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A Chemical Extraction Study of Lead Contaminated Soil from Granite City, IL

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Eastern Illinois University

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A Chemical Extraction Study of Lead Contaminated Soil from Granite City, IL

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Submitted Date: Dec. 12, 1997

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Abstract

Granite City, IL, surface soil (0-10 cm) contaminated with lead was studied by both single- and a four-step sequential chemical extraction procedures designed to establish the partitioning, mobility and availability of lead in soil. The five fractions corresponding to the selected extractants were exchangeable, carbonates-bound, Fe-Mn oxides bound, organic matter and residual. Lead contamination of the soil was determined as a function of particle size and soil depth.

The contaminated sample had the highest lead content of 573.1 mg/kg at the 4 cm soil depth level, and on average was about 8.8 times that of background soil. Most of the lead (over 87%) is concentrated in the Fe-Mn oxides bound, organic matter, and residual fractions, and only about 9-13% of the total lead remain in the first two fractions. The lead content in the residual fractions decreased as the depth increased and suggests the presence of undefined lead-containing large particles.

The intermediate particle size range (90-125 µm) contained the highest lead content, 563.3 mg/kg. Here, over 80% of total lead is found in the Fe-Mn oxides bound, organic matter and residual fractions. Lead content in the more accessible fractions,
exchangeable and carbonates-bound, increased slightly as particle size decreased.

Extraction experiments showed that low pH water may cause mobilization of lead from soil to water. Oxalic acid releases only a limited amount of lead into solution, and surfactant Triton solution may be used as a soil containment reagent to prevent lead release from soil.
DEDICATION

To my mother and father
Acknowledgments

I would like to thank Dr. Douglas G. Klarup for his knowledgeable guidance and encouragement.

I would also like to thank the faculty and staff of the Chemistry Department at Eastern Illinois University for their advice and help.

I also wish to express my thanks to my wife, Yibing Li, for her understanding and support.
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I. Introduction

1. Health Effects of Lead

Lead has long been used in the production of batteries, ammunition, metal products (solder and pipes), roofing, and devices to shield x-rays. People have obtained a lot of benefit from it, but it also has been harmful to our health\textsuperscript{1,2}. Lead can affect almost every organ and system in our body. The most sensitive is the central nervous system, particularly in children, but it also can seriously damage kidneys and the immune system. The effects are the same whether it is breathed or swallowed.

Lead exposure is particularly dangerous for young and unborn children. Unborn children can be exposed to lead through their mothers, while young children are more likely to play in contaminated dirt and place their hands and other objects in their mouths, thereby increasing the opportunity for lead ingestion. Harmful effects include premature birth, smaller babies, decreased mental ability in the infant, learning difficulties, and reduced growth in young children.

Although less common, lead is toxic for adults as well. It may cause anemia, weakness in fingers, wrists, or ankles, decreased reaction time, disorder of the blood, abortion and damage to the male reproduction system. Due to its frequency of occurrence,
toxicity and potential for human exposure, lead is ranked as the number one priority hazardous substance in the U.S. Environmental Protection Agency’s (EPA) National Priorities List (NPL).

2. Lead Contamination in Soil

Lead is a naturally occurring metal found in small amounts in the earth’s crust. Most of the contaminant lead in our environment comes from human activities like mining, manufacturing, and the burning of fossil fuels. Lead contaminated soil, as a result of deposition of flaking lead paint, airborne lead fallout and past environmental disposal practices, particularly at sites of past industrial activities, is one of several major sources of lead exposure which have been identified. When lead enters the soil, it may change into different forms due to the action of sunlight, air, and water via chemical and biological processes.

Lead may mobilize from soil when lead-bearing soil particles run off to surface waters during heavy rains. This may result in the downward movement of lead and the fixation of lead in soil by leaching into various phases of soil. This decreases the possibility of lead exposure but increases the possibility of lead getting into the food chain by plant uptake and making it difficult to remove the lead from soil.
Soils consist of different size particles and different particle sizes contribute differently to the environment. Smaller particles are found[^4][^5][^6] to have significantly higher bioavailability than larger ones because of their high surface area for absorbing lead, better dissolution during the short exposure period in the acidic environment of the stomach, and light weight so that they can be easily entrained in the prevailing wind and inhaled by humans.

It is estimated that the range of children, in the U.S., potentially exposed to lead in dust and soil is 5.9 million to 11.7 million. Because of health concerns, lead from gasoline, paints and some other products has been dramatically reduced in recent years, but the lead contaminated soils are still there. So the evaluation and possible remediation of lead contaminated soil is very important.

Proper evaluation of the impact of contaminated soil is difficult, largely because the soil environment is a very complex setting and the mechanism of adsorption and de-sorption of metal contaminants from the different parts of the soil is complicated and poorly understood. In addition, the bioavailability of lead in soil depends on human exposure factors, soil condition and forms of lead in soil.
3. Soil Interactions

Regardless of the origin, most soils consist of four basic components: mineral matter, water, air, and organic matter. These materials are present in a fine state of subdivision (individual particles), are intimately mixed and subjected to physical, biological and chemical changes. Soils have significant variations in appearance, fertility, and chemical characteristics, depending on the mineral and plant materials from which they were formed. Soils continue to be transformed as they are in a dynamic environment where a large number of reactions occur simultaneously. A few of the reactions are relatively simple and well understood, but the vast majority are not yet completely explained.

The fate of lead in soil is affected by specific or exchange adsorption at mineral interfaces, the precipitation of sparingly soluble solid phases, and formation of relatively stable organo-metal complexes or chelates with the organic matter in soil. Many reactions depend on the participation of water, mineral, and biological factors in a dynamic setting. The complexity of the soil environment results in a variety of forms of lead existing in different parts of the soil.
4. Lead Determination in Soils

Total lead concentration, which is obtained by using a strong digestion procedure, used to be cited as a criterion to assess the potential effects of soil contamination. But the use of total lead concentration implies that all forms of lead have an equal impact on the environment. This obviously is not true, because soils are not homogeneous but are complex mixtures of components of different origin and chemical behavior and so the biological availability of lead depends on the forms of the metal in the soil. Allcroft\textsuperscript{4} reported on long term feeding studies in which several lead compounds were fed to cattle and observed great differences in intake of lead. Thus although the use of total concentration can be used to identify areas possessing content levels of lead higher than background, which is useful for environmental pollution monitoring, it fails to provide more definitive information of the geochemical partitioning of lead in soils and bioavailability.

The evaluation of biological availability of lead, the recycling of metals in soils, and other increasing needs (e.g., legal cases dealing with, say, pollution problems) require clearer resolution of the forms of metal in the soil and possibly absolute specification of the chemical forms responsible for undesirable effects. However, direct determination of specific soil lead associations is difficult, if not impossible, because of the great
variety of solid phases that can bind lead, their amorphous character, and the low metal concentration involved. As an alternative, methods for fractionating the soil chemically and using selective chemical extraction to obtain information about the phase speciation of metal in soils have been developed.

5. Soil Fractionation

The metal content of a soil can be distributed between a number of component phases which range in nature from fragments of the initial base rock (minerals, carbonates, sands) to accumulations of weathering products (hydrous oxides, clay minerals, organic matter). The metal may be bound to the various components by a range of chemical processes (e.g., ion exchange, adsorption, compound formation, etc.). Analytical determination of the distribution of metals among these phases can be approached by phase-selective extracting reagents.

The fractions of soils usually separated are:

1.) Exchangeable, in which the sorption-desorption processes are likely affected by changes in water ionic composition;

2.) Bound to carbonates. This fraction generally has significant trace metal concentrations associated with it; the amount is susceptible to changes of pH;
3.) Fe and Mn oxides, which exist as nodules, concretions, cement between particles, or simply as a coating on particles and are excellent scavengers for trace metals and are thermodynamically unstable under anoxic conditions\(^8\).

4.) Organic matter. Various forms of living organisms, detritus, coatings on mineral particles, etc. that trace metals may be bound to.

5.) Residual mineral fractions, which may hold trace metals within their crystal structure and are not expected to release them when mild reagents are used.

For some fractions, the release of metal ion may require selective dissolution of that particular substrate because of strong bonding between metal ion and soil component, and in most cases, a number of alternatives are available.

For evaluation of the ion exchangeable component, Gupta et al.\(^9\) employed 1M NH\(_4\)OAc; Gibbs\(^10\) and Shuman\(^11\) reported using 1M MgCl\(_2\), and other extractants used include 5M NH\(_4\)Cl (pH=8)\(^12\), 1M NaOAc\(^13\), and 0.05M CaCl\(_2\)\(^14\).

To release metal ions weakly bound to specific inorganic sites (e.g., on carbonates), McLaren\(^14\) used 0.4M HOAc and Tessier et al.\(^13\) selected the procedure involving 1M NaOAc and adjustment
of the pH to 5 with HOAc because the lower pH value led to a partial attack of Fe and Mn oxides.

The poorly ordered hydrous oxides of Al, Fe, and Mn have large surface areas and reactivity. This can result in the retention of large amounts of metal ions by such species\textsuperscript{15,16}. For this particular determination, the recommended extractants include sodium carbonate solutions, sodium fluoride, and sodium dithionite/potassium pyrophosphate mixtures\textsuperscript{17}. Chao\textsuperscript{18} reported a 0.1M NH\textsubscript{2}OH·HCl solution prepared in 0.01M HNO\textsubscript{3} (pH=2) to be a reagent that selectively dissolves the metal associated with Mn oxides. Shuman\textsuperscript{19} tested seven reagents designed to remove amorphous and/or crystalline Fe or Mn oxides and decided that NH\textsubscript{2}OH·HCl alone solubilized as much Mn as most of the other extractants indicating that it is specific for Mn oxides. Metals associated with amorphous Fe and Al oxides have been determined using acidic ammonium oxalate\textsuperscript{20} and 0.25M NH\textsubscript{2}OH·HCl-0.25M HCl combined solution, modified to extract at 50 °C for 30 min\textsuperscript{21}. A dithionite / citrate mixture also has been widely used to release the trace metals bound to the Fe, Mn oxides present in soils\textsuperscript{9,13}.

Total retrieval of the fraction associated with organic matter has been sought through oxidation of this component by using H\textsubscript{2}O\textsubscript{2}\textsuperscript{9}. Other methods proposed have been 1M K\textsubscript{4}P\textsubscript{2}O\textsubscript{7}, described by McLaren \textit{et al.}\textsuperscript{14} and NaOCl, used by Gibbs\textsuperscript{10}.
Strong acidic extractants are used for dissolving silicate or minerals that have not been attacked by the milder reagents. Acid mixtures appear to release a high proportion of the total content of metal (by effectively dissolving precipitated components, releasing adsorbed and complexed material, etc.), but leaching from silicate lattices tends to be partial, and, for maximum recovery, HF has to be included in the mixture. Gupta used HF-HNO$_3$-HClO$_4$ digesting the residual or determining the total contents of metal, where Shuman employed HF-HNO$_3$-HCl as the extractant.

6. Fractionation Procedure

All extraction procedures can be grouped into: (1) methods designed to effect the separation between residual and nonresidual metals only, and (2) more elaborate methods making use of sequential extraction. The former methods normally involve a single extraction and offer a better contrast between anomalous and background samples than does the determination of the total metal concentration because the total lead determination also extracts the normally existed lead. Although they are relatively simple and rapid, these techniques suffer from the difficulty of finding a single reagent effective in dissolving quantitatively the nonresidual forms of metal without attacking the silicate crystal forms. The use of sequential extraction, although more time consuming, furnishes
The fractionation procedures usually involve some compromises or assumptions because of overlapping effects. The selection of a reagent for extracting a given form of the metal from the soil and the sequence of extraction affect not only the partitioning of metals in different fractions, but also the total amount of metals in that fraction. Fractionation schemes have not been standardized, and each researcher uses his or her own scheme or a modification of one developed by another. Some earlier schemes have been used as models for recent ones\(^9,10,14\).

A widely and frequently used scheme is that of Tessier \textit{et al.}\(^{13}\) They proposed a five step sequential extraction procedure as following:

\begin{enumerate}
  \item Fraction 1. Exchangeable.
    \[1\text{M MgCl}_2, \text{pH}=7.0 \text{ or } 1\text{M NaOAc pH}=8.2\]
  \item Fraction 2. Bound to carbonates.
    \[1\text{M NaOAc + HOAc pH}=5.0\]
  \item Fraction 3. Bound to Fe-Mn oxides.
    \[0.3\text{M Na}_2\text{S}_2\text{O}_4 + 0.175\text{M Na-citrate + 0.025M H-citrate or 0.04M NH}_2\text{OH HCl + 25\% (v/v)}\]
    \[\text{HOAc @96±3 °C}\]
\end{enumerate}
Fraction 4. Bound to organic matter.

\[ 0.02M \text{HNO}_3 + 30\% \text{H}_2\text{O}_2 \ \text{pH}=2 \ @ 85\pm2 \ ^\circ\text{C} \]

then 3.2M NH\textsubscript{4}OAc in 20\% (v/v) HNO\textsubscript{3}

Fraction 5. Residual.

HF-HClO\textsubscript{4}

Miller et al.\textsuperscript{22} examined the order of extraction for key steps in the sequential procedure. They proposed a nine step sequential method to characterize trace metals in agricultural, polluted, and waste-amended soils. They found that NH\textsubscript{2}OH·HCl reagent and K\textsubscript{4}P\textsubscript{2}O\textsubscript{7} used for Mn oxide and organic metal removal, respectively, solubilize significantly different amounts of Cu and Mn depending on sequence, with K\textsubscript{4}P\textsubscript{2}O\textsubscript{7} extracting more metal when used first. As NH\textsubscript{2}OH·HCl has little effect on organic metals, it should be used before K\textsubscript{4}P\textsubscript{2}O\textsubscript{7}. Noncrystalline and crystalline Fe compounds are solubilized next, using a variety of reagents, and residual (silicate lattice) metals are dissolved in the final step.

7. Argument Presented

Although various sequential extraction approaches have been proposed, their status as useful analytical tools is questioned by some researchers.

Guy et al.\textsuperscript{23} studied model sediments spiked with copper and lead to evaluate the extraction methods, and the results indicated
that chemical extraction procedures can not be used to determine unequivocally the site of adsorbed metals in sediments. The inter-component interference prevented 100% removal of trace metal by \( \text{H}_2\text{O}_2 \) and \( \text{NH}_4\text{Cl} \).

Tipping \textit{et al.}\textsuperscript{24} employed electron probe microanalysis (EPMA) of the solid material and observed that lead was in the manganese phase before extraction and it was present in the iron phase after extraction. The reason is the transfer of a large amount of lead from manganese to iron oxide during hydroxylamine treatment.

Kheboian and Bauer\textsuperscript{25} criticized the accuracy of Tessier's sequential extraction for metal partitioning by using model aquatic sediments. Trace elements of \( \text{Pb} \), \( \text{Zn} \), \( \text{Cu} \), and \( \text{Ni} \) were doped into each phase by adsorption or co-precipitation. Then the model aquatic sediments were treated with a sequential extraction procedure proposed by Tessier \textit{et al.}\textsuperscript{13}. Generally speaking, none of the trace elements were removed at the stage predicted according to Tessier's method. The main reason for this is because of the elemental redistribution.

Tessier\textsuperscript{26} argued the validity of the approach and experimental problems associated with the methods used by Khebian and Bauer and some others. The properties of the model aquatic sediments are unlikely to be sufficiently representative of
real sediments because soils and sediments are a complex mixture of mineral fragments and decomposition products, reflecting the nature of the original base rock, the degree of degradation and leaching introduced by weathering cycles, and the influence of external inputs such as debris or contamination introduced by human activities. The drawback of the model sediment as prepared by mixing a phase doped with a trace metal with other phases not doped with that metal is non-equilibrium distribution of trace metals among various solid phases.

Shan et al.\textsuperscript{27} used a model soil synthesized with several natural minerals and humic acid to evaluate the sequential extraction for speciation analysis of trace elements in soil. They concluded that, when the single natural mineral is used, Tessier’s method is able to remove the trace elements bound to the particular geochemical phase at the appropriate stage. However, when the model soil synthesized with several natural minerals and humic acid is used to examine the validity of Tessier’s method for speciation analysis of trace elements, readsoption and redistribution of trace metals onto the remaining solid phases are quite evident.

Belzile et al.\textsuperscript{28} evaluated the importance of postextraction readsoption of As, Cd, Cu, Ni, Pb, and Zn for each step of a sequential extraction procedure by measuring the recovery of small amounts of trace elements added during the extraction of oxic lake
sediments. They found that, for all the cases but one, the trace element spikes (<100% of the amount present in control samples) were recovered within the limits given by the experimental errors. These results contradicted the large percentages of postextraction readsorption observed for these trace elements in previous studies which used either large spikes (greatly exceeding the amounts present in the control samples) during extraction of natural sediments or simple model sediments.

It is generally recognized that the partitioning of trace elements obtained by the procedures suggested for separating trace elements present in the soil into broad geochemical classes is operational. It is influenced by experimental factors such as the choice of reagents, the time of extraction, and the ratio of extractant to sediment, as well as by inherent analytical problems such as incomplete selectivity and readsorption. Rapin et al.29 further found that the partitioning of trace metals in sediments obtained with a sequential extraction procedure may be affected by the techniques used to preserve the sediments before analysis and the presence or absence of atmospheric oxygen during the extraction steps.

Despite these drawbacks, partial extractions are one of the few ways of exploring an important aspect of environmental trace
element chemistry. They furnish us detailed information about the origin, mode of occurrence, biological and physicochemical availability, mobilization, and downward movement in agricultural and polluted soils, and they have gained considerable success in obtaining information on the bioavailability\textsuperscript{30-33} and the geochemistry of contaminated metals\textsuperscript{34-39}.

8. Objective of Research

Variation in soil properties plays a major role in influencing the distribution of trace metals among various chemical forms. The assessment of bioavailability of lead and possible remediation of a specific site contaminated with lead need the unique soil information available through sequential extraction steps.

The objective of this research was to employ single and sequential extraction procedures to investigate the distribution of lead among various fractions and the relationships of these fractions with respect to the depth of the soil and the different particle size of the soil contaminated by a lead smelter located in Granite City, IL. Due to the soil washing techniques\textsuperscript{40,41} that have recently become popular for remediating sites contaminated with organics and heavy metals, some of the extractants were tested to determine their potential for remediating the soil at this site.
II Experimental Section

1. Soil Sample Collection and Treatment

The soil samples used in the experiments were obtained from the city of Granite City, Illinois. The sample area was about 600 m$^2$ and about 1 km to the southwest of a discontinued smelter site. The sample area was divided into 20 evenly spaced squares and a soil core removed from the center of each square using a LaMotte model EP Soil Sampling Tube. Only the top 10 cm of soil was collected to ensure that the soil samples were oxic. Every sample core was carefully extruded in one piece from the sample tube and put into separate polyethylene bags and sealed shut.

A background sample of 3 sub-samples was collected in the same manner from an area about 10 km to the northeast of the smelter.

The extruded soil sample cores were brought back to the laboratory and cut into ten 1 cm segments. The sample pieces of the same depth in different sample cores were mixed together and air dried in a isolated area at room temperature. After 1 week of drying, the soil sample aggregate particles were broken apart using a ceramic mortar and pestle. This took about 15 min for each mixed
sample. These final depth-separated, composite, disaggregated soil samples were stored in acid-washed polyethylene containers.

For comparison studies of oven-dried vs. air-dried soil, a portion of the original soil sample was oven dried at 50 °C. The remaining original soil samples were placed in sealed polyethylene bags directly and kept in the refrigerator at 4 °C.

2. Material, Apparatus and Measurement

All glassware, polyethylene containers, syringes and plastic filter holders were soaked in >3M HCl overnight and rinsed with Milli-Q® water prior to use. All chemical reagents used in the experiment were of analytical grade and Milli-Q® water was employed in all experiments.

All pH measurements were made using a Fisher Scientific Accumet pH Meter, model 915. The system was calibrated using standard buffer solutions (Micro Essential Lab, Inc.) of pH 4.0 and 7.0 before use. A Burrell Wrist Action Shaker machine was used when agitation was required and centrifugation was done by a Sorvall Superspeed Centrifuge machine (Ivan Sorvall, Inc.).

For filtration, Gelman Sciences Supor-450 (47mm, 0.45 µm), Membrane Filter paper with a Poretics 47mm In Line Holder and Lluer Llok 30cc Single-use Syringe were used.
A Perkin-Elmer 2380 Atomic Absorption Spectrophotometer (AAS) equipped with an air-acetylene premix atomizer-burner was used at 283.3 nm wavelength and 0.7 nm slit width for the determination of Pb concentration. The concentrations were obtained directly from appropriate calibration curves prepared with standard solution prepared from 99.9999% Pb shot (Alfa® AESAR®).

3. Sequential Extraction Procedure

This extraction procedure is based on that used by A. Tessier et al.\textsuperscript{13} for the first four fractions. Some procedural modifications were made to fit our experimental circumstances.

1.) Fraction 1: Exchangeable

In three separate polyethylene centrifuge tubes (50 ml), 1.0g of the soil sample was weighed and 8.00 ml of 1M MgCl\textsubscript{2} (pH=7.0) added. The soil samples were continuously agitated at room temperature for 1 hr. After extraction, the sample tubes were centrifuged 15 min, and the supernatant pipetted, filtered, and measured by AAS. The remaining sample in each of the three tubes was mixed with 8.00 ml de-ionized water, shaken for 10 min and centrifuged for 15 min. This second supernatant was discarded.
2.) Fraction 2: Bound to Carbonates

8.00 ml of 1M CH₃COONa solution, which had been adjusted to pH=5.0 with diluted CH₃COOH, was added to each of the three sample tubes from Fraction 1 and continuously agitated for 5 hr at room temperature. After agitation the sample tubes were centrifuged 15 min and the supernatant was pipeted, filtered, and measured by AAS. The remaining sample in each of the three tubes was mixed with 8.00 ml de-ionized water, shaken for 10 min and centrifuged for 15 min. This second supernatant was discarded.

3.) Fraction 3: Bound to Iron and Manganese Oxides

A solution of 20.0 ml of 0.04 M NH₂OH·HCl in 25% (V/V) CH₃COOH was added to each of the three sample tubes from Fraction 2. The sample tubes were placed into a water bath at 96±3 °C and agitated every hour for 6 hr. After agitation, the sample tubes were centrifuged 15 min. The supernatant was pipeted, filtered, and measured by AAS. The remaining sample in each of the three tubes was mixed with 8.00 ml de-ionized water, shaken for 10 min and centrifuged for 15 min. This second supernatant was discarded.
4.) Fraction 4: Bound to Organic Matter

To the sample residue in the tubes from Fraction 3 were added 5.00 ml 30% H₂O₂ adjusted to pH=1.80 with concentrated HNO₃. The sample tubes were placed into a water bath at 85±2 °C and extracted for 2 hr with agitation once per hour.

Another 3.00 ml of 30% H₂O₂ adjusted to pH=1.80 with concentrated HNO₃ were added to each of three sample tubes. Again the samples were placed in the 85±2 °C water bath for three hours. After the sample tubes cooled, a solution of 5.00 ml of 3.2 M CH₃COONH₄ in 20% (V/V) HNO₃ was added as well as 7.00 ml of Milli-Q® water, diluting the sample solution to 20 ml. The sample tubes were then agitated 30 min. After extraction, the sample tubes were centrifuged 15 min. The supernatant was pipeted, filtered, and measured by AAS.

4. Particle Size Distribution

Stacked U. S. A. Standard Testing Sieves (Fisher Scientific Company) of No. 60 (250 µm of opening), No. 80 (180 µm of opening), No. 120 (125 µm of opening), No. 170 (90 µm of opening) and No. 230 (63 µm of opening) were used for particle size analyses. A 20.0g sample of soil was precisely weighed into
the top sieve. The sieves were hand shaken in a plane for 30 min. After the shaking was done, the soil sample retained in each sieve was weighed. Four replications were made and the particle size distribution calculated.

5. Extraction by Aqua Regia

Three samples of 1.0 g soil were weighed into polyethylene centrifuge tubes. 1.00 ml de-ionized water, 2.50 ml concentrated HNO₃ and 7.50 ml concentrated HCl were added to each tube. The soil samples were placed into a water bath at 95±3 °C and extracted for 4 hr.

After cooling, the sample tubes were centrifuged 15 min and the supernatant was pipetted and filtered into a 100 ml volumetric flasks. The residue sample in the tubes was washed with 10 ml de-ionized water for 10 min and then centrifuged 15 min. The supernatant was pipetted and filtered into the same volumetric flask. This wash step was repeated 3 times. Then the volumetric flasks were diluted to the mark and the solutions measured with AAS.

6. Extraction by Water (pH=7.0)

Three samples of 1.0 g soil were weighed into polyethylene centrifuge tubes and 20.0 ml de-ionized water pipetted into each tube. The tubes were shaken (24 hr., 48 hr., and 192 hr. of time
intervals were measured) and centrifuged for 15 min. The supernatant was pipetted, filtered and measured with AAS.

7. Extraction by Acidic Water (pH=2.00±0.05)

Three samples of 2.0 g soil were weighed into polyethylene centrifuge tubes and 20.0 ml de-ionized water, adjusted to pH=2.00±0.05 with diluted HNO₃, was pipetted into each tube. The tubes were agitated for 2 hr, 5 hr, 12 hr and 24 hr. The pH of the solutions was monitored and adjusted to pH=2.00±0.05, if necessary, at 0.5 hr and 4 hr. Then the sample tubes were centrifuged 15 min and the supernatant pipetted, filtered, and measured by AAS.

8. Extraction by Oxalic Acid Solution.

Three 1.0 g samples of soil were weighed into polyethylene centrifuge tubes and 20.0 ml 0.01 M (or 0.02 M) oxalic acid solution pipetted into the tubes. The tubes were wrapped in aluminum foil and agitated for different time intervals (1 day, 2 days, 4 days and 8 days of time interval were used). Then the sample tubes were centrifuged for 15 min and the supernatant was pipetted, filtered, and measured by AAS.
9. Extraction by Triton Solution

1.) Extraction by 1% Triton Solution.

Three samples of 1.0 g soil were weighed into polyethylene centrifuge tubes and 20.0 ml 1%(Wt%) Triton solution pipetted into each tube. The sample tubes were agitated for 5 hr (or 48 hr) and then were centrifuged for 15 min. The supernatant was pipetted, filtered, and measured by AAS.

2.) Extraction by 1% Triton Solution at pH=2.8.

The procedure was the same as that for extraction by 1% Triton solution except that the pH of 1% Triton solution was adjusted to 2.8 with 6 M HNO₃.

10. pH Changes with Time

Three 1.22 g samples of wet soil (corresponding to 1.0 g dried soil) were weighed into polyethylene centrifuge tubes and 10.0 ml of 0.01M CaCl₂ solution added into each tube. The tubes were agitated in a 25 °C water bath for different time intervals (a total of 13 different time intervals were measured). The tubes were then centrifuged for 5 min and the supernatant decanted and the pH measured by immersing the pH electrode into the solution for 15 min.
Air dried and oven dried soil samples were tested by using the same procedure.

11. Determination of Total Soil Organic Matter

Three soil samples of approximately 2-5 g were weighed into 50 ml beakers and placed into a drying oven set at 105 °C for 4 hr. After cooling in a desiccator, the sample beakers were weighed to the nearest 0.001 g. Next the sample beakers were placed into a muffle furnace and the temperature raised to 400 °C for 4 hours. The sample beakers were removed from the muffle furnace, cooled in a desiccator, and re-weighed to the nearest 0.001 g.

The following equation was used to calculate the total soil organic matter:

\[ \%OM = \frac{\left( W_{t_{105^\circ C}} - W_{t_{400^\circ C}} \right) \times 100}{W_{t_{105^\circ C}}} \]

\( W_{t_{105^\circ C}} \): Weight of the soil sample at 105 °C.
\( W_{t_{400^\circ C}} \): Weight of the soil sample at 400 °C.
III Results and Discussion

1. Soil Sample Collection and Pretreatment

a. Sample Collection

The soil samples were collected from an open area, about 1 km to the southwest of the old smelter site property, between railroad tracks and a city road, about 50 m from the road and 100 m from the railroad tracks. There were no residences near the site. Cars occasionally passed on the road. This area should reflect primarily the contamination by the smelter with only minimal impact by traffic fallout, agricultural turnover and any other human activities.

The background soil sample was collected from an area about 10 km from the smelter, in an open area near a community college outside of town and about 200 m from a road. Surveys\textsuperscript{43,44} around smelters have shown maximum soil lead accumulations close to the stack and which decrease rapidly with distance. The distance-decline curve is often exponential and soil contamination with metals from smelter fallout appeared centered within 2-3 km of the smelter. So the background soil sample should reflect the normal soil lead condition of this area.
b. Effects of Sample Pretreatment

In addition to procedural and analytical problems in determining the soil phase of lead, other factors may influence sequential extraction results. The extraction sequence, the time of extraction, the ratio of extractant to the sample, incomplete selectivity, readsorption, sample pretreatment, and sample storage may also affect the partitioning of trace metals.

Rapin et al.\textsuperscript{29} reported that several statistically significant decreases or increases in trace metal concentrations were observed after anoxic sediment samples were exposed to atmospheric oxygen. They ascribed this result to the oxidation of sulfides and iron present in sediment (followed by the precipitation of ferric hydroxide), leading to the production of H\textsuperscript{+} ions, which would release trace metals from the solid phases and the newly formed Fe-Mn oxides would tend to scavenge the trace metals.

Surface soil is different from the sediment in that it contacts directly with oxygen. Nevertheless, we wanted to test if sample pretreatment had any possible effect on our extraction process. We used a pH to monitor the behavior of soil samples of different pretreatment: original wet, air-dried, and oven-dried. In 0.01 M CaCl\textsubscript{2} solution, we found, in Figure 1, three different curves for the different pretreated samples. The dried soil sample solutions have higher pH at the beginning than wet soil probably because they need
to consume more \( \text{H}^+ \) on their dried surface sites and exchange with other cations. The reason for the final difference of pH is probably the oxidation of sulfides and iron that stated above by Rapin et al. This result indicates that the soil samples are also affected by different pretreatments. In this study, air-dried soil sample was used for particle size and depth analysis considering that surface soil is oxic. All results were subjected to this processing method.

The addition of a secondary exchange cation \( \text{Ca}^{2+} \), can promote the removal of heavy metal held via cation exchange. pH change furnishes some indication of the solution behavior during the course of the extraction. Figure 2 displays the curve of pH value changes with extraction time when 1.0 g original wet soil was mixed with 10.0 ml 0.01 M \( \text{CaCl}_2 \) solution. The pH increased rapidly in the first 1 hour, then the change slowed down and after about 6 hours, the pH tended to be constant and the system seems to have reached an equilibrium. This curve is important for deciding the extraction time of the experiment or soil washing process.

2. Lead Distribution vs. Particle Size

a. Distribution of Particle Size

The particle size distribution of the sample soil from Granite City was determined by sieve analysis because it is quick and simple to use. Resources required the use of a hand-shaking sieve
All analytical results related to particle size were based on this method. The shaking time was long enough for the soil particles to reach the sieve where they do not pass, but not too long to cause the natural particles to be broken by mechanical force.

Figure 3 is the particle size distribution. Over fifty percent (by mass) of the particles are larger than 250 µm. They were either large particles or aggregated soil because we did not grind the samples. About 15% of the particles belong to the smallest (<63 µm) particle group. The particles setting on the intermediate sieves have similar weight percentage, from 6% to 10%.

The smaller the soil particles, the more bioavailable the lead of contaminated soil. Barltrop and Meek\textsuperscript{5} reported that, based on the animal feeding test, the absorption of metallic lead (particle size 180-250 µm) was lower than the absorption of lead salt (particle size < 50 µm) and decreasing the lead particulate size from 197 µm to 6 µm resulted in a 5 fold enhancement in absorption. Different particles have different surface areas and thus different interactions between particles and trace elements, and particles and humans. Small particles are more easily digested, more easily disturbed by wind, and expected to absorb more lead than large particles because of their larger surface area.
b. Lead Content (aqua regia extraction) vs. Particle Size

Hot HNO₃ has been repeatedly shown to extract total non-matrix soil lead, or at least 95% of soil lead, compared to total soil dissolution method (HF)⁴³. We chose aqua regia digestion because this digestion is stronger than HNO₃ and easy to use. The method selected here does not represent the total extraction of lead, but the breakdown of the organic material and the leaching of lead from the inorganic soil fraction. In this discussion, this lead content is used as the total lead contained in the soil sample because it stands for over 95% of soil lead.

In order to obtain significant differences of lead content between different soil particles, the largest particle (>250 µm), the smallest (<63 µm), and one intermediate (90 µm-125 µm) of the soil sample from 4 cm depth (which has the highest lead concentration) were digested by aqua regia. Figure 4 is the result of the lead content of different particles. The intermediate particle shows the highest lead content, 563.3 mg/kg, while the smallest particle contains the lowest, 456.6 mg/kg and the largest particle contains 504.5 mg/kg. This result contradicts our expectation that the smallest particle should have the highest lead content because of their larger surface area. Other studies⁴⁵ report that the lead content of soil, street dust, city dust, and house dust increases as the particle size decreases. One⁴⁶, however, said that lead content
of soil and dust varies dramatically as a function of particle size. It seems that the particle size from the lead emission source may sometimes contribute most to the particle size group that contains the highest lead content. Low lead content in smallest particle means a low possible bioavailability of lead in the gastrointestinal tract.

c. Sequential Extraction of Different Particle Size

Lead particles are emitted from smelters primarily in the form of PbSO₄, PbO·PbSO₄ and PbS. The fate of lead in soil is affected by the specific or exchange adsorption at mineral interfaces, the precipitation of sparingly soluble solid phases, and the formation of relatively stable organo-metal complexes or chelates with the organic matter in soil⁷.

For the total lead content in different particle size, the results of sequential extraction furnished us detailed information about how the lead contained in certain particle sizes distributed among different fractions. Table 1 contains results of sequential extractions for three different particle size: >250 µm, 180-125 µm and <63 µm.

For the same particle size, the exchangeable fractions contained 31.3-38.3 mg/kg, about 6-8% of total lead; bound to carbonates fractions 30.8-45.0 mg/kg, about 6-9%; bound to Fe-Mn
oxides 171.3-204.5 mg/kg, about 35-40% of total lead; bound to organic matter 118.7-183.3 mg/kg, about 26-33%. Residual fractions, which are obtained by subtracting the lead content of the first four fractions from the total lead content, contained 88.7-99 mg/kg, about 18-19.4%. Figure 5 shows how the lead was partitioned among various fractions for different particle sizes. Over 80% (83.4-88%) of total lead is found in the final three fractions, especially the Fe-Mn oxides and organic matter fractions. Thus mobility of lead in the soil will be influenced by interactions associated with the oxide and organic soil fractions.

Among the different particle sizes, the percentage lead content in exchangeable fractions and carbonate fractions increase slightly as particle size decreases, considering the total lead content in the smallest particle size, <63 µm, is the least of the three, while they are smaller in Fe-Mn oxides and organic matter fractions as both the particle size and total lead content decreased. The lead content of the residual fraction seems to remain unchanged with the particle size and the total lead content.

Comparing results of the large particle and the smallest particle and considering the decrease of the total lead content from large to smallest particle, it seems that slightly more lead is concentrated in exchangeable and carbonates fractions in the smallest particle, while the concentration of lead in Fe-Mn oxides
and organic matter fractions are decreased with more drop in the organic matter fraction.

In general, the free ion Pb$^{2+}$ can react with biological membranes and have a direct toxic effect. The bioavailability of heavy metals bound to organic matter or inorganic anions will depend on the strength of the binding; strongly bound metals will tend to be non-bioavailable while weakly bound metals may be readily taken up by plants. Among the five fractions of our sequential procedure, exchangeable and bound to carbonates fractions are considered more accessible to animals and plants than the other three fractions because of weak interaction between lead ion and soil particles, and changes in water ionic composition and pH are likely to affect sorption-desorption processes. The exchangeable fraction is generally considered to be the one which constitutes the immediate nutrient reservoir for the soil solution, and lead carbonate was reported$^5$ to have the highest absorption in animal feeding studies, which may reflect the greater solubility of this compound in gastric juice.

So this increase of lead in more accessible fractions means more bioavailability of lead in the smallest particles compared to the other particles even though they had less total lead content.
3. Lead Distribution vs. Depth of the Soil

a. Lead Content (aqua regia extraction) vs. Depth of the Soil

Figure 6 shows the profile of lead content in both contaminated and background soil as a function of soil depth. The lead content of different depths for the contaminated soil are presented in Table 2. Values range from 483.5 mg/kg for the 2 cm soil to 573.1 mg/kg from the 4 cm soil. The background soil exhibited lead concentration ranging from 30.2 mg/kg for the 9 cm soil to 77.0 mg/kg for the 2 cm soil. On average, the lead content of contaminated soil is about 8.8 times that of background soil. As the depth of soil increases, the lead contents of both contaminated soil and background soil showed a decreasing trend, but this was minor for contaminated soil.

b. Sequential Extraction of Different Depths

To obtain detailed information about how the lead content in the soil of different depths distribute among different fractions, three different depths of soil were analyzed with sequential extraction: 1 cm, 5 cm and 10 cm.

The results of sequential extractions of different depths are listed in Table 3. The relative contributions of each fraction to the total lead concentration are displayed in Figure 7.
For the same depth of soil, lead contents of the exchangeable fractions range from 25.0 to 35.5 mg/kg, about 5% to 7.2% of total lead concentration. The carbonates fractions contain 22.2-27.2 mg/kg, or 4.3% to 5.5%; Fe-Mn oxides fractions 142.0-191.1 mg/kg, 27.3% to 39%; organic matter fractions 130.3-147.4 mg/kg, 25.8% to 28.4%; and residual fractions 97.3-183.4 mg/kg, 19.8% to 35.3%. Most of the lead (over 87%) is concentrated in the last three fractions, and only about 9-13% of the total lead remain in the first two fractions, the most accessible fractions.

Table 4 compares the results of chemical partitioning (percentage of total) of lead in Granite City soil, Saint-Marcel and Pierreville (Quebec, Canada) sediments, reported by Tessier et al.\textsuperscript{13}, Glasgow soil (Great Britain), investigated by Gibson et al.\textsuperscript{47} and Lancaster soil (Great Britain), studied by Harrison et al.\textsuperscript{48}. Similar multi-step sequential extraction procedures were used for all studies. Lead content of Granite City soil is relatively higher in exchangeable and organic matter fractions, but lower in carbonates and Fe-Mn oxides fractions than the other soils. But one thing is true for all the soils and sediments: most of the lead is concentrated in the last three fractions, namely Fe-Mn oxides, organic matter and residual. Lead in these fractions is considered to be held by covalently bound, organo-metal complex or chelates and in the silicate crystal lattice. This large portion of lead, firmly held
in the final three fractions, severely restricts the mobility of lead. This means that the surface soil will remain highly contaminated and could have severe long term environmental implications, even though the legislation to reduce lead levels in gas and other products has undoubtedly caused a substantial and rapid drop in atmospheric lead concentration.

For different depths of soil, lead concentration (Table 3) in exchangeable and Fe-Mn oxides fractions shows a slight increase as the soil depths increase while it drops significantly in the residual fractions. Decreased lead content in exchangeable fraction of the surface soil will lower its bioavailability by uptake of lead into food crops or the direct intake and absorption of lead by humans.

Correlation between Fe-Mn oxides and lead accumulation has previously been reported. Zimdahl and Skogerboe\textsuperscript{49} further suggested that lead fixation by organic material is more important than precipitation by carbonate or sorption by hydrous oxides. They proposed that, because of the significant linear correlation for the association of the Fe-Mn oxides with organic carbon, organic carbon may serve as a fixation medium for Fe-Mn oxides as well as lead; or oxidic Fe and Mn particles may serve as accumulators for both organic carbon and ionic lead.

In our study, we obtained a significantly higher lead concentration in organic matter fraction, but lower in Fe-Mn oxides.
fraction than other comparative soils. The total soil organic matter tested (also listed in Table 3) decreased as the soil depth increased. It dropped rapidly in the upper 5 cm. But this dramatic drop in total organic matter did not result in a big decrease of lead concentration in organic fraction. At the same time, lead content in Fe-Mn oxides fractions increased with the depth. This observation is perhaps either because the organic matter is not saturated with lead and the loss of some kind of organic matter does not affect the lead content in this fraction, or consistent with there being an association existing between Fe-Mn oxides and organic matter.

Lead concentration in the residual fractions (Table 3) showed a significant decrease as the soil depth increased. Mineral-lattice-bound lead is representative of the natural metal content of the integral soil matrix and should not vary directly with total lead concentration found in contaminated soil.

However, changes in the residual fraction do not necessarily correspond to changes in mineral bound lead. Tessier et al.\(^ {13} \) and Catanzaro\(^ {50} \) found that heterogeneity or the presence of relatively large lead-rich particles in the sample will cause low reproducibility for "acid leachable" lead in the sediments. Gibson et al.\(^ {47} \) proposed two reasons to explain that the final fraction may not comprise merely the mineral-lattice-bound metal component when general increases in the actual residual content of each
element in their sample happened as the total concentration increased. First, the individual extractants in single- or multi-step schemes are probably not truly selective. It is virtually impossible to ensure that metals are released solely from the defined specific phase considered most susceptible to attack by the chosen chemical reagent. So the more the total lead concentration, the more the residual content of lead left. Second, it is possible that the increase in measured residual content is directly related to the physicochemical nature of the original particulate contamination, a component of which may persist in the soil environment and remain inaccessible to all chemical measures except total dissolution.

Even though our data showed a decrease in total lead content as the depth increases, this change is not as significant as that of residual lead. So the second reason may be the main reason. In our case, it may be that a large portion of the undefined lead-containing large particles still exist in the top soil. Our result of particle size analysis also showed that large particles had higher lead concentration. If this is the case, long term environmental problems may result because of slow release of lead from these particles.

Besides the two reasons above, there is a third reason for this significant decrease in the residual fraction as the soil depth increases. It is perhaps due to different soil weathering conditions. Deeper soil may break down over time and retain less "residual"
lead. Oxides represent the end product of weathering. Our results of sequential extraction of different soil depths showed a significant increase in lead content in Fe-Mn oxides fractions when soil depth increased. This increase of lead content in Fe-Mn oxide fractions may be due to the increased Fe-Mn oxide from the more weathered soil and the movement of lead from the decreased residual fractions as the depth increased.

4. Mobility of Lead and Remedial Action by Lead Extraction

Lead may mobilize from soil when lead-bearing soil particles run off to surface waters during heavy rains. The downward movement of lead from soil by leaching is very slow under most natural conditions. But some conditions, such as lead concentration in soil approaching or exceeding the sorption capacity of the soil, the presence of materials that can form soluble chelates with lead or low pH of leaching solution, may cause leaching. Partial favorable conditions for leaching may be present in some soils near a lead smelter.

Remedial action methods which require some form of soil treatment to reduce potential health risks include soil removal, soil containment, contaminant extraction which includes soil washing and flushing, and deep tilling. Contaminant extraction involves chemically treating the contaminated soil and can effectively
remove the metal. Because of this advantage, soil washing is often employed. It should be noted that extraction efficiency is not the only factor to be considered in choosing the extractant. Other factors include cost, toxicity to the environment, recovery of the soil extracted and recycling of the extractant. These factors were not considered in this study.

**a. Extraction by Water (pH=7.0)**

Most soils contain water. Ionic lead can move between different soil fractions through the interaction of soil and water. Water is also the often used extractant for soil washing.

We studied the potential of water for lead mobilization. Table 5 lists the result of lead concentration of a pure water extraction solution measured at different extraction times. These results indicated that, after as long as 192 hours (8 days) of extraction, there was still no significant lead released from the soil under our experimental conditions. This means that the lead was so firmly fixed in the soil phase that the contamination will be limited on site. Downward movement and flowing with rain will be very slow. Our results show that the soil washing by water is not feasible for this site.
b. Extraction by Acidic Water (pH=2.0)

By using HNO$_3$ to keep the solution pH at 2.0, we studied the soil behavior in the acidic water. Lead concentration in the extraction solution showed an increase with the extraction time during our tested time interval (Figure 8). One reason for this observation is because of the presence of hydrous oxides. A general mechanism of adsorption of metal ions on hydrous oxides has been described$^8$ as the exchange of bound H ions of the oxide surface with metal ions by the following scheme:

\[
M^{n+} + x (≡OH) \leftrightarrow M(OH)_{x}^{(n-x)+} + x H^+
\]

in which M is the metal ion to be absorbed and (≡MeOH) and (MeO) are surface sites. This model explains the pH dependence of the adsorption of metal ions by hydrous Mn and Fe oxides. The equilibrium will be driven to the left and more metal will be released as the pH decreases. Carbonates will also be dissolved when H$^+$ concentration increases. It follows that acid rain may cause mobilization of lead from soil to water and increase the bioavailability of lead from soil.
c. Extraction by Oxalic Acid Solution

Oxalate treatment is known to dissolve amorphous oxides\textsuperscript{17}. We studied the soil extraction by 0.01 M H\textsubscript{2}C\textsubscript{2}O\textsubscript{4} at different extraction times. The result in Table 6 showed that lead concentration did not change with the extraction time, and their values were close to 1.00 ppm standard solution. We calculated the solubility of PbC\textsubscript{2}O\textsubscript{4}, which is 1.08 mg/l (1.08 ppm), from its K\textsubscript{sp}. Only the amount corresponding to the solubility of PbC\textsubscript{2}O\textsubscript{4} can be dissolved in the extraction solution. To verify this, we doubled the concentration of extractant H\textsubscript{2}C\textsubscript{2}O\textsubscript{4}. Table 7, which is the result of using 0.02 M H\textsubscript{2}C\textsubscript{2}O\textsubscript{4} as the extractant, indicated the same result as that of 0.01 M H\textsubscript{2}C\textsubscript{2}O\textsubscript{4}. It suggests that oxalic acid may precipitate lead from soil and so only a limited amount of lead can get into solution.

d. Extraction by 1\% Triton Solution

Surfactant solution sometimes is sprayed on the contaminated soil. To test its effect on lead mobility, we used 1\% Triton solution as the extractant. Table 8 lists the result of lead concentration measured after 5 hours and 48 hours extraction. This result shows that there is no significant lead released during the extraction.

Table 9 is the result of acidified Triton solution (pH=2.8) as the extractant. Unlike the acidic water, acidified 1\% Triton solution
Triton, C_{14}H_{22}O(C_2H_4O)_n, consists of long chain molecules which coat soil particles and protect them from attack by H^+ ions in the solution. This implies that Triton may be used as a soil containment reagent to prevent lead release from soil.

5. Conclusions

Single- and multi-step chemical extraction studies of Granite City soil let us make the following conclusion:

1. Soil sample pretreatment and storage may also affect the result of analysis, so care must be taken on storage and processing of soil sample after collection, even of oxic samples.

2. For different soil particles from the Granite City, IL, site, the smallest particles, despite expectations, do not have the highest lead content. The result of sequential extraction of different soil particles indicates that the lead content in the more accessible fractions, exchangeable and carbonates, increases as the soil particle gets smaller, while in large particles more lead was fixed by Fe-Mn oxides, organic matter, and residual lattice. The smaller particles, even
though they have less total lead content, are more dangerous to the environment than larger ones.

3. As the depth of soil increases, the lead content in the soil tends to decrease. Most of the lead is fixed in Fe-Mn oxides, organic matter and residual fractions and severe long term environmental problems are inevitable. That lead concentration in organic matter fraction does not drop rapidly with that of total organic matter as the soil depth increases, may be because either there is an association existing between Fe-Mn oxides and organic matter, or the organic matter is not saturated with lead. High lead content of the residual fraction in surface soil may be mainly caused by a portion of the undefined lead-containing large particles. Non-selective reagents and different weathering conditions may also be responsible for this increase.

4. Bench scale extraction results indicate that soil washing by pure water is not feasible for this site but a lower pH in solution can significantly release lead from soil; oxalic acid can extract only a limited amount of lead into solution, most precipitate as lead oxalate; Triton is an effective soil containment reagent to prevent lead release from soil.
Table 1. Results of Sequential Extraction of Different Particle Size

<table>
<thead>
<tr>
<th></th>
<th>&gt;250 µm</th>
<th>180-125 µm</th>
<th>&lt;63 µm</th>
</tr>
</thead>
<tbody>
<tr>
<td>(1) Exchangeable</td>
<td>31.3 ± 2.1 (6.2%)</td>
<td>38.3 ± 1.1 (6.8%)</td>
<td>38.0 ± 1.1 (8.3%)</td>
</tr>
<tr>
<td>(2) Bound to Carbonates</td>
<td>30.8 ± 2.1 (6.1%)</td>
<td>45.0 ± 2.7 (8.0%)</td>
<td>39.9 ± 1.1 (8.7%)</td>
</tr>
<tr>
<td>(3) Bound to Fe-Mn Oxides</td>
<td>204.5 ± 7.6 (40.5%)</td>
<td>197.8 ± 9.4 (35.1%)</td>
<td>171.3 ± 21.8 (37.5%)</td>
</tr>
<tr>
<td>(4) Bound to Organic Matter</td>
<td>147.7 ± 12.6 (29.3%)</td>
<td>183.3 ± 4.8 (32.5%)</td>
<td>118.7 ± 17.6 (26%)</td>
</tr>
<tr>
<td>(5) Residual(^a)</td>
<td>90.3 (17.9%)</td>
<td>(98.9)(^b) (17.6%)</td>
<td>88.7 (19.4%)</td>
</tr>
</tbody>
</table>

a. The residual is calculated by subtracting the values of the first four fractions from the total lead content obtained from the aqua regia extraction.

b. Due to lack of sample, this value is estimated by using the total lead content of 125-90 µm size particle.
Table 2. Lead Content in Different Depth of Soil for both Contaminated and Background Soil Sample

<table>
<thead>
<tr>
<th>Soil Depth</th>
<th>1 cm</th>
<th>2 cm</th>
<th>3 cm</th>
<th>4 cm</th>
<th>5 cm</th>
</tr>
</thead>
<tbody>
<tr>
<td>Contaminated</td>
<td>519.9 ± 12.5</td>
<td>483.5 ± 13.3</td>
<td>550.0 ± 13.3</td>
<td>573.1 ± 13.4</td>
<td>504.5 ± 13.9</td>
</tr>
<tr>
<td>Background</td>
<td>76.3 ± 4.7</td>
<td>77.0 ± 14.5</td>
<td>57.0 ± 3.0</td>
<td>63.9 ± 3.0</td>
<td>69.8 ± 9.4</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Soil Depth</th>
<th>6 cm</th>
<th>7 cm</th>
<th>8 cm</th>
<th>9 cm</th>
<th>10 cm</th>
</tr>
</thead>
<tbody>
<tr>
<td>Contaminated</td>
<td>551.2 ± 14.1</td>
<td>560.4 ± 13.8</td>
<td>488.6 ± 14.1</td>
<td>485.5 ± 15.0</td>
<td>490.1 ± 28.8</td>
</tr>
<tr>
<td>Background</td>
<td>65.5 ± 6.6</td>
<td>39.0 ± 8.4</td>
<td>55.4 ± 5.9</td>
<td>30.2 ± 10.1</td>
<td>57.3 ± 11.7</td>
</tr>
</tbody>
</table>

mg/kg
Table 3. Results of Sequential Extraction of Different Depth

<table>
<thead>
<tr>
<th></th>
<th>1 cm</th>
<th>5 cm</th>
<th>10 cm</th>
</tr>
</thead>
<tbody>
<tr>
<td>(1) Exchangeable</td>
<td>24.9 ± 1.7</td>
<td>30.1 ± 1.0</td>
<td>35.5 ± 1.0</td>
</tr>
<tr>
<td>(2) Bound to Carbonates</td>
<td>22.2 ± 1.0</td>
<td>27.8 ± 1.0</td>
<td>27.2 ± 1.0</td>
</tr>
<tr>
<td>(3) Bound to Fe-Mn Oxides</td>
<td>142.0 ± 5.1</td>
<td>176.6 ± 17.6</td>
<td>191.1 ± 11.5</td>
</tr>
<tr>
<td>(4) Bound to Organic Matter</td>
<td>147.4 ± 9.9</td>
<td>130.3 ± 6.8</td>
<td>139.2 ± 10.3</td>
</tr>
<tr>
<td>(5) Residuals a</td>
<td>183.4</td>
<td>139.8</td>
<td>97.3</td>
</tr>
<tr>
<td>Total Soil Organic Matter %</td>
<td>12.0 ± 0.1</td>
<td>6.6 ± 0.5</td>
<td>4.3 ± 1.9</td>
</tr>
</tbody>
</table>

a. The residual is calculated by subtracting the values of the first four fractions from the total lead content obtained from the aqua regia extraction.
Table 4. Chemical Partitioning (Percent of Total) of lead in Granite City Soil, Saint-Marcel and Pierreville Sediments, Glasgow Soil and Lancaster Soil

<table>
<thead>
<tr>
<th></th>
<th>Exchangeable</th>
<th>Carbonates</th>
<th>Fe-Mn Oxides</th>
<th>Organic Matter</th>
<th>Residual</th>
</tr>
</thead>
<tbody>
<tr>
<td>Granite City Soil</td>
<td>4.8 - 7.2 %</td>
<td>4.3 - 5.5 %</td>
<td>27.3 - 39 %</td>
<td>25.8 - 28.4 %</td>
<td>19.8 - 35.3 %</td>
</tr>
<tr>
<td>Sediments \textsuperscript{13}</td>
<td>&lt; 3.6 %</td>
<td>15.4 - 24.9 %</td>
<td>22.5 - 27 %</td>
<td>16 - 20.7 %</td>
<td>26.8 - 46.2 %</td>
</tr>
<tr>
<td>Glasgow Soil\textsuperscript{47}</td>
<td>2 %</td>
<td>11 %</td>
<td>51 %</td>
<td>19 %</td>
<td>17 %</td>
</tr>
<tr>
<td>Lancaster Soil\textsuperscript{48}</td>
<td>1 %</td>
<td>26 %</td>
<td>44 %</td>
<td>12 %</td>
<td>17 %</td>
</tr>
</tbody>
</table>
Table 5. Lead Concentration of Water Extraction Solution (pH=7.0)

<table>
<thead>
<tr>
<th>Time</th>
<th>Milli-Q®</th>
<th>Sample 1</th>
<th>Sample 2</th>
<th>Sample 3</th>
</tr>
</thead>
<tbody>
<tr>
<td>24 hour</td>
<td>±0.26</td>
<td>0.00 (0.26)</td>
<td>±0.26</td>
<td>±0.26</td>
</tr>
<tr>
<td>48 hour</td>
<td>±0.26</td>
<td>±0.26</td>
<td>±0.26</td>
<td>0.26</td>
</tr>
<tr>
<td>192 hour</td>
<td>±0.23</td>
<td>±0.23</td>
<td>0.23</td>
<td>0.00 (0.23)</td>
</tr>
</tbody>
</table>
Table 6. Lead Concentration of Sample Solution Extracted by 0.01 M H$_2$C$_2$O$_4$

<table>
<thead>
<tr>
<th></th>
<th>Sample 1</th>
<th>Sample 2</th>
<th>Sample 3</th>
<th>Mean ± s</th>
</tr>
</thead>
<tbody>
<tr>
<td>24 hour</td>
<td>0.64</td>
<td>0.42</td>
<td>0.86</td>
<td>0.64 ± 0.20</td>
</tr>
<tr>
<td>48 hour</td>
<td>1.32</td>
<td>0.86</td>
<td>0.64</td>
<td>0.86 ± 0.42</td>
</tr>
<tr>
<td>96 hour</td>
<td>0.86</td>
<td>1.09</td>
<td>0.86</td>
<td>0.86 ± 0.20</td>
</tr>
<tr>
<td>192 hour</td>
<td>0.86</td>
<td>0.64</td>
<td>0.86</td>
<td>0.86 ± 0.20</td>
</tr>
</tbody>
</table>

Table 7. Lead Concentration of Sample Solution Extracted by 0.02 M H$_2$C$_2$O$_4$

<table>
<thead>
<tr>
<th></th>
<th>Sample 1</th>
<th>Sample 2</th>
<th>Sample 3</th>
<th>Mean ± s</th>
</tr>
</thead>
<tbody>
<tr>
<td>96 hour</td>
<td>0.99</td>
<td>0.74</td>
<td>0.99</td>
<td>0.99 ± 0.25</td>
</tr>
</tbody>
</table>
Table 8. Lead Concentration of Sample Solution Extracted by 1% Triton

<table>
<thead>
<tr>
<th></th>
<th>Milli-Q®</th>
<th>1 % Triton</th>
<th>Sample 1</th>
<th>Sample 2</th>
<th>Sample 3</th>
</tr>
</thead>
<tbody>
<tr>
<td>5 hour</td>
<td>±0.24</td>
<td>±0.24</td>
<td>0.24</td>
<td>0.24</td>
<td>0.24</td>
</tr>
<tr>
<td>48 hour</td>
<td>±0.23</td>
<td>±0.23</td>
<td>0.00 (0.23)</td>
<td>0.23</td>
<td>0.00</td>
</tr>
</tbody>
</table>

Table 9. Lead Concentration of Sample Solution Extracted by 1 % Triton ( pH=2.8 )

<table>
<thead>
<tr>
<th></th>
<th>Milli-Q®</th>
<th>1 % Triton</th>
<th>Sample 1</th>
<th>Sample 2</th>
<th>Sample 3</th>
</tr>
</thead>
<tbody>
<tr>
<td>5 hour</td>
<td>±0.22</td>
<td>±0.22</td>
<td>0.00 (0.22)</td>
<td>0.00</td>
<td>0.00</td>
</tr>
<tr>
<td>48 hour</td>
<td>±0.23</td>
<td>±0.23</td>
<td>0.00</td>
<td>0.23</td>
<td>0.23</td>
</tr>
</tbody>
</table>
pH of 1.0 g soil (dry weight) in 10.0 ml 0.01 M CaCl$_2$ solution changes with time at 25 °C. Three curves were obtained from soil samples pretreated with three different methods: air-dried, oven-dried and original wet sample.
Figure 1. pH of Soil Solutions of Different Pretreatment Samples vs. Time

- Air Dried Sample
- Oven Dried Sample
- Wet Sample

Hd

Time, min.

0 100 200 300 400 500

7.2 7.15 7.1 7.05 7.0 6.95 6.9 6.85 6.8
Figure 2

pH of 1.22 g original wet soil (1.0 g dry weight) in 10.0 ml 0.01M CaCl$_2$ solution changes with time at 25 °C.
Figure 2. pH of Soil Solution vs. Time
Figure 3

Particle size distribution of air-dried contaminated soil sample. Stacked U. S. A. Standard Testing Sieves (Fisher Scientific Company) of No. 60 (250 µm opening), No. 80 (180 µm opening), No. 120 (125 µm opening), No. 170 (90 µm opening) and No. 230 (63 µm opening) were used with hand-shaking 30 min.
Figure 3. Particle Size Distribution

- 50.4
- 9.9
- 9.6
- 6.7
- 1.5
- <63
- 90-63
- 125-90
- 180-125
- >250
Figure 4

Lead content of three particle size of 1.0 g soil samples, the largest particle (>250 µm), intermediate (90-125 µm) and the smallest (<63 µm), extracted by 10.0 ml aqua regia at 95 ± 3 °C for 4 hours.
Figure 4. Lead Content (aqua regia extraction) vs. Particle Size
Figure 5

The chemical partitioning of lead among various fractions (expressed as percentage of the total) for three different particle sizes: >250 µm, 180-125 µm and <63 µm. The 100% of lead stands for different values for different particles: 504.5 mg/kg for >250 µm, 563.3 mg/kg for 125-90 µm and 456.6 mg/kg for <63 µm. Sequential extraction procedural order is: 1. Exchangeable fraction; 2. Bound to carbonates fraction; 3. Bound to Fe-Mn oxides fraction; 4. Bound to organic matter fraction; 5. Residual fraction.
Figure 5. The chemical partitioning of lead among various fractions (expressed as percentage of the total) for different particle sizes.
Figure 6

The profile of lead content of 1.0 g of soil sample extracted by 10.0 ml aqua regia at 95 ± 3 °C for 4 hours in both contaminated and background soil as a function of soil depth.
Figure 6. Lead Content vs. Soil Depth
The chemical partitioning of lead among various fractions (expressed as percentage of the total) for three different soil depths: 1 cm, 5 cm and 10 cm. The 100% of lead stands for 519.9 mg/kg, 504.5 mg/kg and 490.1 mg/kg for 1 cm, 5 cm and 10 cm soil samples respectively. The sequential extraction procedural order is: 1. Exchangeable fraction; 2. Bound to carbonates fraction; 3. Bound to Fe-Mn oxides fraction; 4. Bound to organic matter fraction; 5. Residual fraction.
Figure 7. The chemical partitioning of lead among various fractions (expressed as percentage of the total) for different depth.
Figure 8

Lead content of 2.0 g soil sample extracted by 20.0 ml deionized water, adjusted to pH=2.0 with diluted HNO₃, for 4 different extraction times.
Figure 8. Lead Content of Acidic Water Extraction vs. Extraction Time
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