Old Dominion University

ODU Digital Commons

Summer 2004

Anthropogenic Lead Deposition and Four National Parks in Poland as Determined by Lead Isotope Ratios

Shannon Simcoe
Old Dominion University

Recommended Citation

ANTHROPOGENIC Pb DEPOSITION IN FOUR NATIONAL PARKS IN POLAND AS DETERMINED BY Pb ISOTOPE RATIOS

by

Shannon Simcoe
B.S. May 2002, Old Dominion University

A Thesis Submitted to the Faculty of
Old Dominion University in Partial Fulfillment of the
Requirement for the Degree of

MASTER OF SCIENCE

GEOLOGY

OLD DOMINION UNIVERSITY

AUGUST 2004

Approved by:

Joseph H. Rule (Director)

Dennis A. Darby (Member)

Zhongxing Chen (Member)

ABSTRACT

ATMOSPHERIC Pb DEPOSITION IN FOUR NATIONAL PARKS IN POLAND AS DETERMINED BY Pb ISOTOPE RATIOS

Shannon Simcoe
Old Dominion University, 2002
Director: Dr. Joseph Rule

Polluted soils are recognized by having high concentrations of heavy metals, including Pb. Partitioning of metals in geochemical fractions, by sequential chemical extractions, may indicate whether a metal has been recently deposited in the soil. While concentration levels alone cannot distinguish between natural and anthropogenic Pb, studies have demonstrated that anthropogenic pollution is accurately recorded by specific Pb isotope signatures, which differ from natural Pb isotopes. The objective of this project was to use $^{206}Pb/^{207}Pb$ and $^{206}Pb/^{204}Pb$ isotope ratios to differentiate between the anthropogenic Pb input and the naturally occurring Pb in four national parks in Poland. A second goal was to test the postulate that sequential chemical extractions could be used to evaluate the pollution status of the soils. Soils from Tatry National Park underwent sequential chemical extractions and total acid extractions, while soils from Biesczcady National Park, Roztocze National Park, and Poleski National Park underwent total acid extractions. This project supports the fact that by coupling Pb isotope signatures with Pb concentrations in different geochemical phases an accurate characterization of soil pollution status may be reached. Soils in all of the national parks in this study contain Pb isotope ratio signatures indicative of anthropogenic Pb. Isotope signatures recorded from soil samples taken within Biesczcady National Park and Roztocze National Park indicate that anthropogenic Pb is dominant. Soil samples from Poleski National Park show

mostly Pb isotope signatures indicative of anthropogenic Pb in surface samples, while most subsurface samples contain Pb isotope signatures consistent with natural Pb. In Tatry National Park, a majority of the total and sequential chemical extraction Pb isotope ratios recorded indicate anthropogenic input. In soil samples that portrayed natural total Pb isotope signatures, there were still anthropogenic Pb isotope signatures present in the more easily soluble geochemical phases. This indicates that these soils have been affected by Pb pollution. Data from this portion of the study is consistent with the postulate that elevated amounts of Pb in the more easily soluble geochemical phases indicate anthropogenic input. The Pb pollution in the soils is most likely attributed to the release of local automobile emissions and atmospheric deposits of industrial emissions originating in Upper Silesia and Slovakia.

ACKNOWLEDGMENTS

I would like to thank Dr. Joseph Rule, Dr. Dennis Darby, and Dr. Zhongxing Chen for their guidance throughout this project. I would especially like to thank Dr. Rule for the numerous hours he gave me, and his constant support. I am grateful to my parents, Tom and Barb Simcoe, for their support. I greatly appreciate Michael Labocki for his care and patience through all stages of this project.

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

CHAPTER I

INTRODUCTION

More than 95% of the Pb deposited in the soils and sediment is of anthropogenic origin (Luck and Othman, 2002). Anthropogenic Pb is added to soil by atmospheric dust settling and precipitation scavaging (Flament et. al., 2002). High concentrations of Pb in surface soils are frequently attributed to coal ash, Pb additives in gasoline, metal mining and smelting activities, and agricultural input (Semlali et. al., 2001). Up to 53% of the anthropogenic Pb input is due to gasoline consumption of tetraethyl lead (Farmer et. al., 1996). Natural Pb is transported to sediment or soil by the weathering of Pb rich soils or bedrock (Renberg et. al., 2002).

Polluted soils are generally recognized by having elevated concentrations of Pb and other heavy metals. Concentration levels alone cannot distinguish between natural and anthropogenic Pb sources. Lead isotope studies have demonstrated that anthropogenic pollution is accurately recorded by specific Pb isotopic signatures, which differ from those of natural Pb isotopes (Hansmann and Koppel, 2000).

The four stable naturally occurring Pb isotopes are: ^{206}Pb (formed by the decay of ^{238}U), ^{207}Pb (formed by the decay of ^{235}U), ^{208}Pb (formed by the decay of ^{232}Th), and ^{204}Pb (not decay product)(Charalampides and Manoliadis, 2002). When the common lead ore galena (PbS) is mined, its isotopic signature is fixed in time. Meanwhile, the reservoir will continue to evolve because it still contains concentrations of U and Th. The differences in fixed Pb signatures versus changing signatures will allow us to

---

The model journal for this thesis was the Journal of Environmental Quality.

recognize extracted and processed Pb from natural Pb (Chiaradia and Cuplin, 2000).

$^{206}Pb/^{207}Pb$ ratio is the most widely used Pb isotope ratio in studies because it can be the most accurately measured (Watmough et. al., 1999). Other ratios commonly used in Pb isotope studies include $^{206}Pb/^{204}Pb$, $^{207}Pb/^{204}Pb$, $^{208}Pb/^{204}Pb$, $^{207}Pb/^{206}Pb$, $^{208}Pb/^{206}Pb$ and $^{207}Pb/^{208}Pb$.

Anthropogenic Pb is commonly derived from ore bodies, which tend to have distinctly lower $^{206}Pb/^{207}Pb$ and $^{206}Pb/^{204}Pb$ ratios. Natural (unpolluted) soils and sediments have a $^{206}Pb/^{207}Pb$ signature of 1.20-1.24 (Aberg et. al., 2001; Marcantonio et. al., 2002; Semlali et. al., 2001), and a $^{206}Pb/^{204}Pb$ signature >18.8 (Hansmann and Koppel, 2000). $^{206}Pb/^{207}Pb$ and $^{206}Pb/^{204}Pb$ ratios will be discussed further in my analysis simply because there is more scientific reference data available for these ratios.

Some of the most important lead ores in the world are located in Australia ($^{206}Pb/^{204}Pb$=16.0-16.1), Europe ($^{206}Pb/^{204}Pb$=17.9-18.4) and North America ($^{206}Pb/^{204}Pb$= >19) (Hansmann and Koppel, 2000). Ore signatures vary slightly, depending on the age of the ore, and the specific time of mining. Other significant Pb isotopic signatures are included in Table 1.

Heavy metals are not held uniformly by soil. Lead commonly accumulates in the surface soil, and tends not to migrate lower in the soil profile. This type of behavior indicates the persistent nature of Pb in soils and its relative immobility. This lack of movement indicates that lead is being stored rather than being dispersed by natural processes (Bacon et. al., 1996).

Sequential chemical extraction techniques have been used to help characterize chemical forms of trace elements in soils. This characterization helps determine trace

element environmental availability, toxicity and hazards to living organisms. There are

many different ways sequential chemical extractions can be performed. A basic

requirement for any selective chemical extraction sequence procedure is that it should be

able to dissolve specific components of the soil. It also should provide information on

the trace element behavior in soils over time and at various concentrations, and provide

insight into how that behavior affects organisms' uptake of trace elements (Berti et. al.,

1995).

Partitioning of metals in geochemical fractions, by sequential chemical

extractions, may indicate whether a metal has been recently deposited in the soil.

Recently deposited metals are thought to be more abundant in easily soluble phases

(Rule, 2003).

Table 1. Commonly used Pb isotopic signatures ([a] Hansmann and Kopell, 2000; [b] Flament et. al., 2002; [c] Maracantoino, et. al., 2002; [d] Charalampides and Manoliadis, 2002; [e] Aberg et. al., 2001; [f] Semlali et. al., 2001; [g] Watmough et. al., 1999).

	$^{206}Pb/^{204}Pb$	$^{208}Pb/^{204}Pb$	$^{207}Pb/^{206}Pb$	$^{206}Pb/^{207}Pb$
European ore	17.9-18.4[a]			
Australian ore	16.0-16.1[a]			1.03-1.04[b]
Mississippi Valley ore	>19.0[a]			1.28-1.33[c]
Sweden ores				0.99-1.04[b]
Morocco ores				1.16-1.18[b]
European gasoline				1.10[d,e]
Greek gasoline				1.20[d] 1.06[e]
Italy gasoline				1.067-1.155[b]
Switzerland gasoline				1.075-1.136[b]
Hungarian gasoline				1.07[e]
Austrian gasoline				1.11[e]
French gasoline				1.069-1.094[f]
Swiss Fly ash/industrial	17.95[a]	37.8[a]	1.15[a]	
France Fly ash/industrial	17.98-18.06[a]	37.95-38.25[a]	1.14-1.15[a]	1.143-1.155[f]
Germany Fly ash/industrial			1.14-1.16[a]	
Belgian coal	18.28-18.57[a]			
U.K. coal				1.18[g]

The leaching of soils with strong acid allows for the separation of anthropogenic lead from natural lead (Zhu et. al., 2001). Nearly 95% of anthropogenic Pb can be removed by a strong acid extraction (Monna et. al., 1999). The natural Pb in the soil will remain in the residual phase (Rule, 2003).

Previous Pb Isotope Studies

Lead isotopic studies have been utilized in a number of different ways, by a variety of different scientists. Charalampides and Manoliadis (2002) used Sr and Pb isotopes as environmental indicators of pollution in western Macedonia, Greece. They gathered samples from a nearby lignite mining area ($^{206}Pb/^{207}Pb= 1.20$), an air filter close to the town ($^{206}Pb/^{207}Pb= 1.12$), and wheat samples. By using Pb isotopic signatures they were able to determine that the isotopic signature of the wheat more closely matched that of the air filter than the lignite mining area, suggesting that atmospheric deposition of Pb was the main cause of their polluted wheat.

Stable Pb isotopes have been used by scientists to construct historical records of Pb input in environments worldwide. Watmough et. al. (1999) used Pb isotope ratios and Pb concentrations in tree rings to monitor environmental changes from 1965 to present day in northwest England. By comparing sycamore tree ring samples, this group of scientists was able to correlate changes in $^{206}Pb/^{207}Pb$ ratios to historical dates. For example, they found an increase in $^{206}Pb/^{207}Pb$ ratios in tree rings formed in 1993 and attribute this increase in ratios to the reduction of Pb additives in vehicle emissions. Watmough et. al. (1999) were able to conclude that $^{206}Pb/^{207}Pb$ ratios in sycamore tree rings may be used to document historical changes in sources and boiavailability of Pb in an area.

Lead isotopes and Pb concentrations in Lake Geneva, France were measured in order to investigate the origin and history of Pb inputs in the lake. Samples were collected from many areas in and around the lake, and $^{206}Pb/^{207}Pb$, $^{208}Pb/^{204}Pb$, and $^{206}Pb/^{204}Pb$ ratios were compared. Material was dated by cosmogenic ^{210}Pb and ^{137}Cs methods. Based on their data, Monna et. al. (1999) were able to construct a stable Pb isotope record dating back almost 150 years, and were able to distinguish predominant contamination sources during this time period. Renberg et. al. (2002) conducted a similar study in lake sediments in 31 lakes in Sweden. $^{206}Pb/^{207}Pb$ ratios were used to show changes in the pollution trend over time. Both groups of scientists concluded that over the last 20 years gasoline-derived Pb accounted for a minor portion of Pb contamination in the area, while most of the contamination stemmed from industrial and domestic activities.

Some scientists have used more unconventional techniques to differentiate between recent and ancient sources of pollution. Aberg et. al. (2001) collected recent and ancient teeth samples, in western Macedonia, Greece, and compared the Pb isotopic signatures of them to samples collected at a lignite mine, air filter samples, and wheat samples all from the same area. By comparing the Pb isotopic signatures from the samples they collected to Pb isotopic signatures derived from other sources, they were able to conclude that the $^{206}Pb/^{207}Pb$ ratios of the teeth samples were closely related to the $^{206}Pb/^{207}Pb$ ratios collected from the local lignite mine site. This conclusion infers that a majority of the local pollution in this area was caused by lignite mining activities.

Isotope ratios of Pb are commonly employed to determine anthropogenic Pb from natural Pb in soil and air samples, and to distinguish between possible anthropogenic

sources (Flament et. al., 2002; Hansmann and Koppel, 2000; Monna et. al., 1999; Renberg et. al., 2002; and Teutsch et. al., 2001). The National Park in Switzerland was examined to determine anthropogenic Pb from natural Pb, and to identify the anthropogenic sources of pollution. In order to identify suspected sources accurately, samples were collected from the exhaust pipes of cars ($^{206}Pb/^{204}Pb=$ 17.13-17.52), sewage sludge ($^{206}Pb/^{204}Pb=$ 17.74-17.88), filter ashes from waste incinerators ($^{206}Pb/^{204}Pb=$ 17.92-17.96), ZnO-rich filter dust from a metal processing plant, and filters from air samples near the city of Zurich ($^{206}Pb/^{204}Pb=$ 17.99). By comparing soil profile data to the Pb isotopic composition of suspected sources, Hansmann and Koppel (2000) concluded that pollution was caused by air fall deposition. The Pb isotopic composition of the pollutants did not allow the two to clearly identify a specific source because of anthropogenic inputs from several sources and atmospheric mixing.

Other attempts have been made in Switzerland to distinguish between possible sources of Pb pollution. Air filters were sampled from an urban city and an agricultural area. Then, leaded gasoline samples were collected from four different gas stations, representing four different companies (Shell, Coop, Agip, and BP). Samples were also collected from ashes from household waste incinerators, heating oil, and coal. By comparing the $^{206}Pb/^{204}Pb$ isotopic signatures, Chiaradia and Cupelin (2000) were able to determine that a mixture of leaded gasoline, from all four companies, was the main source of Pb pollution in the city, and household waste incineration was the main source of Pb pollution in the agricultural area.

Zhu et. al. (2001) used Pb isotopes to determine the source of pollution in the Pearl River Delta, China. By collecting and comparing samples of aeolian dust, aerosols,

and soils to previously reported Pb isotopic data on automobile exhaust and industrial materials, they were able to conclude that 45-64% of the total Pb in the soil was attributed to automobile exhaust.

Lead isotope signature have been investigated to support a source appointment on a continental scale. Atmospheric aerosols were collected over Cap Gris-Nez, France to determine the extent to which various continental sources influence the lead abundance in aerosols. Lead concentrations in aerosols are seven times higher when air masses are derived from continental Europe, versus marine air masses (Flament et. al.,2002). Gasoline and industrial Pb isotopic signatures are closely related to the Pb isotopic signatures present in aerosol samples.

The practice of studying the distribution of anthropogenic Pb in different soil fractions in soil samples is not as common. Teutsch et. al. (2001) studied the distribution of natural and anthropogenic Pb in Mediterranean soils. Soil samples were collected within 8-23m of a busy highway and 500m away from that same highway, then a selective extraction sequence was employed to determine the distribution of Pb in the different soil components: soil carbonate, organic matter, Fe-oxides and hydrous oxides, and aluminosilicates. Teutsch et. al. (2001) determined that natural Pb is mainly associated with aluminosilicates (60%) and Fe-oxides (30%). In contrast, anthropogenic Pb is mainly associated with soil carbonates (40%), Fe-oxides (35%). Most of the anthropogenic Pb accumulates in the top 10cm of the soil profile. By comparing their Pb isotopic signatures with other published isotopic signatures, a determination was made that the anthropogenic Pb present in their soil profiles is attributed to a mixture of American and European petrol Pb.

Sources of Pollution in Poland

Poland has been subjected to significant environmental contamination for quite some time. The extensive pollution can be attributed to Poland's continued reliance on coal as a primary source of energy, coupled with industrial emissions, the use of leaded gasoline, and atmospheric deposition (Szpunar et. al., 1990).

Upper Silesia, located in south-central Poland, is one of the most polluted regions in Poland. This region houses many of the country's major industrial plants and is the center of Poland's coal and lignite mining industry. Other large coal and lignite-fired power plants are scattered throughout the country and contribute to air and water pollution (Szpunar et. al., 1990).

Generally, the wind flow pattern throughout Poland is from the west-southwest to the east-northeast. Some northeasterly airflow is common in the summer. In the winter, Central Asia's high-pressure system may cause east-southeasterly airflow (Szpunar et. al., 1990). The predominant westerly winds over Poland make it feasible that emissions originating in central and western Poland can be transported through the atmosphere and deposited in eastern Poland.

Atmospheric Pb

Metal compounds in the atmosphere originate from both natural and man-made processes. Metal compounds, including Pb, can occur naturally through terrestrial, marine, volcanic or biogenic activity. More specifically, volcanoes, forest fires, sea spray and gaseous emissions from the ocean are the most important natural sources of metal compounds in the atmosphere. Anthropogenic emissions of many metals, including As, Cd, Cr, Ni, Pb and Zn often exceed the input of the trace elements from natural sources.

Lead is a good example of this trend, with its natural atmospheric levels, which range from $4\text{-}19\times10^6$ Kg/yr compared to its anthropogenic emissions levels ranging from 400-450×10^6 Kg/yr (Puxbaum, 1991). The most common anthropogenic sources of metal compounds in the atmosphere are coal combustion, smelting, and automobiles.

Metal particles in the atmosphere occur in a wide variety of sizes. Particulate matter with a 50% cut-off diameter of $10\mu M$ is referred to as PM_{10}, and considered inhalable (Fang et. al., 1999). Inhalable particles (PM_{10}) and coarse particles ($PM_{2.5\text{-}10}$) are formed during mechanical processes such as erosion or abrasion. Particulate matter with a size range less than $2.5\mu M$ ($PM_{2.5}$) is considered fine and formed from coagulation and condensation processes. Lead usually occurs in the finer fraction of particulate matter, ranging from $0.3\text{-}0.8\mu M$ in size (Puxbaum, 1991).

Particle size is a governing factor for the amount of time a particle spends in the atmosphere. In general, finer sized particles will remain in the atmosphere for a longer period of time and presumably be able to travel greater distances from the source, compared to coarser particles (Puxbaum, 1991). This means that we can expect to find Pb contamination significant distances from the source. Continental air masses generally carry higher concentrations of trace metals farther distances, compared to marine air masses (Flament, 2002).

Atmospheric Pb is commonly found in association with atmospheric Zn and Cd, presumably because of their similar particulate matter size. Chemical speciation is common among trace metals in the atmosphere. Trace metals in polluted atmospheres are found in the carbonate, sulfate, nitrate or chloride fractions (Puxbaum, 1991).

Kyotani and Iwatsuki (2002) recently proved that a large part of atmospheric Pb can be removed in the water soluble, carbonate and sulfate fractions.

Atmospheric deposition is a major source of trace metal input in soils and waterways worldwide. Atmospheric particles can be deposited by dry deposition, which is dependent on particle size and air mass movement, or by wet deposition, which is dependent on rainfall and atmospheric metal concentrations. Wet deposition accounts for the majority of atmospheric deposition of trace metals, including Pb (Puxbaum, 1991).

Soil Geochemical Phases

Metal cations in soil systems may occur in different geochemical forms: free or complexed ions in solution, exchangeable (or specifically sorbed), and metal hydroxide and carbonate. The geochemical form of the metal cation determines the availability of the metal for bioaccumulation and potential groundwater contamination. Adsorbed, or exchangeable metals are the most bioavailable geochemical forms in the soil. There are associations of certain metals to certain geochemical phases depending on the nature of the soil (i.e. soil composition, soil mineralogy, soil pH, soil organic matter content, etc.).

Water soluble phase: Metals exist in the water soluble phase as free or complexed ions. The metals associated with this phase commonly have a high bioavailability. Contaminated soils commonly have an abundance of water soluble metals.

Exchangeable/specifically sorbed phase: When significant amounts of anthropogenic metals are present in the soil, this geochemical fraction will be high. In uncontaminated soils most trace metal cations are chemisorbed (specifically sorbed), and only small amounts are readily exchangeable.

Carbonate phase: Carbonates can contain various amounts of trace metals, generally by coprecipitation. Most trace metal cations precipitate as oxides and hydroxides at higher pH levels.

Fe-Mn oxide phases: Different extraction techniques may be employed to distinguish Mn oxides from Fe oxides, but since the two elements are so closely associated, extracting both fractions at the same time is more convenient. More recent inputs of trace metals should be associated with more reducible forms of Fe-Mn oxides.

Organic (sulfide) phase: Humic substances account for roughly 60-80% of soil organic matter. Moderate amounts of trace metals are associated with the organic fraction in soils, unless the soil texture is very sandy or the organic content is very high. In these soils a high proportion of trace metals are bound to the organic matter. The sulfide fraction may be extracted separately, but would not be a significant fraction unless dealing with wetland soils.

Residual phase: This fraction would include trace metals that are matrix bound to the phylosilicate structure and any other portion of trace metal that may not have been completely removed by the other extractions. Nearly 95% of trace metals can be removed in this fraction.

(All of the above information was obtained form Betri et. al., 1995; Rule, 1998; Wenzel and Blum, 1999).

Operationally Based Extractions

Due to questionable specificity of the extractants, operationally based fractions are commonly used instead of naming the geochemical fraction.

Water soluble phase (WSP): When attempting to extract water soluble metals out of the soil, one would simply extract with DI water.

Exchangeable phase (EP): Exchangeable cations are measured after displacement with a neutral salt solution. Extraction with NH_4NO_3 seems to be the most desirable reagent, because of its efficiency to displace adsorbed cations and its volatility (which decreases background interference during analysis).

Carbonate phase (CP): The extraction of the carbonate fraction should also remove oxides and hydroxides. This extraction employs acetic acid, and sodium acetate (which should have a minimal effect on the other soil fractions).

Easily reducible phase (ERP): The easily reducible fraction will involve the use of NH_2OH-HCl in HNO_3, and will extract predominantly Mn oxides.

Moderately reducible phase (MRP): To remove the moderately reducible fraction, mainly Fe oxides, NH_2OH-HCl in HOAc is employed.

Organic (sulfide) phase (OSP): For the organic (sulfide) extraction technique, H_2O_2 is used. Extraction with NH_4Oac is then used to prevent readsorption.

Acid extracted phase (AEP): To extract the residual fraction from the soil sample, strong acid digestion with concentrated NHO_3 and H_2O_2 are commonly used.

A more specific version of the general procedure for the extraction of contaminated soils is included in Appendix B.

(All of the above information was obtained from Betri et. al., 1995; Rule, 1998; Wenzel and Blum, 1999).

Purpose

Measuring Pb isotope ratios in each geochemical phase will allow us to indicate the percent of anthropogenic Pb that is water soluble, exchangeable, easily reducible, etc. Determining Pb abundance in these geochemical fractions may allow us to determine the potential health or environmental risk.

The original objective of this project was to use Pb isotope ratios to assess the anthropogenic Pb input from the naturally occurring Pb in four national parks in Poland. More specifically, to test Pb isotope ratios in each geochemical phase, and to determine if the majority of Pb is present in the water soluble phase, exchangeable phase, etc. A second goal was to test the postulate that sequential extractions can be used to evaluate the pollution status of the soils.

After a cost analysis, I determined that the experiment would be very expensive to complete. The new objective of this project is to test the acid extractable Pb isotope ratios in the samples from the four chosen national parks in Poland, by means of concentrated HNO_3/H_2O_2 extraction. Sequential extractions from Tatry National Park will be analyzed to determine the Pb isotope ratios in each geochemical phase.

CHAPTER II

METHODS

Study Area

Soils from four National Parks in Poland were collected, sampled and compared. Two Parks, Tatry National Park and Bieszczady National Park, are located in southern Poland and two Parks, Roztocze National Park and Poleski National Park, are located in eastern central Poland.

The Tatry National Park lies 80km south of the City of Krakow, along the Polish-Slovakian border, within the Carpathian Range (Appendix A). The popular tourist town of Zakopane is located at the northern border of the Park. Heavily industrialized areas are situated to the southeast of the Park in Slovakia. Tatry National Park encompasses an area of 21km^2 which is 71% forested with elevations ranging from 1100m to 2500m. This area is geologically complex, but consists mostly of metamorphic and sedimentary rocks. Soil samples were obtained within meadows, from areas containing granitic or sedimentary rocks, from 1110-1350m elevations of the Park.

The Bieszczady National Park is located in the southeast portion of the country, also within the Carpathian Range (Appendix A). This park is situated in a sparsely populated area. Bieszczady National Park encompasses an area of 15km^2 which is 60% forested with elevations ranging from 600-1300m. The Park contains mostly clastic with some carbonate rocks. Soil samples from this Park were taken at 900m elevations, in an area of fine textured clastic rocks.

The Roztocze National Park lies 80km south of the City of Lublin, in eastern Poland, in a moderately populated agricultural region (Appendix A). This 7.8km^2 area is approximately 93% forested with elevations ranging from 100m to 350m. Between this area's limestone hills are wide valleys covered with thick post-glacial sands, containing numerous peat bogs. Soil samples obtained in Roztocze National Park were taken in sandy soils and peat deposits at 200m elevations.

The Poleski National Park lies 60km northwest of the City of Lublin, in a sparsely populated agricultural region of the country (Appendix A). This nearly flat area encompasses 4.8km^2, is about 80% forested, and ranges in elevations from 170m to 250m. Glacial sands, boulder clays and silty peat deposits form the soils in Poleski National Park. Soil samples were taken from 170m elevations in sandy and peat parent material.

Soil samples were collected for comparison from two other locations: Nowa Huta (an iron and steel manufacturing plant) located on the northern outskirts of the City of Krakow, and near the town of Polaniec (a non-cultivated area of agricultural fields) 90km northeast of Nowa Huta.

(All of the above information was obtained from Rule, 2003).

Field and Laboratory Procedures

Surficial soils, from the depth of 0-15 cm, were collected from all four parks. Samples from 15-30 cm depth were also collected in Poleski National Park. Either plastic or stainless steel tools were used to collect all samples. Up to 15 locations were sampled in each park. Samples were mixed using material from three separate locations

within a 10m^2 area. All samples were air-dried, crushed and sieved through a 2mm

plastic sieve. The samples were then stored in plastic bags (Rule, 2003).

The Tatry National Park samples were subjected to selective chemical extractions

(Rule, 1998) to determine the fraction of Pb present in each of the following phases:

water soluble, exchangeable (NH$_4$ NO$_3$), carbonate (pH5, NH$_2$OH. HCl in 25% HOAc),

organic-sulfide (30% H$_2$O$_2$ in 0.01M HNO$_3$; extract with HNO$_4$ OAc) and acid

extractable (concentrated HNO$_3$ and 30% H$_2$O$_2$) (Appendix B). Samples from all four

national parks were subjected to a total chemical extraction, using concentrated HNO$_3$

and 30% H$_2$O$_2$, to determine the total Pb present (Appendix B).

Sequential chemical extraction samples from Tatry National Park, samples

obtained from the total chemical extractions, and procedural blanks underwent Pb

analysis, at the Laboratory for Isotope and Trace Element Research of Old Dominion

University. All of the solutions were diluted to a ratio of 1% HNO$_3$, with the exception

of the total acid extraction samples 01-27, which have a 1:1 dilution factor. The dilution

matrix consisted of a sodium solution, prepared previous to our analysis in a Class 100

clean lab. Pb concentrations and Pb isotope ratios were measured by the Finnigan

element 2 high resolution inductively coupled plasma mass spectrometer (HR-ICP-MS).

To correct for mass bias all solutions were spiked with 20 ppbTI and the NIST 982

certified reference material was run in conjunction with our samples to ensure precision

and accuracy.

CHAPTER III

RESULTS AND DISCUSSION

As mentioned in the introduction, $^{206}Pb/^{204}Pb$ and $^{206}Pb/^{207}Pb$ ratios will be used

to differentiate between natural and anthropogenic Pb sources for this discussion. All of

the $^{206}Pb/^{204}Pb$, $^{206}Pb/^{207}Pb$, $^{206}Pb/^{208}Pb$, and $^{208}Pb/^{207}Pb$ isotope ratios obtained from the

total acid extractions taken from all four National Parks and the Tatry National Park

sequential extractions are presented in Appendix D. Total Pb concentrations obtained

from all four National Parks, and sequential extraction Pb concentrations for Tatry

National Park were previously determined by Rule (2003), and will be incorporated in

this discussion (Appendix C).

Tatry National Park

Within the four National Parks studied, Tatry National Park has the highest

recorded Pb concentrations, ranging from 42.08-113.3 mg/kg (Table 2; Appendix C).

These concentrations are higher than recently determined background levels of Pb in

Polish soils, which range from 12-18 mg/kg in central, northeast and eastern Poland; and

slightly higher (25-50 mg/kg) concentrations in northwest and western Poland (Lis and

Pasieczna, 1995). Because of these higher Pb concentrations, sequential extractions were

performed on all of the Tatry samples to determine which phase holds the majority of Pb.

Pb isotope ratios were determined for both the total acid extraction samples and the

sequential extraction samples to determine if the different phases contained natural or

anthropogenic Pb signatures.

In general, the highest Pb concentrations were found in the acid extractable phase. The organic sulfide phase held the second highest concentrations (Table 2). This means that a majority of Pb found in these samples is matrix bound, or bound to the organic matter in the soil.

There seems to be a relationship between elevation and Pb concentration. Samples taken from higher elevations within the park tend to have higher total Pb concentrations (Table 2; Figure 1). There is also a trend between Pb isotope ratios and elevation. As the ^{206}Pb/^{207}Pb and ^{206}Pb/^{204}Pb isotope ratios decrease (indicating more anthropogenic Pb) elevations increase (Figure 2; Figure 3). This is most likely because higher elevations serve as catchments for wind and precipitation carrying Pb.

Table 2. Tatry National Park Pb concentrations measured in each sequential extraction and the total Pb present in each sample (mg/kg) (Rule, 2003).

Sample #	Location	Elevation (m)	EP	CP	ERP+MRP	OSP	AEP	TOTAL
6	Mala Lake	1325	43.18	13.84	10.57	9.08	18.53	95.20
7	Mala Lake	1250	13.45	9.55	9.17	9.56	20.26	61.99
8	Mala Lake	1160	0.00	5.73	8.98	9.76	26.50	50.97
9	Mala Lake	1140	2.20	8.55	10.42	10.81	21.49	53.47
10	Mala Lake	1120	2.11	9.60	12.12	11.35	24.64	59.82
11	Rusinowa	1225	0.00	3.85	28.25	4.97	8.6	45.67
12	Rusinowa	1200	4.14	1.48	15.41	13.69	29.09	63.81
13	Rusinowa	1200	18.22	7.08	16.99	14.40	19.87	76.56
14	Chocholowska	1350	49.42	15.77	13.11	8.06	26.94	113.30
15	Chocholowska	1110	16.08	6.60	5.52	5.12	8.76	42.08
16	Chocholowska	1110	0.00	6.61	30.35	4.97	24.91	66.84
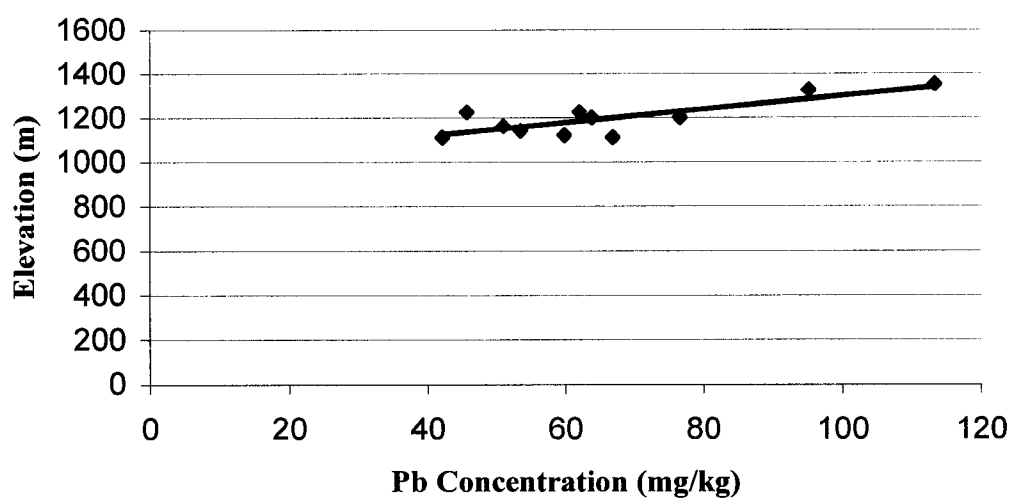
Fig. 1 Tatry National Park elevation (m) vs. total Pb concentration (mg/kg).
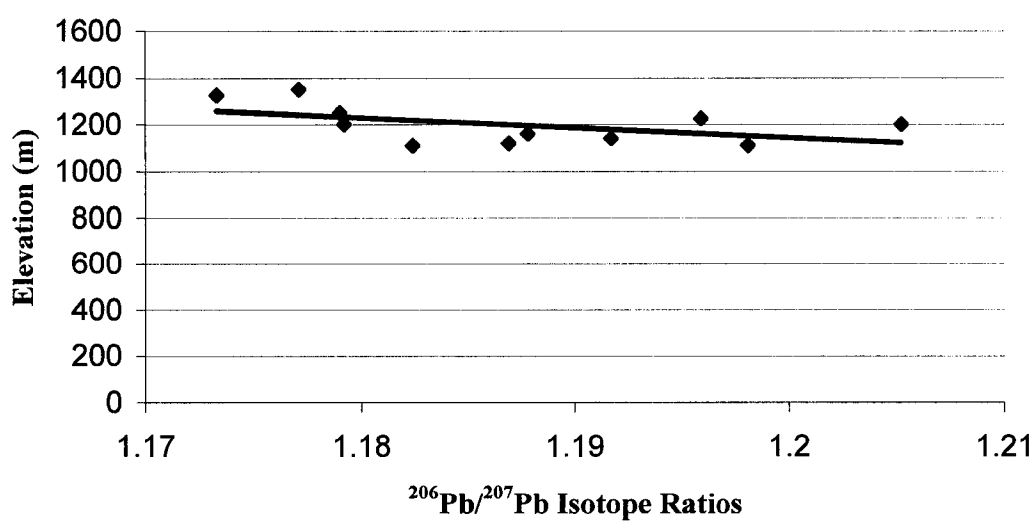
Fig. 2. Tatry National Park total $^{206}Pb/^{207}Pb$ isotope ratios vs. elevation (m).
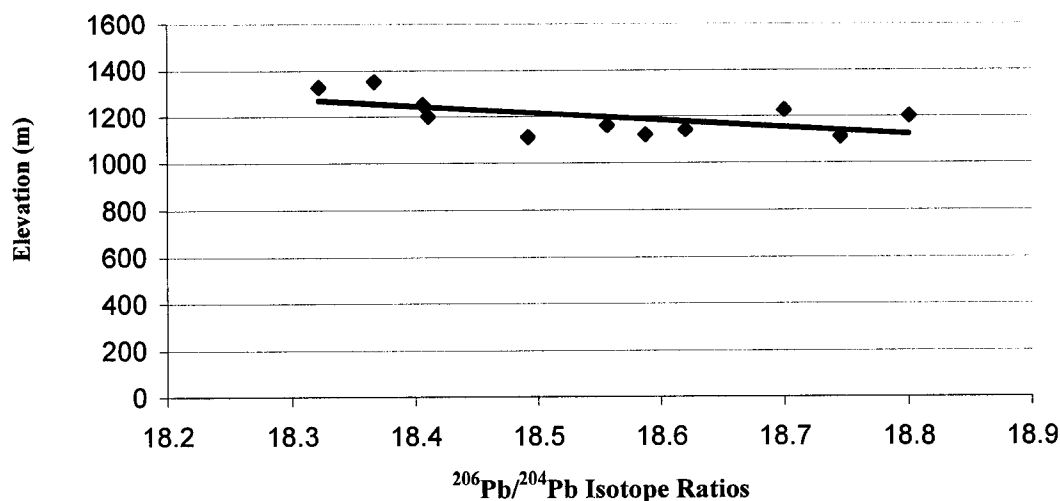
Fig. 3. Tatry National Park ^{206}Pb/^{204}Pb isotope ratios vs. elevation (m).

The ^{206}Pb/^{207}Pb and ^{206}Pb/^{204}Pb data indicates that a majority of the total Pb present in the Tatry National Park samples is anthropogenic in origin. This was expected considering that Tatry lies northwest of a heavily industrialized area in Slovakia, and southwest of the heavily industrialized region of Upper Silesia.

All of the samples taken from the Mala Lake region indicate that the Pb present in each geochemical phase is anthropogenic. The sequential extraction Pb isotope ratios from this region tend to closely mimic the total Pb extraction ratios. Out of the three samples obtained near Rusinowa, two (Samples 11 and 13) contain anthropogenic Pb in all phases, while the other (Sample 12) shows both anthropogenic and natural Pb ratios. Upon examination of the sequential extraction results for Sample 12, it is clear that the natural ^{206}Pb/^{207}Pb ratios occur in the moderately reducible, the organic sulfide, and the acid extractable phases, while the natural ^{206}Pb/^{204}Pb ratio occurs in the acid extractable phase. Even though the ^{206}Pb/^{207}Pb and ^{206}Pb/^{204}Pb isotope ratios in the exchangeable,

carbonate, and easily reducible phases clearly indicate anthropogenic input indicative of pollution, the Pb concentrations in Sample 12 are the highest in moderately reducible, organic sulfide, and acid extractable phases, which gives the overall sample a natural Pb isotope signature. Samples collected from Chocholowska contain Pb ratios that are constant with anthropogenic ratios, with one exception. Sample 16 contains a natural $^{206}Pb/^{207}Pb$ ratio of 1.2035 in its acid extractable phase, even though its total extraction $^{206}Pb/^{207}Pb$ ratio is 1.19 and considered anthropogenic. From this one can infer that the Pb present in the acid extractable phase is natural in origin, but the remainder, and majority of the Pb present in the sample is anthropogenic (Appendix D).

The patterns exhibited by Samples 12 and 16 are more expected. Most soils contain natural (residual) Pb. This natural Pb is usually incorporated in the soil matrix and would be expected in the more insoluble geochemical phases (moderately reducible, organic sulfide, and acid extractable phases). More recently deposited anthropogenic Pb would tend to reside in the more soluble phases (exchangeable, carbonate, and easily reducible phases). In fact, it is surprising that more natural Pb isotope signatures were not predominant for the more insoluble geochemical phases throughout more areas in Tatry National Park.

Bieszczady National Park

The Bieszczady National Park samples contain somewhat higher Pb concentrations than what was expected, considering that these samples were taken from lower elevations (900m) and this park is situated in a sparsely populated area. These concentration levels are similar to Tatry National Parks concentration levels in that they

exceed the expected average background levels of Pb expected in Polish soils.

All of the isotope ratios calculated for this region indicate that the Pb present is of anthropogenic origin (Table 3). Since this National Park is located in such a sparsely populated area, one can assume that the anthropogenic Pb found in these samples was caused by atmospheric deposition.

Table 3. Total Pb concentrations (mg/kg), ^{206}Pb/^{207}Pb, and ^{206}Pb/^{204}Pb isotope ratios measured from sampled taken within Bieszczady National Park (* indicates natural Pb).

Sample #	Elevation (m)	Pb Concentration	^{206}Pb/^{207}Pb	^{206}Pb/^{204}Pb
17	900	62.92	1.1851	18.5149
18	900	62.19	1.1910	18.5179
19	900	53.87	1.1860	18.5692

Roztocze National Park

Samples were collected from Roztocze National Park in a variety of areas containing different soil material, all at elevations of approximately 200m. Samples obtained from a peat meadow contain the highest Pb concentrations obtained in the National Park. This was expected because peats and clays tend to sorb trace metals more tightly than other soil constituents. The remainder of the samples were retrieved from sandy soils and have relatively low Pb concentrations, which is typical (Table 4).

All of the ^{206}Pb/^{207}Pb and ^{206}Pb/^{204}Pb isotope ratios recorded in this area are anthropogenic in origin (Table 4). Since Roztocze National Park lies in a moderately populated area of Poland, the likely causes for the anthropogenic Pb in the region could be the release of automobile emissions in the area coupled with atmospheric deposition of industry emissions originating in Upper Silesia and Slovakia.

Table 4. Total Pb concentrations (mg/kg), ^{206}Pb/^{207}Pb, and ^{206}Pb/^{204}Pb isotope ratios measured from samples taken within Roztocze National Park (* indicated natural Pb).

Sample #	Location	Elevation (m)	Pb Concentration	^{206}Pb/^{207}Pb	^{206}Pb/^{204}Pb
20	Peat Meadow	200	76.55	1.1699	18.1706
21	Peat Meadow	200	86.57	1.1715	18.2124
22	Peat Meadow	200	80.18	1.1735	18.3241
23	Meadow	200	14.61	1.1727	18.2744
24	Meadow	200	12.50	1.1789	18.3352
25	Meadow	200	13.62	1.1779	18.3621
26	Birch Sand	200	13.49	1.1749	18.2852
27	Birch Sand	200	6.74	1.1756	18.2608
28	Birch Sand	200	11.62	1.1765	18.3197

Poleski National Park

A total of 30 soil samples were analyzed from Pokeski National Park. A different sampling scheme was employed at this Park. Soil samples were collected from five different areas, and at two different depths within each area. Samples taken from the other National Parks were all surface soils. Results from this study found that there are distinctive differences in Pb concentration and Pb isotope ratios at varying depths.

In general, surface Pb concentrations exceeded subsurface levels. This is an indication that there is anthropogenic input in this area. Samples obtained from areas containing peaty soils (Duren Bango, Jez Dkugie, and West Meadow) have higher surface Pb concentrations compared to samples taken from areas containing sandy soils (Lowiszow Polana and a forest near Jez Dkugie) (Table 5).

Poleski National Park shows the greatest variation in Pb isotope ratios, out of all four National Parks studied. The subsurface samples collected in Poleski National Park

contain the lowest Pb concentrations observed in this study. A majority of the subsurface samples contain Pb isotope ratios indicative of natural Pb, which was expected. Soils taken from the subsurface should be more protected from anthropogenic input, giving the soils natural Pb isotope signatures (Table 5).

Almost all of the surface samples contain Pb isotope ratios consistent with ratios caused by anthropogenic input. The one exception is the samples obtained from the Lowiszow Polana region of the Park. Pb isotope ratios measured from Lowiszow Polana indicate that all of the Pb present there is natural (Table 5). Since Poleski National Park is located in the eastern portion of Poland, in a sparsely populated agricultural region, the most logical source of anthropogenic Pb would be atmospheric deposition of Pb transported from Upper Silesia or Slovakia and local automobile traffic.

Table 5. Total Pb concentrations (mg/kg), ^{206}Pb/^{207}Pb, and ^{206}Pb/^{204}Pb isotope ratios measured from samples taken within Poleski National Park (* indicates natural Pb).

Sample #	Location	Sample Depth	Pb Concentration	^{206}Pb/^{207}Pb	^{206}Pb/^{204}Pb
30	Durne Bango	0-15 (cm)	23.10	1.1778	18.3530
31	Durne Bango	15-30 (cm)	2.84	*1.2014	18.6898
32	Durne Bango	0-15 (cm)	29.78	1.1777	18.3430
33	Durne Bango	15-30 (cm)	2.27	*1.2104	*18.8713
34	Durne Bango	0-15 (cm)	27.57	1.1774	18.3237
35	Durne Bango	15-30 (cm)	3.56	*1.2052	18.7411
36	Lowiszow Polana	0-15 (cm)	8.67	1.1975	18.6754
37	Lowiszow Polana	15-30 (cm)	11.10	*1.2447	*19.5000
38	Lowiszow Polana	0-15 (cm)	13.70	*1.2028	*18.8097
39	Lowiszow Polana	15-30 (cm)	8.59	*1.2692	*19.9394
40	Lowiszow Polana	0-15 (cm)	10.20	1.1999	18.7242
41	Lowiszow Polana	15-30 (cm)	3.93	*1.2415	*19.3974
42	Jez Dkugie	0-15 (cm)	12.82	1.1857	18.4952
43	Jez Dkugie	15-30 (cm)	8.03	*1.2271	*19.2041
44	Jez Dkugie	0-15 (cm)	10.14	1.1895	18.4981
45	Jez Dkugie	15-30 (cm)	7.47	1.1959	18.5816
46	Jez Dkugie	0-15 (cm)	7.15	1.1864	18.3605
47	Jez Dkugie	15-30 (cm)	6.67	*1.2035	18.6893
48	Forest near Jez Dkugie	0-15 (cm)	9.43	1.1834	18.4532
49	Forest near Jez Dkugie	15-30 (cm)	8.42	*1.2009	18.7095
50	Forest near Jez Dkugie	0-15 (cm)	11.05	1.1900	18.5355
51	Forest near Jez Dkugie	15-30 (cm)	2.00	*1.2375	*19.2213
52	Forest near Jez Dkugie	0-15 (cm)	3.04	*1.2082	*18.8118
53	Forest near Jez Dkugie	15-30 (cm)	7.16	1.1834	18.4645
54	West Meadow	0-15 (cm)	25.17	1.1781	18.4258
55	West Meadow	15-30 (cm)	12.98	1.1818	18.4399
56	West Meadow	0-15 (cm)	36.06	1.1791	18.3234
57	West Meadow	15-30 (cm)	17.61	1.1807	18.4209
58	West Meadow	0-15 (cm)	41.63	1.1786	18.3566
59	West Meadow	15-30 (cm)	17.77	1.1783	18.3704

Pb Concentrations vs. Pb Isotope Ratios

Contaminated soils are generally recognized by containing elevated levels of

heavy metals and trace elements. However, concentration levels alone cannot

differentiate between metals that occur naturally in the soil and metals that occur because

of anthropogenic input. Sequential chemical extractions are a good way to determine

environmental availability of certain trace elements.

While excess Pb concentration levels may indicate anthropogenic contamination,

slightly elevated Pb concentration levels do not. Tatry National Park exhibited the

highest Pb concentrations out of all four Parks studied (Appendix C). The sequential

chemical extraction results showed that most of the Pb present was being stored in the

moderately reducible, organic sulfide, and acid extractable phases, which indicate that the

majority of the Pb is matrix bound, or bound to the organic matter in the soil. The greater

than expected amounts of Pb in the exchangeable phase, carbonate phase, and easily

reducible phase fractions were postulated to indicate anthropogenic input (Rule, 2003).

A majority of the Pb isotope ratios recorded prove that the predominant Pb signature

present is anthropogenic, with two exceptions (Samples 12 and 16). Sample 12 showed

anthropogenic Pb isotope signals in the exchangeable, carbonate, and easily reducible

phases and natural Pb isotope signals in the moderately reducible, organic sulfide, and

acid extractable phases, giving the sample an overall natural signal. Sample 16 exhibited

a natural Pb isotope signal in the acid extractable phase, but the remainder of the

sequential extraction Pb isotope ratios gave off anthropogenic signals giving the sample

an overall anthropogenic Pb isotope signal.

All of the Pb isotope ratios recorded from the Tatry National Parks exchangeable phases, carbonate phases, and easily reducible phases indicate anthropogenic origin of Pb. Recently deposited metals are generally more abundant in these more easily mobile phases. One would expect natural Pb isotope signals in the moderately reducible, organic sulfide, and acid extractable phases in all soils, even those with anthropogenic input, because Pb tends to be relatively abundant in the Fe-Mn oxide, residual, and organic fractions naturally. The fact that natural Pb was found in the more insoluble phases, and bound to the soils matrix was expected. It was actually a surprise that more natural Pb was not found in the more insoluble phases since most soils start out with natural concentrations of Pb. This information is consistent with the postulate that based on metal concentrations in different geochemical fractions, sequential extractions can be used to evaluate the pollution status of a soil.

Samples obtained from Bieszczady National Park and Roztocze National Park contain various Pb concentration levels ranging from 6.74-86.57mg/Kg, and all of these samples Pb isotope ratios showed that the majority of the Pb present was anthropogenic in origin.

In Poleski National Park, where Pb concentrations were the lowest recorded out of all four Parks, the Pb isotope ratios showed the presence of both natural and anthropogenic Pb. Surface soil Pb concentrations for the most part exceeded subsurface concentrations. Upon examination of Pb concentrations in the soil geochemical phases, a good portion of the Pb present in the surface soils was bound to the exchangeable and carbonate phases. A majority of the Pb present in the subsurface samples was bound to the organic sulfide and acid extractable phases (Appendix C). This data is consistent

with the fact that more recently deposited, anthropogenic Pb may be held in more soluble geochemical phases, and natural Pb is bound to the more insoluble geochemical phases.

A majority of the surface samples collected exhibited anthropogenic Pb isotope ratios, while a majority of the subsurface samples collected show no sign of anthropogenic Pb input. This is a very important observation and proves that sparsely populated regions of the country are affected by anthropogenic Pb input in surface soils, most likely caused by atmospheric deposition of emissions originating in Upper Silesia and Slovakia and local automobile traffic.

Natural Pb cannot be distinguished from the anthropogenic Pb by concentration levels. Since overall Pb concentration levels in Poleski National Park were low, an examination of Pb isotope ratio distribution within different geochemical phases to determine which geochemical fractions held a majority of the anthropogenic Pb or natural Pb would have been useful. Data from Pb isotope ratio distribution within different geochemical phases could strengthen the postulate that elevated amounts of Pb in the exchangeable, carbonate, and easily reducible phases indicate anthropogenic input.

There is a slight trend between total Pb concentration and Pb isotope ratios (Figure 4; Figure 5). Generally, as Pb concentrations increase, $^{206}Pb/^{207}Pb$ and $^{206}Pb/^{204}Pb$ isotope ratios decrease (clearly indicating anthropogenic input). However, when lower Pb concentrations are measured, it is harder to establish a trend. Some areas exhibiting low Pb concentration levels gave off natural Pb isotope ratios, while some areas with low Pb concentrations showed anthropogenic Pb isotope signatures.
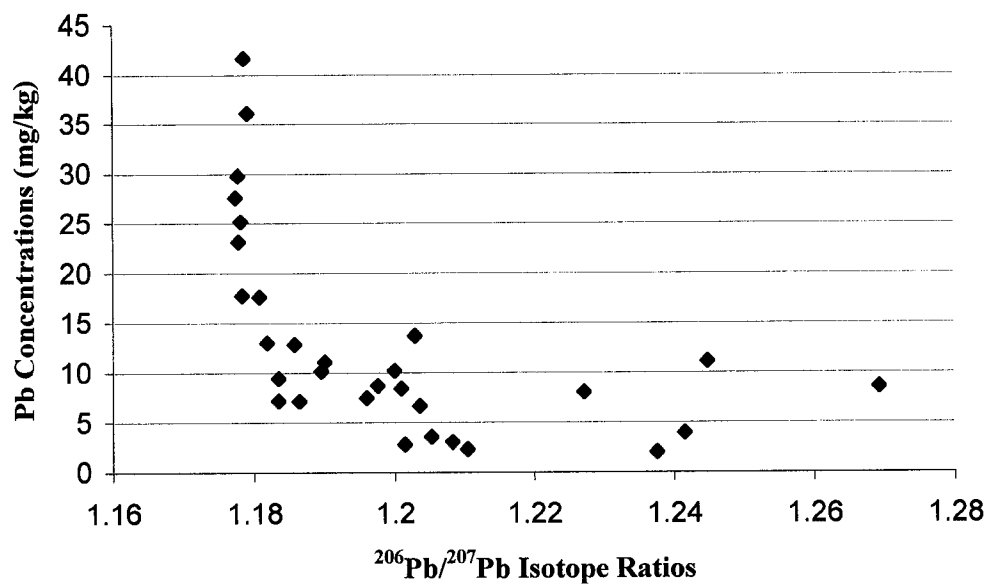
Fig. 4. Pokeski National Park ^{206}Pb/^{207}Pb isotope ratios vs. total Pb concentration (mg/kg).
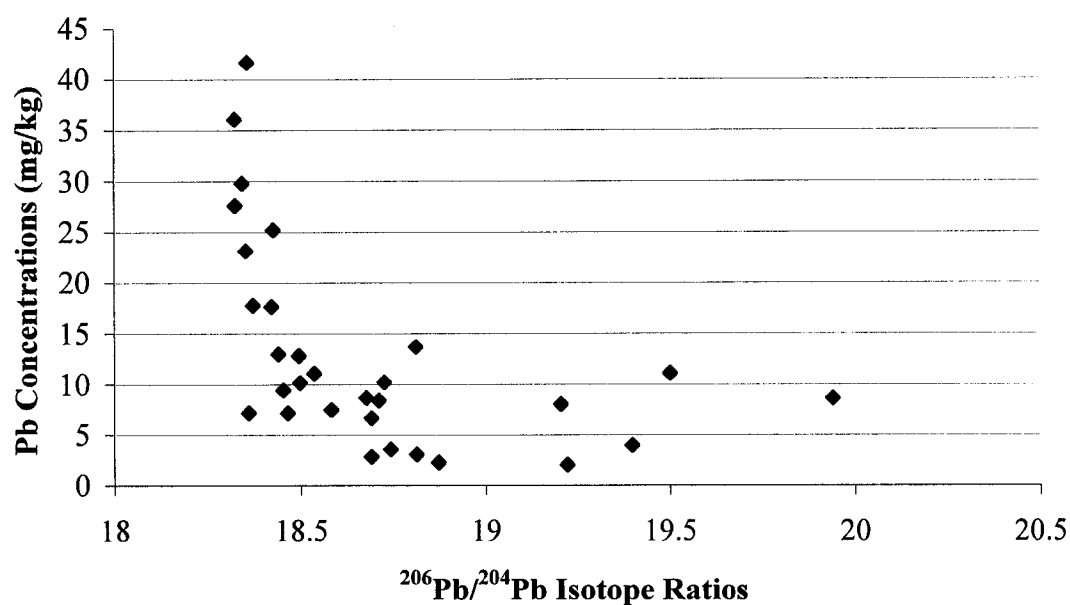
Fig. 5. Pokeski National Park ^{206}Pb/^{204}Pb isotope ratios vs. Pb concentration (mg/kg).

CHAPTER IV

SUMMARY AND CONCLUSIONS

Pb isotope ratio signatures enable distinction between naturally occurring Pb and anthropogenic Pb. By coupling Pb isotope signatures with Pb concentrations in different geochemical phases, an accurate characterization of soil pollution status may be reached.

Soils in all of the National Parks in this study contain Pb isotope ratios indicative of anthropogenic Pb input. The Pb pollution in all of the National Parks could be attributed to the release of local automobile emissions, coupled with atmospheric deposition of industrial emissions originating in Upper Silesia and Slovakia.

There is a relationship between Pb concentrations, Pb isotope ratios, and elevation. As elevations increase, Pb concentrations increase; as elevations increase, $^{206}Pb/^{207}Pb$ and $^{206}Pb/^{204}Pb$ isotope ratios decrease. There is also a slight trend between Pb concentrations and Pb isotope ratios. As Pb concentrations increase, the Pb isotope ratios decrease.

In Tatry National Park, a majority of the total and sequential extraction Pb isotope ratios recorded indicate anthropogenic input. In soil samples that portrayed natural total Pb isotope signatures, there were still anthropogenic Pb isotope signatures present in the more soluble geochemical phases (exchangeable phase, carbonate phase, and easily reducible phase), which indicates that these soils have been affected by Pb pollution. Data from this portion of the study, concerning Pb isotope ratio distribution within different geochemical phases, is consistent with the postulate that elevated amounts of Pb in the more easily soluble phases indicates anthropogenic input. This data also supports

the fact that one should be cautious when characterizing a soil as being influenced by contamination or receiving anthropogenic inputs based on total Pb content alone.

There were no natural total Pb isotope signatures recorded for samples taken from either Bieszczady National Park or Roztocze National Park. All of the Pb isotope signatures recorded in these two National Parks indicate that anthropogenic Pb is dominant in these soil samples.

Poleski National Park shows the greatest variation in Pb isotope ratios, out of all four National Parks studied. A majority of the subsurface samples contain total Pb isotope ratios indicative of natural Pb, while almost all of the surface samples contain Pb isotope ratios consistent with anthropogenic Pb isotope signatures.

This project was significant in that its results showed that many areas of Poland, including sparsely populated regions, are affected by anthropogenic Pb input. This project's results also strengthened the validation of using sequential geochemical extractions to measure anthropogenic input of Pb in soil.

REFERENCES

Aberg, G., Charalampides, G., Fosse, G., and Hjelmseth, H. 2001. The use of Pb isotopes to differentiate between contemporary and ancient sources of pollution in Greece. Atmospheric Environ. 35:4609-4615.

Bacon, J.R., Jones, K.C., McGrath, S.P., and Johnston, A.E. 1996. Isotopic character of lead deposited from the atmosphere at a grassland site in the United Kingdom since 1860. Environ. Sci. Technol. 30:2511-2518.

Berti, W.R., Cunningham, S.D., and Jacobs, L.W. 1995. Sequential chemical extraction of trace elements: Development and use in remediating contaminated soil. p. 121-131. Proceedings of the Third International Conference on the Biochemistry of Trace Elements. 15-19th May, Paris, France.

Charalampides, G., and Manoliadis, O. 2002. Sr and Pb isotopes as environmental indicators in environmental studies. Environ. Intern. 28:147-151.

Chiaradia, M., and Cupelin, F. 2000. Behavior of airborn lead and temporal variations of its source effects in Geneva (Switzerland): comparison of anthropogenic versus natural processes. Atmospheric Environ. 34:959-971.

Fang, G.C., Chang, C.N., Wu, Y.S., Wang, V., Fu, P.P., Yang, D.G., Chen, S.C., and Chu, C.C. 1999. The study of fine and coarse particles, and metallic elements for the daytime and nighttime in a suburban area of central Taiwan, Taichung. Chemosphere 41:639-644.

Farmer, J.G., Eades, L.J., Mackenzie, A.B., Kirika, A., and Bailey-Watts, T.E. 1996. Stable lead isotope record of lead pollution in Loch Lomond sediments since 1630 A.D. Environ. Sci. Technol. 30:3080-3083.

Flament, P., Bertho, M.L., Deboudt, K., Veron, A., and Puskaric, E. 2002. European isotopic signatures for lead in atmospheric aerosols: a source apportionment based upon ^{206}Pb/^{207}Pb ratios. The Sci. of the Total Environ. 296:35-57.

Hansmann, W., and Koppel, V. 2000. Lead-isotopes as tracers of pollutants in soils. Chem. Geol. 171:123-144.

Kyotani, T., and Iwatsuki, M. 2002. Characterization of soluble and insoluble components in PM$_{2.5}$ and PM$_{10}$ fractions of airborne particulate matter in Kofu City, Japan. Atmospheric Environ. 36:639-649.

Lis, J. and A. Pasieczna. 1995. Geochemical Atlas of Poland. Polish Geological Institute, Warsaw, Poland.

Luck, J.M., and Othman, D.B. 2002. Trace element and Pb isotope variability during rainy events in the NW Mediterranean: constraints on anthropogenic and natural sources. Chem. Geol. 182:443-460.

Marcantonio, F., Zimmerman, A., Xu, Y., and Canuel, E. 2002. A Pb isotope record of Mid-Atlantic US atmospheric Pb emissions in Chesapeake Bay sediments. Marine Chem. 77:123-132.

Monna, F., Dominik, J., Loizeau, J.L., Pardos, M., and Arpagaus, P. 1999. Origin and evolution on Pb in sediments of Lake Geneva (Switzerland-France). Establishing a stable Pb record. Environ. Sci. Technol. 33:2850-2857.

Puxbaum, H. 1991. Metal compounds in the atmosphere. p. 257-284. *In* E. Merian (ed). Metals and their compounds in the environment. VCH New York, NY.

Renberg, I., Brannvall, M.L., Bindler, R., and Emteryd, O. 2002. Stable lead isotopes and lake sediments-a useful combination for the study of atmospheric lead pollution history. The Sci. of the Total Environ. 292:45-54.

Rule, J.H. 1998. Trace metal cation adsorption in soils: selective chemical extractions and biological availability. p. 319-349. *In* A. Dabrowski (ed). Adsorption and its applications in industry and environmental protection. Vol. II: Studies in environmental protection, studies in surface science and catalysis, Vol. 120, Elsevier Sci., Amsterdam.

Rule, J.H. 2003. Trace element concentrations and distributions in geochemical fractions in surficial soils in four national parks in Poland. Unpublished.

Semlali, R.M., Van Oort, F., Denaix, L., and Loubet, M. 2001. Estimation distributions of endogenous and exogenous Pb in soils by using Pb isotopic ratios. Environ. Sci. Technol. 35:4180-4188.

Szpunar, C.B., N. Bhatti, W.A. Buehring, D.G. Streets, and H.W. Balaldynowicz. 1990. Poland: An Energy and Environmental Overview. Office of Energy, Bureau of Science and Technology, United States Agency for International Development, Report No. 90-12. Prepared by: International Coal and Environmental Studies, Environmental Assessment and Information Sciences Division, Argonne National Laboratory, Argonne, IL 60439. 176p.

Teutsch, N., Erel, Y., Halicz, L., and Banin, A. 2001. Distribution of natural and anthropogenic lead in Mediterranean soils. Geochimica et Cosmochimica Acta 65:2853-2864.

Watmough, S.A., Hughes, R.J., and Hutchinson, T.C. 1999. ^{206}Pb/^{207}Pb ratios in tree rings as monitors of environmental change. Environ. Sci. Technol. 33:670-673.

Wenzel, W.W., and Blum, W.E.H. 1999. Effects of Sampling, Sampling Preparation and Extraction Techniques on Mobile Metal Fractions in Soil. In: Adriano, D.C., Chen, Z.-S., Yang, S.-S., Iskandar, I.K. (Eds.): Biogeochemistry of trace metals. Advances in Environmental Sciences, 121-172, Northwood: Science Reviews.

Zhu, B.Q., Chen, Y.W., and Peng, J.H. 2001. Lead isotope geochemistry of the urban environment in the Pearl River Delta. App. Geochem. 16:409-417.

APPENDIX A

MAP OF POLAND INCLUDING LOCATIONS

OF NATIONAL PARKS STUDIED

Fig. A1. Map of Poland Including Tatry National Park, Bieszczady National Park, Roztocze National Park, and Poleski National Park.

APPENDIX B

SELECTIVE EXTRACTION SEQUENCE AND

ACID EXTRACTABLE TRACE METALS IN SOILS

CONCENTRATED HNO_3/H_2O_2 EXTRACTION

PROCEDURES

Selective Extraction Sequence Procedure (Rule, 1998)

1. Water Soluble Phase: Add 24mL of ASTM Type I deionized H_2O to 3.0g sample, shake tubes end-to-end for 1 hour. Centrifuge, remove extract, wash, and centrifuge.

2. Exchangeable Phase: Add 24mL of 1.0M pH 7 NH_4NO_3 to 3.0g sample, shake tubes end-to-end for 1 hour. Centrifuge, remove extract, wash, and centrifuge.

3. Carbonate Phase: Add 24mL of 1.0M, pH 5 NaOAc and place on shaker for 5 hours. Centrifuge, remove extract, wash, and centrifuge.

4. Easily Reducible Phase- predominantly Mn oxides: Add 24mL of 1.0M NH_2OH-HCl in 0.01M HNO_3 and place on shaker for 1 hour. Centrifuge, remove extract, wash, and centrifuge.

5. Moderately Reducible Phase- predominantly Fe oxides: Add 24mL of 0.04M NH_2OH-HCl in 25% HOAc and place samples in a 96°C water bath for 6 hours. Centrifuge, remove extract, wash, and centrifuge.

6. Organic (Sulfide) Phase: a) Add 0.1mL of 1.0M HNO_3 + 5mL 30% H_2O_2, pH 2 and place in 85°C water bath; b) add 5mL 30% H_2O_2, wait for the reaction to subside, add 5mL H_2O_2 and heat on 85°C hot plate for 1 hour; c) add 5mL 30% H_2O_2 and place on 85°C hotplate for 3 hours; d) cool samples, add 7mL of 4M NaOAc in 20% HNO_3, cover beaker opening with parafilm, place on shaker for 30minutes; e) centrifuge, remove extract, wash, and centrifuge.

7. Residual Phase: we will use the concentrated HNO_3 + 30% H_2O_2 procedure (Acid Extractable Residual).

Acid Extractable Trace Metals in Soils

Concentrated HNO_3/H_2O_2 Extraction Procedure (Rule, 1998)

1. Place 3-5g dried, sieved soil into a 180mL digestion beaker; add enough DI H_2O to just wet the entire sample. Record weight.

2. Add 15mL of 15.4 M Trace Metal Grade HNO_3, cover with a watch glass and let stand over night.

3. Gently heat at 110°C on large hotplate for 4 hours, adding more acid if necessary.

4. Remove all samples from hotplate onto heat resistant surface, cool for 15 minutes and carefully add 5mL of 30%H_2O_2.

5. Return the samples to the hotplate, cover with watch glasses and heat for an additional 1.5 hours.

6. Remove the watch glasses and evaporate liquid until about 5mL remains.

7. Add 10mL of DI H_2O and warm to dissolve all salts.

8. All filters should be prepared in racks ahead of time. Whatman 541 filter paper in plastic funnels should be washed with 10% Trace Metal Grade HNO_3.

9. Cool the samples and decant the digestate through the pre-washed filters into 50mL volumetric flasks.

10. Rinse the digestion beaker with small amounts of DI H_2O and add to the filter.

11. Rinse the filter paper with small amounts of DI H_2O taking care not to exceed the 50mL volume in the flask.

12. Thoroughly mix each sample in the flask and transfer to storage bottles.

APPENDIX C

SEQUENTIAL EXTRACTION Pb CONCENTRATIONS

FROM TATRY NATIONAL PARK AND POLESKI NATIONAL PARK

TOTAL ACID EXTRACTION

Pb CONCENTRATIONS FROM TATRY NATIONAL PARK, BIESZCZADY

NATIONAL PARK, ROZTOCZE NATIONAL PARK, AND

POLESKI NATIONAL PARK

Table A1. Sequential extraction Pb concentrations (mg/kg) from Tatry National Park (Rule, 2003).

Location	Sample	EP	CP	ERP+ MRP	OSP	AEP	TOTAL
Mala Lake	6	43.18	13.84	10.57	9.08	18.53	95.20
Mala Lake	7	13.45	9.55	9.17	9.56	20.26	61.99
Mala Lake	8	0.00	5.73	8.98	9.76	26.50	50.97
Mala Lake	9	2.20	8.55	10.42	10.81	21.49	53.47
Mala Lake	10	2.11	9.60	12.12	11.35	24.64	59.82
Rusinowa	11	0.00	3.85	28.25	4.97	8.60	45.67
Rusinowa	12	4.14	1.48	15.41	13.69	29.09	63.81
Rusinowa	13	18.22	7.08	16.99	14.40	19.87	76.56
Chocholowska	14	49.42	15.77	13.11	8.06	26.94	113.30
Chocholowska	15	16.08	6.60	5.52	5.12	8.76	42.08
Chocholowska	16	0.00	6.61	30.35	4.97	24.91	66.84

Table A2. Sequential extraction Pb concentrations (mg/kg) from Poleski National Park. (Rule, 2003).

Location	Sample	Depth (cm)	EP	CP	ERP/ MRP	OSP	AEP	TOTAL
Durne Bango	30	0-15	14.45	1.24	1.62	4.40	1.39	23.10
Durne Bango	31	15-30	1.77	0.00	0.21	0.01	0.85	2.84
Durne Bango	32	0-15	23.32	1.19	1.75	0.38	3.14	29.78
Durne Bango	33	15-30	0.52	0.00	0.05	0.00	1.70	2.27
Durne Bango	34	0-15	23.50	0.00	1.14	0.00	2.93	27.57
Durne Bango	35	15-30	0.48	0.01	0.00	1.93	1.14	3.56
Lowiszow Polana	36	0-15	1.22	0.97	1.47	2.63	2.38	8.67
Lowiszow Polana	37	15-30	0.00	0.00	0.52	6.25	4.33	11.10
Lowiszow Polana	38	0-15	1.15	0.00	3.18	5.58	3.79	13.70
Lowiszow Polana	39	15-30	0.46	0.00	2.30	3.47	2.36	8.59
Lowiszow Polana	40	0-15	3.34	0.00	1.88	3.35	1.63	10.20
Lowiszow Polana	41	15-30	0.33	0.00	0.92	1.88	0.80	3.93
Jez Dkugie	42	0-15	0.90	0.66	1.66	2.93	6.67	12.82
Jez Dkugie	43	15-30	0.00	0.00	0.18	5.54	2.31	8.03
Jez Dkugie	44	0-15	0.22	0.00	3.02	5.41	1.49	10.14
Jez Dkugie	45	15-30	0.00	0.00	2.12	4.42	0.93	7.47
Jez Dkugie	46	0-15	0.00	1.24	1.47	3.40	1.04	7.15
Jez Dkugie	47	15-30	0.00	0.97	0.98	3.35	1.37	6.67
Forest near J. Dkugie	48	0-15	4.84	0.90	0.38	1.39	1.92	9.43
Forest near J. Dkugie	49	15-30	1.85	0.02	0.12	4.81	1.62	8.42
Forest near J. Dkugie	50	0-15	1.11	1.29	1.35	5.54	1.76	11.05
Forest near J. Dkugie	51	15-30	0.00	0.00	1.19	0.45	0.36	2.00
Forest near J. Dkugie	52	0-15	0.33	0.00	2.09	0.25	0.37	3.04
Forest near J. Dkugie	53	15-30	2.35	1.46	2.60	0.31	0.44	7.16
West Meadow	54	0-15	8.28	2.34	3.20	0.41	10.94	25.17
West Meadow	55	15-30	2.28	1.35	2.50	0.29	6.56	12.98
West Meadow	56	0-15	11.62	3.20	4.16	0.00	17.08	36.06
West Meadow	57	15-30	4.73	0.51	2.60	0.29	9.48	17.61
West Meadow	58	0-15	6.47	3.63	4.34	21.28	5.91	41.63
West Meadow	59	15-30	3.28	2.59	2.40	2.15	7.35	17.77

Table A3. Total acid extraction concentrations from Tatry National Park, Bieszczady National Park, Roztocze National Park, and Poleski National Park (Rule, 2003).

National Park	Location	Sample	Concentration (mg/kg)	National Park	Location	Sample	Concentration (mg/kg)
Tatry	Mala Lake	6	95.20	Poleski	Durne Bagno	30	23.10
Tatry	Mala Lake	7	61.99	Poleski	Durne Bagno	31	2.84
Tatry	Mala Lake	8	50.97	Poleski	Durne Bagno	32	29.78
Tatry	Mala Lake	9	53.47	Poleski	Durne Bagno	33	2.27
Tatry	Mala Lake	10	59.82	Poleski	Durne Bagno	34	27.57
Tatry	Rusinowa	11	45.67	Poleski	Durne Bagno	35	3.56
Tatry	Rusinowa	12	63.81	Poleski	Lowiszow P.	36	8.67
Tatry	Rusinowa	13	76.56	Poleski	Lowiszow P.	37	11.10
Tatry	Chocholowska	14	113.30	Poleski	Lowiszow P.	38	13.70
Tatry	Chocholowska	15	42.08	Poleski	Lowiszow P.	39	8.59
Tatry	Chocholowska	16	66.84	Poleski	Lowiszow P.	40	10.20
				Poleski	Lowiszow P.	41	3.93
Bieszczady		17	62.94	Poleski	Jez Dkugie	42	12.82
Bieszczady		18	62.19	Poleski	Jez Dkugie	43	8.03
Bieszczady		19	53.87	Poleski	Jez Dkugie	44	10.14
				Poleski	Jez Dkugie	45	7.47
Roztocze	peat meadow	20	76.55	Poleski	Jez Dkugie	46	7.15
Roztocze	peat meadow	21	77.41	Poleski	Jez Dkugie	47	6.67
Roztocze	peat meadow	22	86.57	Poleski	Forest	48	9.43
Roztocze	meadow	23	14.61	Poleski	Forest	49	8.42
Roztocze	meadow	24	12.50	Poleski	Forest	50	11.05
Roztocze	meadow	25	13.62	Poleski	Forest	51	2.00
Roztocze	birch sand	26	13.49	Poleski	Forest	52	3.04
Roztocze	birch sand	27	6.74	Poleski	Forest	53	7.16
Roztocze	birch sand	28	11.62	Poleski	west meadow	54	25.17
				Poleski	west meadow	55	12.98
				Poleski	west meadow	56	36.06
				Poleski	west meadow	57	17.61
				Poleski	west meadow	58	41.63
				Poleski	west meadow	59	17.77

APPENDIX D

^{206}Pb/^{204}Pb, ^{206}Pb/^{207}Pb, ^{206}Pb/^{208}Pb, and ^{208}Pb/^{207}Pb

ISOTOPE RATIOS FROM SEQUENTIAL EXTRACTIONS AND

TOTAL ACID EXTRACTIONS

Table A4. Pb isotope ratios of sequential extractions from Tatry National Park.

Sample	$^{206}Pb/^{204}Pb$	RSD (%)	$^{206}Pb/^{207}Pb$	RSD (%)	$^{206}Pb/^{208}Pb$	RSD (%)	$^{208}Pb/^{207}Pb$	RSD (%)
EP6	18.2067	0.19	1.1743	0.05	0.4794	0.20	2.4498	0.15
EP7	17.8710	0.16	1.1756	0.09	0.4796	0.19	2.4512	0.15
EP8	18.5768	0.65	1.1832	0.06	0.4826	0.12	2.4517	0.15
EP9	18.7020	0.38	1.1821	0.18	0.4803	0.21	2.4610	0.11
EP10	18.6074	0.50	1.1826	0.18	0.4808	0.03	2.4595	0.16
EP11	18.7289	1.04	1.1846	0.34	0.4828	0.34	2.4537	0.12
EP12	18.2473	0.02	1.1609	0.13	0.4857	0.14	2.3901	0.01
EP13	18.2536	0.16	1.1770	0.08	0.4802	0.12	2.4513	0.05
EP14	18.3516	0.20	1.1766	0.18	0.4795	0.29	2.4537	0.11
EP15	18.6987	.036	1.1853	0.11	0.4827	0.29	2.4554	0.27
EP16	18.3764	0.41	1.1811	0.12	0.4813	0.10	2.4541	0.21

Sample	$^{206}Pb/^{204}Pb$	RSD (%)	$^{206}Pb/^{207}Pb$	RSD (%)	$^{206}Pb/^{208}Pb$	RSD (%)	$^{208}Pb/^{207}Pb$	RSD (%)
CP6	18.2872	0.04	1.1748	0.02	0.4798	0.03	2.4485	0.01
CP7	18.2957	0.09	1.1769	0.03	0.4802	0.07	2.4508	0.05
CP8	18.3485	0.03	1.1834	0.02	0.4828	0.03	2.4513	0.02
CP9	18.4123	0.08	1.1866	0.05	0.4833	0.05	2.4552	0.05
CP10	18.3841	0.08	1.1839	0.07	0.4828	0.05	2.4522	0.08
CP11	18.3598	0.06	1.1869	0.05	0.4847	0.05	2.4490	0.01
CP12	18.5705	0.09	1.1970	0.07	0.4877	0.10	2.4541	0.08
CP13	18.3193	0.09	1.1755	0.06	0.4791	0.6	2.4536	0.04
CP14	18.3403	0.06	1.1757	0.01	0.4798	0.07	2.4505	0.07
CP15	18.3857	0.07	1.1794	0.05	0.4711	0.04	2.4515	0.01
CP16	18.4743	0.12	1.1917	0.04	0.4860	0.05	2.4519	0.05

Sample	$^{206}Pb/^{204}Pb$	RSD (%)	$^{206}Pb/^{207}Pb$	RSD (%)	$^{206}Pb/^{208}Pb$	RSD (%)	$^{208}Pb/^{207}Pb$	RSD (%)
ERP6	18.1152	0.16	1.1738	0.01	0.4797	0.14	2.4471	0.14
ERP7	18.1000	0.35	1.1772	0.08	0.4807	0.12	2.4488	0.04
ERP8	18.6036	0.25	1.1828	0.13	0.4808	0.01	2.4602	0.12
ERP9	18.7134	0.21	1.1898	0.22	0.4814	0.12	2.4715	0.10
ERP10	18.6242	0.22	1.1830	0.14	0.4799	0.17	2.4652	0.03
ERP11	18.6967	0.61	1.1882	0.09	0.4824	0.18	2.4630	0.11
ERP12	18.4775	0.22	1.1987	0.02	0.4886	0.08	2.4535	0.06
ERP13	18.1737	0.15	1.1760	0.10	0.4799	0.12	2.4505	0.06
ERP14	18.2847	0.11	1.1763	0.19	0.4798	0.07	2.4515	0.14
ERP15	18.2326	0.14	1.1807	0.04	0.4821	0.06	2.4492	0.07
ERP16	18.4002	0.20	1.1931	0.15	0.4862	0.12	2.4538	0.18

Table A4. Continued.

Sample	$^{206}Pb/^{204}Pb$	RSD (%)	$^{206}Pb/^{207}Pb$	RSD (%)	$^{206}Pb/^{208}Pb$	RSD (%)	$^{208}Pb/^{207}Pb$	RSD (%)
MRP6	18.3377	0.05	1.1734	0.07	0.4790	0.09	2.4496	0.02
MRP7	18.3542	0.19	1.1783	0.06	0.4808	0.08	2.4509	0.05
MRP8	18.4894	0.16	1.1856	0.08	0.4835	0.11	2.4524	0.11
MRP9	18.5423	0.08	1.1885	0.15	0.4843	0.04	2.4541	0.15
MRP10	18.5220	0.09	1.1866	0.09	0.4836	0.07	2.4535	0.01
MRP11	18.6389	0.07	1.1926	0.13	0.4863	0.12	2.4524	0.07
MRP12	18.7638	0.03	1.2001	0.12	0.4888	0.13	2.4550	0.07
MRP13	18.4054	0.15	1.1766	0.05	0.4794	0.11	2.4542	0.08
MRP14	18.3543	0.05	1.1767	0.06	0.4804	0.11	2.4495	0.06
MRP15	18.4422	0.01	1.1793	0.01	0.4810	0.18	4.4520	0.18
MRP16	18.6664	0.08	1.1938	0.03	0.4862	0.08	2.4553	0.06

Sample	$^{206}Pb/^{204}Pb$	RSD (%)	$^{206}Pb/^{207}Pb$	RSD (%)	$^{206}Pb/^{208}Pb$	RSD (%)	$^{208}Pb/^{207}Pb$	RSD (%)
OSP6	18.3086	0.11	1.1773	0.19	0.4809	0.08	2.4479	0.11
OSP7	18.3898	0.14	1.1788	0.10	0.4802	0.14	2.4549	0.04
OSP8	18.5371	0.05	1.1863	0.09	0.4826	0.05	2.4580	0.10
OSP9	18.5819	0.06	1.1889	0.09	0.4842	0.09	2.4555	0.04
OSP10	18.5721	0.22	1.1860	0.12	0.4829	0.03	2.4560	0.10
OSP11	18.4879	0.26	1.1956	0.04	0.4883	0.15	2.4483	0.15
OSP12	18.7670	0.09	1.2019	0.18	0.4899	0.22	2.4534	0.07
OSP13	18.4009	0.12	1.1791	0.10	0.4808	0.21	2.4523	0.15
OSP14	18.4056	0.09	1.1800	0.11	0.4820	0.13	2.4479	0.15
OSP15	18.3524	0.21	1.1836	0.07	0.4822	0.21	2.4548	0.26
OSP16	18.5492	0.24	1.1928	0.02	0.4864	0.06	2.4521	0.06

Sample	$^{206}Pb/^{204}Pb$	RSD (%)	$^{206}Pb/^{207}Pb$	RSD (%)	$^{206}Pb/^{208}Pb$	RSD (%)	$^{208}Pb/^{207}Pb$	RSD (%)
AEP6	18.3583	0.19	1.1776	0.13	0.4810	0.29	2.4479	0.18
AEP7	18.4806	0.14	1.1841	0.09	0.4814	0.18	2.4596	0.10
AEP8	18.6306	0.12	1.1926	0.09	0.4849	0.08	2.4596	0.04
AEP9	18.6823	0.12	1.1957	0.02	0.4858	0.05	2.4615	0.04
AEP10	18.6012	0.23	1.1934	0.08	0.4858	0.07	2.4562	0.05
AEP11	18.7254	0.08	1.1982	0.12	0.4875	0.13	2.4579	0.08
AEP12	18.8739	0.17	1.2051	0.08	0.4890	0.02	2.4644	0.09
AEP13	18.4122	0.13	1.1794	0.13	0.4801	0.13	2.4566	0.01
AEP14	18.4890	0.07	1.1818	0.14	0.4814	0.18	2.2552	0.04
AEP15	18.5932	0.11	1.1907	0.19	0.4831	0.11	2.4644	0.09
AEP16	18.8160	0.11	1.2035	0.04	0.4903	0.07	2.4546	0.03

Table A5. Pb isotope ratios of total acid extractions from near Polance, Nowa Huta, Tatry National Park, Bieszczady National Park, Roztocze National Park, and Poleski National Park.

Area	Sample	$^{206}Pb/^{204}Pb$	RSD (%)	$^{206}Pb/^{207}Pb$	RSD (%)	$^{206}Pb/^{208}Pb$	RSD (%)	$^{208}Pb/^{207}Pb$	RSD (%)
Polanice	TAE1	18.5737	0.11	1.1900	0.02	0.4814	0.09	2.4719	0.07
Polanice	TAE2	18.4908	0.11	1.1848	0.09	0.4799	0.16	2.4689	0.09
Polanice	TAE3	18.4559	0.02	1.1822	0.06	0.4801	0.15	2.4625	0.10

Area	Sample	$^{206}Pb/^{204}Pb$	RSD (%)	$^{206}Pb/^{207}Pb$	RSD (%)	$^{206}Pb/^{208}Pb$	RSD (%)	$^{208}Pb/^{207}Pb$	RSD (%)
Nowa	TAE4	18.6777	0.14	1.1955	0.06	0.4835	0.12	2.4727	0.08
Nowa	TAE5	18.6282	0.06	1.1919	0.03	0.4827	0.01	2.4690	0.04

Area	Sample	$^{206}Pb/^{204}Pb$	RSD (%)	$^{206}Pb/^{207}Pb$	RSD (%)	$^{206}Pb/^{208}Pb$	RSD (%)	$^{208}Pb/^{207}Pb$	RSD (%)
Tatry	TAE6	18.3218	0.06	1.1733	0.04	0.4791	0.09	2.4488	0.06
Tatry	TAE7	18.4062	0.12	1.1790	0.05	0.4804	0.03	2.4545	0.03
Tatry	TAE8	18.5564	0.08	1.1878	0.05	0.4840	0.02	2.4541	0.04
Tatry	TAE9	18.6202	0.06	1.1917	0.09	0.4848	0.06	2.4579	0.07
Tatry	TAE10	18.5877	0.12	1.1869	0.13	0.4830	0.21	2.4572	0.15
Tatry	TAE11	18.7004	0.13	1.1959	0.04	0.4876	0.14	2.4524	0.10
Tatry	TAE12	18.8014	0.16	1.2052	0.13	0.4902	0.23	2.4588	0.10
Tatry	TAE13	18.4106	0.31	1.1792	0.18	0.4814	0.35	2.4495	0.18
Tatry	TAE14	18.3668	0.14	1.1771	0.06	0.4806	0.21	2.4492	0.21
Tatry	TAE15	18.4919	0.34	1.1824	0.31	0.4815	0.29	2.4554	0.02
Tatry	TAE16	18.7454	0.28	1.1981	0.04	0.4877	0.09	2.4569	0.06

Area	Sample	$^{206}Pb/^{204}Pb$	RSD (%)	$^{206}Pb/^{207}Pb$	RSD (%)	$^{206}Pb/^{208}Pb$	RSD (%)	$^{208}Pb/^{207}Pb$	RSD (%)
Bieszczady	TAE17	18.5149	0.22	1.1851	0.22	0.4814	0.16	2.4618	0.27
Bieszczady	TAE18	18.5179	0.75	1.1910	0.30	0.4844	0.28	2.4588	0.26
Bieszczady	TAE19	18.5692	0.37	1.1860	0.04	0.4828	0.08	2.4564	0.11

Area	Sample	$^{206}Pb/^{204}Pb$	RSD (%)	$^{206}Pb/^{207}Pb$	RSD (%)	$^{206}Pb/^{208}Pb$	RSD (%)	$^{208}Pb/^{207}Pb$	RSD (%)
Roztocze	TAE20	18.1706	0.44	1.1699	0.03	0.4783	0.19	2.4459	0.21
Roztocze	TAE21	18.2124	0.76	1.1715	0.36	0.4782	0.80	2.4497	0.46
Roztocze	TAE22	18.3241	0.36	1.1735	0.19	0.4786	0.13	2.4522	0.11
Roztocze	TAE23	18.2744	0.74	1.1724	0.27	0.4793	0.39	2.4467	0.12
Roztocze	TAE24	18.3352	0.09	1.1789	0.14	0.4807	0.16	2.4521	0.05
Roztocze	TAE25	18.3621	0.25	1.1779	0.20	0.4794	0.59	2.4572	0.39
Roztocze	TAE26	18.2852	0.24	1.1749	0.18	0.4796	0.29	2.4495	0.12
Roztocze	TAE27	18.2608	0.16	1.1756	0.20	0.4792	0.35	2.4533	0.15
Roztocze	TAE28	18.3197	0.10	1.1765	0.09	0.4790	0.08	2.4562	0.16

Table A5. Continued.

Area	Sample	$^{206}Pb/^{204}Pb$	RSD (%)	$^{206}Pb/^{207}Pb$	RSD (%)	$^{206}Pb/^{208}Pb$	RSD (%)	$^{208}Pb/^{207}Pb$	RSD (%)
Poleski	TAE30	18.3530	0.06	1.1778	0.08	0.4794	0.05	2.4566	0.08
Poleski	TAE31	18.6898	0.09	1.2014	0.09	0.4802	0.08	2.5022	0.03
Poleski	TAE32	18.3430	0.13	1.1777	0.09	0.4800	0.05	2.4539	0.12
Poleski	TAE33	18.8713	0.11	1.2104	0.13	0.4882	0.16	2.4791	0.09
Poleski	TAE34	18.3237	0.09	1.1774	0.04	0.4797	0.08	2.4543	0.07
Poleski	TAE35	18.7411	0.14	1.2052	0.14	0.4873	0.11	2.4730	0.07
Poleski	TAE36	18.6754	0.04	1.1975	0.11	0.4834	0.08	2.4772	0.04
Poleski	TAE37	19.5000	0.03	1.2447	0.06	0.4943	0.13	2.5179	0.09
Poleski	TAE38	18.8097	0.25	1.2028	0.06	0.4833	0.15	2.4886	0.09
Poleski	TAE39	19.9394	0.08	1.2692	0.10	0.4958	0.11	2.5598	0.02
Poleski	TAE40	18.7242	0.09	1.1999	0.05	0.4831	0.07	2.4837	0.10
Poleski	TAE41	19.3974	0.20	1.2415	0.06	0.4879	0.09	2.5445	0.04
Poleski	TAE42	18.4952	0.07	1.1857	0.05	0.4820	0.06	2.4599	0.08
Poleski	TAE43	19.2041	0.05	1.2271	0.01	0.4908	0.04	2.4999	0.03
Poleski	TAE44	18.4981	0.30	1.1895	0.28	0.4815	0.16	2.4704	0.13
Poleski	TAE45	18.5816	0.14	1.1959	0.14	0.4830	0.06	2.4763	0.15
Poleski	TAE46	18.3605	0.28	1.1864	0.04	0.4805	0.10	2.4693	0.06
Poleski	TAE47	18.6893	0.09	1.2035	0.24	0.4851	0.16	2.4810	0.24
Poleski	TAE48	18.4532	0.07	1.1834	0.03	0.4803	0.08	2.4636	0.08
Poleski	TAE49	18.7095	0.05	1.2009	0.19	0.4829	0.05	2.4867	0.13
Poleski	TAE50	18.5355	0.06	1.1900	0.18	0.4825	0.08	2.4663	0.13
Poleski	TAE51	19.2213	0.04	1.2375	0.24	0.4829	0.21	2.5629	0.05
Poleski	TAE52	18.8118	0.06	1.2082	0.09	0.4853	0.16	2.4894	0.07
Poleski	TAE53	18.4654	0.20	1.1834	0.08	0.4808	0.17	2.4612	0.12
Poleski	TAE54	18.4258	0.09	1.1781	0.04	0.4790	0.06	2.4595	0.09
Poleski	TAE55	18.4399	0.07	1.1818	0.11	0.4801	0.05	2.4616	0.08
Poleski	TAE56	18.3234	0.05	1.1791	0.08	0.4811	0.40	2.4510	0.38
Poleski	TAE57	18.4209	0.17	1.1807	0.06	0.4794	0.24	2.4627	0.21
Poleski	TAE58	18.3566	0.19	1.1786	0.09	0.4796	0.15	2.4572	0.23
Poleski	TAE59	18.3704	0.12	1.1783	0.05	0.4792	0.14	2.4588	0.14

VITA

Shannon Michele Simcoe received a B.S. in Geology from Old Dominion University, Norfolk, VA. in May 2002. In August 2002 Shannon began working towards her Masters of Science degree in Geology at Old Dominion University, Norfolk, VA. While working towards her degree, Shannon worked as a Graduate Teaching Assistant for Introductory Geology Laboratories. As a Teaching Assistant, some of her responsibilities included running laboratory exercises, answering elated laboratory and lecture questions, and grading student exams. Shannon received her M.S. in Geology from Old Dominion University, 4600 Elkhorn Avenue, Norfolk, VA. In August 2004.