope separation.

Pb resin column preconditioned with 5ml of 1M HNO_3

↓

Load solution passed through the column.

↓

Column rinsed with 20ml of 1M HNO_3 (This rinse helps to remove ^{210}Bi and Fe)

↓

Column rinsed with 10ml of 0.1M HNO_3 (This helps to remove ^{210}Po)

↓

Eluted Pb with 40ml of 0.1M citric acid.

↓

Solution heated to complete dryness and volume made up to 10ml with 2% HNO_3.

↓

Quantified by SF-ICP-MS.
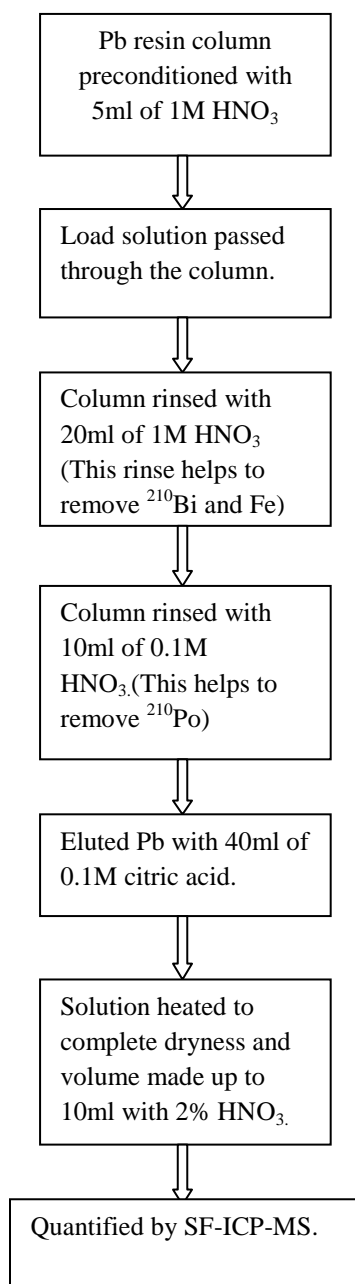
COLUMN CHEMISTRY

The extractant in Pb resin 4,4"(5)-di-t-butylcyclohexano 18-crown-6 in isodecanol (figure 19). Figures 20 and 21 show the uptake of Pb with monovalent and divalent metal ions respectively. The retention capacity (k') of Pb is higher than 100 in nitric acid concentrations ranging from 0.1M to 10M [24].

di-t-butylcyclohexano 18-crown-6

Figure 19. 4,4"(5)-di-t-butylcyclohexano 18-crown-6 in isodecanol [24]

The assumed extraction equilibrium is as follows [24]:

$$Pb^{2+} + 2NO_3^- + \overline{E} \Leftrightarrow \overline{Pb(NO_3)_2 E}$$

with E = crown ether.

Figure 20. Nitric acid dependancy of selected monovalent metals on Pb resin [24].

Figure 21. Nitric acid dependancy of selected divalent metals on Pb resin [24].

ICPMS Analysis

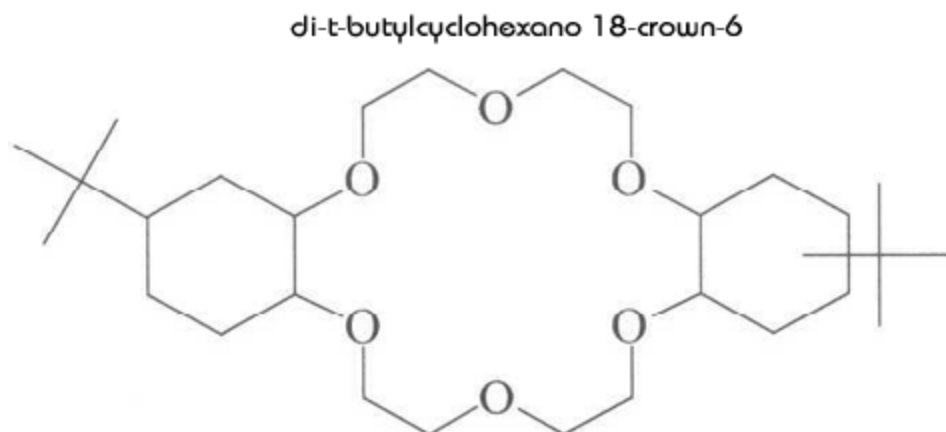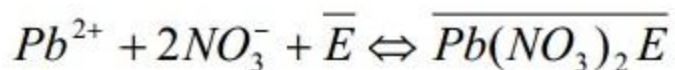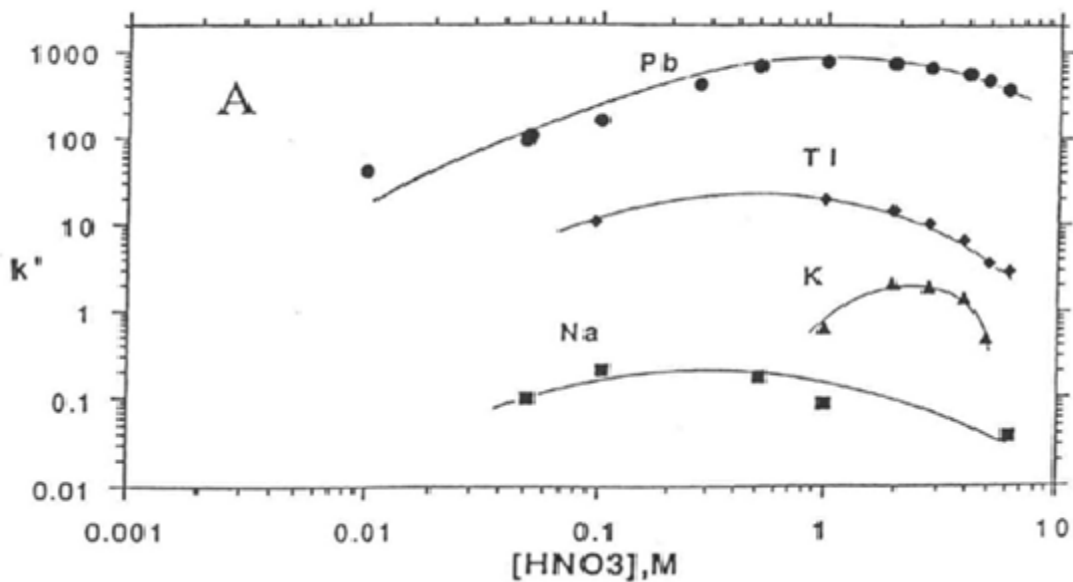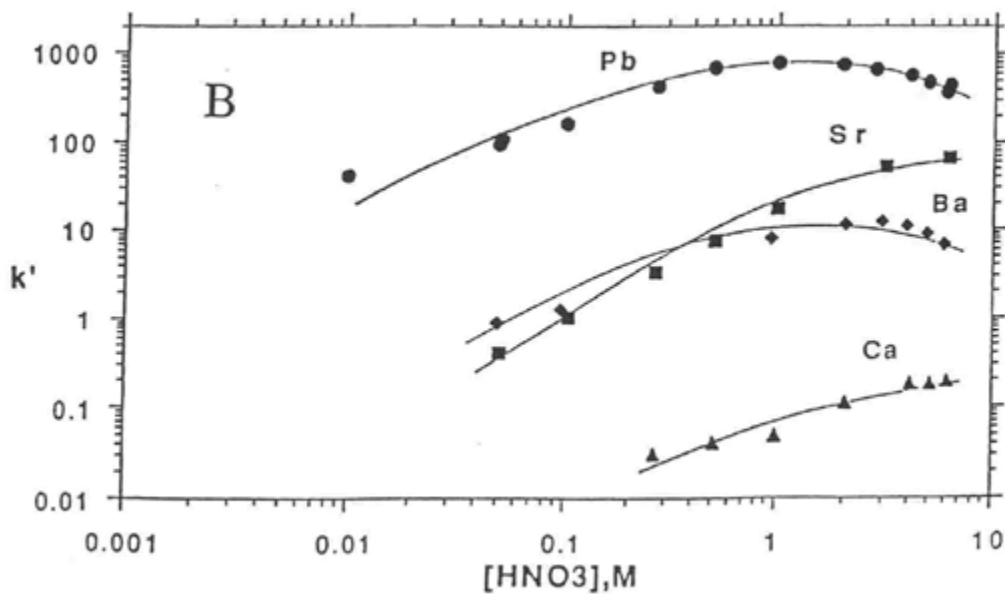Sample handling preparation of standards and reagents were performed in clean rooms under laminar flow clean air benches to minimize the risk of contamination. All ICP-MS measurements were carried out using an Element XR (Thermo Fisher), figure 20. For total Pb and isotopic measurements (^{206}Pb, ^{207}Pb, ^{208}Pb and ^{210}Pb), a high efficiency sample introduction system APEX Q desolvation unit was utilized to minimize hydride formation. SF-ICP-MS operating conditions are summarized in table 4. Use of SF-ICP-MS provides good accuracy and precision and detection limits within femtogram levels.

The common polyatomic interferences in the detection of ^{210}Pb are the following:

a) Formation of a massive peak at mass 208. This peak tails to the adjacent masses 209 and 210. This is from the ions losing energy by collisions with residual gas molecules in the analyzer [25].
b) Formation of ^{208}Pb^{1}H^{1}H. Since separation of stable and radioactive isotopes using chromatographic resins is impossible, the solution to this could be through hydrogen removal [25].

Table 4. Operating Conditions of the SF-ICP-MS

Parameter	Operating Condition
Forward Power	1450
Cool gas flow rate	16 L/min
Auxiliury gas flow rate	1.0 L/min
Sample gas flow rate	1.2 L/min
Mass Window	5
Scan type	Escan
Integration window	5
Samples/peak	100
Dwell time	0.05s

RESULTS AND DISCUSSION

Total-Pb: The average lead concentrations and lead isotopic compositions of Washington Lake (WL1A and WL2) cores and Hampton Lake (HL2A) cores are given in table 5. Detailed Pb concentrations for the cores (WL1A, WL2, HL2A) are presented in the appendix (tables 9 and 10). Total Pb concentrations ranged from about 4-12 ppm in all the three sediment cores, which is slightly below the natural Pb content in soil [26]. The variation in total-Pb concentration with depth (time) for HL is presented in figure 21; the WL cores are not shown because chronology suggests that they were mixed since deposition. The concentration rises from about 6 ppm during the early part of last century to ~12 ppm during the 1950's and early 1960's, a time when leaded gasoline use was relatively high, then diminishes to ~7 ppm in the most recent (surface) sediment. The 6 ppm concentration likely reflects the background levels

from naturally-occurring lead. Nevertheless, this profile should be viewed with caution until a more detailed profile with greater resolution (more samples) is determined.

Table 5. Mean Pb Concentration and Pb Isotopic compositions in Washington and Hampton Lakes.

Oxbow Lake ID	Total-Pb (ppm)	$^{208}Pb/^{207}Pb$	$^{206}Pb/^{207}Pb$	$^{208}Pb/^{206}Pb$	$^{207}Pb/^{206}Pb$	^{210}Pb (cps)
WL1A	7.86	2.49	1.22	2.02	0.81	294
WL2	4.03	2.47	1.22	2.03	0.82	219
HL2A	8.48	2.48	1.22	2.03	0.82	400
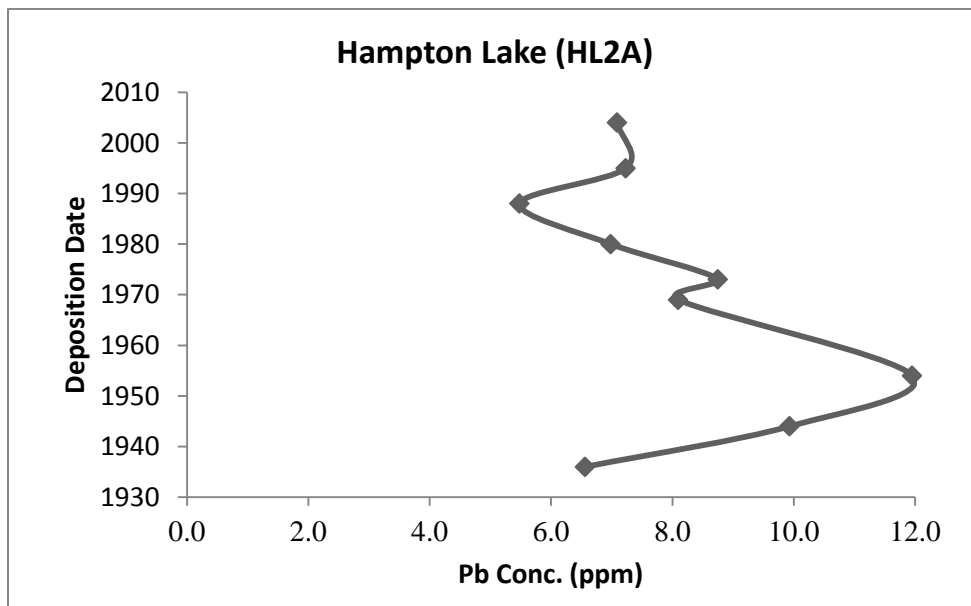
Figure 22. Deposition date vs. Pb conc. in Hampton Lake

LEAD ISOTOPES: Lead isotopes are the products of radioactive decay of other isotopes. Their levels and distribution in a geologic sample depends in part upon the age and environmental conditions of the source material. Isotopes of Pb have long been used in fingerprinting sources of Pb contamination [27]. This can be accomplished using a two component mixing diagram (isotopic plot). A mixing diagram (figure 23) can be constructed by plotting two different ratios with common denominator of any two well established Pb sources.

Samples that plot along a mixing line comprise of mixtures of both the end members. Samples that deviate from the line indicate a different source.

Results for the three sediment cores (WL1A, WL2 and HL2A) are provided in the Appendix (Tables 9-10). Overall, the mean $^{207}Pb/^{206}Pb$ isotopic ratio was 0.82, and the mean $^{208}Pb/^{206}Pb$ ratio was 2.03. Replicate analysis of NIST 981 (~1.7 µg on column) resulted in a relative standard deviation (RSD) of 0.27 and 0.48 for 208/206 and 207/206, respectively. Experimentally established ratios differed from certified ratios by no more 0.42%. Data herein were not corrected for mass bias, which is expected to be smaller than the observed experimentally variability.

A mixing diagram was constructed based upon literature values, with "natural" Pb from mineral phases (e.g., iron oxides, aluminosilicates) in soil, American ores/leaded gasoline, and coal as possible end members (figure 24) [28, 29, 30, 31]. The lead isotopic signatures for the sediment samples generally fall on a straight line within the "natural" Pb region, but gasoline and coal can't be ruled out. Data scattering around the line between the end members likely reflects variability in the analysis rather than additional sources with different isotopic signatures.

Courtesy of M. Ketterer (NAU)
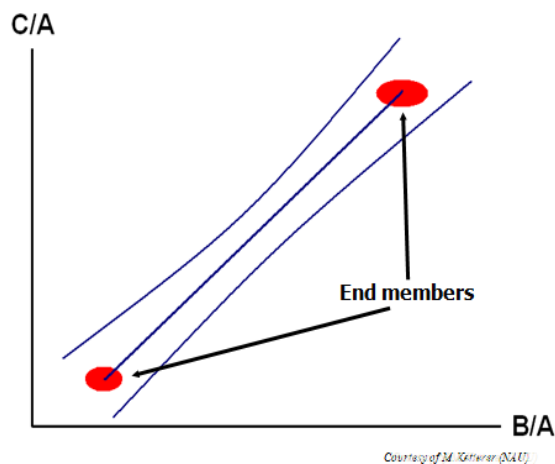
Figure 23. An example of two component mixing diagram [7].

Three isotope plot showing compositions of possible Pb sources
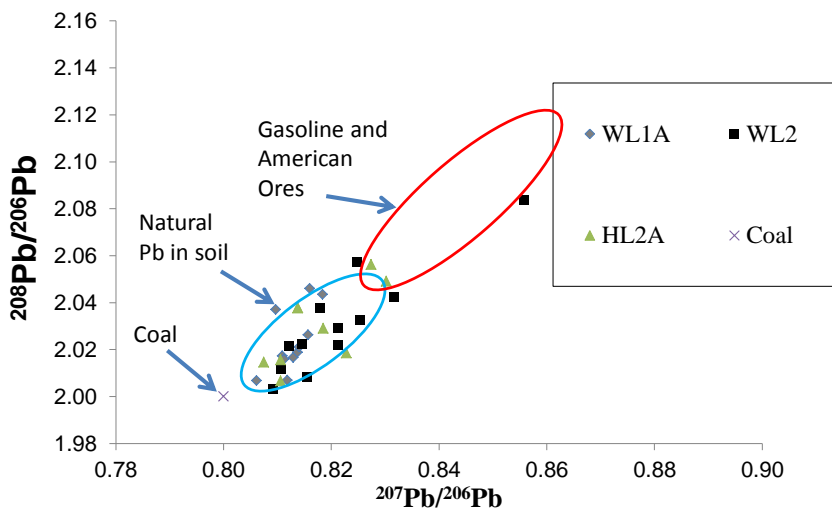
Oval regions generalized from Ettler et al. (2004) Anal. Bioanal. Chem 378:311-317[46]

Figure 24. ^{208}Pb/^{206}Pb vs. ^{207}Pb/^{206}Pb mixing diagram for sediments from Hampton and Washington Lakes [11].

^{210}Pb: Determination of ^{210}Pb in the sediment samples by ICP-MS proved to be difficult. The levels of ^{210}Pb were expected to decrease with depth but instead we found a correlation with total Pb (figure 25) in Hampton Lake open water. This suggests that interference from stable Pb perhaps a ^{208}PbHH$^+$ and /or the tail of the large ^{208}Pb (referred to as abundance sensitivity) peak is present. Because we were unable to mitigate these interferences using different instrumental parameters and sample introduction techniques, further study was stopped. Possible solutions to this problem include using a collision cell to minimize polyatomic interferences, and to increase sensitivity using the new jet-interface option for the ICPMS, which has been shown to enhance signal 100x.

Figure 25. ^{210}Pb counts and total-Pb concentration versus depth (x axis).

SIGNIFCANT FINDINGS AND RECOMMENDATIONS

Analyses of an undisturbed core yielded a Pu peak at a depth which is in good agreement with conventional ^{137}Cs and ^{210}Pb dating. The column method yielded better recoveries compared to the batch method. Open water cores provided Pu profiles more conducive for dating compared to wetland cores; wetlands generally had lower sedimentation rates and appeare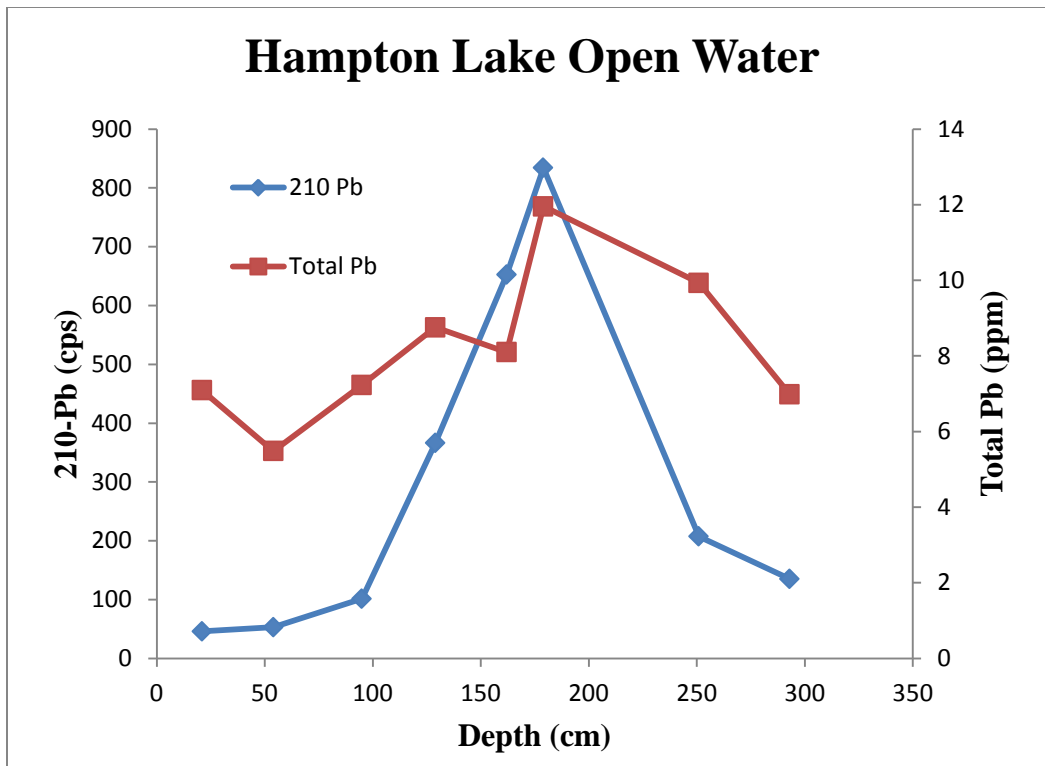d (sometimes) to have been mixed since deposition. It is recommended that future work utilize the column method and include more samples to obtain a higher resolution chronology. Overall, this study has demonstrated that ICPMS can serve a useful role in rapidly identifying sediments that have experienced a degree of mixing since deposition, and thus can be used as a screening tool, eliminating time-consuming and costly ^{210}Pb analyses on such cores. Moreover, because the methodology has now been established in our lab (there is a significant learning curve), we can provide Pu analyses with isotopic ratios when needed by the Mississippi water resources research community.

For lead, the analytical procedure developed in this work and detailed in this report allows total-Pb and Pb isotope (^{206}Pb, ^{207}Pb, ^{208}Pb) determinations at ppm levels in sediment samples using ICP-MS.   Isotopic plots suggest that the Pb likely stems from natural sources, although both coal and leaded gasoline may provide a slight contribution. This study demonstrates that ICP-MS is a powerful tool for environmental studies using Pb ratios to detect different sources of Pb. Unfortunately, the results for ^{210}Pb by ICPMS were less promising. The counts at mass 210 were low and subject to interferences. Two approaches are suggested to overcome these issues: increase sensitivity (a new jet-interface option has been shown to enhance signal >100x), and remove polyatomic interferences using a collision cell.

Information transfer: Publications resulting from this work include a paper in the 2012 Mississippi Water Resource Conference Proceedings. This work also contributed toward a Master's thesis by Ms. Pragya Chakravarty titled "Elemental and Isotopic Analysis of Sediments from Oxbow Lakes in the Mississippi Delta" (University of Mississippi, 2012). The current report contains elements from each of those reports.

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APPENDIX

Table 6. Pu concentration, ^{240}Pu/^{239}Pu ratio and $^{239+240}$Pu activity for Roundaway Lake (RL1A)

Year	Depth(cm)	Concentration (ppt)	Concentration (ppt)	Ratio	Activity (Bq/Kg)
		^{239}Pu	^{240}Pu	^{240}Pu/^{239}Pu	$^{239+240}$Pu
1991	11	0.03	0.01	0.17	0.13
1982	16	0.04	0.01	0.18	0.14
1973	21	0.04	0.01	0.18	0.16
1963	26	0.04	0.01	0.18	0.16
1954	31	0.05	0.01	0.17	0.18
1945	36	0.05	0.01	0.17	0.18
1925	46	0.05	0.01	0.17	0.20
1906	51	0.06	0.01	0.17	0.22
1886	56	0.05	0.01	0.16	0.18
Avg		0.05	0.01	0.17	0.17
SD		0.008	0.001	0.007	0.028
		Activity(mBq/g)	Recovery (%)	Atom Ratio (^{240}Pu/^{239}Pu)	
Reference Material* (Cert. Value)		6.56±0.20	100.9	0.1915±0.0030	
Reference Material* (Found Value)		6.62		0.17	

Table 7. Pu concentration, ^{240}Pu/^{239}Pu ratio and $^{239+240}$Pu activity for Washington Lake (WL1A)

Year	Depth	Concentration (ppt)		Ratio	Activity (Bq/Kg)
		^{239}Pu	^{240}Pu	^{240}Pu/^{239}Pu	$^{239+240}$Pu
2008	1	0.14	0.03	0.18	0.54
2000	8	0.15	0.02	0.16	0.56
1995	11	0.11	0.02	0.19	0.43
1989	15	0.15	0.03	0.18	0.58
1980	21	0.20	0.03	0.16	0.73
1977	23	0.03	0.00	0.16	0.09
1971	26	0.06	0.01	0.17	0.23
1969	27	0.05	0.01	0.21	0.21
1963	30	0.14	0.03	0.18	0.54
1958	33	0.02	0.00	0.17	0.06
	Avg	0.11	0.02	0.18	0.40
	SD	0.06	0.01	0.01	0.23

Table 8. Pb concentration and Isotopic Pb signatures for WL1A.

Sample ID	Depth (cm)	Deposition Date	Total-Pb (ppm)	$^{208}Pb/^{207}Pb$	$^{208}Pb/^{206}Pb$	$^{207}Pb/^{206}Pb$	$^{206}Pb/^{207}Pb$	^{210}Pb (cps*)
WL1A-1	3	2006	9.29	2.48	2.02	0.81	1.23	90.4
WL1A-2	11	1995	10.48	2.49	2.02	0.81	1.23	153.2
WL1A-3	15	1989	8.94	2.48	2.03	0.82	1.21	415
WL1A-4	23	1978	8.81	2.50	2.04	0.82	1.21	227.4
WL1A-5	27	1968	5.25	2.47	2.01	0.81	1.23	58.6
WL1A-6	33	1958	6.00	2.52	2.04	0.81	1.23	287.5
WL1A-7	40	1948	5.95	2.49	2.01	0.81	1.20	644.2
WL1A-8	44	1939	7.94	2.48	2.02	0.81	1.22	497.4
WL1A-9	50	1928	8.29	2.48	2.02	0.81	1.23	110.3
WL1A-10	57	1916	9.27	2.48	2.02	0.81	1.21	34.9
WL1A-11	62	1908	4.38	2.51	2.05	0.82	1.21	618.5
		Avg	7.69	2.49	2.02	0.81	1.22	285.22
		SD	1.97	0.01	0.01	0.00	0.01	224.76

Table 9. Pb concentration and Isotopic Pb signatures for WL2.

Sample ID	Depth (cm)	Deposition Date	Total-Pb (ppm)	$^{208}Pb/^{207}Pb$	$^{208}Pb/^{206}Pb$	$^{207}Pb/^{206}Pb$	$^{206}Pb/^{207}Pb$	^{210}Pb (cps*)
WL2-1	10	1992	6.42	2.48	2.01	0.81	1.21	104.9
WL2-2	11	1990	6.75	2.46	2.02	0.82	1.22	39.4
WL2-3	12	1988	2.20	2.46	2.03	0.83	1.20	73.1
WL2-4	13	1985	6.89	2.49	2.04	0.82	1.22	51.2
WL2-5	17	1977	6.54	2.43	2.08	0.86	1.23	436
WL2-6	20	1968	3.80	2.48	2.02	0.81	1.17	1389.6
WL2-7	23	1956	7.31	2.46	2.04	0.83	1.22	48.6
WL2-8	25	1948	4.98	2.47	2.03	0.82	1.21	422.4
WL2-9	28	1937	1.52	2.48	2.00	0.81	1.22	51.9
WL2-10	30	1927	1.23	2.49	2.02	0.81	1.22	63.6
WL2-11	31	1922	1.62	2.49	2.06	0.82	1.22	66.8
WL2-12	34	1907	1.73	2.46	2.01	0.82	1.20	33.7
WL2-13	31	1922	1.46	2.48	2.03	0.82	1.22	67.9
		Avg	4.03	2.47	2.03	0.82	1.21	219.16
		SD	2.49	0.02	0.02	0.01	0.01	378.03

Table 10. Pb concentration and Isotopic Pb signatures for HL2A

Sample ID	Depth (cm)	Deposition Date	Total-Pb (ppm)	$^{208}Pb/^{207}Pb$	$^{208}Pb/^{206}Pb$	$^{207}Pb/^{206}Pb$	$^{206}Pb/^{207}Pb$	^{210}Pb (cps*)
HL2A-1	21	2004	7.09	2.50	2.04	0.81	1.21	46.00
HL2A-2	54	1995	7.23	2.45	2.02	0.82	1.22	52.90
HL2A-3	95	1988	5.48	2.50	2.04	0.81	1.23	101.30
HL2A-4	129	1980	6.99	2.47	2.05	0.83	1.22	366.10
HL2A-5	162	1973	8.76	2.48	2.06	0.83	1.22	652.30
HL2A-6	179	1969	8.10	2.48	2.03	0.82	1.24	834.20
HL2A-7	251	1954	11.95	2.49	2.02	0.81	1.22	207.20
HL2A-8	293	1944	9.93	2.49	2.01	0.81	1.22	135.10
HL8A-9	332	1936	6.57	2.48	2.01	0.81	1.21	978.00
HL2A-10	129	1980	10.00	2.47	2.01	0.81	1.22	331.80
HL2A-11	162	1973	11.23	2.46	2.03	0.82	1.22	696.20
		Avg	8.48	2.48	2.03	0.82	1.22	400.10
		SD	2.06	0.02	0.02	0.01	0.01	334.99