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Omaha Soil Mixing Study: Redistribution of Lead in Remediated Residential Soils Due to Excavation or Homeowner Disturbance

Office of Research and Development
Nation Risk Management Research Laboratory

Omaha Soil Mixing Study: Redistribution of Lead in Remediated Residential Soils Due to Excavation or Homeowner Disturbance.

Omaha Lead Superfund Site, Omaha, Nebraska

Engineering Technical Support Center
Land Remediation and Pollution Control Division
National Risk Management Research Laboratory
Office of Research and Development

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This document presents results from the fiscal years 2011-2012 field investigation at the Omaha Lead Superfund (OLS) Site to fulfill objectives outlined in the proposal 'Redistribution of Lead in Remediated Residential Soils Remaining at Depth Due to Excavation or Homeowner Disturbance' (Dr. Todd Luxton, EPA/ORD and Dr. Bradley Miller, ORISE) Draft 2, March, 15 2011 for the Superfund Remedial Project Manager, Don Bahnke (EPA/Region 7) and Robert Weber (EPA/ORD). The purpose of the study was to investigate the redistribution of Pb in remediated residential soils after "normal" home owner excavation within the OLS.

Forward

The US Environmental Protection Agency (US EPA) is charged by Congress with protecting the Nation's land, air, and water resources. Under a mandate of national environmental laws, the Agency strives to formulate and implement actions leading to a compatible balance between human activities and the ability of natural systems to support and nurture life. To meet this mandate, US EPA's research program is providing data and technical support for solving environmental problems today and building a science knowledge base necessary to manage our ecological resources wisely, understand how pollutants affect our health, and prevent or reduce environmental risks in the future.

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Cynthia Sonich-Mullin, Director
National Risk Management Research Laboratory

Abstract

Urban soils within the Omaha Lead Superfund (OLS) Site have been contaminated with lead (Pb) from atmospheric deposition of particulate materials from lead smelting and recycling activities. In May of 2009 the Final Record of Decision stated that any residential soil exceeding the preliminary remediation goal (PRG; 400 mg_{Pb} kg^{-1}_{soil}) would be excavated, backfilled and re-vegetated. The remedial action entailed excavating contaminated soil in the top 12 inches and excavation could stop when the concentration of soil Pb was less than 400 mg kg^{-1} in the top 12 inches, or less than 1200 mg kg^{-1} at depths greater than 1 ft. After removal of the contaminated soil, clean backfill was applied and a grass lawn was replanted. A depth of 12 inches was based on the assumption that Pb-contaminated soil at depth greater than 1 ft would not represent a future risk (ASTDR Health Consult, 2004). This assumption was based on the principal that mixing and other factors encountered during normal excavation practices would not result in Pb surface concentrations greater than the PRG.

The goal of the current study was to investigate the redistribution of Pb in remediated residential surface soils after typical homeowner earth-disturbing activities in the OLS Site. Of specific interest to the region for protection of human health is determining whether soil mixing associated with normal homeowner excavation practices results in surface Pb concentrations greater than the preliminary remediation goal (PRG) (400 mg_{Pb} kg^{-1}_{soil}). Results from the 18 properties investigated indicate that when the concentration of Pb was less than 1200 mg_{Pb} kg^{-1}_{soil} below 12 inches, the surface concentration of Pb remained below 400 mg_{Pb} kg^{-1}_{soil}.

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Acronyms

The following acronyms appear frequently in the report and are listed in alphabetical order.

B1	Initial soil surface Pb soil concentration
B2	Bottom of the excavation hole Pb soil concentration
B3	Excavated spoil Pb soil concentration
B4	Final Soil Surface Pb soil concentration
CERCLA	Comprehensive Environmental Response Compensation and Liability Act
ICP-AES	Inductively Coupled Plasma Atomic Emission Spectroscopy
LCF	Linear Combination Fitting
LCRSH	Lead Contaminated Residential Site Handbook
OLS	Omaha Lead Superfund Site
Pb	Lead
PRG	Preliminary Remediation goal
QAPP	Quality Assurance Project Plan
USEPA	United States Environmental Protection Agency
XRD	X-ray Diffraction
XAFS	X-ray Absorption Fine Structure
XANES	X-ray Absorption Near Edge Structure
XRF	X-ray Fluorescence Spectroscopy

Acknowledgements

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Executive Summary

Urban soils within the Omaha Lead Superfund Site have been contaminated with lead (Pb) from atmospheric deposition of particulate materials from lead smelting and recycling activities. In May of 2009 the Final Record of Decision stated that any residential soil exceeding the preliminary remediation goal (PRG) of 400 milligrams of lead per kilogram of soil (mg_{Pb} kg^{-1}_{soil}) would be excavated, backfilled and re-vegetated. The remedial action entailed excavating contaminated soil in the top 12 inches (1 foot) and excavation could stop when the concentration of soil Pb was less than 400 mg kg^{-1} in the top foot, or less than 1200 mg kg^{-1} at depths greater than a foot (ft). After removal of the contaminated soil, clean backfill was applied and a grass lawn was replanted

The current study investigated the degree of soil mixing and the redistribution of lead within the soil profile after typical Homeowner earth-disturbing or excavation activities. Two methods were employed to evaluate soil mixing. The first method (Homeowner) entailed excavating soil using a common garden spade to a depth of 18 inches. The second (Standard) used a two-man auger to excavate a hole 2 ft in depth. Prior to excavation surface soil samples and an undisturbed soil core were collected to determine the initial concentration and distribution of lead with in the soil. After excavation a composite soil sample was collected from the spoil pile prior to backfilling the hole. A final soil core was collected to evaluate the redistribution of within the soil profile, and a final surface soil sample. Samples were dried and digested following EPA method 3051a.

Data were collected from 18 properties, including duplicate and triplicate samples taken from properties to evaluate soil heterogeneity within a single remediation quadrant. The results from the duplicate and triplicate sampling were mixed. Two of the properties exhibited a large degree of variability between the duplicate and triplicate samples. The other two properties showed a similar distribution and concentration of within the soil profile. Results from the soil analysis of the pre-excavation soil cores revealed a stark contrast in the soil lead concentration at the remediation interface. Of the 18 properties sampled 17 were previously remediated. Seven of the 14 properties had maximum lead concentration at the remediation interface. The remaining 7 properties show that soil Pb concentrations increased below the remediation interface.

Post excavation cores revealed a heterogeneous distribution of lead within the soil profile demonstrating that the soils were not well mixed. Attempts to model soil mixing based on soil Pb concentrations and the geometry of the excavation failed due to the high variance in the data. A future study expanding the number of properties sampled and adding composite samples to the current study design may reduce the high levels of variance in the data. Based on the statistical analysis, the current study should be viewed as a pilot study. The high variances within the data make it impossible to derive any conclusions on the degree of soil mixing based on soil excavation or disturbance.

A frequency analysis showed that for all of the properties sampled and both excavation techniques (n= 40), 5 or 12.5% of the samples had soil lead concentrations in excess of 400 mg kg^{-1} in the top 12 inches of soil after excavation and backfilling. Of the 5 properties with elevated soil lead concentrations 3 were from the Homeowner excavation technique and two from the Standard excavation technique. Frequency analysis limited to properties with soil lead concentration > 1200 mg kg^{-1}at depth showed that intrusion into the contaminated soil resulted in surface soil lead concentrations exceeding 400 mg kg^{-1} at three of 11 sites. However, the post surface lead concentration did not exceed 400 mg kg^{-1} of lead when the maximum lead concentration at depth was less than 1200 mg kg^{-1}.

Lead speciation data obtained from X-ray absorption fine structure (XAFS) spectroscopy analysis of the soils indicates that the predominant lead species present in the soils analyzed included: anglesite, hydroxypyromorphite, plumboferrite, and galena. Hydroxypyromorphite is not a constituent/lead species associated with atmospheric emissions from lead smelting or recycling activities. It is most likely that the lead phosphate mineral formed in the soil. Soil phosphorus to lead (P:Pb) molar ratios were between 4 and 14. This would indicate there was ample P available for the *in-situ* formation of phosphates. The precipitation of the lead phosphates is extremely advantageous due to the low bioavailability of lead from pyromorphites. The precipitation of the phase is effectively offering a secondary remediation technology by binding the lead in place in an extremely low bioaccessible form.

1. Introduction

The Omaha Lead Superfund Site (OLS; Site [CERCLIS ID # NESFN0703481]) was first investigated by the Environmental Protection Agency (USEPA) in 1998 under the authority of the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) after the Omaha City Counsel petitioned the EPA to address the frequency of elevated blood lead (Pb) levels in children (U.S. EPA-OLS, 2009). The source of the Pb was attributed to particulate matter released from former Pb smelting and refining activities over the past 125 years. The subsequent deposition of expelled particulates contaminated soils in the residential area surrounding the former smelting facilities. EPA began sampling soils on residential properties and licensed child care providers in March of 1999. By August, a response action was initiated under CERCLA and EPA began excavating and replacing soil contaminated with Pb at concentrations exceeding 400 mg kg^{-1} at child care facilities and residences where children with elevated blood levels resided (U.S. EPA-OLS, 2009). In 2002 a second removal action was enacted at residential properties where the soil Pb levels exceeded 2,500 mg kg^{-1} in soils not adjacent to foundational structures. The OLS was placed on the National Priorities list in 2003 and the extent of the contamination was determined. The final area encompassed in the OLS consisted of 25.7 square miles with an estimated 16,000 homes that could exceed 400 mg kg^{-1} of Pb. In May of 2009 the Final Record of Decision Declaration for the Omaha Pb Site stated that any residential soil exceeding the preliminary remediation goal (PRG; 400 mg_{Pb} $kg^{-1}{}_{soil}$) would be excavated, backfilled and re-vegetated.

Briefly, residential properties were divided into sections. Soils in each section were sampled according to the procedures described in the Superfund Lead-Contaminated Residential Sites Handbook (LCRSH) (OSWER Directive 9285.7-50, 2003). A single multi-composite sample was collected from each section and analyzed by handheld X-ray Fluorescence spectroscopy (XRF). If one or more of the residential yard sections exceeded the PRG, the property was eligible for EPA response and remediation. Remedial action entailed excavating soils where the Pb concentration exceeded 400 mg kg^{-1} and replacing the excavated material with clean soil. Excavation and removal of the soil continued until the concentration of Pb at the soil surface was less than 400 mg kg^{-1} in the top 12 in or less than 1200 mg kg^{-1} at depths greater than 1 ft. When Pb soil concentrations exceeded 1200 mg kg^{-1} at one foot a visual barrier was installed (Figure 1.1). After excavation, clean soil was backfilled into the excavated areas to the original grade and a grass lawn was restored.

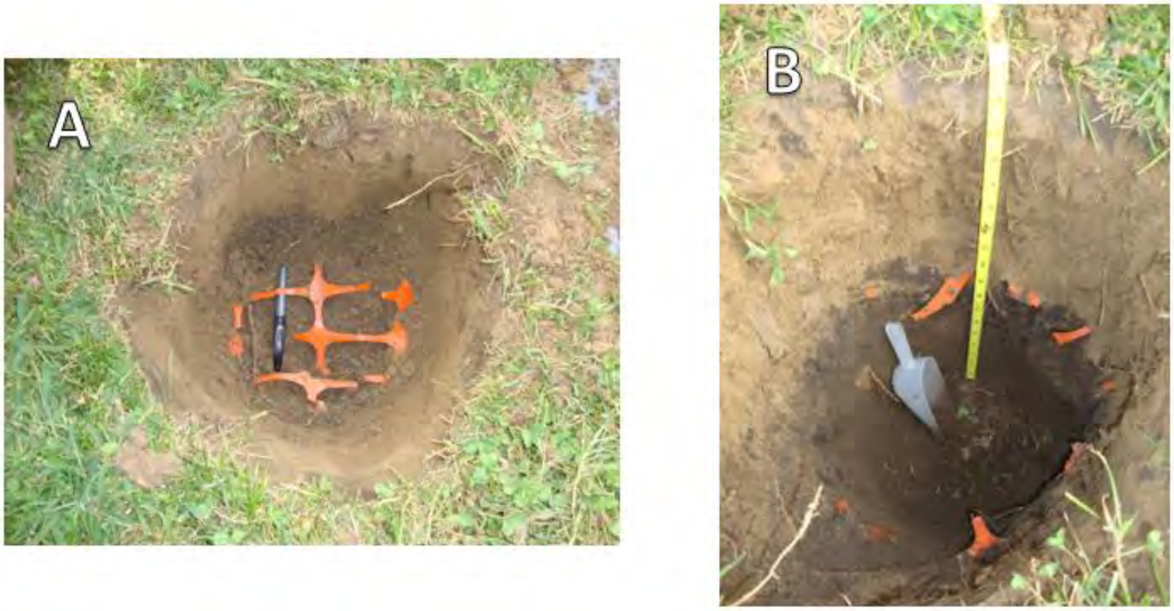

Figure 1.1 A) Visual barrier placed at 12 inches to indicate underlying soil exceeds 1200 mg kg^{-1}, B) Image showing the remediation interface and the visual distinction between the clean soil and intact subsoil.

In addition to the active remedial measures a Pb hazard registry was established as an institutional control. The registry provides information to the public about conditions at specific properties, Pb hazard information, and the current status of EPA investigations and response actions.

Excavation of contaminated soils and replacement with a soil cover is the preferred method recommended by the LCRSH for relatively shallow contamination of Pb typically associated with smelter sites (OSWER Directive 9285.7-50, 2003). However, when integrity of the remedial action is compromised, exposure to soil Pb levels in excess of the PRG (400 mg kg^{-1}) is possible. Any excavation event in soils where the Pb concentration exceeds the PRG at depths greater than the remediation depth may result in exposure to elevated soil Pb concentrations. Numerous excavation activities routinely performed by residential property owners may comprise the integrity of the of the soil cap by excavating soils below the remediation depth. Activities resulting in the excavation of soils up to 36 inches deep and intrusion into the contaminated soils (remediation interface at 12 in. deep) include, but are not limited to: landscaping (planting trees and bushes), establishing a garden, fence installation, construction of an outdoor structure (deck or garage), home addition/remodel, and installation of a driveway. A “normal” Homeowner excavation would likely entail the use of a shovel or other hand tool for excavation while larger projects would require the use of mechanical equipment.

Following any excavation several scenarios exist for the excavated soil:

1. Soil is removed and disposed of offsite
2. Soil is back filled into the excavated hole
3. Spoil pile is left at the surface
4. Soil is relocated to another location or spread over another portion of the property.

The best option would be scenario 1, this would offer the most protection against the potential exposure of elevated soil Pb concentrations. However, scenarios 2-4 are more likely to occur. The result of the scenarios 2-4 is the potential exposure to elevated concentrations of Pb in soils. Exposure to elevated soil Pb concentrations will largely be dependent on how the soil is mixed during excavation. If there is a high degree of mixing that occurs during the excavation then the higher concentrations of Pb remaining at depth will be diluted. However, if there is little to no mixing during excavation, then pockets of soil will exist with Pb concentrations in excess of the PRG.

Soil mixing due to Homeowner excavation is expected to be highly variable based upon the type of soil encountered (texture, water content, and presence of coarse fragments). Differences in properties will result in different quantities of soil being removed by a shovel or other conventional excavation tool. Further complicating the matter is the operator method (shoveling technique) and operator strength (gender and/or age). Both of these variables may introduce a large degree of variability in the natural mixing that occurs during excavation, and replacement of soil after excavation. To help account for variability in soil composition and operator variability, the current study employed the use of a Standardized excavation technique (gas powered auger) in addition to the traditional Homeowner excavation (shovel). The Standardized excavation technique in this study used a gas powered posthole digger with a 10 in diameter bit (earthen drill), while the Homeowner excavation used a traditional garden spade. The Standardized excavation technique will: (1) provide holes with standard dimensions (2) have minimal impact on operator variability, (3) help reduce mixing variability from soils with different physical properties, and (4) standardize how the excavated soil was removed from the hole and how it was deposited on the surface.

Currently, there has been no research investigating the potential hazards associated with the re-distribution of Pb contaminated soils beneath a soil cap following intrusion into the contaminated zone. *Therefore, the goal of the study was to investigate the redistribution of Pb in remediated residential surface soils after typical Homeowner earth-disturbing activities in the Omaha SF Site. Of specific interest was determining whether soil mixing associated with normal Homeowner excavation practices results in surface Pb concentrations (top inch) greater than the PRG (400 mg kg^{-1} of Pb).*

2. Study Site Selection

The residential properties selected for the current study were previously remediated following the protocol outlined in the Final Record of Decision for the Omaha Lead Site Operable Unit 2 Decision Summary (May 2009). The selection criteria for residential properties in the current study were based on the concentration of soil Pb (mg kg^{-1}) 12 inches (1 foot) deep as reported in the Omaha Lead database, logistical constraints for sampling at each location, and property owner permission. Residential properties with soil Pb concentrations greater than 800 mg kg^{-1} were identified in the soil Pb database. Logistical constraints at each site included the collection of soil samples from areas that were at least 6.5 ft (2 meters, or 2 m) away from the foundation of a building, structure, fence, paved surface (road, sidewalk, driveway, or front walk), garden/flower beds, and playground equipment. Soil sampling locations were also located at least 2 m away from the drip zone of building and other structures. Finally, property owners were contacted by either Region 7 staff or the Omaha Lead Superfund contractor in the form of a letter or phone call to request permission for property access.

Based on the site selection process 16 properties were identified for inclusion in this study (Figure 2.1 and Table 2.1). Of the properties identified four (1, 3, 7, 9) were located on vacant lots. In addition to the 16 properties identified, a vacant lot that had not been remediated was included. In order to evaluate quadrant heterogeneity, four of the sites were sampled multiple times (3, 4, 7, 1).

3. Site Locations

The residential properties sampled were located within 1 mile (east or west) of U.S. Route 75 and extended throughout the entire OLS site. The properties were grouped into 4 geographical locations based on their proximity to each other (Figure 2.1). The groupings were used to determine if Pb soil concentrations were related to geographical location. Only one property north of the former smelting observations met all of the sampling criteria, and is the only property in Group A (Figure 2.1). South of Site 4 there was a grouping of 9 residential properties all less than a mile from each other (Group B). The third grouping of 5 properties was located further south (Group C) and these properties were more dispersed than the second group, but still within a mile of each other. The final two, most southern properties, encompass Group D.

Table 3.1 Property addresses, remediation quadrants, excavation depth, and Pb concentration at depth.

Experimental Unit	Sample ID	Address	Quad	Group[†]	Excavation Depth (inches)[††]	Soil Pb Concentration at Excavation Depth (mg kg^{-1}) [††]
1	27966	2113 Grant St*[§]	B1	B	13	1016
2	27598	2524 Patrick Ave**	B1	B	N/A	129
3	27595	2528 Patrick Ave[§]	B1	B	13	980
4	36021	2611 Browne St[§]	B1	A	13	1016
5	20953	1112 South 31st St	F2	C	6	118
6	47857	3126 R St	B1	D	12	961
7	22393	704 South 25th Ave*[§]	B1	C	13	938
8	27507	2033 North 20th St	B1	B	12	840
9	29827	2518 Maple St*	B2	B	13	981
10	28971	2238 Ohio St	B2	B	12	1073
11	26975	2094 Parker Cr	B2	B	13	1075
12	27319	2422 Blondo St	F2	B	12	920
13	26807	2921 Parker St	B1	B	13	806
14	12299	2621 E ST	F1	D	12	1037
15	2289	2530 Patrick Ave	B2	B	12	1530
16	18470	1914 South 36th St	B1	C	13	866
17	20319	1516 William St	B1	C	12	1237
18	94631	2210 South 13th St	F2	C	17	816

[†] Refers to the property grouping identified in Figure 2
[††] Values obtained from the Omaha Soil Lead database
*Vacant Lot
**Site 2 was not previously remediated.
[§] Locations where replicate samples were collected

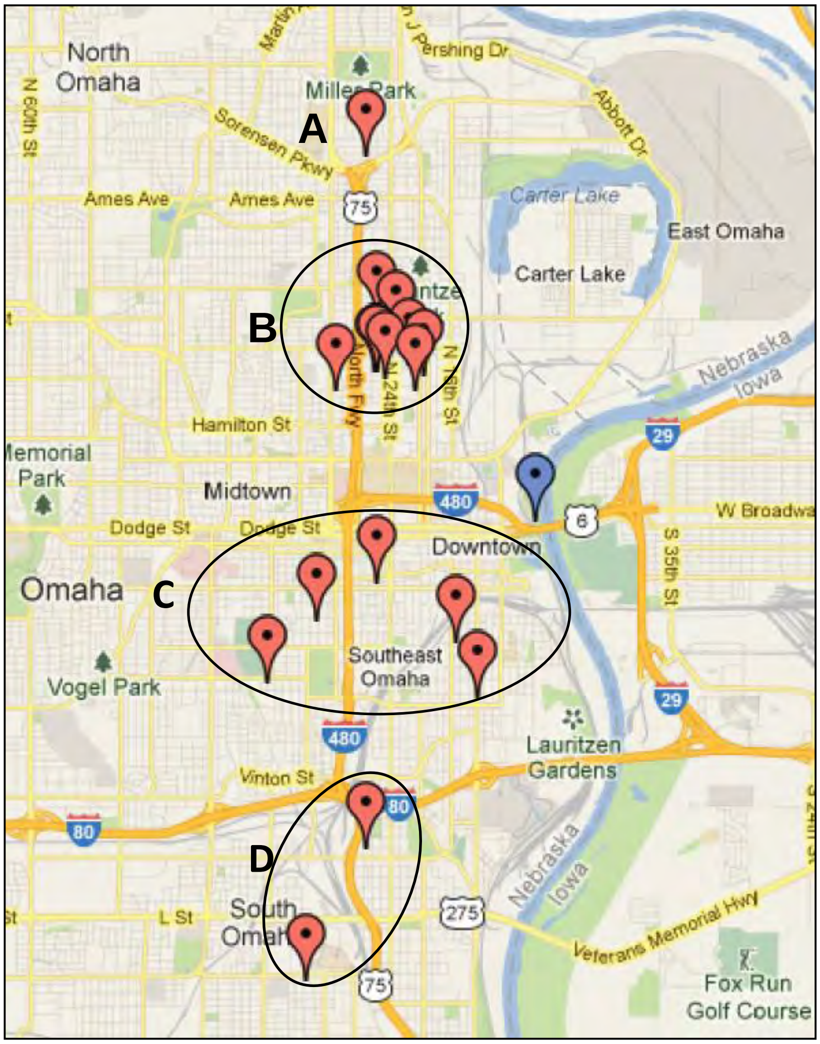

Figure 2.1 Map showing the locations of the sampled residential properties (red markers) and the former Arcos Lead recycling and smelting facility. The Numbers refer to the four grouping of properties investigated. A list of properties within each grouping is listed in Table 1.

4. Methods/Materials

4.1. Field Methods

<u>Sampling Locations</u>

Soil samples collected were obtained from OLS residential yards that have already undergone remediation. Exclusion zones were delineated as at least 6.5 ft (2 m) from the foundation of any building or fence and 6.5 ft from paved surfaces (road, sidewalk, driveway, or front walk). Soil samples were collected outside the exclusion area to prevent sampling of secondary Pb sources (e.g., Pb paint chips, contaminates from roads). The locations sampled within a remediated OLS residential yard were chosen randomly outside the exclusion zone, and all locations were recorded.

Soil Mixing Techniques

Two mixing techniques were tested at each of the yards, Standardized and Homeowner. The two different sampling locations for each technique were located at least 1.5 m (5 ft) apart to prevent cross contamination. All excavation equipment was cleaned and dried prior to sampling to remove any adhering soil or debris.

The Standardized excavation was performed using a gas powered 2-person auger with a 10 inch diameter bit. The auger was used to excavate the soil to a depth of 24 inches (Figure 4.1 and Supplemental Figure 1). Prior to excavation a 14 ft^2 plastic board, with an 11 inch inner diameter hole, was laid on the ground to catch excavated soil (Figure 4.1). Then the soil surface was cleared of grass or debris and a soil sample was collected to a depth of 1 inch, followed by auguring to 24 inches. After excavation a subsample from each of the four quadrants of the plastic board were collected for analyses. A grab sample from the bottom of the pit was also collected. The depth to the remediation interface was measured and the excavated soil was returned to the hole by hand or with a spade. The soil was lightly compacted to bring the back filled soil level with the yard. A soil core followed by bulk surface soil samples (1 in) was then collected.

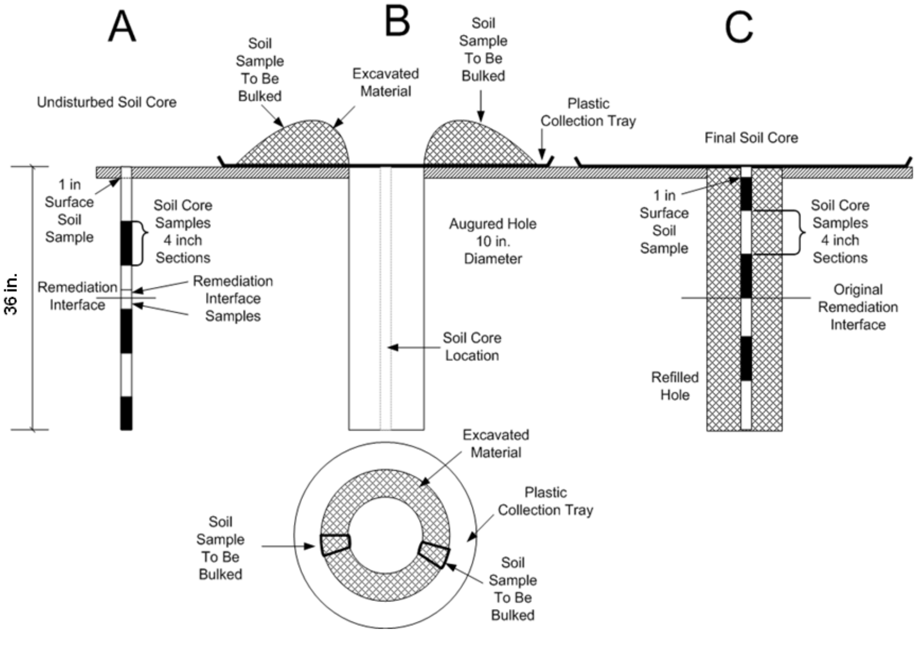

Figure 4.1 Schematic representation of the Standard Excavation Technique. A. First undisturbed soil core was collected. B. After soil core was collected a 2-person auger was used to dig a hole in the same location as undisturbed soil core. C. Soil core collected from backfilled hole.

The Homeowner excavation was performed with a standard 5' tall garden spade. Prior to digging a 3 ft^2 plastic board was placed adjacent to the sample area (Figure 4.2 and Supplemental Figure 2). The soil surface was cleared of grass or debris and a soil sample was collected to a depth of 1 in. An 18 inch diameter hole was dug with the garden spade and all material was deposited on the plastic board (Figure 4.2). After excavation a subsample from each of the four quadrants of the plastic board were collected for analyses. A grab sample from the bottom of the pit was also collected. The depth to the remediation interface was measured and the excavated soil was returned to the hole by hand or with a spade. The soil was lightly compacted to bring the back filled soil level with the yard. A soil core was collected followed by bulk surface soil samples (1 in).

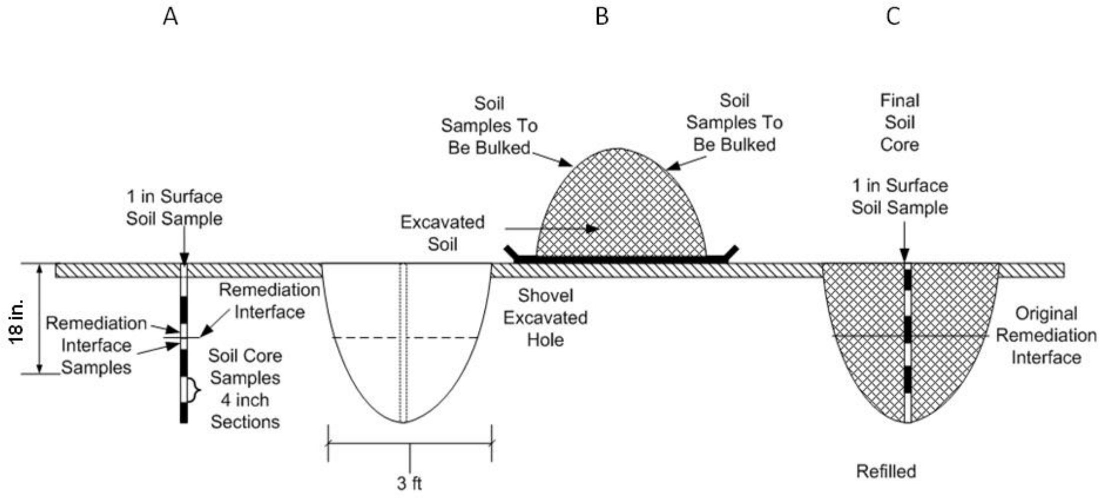

Figure 4.2 Schematic representation of the Homeowner Excavation Technique. A. First undisturbed soil core was collected. B. After soil core was collected a spade was used to dig a hole in the same location as undisturbed soil core. C. Soil core collected from backfilled hole.

Soil Cores and Processing

Undisturbed soil cores were also collected from each site. All soil cores were collected using a JMC Environmentalist's Sub-Soil Probe using a "kick style" soil probe (Supplemental Figure 3). Each core was collected using a1 inch (2.5 cm) diameter transparent plastic tube driven into the ground encased within a steel tube to a depth of 36 in. The soil cores were extracted from the steel probe, capped, sealed, and labeled (Figure 4.3). The depth to remediation interface was immediately identified and delineated on the plastic tube from the undisturbed soil cores. The remediation interface was identifiable based upon changes in soil color and texture. After the soil core was removed, the depth to the bottom of the excavated soil core hole was measured as well as length of each soil core. The measurements were conducted to account for any soil compaction due to sample collection. Compaction was determined by dividing the length of the recovered soil core by sampled depth. For example, if the recovered soil core is 32 inches, and the sampled depth is 36 inches the sample compaction is 11% (1-(32/36)*100 = 11%). All cores were then shipped to the EPA's Center Hill laboratory in Cincinnati, OH. Soil cores received at the Center Hill laboratory were placed in a -80°C freezer. Soil depths, on the cores, were delineated as surface (1 in) deep, and then portioned according to depth of remediation interface and corrected for soil compaction. The frozen cores were then cut into sections with a band saw, transferred to plastic bags and air-dried.

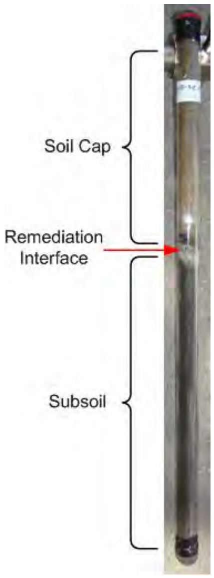

Figure 4.3 Intact soil core collected pre-excavation. Visual changes in soil color or texture were used to identify the remediation interface when the barrier was not present.

All soil samples, bulk samples and sections from each soil core, were force air dried at 105°C, fractured with a mortar and pestle, and passed through an ASTM No. 10 sieve to isolate the < 2mm fraction. The soils were homogenized and stored in plastic containers until chemical analyses. Three replicate subsamples from each air-dried soil were collected and dried at 105°C for moisture corrections.

4.2. Laboratory Analysis

Extractable soil Pb concentrations were quantified following the procedures of EPA Method 3051A. Triplicate 0.5 gram subsamples of the homogenized soil were added to microwave digestion vessels to determine elemental content. Next, 9 ml concentrated nitric acid and 3 ml of concentrated hydrochloric acid were added to each the vessel. The samples were then subjected to microwave assisted digestion using a MARS Express Microwave system with temperature monitoring. The digestates were quantitatively transferred to a volumetric vessel and brought to final volume with double distilled water (≤ 18.2 MOhms) for ICP-AES (Inductively Coupled Plasma-Atomic Emission Spectroscopy) analyses. Quality control and quality assurance protocols were followed as outlined in the project QAPP and EPA Method 3051A.

The digestates were analyzed for Al, As, Ca, Co, Cr, Cu, Fe, K, Mg, Mn, Na, Ni, P, Pb, S and Zn concentration by ICP-AES. Quality control and quality assurance protocols were followed as outlined in the project QAPP and according to the procedures of EPA Method 6010C. If the relative standard deviation of the concentration of Pb from a soil sample exceeded 10%, the results were discarded and triplicate soil samples were digested and analyzed again.

4.3. Lead X-ray Absorption Fine Structure Spectroscopy

Lead speciation, in a sub set of the soils collected from residential properties, was determined using X-ray absorption fine structure (XAFS) spectroscopy. Lead L3-edge (13, 035 eV) X-ray absorption spectra (XAS) were collected at the Materials Research Collaborative Access Team's (MRCAT) beamline 10-ID, Sector 10 at the Advanced Photon Source at the Argonne National Laboratory, Argonne, IL. The electron storage ring was operated in top-up mode at 7 GeV. Spectra were collected in fluorescence mode with either a Lytle or a solid-state silicon drift detector at room temperature. The samples were prepared using, the < 250 µm soil fraction, as thin pellets using an IR pellet press and samples were secured to sample holders using Kapton tape. For each sample, a total of fifteen to seventeen scans were collected using the Lytle detector or 4 to 5 scans using the solid state detector and averaged. Data were analyzed using the Athena software program (Ravel and Newville, 2005). Sample spectra were compared with synthesized minerals and mineral specimens acquired from the Smithsonian National Museum of Natural History (USA). All minerals were verified with X-ray Diffraction (XRD) before use as reference materials.

Soil Pb speciation was determined by comparison of Pb standards to the field samples via Linear Combination Fitting (LCF). Linear Combination Fitting refers to the process of selecting a multiple component fitting function with a least-squares algorithm that minimizes the sum of the squares of residuals. A fit range of −20 to 50 eV was utilized for the X-ray absorption near-edge structure (XANES) portion of the XAFS spectra and up to four variables. The best fitting scenarios are determined by the smallest residual error (χ^2) and the sum of all component fractions being close to 1. Detailed descriptions of the fitting procedure are described elsewhere (Isaure et al., 2002; Roberts et al., 2002, Scheinost et al., 2002). The reference samples used in the LCF model were plumboferrite ($PbFe_4O_7$), plumbonacrite ($Pb_5O(OH)_2(CO_3)_3$), chloropyromorphite ($Pb_5(PO_4)_3Cl$), Pb-sorbed to hydroxyapatite complex ($Ca_5Pb_5(PO_4)_6(OH)_2$), galena (PbS), hydrocerussite ($Pb_3(CO_3)_2(OH)_2$), anglesite ($PbSO_4$), plumbomagnetite ($PbFe_2O_4$), litharge (PbO), lead hydroxide ($Pb(OH)_2$), and Pb sorbed to humic and fulvic acids, goethite, gibbsite, kaolinite, bentonite, and calcite.

5. Results

5.1. Soil Samples Types

Soil samples types were used to explore different potential end points for the excavated soil. Previously 4 potential outcomes were identified. The soil samples collected were designed to establish the pre-excavation conditions and to mimic different post excavation scenarios.

Two types of soil samples were collected in the field, bulk and core. Bulk soil samples were collected as loose soil from four locations: initial soil surface (B1), bottom of the excavation hole (B2), excavated spoil (B3), and final soil surface (B4). The two surface bulk soil samples (B1 and 4) were collected to compare the concentration of Pb measured in the surface core sample and the bulk sample. To ensure enough soil, free of vegetation/plant debris, was collected for analysis purposes a bulk sample was collected from the top inch before and after excavation. The spoil sample (B2) provided an average soil Pb concentration in the excavated material and mimicked potential end point scenarios 3 and 4 (spoil left in place, and soil is relocated to another or spread over another portion of the property). As discussed in the Material and Methods section, the B2 sample was thoroughly mixed in the field prior to collection. Finally the Bulk sample collected from the bottom of the excavation was used to determine if the soil Pb concentration at the bottom of the hole was less than the maximum soil Pb concentration in the excavated material.

Core soil samples were sections were collected from the intact soil cores at specific depth intervals identified in the Materials and Methods. The soil core data provided detailed information regarding the distribution and mixing of Pb throughout the soil profile pre and post excavation. The post excavation core also mimicked scenario 2, backfilling of the soil.

5.2. Pre-Excavation Soil Lead Distribution

The total Pb concentration in the soil is presented as Pb soil concentration (mg kg^{-1}). A profile of extractable soil Pb concentrations by depth for the 18 properties investigated are presented in Figure 5.1. Soil Pb concentration in Figure 5.1 was corrected for soil core compaction. As expected, soil Pb concentrations at the surface were low pre-excavation. In general soil Pb concentrations increased at the remediation interface and decreased with depth. The soil Pb profile for the remediated lots were characterized by a dramatic increase in soil Pb concentration at or near the visually identified remediation interface (Figure 5.1). The maximum soil Pb concentration occurred either at or below the remediation interface and decreased with depth. The drastic change was not present for properties 5, 12, and 16. Following the same trend as the remediated properties, Property 2, un-remediated, exhibited a significant decrease in soil Pb concentration at a depth similar to the remediated soil.

Property 5 differed from 2 in that the entire profile had a similar soil Pb concentration near 25 mg kg^{-1}. Interestingly the highest concentration of Pb was at the soil surface.

The concentration of soil Pb at Properties 5, 12 and 16 did not exhibit the same distribution as the other remediated properties. For each of these three sites there was no apparent remediation interface identified by the soil Pb concentrations. Visually there was no discernible remediation interface observed for any of the three properties. The Omaha Lead data base indicates that the quadrants sampled for Properties 5, 12 and 16 had previously been remediated and that the soil Pb concentrations at 12 and 13 inches for Property 12 and 16 were 912 and 866 mg kg^{-1}, respectively. As evident from Figure 6 the maximum Pb concentration in the soil was significantly less than 60 and 225 mg kg^{-1} for 12 and 16 respectively, indicating that no additional contamination was left at depth.

In general the visual appearance of the remediation interface was in good agreement with the chemical data. The soil Pb concentration for a portion of the properties continued to increase with depth (1, 10, 11, 13, 15, 16, 17, and 18) which encompassed geographical units (B, C, and D) The principal source of Pb contamination in soils within the Omaha Lead superfund site is atmospheric deposition of Pb particulate matter. The elevated concentration of Pb in the sampled soils at depth, and the increasing soil Pb concentration with depth, would suggest that a portion of the Pb deposited on the soil surface is mobile and is currently being leached through the soil profile. Lead has a high affinity for organic matter, and hydrous (oxide) minerals and is generally considered immobile in the soil. However, previous research has shown that significant quantities of Pb may be leached through a soil profile under specific geochemical conditions and mineralogical properties. (Kim et al. 2008).

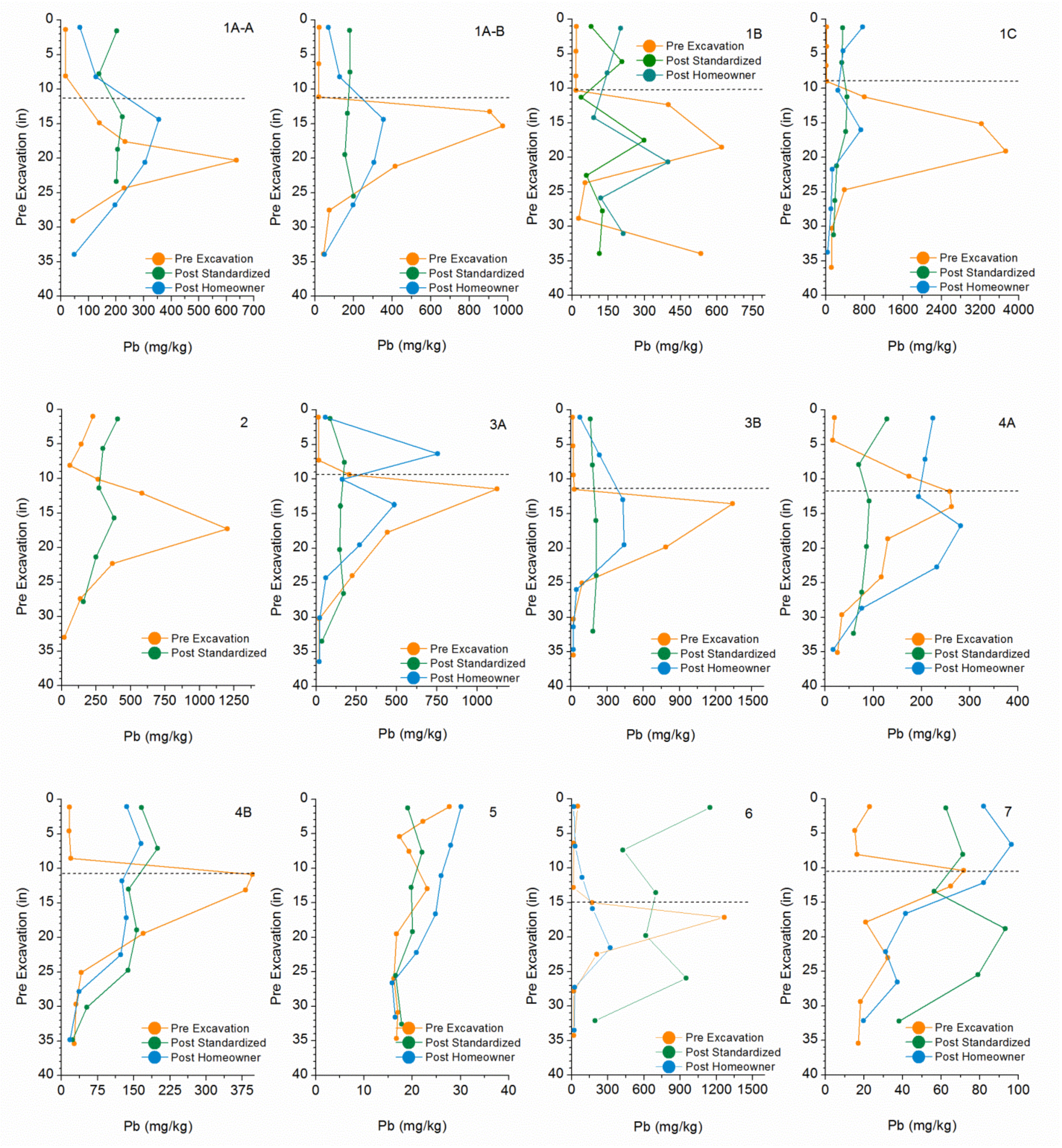

Figure 5.1 Soil Pb concentration as a function of depth for each of the excavation units pre- and post-excavation. Numbers refer to the property address/location. Letters refer to duplicate samples collected from the same property. For property 1, replicate A the –A and –B refer to samples collected within three feet of each other. Dashed line indicates the location of the remediation interface.

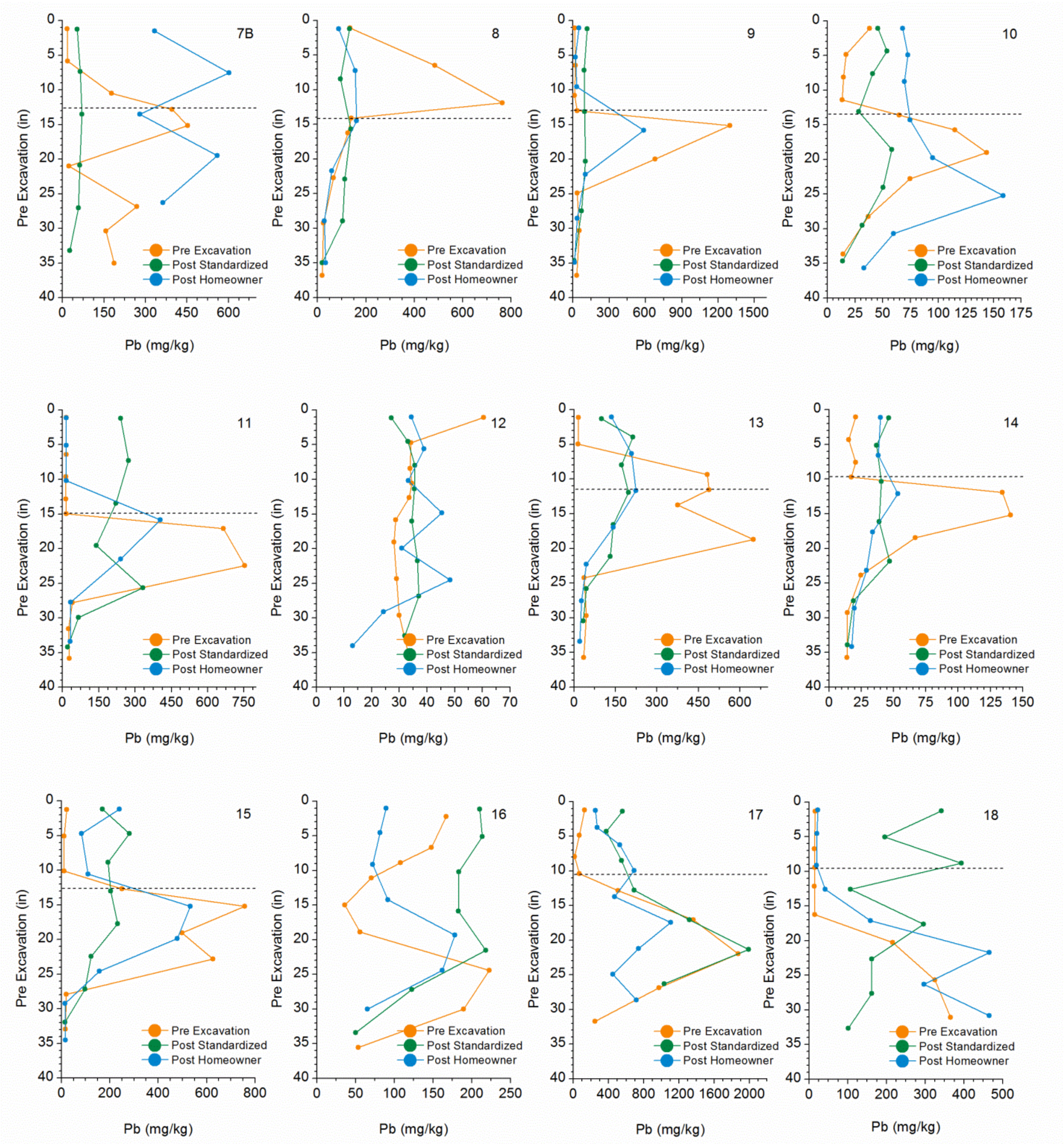

Figure 5.1 (cont.). Soil Pb concentration as a function of depth for each of the excavation units pre- and post-excavation. The dashed line in each plot corresponds to the visually identified remediation interface. In the upper right corner of the plots the numbers refer to the property address/location, and the letters refer to duplicate samples collected from the same property. For property 1, replicate A the –A and –B refer to samples collected within three feet of each other.

In general, the visual appearance of the remediation interface was in good agreement with the chemical data. The soil Pb concentration for a portion of the properties continued to increase with depth (1, 10, 11, 13, 15, 16, 17, and 18) which encompassed geographical units (B, C, and D) The principal source of Pb contamination in soils within the Omaha Lead superfund site is atmospheric deposition of Pb particulate matter. The elevated concentration of Pb in the sampled soils at depth, and the increasing soil Pb concentration with depth, would suggest that a portion of the Pb deposited on the soil surface is mobile and is currently being leached through the soil profile.

Immediately evident is the remediation interface between the clean fill and the underlying soil (Figure 5.1). The heterogeneity shown in the distribution and concentration of Pb in the soils between properties was expected and readily apparent in Figure 5.1. There were no discernible patterns of maximum soil Pb at depth among the four geographical groups (Figure 5.2). Likewise, there was large variability in soil Pb concentrations at depth among properties in close proximity to each other within geographical groups. A prime example of soil Pb heterogeneity at depth are properties 8, 9, and 10 located in geographical Group B. The properties are less than 0.25 miles apart but the maximum Pb concentration in the soil profile varies from approximately 150-1500 mg kg^{-1}. Large variation in soil Pb concentration was also present within a single property. Property 1 included three different excavation reps (1A, B, and C) and one duplicate rep for 1A (Figure 5.1). Visual comparison of the soil Pb distribution through the profile and the maximum concentration of soil Pb present in any of the 4 profiles varied greatly. As previously mentioned samples 1A-A and 1A-B were collected within three feet of each other, and even these two samples show significant differences. The large increase in soil Pb concentration for 1C compared to 1A and 1B is due to the presence of what appeared to be smelter slag-like material in the pre-excavation core. The same variation in soil Pb distribution within a single property was is evident in property 7 as well. However, the maximum concentration of soil Pb and the soil Pb profiles were similar for Property 3 and 4. The wide variation in the distribution of soil Pb throughout the profiles and within individual properties highlights the heterogeneity that exists over the entire Omaha Lead site. It is unlikely that the atmospheric deposition of Pb was significantly different within a single property given the nominal size of residential properties sampled, less than 0.25 acres. Therefore, the heterogeneity is likely related to previous anthropogenic disturbances to the property pre-remediation. Changes in soil compaction, leveling of the property, introduction of contaminants, and chronic drainage issues may have influenced the local distribution of Pb through the soil profile.

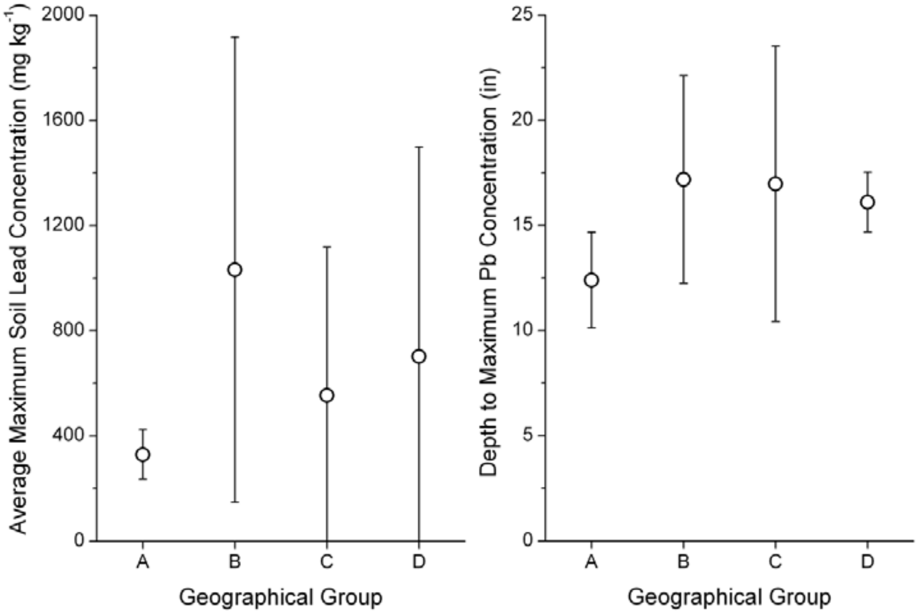

Figure 5.2 Average maximum concentration of lead and depth at which maximum concentration occurs for the four different geographical locations.

5.3. Lead Spoil Concentrations

The slag-like material was also present in both the Homeowner and standard excavation holes. The slag-like material was dark grey friable channers and flagstones[1] present at 18 to 20 inches. The slag-like material was present at depths greater than 12 inches and would not have been identified during the initial investigation. If the slag-like material was well mixed within the soil, the concentrations of soil Pb and Pb in the slag-like material should be similar. Figure 5.3 shows a poor relationship between the Pb concentrations in the soil and spoil. A linear regression of the concentration of Pb in the two excavation techniques indicated there was no relationship between the soil Pb and the spoil for the Homeowner excavation technique (p-value 0.5; $R^2 = -0.1$) and only a weak relationship for the standard technique (p-value 0.013; $R^2 = 0.37$). The relationship between the spoil-like material and the soil Pb concentration improves at lower spoil Pb concentrations for both techniques; however the relationship is still weak. Interestingly, the slope for the Homeowner was close to 1 (1.1) but the very low R^2 value (0.159) indicating the variability between the two soils is still very high.

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[1] Channers and flagstone are terms used to describe flat rock fragments present in soils between 2-15 mm and 15-380 mm, respectively.

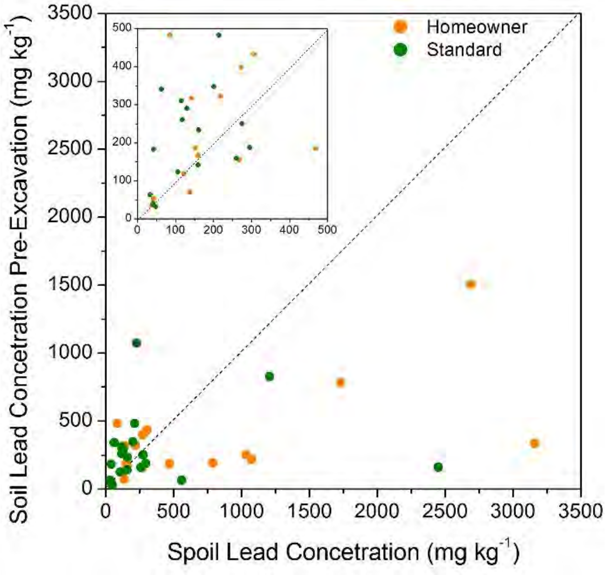

Figure 5.3 Soil Pb concentration in the top 18 or 24 inches of the pre-excavation soil as a function of the Pb concentration in the spoil. The concentration in the soil was determined from calculating the average concentration of Pb in the soil pre-excavation from the soil core data.

Post excavation Soil Lead Distribution

The redistribution of Pb through the soil after backfilling is presented in Figure 5.1 for both excavation techniques. If the quantity of Pb in the pre-excavation core is equal to the quantity of Pb in the post excavation core then the integration of the area along the y-axis for the pre-, post Homeowner, and post standard soil Pb should be nearly identical. Visual inspection of the soil profiles pre- and post-excavation indicates the total concentration of Pb in the pre and post excavations is true for a portion of experimental units (1A-A, 1B, 4A, 10, 15, 17, and 18; Figure 5.1). Conversely, the assumption does not hold for several of the properties (1C, 3B, 8, 9 and 13). Finally, in some instances the assumption was only true for one of the specific excavation techniques (3A, 6, and 7B).

The lack of conservation of mass between the pre- and post-excavation soil cores is not immediately understood. Non-sample heterogeneity of the core section prior to analysis may have contributed to the issue. However, every attempt was made to thoroughly homogenize samples prior to acid digestion (EPA Method 3051A). Further, all digestions and analyses were conducted in triplicate and average values are reported. Significant heterogeneity within the specific quadrant may also have contributed to the issue. Sample location 1, 3, and 7 were all vacant lots. Visual inspection of the soil cores indicated that the soils were heavily disturbed at depth below the remediation interface. Heavily disturbed soils often exhibit a high degree of heterogeneity in the soil over very short distances. Therefore the previous anthropogenic activities may have contributed to the issue. As previously discussed the heterogeneity of soils within a single quadrant was evident from the duplicate samples within a single quadrant (Figure 5.1). Based on the known heterogeneity within the quadrant it is very possible that the centralized location of the pre-excavation soil core Pb concentration between the shovel and auger differed from the soil Pb concentrations at each excavation location. One potential option for determining if the reason is due to soil heterogeneity or poor homogenization of the analytical sample would be to collect a pre-excavation sample for each excavation technique. If the total soil Pb concentrations pre and post exaction were similar then the differences may be attributed to soil heterogeneity. However, if the same issue occurs the reason is related to poor sample homogenization

For the purposes of evaluating mixing of the soils based on excavation technique, the discussion will focus on profile distribution of Pb rather than the absolute quantity of Pb present.

If a soil was well mixed then the post excavation profile should exhibit little change in the soil Pb concentration as a function of depth as seen in experimental units 1C, 3B Standardized, and 9 Standardized (Figure 5.1). If a soil was not well mixed then the Pb soil profile will include large variations in the soil Pb concentration as a function of depth as seen in Figure 5.1 properties 1B, 3A, 4A, 6, 7, 7B, 10, 16, 17, and 18. In most instances the redistribution of Pb throughout the soil profile post-excavation was more homogeneous (regardless of excavation technique) however, excavation resulted is an increase of Pb at the soil surface, occasionally exceeding 400 mg Pb kg^{-1} (Figure 6 properties 6, 17 and 18). Property 2 had a similar Pb profile distribution to the properties that had undergone remediation. In this instance the Standardized technique did result in a fairly homogeneous distribution of Pb through the soil profile

5.4. Soil Properties

For the purposes of the current study only the soil moisture content and chemical composition, and were determined. Excel files containing all of the raw and processed data are located in Appendix 1.

Moisture Content

Moisture content is the percent mass of water present in the soil. The moisture content will influence how the soil forms clods/aggregates during excavation and the overall strength/stability of the clods/aggregates. The average moisture content for both the bulk and core soil samples was 19.19% with a relatively low standard deviation of 5.8%. The mass moisture content for just the spoil was 19.5 % with a standard deviation of 3.7%. The lower moisture content, narrow variation between all of the samples, and visual observations in the field indicate that the aggregates formed during excavation were friable (easily breakable) and collection of bulk soil samples were not impacted by the presence of large strong soil clods. Further, small variability in soil moisture content ensures all of the soils had similar moisture content at the time of sampling.

Soil Chemical Composition

Obtaining a background or baseline concentration of elements in the OLS for comparative purposes was not feasible in this preliminary study. The incorporation of fill materials with potentially high levels of contaminates and length of time since the disturbance are a just a couple of the factors that makes it very difficult. In the current study, trends in the chemical composition of the entire soil data set including average chemical concentration and standard deviation for the fill/cap material and the underlying soil were calculated separately (Table 5.1). The calculated standard deviations for the chemical analysis for both the fill and underlying soil are extremely large with respect to the average value calculated. The large standard deviations suggest that different materials being used as fill and the natural heterogeneity is persistent in soils.

Table 5.1 Average total elemental concentrations for the fill material and underlying soil. Data used in the calculation of the average elemental concentration and the t-test does not include soil samples collected from Properties 2, 5, 12, and16, α=0.05.

Element	Fill Material	Underlying Soil	Average	Standard Deviation	Average mg kg^{-1}	Standard Deviation	p-value
Al	12828.2		3743	12210.4	3080.2		0.232
As	11.5		3.1	20.5	13.6		< 0.001
Ca	11052.9		5453.2	9855.6	7965.3		0.21
Co	9.2		0.9	10.2	1.7		< 0.001
Cr	15		4.1	17.2	5.4		0.0013
Cu	26.7		25.9	40	39.3		< 0.001
Fe	18512.3		4197.4	22566.1	6876.1		< 0.001
K	4709.8		2849.3	2790.5	1468.6		< 0.001
Mg	5476.3		2041.7	3678.5	1296.2		< 0.001
Mn	609.8		91.3	634.7	125.5		0.115
Na	376.4		345.3	259.7	227.8		0.0102
Ni	21.7		4.8	25.6	10.3		< 0.001
P	2265.5		2026.3	1134.1	916.9		< 0.001
Pb	51.1		95.1	353.3	565.2		< 0.001
S	868.6		864.9	608.2	601		0.023
Zn	130		136.9	470.2	1236.4		0.0043

Using an unequal variance t-test the mean elemental composition of the fill and the underlying soil were tested to see if there was a statistical difference in the chemical composition (Table 2).

There was a statistical difference ($\alpha \leq 0.05$) for all but three of the elements (Al, Ca, and Mn) (Table 5.1). Aluminum and calcium are common components of nearly all major silicate minerals present in soil, and the lack of differences in the concentration of the two elements in the fill and underlying soil is expected. The lack of a difference in the Mn was not expected and the reason is not apparent. Overall there is an enrichment of first row transition metals (Cr, Fe, Co, Ni, Cu, Zn), As, and Pb in the subsoil and an enrichment of P and S in the cap material. The enrichment of the metals in the subsoil was expected. Similar to the soil Pb data there were extremely large variations in the elemental composition of soils as a function of depth. There were no statistical differences in excavation techniques for any of the elements analyzed. In nearly all instances the calculated averages had large standard deviations.

5.5. Elemental Correlations

Correlations between Pb and other elements were performed to determine if elemental correlations could be used to predict the degree of mixing. Elemental correlations were evaluated for the entire soil profile pre-excavation, the clean fill/cap, the underlying subsoil, the post Standardized excavation soil cores and the post Homeowner soil cores. For all of the data sets analyzed only a few weak elemental correlations with Pb were identified. In the capping material used for remediation there was a weak correlation between Pb and As (R^2=0.43) and Cu (R^2=0.58). In the subsoil prior to excavation Pb was again weakly correlated with Cu (R^2=0.59). The correlation between As, Cu, and Pb in the capping material is likely related to the very low concentrations of the three elements present. The relationship between Cu and Pb in the subsoil is more likely related to the quantity of copper present in Pb ore (galena) which may have been deposited together via atmospheric deposition from the refinery. In the post excavation soil cores there was again a weak correlation with Cu in both the Homeowner and Standardized soil cores (R^2= 0.47 and 0.44, respectively). Based on the presence of the weak Pb/Cu relationship in the soil pre-excavation samples the relationship may be related.

5.6. Lead Speciation

XAFS spectroscopy was used to determine Pb speciation in a select subset of the collected soil samples. A total of 5 samples were analyzed. Soil samples selected for XAFS analysis exhibited high Pb concentrations present in the sub soil (below the depth of remediation) or elevated Pb concentration in the post-excavation soil at the surface. Two soil samples were analyzed from the same experimental unit (residential property 1), one sample from an un-remediated soil (residential property 2), an additional sub soil sample from residential property 3, and a post excavation surface soil sample (residential property 6). XANES spectra and the first derivative of the XANES spectra for each of the soil samples are presented in Figure 5.4. Subtle differences exist in the shape, peak locations, and spectral features between each of the XANES spectra and are related to the speciation of Pb. Differences in the spectra of the 5 soils analyzed are indicated by dashed lines in Figure 5.4.

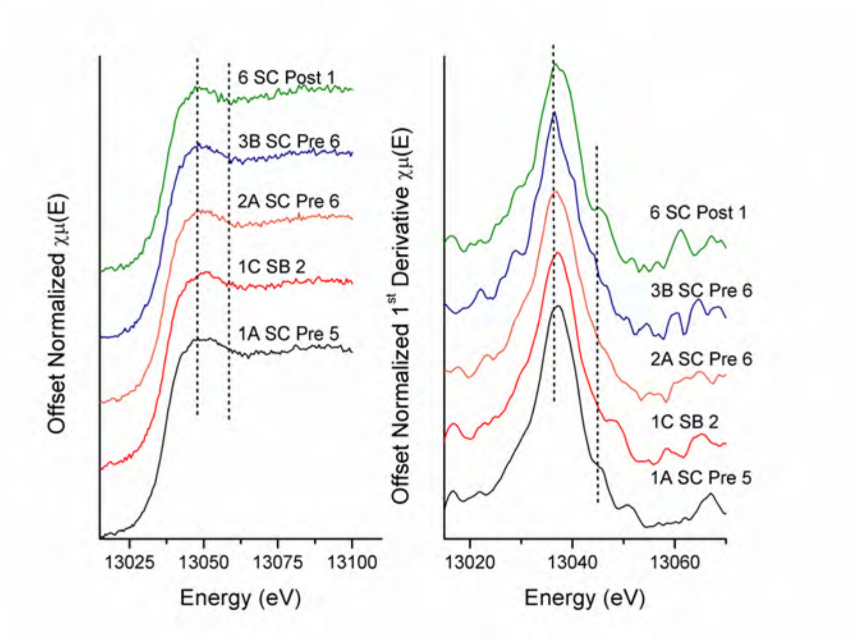

Figure 5.4 Normalized Pb L3 XANES spectra and the first derivative of the XANES spectra. Dashed lines indicate highlight areas where differences exist in the location, shape, and/or presence of spectral features.

Linear combination fitting was used to determine the Pb species present and their relative abundance in the soil. Potential Pb species for inclusion in the LCF were chosen based on: 1) previously published data on the composition and speciation of Pb atmospheric particulates typically released during Pb smelting and recycling operations (galena, anglesite, cerussite, plumboferrite); 2) Pb species that are commonly found in soils with similar chemical properties and mineralogy (plumbonacrite, Pb sorbed to different mineral surfaces, Pb organic complexes); 3) Pb dissolution products from the primary particulates previously identified (plumbonacrite, hydrocerussite, and plumbojarosite); 4) a Pb(IV) compound typically found in paint (platternite); and 5) several pyromorphites species (pyromorphite, chloropyromorphite, and hydroxypyromorphite). The pyromorphite species were included in the fitting process based on the existing P to Pb molar ratios present in the soil (between 4 and 14; Table 5.2). Similar molar ratios have been used successfully in laboratory and field trials for immobilizing Pb through the formation of pyromorphite. LCF modeling results indicate that four different Pb species could be used to successfully model the 5 different soils samples: plumboferrite, Anglesite, galena, and Hydroxyapatite. LCF was performed on both the normalized and the first derivative of the normalized spectra. The LCF results were similar for the normalized and 1st derivative spectra, results from the LCF analysis are presented in Table 5.2 and an example fit is presented in Figure 5.5.

Previous research has not identified Pb phosphate species present in the atmospheric particulates released during Pb smelting and recycling operations (Ettler et al., 2005; Manceau et al., 1996; Morin et al., 1999). This would suggest that hydroxypyromorphite formation occurs during active weathering of the primary Pb phases initially present in the soil. *In-situ* formation of Pb phosphates sequesters the free Pb present in the soil and may significantly reduce bioavailability/bioaccessibility (Scheckel et al., 2013). The relative abundance of hydroxyapatite in the sample was related to the total P present. A nonlinear regression of the data using an exponential function indicates a potential maximum of Pb transformation above a specific phosphorus to lead (P:Pb) ratio (Figure 5.6). However, additional research would be required to more fully characterize the system and determine the influence of other Pb species present on the formation of Pb phosphates.

Table 5.2 Linear Combination Fitting Results for the normalized and first derivative of the Pb L3 XANES spectra. Ang = Anglesite, Hy-Py = Hydroxypyromorphite, and Pb-Ferr = Plumboferrite

Soil Sample	Pb	P/Pb	Spectra Modeled*	Normalized LCF Fit				Fit Red chi^2
				Ang	Hy-Py	Pb-Ferr	Galena	
	mg kg^{-1}	mol/mol		%				
1A SC Pre 5	1541	4	Norm	24	29	48		1.00E-04
			1st Der	24	37	42		1.00E-04
1C SB 2	2692	6	Norm	21	35	45		1.00E-04
			1st Der	23	32	46		1.00E-04
2A SC Pre 6	1202	14	Norm	13	49	38		9.00E-05
			1st Der	10	57	33		2.00E-04
3B SC Pre 6	1342	7	Norm	13	50	37		1.00E-04
			1st Der	17	43	41		2.00E-04
6 SC Post 1	1147	11	Norm	29	39		32	2.00E-04
			1st Der	24	55	0	21	4.00E-04

*Norm refers to the normalized Pb L3 XANES spectra and 1st Der refers to the first derivative of the normalized Pb L3 XANES spectra

Two samples were analyzed from Residential Property 1. One sample was from the subsoil and the other from the spoil pile. The subsoil sample represents the Pb speciation at a specific depth (21 inches) while the spoil sample is a bulk sample of entire excavated soil. The two samples differed in their exact location within the quadrant and total concentration of Pb (1541 and 2692 mg kg^{-1} for the subsoil and spoil, respectively), however the Pb speciation and relative abundance of each species remained similar (Table 5.2). This would suggest that the Pb speciation within each quadrant is similar and that the vertical speciation of Pb may be similar throughout the quadrant. A relatively homogenous distribution of the Pb species and abundances within a single quadrant enables a more complete understanding of the potential bioaccessibility.

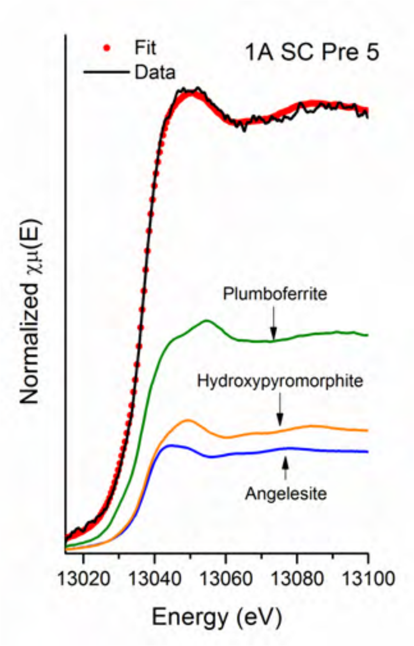

Figure 5.5 Linear combination fit results for a sub soil sample collected prior to excavation at residential Property 1.

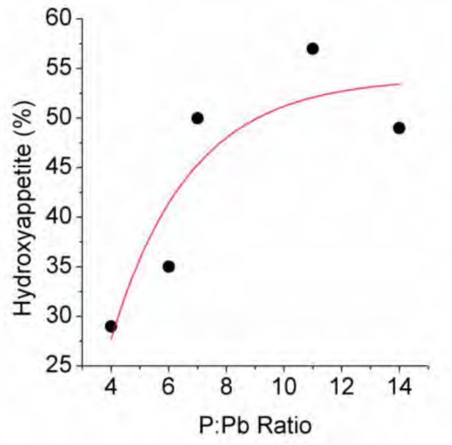

Figure 5.6 Relative abundance of hydroxypyromorphite in soil samples, from the LCF analysis, as a function of the P:Pb molar ratio. An exponential function was used for the nonlinear regression of the data: Adjusted R2 = 0.60, p-value = 0.016.

6. Discussion

6.1. Statistical Analysis of Soil Mixing

Several empirical models were developed to predict the degree of soil mixing and resulting Pb concentrations and redistribution after soil mixing based upon the Standard and Homeowner excavation techniques. The decision to leave soils with Pb concentrations <1200 mg kg^{-1} soil was based upon the assumption that the excavated soil would be well mixed and result in an average soil Pb concentrations <400 mg kg^{-1}. To test this hypothesis, statistical models were created to:

1. Use the geometry of the hole to predict the ratio of un-remediated soil in a specific sample as a function of the depth to the remediation interface and total depth excavated
2. Conduct matching means and matching means and variances to predict the distribution and concentration of Pb in the mixed soil
3. Use Bayesian estimation analysis to estimate the mixing distribution at each location.

Modeling the degree of soil mixing and the concentration of Pb in the resulting mixture is dependent upon the relative proportions of clean and un-remediated soil present. For example, the soil profile can be viewed as a series of compartments above and below the remediation interface (Figure 6.1). When the soil is disturbed, the distribution of the soil compartments changes. A random sample from the new distribution will contain a certain number of clean and un-remediated soil compartments. Therefore, the total concentration of any analyte of interest is based on the relative number of clean and un-remediated soil compartments in the random sample. The geometric model provides an estimate of the analyte of interest by predicting the amount of un-remediated soil in a given sample.

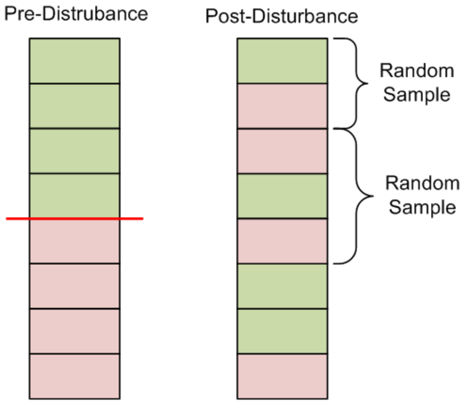

Figure 6.1 Schematic representation of soil mixing. In the figure the green blocks designate the clean soil, the red line the remediation interface, and the red blocks the un-remediated soil. The brackets next to the Post-Disturbance column indicate different random samples taken. The groupings of blocks contained within the brackets differ based on the redistributed soil compartments. The red line indicates the location of the remediation interface.

For our first model, a cylinder was used to model the geometry of the hole created using the Standard technique, and a hemisphere or hemispherical cylinder was used to model the geometry of the Homeowner excavation technique (Figure 4.1, 4.2). For comparison of all the experimental units, the depth of the remediation interface was normalized to 1 by evaluating the total excavation depth as a fraction of the remediation depth (Eq.1).

Equation 1 $$r = \frac{E}{RI}$$

Where r is the normalized depth, E is the excavation depth and RI is the remediation depth.

For a cylindrical (Eq. 2) and hemispherical (Eq.3) shaped exaction the expected fraction of un-remediated soil (w) is

Equation 2 $$w = \frac{E-RI}{E} = 1 - \frac{1}{r}$$

Equation 3 $$w = \frac{(r-1)^2(2r+1)}{2r^3} = 1 - \frac{(3r^2-1)}{2r^3}$$

For both the cylindrical and hemispherical the equation are true for $r \geq 1$. At r values < 1 $w = 0$

A schematic representation of the geometric model is presented in Figure 6.2 and the normalized ideal mixing model for the Standard and Homeowner excavation techniques, is presented in Figure 6.3. A value of 1 on the x-axis indicates the depth at which excavation has reached the remediation interface. Therefore, at excavation depths less than 1, y = 0 because the subsoil remains undisturbed. As the excavation depth exceeds the remediation interface the ratio will be greater than 1. The exact value of the ratio is dependent on the geometry of the hole. For example, at an x-axis value of 2 the excavation depth is twice that of the remediation interface. The ideal degree of mixing (*w*) for the Standard excavation technique (cylinder) is 0.5 or 50%, but the degree of mixing for the Homeowner excavation (hemispherical) is only 0.3 or 30% (Figure 6.3).

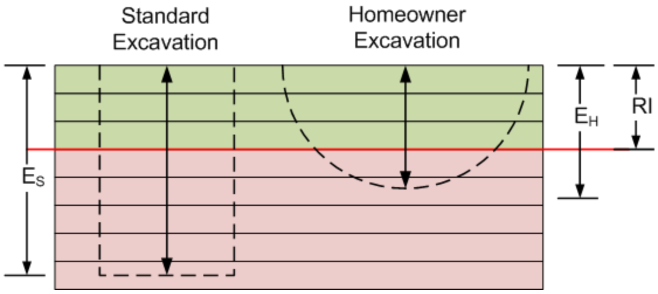

Figure 6.2 A Schematic Representation of the geometry of the standard and Homeowner excavations. The image illustrates how the geometry of the hole will impact the mixing of clean and un-remediated soil.

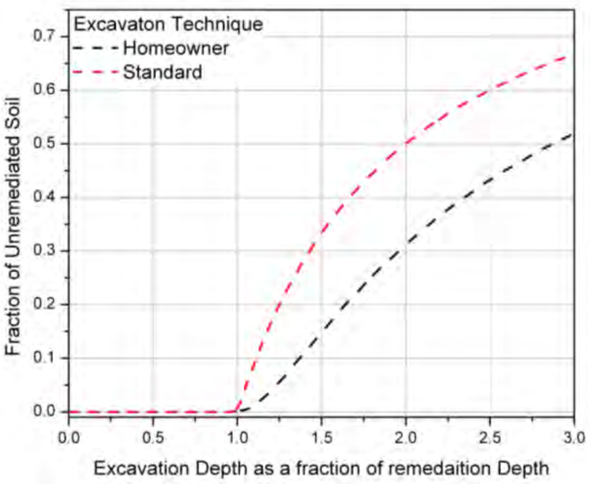

Figure 6.3 Expected fraction of contaminated or "un-remediated" soil based upon geometry of the excavation. The excavated fraction of un-remediated soil versus ratio of depth of excavation to remediation interface.

The geometric model was validated by predicting the mean concentration of a specific analyte in the spoil pile based on the relative contribution of the given analyte above and below the remediation interface within the spoil. The equation for the predicted concentration of an analyte in the spoil pile is

Equation 4 $$P_{spoil} = \frac{([Pb_{below\ RI}]*w)+([Pb_{below\ RI}]*(1-w))}{Spoil\ mass}$$

where w is the percentage of un-remediated soil in the sample/spoil.

As an example assume a spoil sample mass of 1 kg, 15 mg Pb kg^{-1} above the RI, 800 mg Pb kg^{-1} below the RI, and a 20% fraction of un-remediated soil in the spoil, the predicted spoil (P_{spoil}) concentration is

Equation 5 $$P_{spoil} = \frac{(800\ mg\ Pb\ kg^{-1} * 0.2) + (15\ mg\ Pb\ kg^{-1} * 0.8)}{1\ kg\ soil} = 172\ mg\ Pb\ kg^{-1}\ soil$$

Correlation coefficients from the validation of the geometric model for the analytes of interest varied (Table 6.1). An example of the correlation plots for Pb is presented in Figure 6.4. Plots for other analytes are presented in Appendix 2. Dot plots were also developed to depict the range of elemental values compared to the actual concentration (Figure 6.5). Each point on the plot represents an individual sample. The spread of data along the x-axis provides a visual interpretation of the distribution of analyte concentrations and the variability. Additionally, the degree to which the predicted sample concentrations line up with the actual sample concentrations provides an insight as to the robustness and accuracy of the geometric model predictions.

Overall, the predicted soil concentration in the spoil was better for the Standard excavation technique as compared to the Homeowner (Table 6.1). However, this was not the case for Pb or nickel. The correlations were also higher for analytes whose soil concentration above and below the remediation interface were similar, e.g. aluminum, calcium, potassium, sodium, and phosphorus (Table 6.1; Figure 6.5). This is was expected, since a poorly mixed or well mixed soil would have virtually the same analyte concentrations.

Less robust correlations for the model were also noted for analytes whose total concentration in the soil was low e.g. arsenic, cobalt, copper and nickel (Table 6.1; Figure 6.5). Examining the dots plots specifically for cobalt and arsenic the range of concentrations for the two elements in the clean soil (1) is significantly less than the un-remediated soil (2) (Figure 6.5). The range of average concentrations in the spoil (H and S) visually appears to more closely resemble the element distribution in the un-remediated soil. This would suggest that the soil may not be well mixed in the spoil. Iron, Zn, and Pb also had significantly higher concentrations in the un-remediated soil compared to the surface soil. Unlike the previous analytes the concentrations in the un-remediated soil were in excess of 1000 mg kg^{-1}. However, the correlation coefficients for these elements were also low. The smaller correlation values indicate that geometric ideal mixing model may not be representative of the field observations. The inability of the model to accurately predict the average spoil concentration is related to the degree of soil mixing that occurs during excavation. Results from the geometric model are in agreement with the data for the redistribution of Pb (Figure 5.1) indicating a heterogeneous distribution of Pb after excavation and back filling.

Table 6.1 Correlation coefficients for the predicted elemental concentrations in the excavated material based on the geometric model as a function of the average concentration of specific elements in the excavated spoil.

Element	Excavation Type	
	Standard	Homeowner
	Correlation Coefficient	
Al	0.858	0.8
As	0.703	0.648
Ca	0.886	0.863
Co	0.727	0.594
Cr	0.766	0.687
Cu	0.698	0.623
Fe	0.338	0.482
K	0.928	0.964
Mg	0.908	0.96
Mn	0.875	0.636
Na	0.87	0.917
Ni	0.182	0.4
P	0.906	0.94
Pb	***0.406***	***0.737***
S	0.831	0.894
Zn	0.397	0.264

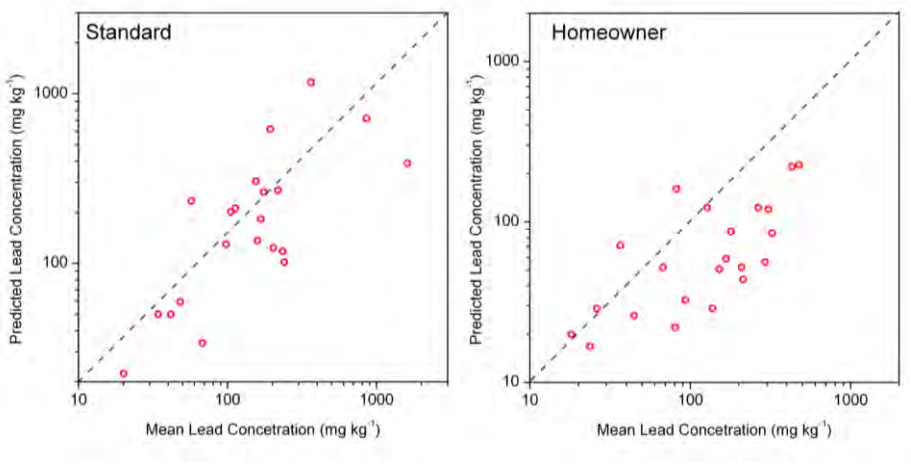

Figure 6.4 The predicted concentration of soil Pb, based on the geometric model, as a function of the average concentration of Pb in the excavated spoil for the standard and Homeowner excavation techniques. Dashed line indicates a 1:1 correlation. Correlation values are presented in Table 3.

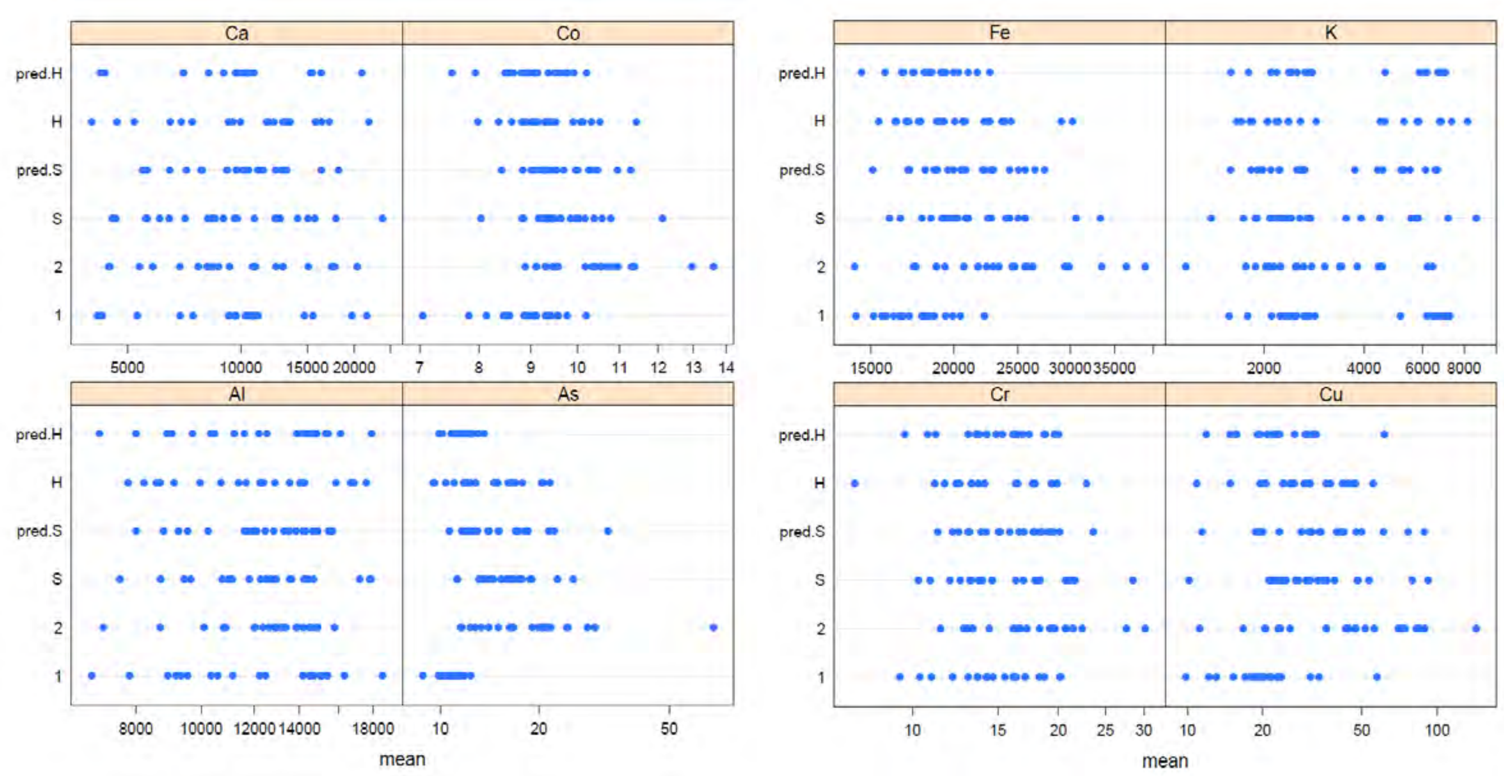

Figure 6.5 Dot plots for the results predicted and actual values for the analyte concentration in the spoil for the geometric model. Each dot represents a single sample location and a single predicted value for a sample location. H indicates the Homeowner excavation method, S indicates the standard method, 1 indicates the surface/clean soil analyte concentration, and 2 indicates the subsurface/un-remediated analyte concentration

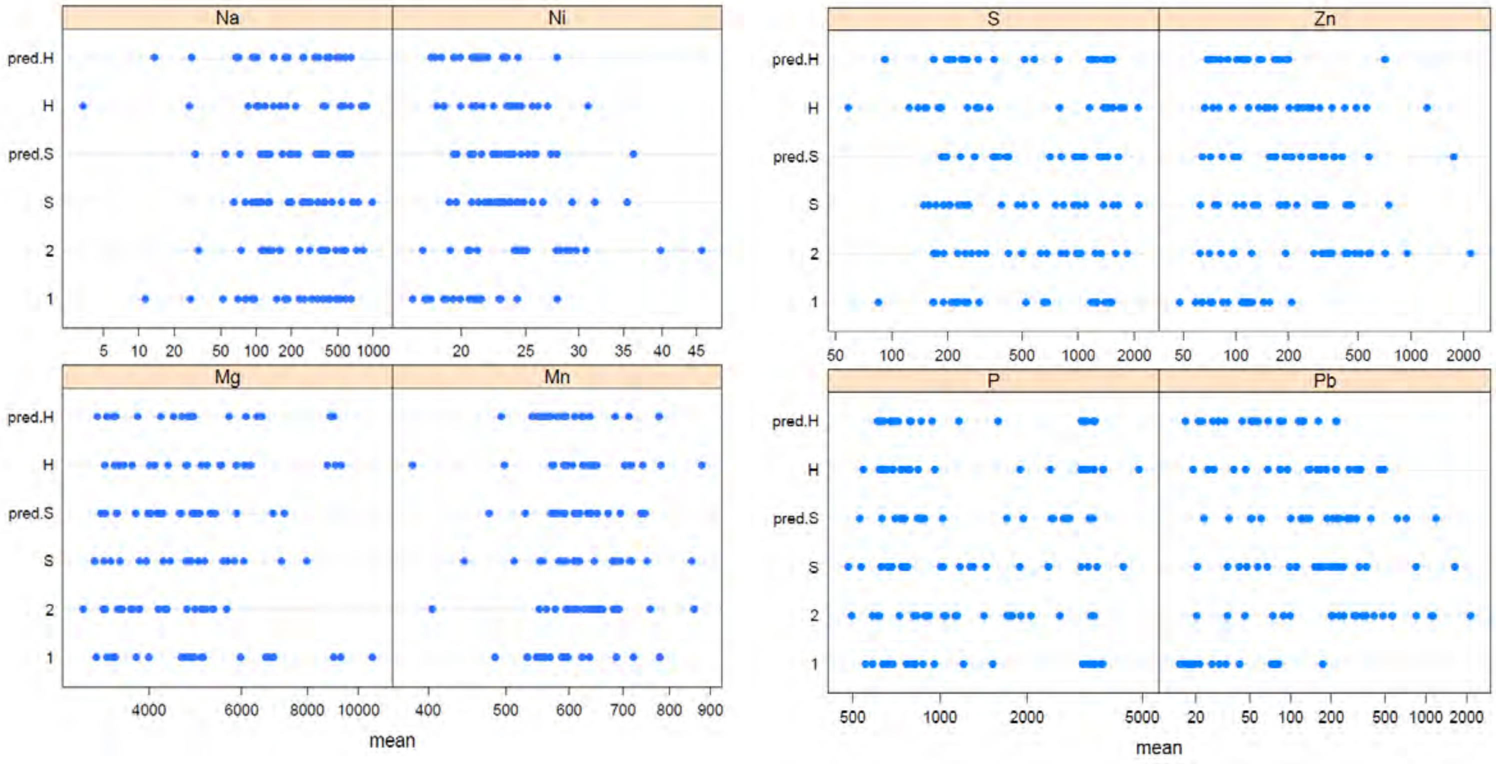

Figure 6-5 cont. Dot plots for the results predicted and actual values for the analyte concentration in the spoil for the geometric model. Each dot represents a single sample location and a single predicted value for a sample location. H indicates the Homeowner excavation method, S indicates the standard method, 1 indicates the surface/clean soil analyte concentration, and 2 indicates the subsurface/un-remediated analyte concentration.

An attempt was made to model the redistribution of Pb following excavation and backfilling using a matching means and a matching means with variances approach. Matching Means, in its simplest form, estimates the analyte means of the 'clean', 'un-remediated' and mixed soil for each location. For the purposes of this analysis, clean is defined as average concentration of the analyte of interest in all of the soil samples (all properties) collected above the remediation interface, and un-remediated is defined as the average concentration below the remediation interface. For matching means the mixing variance is assumed to be 0. Under this assumption the mixing fractions (clean/un-remediated) are estimated using only the means values for the specific analyte of interest. For a given mixing fraction, *w*, the mean of the mixture is modeled as

Equation 6 Figure 6-5 cont. Dot plots,

with the subscripts *m, c* and *u*, designating mixed, clean and un-remediated soil, respectively, and μ being a mean.

Theoretically, this should give the best agreement between the mixing fractions estimated from geometry and those estimated based on analytical data. Unfortunately, as seen in Figure 6.6 for Pb, the agreement is so extremely poor as to render the estimates of little worth. The lack of any significant agreement between the model and analytical data highlights even on a small scale demonstrates significant heterogeneity in the distribution of Pb in the soil.

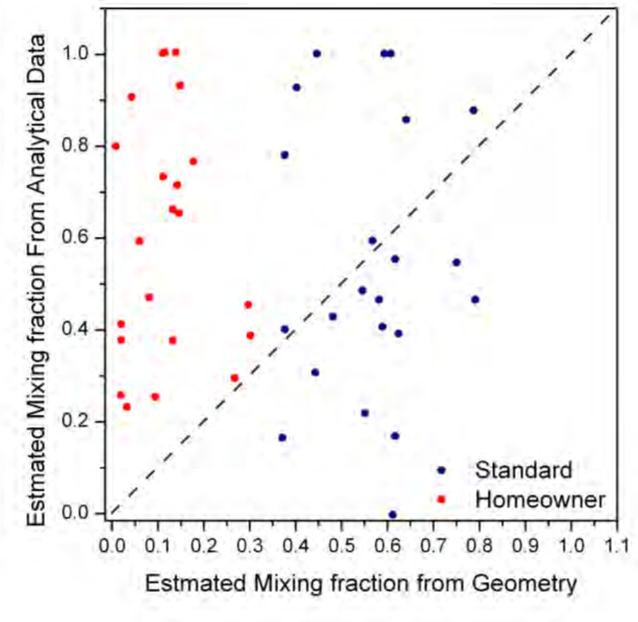

Figure 6.6 Estimated fraction of soil mixing as a function of depth and geometry based on the Pb soil concentrations in the post soil core data. A) Standard Excavation Technique. B) Homeowner Excavation technique.

Matching Means and Variances, A more sophisticated method of estimating the distributional parameters of the mixing distribution is to match both means and their variances. This can be done by using the formula for the variance of the product of two independent random variables.

Equation 7 $$V(XY) = \mu_X^2\sigma_Y^2 + \mu_Y^2\sigma_X^2 + \sigma_X^2\sigma_Y^2 .$$

Then under our model, the variance of the mixed soil should be

Equation 8 $$\sigma_m^2 = \sigma_c^2 + \mu_w^2\left(\sigma_c^2 + \sigma_u^2\right) + \sigma_w^2\left(\mu_u - \mu_c\right)^2 + \sigma_w^2\left(\sigma_c^2 + \sigma_u^2\right) - \mu_w\sigma_c^2 ,$$

where the subscript *w* indicates the distribution of the mixing fraction. In order to ensure legitimate values for the mean and variance of the weighting distribution, they were taken to follow the form of those parameters for a beta distribution. The beta parameters were then optimized and back-transformed. Again, this approach produced extremely poor results (data not shown).

Finally, an attempt was made to use Bayesian estimation to estimate the mixing distribution for each location. This was done assuming gamma and lognormal distributions for the clean and un-remediated soil and a beta distribution. Bayesian estimation of the distributions for each analyte at each location of the clean and un-remediated soil worked better. It confirmed that these data were better modeled using lognormal distributions than gamma distributions. However, modeling the distribution of a randomly weighted mean using either Bayesian Markov Chain Monte Carlo (as implemented in BUGS and JAGS software) or Laplace approximation methods proved infeasible.

The inability to develop a model to predict the concentration of Pb in the top 12 inches of soil following excavation or the redistribution of Pb within the soil profile is due to sample variance. The variances are so large that that it is impossible to provide reliable estimates for the distribution of mixing fractions. The variances were so large because of the nature of the research objective which was to estimate the degree of mixing following Homeowner intrusion into the un-remediated soil. We attempted to control for the expected difficulty of this research by using a Standardized excavation technique to represent "a best case scenario" of soil mixing which would result in a 1:4 ratio of clean fill to un-remediated soil. Regardless of using an "idealized" mixing technique we were not able to develop a valid predictive model. Further, based on statistical analysis the sampling campaign and data analysis should be regarded as a pilot study and used as the basis to design a full study of soil mixing and risk for the OLS site. The methodology, if not the results, should be applicable to other sites.

6.2. Frequency Analysis

As discussed in the previous section, the small sample size and the variability of the data prevent any us from developing predictive models to then make inferences the degree of soil mixing following Homeowner intrusion into contaminated soil. A frequency analysis can be used to evaluate the impact of soil mixing on the redistribution of Pb within the soil profile. A frequency analysis, in this case, only allows for conclusions to be drawn from the current data set and is observational not predictive. However, it is useful for evaluating how often surface soil Pb concentrations exceeded 400 mg kg^{-1} after mixing.

In this study only properties that had been previously remediated and Property 2 were used. Property 2 was included based on the similarity of the pre-excavation soil Pb profile and that of the properties that were previously remediated. Further replicate samples from the same quadrant were treated as individual experimental units. For the frequency analysis the concentration of Pb in the top 1, 6, 12, 18, and 24 inches of the soil post excavation were calculated (Tables 6.2).

In the May 2009 Final Record of Decision for the Omaha Lead Site properties exceeding 400 mg kg^{-1} Pb (equivalent to mg Pb kg^{-1}) in the top 1 inch would trigger a remedial action. Results of our study are broken into three categories and reported on Table 6.3.

Table 6.2 Post Homeowner and Standardized excavation soil total Pb concentrations in the top 1, 6, 12, 18, and 24 inches of the soil profile. Bolded numbers indicate where the soil lead concentration exceeds 400 mg kg^{-1}.

Experimental Unit	Soil Pb Concentration (mg kg^{-1}) Homeowner					Soil Pb Concentration (mg kg^{-1}) Standardized				
	0-1	0-6	0-12	0-18	0-24	0-1	0-6	0-12	0-18	0-24
	Inches					Inches				
1A	69	121	247	267	246	202	153	184	190	192
1B	202	155	123	219	196	80	184	118	195	160
1C	**765**	**462**	348	**504**	**403**	351	341	383	393	353
2						**407**	326	301	327	313
3A	57	**625**	**457**	**408**	334	86	159	156	153	157
3B	76	212	331	368	285	159	175	191	191	198
4A	224	210	203	225	227	128	82	86	86	84
4B	135	161	143	140	136	166	193	170	165	159
5	30	28	28	27	25	19	22	21	21	19
6	20	27	52	86	145	**1147**	**516**	**603**	**607**	**689**
7	82	94	89	75	63	62	70	65	73	75
7B	333	**562**	**436**	**477**	**445**	53	63	66	65	63
8	87	146	154	123	98	133	102	119	117	114
9	51	26	266	219	176	120	96	95	98	91
10	68	71	72	79	96	45	47	38	45	46
11	16	16	16	139	166	240	268	246	213	238
12	34	38	36	37	39	27	34	34	34	35
13	136	197	209	185	146	100	185	177	172	162
14	40	38	46	42	38	46	38	40	39	42
15	240	118	114	281	260	170	260	214	220	195
16	90	83	83	112	124	210	213	195	190	199
17	249	377	**488**	**639**	**625**	**556**	**449**	**573**	**774**	**1048**
18	23	21	26	73	155	342	234	242	257	237

The first is the total number of excavations conducted for each experimental unit. In this case each experimental unit had two excavations conducted (except Property 2) the Homeowner and Standard techniques. These results are then broken out by excavation technique, either Homeowner or Standard. In the Table the headings indicates the conditions under which the analysis was conducted. The category, Total Excavation, refers to the number of excavation units used in the analysis. The category, Soils with Pb > 400 mg kg^{-1}, refers to the number of properties that exceed the 400 mg kg^{-1} concentration in a given depth interval, e.g. 0 to 1 inch or 0 to 12 inches. Finally, we report the percentage refers the percentage of properties that exceed 400 mg kg^{-1}.

The frequency analyses were conducted for several different soil Pb conditions to analyze specific questions. The analysis was for the total number of excavations (all experimental units; Table 6.3). This analysis is the most robust since it includes the largest number of observations. For the entire study 10% of the excavation units resulted in a final soil Pb concentration exceeding 400 ppm in the top inch after excavation (Table 6.3). The excavation units exceeding 400 included one property from the Homeowner excavation group and three from the Standard excavation group. The significance of the finding is questionable due to the small sample size.

In the top 12 inches of soil, 12.5% of the excavation units resulted in a final soil Pb concentration exceeding 400 ppm (Table 6.3). Interestingly, the 0-12 and 0-6 inch groups both included five properties. However, the specific properties in each group were not all the same. Breaking the information down by excavation technique shows that one more property in the Homeowner excavation group exceeded the 400 value compared to the Standard. The significance of this finding is questionable. The number of total samples analyzed was small. Further, the number of properties exceeding the 400 mark was only 10 % for the 0-1 inch and 12.5% of the total samples for 0-12 inches. Lastly, the highest concentration of Pb in each soil property investigated varied greatly. All of these factors make it difficult to place significance on the degree of soil mixing attributed to either excavation technique. The visual evaluation of the Pb soil profiles in Figure 5.1 provides a greater insight into the difference in the degree of mixing based on excavation technique.

Of specific interest in the current study was potential to exceed 400 ppm of Pb in the top inch and 12 inches of the soil after mixing when the maximum concentration of Pb exceeded 1200 ppm at the remediation interface. The second section of Table 6.3 uses data obtained from the Omaha Lead database to answer the question. Based on the database information, only 2 the properties investigated have soil Pb concentrations exceeding the 1200 value. Of the four excavations, one (property 17) exceeded the 400 value in the top inch and both excavation techniques resulted in an excess of 400 ppm in the top 12 inches.

Based on the frequency analysis using the database values, the same analysis was again performed on soils with a maximum Pb concentration greater than 1000 ppm and less than 800 ppm using data from the Omaha Lead database and the current study (Table 6.4). The number of properties exceeding 400 ppm Pb in the soil surface after excavation decreases when soil Pb concentration at depth is less than 1200 ppm. These data are observational only. They are not predictive of what surface soil Pb concentrations may be after Homeowner intrusion into contaminated soils at other OLS properties.

Table 6.3 Frequency analysis of the number of properties that exceeded Pb concentrations of 400 mg kg^{-1} in either the top 1, 6, 12, 18, or 24 inches. For all of the properties sampled, properties where the soil Pb concentration exceeded 1200 mg kg^{-1} according to the OLS database, and properties where the maximum soil Pb concentration exceeded 1200 mg kg^{-1} based on the current study. Data corresponding to the frequency that 400 mg kg^{-1} was exceeded in the top 12 inches in italics. Bolded heading refer to the type of soils included in the analysis.

	Soil Depth (inches)				
	0-1	0-6	0-12	0-18	0-24
Total Excavations Standard + Homeowner					
Total Excavations	40				
Soils with Pb > 400 mg kg^{-1}	4	5	*5*	6	5
Percentage	10	12.5	*12.5*	15	12.5
Homeowner Excavations	19				
Soils with Pb > 400 mg kg^{-1}	1	3	*3*	4	3
Percentage	5.3	15.8	*15.8*	21.1	15.8
Standard Excavations	21				
Soils with Pb > 400 mg kg^{-1}	3	2	*2*	2	2
Percentage	14.3	9.5	*9.5*	9.5	9.5
Soils with soil Pb > 1200 mg kg^{-1}, data from the Omaha Lead Database					
Total Excavations	4				
Soils with Pb > 400 mg kg^{-1}	1	1	*2*	2	2
Percentage	25	25	*50*	50	50
Homeowner Excavations	2				
Soils with Pb > 400 mg kg^{-1}	0	0	*1*	1	1
Percentage	0	0	*50*	50	50
Standard Excavations	2				
Soils with Pb > 400 mg kg^{-1}	1	1	*1*	1	0
Percentage	50	50	*50*	50	0
Soils with soil Pb > 1200 mg kg^{-1}, Current Study					
Total Excavations	11				
Soils with Pb > 400 mg kg^{-1}	4	3	*3*	4	4
Percentage	36.4	27.3	*27.3*	36.4	36.4
Homeowner Excavations	5				
Soils with Pb > 400 mg kg-1	1	1	*1*	2	2
Percentage	20	20	*20*	40	40
Standard Excavations	6				
Soils with Pb > 400 mg kg^{-1}	3	2	*2*	2	2
Percentage	50	33.3	*33.3*	33.3	33.3

Table 6.4Frequency analysis of the number of properties that exceeded Pb concentration of 400 mg kg^{-1} in either the top 1, 6, 12, 18, or 24 inches for properties where the soil Pb concentration exceeded 1000 mg kg^{-1} at the remediation interface according to the Omaha Lead database, properties where the maximum soil Pb concentration exceeded either 1000 or 800 mg kg^{-1} based on

the current study. Data corresponding to the frequency that 400 mg kg^{-1} was exceeded in the top 12 inches in italics. Bolded heading refer to the type of soils included in the analysis.

	Soil Depth (inches)				
	0-1	0-6	0-12	0-18	0-24
Soils with soil Pb ,> 1000 mg kg^{-1}, data from the Omaha Lead Database					
Total Excavations	21				
Soils with Pb > 400 mg kg^{-1}	3	2	*2*	3	3
Percentage	14	9.5	*9.5*	14	14
Homeowner Excavations	10				
Soils with Pb > 400 mg kg^{-1}	1	1	*1*	2	2
Percentage	10	10	*10*	20	20
Standard Excavations	11				
Soils with Pb > 400 mg kg^{-1}	2	1	*1*	1	1
Percentage	18	9	*9*	9	9
Soils with soil Pb > 1000 mg kg^{-1}, Current Study					
Total Excavations	13				
Soils with Pb > 400 mg kg^{-1}	4	3	*3*	4	4
Percentage	31	23	*23*	31	31
Homeowner Excavations	6				
Soils with Pb > 400 mg kg^{-1}	1	1	*1*	2	2
Percentage	43	29	*29*	29	29
Standard Excavations	7				
Soils with Pb > 400 mg kg^{-1}	3	2	*2*	2	2
Percentage	43	29	*29*	29	29
Soils with soil Pb < 800 mg kg^{-1}, Current Study					
Total Excavations	27				
Soils with Pb > 400 mg kg^{-1}	0	1	*1*	1	1
Percentage	0	4	*4*	4	4
Homeowner Excavations	13				
Soils with Pb > 400 mg kg-1	0	1	*1*	1	1
Percentage	0	8	*8*	8	8
Standard Excavations	14				
Soils with Pb > 400 mg kg^{-1}	0	0	*0*	0	0
Percentage	0	0	*0*	0	0

6.3. Bioavailability/Bioaccessibility

XAFS data indicate that Hydroxy/Chloropyromorphite was present in all of the soils sampled at relative abundances exceeding 30%. Based on the known speciation of Pb emitted from Pb smelting/recycling activities and existing P:Pb molar ratios in the soils analyzed it is reasonable to assume that phosphorus concentrations in the soil were high enough to promote precipitation of a pyromorphite species. The addition of P amendments to Pb contaminated soils to induce pyromorphite precipitation is a remediation technique utilized to reduce Pb bioavailability. The *in-situ* formation of pyromorphite without additions of phosphorus is highly advantageous due to the inherent reduction in potential bioavailability of soil Pb. Additional research evaluating the geographic distribution and abundance of pyromorphite phases will aid in a better understanding of the conditions under which phase form and determine if geographical location/soil properties control the precipitation of Pb phosphate minerals. Currently additional soils are being investigated by XAFS analysis to further evaluate the abundance and presence of Pb phosphates.

7. Summary/Conclusions

Urban soils within the OLS have been contaminated with Pb from atmospheric deposition of particulate materials from Pb smelting and recycling activities. In May of 2009 the Final Record of Decision Declaration for the Omaha Lead Site (OLS) stated that any residential soil exceeding the preliminary remediation goal (PRG; 400 mg_{Pb} $kg^{-1}{}_{soil}$) would be excavated, backfilled and re-vegetated. The remedial action entailed excavating contaminated soil in the top 12 inches and excavation could stop when the concentration of soil Pb was less than 400 mg kg^{-1} in the top 12 inches or less than 1200 mg kg^{-1} at depths greater than 1 ft. After removal of the contaminated soil, clean backfill was applied and a grass lawn was replanted

The initial recommendation was that soils with Pb concentration less than 1200 mg kg^{-1}, at depths greater than 1 ft, be left in place. The recommendation was based on the assumption that Pb-contaminated soil at depth greater than 1 ft would not represent a future risk. This assumption was based on the principal that mixing and other factors encountered during normal excavation practices would not result in Pb surface concentrations greater than the PRG. The current study was designed to evaluate the degree of soil mixing and the redistribution of Pb within the soil profile after typical Homeowner earth-disturbing or excavation activities. Two methods were employed to evaluate soil mixing. The first method (Homeowner) entailed excavating soil using a common garden spade to a depth of 18 inches. The second (Standard) used a 2-person auger to excavate a hole 2 ft in depth and would represent the best case scenario where the excavated soil would be well mixed, and surface soil Pb concentrations would remain below the PRG. Prior to excavation, surface soil samples and an undisturbed soil core were collected to determine the initial concentration and distribution of Pb within the soil. After excavation, a composite soil sample was collected from the spoil pile prior to backfilling the hole. Lastly, a final soil core and surface soil sample were collected to evaluate the redistribution of Pb within the soil profile. Samples were dried and digested following EPA method 3051a.

Data were collected from 18 properties. This includes duplicate and triplicate samples taken from properties to evaluate soil heterogeneity within a single remediation quadrant. The results from the duplicate and triplicate sampling were mixed. Two of the properties exhibited a large degree of variability between the duplicate and triplicate samples. The other two properties showed a similar distribution and concentration of Pb within the soil profile. It should be noted that large difference in soil Pb concentration from the triplicate samples collected from property 1 is likely caused by the presence of the slag-like material at depths below the remediation interface. Results from the soil analysis revealed a stark contrast in the soil Pb concentration at the remediation interface, as would be expected. Of the 18 properties sampled, 17 were previously remediated, two did not have the expected high Pb concentration below the remediation interface. A fourth property did have a slight increase in Pb below the remediation interface, however, the increase was less than what was expected based on data obtained from the Omaha Lead Database. Seven of the 14 properties had maximum Pb concentration at the remediation interface. The remaining 7 properties show that soil Pb concentrations increased below the remediation interface. Four of the properties (Figure 6; 1C, 3B, 9, 17) had soil Pb concentrations greater than 1200 mg kg^{-1} below the remediation interface.

Post excavation cores revealed a heterogeneous distribution of Pb within the soil profile demonstrating that the soils were not well mixed. Our attempts to model soil mixing based on soil Pb concentrations and the geometry of the excavation failed due to the high variance in the data despite attempting to reduce the variance before beginning the study. While a conceptual model could be developed in Excel with assumed means and variances to predict mixing, we believe this pilot study has demonstrated the need for further investigations to develop an empirical model. We believe a future study expanding the number of properties sampled and adding composite samples to the current study design would reduce the high levels of variance in the data, and would therefore validate our model. From the statistical analysis it was determined that mixing fractions for the un-remediated and clean soil could be estimated approximately from the geometry of the excavation and the measured depths of remediation and total excavation depth. The mixing fraction should be viewed as a random variable with a distribution whose mean depends on the geometry of the excavation and the relative depths of the excavation and remediation. This conceptual model may be implemented in an Excel spread sheet with assumed means and variances. Finally based on the statistical analysis the current study should be viewed as a pilot study. The high variances within the data make it impossible to analyze.

A frequency analysis was conducted to evaluate soil mixing. The analysis showed that for all of the properties sampled and both excavation techniques (n= 40), 5 or 12.5% of the samples had soil Pb concentrations in excess of 400 mg kg^{-1} in the top 12 inches of soil after excavation and backfilling. Of the 5 properties with elevated soil Pb concentrations, 3 were from the Homeowner excavation technique and two from the Standard excavation technique. Frequency analysis limited to properties with soil Pb concentration > 1200 mg kg^{-1}at depth showed that intrusion into the contaminated soil resulted in surface soil Pb concentrations exceeding 400 mg kg^{-1} at three of 11 sites. However, the surface Pb concentration after excavation did not exceed 400 mg kg^{-1} of Pb when the maximum Pb concentration at depth was less than 1200 mg kg^{-1}. As previously mentioned frequency analysis are observational and are not predictive of other sites.

Lead speciation data obtained from XAFS analysis of the soils indicates that the predominant Pb species present in the soils analyzed included: anglesite, hydroxypyromorphite, plumboferrite, and galena. Hydroxypyromorphite (i.e., hydroxyapatite) is not a constituent/Pb species associated with atmospheric emissions from Pb smelting recycling activities. It is most likely the Pb phosphate mineral formed in the soil. Soil phosphorus to lead (P:Pb) molar ratios were between 4 and 14. This would indicate there was ample P available for the *in-situ* formation of Pb phosphates. The precipitation of the Pb phosphates is extremely advantageous due to the low bioavailability of Pb from pyromorphites. The precipitation of the phase is effectively offering a secondary remediation technology by binding the Pb in place in an extremely low bioaccessible form.

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Supplemental Figures

Supplemental Figure 1 Standardized excavation used a gas powered posthole digger with spoil material brought to soil surface. Notice loss of soil structure.

Supplemental Figure 2 The Homeowner technique used a traditional garden spade to excavate a hole 18 inches in depth. Notice large soil clods.

Supplemental Figure 3 JMC Environmentalist's Sub-Soil Probe. Soil core tube was driven into the soil by hand and withdrawn using a jack.

Appendices

Appendix 1. Sample Data Sets

The imbedded excel documents contained all of the analytical data collected for the current study. The Complete Data Set file contains all of the raw and processed data. The Bulk Soil Sample Data Set contains only the data for the bulk soil samples and the Soil Core Data Set contains just the soil core data

Complete Data Set.xlsx

Bulk Soil Sample Data Set.xlsx

Soil Core Data Set.xlsx

Appendix 2. Correlation Figures

Correlation plots for the geometric model for all of the analytes are located in the attached adobe file.

Adobe Acrobat Document

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Environmental Protection
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Washington, DC 20460

EPA/600/R-15/054