A 94-YEAR LAKE SEDIMENT RECORD OF INDUSTRIAL POLLUTANTS IN THE PITTSBURGH METROPOLITAN AREA

by

Brianne Michelle Cassidy

B.A., University of Pittsburgh, 2003

Submitted to the Graduate Faculty of

The College of Arts and Sciences in partial fulfillment

of the requirements for the degree of

Master of Science

University of Pittsburgh

2008

UNIVERSITY OF PITTSBURGH

COLLEGE OF ARTS AND SCIENCES

This thesis was presented

by

Brianne Michelle Cassidy

It was defended on

November 21, 2008

and approved by

Michael F. Rosenmeier, PhD, Geology and Planetary Science

Daniel J. Bain, PhD, Geology and Planetary Science

Thesis Director: Mark B. Abbott, PhD, Geology and Planetary Science

A 94-YEAR LAKE SEDIMENT RECORD OF INDUSTRIAL POLLUTANTS IN THE PITTSBURGH METROPOLITAN AREA

Brianne Michelle Cassidy, M.S.

University of Pittsburgh, 2008

A 47.0 cm lake core was taken from Panther Hollow Lake, a small manmade lake in Schenley Park within the City of Pittsburgh. The core was analyzed for geochemical evidence of the region's industrial history during the twentieth century. Physical and geochemical proxies showed that the lake sediments contained trace metal concentrations that are an order of magnitude above natural background levels, including high levels of heavy metals throughout the period of study and increasing concentrations of alkali and alkali earth metals. Lead was found at concentrations as high as 350 ppm in the core although chromium, arsenic, nickel, and vanadium are all well above background levels throughout the twentieth century. Depths were converted to age assuming a 0.5 cm/yr sedimentation rate. Using this age model, the shifts in concentrations of the industry-related metals align with changes made to environmental laws and industrial output in the region.

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

PREFACE

I would like to thank everyone who helped me collect and analyze my samples and my committee for all their help. I would also like to thank Paul Coyle for his encouragement, and my family and Adam for their love, support, and understanding through the duration of this project.

1.0 INTRODUCTION

Lacustrine sediment archives provide a means to investigate environmental change beyond the temporal limits of instrumental and historical records. Lakes are found over a wide geographic range and can be used to study natural and anthropogenic changes over the landscape and through history. Paleolimnology has been used to constrain pollution records around the globe (Couillard et al., 2004, Vermillion et al., 2005, Erel et al., 1997, Gasse, 2001). Air pollution is often regarded as a recent phenomenon; however, atmospheric metal pollution dating back to the Roman Empire has been identified using a variety of methods including lake sediment studies (Nriagu, 1996). Polar ice cores (Murozumi et al., 1969, and Hong et al., 1996), peat bogs (Bindler, 2006), and aquatic sediments, including those from lacustrine settings (Renberg, 1994), collectively archive nearly three thousand years of metal pollution in the northern hemisphere.

1.1 STUDY AREA

Pittsburgh is at the convergence of two major rivers, the Lower Allegheny (drainage area: 839 km^2) and the Monongahela (523 km^2) (PA DEP, 2008) which come together to form the Ohio (See Figure 1). Erosion from the rivers formed the topography of the Pittsburgh area throughout the Holocene, cutting deep valleys across the Allegheny Mountains. The characteristics of the area, including available river transportation and rich natural resources (namely bituminous coal), enabled it to become a global center for iron and steel production (See Figure 2). Coal supplies the majority of energy required for iron making and was generally transported by rail (Tarr, 2003). Railroads began to blanket the area, their smoke becoming a major contributor to the city's air pollution problem.

High-volatile commodities, such as coal, heating oil, and gasoline, were extensively used in the region by railroads, industry, and in home heating, producing vast amounts of smoke and soot. Solutions to this air quality problem were sought during the 1940s to the 1960s. This problem was highlighted when an extreme pollution disaster affected the small town of Donora, Pennsylvania, located 28 km southeast of Pittsburgh. Twenty people died and thousands were sickened when a temperature inversion (made possible because of the deep river valleys in the region) trapped smoke associated with steel production along the Monongahela River in October of 1948 A.D. (Ciocco et al., 1961). Local natural gas was sought as an alternative and became

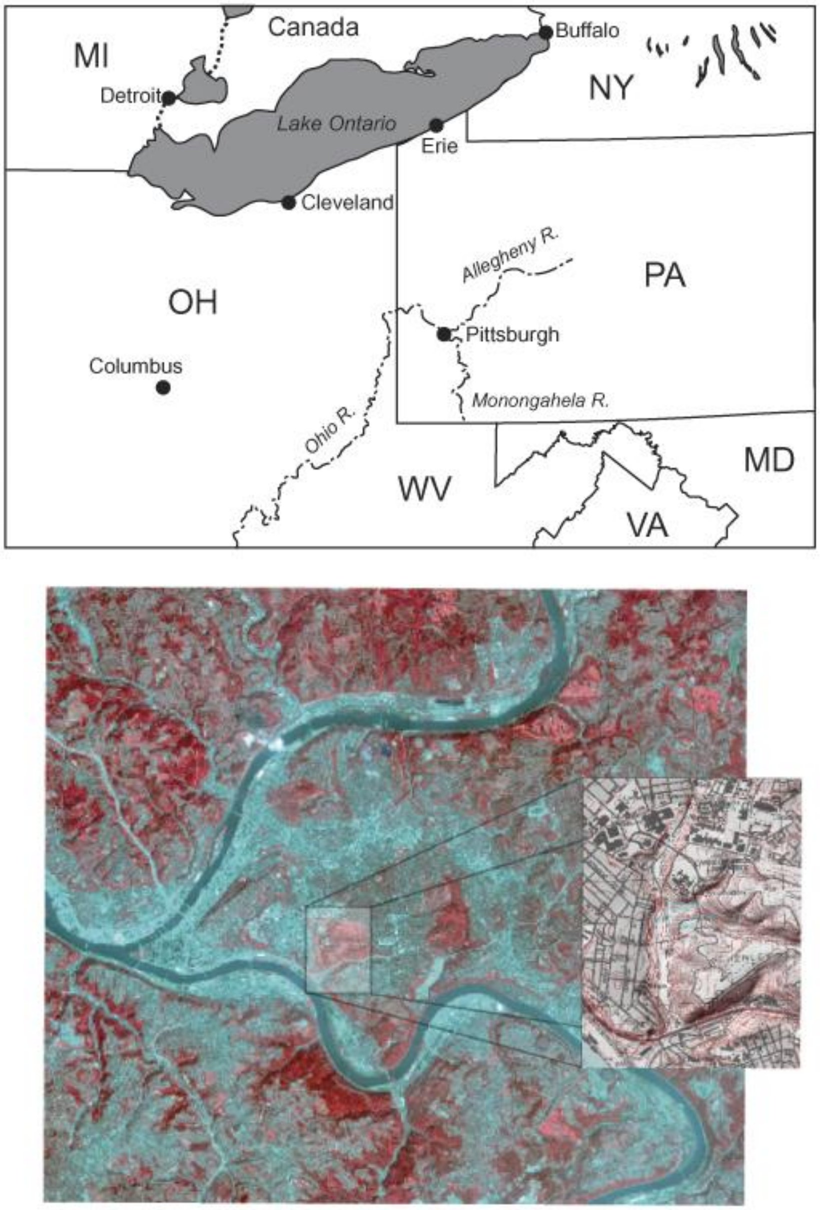


Figure 1. Study site. Shows the location of the Pittsburgh area in ASTER VNIR (bands 3, 2, 1 in R, G, B, respectively). Shaded relief image of Schenley Park area created from 10 meter USGS Digital Elevation Model (DEM) with Digital Raster Graphic (DRG) overlay.

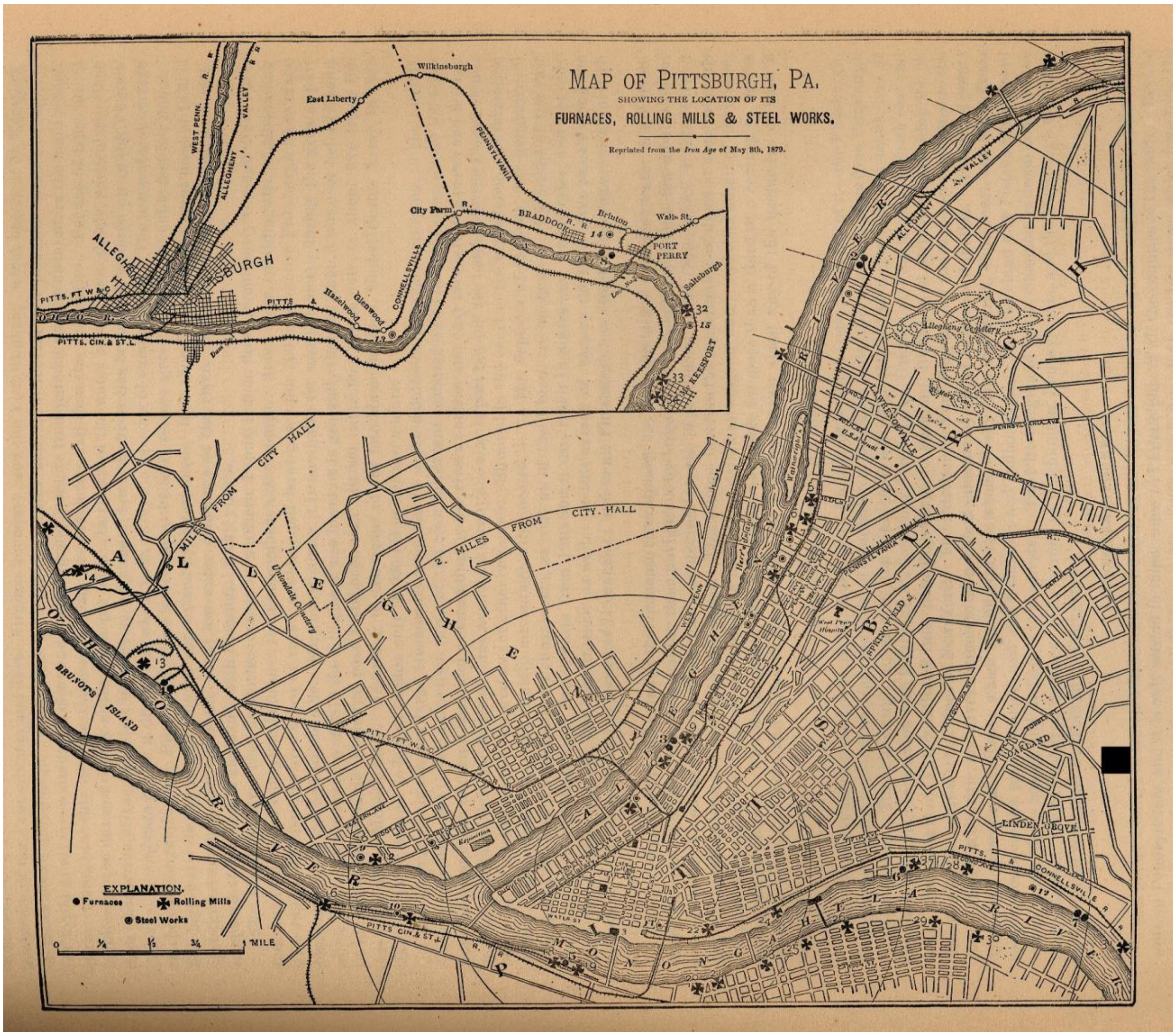


Figure 2. Map of Pittsburgh, PA ca. 1880 A.D., showing the location of its furnaces, rolling mills, and steel works (The Univ. of Texas at Austin, 2007). The black square marks the approximate future location of Panther Hollow Lake.

the main fuel for home heating for a short period between 1945 and 1950 A.D. The sources of the smoke problem changed when the railroads, with their incredible rates of consumption, were forced to alter their fuel sources and methods of burning (Merschon et al., 2003). Smokeless coal and burning technologies were adopted. This left the home-use of carbon fuels as one of the major sources of the air quality problems (Gugliotta, 2003). Later, homeowners were asked to burn the smokeless fuel, but the technology was not yet available to mass-produce the required furnaces. Homes could not be regulated because of administrative reasons and cost.

2.0 METHODS

2.1 CORING AND SAMPLE COLLECTION

On January 6, 2003 A.D., a 47.0 cm sediment core with an intact sediment-water interface was collected from Panther Hollow Lake, in the City of Pittsburgh's Schenley Park (See Figure 3). The lake was cored through the ice in 1 m of water using a K-B style surface coring device fitted with a 7.0 cm diameter polycarbonate tube. The core used for metal analysis was recovered from the middle-west end of the lake (See Figure 4), furthest from any possible disturbance by turbulent inflow. Sediments were extruded in the field at continuous 0.5 cm increments (94 samples) to eliminate potential disturbance during transport to laboratories at the University of Pittsburgh. Soil samples were also collected from twelve sites within the Panther Hollow Lake watershed for geochemical analysis. Soil samples were collected at representative soil pits and sampled by soil horizon, described in Appendix A.

2.2 SEDIMENTOLOGY

Sediments and soils were analyzed shortly after collection for a variety of physical and chemical parameters. Initially, bulk sediment sub-samples were transferred to 2.33 cm^3 micromount boxes

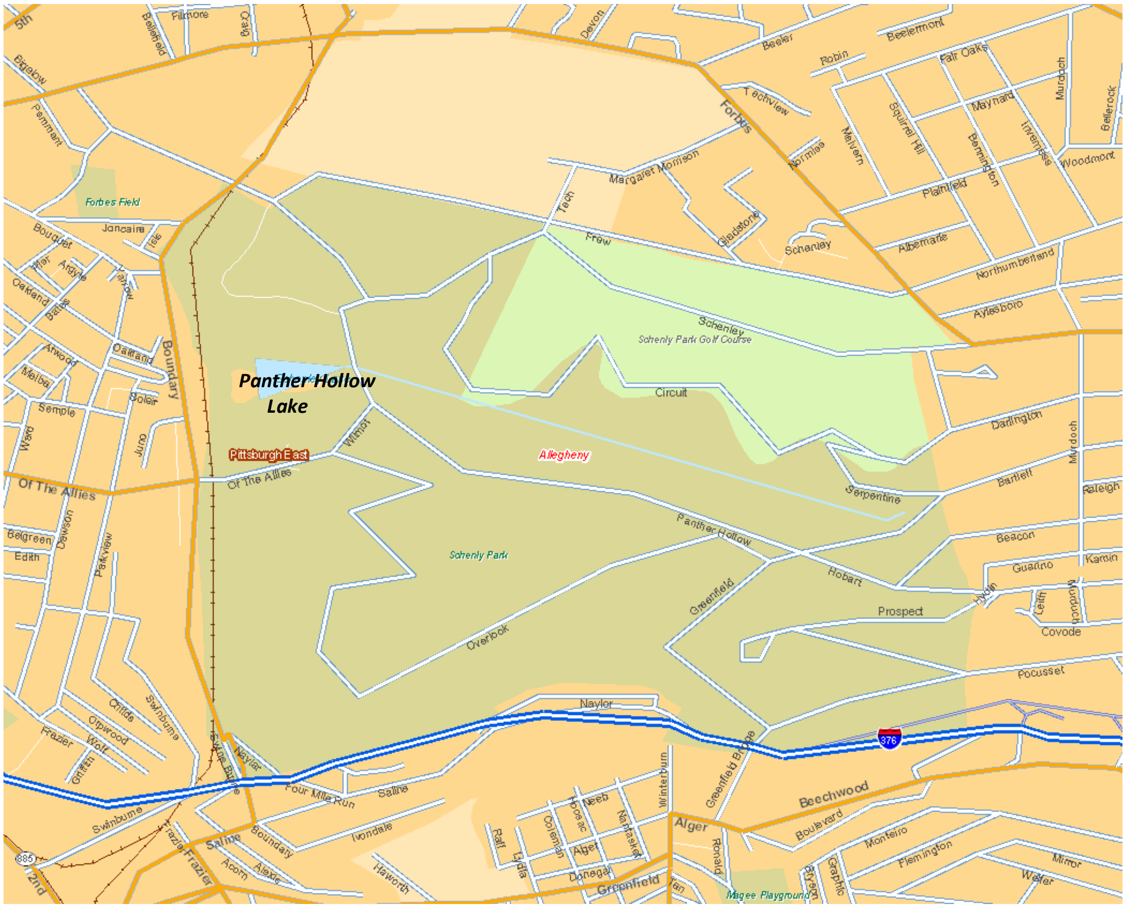


Figure 3. Map of Schenley Park located just north of the Monongahela River, showing the thoroughfares and trails that cross the park. Panther Hollow Lake resides in a valley in the eastern part of the park.

Figure 4. A USGS High Resolution Ortho-Image (USGS, 2005) showing the locations of samples collected in Schenley Park (one core sample and twelve soil samples).

using plastic utensils (in an effort to limit the introduction of metal contamination). Each filled cube was weighed, freeze dried for 36 hours, then weighed again. Water content of the sediment was calculated as the difference between the weights of the cubed wet and dry sediments. Sediment wet and dry bulk densities were also calculated from the known sample weights and volumes. Following drying and weighing, the samples were measured for bulk sediment magnetic susceptibility at both high and low frequencies using a Bartington MS2B Dual Frequency sensor. The reported susceptibility is the average of the high and low frequency measurements.

Organic matter and carbonate content were determined by loss-on-ignition at 550ºC and 1000ºC, respectively (Dean, 1974) at 1.0 cm intervals throughout the Panther Hollow Lake sediment core. Percent organic carbon (% Organic C) and calcium carbonate (% $CaCO_3$) were estimated from organic matter and carbonate content, respectively (Heiri et al., 2001).

2.3 BULK METAL EXTRACTION: CORE AND SOILS

In order to liberate the metals bound in the sediment, 1.0 g dried sediment (in a 15 mL centrifuge tube), from each of the ninety-four 0.5 cm core samples, was disaggregated so as to pass through a 2 mm nylon sieve and treated with 10 mL of 1.60 M nitric acid (See Figure 5). This procedure was repeated with a single blank (10 mL of 1.60 M nitric acid) to determine if any contaminants were introduced in during lab procedures. Samples were agitated in a mechanical shaker at 30 rpm at 22°C for 24 hours. Following acidification, samples were then centrifuged at 3000 x g for 10 minutes. The separated liquid was poured off into a second 15 mL centrifuge tube, and the

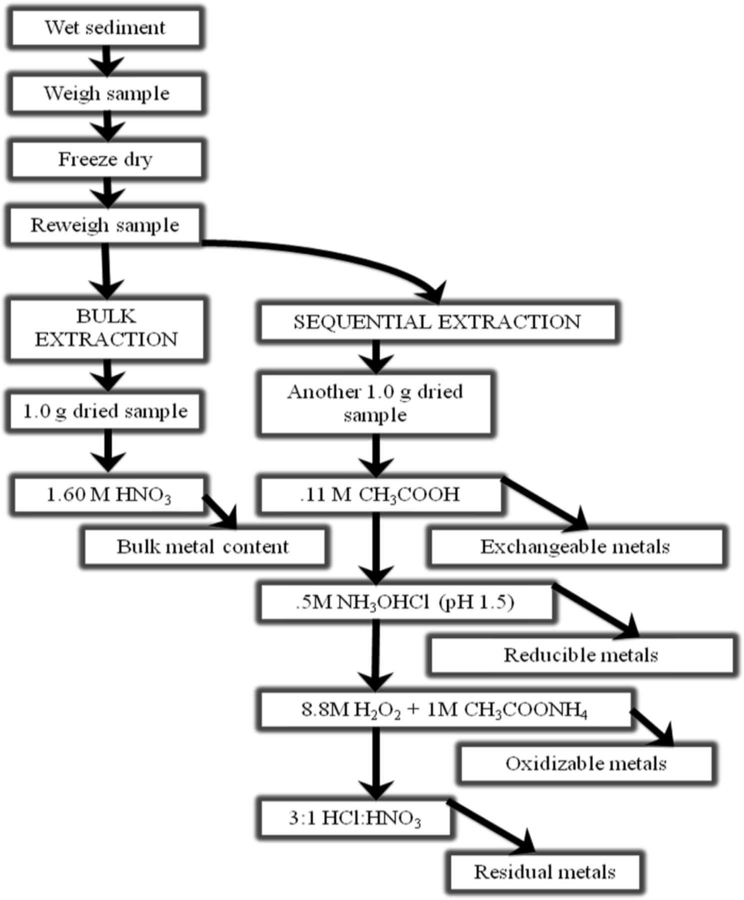


Figure 5. Flow chart of the extraction procedures performed on Panther Hollow Lake core sediments. The same extraction procedures were done on the soil samples.

decanted liquid was then centrifuged again at 3000 x g for an additional 10 minutes. Samples were stored at 4°C until elemental analysis. Analyses were completed using a Spectro Analytical Instruments, Inc. (Marlborough, MA, USA) axial Spectro-Flame Modula EOP inductively coupled plasma atomic emission spectrometer (ICP-AES).

Nine of the twelve soil samples taken from the watershed were also subject to a bulk metal extraction using the method described for the core sediments. The soil samples that underwent this nitric acid bulk metal extraction are numbered 1-9.

2.4 SEQUENTIAL EXTRACTION: CORE AND SOILS

A second, dried, 1.0 g sub-sample was taken from three discrete depths within the sediment core (5 cm, 14 cm, and 23 cm). These samples were disaggregated and passed through a 2 mm nylon sieve, and were transferred to acid-washed high-density polyethylene (HDPE) containers. The samples were then treated sequentially with acetic acid (exchangeable extraction), hydroxylamine hydrochloride (pH 1.5) (reducible extraction), hydrogen peroxide and ammonium acetate (pH 2.0) (oxidizable extraction), and aqua regia (residual extraction). Exact methods follow (See Figure 5). This sequential extraction was based on a previous study made by Pueyo et al. (2003) and Rauret (1999). Duplicate samples were prepared for each level as well as analytical blanks for each step. To determine corrections and percent recovery, one spiked sample was included during this sequential extraction process. The extracts from the samples and the blank were stored at 4°C until elemental analyses.

The first step was an exchangeable extraction with 0.11 M acetic acid, to dissolve the carbonate phases and cause exchange reactions mobilizing organic and mineral bound trace metals. An aliquot of 40.0 mL of 0.11 M acetic acid was added to each 1.0 g of sample in a 50 mL centrifuge tube. The mixture was shaken in a Boekel Grant ORS 200 mechanical shaker at 30 rpm at 22°C for 16 hours. The samples were separated by centrifugation at 3000 x g for 20 min. The supernatant was decanted with a pipette into HDPE containers and stored at 4°C until analysis. The residue was washed to remove any remaining solvent by adding 20 mL of double de-ionized water and shaken at 30 rpm for 15 minutes. It was then centrifuged for 20 min at 3000 x g, the liquid decanted and discarded.

The second (reducible) extraction utilized hydroxylammonium chloride to liberate metals bound to iron and manganese oxides. An aliquot of 40.0 mL of 0.5 M hydroxylammonium chloride, adjusted to pH 1.5 with 2.0 M nitric acid, was added to the residue from the first extraction. The residue was re-suspended by manual shaking and then mechanically agitated at 30 rpm at 22°C for 16 hours. The sample was centrifuged, the liquid decanted and stored, and the residue washed as in the previous step.

Step three (oxidizable extraction) involved digestion with hydrogen peroxide and ammonium acetate, to free the oxidizable fraction of the samples from organic matter and sulfide minerals. An aliquot of 10.0 mL of 8.8 M hydrogen peroxide was added to the residue and digested at 22°C for one hour, and then at 85°C (in a water bath) until the volume of the liquid was reduced to less than 3 mL. A second aliquot of 10.0 mL of 8.8 M hydrogen peroxide was added and the mixture was again digested at 85°C until the volume was reduced to 1 mL. Finally, 50.0 mL of 1.0 M ammonium acetate, adjusted to pH 2.0 with concentrated nitric acid, was added to the cool, moist residue. The mixture was shaken mechanically at 30 rpm at 22°C for 16 hours. The sample was then centrifuged, decanted, stored, and washed as in previous steps.

Aqua regia (residual extraction) was used in the last step of the procedure to liberate any residual metals bound to resistant sulfide material and organic matter. The residue from the third step was digested with 7.0 mL of aqua regia (3:1, hydrochloric acid: nitric acid), loosely covered. The solution was shaken at 30 rpm at 22°C for 16 hours. The sample was again centrifuged, decanted, stored, and washed as in previous steps.

Three soil samples were also subjected to the sequential extraction procedure described for the sediments. These samples are numbered 10-12.

2.5 QUALITY CONTROL

Quality analysis and quality control protocol followed EPA Method 6010 (EPA, 2000). Specifically, control standards were run at the beginning of each sample analysis set, at the end of each sample set, and throughout the set after no more than ten analyses (See Appendix B). Additionally, one sample duplicate per every ten samples was run, as well as a total of one analytical spike, and a blank for each of the four extraction steps. The reported values are the ICP-AES averages for three sequential runs.

3.0 RESULTS

Age-depth values for the Panther Hollow Lake sediments were determined by assuming a linear sedimentation rate (0.5 cm/yr) between the basal deposits (ca. 1908 A.D., the year of lake construction) and the core top, considered 2003 A.D., when the core was collected. Geochemical results are discussed as a function of depth and assumed year. The core was broken into four sediment units based on the physical characteristics and metal concentrations of the sediments. Upper unit delineations are placed at the depths of 41, 26, 13, and 0.0 cm, for Units 1, 2, 3, and 4, respectively. Units are described at the end of this chapter.

3.1 SEDIMENTOLOGY

Generally, bulk density in the core decreased through time, from maximum values near 1.2 g/cm^3 to minimum values near 0.30 $g\ cm^{-3}$ (See Figure 6a). Similarly, sediment magnetic susceptibility decreased through time with the exception of brief excursions toward higher values centered near 44, 31, and 28 cm depth (approximately 1914, 1940, and 1946 A.D.) (See Figure 6b). Organic matter content in the core was relatively low (averaging ~8%), but variable (See Figure 6c). Calcium carbonate concentrations in the Panther Hollow Lake sediments were also

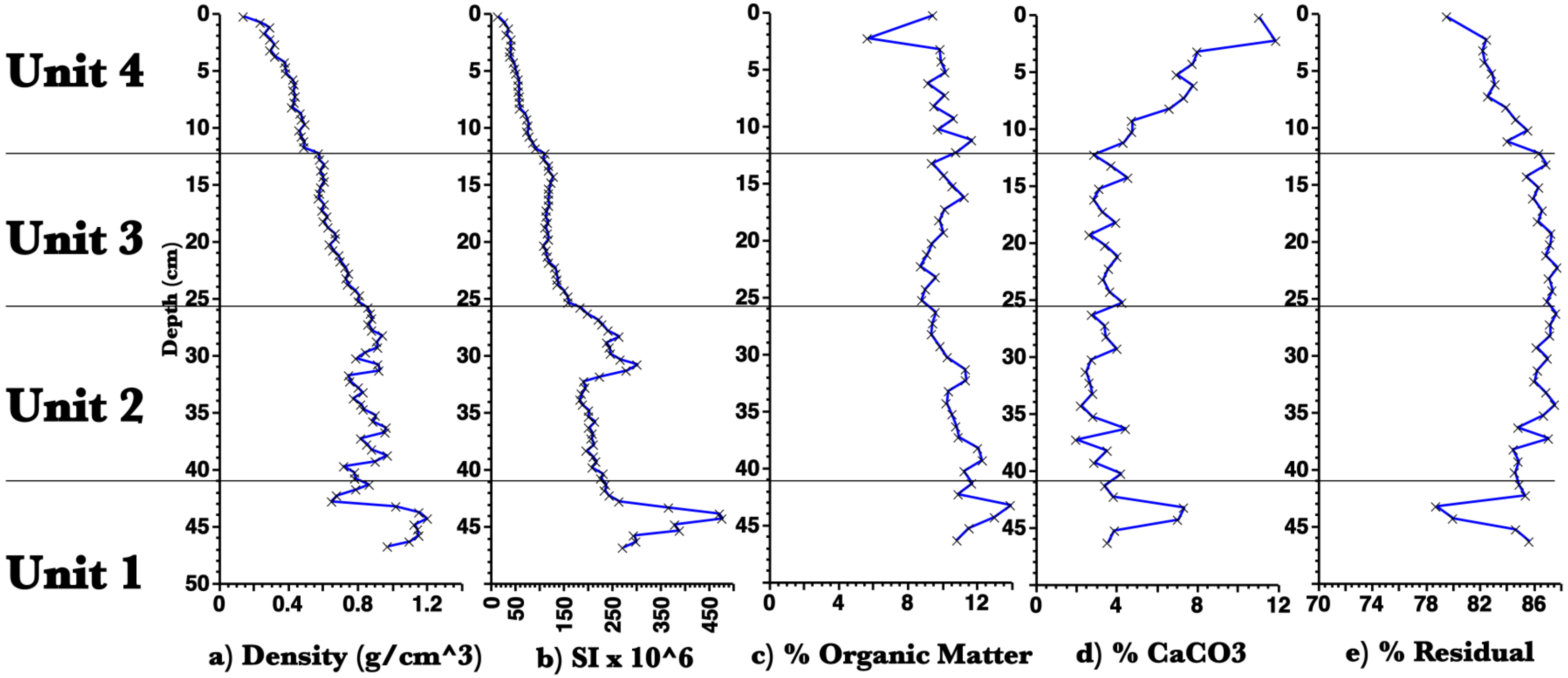


Figure 6. a) Bulk density, b) magnetic susceptibility values for the Panther Hollow sediment core, c) organic matter, d) calcium carbonate, and e) residual matter concentrations derived from loss-on-ignition measurements.

relatively low, typically <5%, below 12 cm (1978 A.D.), but increased abruptly above 9 cm (1984 A.D.) (See Figure 6d).

3.2 BULK METAL EXTRACTION: CORE

The bulk metal analyses of the core sediments included Al, As, Ba, Ca, Co, Cr, Cu, Fe, K, Mg, Na, Ni, Pb, Sr, and V. The results of this extraction can be found in Appendix C. All elements increase at varying levels and exhibit concentrations greater than the background established from the bottom of the core. Aluminum varies from 1,900 – 3,500 ppm. It shows a trough near 45 cm depth (1912 A.D.), followed by an increase to its peak at 41 cm (1920 A.D.) followed by a nearly constant concentration of approximately 2,500 ppm. Aluminum has another increase to 3,500 ppm starting near 12 cm depth (1978 A.D.). Arsenic peaks at 44 cm (1914 A.D.), followed by a near constant concentration of approximately 5 ppm to the top of the core. Barium shows concentrations of 45 ppm throughout the core. Calcium varied throughout the core. Its lowest concentration of just under 4,000 ppm was near the base of the core. It then shows a sharp increase at a depth of 40 cm (1922 A.D.) to nearly 18,000 ppm. It continues with an average concentration of 12,000 ppm to a depth of 14 cm (1974 A.D.), where the concentration saturates the analytical limits of the instrument. Iron concentrations remain constant throughout the entire core at about 10,000 ppm. Co, Cr, K, Mg, Ni, Pb, and V all exhibit relatively constant concentrations down core, with the exception of the interval from 26 cm to 13 cm (1950 to 1976 A.D.), where they are elevated. Thereafter (above 13 cm depth), each element returns to or decreases below its concentration. Sodium and strontium appear to be coupled, exhibiting similar, unchanging profiles by depth. Both have unvarying concentrations (approximately 200 ppm Na, and 40 ppm Sr) until the depth of 14 cm (1974 A.D), where both elements show marked increases (to >800 ppm Na, and >110 ppm Sr).

3.3 BULK METAL EXTRACTION: SOILS

Nine soils samples were taken from representative locations and soil horizons throughout the Panther Hollow Lake watershed (See Figure 3 and Appendix A). The results of these extractions are found in Table 1. Soil samples were analyzed for concentrations of As, Cu, Ni, V, and Pb. In all samples, lead had the highest concentrations of the five metals. In comparison, the next most available metal was Cu. Each soil analyzed had concentrations comparable to those found in the core. In each sample, Pb was two to eight times more concentrated than Cu. Cu, V, and Ni generally had concentrations similar to each other. Arsenic had the lowest concentrations overall; and two of the nine samples had As concentrations below the detectable limits of the ICP. Samples 4 and 5 were taken at the same location from different soil horizons. Sample 4, taken from the O horizon, had a Pb level 1.8 times greater than that found in sample 5, the A horizon. Arsenic was nearly 9x greater in the O horizon than in the A horizon. The remaining three metals consistently had somewhat higher concentrations in the upper horizon versus the lower one.

3.4 SEQUENTIAL EXTRACTION: CORE

The results for the sequential extractions are shown in Table 2 and are the result of the average of the sum of the sample and its duplicate, with the concentration established by the blank deducted. Sr, Na, Ca, and Zn show significant availability in the acetic acid extraction designed to release the weakly bound fractions of the sediment and metals bound to the carbonates. Most elements from the core were more mobile during the hydroxylamine chloride (reducible) extraction, which reduces those elements bound to manganese and iron oxides. Metals released during this extraction included Ba, Al, Fe, and Pb, and to a lesser extent, Ti, Cu, V, and Cr. Ni

Table 1. Results of bulk metal extraction from soil samples 1-9.

Soil Sample	As ppm	Pb ppm	Ni ppm	Cu ppm	V ppm
1	-1.16	22.8	6.53	4.02	7.24
2	2.44	23.93	6.47	6.84	6.73
3	2.85	84.69	7.43	17.36	8.82
4	1.81	122.21	7.41	20.29	10.1
5	0.216	68.35	6.04	16.52	8.34
6	1.7	17.65	6.6	7.26	7.77
7	2.96	88.69	7.32	13.09	9.78
8	-1.83	51.04	5.81	5.16	6.72
9	3.36	305.94	11.07	40.22	17.62

Table 2. Results (in ppm) from the sequential extraction on Panther Hollow Lake sediments.

Sample	**Step**	**Mn**	**Sr**	**Ba**	**Zn**	**Al**	**Na**
5.0 cm	acetic acid	> *	41.89	10.06	>	17.22	799.61
	NH3OHCl	312.8	19.16	53.44	480.72	1090.62	58.22
	aqua regia	5.11	0.13	*	6.6	236.8	BDL*
	Total		61.18		>	1344.64	857.34
14.0 cm	acetic acid	>	16.43	5.35	>	31.8	502.8
	NH3OHCl	111.04	7.46	62.82	509.12	926.42	22.84
	aqua regia	5.57	0.15		4.33	136	BDL
	Total		24.04		>	1094.23	524.99
23.0 cm	acetic acid	>	15.15	5.63	>	49.54	138.28
	NH3OHCl	262.2	6.5	36.26	487.92	1204.02	11.46
	aqua regia	6.09	0.16		6.79	261	BDL
	Total	>	21.18		>	1514.56	148.54
Sample	**Step**	**Ca**	**Fe**	**Ti**	**As**	**Pb**	**Co**
5.0 cm	acetic acid	>	22.57	0.62	1.37	5.09	0.41
	NH3OHCl	14715.84	4439.06	2.04	1.15	143.52	2.82
	aqua regia	6.62	>	4.03	BDL	2.06	0.68
	Total	>	>	6.68	2.46	150.67	3.91
14.0 cm	acetic acid	>	120.16	0.77	1.66	10.54	1.33
	NH3OHCl	2298.44	3433.06	1.98	25.57	136.98	4.8
	aqua regia	5.91	>	3.35	1.34	2.21	0.73
	Total	>	>	6.11	28.57	149.73	6.87
23.0 cm	acetic acid	>	234.88	0.82	BDL	9.19	1.74
	NH3OHCl	2461.84	4931.06	0.95	1.78	148.88	3.98
	aqua regia	6.05	>	3.92	BDL	1.95	0.79
	Total		>	6.7	0.34	160.02	6.51

Table 2 (continued)

Sample	**Step**	**Ni**	**Cu**	**V**	**Cr**	**Se**	
5.0 cm	acetic acid	0.51	1.11	0.18	0.26	0.82	
	NH3OHCl	1.76	10.79	3.82	1.64	0	
	aqua regia	2.45	0.73	1.10			
	Total	4.72	12.63	5.1			
14.0 cm	acetic acid	2.5	1.51	1.47	1.22	0.73	
	NH3OHCl	3.85	9.56	6.72	2	0	
	aqua regia	2.3	0.91	1.02			
	Total	8.66	11.98	9.2			
23.0 cm	acetic acid	1.19	2.1	0.46	0.52	0.44	
	NH3OHCl	2.62	9.86	4.57	1.29	0	
	aqua regia	2.66	0.74	1.42			
	Total	6.46	12.71	6.44			

*(>) indicates a result that was greater than ICP detection limits and (BDL) indicates a result that was below detection limits. Blanks indicate results unable to be extrapolated by the instrument.

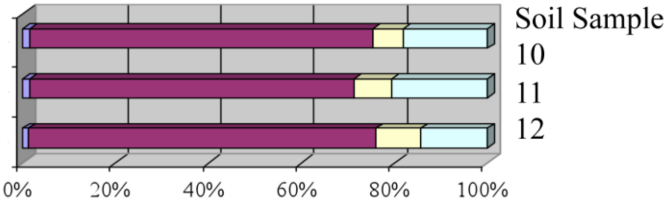
was unique in that it had similar extraction yields in both the reducible and the residual extractions. Approximately 30% of the Ti made available during the sequential extraction procedure was released during the hydroxylamine chloride (reducible) extraction. Another 60% was released from the sediments when the remaining sediments were dissolved in aqua regia. Ti was the only element that exhibited its greatest yield in the final step of the extraction.

3.5 SEQUENTIAL EXTRACTION: SOILS

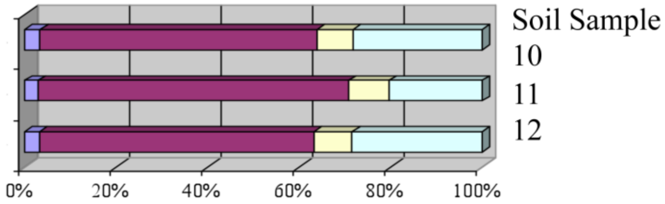
The major and minor elemental concentrations (Al, Ca, Fe, Na, Mn; Sr, Ba, Zn, Ti, Pb, Co, Ni, Cu, V, and Cr) for the sequential extraction procedure administered on the soils are found in Appendix D. Calcium was predominantly associated with the exchangeable fraction with greater than 50% extraction yield (samples 11 and 12) for that step. Strontium was also mainly made available in this extraction. The majority of extractable Pb (See Figure 7a), Mn, and Ni (See figure 7b) was found in the reducible phases of the soil sediments (hydroxylamine chloride extraction). Sodium was detected with organic matter and sulfide minerals (oxidizable extraction) and Zn, Al, and Fe were found with the residual portion dissolved in the aqua regia extraction.

3.6 UNIT DESCRIPTIONS

The basal section of the core, Unit 1, extends from 47 cm to 41 cm (1908 to 1920 A.D.), and is characterized by high magnetic susceptibility (150 to >450 SI x 10^{-6}), high dry bulk density (>1.0



a) Pb sequential extraction



b) Ni sequential extraction

Figure 7. Sequential extraction yields per step for a) Pb and b) Ni. Solvents used left to right: acetic acid (exchangeable), hydroxylamine chloride (reducible), ammonium acetate (oxidizable), and aqua regia (residual).

g/cm^3), relatively high organic matter content (4 to 8%), and typical calcium carbonate content (average 5.1%). It is assumed that this Unit represents the —base” concentrations for the physical characteristics and the metal content in this core.

The transition between Units 1 and 2 is abrupt and based on a general decrease in magnetic susceptibility (>240 to <200 SI x 10^{-6}) with an abrupt double peak (>300 SI x 10^{-6}) at 31 and 28 cm (1940 and 1946 A.D.), relatively constant bulk density (near 0.8 g/cm^3), and the beginning of relatively steady concentrations of Cr, K, Mg, Ni, Pb, and V. Throughout Unit 2, trace metals fall from their high levels near the base of the core to their lowest concentrations before beginning to increase at the boundary with Unit 3.

Unit 3 is characterized by increases in nearly all metals. The easily exchangeable elements (Ca, Na, and Sr) all exhibit steady, near linear increases from the bottom of Unit 3 at 26 cm (1950 A.D.) to the top at 13 cm (1976 A.D.), at which point the Ca concentration overwhelms the detection limits of the ICP. Nearly the entire set of elements that were found to be the most mobile during the reducible phase of the sequential extractions (i.e. Al, As, Co, Cr, Cu, Ni, Pb, and V) exhibit a smooth increase throughout this Unit. These metals are by-products of the coal combustion and coking processes (Frandsen et al., 1994) that were a major part of the City of Pittsburgh’s industries during the time period represented by this Unit (1950 - 1976 A.D.). These metals reach their Unit 3 peak at the approximate depth of 19 cm (1962 A.D.) and then begin to decrease to the levels seen in Unit 2. Decreasing magnetic susceptibility (150 – 50 SI x 10^{-6}) and decreasing bulk density (0.75 to <0.5 g/cm^3) characterize Unit 3.

The uppermost unit, Unit 4, 13 cm to the sediment-water interface (1976 to 2003 A.D.), is characterized by a marked increase in concentrations of the alkali and alkali earth metals and the decrease of industry-related metal concentrations to levels similar to Unit 2. The bulk density

(<0.5 g/cm^3) follows the same declining trend as the heavy metals, as does carbonate concentration and the sediment magnetic susceptibility. Organic matter increases in Unit 4 to >12%.

4.0 DISCUSSION

4.1 SEDIMENT RECORD INTERPRETATION IN HISTORICAL CONTEXT

Many of the metals analyzed in this core are by-products of coal-combustion and coking processes (Frandsen et al., 1994). The city of Pittsburgh and its surrounding region have had a long history of industrial activity and subsequent air pollution that served to increase heavy metal deposition in the study area. The concentrations of metals in the core from Panther Hollow Lake were examined with this historical context in mind.

By 1868 A.D., forty years before Panther Hollow Lake was created, the Pittsburgh City Council had to ban the use of bituminous coal by railroads due to health concerns over smoke emissions. By 1911 A.D. the Bureau of Smoke Regulation was put in place to enforce this railroad statute, among others, that regulated industrial, commercial, and transportation sources of smoke. Further air pollution reductions were mandated by the City's municipal smoke control policies enacted from 1940 to 1950 A.D. During this time, half of the households in Pittsburgh converted their home heating from coal to natural gas (Tarr et al., 1981). Between 1940 and 1960 A.D., Pittsburgh and Allegheny County experienced a major air quality transformation. This time period corresponds to the transition from Unit 2 to Unit 3 in the core. The smoke ordinance finally passed in 1941 A.D. (Tarr et al., 1981), around the same time (~1940 A.D.) in which one of the region's major industries, Unites States Steel Corporation, had increased its production by nearly 50% (See Figures 8 and 9) to supply the demands of World War II. The Clean Air Act of 1963 A.D. was designed to reduce national air pollution by focusing efforts towards reducing emissions from power plants and steel mills (Fleming et al., 2008). The impacts of this federal effort are seen in the core above the 16 cm (1970 A.D.) level where nearly all trace metals associated with industrial emissions begin to decline from peak concentrations at 20 cm depth (1962 A.D.). At the depth in the core representing the period from 1967 to 1970 A.D. (18 to 16 cm depth) all trace metals continued to decline, whereas alkali and alkali earth metal concentrations increased (See Figures 8 and 9). Further air pollution reductions, including particulates and lead, were forced through the succeeding Clean Air Acts and Amendments in 1970, 1977, and 1990 A.D. (EPA, 2008a).

4.2 CALCIUM, SODIUM, AND STRONTIUM

The stratigraphies of the exchangeable metals (Ca, Na, and Sr) are different than the majority of the other trace metals analyzed for this study. While the industry related elemental concentrations declined, Ca, Na, and Sr increased. They do so throughout Unit 3, and then increase at much greater rates thereafter to the water-sediment interface. Calcium, sodium, and strontium are all easily extractable under the weak acid conditions, and are also known to replace each other in $CaCO_3$, NaCl, and $CaCl_2$. The increased Ca concentrations may be the product of the increased use of calcium carbonate as a filter (wet limestone) in power plant smoke stack ―scrubbers" which are used to lessen the atmospheric pollution released by the plant's combustion processes. During this filtering process, some of the Ca (or Sr, by ionic substitution)

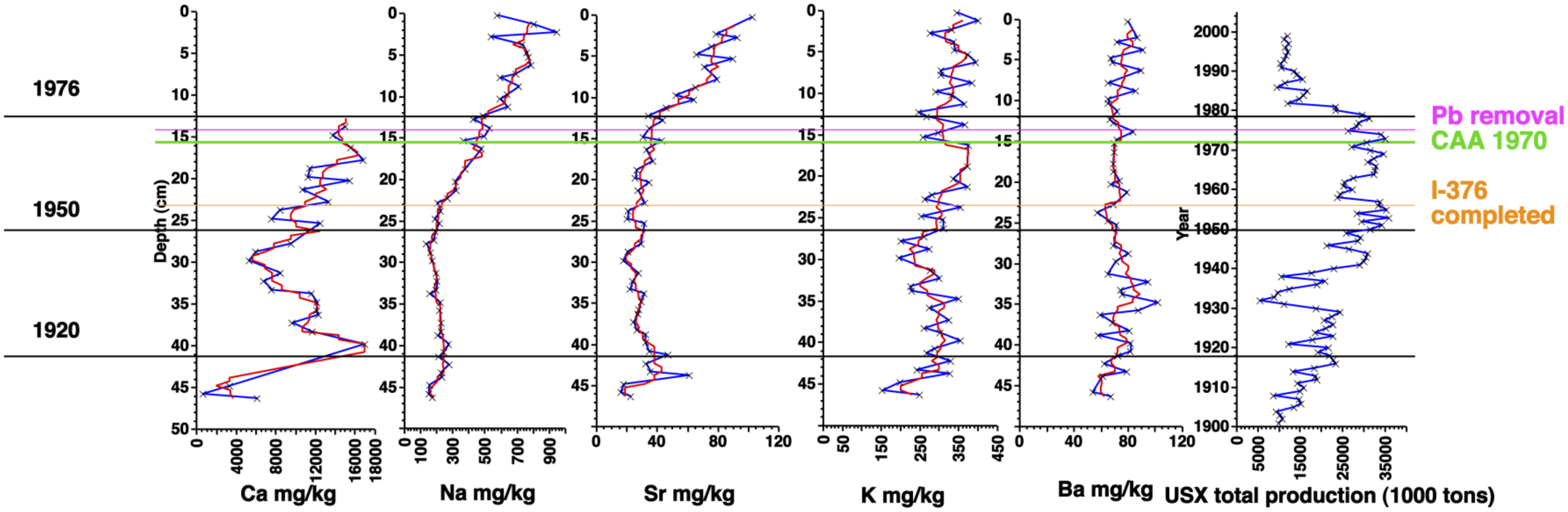


Figure 8. Panther Hollow Lake sediment metal concentrations for the easily exchangeable metals and U.S. Steel's total production by year.

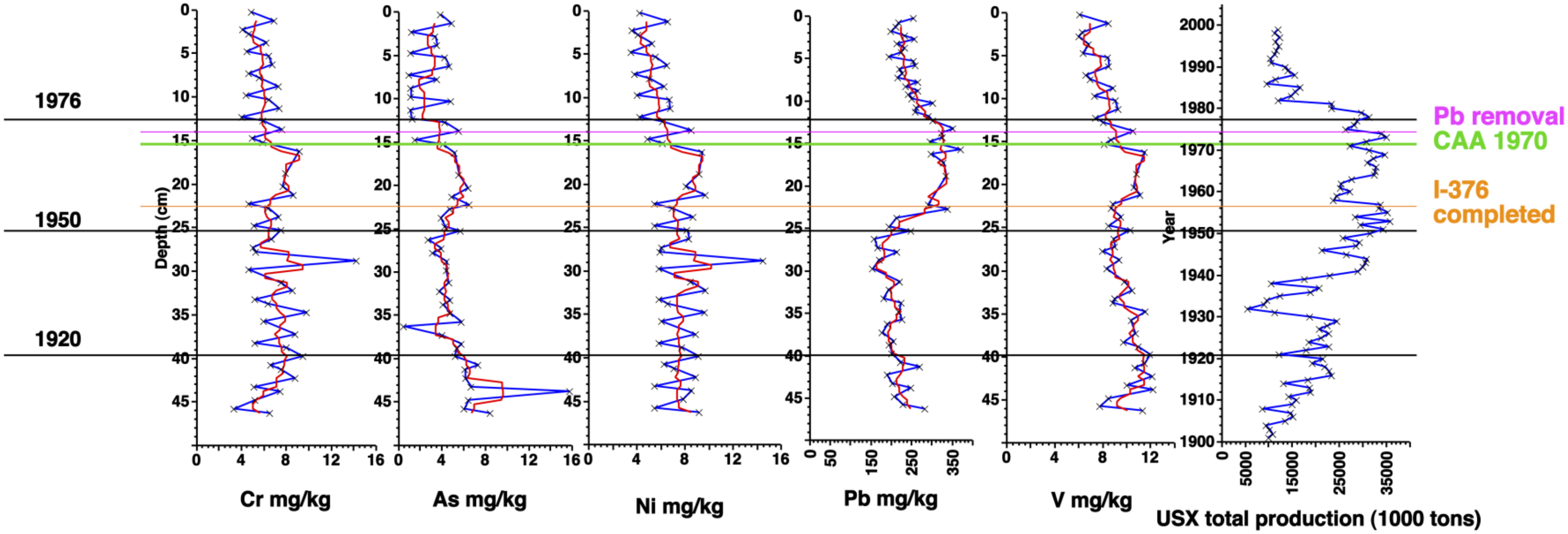


Figure 9. Panther Hollow Lake sediment metal concentrations for the industrial metals and U.S. Steel's total production by year.

may adhere to the carbonaceous spheres that exit the stacks, and could be transported into the lake's basin through atmospheric processes. These filters were implemented in the early 1970s as a pollution control as the result of the Clean Air Act of 1970 (EPA, 2008b) (See Figure 8).

Calcium, sodium, and strontium are also present in road salts used for deicing. In Pittsburgh, calcium magnesium acetate ($Ca_{0.3}Mg_{0.7}(C_2H_3O_2)_2$), fly-ash, and limestone were used as an alternative to NaCl for deicing purposes on area roads (Armhein et al., 1990, Mitchell, 2008), including I-376, which is located near the drainage divide at the south end of the lake. This major thoroughfare was completed in the 1953 A.D. resulting in increased traffic in the proximity of the Panther Hollow watershed. The corresponding point in the core would be placed at the depth of 23 cm (See Figure 8), which coincides with the depth when Ca, Na, and Sr begin to increase more rapidly. Previously deposited particles such as these have the ability to be transported across basins through the process of atmospheric resuspension (Lankey et al., 1998, Sehmel, 1973, and Chen et al., 2006).

These elements were made available during the first phase of the sequential extraction indicating that they are readily released from the sediments under weak acid conditions. The Pittsburgh Metropolitan area has acid precipitation. The average pH of annual rain is <4.36 (PA DEP, 2004) (See Figure 10), which may be low enough to release some of these cations from their depositional environment, but does not reach the pH required to release the other metals analyzed in this study.

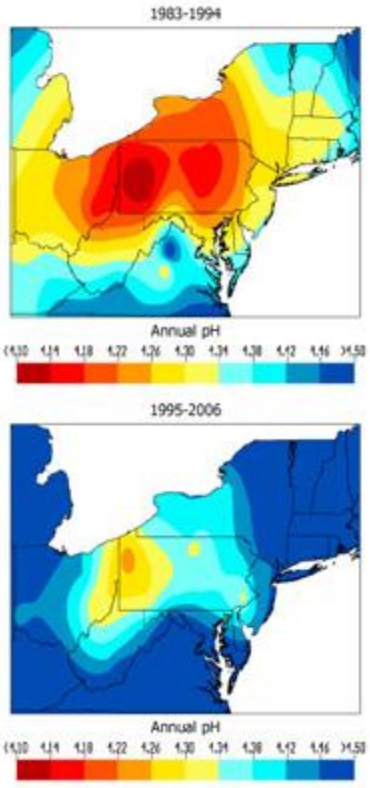


Figure 10. Mean annual pH across the Pittsburgh Metropolitan area and surrounding region before (1982-1994 A.D.) and after (1995-2004 A.D.) the Clean Air Act amendments of 1990 A.D. (PA DEP, 2004)

4.3 ALUMINUM, IRON, AND ARSENIC

Aluminum, Fe, and As concentrations covary throughout the majority of the core. Each decreases dramatically at 45 cm depth. This decrease is followed by an abrupt increase that peaks at about 41 cm depth (1920 A.D.). This may be the result of an increase in sedimentation at this time due to construction in the newly formed park. Iron was the only heavy metal that remained in the sediments until the aqua regia portion of the sediment extraction, indicating that it is most likely found in the silicate material in the sediments. The high As levels, in particular, may be related to the use of pesticides while originally landscaping Schenley Park (Sarkar et al., 2004). Arsenic was extractable during the iron and manganese oxide-reducing step of the sequential extraction, indicating that it is not easily released from the sediments. A reducing event, such as eutrophication, or physical movement of the lake floor, such as dredging, may release high levels of As from the sediments where it is now bound. This contamination may be able to enter the local water system; the drinking water standard is set at 0.01 ppm (EPA, 2008c), 500 to 1,200 times lower than the arsenic concentration in the sediments.

4.4 INDUSTRIAL METALS

The metals Co, Cr, Cu, Ni, Pb, and V are associated with combustion of fossil fuels and covary throughout the core. The initial basal concentrations of these elements reflect the impact of regional industrialization prior to the lake's inception. Through Unit 2, these industry-related elements remain nearly constant. At the beginning of Unit 3 (26 cm depth or ~1950 A.D.), these metals all exhibit an increase through the next 6 cm reaching peak values at 20 cm depth (1962 A.D.). This increase coincides with increased industrial activity in the area (See Figure 9). These metals decrease from peak values to minimum values near 14 cm depth (1974 A.D.). This is the same point at which the alkali and alkali earth metals begin a marked increase (See Figure 8). Both of these variations may be attributed to the changes to environmental regulations enacted at this time, such as changes to the Clean Air Act. The wet limestone scrubbers installed at area mills may have added to the exchangeable metal concentrations while filtering some of the heavy metals from the industrial atmospheric output.

Vanadium, however, may have an alternative source. Often associated with hydrocarbon (gas, oil) combustion, vanadium may therefore be the result of particulate input into the lake via local roadways. This same source may also contribute to the magnitude of Pb. Lead is known as a coal-burning by-product, but was also readily found in gasoline until the early 1970s when it began to be phased out by the passage of the Clean Air Act in 1970 A.D. (EPA, 2008a).

The Pb stratigraphy seems to reflect regional environmental changes, helping to verify the assumed sedimentation rate of 0.5 cm/year and interpretation of the core. The Pb concentration begins a marked increase just after the transition to Unit 3 (26 cm or ~1950 A.D.), which correlates with the completion of the Pittsburgh Parkway East, I-376, in 1953 A.D. (See Figure 9) and is most likely the result of the atmospheric deposition of resuspended Pb from leaded gasoline particles. The level linearly associated with the year 1972 A.D. is the peak of the Pb concentration.

The sequential extractions done here were designed to be similar to a variety of natural geochemical environments, including those affected by acid rain. These industry-related elements were found to mainly be released when the iron and manganese oxides in the sediments were broken down in a reducing reaction involving hydroxylamine chloride. These harsh conditions would not be typical in a watershed under natural conditions. However, the release of the very high concentrations of heavy metals found in these sediments could be attained if a reducing event were to take place in the sediments or if they were to be physically disturbed. Otherwise, these heavy metals do not appear to be readily removed from the sediments.

4.5 CATCHMENT SOILS

The soil samples from the watershed suggest that the entire catchment has been subject to atmospheric deposition that was heavily influenced by industrial activity. The metal concentrations vary by soil depth. The concentrations tend to be higher in the upper horizons and lower in the deeper horizons, possibly indicating a buried soil or a change in input accumulation at the surface. Over time, the particles deposited on the surface are washed into the lake by precipitation runoff. This leaves the remaining soils increasingly more depleted. As the silt from catchment runoff eventually reaches the mouth of the lake, the particles accumulate and become concentrated. An example is Soil Sample 9, which is sediment directly from the input delta. This sample is one of the points with the highest metal concentrations: ~306 ppm Pb, >40 ppm Cu, and >17 ppm V (See Table 1). Another sample with high metal concentrations for all elements analyzed was Sample 3, which was collected at the convergence of the tributaries draining into the lake, and may be a primary depositional environment for the metals exported from that half of the watershed.

5.0 CONCLUSIONS

The results of these analyses showed that Panther Hollow Lake recorded the industrial activity and consequent environmental changes occurring in the region. The 94-year record preserved in the sediments recovered from the lake floor reveals changes in atmospheric metal concentrations reflective of changes in industry. The core record shows high basal concentrations of all metals measured in this study due to the influence of the Pittsburgh Metropolitan area's already smoke-laden atmosphere before the construction of the lake in 1908. Heavy metals associated with industry were present in the sediments in substantial concentrations and varied in accordance with regional industrial developments and environmental controls. The alkali and alkali earth metals varied in response to the environmental stipulations placed on industrial facilities and possibly changes in methods of winter road treatment. The examination of upstream soils from various soil horizons showed that this atmospheric deposition affected the entire catchment. The concentrations found in the soil samples varied by location and depth leading to the conclusion that atmospheric deposition throughout the catchment is picked up by runoff and washed into the lake, ultimately concentrating at the confluence of the valley's streams at the mouth of the lake.

The sequential extraction procedure applied to both the core sediments and the catchment soils extracted the metals found in the exchangeable, reducible, oxidizable, and residual fractions of the samples. The results showed that the metals Ca, Na, and Sr are easily extractable under weak acid conditions. The industry-related heavy metals were mainly released under strong reducing conditions due to their attachment to the Fe/Mn oxides in the samples. These metals will most likely remain where deposited if not disturbed or subject to reducing conditions. Further studies may include sediment dating using Cs-137 of Pb-210 to better constrain the time record, or the use of Pb isotopes to better pinpoint pollution sources.

APPENDIX A

SOIL SAMPLE DESCRIPTIONS AND LOCATIONS

Table 3. Appendix A

Soil Sample	Depth (cm)	Sample Description	Latitude	Longitude
1	14	Rocky Delta	40.43703	-79.94701
2	surface	Side Channel	40.43826	-79.9448
3	surface	Side Channel Further up stream	40.43851	-79.9443
4	6	Soil (O Horizon)	40.43575	-79.9441
5	21	Soil (A Horizon)	40.43575	-79.9441
6	surface	Soil/weathered tree trunk	40.43549	-79.94341
7	surface	Marsh grass	40.43689	-79.9462
8	surface	Soil	40.43646	-79.94528
9	13	Cattails	40.43694	-79.94701
10	3	Side of hill slope, next to bridge (Blvd of the Allies)	40.43471	-79.94912
11	5	Slope of hill, next to railroad track	40.43542	-79.94955
12	surface	Soil	40.43734	-79.9464

.

APPENDIX B

CALIBRATIONS

Table 4. Appendix B

		Date Time	Sample Name	†	Mg mg/L		K mg/lL
1	Average	4/16/2003 12:37	ccv		55.1		49.47
2	RelStdDev	4/16/2003 12:37	ccv		2.513		3.366
3	StdDev	4/16/2003 12:37	ccv		1.384		1.665
4	Average	4/16/2003 12:45	ccb	-	0.0285	-	0.0074
5	RelStdDev	4/16/2003 12:45	ccb		135.619		21.087
6	StdDev	4/16/2003 12:45	ccb		0.0387		0.0016
7	Average	4/16/2003 12:53	inta	>	529	-	0.0127
8	RelStdDev	4/16/2003 12:53	inta		2.24		2.934
9	StdDev	4/16/2003 12:53	inta		11.85		0.0004
10	Average	4/16/2003 1:03	ccv		54.7		46.58
11	RelStdDev	4/16/2003 1:03	ccv		2.067		1.379
12	StdDev	4/16/2003 1:03	ccv		1.13		0.642
13	Average	4/16/2003 1:32	ccv		47.11		49.62
14	RelStdDev	4/16/2003 1:32	ccv		3.874		2.488
15	StdDev	4/16/2003 1:32	ccv		1.825		1.234
16	Average	4/16/2003 1:40	intab	>	463.4		0.0043
17	RelStdDev	4/16/2003 1:40	intab		0.967		34.547
18	StdDev	4/16/2003 1:40	intab		4.483		0.0015
19	Average	4/16/2003 1:48	PH A03D1 B5	-	0.0336		0.016
20	RelStdDev	4/16/2003 1:48	PH A03D1 B5		20.777		29.722
21	StdDev	4/16/2003 1:48	PH A03D1 B5		0.007		0.0048
22	Average	4/16/2003 1:56	PH A03D1 B6	-	0.0545		0.008
23	RelStdDev	4/16/2003 1:56	PH A03D1 B6		54.411		20.101
24	StdDev	4/16/2003 1:56	PH A03D1 B6		0.0297		0.0016
25	Average	4/16/2003 2:06	PH A-03 D-1 2cm		69.8		27.76
26	RelStdDev	4/16/2003 2:06	PH A-03 D-1 2cm		9.475		11.386

Table 4 (continued)

		Date Time	Sample Name		Mg mg/L		K mg/lL
27	StdDev	4/16/2003 2:06	PH A-03 D-1 2cm		6.61		3.161
28	Average	4/16/2003 2:13	PH A03D1 4.5CM		70.4		28.36
29	RelStdDev	4/16/2003 2:13	PH A03D1 4.5CM		6.995		13.976
30	StdDev	4/16/2003 2:13	PH A03D1 4.5CM		4.927		3.963
31	Average	4/16/2003 2:21	PH A03D1 7CM		69.6		25.34
32	RelStdDev	4/16/2003 2:21	PH A03D1 7CM		2.521		3.275
33	StdDev	4/16/2003 2:21	PH A03D1 7CM		1.755		0.83
34	Average	4/16/2003 2:29	PHA03D1 8.5CM		94.1		32.01
35	RelStdDev	4/16/2003 2:29	PHA03D1 8.5CM		2.154		4.202
36	StdDev	4/16/2003 2:29	PHA03D1 8.5CM		2.026		1.345
37	Average	4/16/2003 2:37	PH A03D1 9.5CM		63.1		24.45
38	RelStdDev	4/16/2003 2:37	PH A03D1 9.5CM		3.388		5.261
39	StdDev	4/16/2003 2:37	PH A03D1 9.5CM		2.137		1.286
40	Average	4/16/2003 2:45	PH A03D1 11CM		91.8		30.37
41	RelStdDev	4/16/2003 2:45	PH A03D1 11CM		2.442		3.677
42	StdDev	4/16/2003 2:45	PH A03D1 11CM		2.24		1.117
43	Average	4/16/2003 2:53	PH A03D1 12CM		56.8		20.68
44	RelStdDev	4/16/2003 2:53	PH A03D1 12CM		6.969		9.244
45	StdDev	4/16/2003 2:53	PH A03D1 12CM		3.961		1.912
46	Average	4/16/2003 3:01	PH A03D1 14.5CM		72.1		24.79
47	RelStdDev	4/16/2003 3:01	PH A03D1 14.5CM		10.094		11.431
48	StdDev	4/16/2003 3:01	PH A03D1 14.5CM		7.28		2.833
49	Average	4/16/2003 3:09	PH A03D1 17CM		76.7		26.73
50	RelStdDev	4/16/2003 3:09	PH A03D1 17CM		2.013		5.685
51	StdDev	4/16/2003 3:09	PH A03D1 17CM		1.544		1.52
52	Average	4/16/2003 3:18	CCV		46.72		47.58
53	RelStdDev	4/16/2003 3:18	CCV		0.638		1.761

Table 4 (continued)

		Date Time	Sample Name		Mg mg/L		K mg/lL
54	StdDev	4/16/2003 3:18	CCV		0.2979		0.838
55	Average	4/16/2003 3:27	CCB	-	0.0622		0.0107
56	RelStdDev	4/16/2003 3:27	CCB		54.208		20.122
57	StdDev	4/16/2003 3:27	CCB		0.0337		0.0022
58	Average	4/16/2003 3:35	INTA	>	442.2		0.0072
59	RelStdDev	4/16/2003 3:35	INTA		2.174		38.26
60	StdDev	4/16/2003 3:35	INTA		9.61		0.0027
61	Average	4/16/2003 3:44	INTAB	>	456.9		0.0055
62	RelStdDev	4/16/2003 3:44	INTAB		1.835		32.687
63	StdDev	4/16/2003 3:44	INTAB		8.38		0.0018

Table 4 (continued)

		Na mg/L		Ca mg/L		Fe mg/L		As mg/L		Pb mg/L
1		53.2		55.3		0.943		0.1168		0.0459
2		9.4		4.322		7.448		8.195		11.285
3		4.998		2.39		0.0702		0.0096		0.0052
4	-	0.0601	-	0.0022	-	0.0217	*	0.0045	-	0.0051
5		2.68		274.028		36.715		119.637		55.991
6		0.0016		0.0061		0.008		0.0054		0.0029
7	-	0.0395	#	497.9	>	183.7		0.0497		0.262
8		1.74		1.168		1.75		38.564		4.581
9		0.0007		5.82		3.215		0.0192		0.012
10		48.81		53.1		0.95		0.1184		0.0484
11		0.626		0.299		3.371		4.832		4.181
12		0.3055		0.1588		0.032		0.0057		0.002
13		51.5		50.2		0.793		0.0316		0.0819
14		2.403		1.794		1.006		3.504		0.68
15		1.236		0.901		0.008		0.0011		0.0006
16	-	0.0314	#	467.2	>	157.9		0.1282		0.548
17		2.333		1.898		0.549		1.253		1.472
18		0.0007		8.87		0.867		0.0016		0.0081
19	-	0.0114		0.3484		0.0644	*	0.0038		0.0669
20		33.856		4.324		9.881		75.812		0.184
21		0.0039		0.0151		0.0064		0.0029		0.0001
22	-	0.0125		0.2677		0.0444		0.0061		0.0634
23		6.772		4.737		9.661		90.565		2.02
24		0.0008		0.0127		0.0043		0.0055		0.0013
25		79.1	#	555	>	388		0.0993	>	5.77
26		9.692		0.128		13.175		10.338		10.793

Table 4 (continued)

		Na mg/L		Ca mg/L		Fe mg/L		As mg/L		Pb mg/L
27		7.66		0.712		51.1		0.0103		0.623
28		63.5	#	555	>	417.1		0.0912	>	5.56
29		7.003		0.073		9.59		0.997		5.085
30		4.45		0.4062		40		0.0009		0.2827
31		57.6	#	555	>	400.2		0.0786	>	5.52
32		3.179		0.042		3.759		2.364		3.535
33		1.831		0.2349		15.04		0.0019		0.195
34		59.2	#	557	>	553		0.0924	>	6.54
35		3.197		0.028		4.901		5.493		3.812
36		1.894		0.1562		27.1		0.0051		0.2492
37		53.6	#	558	>	408.9		0.0956	>	6.21
38		4.347		0.038		3.948		5.979		4.09
39		2.328		0.214		16.14		0.0057		0.2542
40		53.4	#	558	>	551		0.0928	>	7.08
41		2.711		0.023		4.346		0.602		1.283
42		1.447		0.1286		23.94		0.0006		0.0908
43		40.84	#	560	>	397		0.1073	>	7.38
44		8.493		0.035		11.337		3.846		8.463
45		3.468		0.1958		45.01		0.0041		0.625
46		41.27	#	560	>	491.3		0.1294	>	8.44
47		10.75		0.044		13.138		6.571		10.323
48		4.436		0.2486		64.5		0.0085		0.871
49		35.4	#	560	>	584		0.116	>	9.21
50		4.821		0.01		4.889		8.267		3.008
51		1.707		0.0564		28.56		0.0096		0.277
52		48.77		47.71		0.828		0.0304		0.083
53		1.107		0.85		6.776		7.734		2.719
54		0.54		0.4056		0.0561		0.0024		0.0023
55	-	0.053	-	0.0135	-	0.0255	*	0.0041		0.0618
56		1.29		18.661		3.754		116.069		1.111
57		0.0007		0.0025		0.001		0.0048		0.0007
58	-	0.0274	#	451.7	>	153		0.0163		0.1707
59		2.134		0.966		3.931		34.793		0.963
60		0.0006		4.363		6.02		0.0057		0.0016
61	-	0.0333	#	441.1	>	154.6		0.1226		0.519
62		3.469		1.824		1.386		1.695		0.908
63		0.0012		8.05		2.142		0.0021		0.0047

Table 4 (continued)

		Co mg/L		Ni mg/L		Cu mg/L		V mg/L		Cr mg/L
1		0.56		0.4525		0.2618		0.578		0.14
2		2.019		2.316		3.63		2.406		3.439
3		0.0113		0.0105		0.0095		0.0139		0.0048
4		0.0305		0.0493		0.0135		0.0548		0.0315
5		24.796		15.356		12.838		5.547		17.962
6		0.0076		0.0076		0.0017		0.003		0.0057
7		0.0371		0.0509		0.0159		0.0616		0.0403
8		3.726		2.976		25.094		4.358		3.23
9		0.0014		0.0015		0.004		0.0027		0.0013
10		0.56		0.4467		0.2641		0.57		0.1441
11		2.32		1.223		2.712		1.225		3.828
12		0.013		0.0055		0.0072		0.007		0.0055
13		0.4997		0.3575		0.2625		0.5		0.1099
14		1.006		1.1		2.001		1.502		1.738
15		0.005		0.0039		0.0053		0.0075		0.0019
16		0.514		0.802		0.509		0.4697		0.4732
17		3.263		1.28		1.291		1.465		1.365
18		0.0168		0.0103		0.0066		0.0069		0.0065
19	*	0.0068		0.0158		0.0367	*	0.0086		0.0124
20		54.988		12.523		4.463		10.671		14.263
21		0.0038		0.002		0.0016		0.0009		0.0018
22	*	0.0053		0.0187		0.0091	*	0.0107		0.0108
23		123.658		2.346		54.093		15.176		20.087
24		0.0066		0.0004		0.0049		0.0016		0.0022
25		0.2785		0.302		2.775		0.529		0.3425
26		13.782		16.888		10.216		11.179		11.296

Table 4 (continued)

		Co mg/L		Ni mg/L		Cu mg/L		V mg/L		Cr mg/L
27		0.0384		0.051		0.2835		0.0591		0.0387
28		0.2869		0.2927		2.758		0.532		0.3731
29		4.788		6.49		5.045		8.391		6.97
30		0.0137		0.019		0.1391		0.0446		0.026
31		0.2881		0.3152		2.613		0.55		0.3873
32		8.405		4.31		2.443		3.016		4.87
33		0.0242		0.0136		0.0638		0.0166		0.0189
34		0.4436		0.521	~	3.412		0.741		0.605
35		0.713		3.076		1.568		3.675		3.504
36		0.0032		0.016		0.0535		0.0272		0.0212
37		0.3102		0.3347		2.652		0.615		0.3734
38		3.227		5.023		3.287		4.177		4.346
39		0.01		0.0168		0.0872		0.0257		0.0162
40		0.4548		0.562	>	3.634		0.772		0.613
41		0.987		1.313		0.416		3.737		1.623
42		0.0045		0.0074		0.0151		0.0289		0.0099
43		0.3218		0.3528		2.555		0.623		0.3356
44		5.974		8.667		8.717		8.257		6.587
45		0.0192		0.0306		0.2227		0.0514		0.0221
46		0.3862		0.4079	~	3.195		0.724		0.4108
47		7.561		9.761		7.834		9.962		7.998
48		0.0292		0.0398		0.2503		0.0721		0.0329
49		0.4332		0.456	~	3.386		0.774		0.4757
50		2.946		1.264		3.362		3.084		2.991
51		0.0128		0.0058		0.1138		0.0239		0.0142
52		0.4705		0.3261		0.2431		0.4714		0.1031
53		0.439		0.046		1.434		0.517		4.235
54		0.0021		0.0002		0.0035		0.0024		0.0044
55		0.009		0.0064	*	0.0026	-	0.0034	*	0.0012
56		26.297		30.045		83.931		70.67		236.043
57		0.0024		0.0019		0.0022		0.0024		0.0029
58		0.01	*	0.0012		0.0072	-	0.0053	*	0.0045
59		45.847		155.981		36.02		73.453		112.556
60		0.0046		0.0019		0.0026		0.0039		0.005
61		0.4922		0.737		0.486		0.4343		0.4413
62		0.799		1.861		1.334		1.011		0.447
63		0.0039		0.0137		0.0065		0.0044		0.002

† (>) indicates a value above the upper calibration curve, (#) indicates a value that caused the machine to overload the integrator, (~) indicates an extrapolated value, and (-) indicates a value below the tolerance limit of the machine.

APPENDIX C

BULK METAL EXTRACTION RESULTS: CORE

Table 5. Appendix C

Avg. Depth	Ca mg/kg	Na mg/kg	Mg ppm	K ppm	Sr mg/kg	Al mg/kg	As mg/kg	Ba mg/kg	Co mg/kg	Zn mg/kg	Cr mg/kg	Cu mg/kg	Ni mg/kg	Pb mg/kg	V mg/kg	Fe mg/kg
0.25		579.18	853.47	347.20	102.65		3.89	79.78	3.44	>	4.86	30.10	4.25	255.45	6.07	11652.29
0.75			0.00	0.00										219.65		
1.25		801.69	1195.33	400.48			4.89		5.11		6.88	41.88	6.58	211.83	8.50	
1.75			0.00	0.00										200.08		
2.25		946.71	835.40	332.25	78.87	2478.68	1.19	86.65	3.33	>	4.10	33.21	3.61	233.51	6.33	7779.52
2.75		536.86	824.64	276.21	92.47		3.40	71.73	3.53	>	4.63	27.80	4.07	257.88	6.00	12188.74
3.25			0.00	0.00										214.47		
3.75		732.83	1077.83	337.01	75.83		3.57	91.00	4.89		6.25	36.11	5.27	233.51	6.84	11067.76
4.25			0.00	0.00										224.38		
4.75		760.30	842.92	339.56	65.85	2308.45	1.09	66.93	3.44		4.47	33.02	3.50	194.69	6.37	7279.76
5.25		768.73	1129.84	373.35	89.60		4.26	68.79	4.67	>	6.44	36.62	5.54	254.61	8.46	12449.07
5.75			0.00	0.00										258.91		
6.25		786.13	1263.08	394.38	70.94	3267.94	4.68	89.64	5.09	>	6.76	38.35	6.51	220.14	8.52	9227.40

Table 5 (continued)

Avg. Depth	Ca mg/kg	Na mg/kg	Mg mg/kg	K mg/kg	Sr mg/kg	Al mg/kg	As mg/kg	Ba mg/kg	Co mg/kg	Zn mg/kg	Cr mg/kg	Cu mg/kg	Ni mg/kg	Pb mg/kg	V mg/kg	Fe mg/kg
6.75			0.00	0.00										228.06		
7.25		692.62	836.91	304.70			0.95		3.46		4.66	31.42	3.79	215.67	6.61	
7.75		595.88	878.05	305.83	79.44		3.57	65.35	4.07	>	5.56	29.82	5.04	265.45	7.00	12340.55
8.25			0.00	0.00										236.65		
8.75		711.28	1130.59	384.59	65.35		1.13	85.40	5.33		7.27	40.99	6.26	266.35	8.90	11382.58
9.25			0.00	0.00										242.80		
9.75		639.40	752.73	291.67	52.35	2712.81	1.14	65.31	3.70		4.45	31.64	3.99	251.92	7.34	8384.07
10.25		596.59	1015.67	333.45	64.20		4.82	65.40	5.27	>	6.43	35.46	6.71	303.38	9.05	14803.86
10.75			0.00	0.00										262.45		
11.25		642.35	1104.27	365.32	45.78		1.12	72.05	5.47		7.37		6.76	258.86	9.29	10044.24
11.75			678.70	247.11										292.75		
12.25		488.00	902.02	268.58	34.35	2580.99	1.28	66.32	3.85		4.01	30.53	4.22	302.07	7.44	7969.99
12.75		429.20			43.90		4.28	68.99	4.94	>	5.88	35.93	6.10		8.03	13488.58
13.25			1202.46	366.36										352.76		
13.75	15051.66	529.80			34.88		5.58	83.99	6.29	>	7.59		8.52	325.08	10.55	10588.81
14.25			866.63	297.97										327.03		
14.75	13738.71	496.06	903.73	259.44	30.55	2646.78	1.56	71.76	4.64		4.94	38.40	4.90	295.33	8.70	7957.16
15.25		368.83			43.00		4.09	69.58	4.88	>	5.87	35.52	6.13		8.17	13964.26
15.75			1359.34	375.74										370.98		
16.25	15598.77	480.57			32.89		5.19	69.65	7.27	>	9.16		9.40	298.89	11.50	10543.28
16.75			0.00	0.00												
17.25														329.34		9989.05
17.75	16863.27		0.00	0.00	37.17			69.15		>						13352.08

Table 5 (continued)

Avg. Depth	Ca mg/kg	Na mg/kg	Mg mg/kg	K mg/kg	Sr mg/kg	Al mg/kg	As mg/kg	Ba mg/kg	Co mg/kg	Zn mg/kg	Cr mg/kg	Cu mg/kg	Ni mg/kg	Pb mg/kg	V mg/kg	Fe mg/kg
18.25			1178.48	372.83												
18.75	11473.44	378.46			26.36		5.58	69.22	6.78		7.93		9.16	334.98	10.83	10179.98
19.25			0.00	0.00												
19.75	11207.02		1103.28	336.22	25.67	2843.11		73.59								8917.67
20.25	15448.37	317.06			34.62		6.43	67.24	6.83	>	7.69		8.08		10.60	13187.05
20.75			1247.27	373.34												
21.25	10706.35	321.19			27.25		4.94	79.31	7.38	>	8.65		9.68		11.14	11883.92
21.75			730.29	281.65												
22.25		265.47	900.73	262.43			6.49		5.21		4.65	35.03	5.45	291.76	8.90	7861.91
22.75	13343.31	206.74			31.68		4.72	69.23	5.61	>	6.41	33.47	6.91	339.33	8.72	13079.80
23.25			1042.49	356.08												
23.75	8438.08	225.02			20.83		3.93	57.18	6.81		7.32	37.33	8.64	214.12	9.55	9670.88
24.25			688.98	254.42												
24.75	7607.46	188.63	1008.26	310.50	20.25	2747.54	4.28	65.31	4.93	>	5.11	29.47	5.47	196.05	8.52	7834.72
25.25	12501.50	216.02			31.37		5.69	71.25	6.73	>	7.52	32.45	8.19	247.99	10.31	13519.34
25.75			945.35	310.73												
26.25		190.86					2.76		6.90		6.69	29.94	8.31	158.83	8.94	9405.70
26.75			786.73	260.69												
27.25		182.73	753.24	201.38			3.96		5.73		5.03	28.28	6.05	166.81	9.05	7532.01
27.75	9511.41	138.05			29.40		3.17	69.33	4.96	209.54	5.31	21.19	5.90	214.46	8.00	10782.80
28.25			957.26	274.82												
28.75	5984.66	162.06			20.76		4.44	80.13	8.50	120.08	14.20	28.12	14.51	170.94	9.40	9320.66
29.25			723.13	196.02												
29.75	5308.12	172.36	1094.01	276.24	17.65	2253.05	4.41	70.88	5.50	83.79	4.64	27.24	5.81	155.14	8.35	6012.13

Table 5 (continued)

Avg. Depth	Ca mg/kg	Na mg/kg	Mg mg/kg	K mg/kg	Sr mg/kg	Al mg/kg	As mg/kg	Ba mg/kg	Co mg/kg	Zn mg/kg	Cr mg/kg	Cu mg/kg	Ni mg/kg	Pb mg/kg	V mg/kg	Fe mg/kg
30.25										154.23						
30.75			1181.26	300.83												
31.25	8466.66	193.83			27.67		4.64	65.16	6.62	122.87	7.53	31.71	8.47	221.18	9.82	8359.64
31.75			726.06	226.11												
32.25	6755.13	201.94	787.43	228.14	23.85	2455.85	3.76	94.98	6.99	96.29	8.52	32.55	9.70	194.34	10.46	8132.27
32.75										179.83						
33.25	7573.10	198.22	1141.04	350.21	21.97		4.78	74.65	5.03		5.23	29.91	5.85	181.15	9.03	6587.40
33.75	11569.90	157.85			31.52		4.12	75.72	5.40	157.52	6.36	25.20	6.55	224.39	8.84	10941.89
34.25			804.49	275.26												
34.75	12163.90	223.78	0.00	0.00	29.40	2919.75	4.78	102.02	6.79	135.04	9.83	37.36	9.64	219.60	11.58	10609.03
35.25										157.73						
35.75	12133.54	220.06	1109.06	324.96	27.90		5.79	87.91	5.43		6.00	33.82	6.02	226.80	10.40	8874.68
36.25	12283.46				27.35		0.50	59.46		137.65				191.30		9857.83
36.75			730.28	261.41												
37.25	9646.06	226.94	972.64	301.35	24.40	2562.58	3.99	68.64	7.20	119.32	8.79	35.31	8.86	178.12	10.74	9084.96
37.75										183.42						
38.25	11679.73	228.32	1124.68	354.88	26.36		5.83	80.94	5.16		5.18	33.48	5.83	205.89	9.76	7434.73
38.75		207.67			32.43		5.36	57.98	5.58	168.82	7.99	33.21	7.74	195.72	10.97	10718.15
39.25			778.96	287.54												
39.75	17001.02	275.11	825.55	267.97	32.29	2745.60	5.21	82.03	6.47	162.28	9.45	38.86	9.12	201.63	11.95	9998.50
40.25										282.15						
40.75		245.83	1006.05	328.89	34.72		7.34	81.86	5.19		6.58	40.43	6.24	223.23	11.52	8811.40
41.25		214.02			46.96	3380.38	6.13	72.58	5.41	175.34	7.52	35.07	7.10	270.62	10.71	14348.06
41.75			648.86	241.64												

Table 5 (continued)

Avg. Depth	Ca mg/kg	Na mg/kg	Mg mg/kg	K mg/kg	Sr mg/kg	Al mg/kg	As mg/kg	Ba mg/kg	Co mg/kg	Zn mg/kg	Cr mg/kg	Cu mg/kg	Ni mg/kg	Pb mg/kg	V mg/kg	Fe mg/kg
42.25		276.66	1022.46	327.05	32.55	2528.15	6.19	62.46	6.15	179.88	8.75	39.05	8.91	190.26	12.13	10325.28
42.75										>						
43.25		227.46	668.84	198.30	35.45		6.70	79.06	4.71		5.14	31.27	5.49	203.19	10.05	9997.24
43.75		233.35			61.04	1981.82	15.76	61.04	6.48	47.49	7.45	34.82	8.55	247.84	12.22	
44.25			436.86	153.51												
44.75	3326.54	154.93	774.48	248.62	18.09	2189.69	6.47		5.82	155.06	5.24	29.45	7.86	208.06	8.53	5214.33
45.25										261.67						
45.75	597.30	151.71	885.57	285.63	16.09		6.06	53.91	4.55		3.34	29.53	5.50	229.48	7.78	9520.93
46.25	6152.71	173.57			22.58	3061.72	8.43	67.39	6.89	193.05	6.54		9.15	282.38	11.32	14184.74

Blanks indicate values not within the limits of the ICP. (>) indicate values extrapolated above the detection limits of the instrument.

APPENDIX D

SEQUENTIAL EXTRACTION: CORE

Table 6. Appendix D

Sample	Step	Mn			Sr			Ba			Zn			Al		
10	acetic acid	64*	±	2	12.7	±	0.3	19.9	±	0.5	> 210			64	±	16
	NH3OHCl	> 1020			19.9	±	4.3	103	±	19	958	±	59	2715	±	205
	H2O2 + CH3COONH4	49	±	16	6.8	±	0.8	14.3	±	1.9	> 118			1181	±	92
	aqua regia	232	±	34	4.9	±	0.8	< 1.5			229	±	39	> 2800		
	Total	899	±	54	24	±	1	90	±	6	1212	±	64	> 4 600		
11	acetic acid	8.3	±	0.6	3.1	±	0.3	10.5	±	1.1	8.4	±	0.7	204	±	31
	NH3OHCl	399	±	43	3.5	±	0.1	<8.5			17.8	±	1.1	1494	±	41
	H2O2 + CH3COONH4	22	±	3	7.1	±	0.3	15.1	±	0.6	13	±	1.7	> 1250		
	aqua regia	130	±	48	1.4	±	0.4	< 1.5			54	±	23	> 2800		
	Total	533	±	25	5	±	0.2	<30			91	±	4	> 4 600		
12	acetic acid	85	±	4	3.2	±	0.1	16.3	±	1	10.2	±	0.3	76	±	1
	NH3OHCl	764	±	20	3.6	±	0.2	< 9.5			16.9	±	1.2	1499	±	33
	H2O2 + CH3COONH4	32	±	1	1.43	±	0.11	12.3	±	1.4	10.2	±	0.3	868	±	21
	aqua regia	201	±	43	1.27	±	0.17	<1.6			87	±	4	> 3 100		
	Total	933	±	16	5.1	±	0.1	<34.1			100	±	0.4	4911	±	12

Table 6 (continued)

Sample	**Step**	**Na**			**Ca**			**Fe**			**Ti**			**Pb**		
10	acetic acid	26	±	2	4311	±	93	12.6	±	7.6	<1.11			8	±	0.9
	NH3OHCl	< 5			4540	±	689	4373	±	438	16.3	±	6.5	432	±	20
	H2O2 + CH3COONH4	150	±	5	1752	±	772	533	±	40	28	±	16	55	±	0
	aqua regia	25	±	6	1587	±	654	> 23 500			166	±	28	84	±	3
	Total	43	±	3	6955	±	397	> 21 000			258	±	19	419	±	22
11	acetic acid	16.5	±	0.8	528	±	27	16.8	±	2.9	< 0.64			1.62	±	0.04
	NH3OHCl	< 5			316	±	47	4496	±	143	13.8	±	0.4	71	±	4
	H2O2 + CH3COONH4	144	±	5	142	±	25	> 1380			7.7	±	1.6	8.3	±	1.6
	aqua regia	< 10			37	±	14	> 18 600			69	±	28	21	±	8
	Total	< 187			577	±	25	> 25 000			166	±	7	67	±	2
12	acetic acid	29	±	7	971	±	21	9.2	±	2.3	0.61	±	0.4	1.75	±	0.31
	NH3OHCl	< 5			670	±	50	2427	±	79	12.3	±	0.2	85	±	3
	H2O2 + CH3COONH4	151	±	3	134	±	148	> 770			24	±	11	7.3	±	0.3
	aqua regia	17.7	±	1.6	62	±	46	> 26 100			97	±	26	21	±	2
	Total	< 213			1265	±	4	> 23 000			127	±	2	84	±	1

Table 6 (continued)

Sample	**Step**	**Co**			**Ni**			**Cu**			**V**			**Cr**		
10	acetic acid	ND			1.21	±	0.03	1.78	±	0.07	0.91	±	0.09	0.74	±	0.19
	NH3OHCl	< 6.0			22	±	14	< 4.3			26	±	16	< 3.3		
	H2O2 + CH3COONH4	<5.8			3	±	0.1	25	±	2	5.3	±	0.9	6	±	0.7
	aqua regia	< 1.0			10.4	±	2.6	22	±	4	16.8	±	3.1	17.1	±	3.6
	Total	< 6.2			18.4	±	1	66	±	5	< 70			24	±	1
11	acetic acid	ND			1.24	±	0.04	1.36	±	0.29	0.71	±	0.11	0.66	±	0.2
	NH3OHCl	< 5.8			27	±	0	< 4.2			< 3.2			< 2.7		
	H2O2 + CH3COONH4	< 0.60			3.6	±	0.2	12.3	±	1.4	4.2	±	0.6	5.4	±	0.1
	aqua regia	< 1.0			8.1	±	2.4	13.7	±	5.5	13.4	±	3.4	11.4	±	3.2
	Total	< 6.1			16.4	±	0.3	32	±	1	25	±	1	19.8	±	0.4
12	acetic acid	ND			1.41	±	0.22	0.7	±	0.12	0.74	±	0.25	0.54	±	0.06
	NH3OHCl	< 6.5			31	±	1	< 4.8			< 3.6			< 3.0		
	H2O2 + CH3COONH4	0.92	±	0	4.04	±	0.44	3.9	±	0.3	3.7	±	0.3	5.3	±	0.6
	aqua regia	< 1.1			14.54	±	1.03	19.1	±	1	21	±	2	19.8	±	1.1
	Total	< 6.9			21	±	0	< 50			26	±	0.3	24	±	0.3

*all values in ppm.

APPENDIX E

WATER QUALITY

Using a Hach Environmental Hydrolab® water quality mini-sonde, the water quality of the lake was measured. The water quality results are as follows: Temperature, 11.26˚C, Specific Conductivity, 0.686, Dissolved Oxygen, 9.43, pH 8.17, and Depth, 1m.

APPENDIX F

ICP OUTPUT AND DETECTION LIMITS

Table 7. Appendix F

Avg. Depth	Ca (d)	Na	Sr (d)	Al (d)	As (d)	Ba	Co	Cr	Cu	Ni	Pb (d)	V	Fe
0.25	#569*	48.8600	0.866	>33.94*	0.0713	0.673	0.2904	0.4100	0.519	0.3588	2.155	0.5120	98.3
0.75					0.0523				0.4702		1.827		>103.0
1.25		66.8000			0.0137		0.4255	0.5730	0.3966	0.5480	1.602	0.7080	>50.4
1.75					0.0306				0.4233		1.668		>100.2
2.25	#466.2	79.1000	0.659	20.71	0.0721	0.724	0.2785	0.3425	0.3694	0.3020	1.951	0.5290	65
2.75	#530	44.5300	0.767	>33.51	0.0709	0.595	0.2926	0.3838	0.4956	0.3374	2.139	0.4973	101.1
3.25					0.0384				0.4511		1.798		>103.9
3.75		63.3000	0.655		0.0382	0.786	0.4224	0.5400	0.4503	0.4554	2.017	0.5910	95.6
4.25					0.037				0.4696		1.866		>108.7
4.75		63.5000	0.55	19.28	0.053	0.559	0.2869	0.3731	0.3067	0.2927	1.626	0.5320	60.8
5.25	#508	62.8000	0.732	>35.36	0.0675	0.562	0.3819	0.5260	0.4914	0.4528	2.08	0.6910	101.7
5.75					0.0061				0.4017		1.888		>62.5
6.25	>456	65.6000	0.592	27.27	0.042	0.748	0.4249	0.5640	0.3807	0.5430	1.837	0.7110	77
6.75					0.0405				0.4738		1.91		>113.3

Table 7 (continued)

Avg. Depth	Ca (d)	Na	Sr (d)	Al (d)	As (d)	Ba	Co	Cr	Cu	Ni	Pb (d)	V	Fe
7.25		57.6000			0.0016		0.2881	0.3873	0.3677	0.3152	1.693	0.5500	>57.3
7.75	#472.3	49.8800	0.665	>37.16	0.0765	0.547	0.3405	0.4657	0.4968	0.4221	2.222	0.5860	103.3
8.25					0.0358				0.4622		1.972		>106
8.75		59.2000	0.515		0.0482	0.673	0.4436	0.6050	0.3958	0.5210	2.099	0.7410	89.7
9.25					0.0434				0.4422		2.021		>104.1
9.75		53.6000	0.3921	20.32	0.0553	0.4892	0.3102	0.3734	0.3047	0.3347	1.887	0.6150	62.8
10.25	>342.7	49.8100	0.536	>42.53	0.075	0.546	0.4403	0.5370	0.542	0.5600	2.533	0.7560	123.6
10.75					0.0473				0.4778		2.176		>117.1
11.25		53.4000	0.3806		0.0554	0.599	0.4548	0.6130	0.4163	0.5620	2.152	0.7720	83.5
11.75					0.0368				0.514		2.45		>119.5
12.25		40.8400	0.2875	21.6	0.0765	0.555	0.3218	0.3356	0.3486	0.3528	2.528	0.6230	66.7
12.75	>183.6	36.0200	0.3684	>41.69	0.0278	0.579	0.4147	0.4937	0.586	0.5120	>3.084	0.6740	113.2
13.25					0.0349				0.3839		2.388		>51.8
13.75	125.8	44.2800	0.2915	>33.04	0.0598	0.702	0.5260	0.6340	0.456	0.7120	2.717	0.8820	88.5
14.25					0.029				0.4289		2.429		>56.6
14.75	114.3	41.2700	0.2542	22.02	0.0497	0.597	0.3862	0.4108	0.3517	0.4079	2.457	0.7240	66.2
15.25	>158.4	30.8500	0.3597	>43.94	0.0689	0.582	0.4083	0.4909	0.563	0.5130	>3.045	0.6830	116.8
15.75					0.0476				0.501		2.831		>74.6
16.25	129.9	40.0200	0.2739	>33.22	0.0502	0.58	0.6050	0.7630	0.4433	0.7830	2.489	0.9580	87.8
16.75					0.0655				0.539		>3.076		>80.6
17.25					0.0764				0.3903		2.786		84.5
17.75	141.2	31.7200	0.3112	>39.54	0.0878	0.579	0.5360	0.6520	0.584	0.6350	>3.133	0.8640	111.8
18.25					0.0444				0.522		>3.414		>72.3
18.75	95.8	31.6000	0.2201		0.0494	0.578	0.5660	0.6620	0.4201	0.7650	2.797	0.9040	85
19.25					0.0459				0.4478		>3.053		>61.4
19.75	93.5		0.2142	23.72	0.0752	0.614			0.4142				74.4
20.25	129.8	26.6400	0.2909	>40.71	0.0886	0.565	0.5740	0.6460	0.614	0.6790	>3.649	0.8910	110.8
20.75													
21.25	89.1	26.7300	0.2268	>34.62	0.0497	0.66	0.6140	0.7200	0.4611	0.8060	>2.987	0.9270	98.9

Table 7 (continued)

Avg. Depth	Ca (d)	Na	Sr (d)	Al (d)	As (d)	Ba	Co	Cr	Cu	Ni	Pb (d)	V	Fe
21.75													
22.25		22.3200			0.0761		0.4379	0.3908	0.3136	0.4581	2.453	0.7480	66.1
22.75	111.4	17.2600	0.2645	>40.08	0.0625	0.578	0.4687	0.5350	0.55	0.5770	2.833	0.7280	109.2
23.25													
23.75	70.5	18.8000	0.174		0.0333	0.4777	0.5690	0.6120	0.3223	0.7220	1789	0.7980	80.8
24.25													
24.75	63.6	15.7700	0.1693	22.97	0.0316	0.546	0.4125	0.4272	0.2516	0.4570	1.639	0.7120	65.5
25.25	104.4	18.0400	0.262	>38.15	0.0755	0.595	0.5620	0.6280	0.4274	0.6840	2.071	0.8610	112.9
25.75													
26.25					0.0288		0.5770	0.5600	0.2724	0.6950	1.329	0.7480	78.7
26.75		15.9700											
27.25		15.2600			0.0383		0.4788	0.4203	0.2424	0.5050	1.393	0.7560	62.9
27.75	79.3	11.5100	0.2451	>35.16	0.0614	0.578	0.4132	0.4424	0.3678	0.4921	1.788	0.6670	89.9
28.25													
28.75	49.89	13.5100	0.1731	>31.41	0.0293	0.668	0.7090	1.1840	0.27	1.2100	1.425	0.7840	77.7
29.25													
29.75	44.41	14.4200	0.1477	18.85		0.593	0.4600	0.3884	0.2327	0.4860	1.298	0.6990	50.3
30.25	71.2	16.3000	0.2327	>31.18	0.0545	0.548	0.5570	0.6330	0.34	0.7120	1.86	0.8260	70.3
30.75													
31.25	56.9	17.0100	0.2009	>30.89	0.0354	0.8	0.5890	0.7180	0.2957	0.8170	1.637	0.8810	68.5
31.75													
32.25	63	16.4900	0.1828	20.43	0.0432	0.621	0.4181	0.4349	0.2576	0.4865	1.507	0.7510	54.8
32.75	95.8	13.0700	0.261	>42.41	0.0654	0.627	0.4469	0.5270	0.3884	0.5420	1.858	0.7320	90.6
33.25													
33.75	101.7	18.7100	0.2458	>33.97	0.0425	0.853	0.5680	0.8220	0.3336	0.8060	1.836	0.9680	88.7
34.25													
34.75	100.9	18.3000	0.232	24.28	0.0535	0.731	0.4513	0.4992	0.3064	0.5010	1.886	0.8650	73.8
35.25	102.8	16.2500	0.2289	>29.18	0.0608	0.4976		0.6190	0.3275	0.6240	1.601	0.8320	82.5
35.75							0.4966						
36.25	80.8	19.0100	0.2044	>30.42	0.038	0.575	0.6030	0.7360	0.2935	0.7420	1.492	0.9000	76.1
36.75													

Table 7 (continued)

Avg. Depth	Ca (d)	Na	Sr (d)	Al (d)	As (d)	Ba	Co	Cr	Cu	Ni	Pb (d)	V	Fe
37.25	97.4	19.0400	0.2198	21.37	0.0463	0.675	0.4299	0.4321	0.2934	0.4860	1.717	0.8140	62
37.75	>146.5	17.3800	0.2714	>29.99	0.0538	0.4852	0.4670	0.6690	0.3442	0.6480	1.638	0.9180	89.7
38.25													
38.75	143	23.1400	0.2716	>32.43	0.043	0.69	0.5440	0.7950	0.3469	0.7670	1.696	1.0050	84.1
39.25													
39.75		20.4500	0.2888	22.84	0.0724	0.681	0.4318	0.5470	0.345	0.5190	1.857	0.9580	73.3
40.25	>253.3	17.8100	0.3908	>37.79	0.1066	0.604	0.4498	0.6260	0.514	0.5910	2.252	0.8910	119.4
40.75													
41.25	>163.1	22.9900	0.2705	28.09	0.0592	0.519	0.5110	0.7270	0.3495	0.7400	1.581	1.0080	85.8
41.75													
42.25	>173.3	18.9300	0.295	21.04	0.0834	0.658	0.3918	0.4274	0.3366	0.4570	1.691	0.8360	83.2
42.75	>180.6	19.6500	0.514	>38.15	0.2409	0.514	0.5460	0.6270	0.4816	0.7200	2.087	1.0290	>167.7
43.25													
43.75	28.3	13.1800	0.1539	1.686	0.0736		0.4953	0.4456	0.3236	0.6690	1.77	0.7260	44.36
44.25													
44.75	5	12.7000	0.1347	18.33	0.0716	0.4513	0.3813	0.2800	0.3322	0.4601	1.921	0.6510	79.7
45.25	51.4	14.5000	0.1886	>31.06	0.1113	0.563	0.5760	0.5460	0.4542	0.7640	2.359	0.9460	118.5
45.75													
46.25	34.95	18.8000	0.1451	25.93	0.05	0.4884	0.5830	0.5920	0.3711	0.9220	1.974	0.9430	83.7
calculated detection limit, lower range	0.0070	0.0085	0.2969	0.1340	0.0424		0.0065	0.0134	0.0128	0.0142	0.0122	0.0202	0.0233

*(#) indicates a value causing integrator overload and (>) indicates a value above the upper calibration curve, (d) indicates a sample that required dilution.

BIBLIOGRAPHY

Abbott, Mark B. and Wolfe, Alexander P. 2003. Intensive Pre-Incan Metallurgy Recorded by Lake Sediments from the Bolivian Andes. Science 301: 1893-1895.

Armhein, Christopher and Strong, James E. 1990. The Effect of Deicing Salts on Trace Metal Mobility in Roadside Soils. Journal of Environmental Quality 19: 765-772.

Bindler, R. 2006. Mired in the past – looking to the future: Geochemistry of peat and the analysis of past environmental changes. Global Planet Change 53: 209-221.

Chen, Jianhua, Zheng, Hongfeng, Wang, Wei, Liu, Hongjie, Lu, Ling, Bao, Linfa, and Ren, Lihong. 2006. Resuspension method for road surface dust collection and aerodynamic size distribution characterization. China Particulology 4 (6): 300-303.

Ciocco, Antonio D.Sc., F.A.P.H.A. and Thompson, Donovan J. Ph.D., F.A.P.H.A. 1961. A FOLLOW-UP OF DONORA TEN YEARS AFTER: METHODOLOGY AND FINDINGS. Journal of Public Health 51 (2): 155-164.

Coal Utilization. 2005. Encyclopædia Brittanica. Encyclopædia Brittanica Premium Service, http://www.britannica.com/eb/article-81715 (accessed October 6, 2005).

Cooke, C.A., Abbott, M.B., Wolfe, A.P., Kittleson, J.L. 2007. A Millennium of Metallurgy Recorded by Lake Sediments from Morococha, Peruvian Andes. Environmental Science and Technology 41: 3469-3474.

Couillard, Yves, Courcelles, Michel, Cattaneo, Antonella, and Wunsam, Sybille. 2004. A test of the integrity of metal records in sediment cores based on the documented history of metal contamination in Lac Dufault (Quebec, Canada). Journal of Paleolimnology 32: 149-162.

Dean, Walter E., Jr. 1974. Determination of Carbonate and Organic Matter in Calcareous Sediments and Sedimentary Rocks by Loss on Ignition: Comparison with other methods. Journal of Sediment Petrology 44: 242-248.

EPA. 2000. Method 6010C (SW-846): Inductively Coupled Plasma-Atomic Emission Spectrometry, Revision 3. http://www.epa.gov/sam/pdfs/EPA-6010c.pdf (accessed November 13, 2008).

EPA. 2008a. History of the Clean Air Act. http://www.epa.gov/oar/caa/caa_history.html (accessed October 1, 2008).

EPA. 2008b. Clean Air Act. http://epw.senate.gov/envlaws/cleanair.pdf (accessed November 5, 2008).

EPA. 2008c. Arsenic in Drinking Water. http://www.epa.gov/safewater/arsenic/index.html (accessed November 30, 2008).

Erel, Yigal, Vernon, Alain, and Halicz, Ludwik. 1997. Tracing the transport of anthropogenic lead in the atmosphere and in soils using isotopic ratios. Geochimca et Cosmochimica Acta 61 (21): 4495-4505.

Fleming, James R. and Knorr, Bethany R. 2008. History of the Clean Air Act. http://www.ametsoc.org/Sloan/cleanair/index.html (accessed October 1, 2008).

Frandsen, Flemming, Dam-Johansen, Kim, and Rasmussel, Peter. 1994. Trace elements from combustion and gasification of coal—An Equilibrium approach. Progress in Energy and Science 20: 115-138.

Gasse, Francoise. 2001. Paleoclimate: Hydrological Changes in Africa. Science 292: 2259-2260.

Gugliotta, Angela. 2003. How, When, and for Whom Was Smoke a Problem in Pittsburgh?. In *Devastation and Renewal The Environmental History of Pittsburgh and its Region*, ed. Joel A. Tarr, 110-126. Pittsburgh, PA: University of Pittsburgh Press.

Hieri, Oliver, Lotter, Andre F., and Lemcke, Gerry. 2001. Loss on ignition as a method for estimating organic and carbonate content in sediments: reproducibility and comparability of results. Journal of Paleolimnology 25: 101-110.

Hong, S., Cadelone, J.-P., Patterson, C.C., and Boulton, C.F. 1994. Greenland Ice Evidence of Hemispheric Lead Pollution Two Millenia Ago by Greek and Roman Civilizations. Science 265: 1841-1843.

Hong, S. Cadelone, J.-P., Patterson, C.C., Boulton, C.F. 1996. History of Ancient Copper Smelting Pollution During Roman and Medieval Times Recorded in Greenland Ice. Science 272: 246-249.

Koerner, R.M. 1977. Devon Island Ice Cap: Core Stratigraphy and Paleoclimate. Science 196: 15-18.

Lankey, Rebecca L., Davidson, Cliff I. and McMichael, Francis C. 1998. Mass Balance for Lead in the California South Coast Air Basin: An Update. Environmental Research 78 (2): 86-93.

Magill, Frank N., ed. 1995. *Great Events From History II: Ecology and the Environment Series.* 2-5. Englewood Cliffs, NJ: Salem Press.

Merschon, Sherrie R. and Tarr, Joel A. 2003. Strategies for Clean Air: The Pittsburgh and Allegheny County Smoke Control Movements. In *Devastation and Renewal The Environmental History of Pittsburgh and its Region*, ed. Joel A. Tarr, 145-174. Pittsburgh, PA: University of Pittsburgh Press.

Mitchell, Tom. 2008. Townships scramble to find road salt. Leader-Times, October 31.

Mudgway, L.B., Duncan, H.P., McMahon, T.A., and Chiew, F.H.S. 1997. Best Practice Environmental Management Guidelines for Urban Stormwater: Background Report to the Environment Protection Authority, Victoria, Melbourne Water Corporation and the Department of Natural Resources and Environment, Victoria. Cooperative Research Center for Catchment Hydrology Report 97: 7: 3.

Murozumi, M., Chow, T.J., and Patterson, C. 1969. Chemical concentrations of pollutant lead aerosols, terrestrial dusts and sea salts in Greenland and Antarctic snow strata. Geochim. Cosmochim. Acta 33: 1247-1294.

Nriagu, Jerome O. 1996. A History of Global Metal Pollution. Science 272: 223-224.

Nriagu, Jerome O. 1979. Global Inventory of Natural and Anthropogenic Emissions of Trace Metals to the Atmosphere. Nature 279:409.

PA DEP. 2004. Monitoring Pollutants in Rain. http://www.dep.state.pa.us/dep/DEPUTATE/airwaste/aq/acidrain/acidrain.htm (accessed October 7, 2008).

PA DEP. 2008. Choose your watershed. http://www.dep.state.pa.us/dep/deputate/watermgt/WC/Subjects/WSNoteBks/shedtable.htm (accessed May 6, 2008).

Pittsburgh Parks Conservancy. 2004. Historical Archives from 1842-2003. 2000 Technology Drive, Suite 300, Pittsburgh, PA 15219.

Pittsburgh Parks Conservancy. 2008. Showcase Projects Ecological Restoration. http://www.pittsburghparks.org/_24.php (accessed October 8, 2008).

Pueyo, M., Sastre, J., Hernandez, E., Vidal, M., Sanchez, J.F. Lopez, and Rauret, G. 2003. Prediction of trace element mobility in contaminated soils by sequential extraction. Journal of Environmental Quality 32: 2054-2066.

Rose, N.L. 1990. An Extraction Method for Carbonaceous Particles from Lake Sediments. Journal of Paleolimnology 4: 61-68.

Rose, Neil. 2001. 12. Fly-ash Particles. *In Tracking Environmental Change Using Lake Sediments. Volume 2: Physical and Geochemical Methods.* eds. W.M. Last and J.P. Smol, 319-349. Boston: Kluwer Academic Publishers.

Rose, Neil L. 1994. A Note on Further Refinements to a Procedure for the Extraction of Carbonaceous Fly-ash Particles from Sediments. Journal of Paleolimnology 11: 201-204.

Rauret, G., Sanchez, J.F. Lopez, Sahuquillo, A., Rubio, R., Davison, C., Ure, A., and Quevauviller, P. 1999. Improvement of the BCR Three Step Sequential Extraction Procedure Prior to the Certification of New Sediment and Soil Reference Materials. Journal of Environmental Monitoring 1: 57-61.

Renberg, I., Persson, M.W., and Emteryd, O. 1994. Pre-industrial atmospheric lead contamination detected in Swedish lake sediments. Nature 368: 323-326.

Sarkar, Dibyendu, Datta, Rupali, and Sharma, Saurabh. 2004. Fate and bioavailability of arsenic in organo-arsenical pesticide-applied soils.: Part-I: incubation study. Chemosphere 60 (2): 188-195.

Sehmel, G.A. 1973. Particle resuspension from an asphalt road caused by car and truck traffic. Atmospheric Environment 7 (3): 291-309.

Shifeng, Dai, and Chou, Chenlin. 2008. Fly ash-airborne particles from Ptolemais-Kozani area, northern Greece, as determined by ESEM-EDX. International Journal of Coal Geology 73 (1): 67-73.

Smol, John P. 2002. Pollution of Lakes and Rivers A Paleoenvironmental Perspective. Oxford University Press, New York, NY. *xxii-xxiii.*

Sutherland, Ross A. 2002. Comparison between non-residual Al, Co, Cu, Fe, Mn, Ni, Pb, and Zn released by a three-step sequential extraction procedure and a dilute hydrochloric acid leach for soil and road deposited sediment. Applied Geochemistry 17: 353-365.

Tarr, Joel A. and Lamperes, Bill C. 1981. Changing Fuel Use Behavior and Energy Transitions: The Pittsburgh Smoke Control Movement, 1940-1950: A Case Study in Historical Analogy. Journal of Social History, Special Issue on Applied History (Summer, 1981) 14 (4): 561-588.

Tarr, Joel A. 2003. The Interaction of Natural and Built Environments in the Pittsburgh Landscape. In *Devastation and Renewal The Environmental History of Pittsburgh and its Region*, ed. Joel A. Tarr, 11-41. Pittsburgh, PA: University of Pittsburgh Press.

United States Geological Survey (USGS). 2005. USGS High Resolution Orthoimage for the Pittsburgh, PA (Allegheny and Beaver Counties), Urban Area. www.pasda.psu.edu (accessed September 29, 2008).

The United States Steel Corporation. 2005. Annual Reports Archives from 1901-2005. 600 Grant St # 450 Pittsburgh, PA 15219.

The University of Texas at Austin. 2007. Map of Pittsburgh, PA showing the location of its furnaces, rolling mills, and steel works, May 8th, 1879.

http://www.lib.utexas.edu/maps/historical/pittsburgh_iron_steel_1879.jpg Feb 22, 2007 (accessed February 22, 2007).

Vermillion, Brian, Brugam, Richard, Retzlaff, William, and Bala, Indu. 2005. The sedimentary record of environmental lead contamination at St. Louis, Missouri (USA) are smelters. Journal of Paleolimnology 33: 189-203.

Voynick, Joyce, and Hill, Col. Stephen L. 2005. U.S. Army Corps of Engineers – Pittsburgh District A Reflection of Transportation. Pittsburgh ENGINEER, PEfall05: 13-15.