

Dating Sediments from Oxbow Lakes in the Mississippi Delta using ^{239}Pu , ^{240}Pu and ^{210}Pb determined by ICPMS: a feasibility study

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Sediments are complex deposits of inorganic and organic matter that can serve as a natural storage system for metals and anthropogenic contaminants. Sediment cores can provide a window on the past because they can go back years, decades, even centuries and serve as environmental proxies. Dating of recent (<100 years) sediments is important in many studies and applications, including determining the source and timing of pollution events, establishing sedimentation patterns, and in reservoir management. Linking sediment "dates" (typically in years) with sediment characteristics or specific chemical constituents is also crucial for examining the effectiveness of both pollution and erosion control measures. Conventional dating techniques which use ^{210}Pb and ^{137}Cs are slow and costly, in part because extended times are needed to measure the radioactive decay emissions from low-activity samples.

In this study, we examined the feasibility of using inductively coupled plasma mass spectrometry (ICP-MS) to: measure global fallout plutonium (Pu) and ^{210}Pb in sediment core samples from Mississippi for dating purposes. Recent advances in mass spectrometry have made it an alternative to radioactive decay spectrometry for determining Pu, and possibly ^{210}Pb , in environmental samples. This study utilized core samples previously collected from strategic locations within the Mississippi Delta region. Select samples were digested with mineral acids and the Pu and Pb isotopes were selectively removed from the matrix using chromatographic extraction resins, effectively pre-concentrating the elements prior to analysis. Plutonium was determined using isotope dilution mass spectrometry and ^{210}Pb using external standardization. In this talk and associated poster we will discuss the methodology and present our findings.

Introduction

Determining the chronology of sediments is important for a number of reasons including: to manage reservoirs more effectively (e.g., calculate sediment rates), to study the spatial and temporal patterns of metal deposition in an area, and, more recently, to monitor the effectiveness of erosion control methods (Wren and Davidson 2011). Dating of sediments is done by using natural radionuclides like ^{210}Pb and ^{14}C and artificial radionuclides like ^{137}Cs , ^{239}Pu and ^{240}Pu .

Plutonium

^{239}Pu and ^{240}Pu are anthropogenic radionuclides introduced into the environment from atmospheric testing of nuclear weapons and from accidental releases from nuclear power plants. Because

plutonium is particle-reactive, fallout from these events are accumulated and preserved in sediments along with other particles washed into lakes. Because the dates for these fallout events are known they can be used for determining sediment chronology. For example, the peak fallout for Pu in the northern hemisphere was in 1963; thus, if a sediment core is divided into intervals (typically 1 cm) the layer/horizon containing the highest activity or concentration of Pu will, in the absence of other major local or regional sources, likely correspond to 1963. Once a sediment layer has been dated, it can be used to estimate the average sedimentation rate (cm/yr) by (continuing with the Pu example) dividing that depth by the years since 1963. Moreover, the isotopic signature ($^{240}\text{Pu}/^{239}\text{Pu}$ atom ratio) is indicative of the source of

Dating Sediments from Oxbow Lakes in the Mississippi Delta using ^{239}Pu , ^{240}Pu and ^{210}Pb determined by ICPMS: a feasibility study
Cizdziel, James

the Pu and can be used for source apportionment. For example, the stratospheric fallout ratio is $^{240}\text{Pu}/^{239}\text{Pu} = 0.180 \pm 0.014$ and the Nevada Test Site fallout ratio is $^{240}\text{Pu}/^{239}\text{Pu} = 0.03 \pm 0.07$ [e.g., Ketterer et al. 2004]. Using these and other known 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 [Donard et al. 2007].

^{210}Pb

^{210}Pb is a member of the ^{238}U decay series. Uranium is ubiquitous in soils and sediments. "Supported" ^{210}Pb in soils and sediments is generated in-situ, whereas "unsupported" or "excess" ^{210}Pb results from deposition from the atmosphere. A precursor of ^{210}Pb is ^{222}Rn , an inert gas, which diffuses from surface soils, decays in the atmosphere, where it becomes charged and can attach to particles that deposit to the earth's surface through wet and dry deposition. The ^{210}Pb dating method is based on measuring and comparing the quantities of supported and unsupported ^{210}Pb and applying the decay equation [Simms et al. 2008]. However, there are two major limitations in applying this method. First, mixing or displacement of sediment particles gives erroneous dates, and second, this method does not hold good for sediments more than ~100 years old as no excess ^{210}Pb can be detected above the background (supported) level. Conventionally, ^{210}Pb has been measured using radiochemical techniques. ^{210}Pb decays by emitting beta particles of energy 17 keV and 63.5 keV and gamma rays of energy 46.5 keV [Amr et al. 2010]. The decay products are ^{210}Bi and ^{210}Po , respectively, Po being an alpha emitter. The count times are long and thus ^{210}Pb analyses are generally time-consuming and costly.

Objectives

An alternative to using radiochemistry is the use of mass spectrometry. Inductively coupled plasma mass spectrometry (ICPMS) has a number of advantages for long-lived radionuclides because it counts atoms instead of decays. It is particularly suitable for routine analysis of large number of samples (utilizing solutions) and can measure isotope ratios. Others have successfully used Pu for dating sediments [e.g., Ketterer et al. 2004]. In contrast, there are, to our knowledge, no reports of using sector field ICPMS to measure ^{210}Pb in sediments.

In this study, our goals were to: 1) transfer and optimize protocols for Pu analyses for our lab using our instrumentation, and 2) examine the feasibility of using sector field ICPMS for dating sediments using both Pu and Pb isotopes. Specific objectives were to:

- Use ICPMS to measure Pu activity and atom ratios to age-date the Oxbow Lake sediments, and to compare the results with conventional ^{137}Cs and ^{210}Pb radioanalytical analysis.
- Determine the likely source(s) of Pu in the sediment using Pu isotopic signatures.
- Test the feasibility of using sector field ICPMS (instead of radiochemical means) to measure ^{210}Pb extracted from sediment and isolated using column chromatography.

Methods

Sediment Collection and Conventional Radiochemical Chronology

Sediment cores were collected as a part of a previous study [Wren and Davidson 2011]. 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. Plastic core pipes were inserted in the vibracorer before sampling. The cores were extruded and stored at 4°C until they were processed. The cores were sliced into 1-cm thick intervals, dried

Dating Sediments from Oxbow Lakes in the Mississippi Delta using ^{239}Pu , ^{240}Pu and ^{210}Pb determined by ICPMS: a feasibility study
Cizdziel, James

at 60°C in an oven, crushed with a mortar and pestle, and sieved through 1-mm screen. The cores were dated using both ^{210}Pb and ^{137}Cs analyses using conventional radioanalytical techniques as described elsewhere [Reimann et al. 2012]. Other sample and lake information, including watershed area, surface area, and GPS coordinates can be found elsewhere [Wren and Davidson 2007, 2011].

Plutonium Extraction, Isolation and Concentration

The main issues associated with the determination of Pu isotopes are: 1) formation of $^{238}\text{U}^{\text{I}}\text{H}$, $^{238}\text{U}^{\text{II}}\text{H}$ that cause interferences with ^{239}Pu and ^{240}Pu , respectively, and 2) tailing effect of ^{238}U on the ^{239}Pu signal. Thus, uranium should be removed from the sample solutions by column chromatography before analysis because resolution of $^{238}\text{U}^{\text{I}}\text{H}$ and ^{239}Pu is not possible using SF-ICPMS.

Here, sediment core samples from Beasley Lake (BL1A), Washington Lake (LW1A) and Roundaway Lake were analyzed for ^{239}Pu , ^{240}Pu and ^{242}Pu (tracer) isotopes. The sample weights ranged from about 2 to 5 grams. The samples were weighed into a 20-ml 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 ml of 16M HNO_3 was added and the mixture was leached at 80°C for 16 hours. The samples were vacuum filtered through 0.45 micron glass fiber filters. The filters were rinsed with 15 ml of DI water and the rinsate was combined with the filtrate. Twenty mg of ascorbic acid were added to the solution for the conversion of all the Pu (III) to Pu (IV).

Columns of TEVA resin (Eichrom Technologies), used for the collection of actinides, were prepared using 5 ml pipette tips and TEVA resin powder. The narrow end of the pipette tips were clogged with glass wool and 0.1 – 0.2 gm TEVA resin powder was added. The columns were conditioned by passing 5 ml of 4M HNO_3 . 5 ml of the sample solution was allowed to pass through the column. During this step, Pu (IV) along with Np, Th and U is retained

within the column and other matrix elements are discarded. The columns were then rinsed with 3 ml of 4M HNO_3 and 5 ml 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 10 ml of 0.02M HCl and analyzed by ICPMS.

Plutonium by ICPMS

A desolvating sample introduction system (APEX) was utilized to minimize uranium hydride formation. SF-ICP-MS operating conditions are summarized in Table 1. The detection limit (3 times the standard deviation of the blank) was determined at femtogram levels.

Parameter	Units or mass	Operating Condition
Forward Power	W	1450
Cool gas	L/min	16
Auxiliary gas	L/min	1.0
Sample gas	L/min	1.2
Mass Window	%	20
Magnet settling	s	0.001
Scan type		E-scan
Integration window	%	80
Samples/peak	239, 240	150
	242	50
Sample time	239, 240	0.1s
	242	0.01s

^{210}Pb Analyses

Wetland and open water sediment core samples from Lake Washington (LW1A and LW2 respectively) and open water sediment samples from Hampton Lake (HL2A) were analyzed for total-Pb and Pb isotopes (^{206}Pb , ^{207}Pb , ^{208}Pb and ^{210}Pb). This report focuses on ^{210}Pb ; results for the other Pb isotopes will be reported elsewhere.

Dating Sediments from Oxbow Lakes in the Mississippi Delta using ^{239}Pu , ^{240}Pu and ^{210}Pb determined by ICPMS: a feasibility study
Cizdziel, James

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 clean 50 ml tubes and leached with 20 ml of concentrated HNO_3 for 8 hours in a hot block. The leached samples were passed through 0.45 micron filters and the leachate volume was made to 50 ml with DI water. 0.5 ml liquid from the diluted leachate was transferred to 15 ml clean centrifuge tube and the volume was made up to 10 ml with 2% HNO_3 .

Sample preparation for ^{210}Pb analysis

Samples were prepared as described above for total-Pb analyses. As noted, 0.5 ml of the diluted leachate was used for total Pb analysis; here the remaining 49.5 ml liquid was used for Pb isotope analysis. The solution was heated to complete dryness in a hot block. The volumes of the samples were made up to 10 ml using 1M HNO_3 . Pb resin columns were prepared by clogging the narrow end of 5 mL pipette tips with glass wool and filling it up with 0.1 - 0.2 gm of Pb resin powder (100 – 150 μm). 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 20 ml of 1M HNO_3 . This wash is performed to remove Bi and Fe. 10 ml of 0.1M HNO_3 was added to the columns to remove any ^{210}Po . Following the last wash, 40 ml of 0.1M citric acid monohydrate solution was added 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 10 ml with 1% HNO_3 . The procedure is summarized in Figure 1.

^{210}Pb by ICPMS

The commonly occurring polyatomic interferences in the detection of ^{210}Pb are: 1) the presence of large peak at mass 208 (the most abundant Pb isotope) which tails into the adjacent mass 209 and 210 (this is partly from the ions losing energy by collisions with residual gas molecules in the

analyzer); and 2) the formation of $^{208}\text{Pb}^1\text{H}^1\text{H}$ (isobaric with ^{210}Pb). Note that it is not possible to separate stable (^{208}Pb) and radioactive isotopes (^{210}Pb) of the same element using chromatographic resins. A possible solution to the later is the use of a desolvating nebulizer to remove hydrogen atoms, which stem mostly from water [Laiviere et al. 2005].

Here we used a desolvating sample introduction system (APEX-Q) for both total-Pb and Pb-isotopes to minimize hydride formation and boost sensitivity. SF-ICPMS operating conditions are summarized in Table 2.

Parameter	Operating Condition
Forward Power	1450 W
Cool gas flow rate	16 L/min
Auxiliary gas flow rate	1.0 L/min
Sample gas flow rate	1.2 L/min
Mass Window	5%
Magnet settling time	1 s
Scan type	E-scan
Integration window	5%
Samples/peak	100
Sample time	0.05s

Results & Discussion

Plutonium. Results for Pu (concentrations, $^{239+240}\text{Pu}$ activities, and $^{240}\text{Pu}/^{239}\text{Pu}$ atom ratios) for the Beasley Lake open water (OW) core are given in table 3 and figure 2. The results for Washington and Roundaway Lake wetland core are presented in Figures 3 and 4. Of the cores analyzed the Beasley Lake OW core has the best defined chronology [Wren and Davidson 2011]. The authors of that report used conventional dating techniques to find a reduction in sediment accumulation rates and attributed it to recent erosion control and cropping practices. We analyzed Beasley Lake sediment samples using two methods: batch mode (mixing resin beads with the solution then collecting them by filtration) and column mode (slowly passing the sample through a column containing the resin).

Dating Sediments from Oxbow Lakes in the Mississippi Delta using ^{239}Pu , ^{240}Pu and ^{210}Pb determined by ICPMS: a feasibility study
Cizdziel, James

Whereas Pu levels were found to be lower in the batch method, the trend (profile) for concentration with depth was similar (figure 2). Nevertheless, the column method appears to yield better results, based on the low counts (recoveries) and unusually high isotope ratios for the batch method (discussed below). Thus, we used the column method for other analyses.

Importantly, the peak Pu depth (~47 cm) was in agreement with peak ^{137}Cs depth (data not shown). This suggests that Pu can be used as an alternative to traditional ^{137}Cs radioanalysis. It should be noted that the inventory of ^{137}Cs (half-life 30 yrs) from global fallout is decreasing and at some point in the future it will be too low in concentration to be used for dating purposes; this will not be the case for Pu with its long half life. As noted, ^{137}Cs and Pu peaks correspond to 1963, the peak year for fallout, but the ^{210}Pb dating places them a few years later (~1970). It is possible that the recent changes in sedimentation rates slightly affected the ^{210}Pb chronology due to different slopes for the "excess" ^{210}Pb (natural log) versus depth for before and after the erosion control structures were put in place.

$^{240}\text{Pu}/^{239}\text{Pu}$ atom ratios averaged 0.19 for the column method, consistent with a global fallout source. The batch method yielded a ratio of 0.21, which is outside the global fallout range. Because

there are no other expected sources of Pu at this location, this suggests that the batch method is less accurate, perhaps a result of the low signal (counts) that it yielded which would introduce analytical error. There was an anomalously high ratio (0.25) at the peak Pu concentration (corresponding to 1963) for both methods. Again, whereas this wouldn't be unexpected near the Pacific Proving Grounds where high yield tests were conducted this is unusual at this location. The cause is unknown but it should be noted that this high reading was not replicated in other cores. Removing the anomalous point changes the mean ratio to 0.18 (column) and 0.20 (batch), more in-line with global fallout ratios.

The Pu activity profile for Washington and Roundaway Lakes are shown in figures 3 and 4. The data suggests that these sediments were, to some extent, mixed since deposition. Importantly, this agrees with conventional dating results which showed data scatter indicative of mixing [Wren and Davidson 2011]. 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. An additional core from Sky Lake, also an Oxbow Lake in the Delta, is being analyzed with more samples for greater resolution; results were unavailable at the time this report was prepared.

Table 3. Pu levels, isotope ratios, and $^{239}+^{240}\text{Pu}$ activities for Beasley Lake open water (BL1A) sediment core determined by Column (C) or Batch (B) modes

Year	Depth (cm)	^{239}Pu (pg/g)		^{240}Pu (pg/g)		$^{240}\text{Pu}/^{239}\text{Pu}$		$^{239}+^{240}\text{Pu}$ (Bq/kg)	
		C	B	C	B	C	B	C	B
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
Mean		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

Dating Sediments from Oxbow Lakes in the Mississippi Delta using ^{239}Pu , ^{240}Pu and ^{210}Pb determined by ICPMS: a feasibility study
Cizdziel, James

Total-Pb: The average lead concentrations for Washington Lake (WL1A and WL2) cores and Hampton Lake (HL2A) were 7.86, 4.03, and 8.48 ppm, respectively. The corresponding signal intensity (counts-per-second) at mass 210 was 294, 219 and 400, respectively. Total-Pb concentrations ranged from about 4-12 ppm in all the three sediment cores. The variation in total-Pb concentration with depth (time) for the Hampton Lake core is presented in figure 5. The Washington Lake 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 in soils.

^{210}Pb : Determination of ^{210}Pb in the sediment samples by ICPMS 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 6), showing data for the Hampton Lake open water core. This suggests that interference from stable Pb, perhaps a $^{208}\text{PbHH}^+$ and /or the tail of the large ^{208}Pb peak (referred to as abundance sensitivity), is present and masking the small ^{210}Pb signal.

Conclusion & Future Work

Plutonium. 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, a potential use is as a screening tool, eliminating time-consuming and costly ^{210}Pb analyses on such cores. Analyses of an undisturbed core yielded a Pu peak at a depth which is in good agreement with conventional ^{137}Cs 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 which appeared to have been mixed since deposition. Future work will include additional samples to

obtain a higher resolution chronology.

^{210}Pb . The ICPMS analytical procedure presented here allows total-Pb and Pb isotopes (^{206}Pb , ^{207}Pb , ^{208}Pb) to be determined at ppm levels in sediment samples. Total-Pb was highest in sediment intervals corresponding to a period when leaded gasoline was used. The results for ^{210}Pb by ICPMS were problematic. The counts at mass 210 were low and subject to interferences that were not resolvable by high resolution ICPMS. 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.

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Dating Sediments from Oxbow Lakes in the Mississippi Delta using ^{239}Pu , ^{240}Pu and ^{210}Pb determined by ICPMS: a feasibility study
Cizdziel, James

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Figure 1. Pb analytical scheme

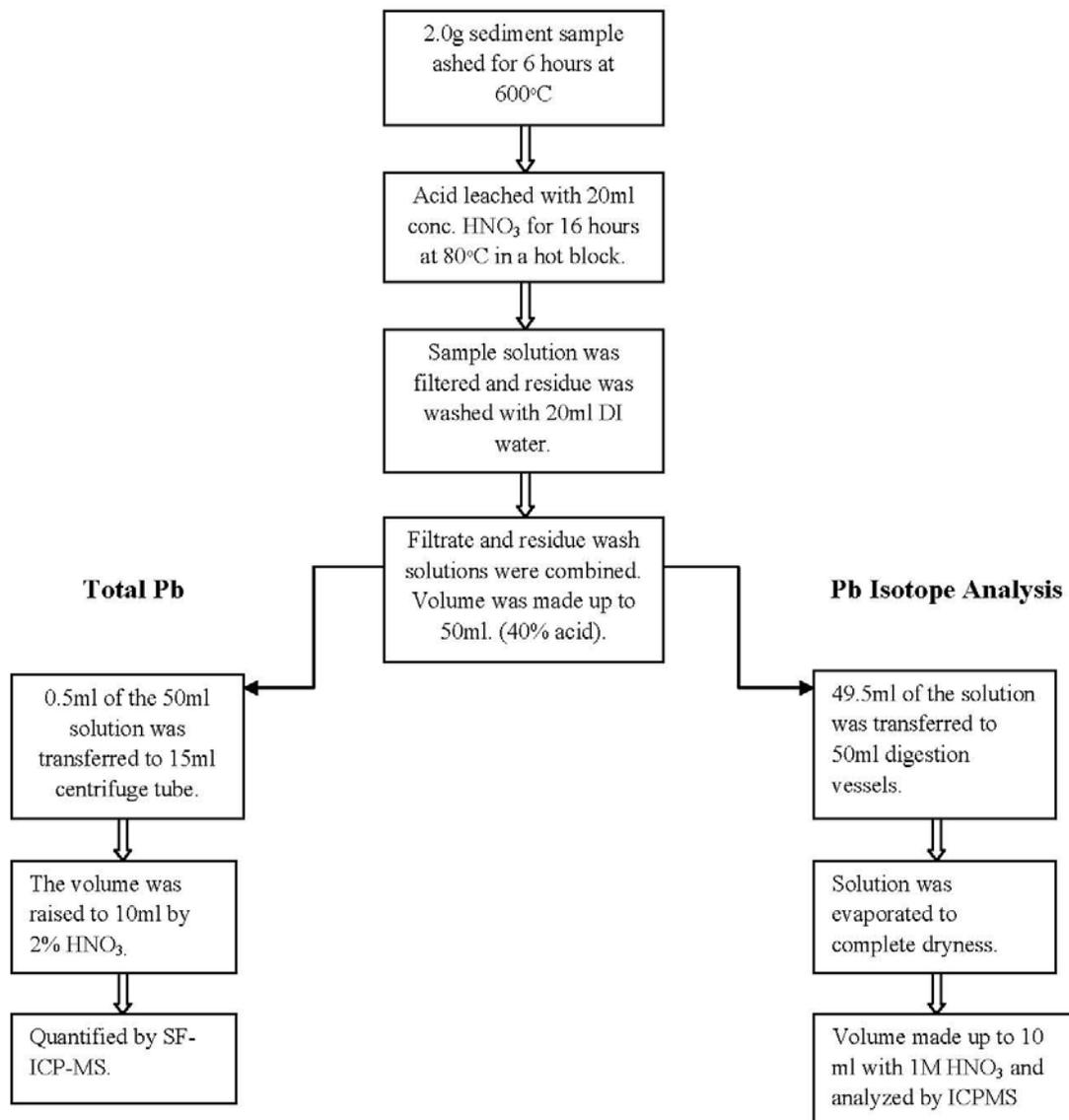


Figure 2. Sample preparation scheme for Pb analysis.

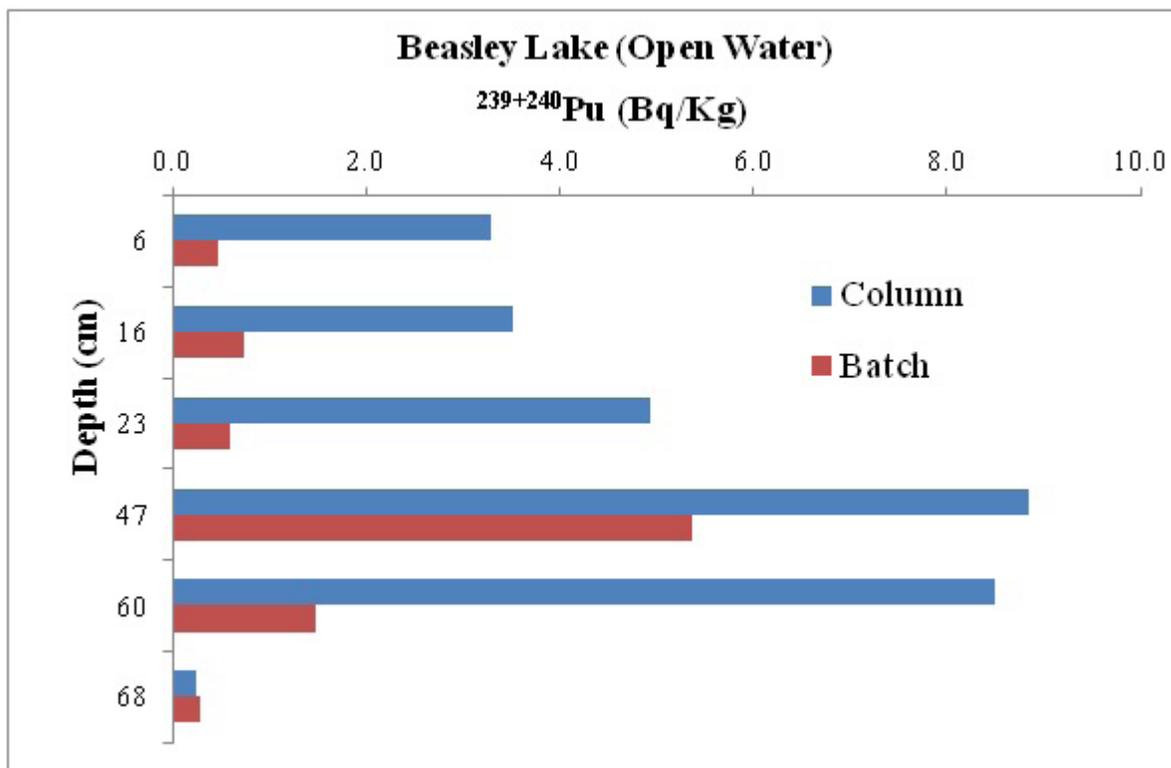
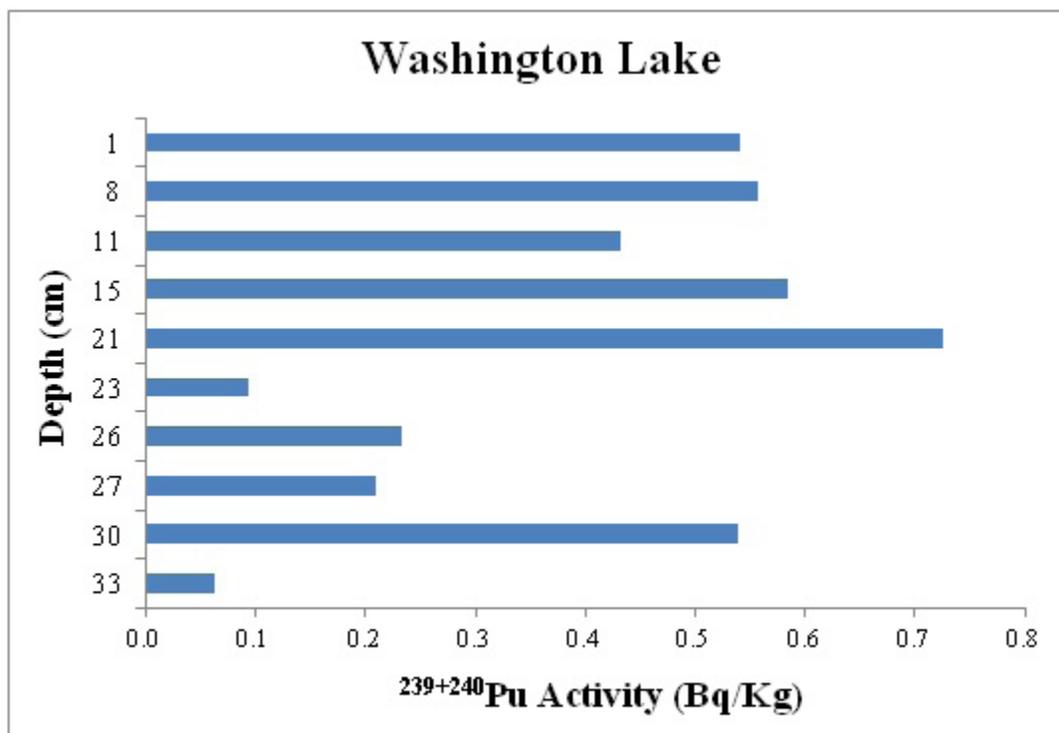


Figure 3. Depth vs. $^{239+240}\text{Pu}$ activity for Beasley Lake



Dating Sediments from Oxbow Lakes in the Mississippi Delta using ^{239}Pu , ^{240}Pu and ^{210}Pb determined by ICPMS: a feasibility study
 Cizdziel, James

Figure 4. Depth vs. $^{239}+^{240}\text{Pu}$ activity (Bq/Kg) for Roundaway Lake

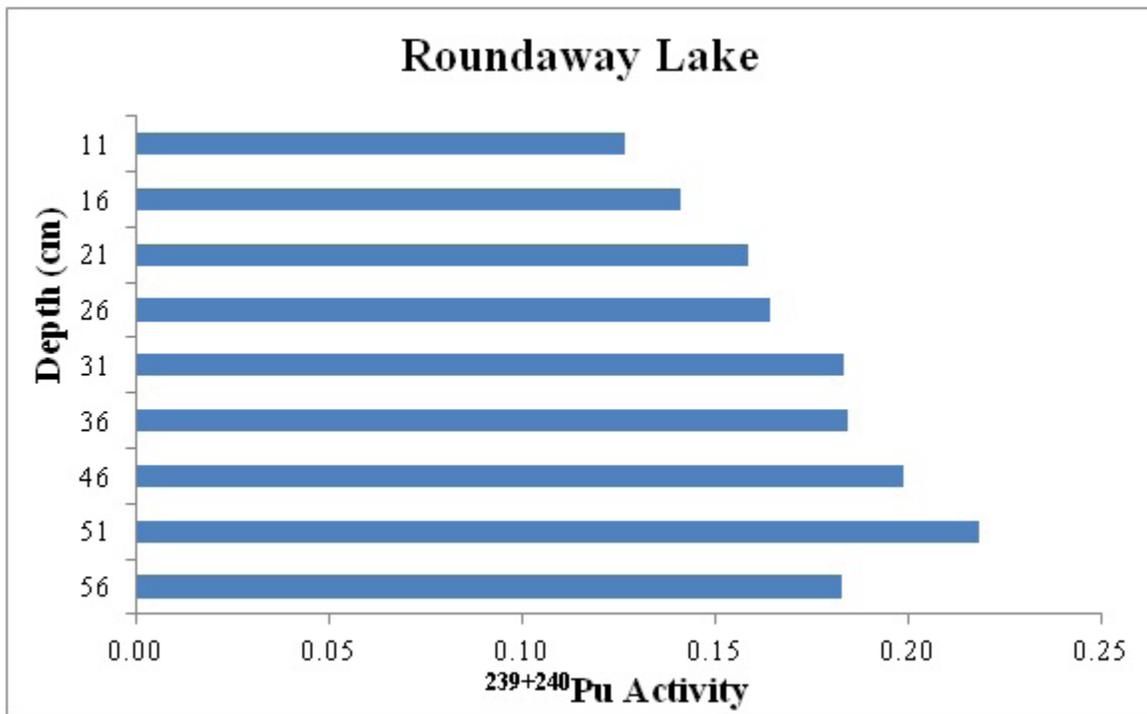
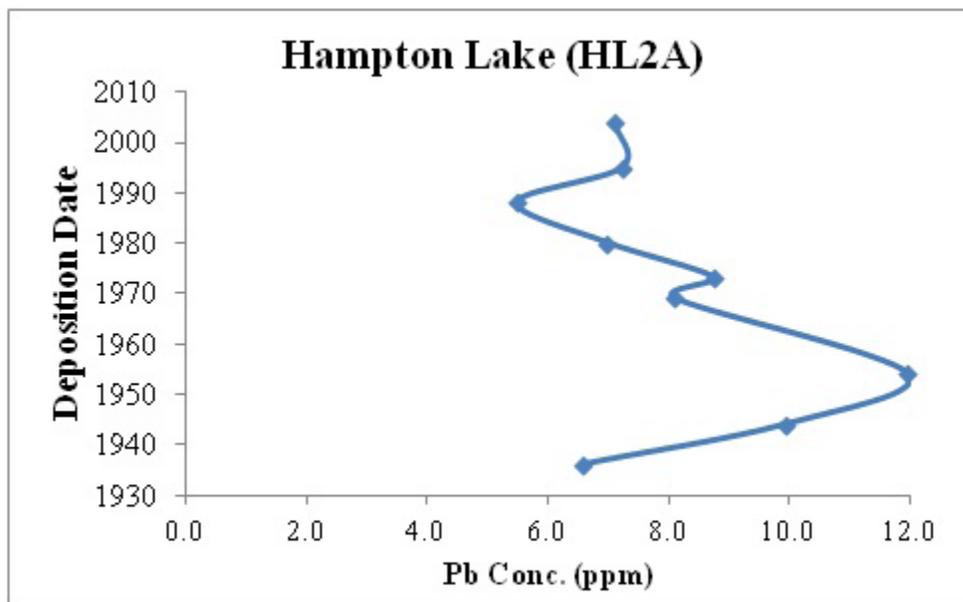


Figure 5. Deposition Date vs. Pb conc. in Hampton Lake



Dating Sediments from Oxbow Lakes in the Mississippi Delta using ^{239}Pu , ^{240}Pu and ^{210}Pb determined by ICPMS: a feasibility study
Cizdziel, James

Figure 6. ^{210}Pb signal intensity and total-Pb concentration versus depth (x-axis)

