January 2020

A Field Study Of Bioaccessible Lead In Detroit Soils: Insight Into The Effectiveness Of Phosphate-Based Lead Sequestration

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A FIELD STUDY OF BIOACCESSIBLE LEAD IN DETROIT SOILS: INSIGHT INTO THE EFFECTIVENESS OF PHOSPHATE-BASED LEAD SEQUESTRATION

by

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THESIS

Submitted to the Graduate School

of Wayne State University,

Detroit, Michigan

in partial fulfillment of the requirements

for the degree of

MASTER OF SCIENCE

2020

MAJOR: CIVL & ENVIRONMENTAL

ENGINEERING

Approved By:

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Advisor   Date

DEDICATION

To the Black, Indigenous, and Latinx children who continue to disproportionately suffer from the burden of environmental racism in this nation and across the world. Your lives matter and you deserve better.

ACKNOWLEDGEMENTS

Infinite thanks to my advisor, Dr. Shawn McElmurry, for his constant support, guidance, understanding, and for giving me the opportunity to research a topic that I am passionate about.

I would like to thank my thesis committee, Dr. Allison Harris, Dr. William Shuster, and Dr. Timothy Dittrich for the constructive criticism they have given me and asking the hardest, but most important questions.

Thank you to Patrick Crouch and Earthworks for your help in sampling and a great thank you to the Erb Family Foundation for funding this important research.

To my parents, Greg and Cathy, and to my life partners, Viktoriya and Caine, thank you eternally for your constant love, advice, and encouragement. Thank you for supporting me in every aspect of my life.

Thanks to Audrey Zarb, Mohammed Dardona, and Chandra Tummala for their help and guidance through this project and for always being respectful mentors and great friends.

Lastly, I would like to thank those who disparaged me in my undergraduate studies, as they served as a driving force and motivation for pursuing my M.S. in Civil and Environmental Engineering.

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CHAPTER 1 "INTRODUCTION"

Lead (Pb) is ubiquitous in the urban environment. Although traditionally useful in many industrial applications, lead is a harmful contaminant which poses a significant public health threat, especially to children. Exposure to lead has been studied for decades. As additional negative health effects of lead exposure have been identified, regulations have followed to reduce or eliminate many sources of environmental lead. Since the 1970s, the geometric mean of blood lead levels (BLLs) has declined across the United States. Despite this decline, minority children living in urban areas continue to remain disproportionately impacted. In the U.S., Black children are 3 times more likely than white children to have elevated blood lead levels (EBLL) (Leech et al., 2016). Of all children with EBLLs between 1997 and 2001, 80% were non-white minority children (Leech et al., 2016). The failure to address these disparities poses social and environmental justice concerns which must urgently be addressed.

The current guideline set by the U.S. Centers for Disease Control and Prevention (CDC) for EBLL in children is 5 µg/dL (CDC, 2020). Despite this guideline, no safe levels of lead in the blood has been identified. Even BLLs less than 5 µg/dL have been linked to negative behavioral and cognitive outcomes, such as decreased IQ, attention deficit disorders, decreased academic achievement, and increased incidence of problem behaviors (Hauptman et al., 2017). Children are at the highest risk from lead, as their bodies are rapidly developing and have an increased rate of absorption into their tissues (Tong et al., 2000). Lead also inhibits the ability of a child's body to absorb minerals such as zinc, calcium, and iron which are essential to proper nerve and brain development (ATSDR, 2017).

Through automotive emissions, industrial emissions, and chipping lead paint, lead has accumulated in urban soils and is potentially the main driving mechanism of childhood lead exposure in urban areas (Laidlaw et al., 2005). Seasonality in children's BLLs have exemplified the relationship between children's BLLs and soil lead, as BLLs increase in summer months when children are playing outside and windows tend to be open, allowing for soil dust to enter the home (Zahran et al., 2013). Remediation efforts in lead-contaminated soils through soil removal or capping have been shown to reduce children's BLLs (Laidlaw et al., 2017). Addressing and remediating soil lead contamination is therefore likely to reduce urban children's BLLs and there is an urgent need for a low-cost, environmentally sustainable method for reducing children's exposure to lead from urban soils.

Remediation strategies for lead in soil most often entail excavation or soil capping. These remediation techniques are expensive, disruptive to the soil environment, and are not logistically feasible for large-scale urban residential areas. However, lead may not need to be removed from the soil to decrease exposure. The portion of lead which is able to be absorbed into the body, the bioavailable fraction, may be reduced through the addition of phosphate-based soil amendments (Scheckel et al., 2013). This is because phosphate and lead can bind together in very insoluble mineral forms (i.e. pyromorphite), which are stable across a wide range of pH conditions, including those found in the gastro-intestinal system (Scheckel et al., 2013).

Animal feeding studies have been used to determine the effectiveness of these soil amendments, providing relationships between soil lead concentrations and lead concentrations across body tissues. However, these tests are expensive and morally unsound. Tests have been developed to determine the *in-vitro* bioaccessibility (IVBA) of lead as a proxy for bioavailability without the need for further animal tests. IVBA is a laboratory measure of the solubility of lead which could dissolve into the bloodstream and be absorbed by the body (U.S. EPA, 2017). IVBA tests can provide a general guidance on how bioavailable lead is from a variety of soils. The U.S. Environmental Protection Agency has developed an Integrated Exposure Uptake Biokinetics (IEUBK) modeling software which can use IVBA results and total soil lead concentrations to predict BLLs in children under 7 years old. These methods and models can be used to test soil amendments for their anticipated effect on children's health. Additional details on the health effects of lead and lead exposure as well as a review of lead in the urban environment and lead remediation are presented in Chapter 2.

In this study, a modified version of the physiologically based extraction test (PBET) developed by Ruby et al. (1996) was used to assess IVBA of lead in soils from Detroit, MI. Soils were collected from across Detroit, Highland Park, and Hamtramck and were characterized for total soil lead, lead IVBA, and a variety of soil characteristics (pH, organic matter, CEC, phosphorus, and nutrients). Detailed methods for our analyses are included in Chapter 3.

In Chapter 4, we attempted to characterize and identify relationships between these soil properties and IVBA using multiple variable linear regression. In this chapter, we also investigated the relationship between IVBA and proximity to smelters.

Chapter 5 describes a randomized treatment-control experiment at 142 locations around Detroit intended to evaluate the effectiveness of bone meal soil amendments. Phosphates in bone meal can bind lead to form insoluble minerals, effectively reducing bioavailability. After initially characterizing soils, liquified bone meal was applied to 61% of soil sites, while 39% served as a control. After treatment soil properties where again measured and we explored relationships between soil properties and IVBA. Results from this study should provide guidance on the effectiveness of using a bone meal soil amendment as a low-cost, readily available remediation technique for reducing bioavailable lead exposure to urban populations.

CHAPTER 2 "BACKGROUND & LITERATURE REVIEW"

Sources of Lead in the Environment

Lead is a naturally occurring heavy metal that has many historic and current uses in industry, despite its acknowledged toxic effects on humans and animals (EPA, 2019). Its physical and chemical properties have led to use of lead and its compounds in gasoline, paint, pipes, batteries, ceramics, solder, and ammunition. As negative health effects of lead have been studied and proven, regulations have removed or reduced the use of lead in products manufactured in the United States. The sale of lead-based paint was prohibited in 1976 under the Lead Paint Poison Protection Act, and the use of lead in gasoline was phased out and eventually banned in 1990 (Dignam et al., 2019), by which time an estimated 4 to 5 million tons of lead had been deposited into the environment through gasoline emissions (Laidlaw et al., 2005). Through these regulations, reduced air emissions and widespread application of lead source control measures, the geometric mean blood lead levels (BLLs) of Americans aged 1 to 74 was reduced from 12.8 µg/dL between 1976-1980 to 0.82 µg/dL between 2015-2016, a 93.6% reduction in BLLs (Dignam et al., 2019). The Centers for Disease Control (CDC), have set guidelines for elevated BLLs (EBLL) in children at 5 µg/dL (CDC, 2020).

Although regulations have decreased lead hazards from air, water, and food, the legacy of lead remains. Legacy lead in soil deposited from past gasoline emissions, dust from and chipping of exterior-interior leaded paint, and emissions from smelting or industrial activities in urban areas remains a public health issue. Lead is a naturally occurring heavy metal. The United States Geological Survey (USGS) reports a national geometric mean background level of lead in soil of 16 mg/kg (Shacklette and Boerngen, 1984). Through anthropogenic uses of lead in gasoline, paints, and industry, lead concentrations in soils can be significantly higher than background levels (U.S. EPA, 2019).

Industrial activities such as smelting have contaminated the regions in which they operate. Historical lead smelting activities in Jasper County, MO contaminated over 2500 residential lots with lead exceeding 800 mg/kg (Yang et al., 2001), much higher than the mean reported by the USGS. Both the

Missouri Department of Health and the City of Joplin, MO Health Department conducted studies which reported BLLs greater than 10 μg/dL in 14% of children younger than 7, directly correlating soil lead with childhood BLLs (Yang et al., 2001). Lead in soil is therefore an important pathway for lead, still contributing to elevated BLLs (EBLL). It has been shown that proximity to smelters is correlated to BLLs (Grigoryan et al., 2016) and that lead in sidewalk dust decreases exponentially with increasing distance from smelters (Pelfrene and Douay, 2018).

For residential areas, the EPA has set a soil screening level (SSL) for lead of 400 mg/kg in bare soil or play areas, and 1200 mg/kg in non-play areas (ATSDR, 2017). This is the level which the EPA has suggested to be protective for human health, although these levels serve as a guideline and are not enforceable. For soil lead, the primary route of exposure of concern is via oral ingestion, although inhalation of suspended soil and dust is significant (Zahran et al., 2013). Once ingested, a portion of the lead is absorbed by the body. The amount of lead which absorbs into the body, defined as the amount of bioavailable lead, by children is typically around 30% of lead present in soil when ingested (U.S. EPA, May 2007).

The amount of bioavailable lead correlates to the total amount of lead present (Roussel et al. 2010). When testing soil amendments for their ability to decrease lead bioavailability, there must be a way to determine how effective these amendments are. Because it would be unethical to intentionally subject children to lead exposure, *in-vitro* methods have been developed to estimate *in-vivo* bioavailability. These *in-vitro* methods measure the amount of lead that is bioaccessible, or the amount of lead that may be available for absorption (U.S. EPA, 2017). Multiple methods for measuring bioaccessible lead, based on reactions that occur in the human stomach and intestines, are found to correlate well with in vivo measurements of lead bioavailability performed in swine and other research animals (Ryan et al., 2004; Ruby et al., 1996).

Health Effects and Pediatric Exposure to Lead

The concentration of lead in blood, or blood lead level (BLL), is an indicator of recent exposure to lead. This metric is used to determine the burden of lead in the body (EPA, 1994), and scale the health impacts of this burden. For example, in adults, BLLs between 20 to 40 µg/dL have been linked to decreased motor function, attention deficit disorder, and decreased reaction times, while BLLs over 40 µg/dL can cause anorexia, fatigue, headaches, pain in the joints, constipation, and myalgia (OSHA, 2020). BLLs over 60 µg/dL can cause anemia, kidney fibrosis, peripheral neuropathy, convulsions, coma, and sometimes death (OSHA, 2020). Children are at higher risk from lead than adults due to their rapid development and increased rate of lead deposition within tissues, increased ratio of lead to body weight, physiological uptake rates, and the tendency to place objects and fingers that may be contaminated into their mouths (Tong et al., 2000). Even at BLLs <5 µg/dL, negative behavioral and cognitive impacts have been reported, including decreased IQ, attention disorders, decreased academic achievement, and increased incidence of problem behaviors (Hauptman et al., 2017).

Reduction or elimination of lead in paint, automotive emissions, and soldered food cans over the last 50 years has resulted in a reduction of median BLLs in children under six from 15-18 µg/dL in 1970 to a substantially lower level of 2-3 µg/dL in 1994 (Ryan et al., 2004). As the adverse effects of lead exposure children continue to be illuminated, what is considered acceptable BLLs has continued to decrease. Prior to the 1970s, elevated BLLs were defined at a concentration of 60 µg/dL or greater. The definition of elevated BLLs decreased from 60 µg/dL to 40 µg/dL in 1971, down to 30 µg/dL in 1978, to 25 µg/dL in 1985, and dropped further to 10 µg/dL under the guidance of the Centers for Disease Control (CDC) and the World Health Organization (WHO) in 1991 (Lanphear et al., 2005). Even at BLLs <5 µg/dL, evidence of the negative intellectual and behavioral impacts of blood lead are observed, notably decreased IQ, increased incidence of problematic behavior, and attention-related disorders (National Toxicology Program, 2012). For this reason, the CDC has decreased the definition of EBLLs to 5 µg/dL (Betts, 2012).

There are no identified BLLs in children that are considered safe (Raymond and Brown, 2017). When lead enters the bloodstream, it resides within the blood and circulates through the body for about 28 to 36 days, after which it is either deposited into soft body tissues, mineralizing body tissues (bones and teeth) or is excreted (ATSDR, 2017). The teeth and bones contain most of the lead burden in the body, about 73% for children, and about 94% for adults (ATSDR, 2017). These percentages represent the majority of storage for lead in the body. Under times of physiological stress (i.e. old age, physical immobilization, pregnancy, broken bones, etc.), the bones and teeth may release lead back to the bloodstream, where they can recirculate and once again deposit in soft tissues (ATSDR, 2017). Children's bodies utilize nutrient metals such as iron, zinc, and calcium for brain, nervous system, soft tissue, and bone development and function. The ability of lead to inhibit and mimic these nutrients can deprive children of the tools necessary for healthy development throughout the entire body (ATSDR, 2017).

Children are exposed to lead through inhalation and ingestion of contaminated air, water, soil, dust, food, and lead-based paint chips. Regulations in the U.S. have decreased airborne and dietary sources of lead by eliminating or reducing lead use in paints, automotive emissions, and soldered food containers (Mielke et al., 2019). Although these sources have decreased, lead in soil and industrial emissions in the air continue to be sources of lead exposure to humans. Ingestion and inhalation are the main routes of lead exposure, with ingestion being the primary route of exposure leading to elevated BLLs (ATSDR, 2017). Soil contaminated with leaded gasoline emissions and deteriorated leaded paint is especially associated with increased BLLs (CDC, 2007). The U.S. EPA reports that children aged 6 weeks to less than 1 year old consume 30 mg/day of soil, 60 mg/day of combined soil and dust, while individuals over 1 and under 21 years old consume 50 mg/day soil and 100 mg/day of soil and dust combined (Moya and Phillips, 2014). Studies conducted by the U.S. EPA indicate that BLLs for children below age 6 generally increase 1-5 µg/dL for every increase of 1000 mg/kg soil lead (Clay et al., 2019).

There are seasonal variations in BLLs among children in the northern hemisphere. Children's BLLs tend to peak in summer and autumn months and decline during spring and winter months (Zahran et al., 2013). This may be due to the increased activity of children and adults outdoors and in gardens, which may lead soil particles to be tracked indoors. Windows in houses are typically open more during the summer months, which could distribute contaminated dust throughout households, allowing it to settle in areas it would not settle during winter months and suspending dust in the air.

Lead in Detroit

Lead poses a specific threat to legacy industrial urban centers like Detroit, Michigan which have a history of waste incineration, smelters, automobile manufacture, power plants, refineries, and leaded gasoline automobile emissions, with many older homes containing lead-based paint and plumbing (e.g., drinking water) pipes (Moody and Grady, 2017). Within the Detroit Metropolitan Area (DMA), increasing proximity to hazardous waste sites, commercial waste facilities, and industrial pollution is correlated with a greater proportion of the population being Black (or identifying as African-American, brown) and low-income (Moody and Grady, 2017). Black children in the DMA have the greatest childhood lead exposure by race, even in neighborhoods with higher household incomes (Moody et al., 2016). In 2014, The Michigan Department of Community Health (MDCH) tested 34.6% of the children under six in Detroit for BLLs. 10.6% of the children tested showed BLLs at or above the 5 µg/dL (Moody et al., 2016). In 2017, 7.4% of children in Detroit had BLLs >5 µg/dL, and in the 48206-zip code, 19.2% of children exceeded this guideline (MDHHS, 2018).

The population in Detroit has been steadily declining over the years. The population of Detroit was about 1.8 million in 1950 and has declined to about 677,000 residents as of 2016 (MacDonald, 2016). As people move away from the city and foreclosures increase, old homes are left abandoned and add to the list of homes to be demolished. Since the election of Detroit Mayor Mike Duggan in 2013, over 18,000 homes have been demolished and thousands more are planned to be demolished (Jayyousi, 2019). Increased blight and its control through demolition in Detroit may impact on the health of Detroit children via a number of exposure pathways. Standing abandoned houses may contaminate areas proximate to the house though demolition can create dust and lead particles across a much broader area. While the demolition of a single home may not have a significant impact on children's health, demolition of multiple old homes within a city block has been linked to a significant increase in childhood BLLs in St. Louis, Missouri (Rabito et al., 2007).

Urban farming is on the rise in Detroit as a means for food security, due to sparse access to markets and grocery stores, and expense of nutritious foods. A plethora of vacant lots exist within the city, occupying about 40 square miles of land (Paddeu, 2017). This combination of factors has led many Detroiters and communities to start their own agricultural gardens, growing their own produce as a means of increasing the availability of nutritious, affordable food. Keep Growing Detroit estimates over 1,500 urban gardens have been developed in the city's boundaries (Keep Growing Detroit, 2017). It is vital to address issues of lead contamination in soil, not only to decrease dust concentrations in homes, but also to ensure that root vegetables and produce that contact soil are safe for ingestion and are not adding any additional lead into the body.

Lead in Soil

Soil properties such as pH, organic matter (OM), cation exchange capacity (CEC), clay content, and the presence of competing cations (e.g., Ca, Mn, Fe), can influence the adsorption, mobility, and bioavailability of heavy metals in soil. Soil pH drives the solubility of metals, as solubility of metals generally increases in acidic conditions and decreases in alkaline conditions (Rieuwerts et al., 1998). Soil organic matter, consisting of living organisms, soluble biochemicals, and insoluble humic material can provide surface sites for metal sorption (McLean and Bledsoe, 1992). These organic materials can form soluble complexes with metal ions, which, depending on soil solution chemistry, can increase heavy metal mobility (McLean and Bledsoe, 1992). It is important to differentiate between mobility and bioavailability. Mobility refers to the association of metals with the aqueous phase of soils, or their ability to move with groundwater (McLean and Bledsoe, 1992). Bioavailability refers to the fraction of a metal in soil which can be absorbed into the bloodstream of living things such as humans (Hettiarachchi and Pierzynski, 2004). Increased mobility does not necessarily mean increased bioavailability. When using *in-vitro* bioaccessibility tests, high organic matter levels have been shown to correlate with decreased lead bioaccessibility, as they provide increased binding sites (i.e. increased CEC), allowing for surface complexation (Yan et al., 2017). The high surface area of soil organic matter likely enhances the sorption of lead, providing sites for adsorption (Strawn and Sparks, 2000). CEC has been correlated with increased lead retention and decreased lead bioaccessibility (Saminathan et al., 2010). The effect of CEC and clay on lead bioaccessibility showed that increasing CEC and clay content promoted decreased lead bioaccessibility (Yan et al., 2017). The adsorption of lead by metal oxides and hydroxides has been reported to decrease bioaccessibility of lead (Sonmez and Pierzynski, 2005). These adsorption reactions are suggested to be strong and mostly irreversible, or very weakly reversible (Sonmez and Pierzynski, 2005). Adsorption and retention of cationic metals, such as lead, in soil are generally favored at neutral to alkaline pH values greater than 7 (McLean and Bledsoe, 1992).

Hagens et al (2009) evaluated the impact of some soil properties (pH, OM, clay content, etc.) but was unable to statistically identify relationships with lead bioaccessibility in Dutch Soils, likely due to the small sample size (n=90). Roussel et al. (2010) studied the impacts of similar soil properties on lead bioaccessibility using the UBM model in 27 urban soils of neutral to alkaline pH. They reported decreased lead bioaccessibility in soils with increases in pH, clay content, nitrogen, iron, and carbonate, and an increase in lead bioaccessibility with increasing total lead concentrations (Roussel et al., 2010). However, Morman et al. (2009) studied 20 soils from a variety of sources to determine how pH, organic carbon, and percent clay affected lead bioaccessibility using the RBALP model and found no correlation between bioaccessible or total lead and these soil characteristics. It is possible that these differences stem from using different bioaccessibility assays and different types of soils.

Remediation

Remediation of lead contaminated soil have shown drastic reductions in childhood BLLs. The Bunker Hill Superfund Site (BHSS) located in the Coeur d'Alene Basin, ID is a historical region of smelting and mining industry. Remediation efforts between 1990 and 2001 in the Kellogg and Smelterville communities, within the BHSS, reduced geometric mean soil lead levels from 700 mg/kg to 175 mg/kg and 750 mg/kg to 175 mg/kg respectively, resulting in reduced vacuum bag house dust lead levels as well (Laidlaw et al., 2017). These reductions in soil lead resulted in drastic reductions in childhood BLLs exceeding 10 µg/dL, from about 46% in 1988 to 3% in 2001 (Laidlaw et al., 2017). Studies analyzing soil lead and child BLLs in New Orleans, LA pre- and 10 years post-Hurricane Katrina showed that median soil lead levels decreased from 280 mg/kg to 132 mg/kg and median BLLs decreased from 5 µg/dL to 1.8 µg/dL, showing that the natural removal of surface lead in soils by flooding decreased BLLs (Laidlaw et al., 2017). Reductions in soil lead levels seem to have a significant influence in reducing childhood BLLs.

The U.S. EPA has set guidelines for lead levels in soils. A soil-lead hazard is defined as bare soil containing 400 mg/kg in play areas or 1,200 mg/kg in remaining parts of the yard (ATSDR, 2017). Remediation of lead-contaminated soil can be *in-situ*, or within the soil, or *ex-situ*, involving removal of the soil. Remediation of lead-contaminated soils often involves the excavation and removal of contaminated soil, and replacement of the contaminated soil with clean soil. *Ex-situ* methods can be expensive for large land parcels, disruptive, unsustainable, and may only be transferring the problem to a landfill.

Complete removal of soil lead may not be necessary to decrease the health risks to children. Reducing the bioavailability, or fraction of a substance that is available to be absorbed into the bloodstream, of soil lead can be an effective remediation technique from cost and human health perspectives (Scheckel et al., 2013). *In-vivo*, or animal feeding studies, have shown that bioavailability of lead is dependent on relative dissolution rates and the specific mineral form of lead (Ruby et al., 1992). Addition of phosphate to soils promotes the formation of lead-phosphate minerals with low solubility (e.g., pyromorphite), which may remain insoluble, therefore less bioavailable, over a wide range of pH conditions, resulting in reduced absorption into the acidic conditions of the gastrointestinal (GI) tract and bloodstream (Henry et al, 2015).

Soil conditions influence the efficacy of lead-phosphate formation. Soil pH plays an important role and effects the rate of pyromorphite formation. A field trial from a legacy contamination site in Joplin, MO discovered that pyromorphite formation was more rapid when using phosphoric acid versus calcium phosphate (Laidlaw et al., 2017). Previous studies have shown that phosphate amendments may also be useful for immobilizing various other environmental contaminants such as cadmium, zinc, copper, and uranium (Freeman, 2012). Fish bones contain the mineral apatite and may be an effective phosphorus source for amendments. The use of fish bones or bone meal as a phosphate source may be a more environmentally conscious method for phosphate-based remediation, as it reduces the potential for phosphate run-off (Freeman, 2012). Therefore, phosphate-based amendments have varying capacities to form stable mineral complexes. If the phosphate source is particularly inefficient or requires specialized soil geochemical conditions, this is difficult to implement at any but the smallest scales (e.g., small raised bed agriculture). Loss of surplus phosphate is driven by erosion of phosphorus-enriched soils, generating sediment-associated phosphorus, which is then available for transport in rainfall runoff. Transport of phosphorus in this way contributes to eutrophication of nearby surface waters which can harm wildlife.

Pyromorphite Formation

Behavior of lead in soil is influenced by soil characteristics including pH, organic matter, clay content, cation exchange capacity (CEC), and concentrations of other ions (e.g., Ca, Fe, Al, Mn). The CEC of a soil describes the availability of negatively charged sites that may attract cations, such as Pb^{2+}, and form electrostatic bonds (Saminathan et al., 2010). Clay content of soil can impact the bioaccessibility of lead in soils through similar mechanisms. Greater amounts of lead can be adsorbed onto high clay soils and soils with high CEC, which has been shown to decrease relative bioavailability of lead in swine

(Wijayawardena et al., 2015). These soil characteristics can influence the formation of stable lead-phosphate minerals.

Soil solution pH influences orthophosphate speciation, with orthophosphate species losing protons as pH increases: $H_3PO_4^0 \rightarrow H_2PO_4^{1-} \rightarrow HPO_4^{2-} \rightarrow PO_4^{3-}$ (Scheckel et al., 2013). Acid dissociation constants (pK_a) of phosphoric acid control the orthophosphate species present under different pH conditions. Below pH 2.12, $H_3PO_4^0$ dominates, between pH 2.12 and 7.21, $H_2PO_4^{1-}$ dominates, and between 7.21 and 12.38, HPO_4^{2-} dominates (Brown et al., 1994). The formation of pyromorphite is favored when $H_3PO_4^0$ and $H_2PO_4^{1-}$ are present in the soil solution, meaning that the soil pH would need to be relatively acidic for transformation of lead into pyromorphite (Porter et al., 2004). Low pH should also promote increased solubility of lead, as most cationic metals are anticipated to be more labile in acidic solutions and less labile in alkaline solutions (McLean and Bledsoe, 1992).

Karna et al. (2018) studied the formation of pyromorphite in a phosphate amended soil with high organic matter. Their study showed no pyromorphite formation, which the researchers attributed to high organic matter and iron oxides (Karna et al., 2018). Lang and Kaupenjohann (2003) hypothesized that organic matter in soil solutions led to an inability of phosphate amendments to immobilize lead in a mineral form. Their studies showed that at low pH values of 3 and 4, chloropyromorphite formation was significantly stunted by high organic matter concentrations, likely due to organic matter adsorption on metal surfaces, effectively coating the “crystal seeds” and preventing reaction with phosphate (Lang and Kaupenjohann, 2003). While organic matter can inhibit the formation of pyromorphite through adsorption on the metal surface, it may help to reduce bioaccessibility of lead in the soil through complexation. Results of a study by Magrisso et al. (2008) showed that up to 200 mg/kg lead could be complexed by 1% soil organic matter, theoretically making it unavailable for absorption into the body.

The presence of calcium, iron, aluminum, and manganese can negatively affect the formation of lead-phosphates in soils, as they readily react with phosphate and compete with lead for available phosphate (Scheckel et al., 2013).

Integrated Exposure Uptake Biokinetic Model

The Integrated Exposure Uptake Biokinetic (IEUBK) Model is a risk assessment tool developed by the U.S. Environmental Protection Agency (EPA) that uses lead concentrations in various environmental substrates to help predict elevated BLLs in children ages 0-84 months, or under the age of seven (U.S. EPA, 2002). The IEUBK Model uses various modules to predict BLLs including exposure, uptake, biokinetics, and probability distribution modules.

The Exposure Module considers the rate at which a child may ingest or inhale contaminated media in the environment. These media may include water, air, dust, soil, diet, and other sources (i.e. lead paint) that may enter the child's body. The EPA defines lead Intake Rate as the concentration of lead in a specific media multiplied by the intake rate of the media. Intake rates vary depending on age of the child. The lead intake rate is then used to calculate lead uptake rate (U.S. EPA, 2002).

The Uptake Module takes data from the Exposure Module to predict uptake of lead into the lungs and gastrointestinal (GI) tract. The fraction of lead that passes from the GI tract or lungs to the bloodstream is defined as uptake. IEUBK uses absorption factors, which are age and media-specific, and intake rate to determine the lead Uptake Rate into the bloodstream. Uptake rate is calculated by multiplying lead intake rate by the absorption factor. The lead uptake rate is utilized in the Biokinetic Module (U.S. EPA, 2002).

The Biokinetic Module assesses the transfer and deposition of lead from the bloodstream into various body tissues and accounts for the release of lead from the body through excretion, and hair, nail, and skin growth to determine a geometric mean blood lead concentration used in the Probability Distribution Module (U.S. EPA, 2002).

The Probability Distribution Module uses the geometric mean blood lead concentration to determine the probability that a child's BLLs will exceed a BLL of concern (U.S. EPA, 2002). The default level of concern for the software is 10 µg/dL, but can be adjusted to specific levels of concern, which would currently be 5 µg/dL.

Bioaccessibility Assays

Bioaccessibility assays have been developed to simulate the conditions of a child's GI tract and determine the amount of lead that may enter the bloodstream. These assays are based on conditions that would generally exist in a child's stomach, mimicking pH, movement, temperature, and chemical composition. The physiologically-based extraction test (PBET) developed by Ruby et al. (1996) reports pediatric gastric fasting pH mean values between 1.7 and 1.8 with a range from pH 1 to 4, rising to above pH 4 after ingestion of food and returning to fasting levels within 2 hours post-consumption. The PBET method has been tested widely and modified versions of the method have shown that data from the stomach phase alone correlate similarly to swine studies as the stomach and intestinal phases combined (Hettiarachchi and Pierzynski, 2004). For this reason, many modified PBET tests include the stomach phase only. The U.S. EPA has developed Method 1340 for determining the *in*-vitro bioaccessibility of lead in soils, however, the method warns that it is not suitable for phosphate-amended soils (U.S. EPA, 2017). Research has indicated that when using EPA Method 1340 on phosphate amended soils, the low pH (1.5) causes overestimation of swine uptake (Obrycki et al., 2016). Zia et al. (2011) reported that phosphate amended soils extracted at pH 1.5 predicted lead bioaccessibility reductions of 18%, while human feeding studies showed a reduction of 69%.

Hettiarachichi et al. (2003) and Brown et al. (2003) tested modified versions of Ruby et al.'s (1996) PBET method on soils amended with phosphate or biosolids. They conducted both *in-vitro* and *in-vivo* experiments using rats to determine an *in-vivo-in-vitro* correlation (IVIVC). The rat is considered an acceptable model for risk assessment due to similarities in stomach pH and food consumption patterns

(Hettiarachchi and Pierzynski, 2004). Brown et al. (2003) tested biosolids amended soils using two main modified methods of the Ruby et al. (1996) PBET method. The first method uses the gastric phase of the Ruby et al. (1996) PBET, adjusting solution pH to 2.0 throughout the procedure to maintain that pH. The second method was the same as the first, but pH was not corrected throughout the procedure. The rat feeding study showed that the PBET method at pH 2.0 correlated to reductions in rat bone data ($r^2 = 0.71$). The modified PBET method also correlated to rat bone data: pH 1.50 ($r^2 = 0.84$) and pH 2.3 ($r^2 = 0.90$). Hettiarachchi et al. (2003) tested the entire PBET (pH 2.0) method on phosphate amended soils, including gastric and intestinal phases. A point estimate, or weighted average across tissue types, was reported to be well correlated to rat studies ($r^2 = 0.95$). Liver ($r^2 = 0.92$) and bone ($r^2 = 0.88$) were better correlated than blood ($r^2 = 0.50$) or kidney ($r^2 = 0.50$) values.

CHAPTER 3 "EXPERIMENTAL DESIGN AND MATERIALS & METHODS"

Introduction

Soils were collected from residential sites across Detroit to determine the impacts of soil properties and a phosphate-based bone meal soil amendment on *in-vitro* lead bioaccessibility. The project consisted of two phases. Phase I included sampling soils for chemical and physical characterization to determine how soil pH, organic matter, cation exchange capacity, soil texture, phosphorus, and various ion concentrations affect bioaccessibility of lead in Detroit soils. Phase II consisted of applying a bone meal soil amendment to determine if this could decrease lead bioaccessibility. During Phase II, all soil properties were recharacterized to determine how they may have changed with time and through the addition of the bone meal amendment.

Sample Selection & Collection

Participants in this study were selected from Detroit, Highland Park, and Hamtramck. EcoWorks conducted participant recruitment through Clear Corp's community health events, phone calls to urban gardeners, and through EcoWorks social media, website, and mailing list. This recruitment resulted in a total of 69 participants with a total of 208 sampling locations, as many participants have more than one lot with different addresses.

Before sample collection, the participant was called to remind them that sampling would take place that day. Upon arrival, the participant is asked which spot they would prefer to be sampled. Samples were not taken along the drip line, or edge beneath the roof where rain tends to drip, of the house nor in the area between the sidewalk and the street as these are areas known to have higher levels of lead contamination due to leaded paint and gasoline, respectively. Once the site was decided, the data collection form (Appendix A) was filled out and two collection bags were labelled. A stake was driven into the sample location and a smartphone equipped with a GPS application was used to determine coordinates. A pre-cut piece of string 8" in length was held with one hand in the center of the stake and held out to the north. The bulb planter was placed at the edge of the string and driven 4” into the ground. Soil from the bulb planter was dumped into the pre-labelled one-gallon bag. After repeating steps for east, south, and west directions, grass and other vegetation were picked out of the bags and placed into the holes created by the bulb planter. The bag was sealed and mixed thoroughly by hand to homogenize the soil. Using a gloved hand, approximately 1.5 cups of soil were added to the second labelled bag to be sent to Dairyland Laboratories, Inc. Samples were shipped to Dairyland Labs no more than 7 days after being removed from the ground to minimize the loss of organic matter. The bag with more soil was labelled with “WSU” to be picked up for lab analysis in the Environmental Chemistry Research Laboratory. A fluorescent flag was left next to the stake as a marker. A measuring tape was used to measure distance from the stake to identifiable markers on site to assist in locating the site for the second sampling portion. After the amendment aged in the soil for 269 ± 29 days, the above procedures were repeated with the exception on sample location direction. The directions for the second sampling were northeast, southeast, southwest, and northwest, 20cm from the stake location. Amendment time in the field could be an important factor in both the kinetic stability of lead-phosphates and the bioavailability of lead in soil, as increased residence time of phosphate amendments have been linked to decreased bioavailability of soil lead (Ryan et al., 2004), and increased stability of chloropyromorphite minerals (Scheckel and Ryan, 2002).

Amendment Application

For each sample site, a pre-drilled wooden board was centered on top of the marker stake. Holes were drilled in a grid so that each hole was 2” apart from the next, both horizontally and vertically. After the board was centered and one edge oriented to the north, a drill was used to aerate the soil to a depth of 4”, marked by a piece on tape in the drill bit. The soil amendment was prepared wearing personal protective equipment and combining 100 mL liquid bone meal (Down to Earth Liquid Bone Meal 0-12-1; Eugene, OR) and 2000 mL tap water to a jug, then mixed thoroughly. The solution was poured evenly into each drill hole. The used board was placed into a bin labelled for contaminated equipment and a new board was used for each site. Sites which served as controls received a 2,100 mL tap water. The boards and bulb planters were cleaned daily with Liquinox soap at a ratio of 1:100 with tap water followed by a final rinse with nanowater. The process for purifying tap water into nanowater is as follows: water is filtered through a LabStrong D00172 deionization cartridge into a Barnstead Fistreem II 2S Glass Still (Model No. A74415) where it is distilled, then passed through a NANOpure DIamond UV ultrapure water system (Model No. D11911) to a resistance of >18.2 mΩ-cm.

Sample Processing

Received sample bags labeled with WSU were opened and placed into a fume hood for two weeks to allow soil to air dry. The soils were covered with large absorbent paper to prevent cross-contamination from dust migration. One week into soil drying, the bag was closed and shaken to expose soil at the bottom to increase airflow. After approximately two weeks, the soils were sieved using a 150 µm stainless-steel sieve (Cole-Parmer, UX-59984-16). This size fraction was chosen according to EPA Method 1340 since it represents the particle size which commonly adheres to a child's hands (U.S. EPA, 2017). In between samples, the sieve was cleaned using a scrub brush and Liquinox soap, then rinsed three times with nano water and left in the incubation chamber for at least one hour, or until dry. The sieved portion of soil was transferred to a polypropylene centrifuge tube (VWR) for storage. Un-sieved soils were left in sample bags, resealed, and set aside for soil texture analysis.

Total lead was determined using EPA Method 3051a (U.S. EPA, 2007). 55 mL MARSXpress digestion tubes are fitted with a disposable Teflon liner (CEM, 404460) pre-fitted to the tube. Digestion tubes were brushed with an anti-static brush to prevent soil from adhering to the tube. To the digestion tube, 0.5 ± 0.05 g of <150 µm soil was added. This soil fraction is chosen as it is the size which adheres to a child's fingers (U.S. EPA, 2017). 10 mL 68% Omnitrace nitric acid (VWR, CAS # 7697-37-2) was added to the digestion tube using an automated dispenser. Tubes were covered with fitted plugs and caps were twisted on and tightened by hand. A total of 24 samples were placed in the turntable and sample spots were recorded. The turntable containing samples was placed into the MARSXpress microwave and the setting for “EPA Method 3051 Xpress for 8-24 Samples” was selected. Samples were digested and left to cool overnight. Empty 50 mL centrifuge tubes (VWR, 89039-660) were labelled and weighed, then 10 mL nanowater was added to the tubes using a pipette. The sample was poured into the centrifuge tube, then 10 mL nanowater was used to rinse the digestion tube and poured into the centrifuge tube. This step was repeated to make a final volume of 40 mL 17% nitric acid. The final weight was recorded, and samples were placed 12 at a time into a wrist-action shaker for 20 minutes. After 20 minutes, 4 centrifuge tubes were placed, evenly spaced, into the centrifuge and centrifuged at 4000 rpm for 20 minutes. New centrifuge tubes or 30 mL HDPE bottles were labelled and set aside for filtration. Then, 0.45 µm PTFE slip-tip filters were attached to 30 mL syringes. The plunger was removed from the syringe and 15 mL of supernatant was poured into it. The plunger was placed back in and the sample was filtered into its labeled clean centrifuge tube or bottle. This step was repeated so that 10 mL sample remained in the original centrifuge tube. The remaining 10 mL sample was poured into a waste bin and lead concentration was recorded for the waste disposal tag after ICP-MS analysis. Digestion quality assurance and quality control checks included a matrix spike, or a spiked blank, a standard addition, or a spike added to a duplicate sample after filtration, a duplicate, a reagent blank, and NIST certified standard reference soils. Control limits and corrective actions are outlined in Table 3.1. These quality control measures were adapted from U.S. EPA guidelines for analysis of lead in paint, soil, and dust (Scalera and Remmers, 1993).

Standard reference materials were analyzed as laboratory control samples, these included NIST 2586: *Trace Elements in Soil Containing Lead From Paint* and NIST 2711a: *Montana II Soil, Moderately Elevated Trace Element Concentrations*. Certified lead concentrations for NIST 2586 (432 ± 17 mg/kg) and NIST 2711a (1400 ± 10 mg/kg) were used to determine percent difference. All NIST 2586 checks were within ± 20% of certified values, with a mean deviation of 7%. NIST 2711a checks were consistently below the certified concentration of 1400 mg/kg, with a mean deviation of 22%. Bismuth is used as an internal standard for lead analysis with ICP-MS, and bismuth interference from the NIST 2711a soil could have caused this underestimation of lead concentrations. Further detail is provided in the error section of this chapter. Since NIST 2586 concentrations and other quality assurance checks were consistently within range of certified values and were digested in the same batch of samples, NIST 2711a samples which were out of range were flagged instead of reanalyzing all samples within the batch.

Table 3.1: Quality Assurance and Quality Control Measures for Total Lead Procedure.

Quality Control Sample (QCS)	Frequency	Method	Control Limits	Corrective Action
Initial Calibration Verification (ICV)	Once per run after calibration	Concentration check made from standards other than those used for calibration curve	± 10% of known value	Reanalyze, repeat procedure if not within limits after analysis
Initial Calibration Blank (ICB)	Once at beginning	Calibration blank containing 2% nitric acid and no spikes	Not more than 20% of the regulatory limit <5x intrument detection limit	Reanalyze, repeat procedure if not within limits after analysis
Continuing Calibration Verification (CCV)	Before and at end of run, every 10 samples	Spike Check	within ± 10% of known value	Reanalyze, repeat procedure if not within limits after analysis
Interference Check Sample (ICS)	Beginning and end of run	Spike Check	Within ± 20% of known value	Reanalyze, repeat procedure if not within limits after analysis
Continuing Calibration Blank (CCB)	After ICS and CCV	Calibration blank containing 2% nitric acid and no spikes	Not more than 20% of the regulatory limit <5x intrument detection limit	Reanalyze, repeat procedure if not within limits after analysis
Laboratory Control Sample (LCS)	5% or 1 in 20	NIST 2711a & NIST 2586	within ± 20% of known value	Reanalyze, repeat digestion if both NIST standards aren't within range
Matrix Spike (MS)	5% or 1 in 20	Duplicate soil spiked with known concentration	within ± 25% of known value	Reanalyze, repeat procedure if not within limits after analysis
Duplicate Sample (D)	5% or 1 in 20	A duplicate sample ran through all steps of digestion, same soil	within ± 25% relative percent difference (RPD)	Reanalyze, repeat procedure if not within limits after analysis
Method Blank (MB)	5% or 1 in 20	Reagent ran through all steps of digestion	Not more than 20% of the regulatory limit	Reanalyze, repeat procedure if not within limits after analysis

The method for bioaccessible lead was derived from the Physiologically Based Extraction Test (PBET) developed by Ruby et al. (1996), the In Vitro Bioaccessibility Assay for Lead in Soil (IVBA) developed by the U.S. Environmental Protection Agency (2017), and experiments that assessed the PBET at various pH levels and on amended soils by Brown et al. (2003) and Hettiarachchi et al. (2003). The modification was deemed necessary because the EPA's IVBA Method is not suitable for phosphate-amended soils. Size fraction, filter type, extraction apparatus, and quality assurance checks were selected from the EPA Method (EPA, 2017). A pH of 2.0 was chosen instead of the EPA's pH of 1.5. This decision was aided by results from Hettiarachchi et al. (2003), which tested the PBET procedure using a pH of 2.0 on soils treated with phosphate and manganese-oxide. Their results showed a significant *in-vivo-in-vitro* correlation (IVIVC) with Sprague-Dawley rats. Correlations between *in-vitro* bioaccessible lead and lead bioavailability to rats were significant in the liver ($r^2 = 0.92$) and bone ($r^2 = 0.88$). Hettiarachchi et al. (2003) calculated a significant ($r^2 = 0.95$) point-estimate, which represents a weighted average of relative bioavailability throughout all tissue types. Brown et al. (2003) tested the PBET procedure with a pH of 2.0 on biosolids amended soils, which showed a significant correlation to rat bone lead levels ($r^2 = 0.71$). The modified PBET procedure used for this study is outlined below.

60 mL HDPE bottles, either new out of the packaging or acid-washed if being reused, were labelled with sample identification, and wiped down with a damp paper towel to minimize static. After dry, the HDPE bottles were set on the scale and tared. 0.4 ± 0.001 g soil sieved to 150 µm were added to the HDPE bottles. Sample weights were recorded to the nearest 0.0001 g. All glassware was properly acid washed before use. Before making the gastric solution, pH buffers were poured in PP centrifuge tubes and placed in a beaker to prevent water from leaking into the tube. Values for pH buffers were 1.0, 2.0, and 4.0. To make a 2 L batch of gastric solution, 2.50 g pepsin, 1.00 g malate, 1.00 g citrate, 840 µL lactic acid, and 1000 µL glacial acetic acid were added to 1990 mL nanowater in a volumetric flask. All weights for solution components were measured to ± 0.0005 g. The flask was covered with Parafilm and stirred using a magnetic stir bar at about 1000 rpm for 10 minutes, or until all components were dissolved. The flask was placed in a temperature-controlled bath at 37°C. While waiting for the solution to heat, pH buffers were removed from the bath and used to calibrate the automated temperature control pH probe. Values bracketed the expected pH, using 1.0 and 4.0 for calibration points. A sample probe and reagent probe were used to minimize contamination. pH 2.0 was checked to ensure the meter was calibrated correctly. After calibration, the gastric solution was removed from the bath and pH was checked. Trace-metal grade hydrochloric acid was used to adjust the solution pH to 2.0 ± 0.05. Volume of acid and resulting pH were recorded, the remaining volume of nanowater required to bring the solution to 2 L was added, and the pH was checked

again. The solution was placed back into the water bath and a subsample of 10 mL was set aside to check using the sample pH probe. The solution was placed into an acid-washed 1 L bottle equipped with an automated dispenser set to 40 mL. After solution was warmed, 40 mL was added to each sample bottle, bottles were vigorously shaken and placed in sealed bags in the water bath. Samples were checked for initial pH and results were recorded. If the sample pH was not within 2.0 ± 0.2, trace metal grade hydrochloric acid was added dropwise until pH was within range and volume of acid added was recorded. To prevent cross contamination, the pH probe was rinsed with nanowater, swirled in a 2% nitric acid solution, rinsed with nanowater again, then dried with a Kimwipe before moving onto the next sample. Start time for extraction was recorded as the time that samples began rotation at 30 ± 2 rpm. To ensure pH of all samples was able to be checked, four rows of six samples were placed into the oven 10 minutes apart. Samples were extracted for an hour, checking pH 20 to 30 minutes into the extraction, and adjusting with hydrochloric acid to ensure samples were at a pH of 2.0 ± 0.2. After 1 hour of rotation, the samples were removed and placed upright on the bench to allow soil to settle to the bottom. A 10 mL syringe was equipped with a 0.45 µm cellulose acetate filter and 10 mL of supernatant were decanted into the syringe and filtered into a 15 mL centrifuge tube. End time was recorded as the time that samples were filtered. Temperature and pH were checked after samples had been filtered and were within 37 ± 2°C and 2.0 0 ± 0.5 pH units. After all samples were filtered, 0.01 mL 68% Omnitrace nitric acid was added to prevent precipitation of metals during storage. Samples were stored in a fridge at 4°C and were placed on a vortex spinner before dilution for ICP-MS analysis. quality assurance and quality control checks included a matrix spike, or a spiked blank, a standard addition, or a spike added to a duplicate sample after filtration, a duplicate, a reagent blank, a certified NIST 2711a Montana II Soil Standard. Control limits and corrective actions are outlined in Table 3.2. ICP-MS analysis quality control measures were the same as those outlined in Table 3.1 (i.e. ICB, ICV, CCV, CCB, and ICS).

Table 3.2. Quality Assurance and Quality Control Measures for In-Vitro Bioaccessibility Procedure.

Analysis	Frequency	Method	Control Limits	Corrective Action
Reagent Blank	Each new batch of extraction fluid	Unprocessed extraction fluid (No extraction/filtration)	Results < LLOQ	Extraction fluid must be re-made, and soil samples must be reprocessed with new extraction fluid
Method Blank	1 in 20 samples (1 per batch, minimum)	Extraction fluid, with no test soil, must run through entire process	Results <LLOQ	Extraction fluid must be re-made, and soil samples must be reprocessed with new extraction fluid
Laboratory Control Sample (LCS) or Blank Spike	1 in 20 samples (1 per batch, minimum)	Extraction fluid is spiked at 10 mg Pb/L	85-115% Recovery	If a sample falls outside of range, analyst review to ensure dilutions and spike concentrations were correctly performed. Flag data in results if no error is found.
Matrix Spike (MS)	1 in 20 samples (1 per batch, minimum)	Prepared after extraction/filtration, sample can be taken from same bottle as duplicate, spiked at 10 mg Pb/L	75-125% Recovery	If a sample falls outside of range, analyst review to ensure dilutions and spike concentrations were correctly performed. Flag data in results if no error is found.
Duplicate Sample	1 in 20 samples (1 per batch, minimum)	Duplicated soil sample must run through entire process	Relative Percent Difference < 20%	Re-extraction of samples or flagging of data
Control Soil NIST SRM 2711a	1 in 20 samples (1 per batch, minimum)	NIST Standard Reference Material must be run through entire process	**Acceptable IVBA Range:** 75.2-96.2% **Total Lead:** 1,300 mg/kg	

These quality control limits were derived from EPA Method 1340 (U.S. EPA, 2017). EPA Method 1340 did not specify corrective action for NIST 2711a checks which were out of range. Many NIST 2711a samples from our study were lower than the acceptable IVBA range. This may be explained by the higher pH used in the modified PBET (pH 2.0) compared to the EPA Method (pH 1.5).

Analysis

Total lead and bioaccessible lead samples were analyzed on the Agilent 7700x ICP-MS in Wayne State University Lumigen Instrument Center courtesy of the Chemistry Department. Samples were diluted using 2% nitric acid made from Omnitrace 68% nitric acid and nanowater. Internal standard for analysis was lead 208, bismuth 209, and thallium 205 diluted to 10 µg/L using the same 2% nitric acid solution as dilutions and 100 ppm Aristar multi-element ICP-MS certified reference standards from VWR. Before each analysis, the Agilent 7700x ICP-MS was put through a tuning test to ensure the instrument was running properly. Calibration curves consisted of 0.1, 0.5, 1, 5, 10, 50, 100, and 200 µg/L points diluted by weight. ICP-MS response values that did not fall within ± 20% of the calculated concentration were removed from the concentration curve. An IV-71 check standard was provided by Lumigen to ensure ICP-MS accuracy. Blank checks, 2% nitric acid, were run after IV-71 checks at a frequency of 1 in 10 to 15 samples depending on the amount of environmental samples analyzed in a day. Results were reported for four gas modes: no gas, helium (He), hydrogen gas (H_2), and High Energy helium (HEHe). Results were taken from the mode that had the most well-fit calibration curve, mainly HEHe and H_2. The average method detection limit using ICP-MS for our analysis was 6.15 µg/L. This calculates to a detection limit of 0.492 mg/kg.

Soil pH, organic matter (OM), phosphorus, and cation exchange capacity (CEC) were analyzed by Dairyland Laboratories, Inc. in Arcadia, WI. Soil pH was determined by a combination of water method and Sikora method, OM was determined by the loss-on-ignition method, phosphorus by the Bray 1 Extraction, and CEC by the Mehlich 3 Extraction technique. A subset of 22 samples were sent to Dairyland Labs for particle size distribution, to determine percentages of clay, silt, and sand, analyzed using the Hydrometer Method. Particle size distribution analysis are used to determine soil texture.

Soil texture was determined by the USDA's National Resources Conservation Service (NRCS) Texture by Feel method (Burt, 2014). The method began by sieving soils to 2 mm. A portion of the sieved soil, about 25 g, was grabbed, wetted, and kneaded until the soil reached a putty-like consistency. The soil was rolled into a ball and tossed into the air to determine if it would keep its shape. If the ball remained solid, the soil was worked between the thumb and forefinger to create a ribbon with even width and depth. As the ribbon breaks by its own weight, the length of the ribbon helped to determine which category the soil would fall under. A small pinch of the soil was placed in the palm and wetted excessively, then rubbed with a finger to determine if the soil was predominately gritty, predominately smooth, or neither predominately gritty nor smooth. The NRCS flowchart used to determine soil texture is shown in Appendix A.

Soil texture categories are a combination of sand, silt, and clay. For statistical analysis, percentages of sand, silt, and clay were determined by plotting the midpoint of each soil texture category on the NRCS soil texture triangle, shown in Appendix A.

Errors

Soil samples used were sieved to <150 µm and were recorded to the nearest 0.0001 g when weighed. Static electricity and small particle size likely caused drift when weighing soils. Depending on the day and environmental conditions, drift was observed mostly to the 0.0001 and occasionally to the 0.001 placements. To counteract static, anti-static gloves, anti-static scoops, and an anti-static brush were used. The anti-static brush was used along the lip of the sample bottle and to brush all sides and the inner ceiling of the weigh chamber to prevent soil from jumping to the sides during measurements. All glassware and plastic materials were moved from the weigh station to prevent static pull. HDPE bottles were wiped with a paper towel dampened with nanowater to neutralize charge on the outside of the bottle and allowed to dry before being placed into the balance chamber.

ICP-MS errors were caused mainly by Bi interference with certain soil samples. This occurred only for total lead analysis. Bioaccessible extractions did not show the same pattern, likely due to lead solubility in various matrices. When looking at internal standard counts, NIST 2711a showed bismuth spikes, leading the software to calculate a lower concentration than NIST's certificate of analysis reported (Gonzalez and Choquette, 2018). NIST 2711a soil was sourced from a previous smelting site in East Helena, Montana (Gonzalez and Choquette, 2018). Butte, Montana, just southwest of Helena, has at least two cosalite mines (Mindat, 2020). Cosalite, $Pb_2Bi_2S_5$, may have been present or processed at the East Helena site leading to bismuth spikes in ICP-MS analysis. Thallium was added to the internal standard after this information was discovered.

Of the 142 sites sampled, 21 sample locations (15%), had total lead concentration differ by more than 20% between pre-treatment and post-treatment sampling. This 20% deviation is greater than our quality assurance/quality control thresholds for total lead measurements. This error is likely attributed to the inherit heterogeneity of lead in soils. For example, if a lead paint chip existed in a 1” by 1” portion of treated soil and a paint chip did not exist in the soil originally sampled, lead results for post-treatment soil fraction could be significantly higher than the pre-treatment sample. Total and bioaccessible lead concentrations have been found to have similar spatial variation in residential soils (Bugdalski et al., 2014).

Results from Dairyland Labs for soil texture were not consistent with results using the Texture by Feel Method (Burt, 2014). This was likely due to the human error from feeling soils as compared to a more quantitative method which relies on instrument measurements.

The pK_{a1} of phosphate is 2.12, meaning that below this pH, phosphate prefers to be in the form of H_3PO_4 (Henry et al., 2015). Although using an extraction pH of 2.0 has been shown to correlate well with animal studies for lead contaminated soils amended with phosphate (Brown et al., 2003; Hettiarachchi et al., 2003), it is possible that using a pH of 2.0 in extraction tests, or any pH below 2.12, could impact phosphate chemistry and give results which underestimate the reductions in bioavailability (Scheckel et al., 2013).

CHAPTER 4 "RELATIONSHIP BETWEEN ENVIRONMENTAL FACTORS AND BIOACCESSIBILITY"

Introduction

In this chapter, we explore the various mechanisms influencing soil lead bioaccessibility. The amount of bioavailable lead correlates to the total amount of lead present (Roussel et al. 2010). Soil characteristics such as organic matter, soil pH, cation-exchange-capacity (CEC), soil texture, and the presence of other metals affect soil lead bioavailability and bioaccessibility. Organic matter may enhance the ability of soils to retain lead, due to its high surface area and through the ability of organic matter to form surface complexes with lead (Yan et al., 2017). The addition of soil organic matter, such as compost or peat, to lead contaminated soils have shown reductions in bioavailability to earthworms and a variety of plants (Fleming et al., 2013).

Soils with greater CEC correlate with increased lead retention and decreased lead bioaccessibility (Saminathan et al., 2010). Due to their high amount CEC, the amount of clay present in soils is expected to influence lead retention (Wijayawardena et al., 2015). This assumption has been confirmed in studies which tested the effect of clay and CEC on lead relative bioavailability, in which results showed that increasing CEC and clay content decreased the relative bioaccessibility of lead (Yan et al., 2017). As the pH of soil decreases, metal ions are typically released from the soil, enter solution, and compete for binding sites (McLean and Bledsoe, 1992). However, under neutral pH conditions, enhanced metal complexation with organic ligands can also contribute to the immobilization of lead (Rieuwerts et al., 1998).

Remediation of soil lead in the historic smelting area of the Coeur d'Alene Basin, ID, through excavation of soils and capping with clean soil (Sheldrake and Stifelman, 2003), resulted in reductions of BLLs exceeding 10 µg/dL from 46% in 1988 to 3% in 2001 (Laidlaw et al., 2017). BLLs are correlated to smelter proximity (Grigoryan et al., 2016), with BLLs decreasing with distance from smelters. This decrease in BLLs could be attributed to a concentration gradient or variation in bioaccessibility.

The bioaccessibility of lead is dependent on the mineral form in soils. Minerals, particularly phosphate minerals such as pyromorphite, are insoluble, even in solutions with low pH such as that found in the human gastrointestinal system (Henry et al., 2015). Regardless of the form, we expect that high levels of lead in soil would result in increased blood lead levels (BLLs) as compared to soils with lower total lead levels. While organic matter seems to inhibit the formation of pyromorphite, conversely it may trap lead in organo-metal complexes, rendering them unavailable for absorption. Despite the two chemical mechanisms working at cross-purposes, we hypothesize that as organic matter increases, bioaccessibility will decrease. However, the organo-complexation process is pH dependent and as pH decreases, the ability of heavy metals to adsorb to organic material decreases (McLean and Bledsoe, 1992). We therefore hypothesize that a decreased soil solution pH will result in increased bioaccessibility. In this study, we use a Physiologically Based Extraction Test (PBET) to determine the *in-vitro* bioaccessibility (IVBA) of lead. We hypothesize that as extraction pH in the PBET method decreases, the bioaccessibility will increase due to increased solubility of lead. To better understand potential smelter related exposure, we evaluate how concentration of lead, both total and bioaccessible, vary with distance from smelters. We hypothesize that increasing proximity to smelters will increase both total lead concentrations and IVBA lead concentrations.

Survey Details and Analytic Methods

A survey of soils from 142 residential sites and urban farms across Detroit were investigated to establish a baseline understanding of lead contamination in the City of Detroit, to determine the bioaccessibility of lead in these soils, and to evaluate how soil properties may affect the bioaccessibility of lead (Figure 4.1). As described in detail in Chapter 3, approximately 2 kg of soil was collected from each site and homogenized. About 1.5 cups of soil was sent to Dairyland Labs, Inc to be analyzed for pH, organic matter, cation exchange capacity, phosphorus, and various other ions. The remaining soil, which was delivered to Wayne State University was dried, and sieved to <150 µm in size. This size fraction is chosen as it is the particle size which generally would adhere to a child’s fingertips (U.S. EPA, 2017). This size fraction was used for both total lead and *in-vitro* bioaccessible lead. Methods for chemical and physical characterization are outlined in Chapter 3. Additionally, the influence of 19 smelters proximate to study sites (MDEQ Remediation and Redevelopment, 2008) was also evaluated.

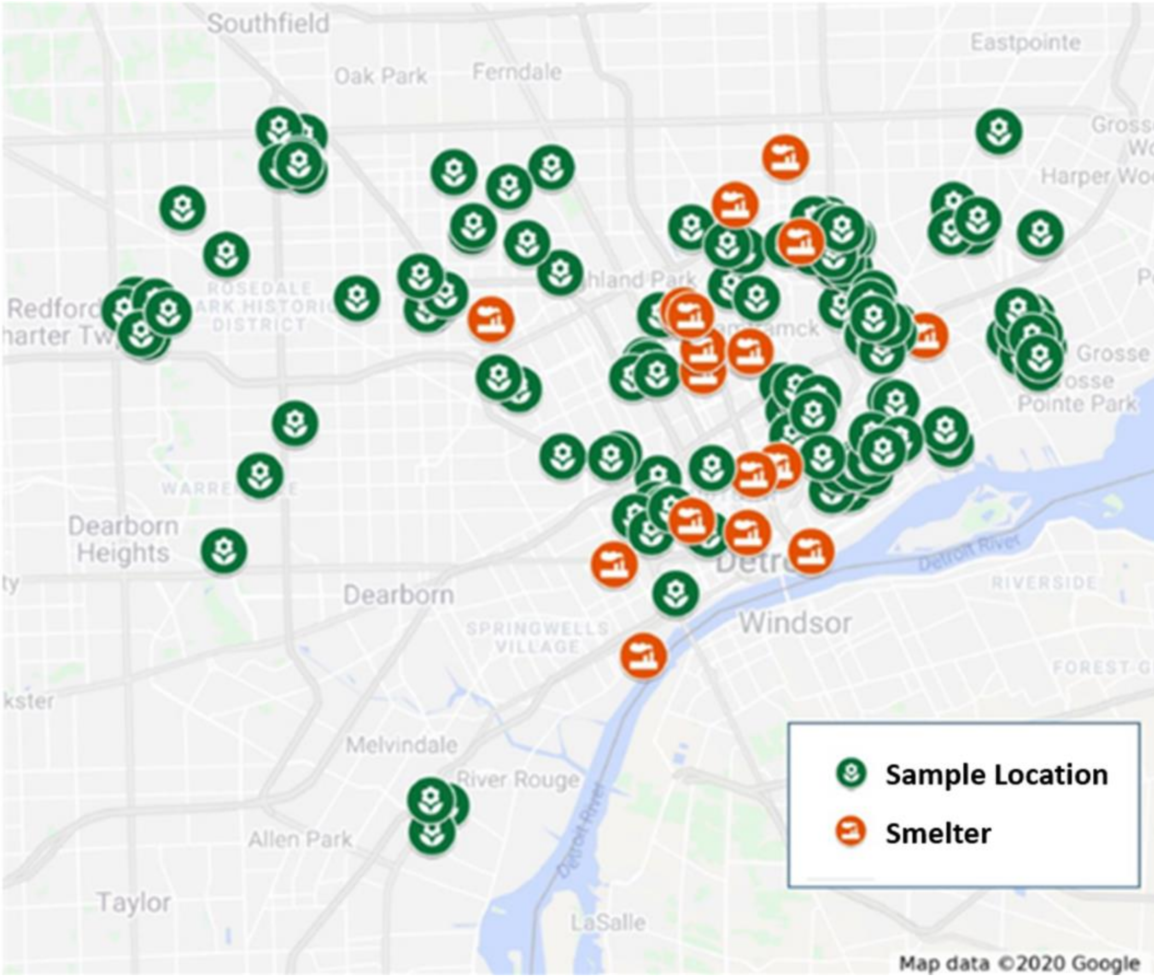

Figure 4.1. Map showing smelters and sampling site locations. Random offset was applied to sample site coordinates.

Chemical Characterization

Total lead was measured according the EPA Method 3051a (U.S. EPA, February 2007). Briefly, 0.5 g of sieved soil was placed in 10mL of 68% trace-metal grade nitric acid and subjected to microwave assisted digestion in a MARSXpress (CEM, 907501). After cooling, samples were diluted, to a 17% nitric acid solution, centrifuged and filtered through a 0.45 µm PTFE filter. *In vitro* bioaccessible lead was measured according to a modified version of the Physiologically Based Extraction Test (Ruby et al., 1996).

Since the standard PBET procedure utilizing a pH of 1.5 underestimates changes in bioavailability following phosphate amendments (Zia et al., 2011) experiments were conducted to evaluate the impact of altering the pH of the extraction solution. Eighteen randomly identified soil samples were subjected to PBET method using extraction solutions with a pH of 1.5 ± 0.2, 2.0 ± 0.2, and 2.5 ± 0.2. Soil pH, cation exchange capacity (meq/100g), organic matter content (%), and cation concentrations (mg/kg) were measured by Dairyland Laboratories (Arcadia, WI).

Physical Characterization

Soil texture analysis via the NRCS Texture by Feel method (Burt, 2014) was performed on all 142 samples. To evaluate the accuracy of this characterization, a random assortment of 22 soil samples sieved <2 mm was evaluated by sieving at Dairyland Laboratories (Arcadia, Wisconsin). Information on the source of soil, fill or native, was also collected to determine if fill-soils or native-soils could predict lead bioaccessibility.

Proximity to Smelters

Potential impacts of smelters on soil lead were assessed by evaluating total and bioaccessible lead concentrations relative to the proximity of sampling locations to these legacy sources and whether these locations were downwind. Distances between the historical location of 19 smelters in the Detroit metropolitan area and each sampling location were determined based on the GPS coordinates, latitude, and longitude, according to the following equation:

$$d = \sqrt{((Lat_1 - Lat_2)^2 + (Long_1 - Long_2)^2)} \qquad \text{Equation 1}$$

where d is the coordinal, straight-line distance, Lat is the latitude, Long is the longitude, and the subscript 1 signifies the coordinates of the sampling location and subscript 2 signifies the coordinates of the smelter. Because it was anticipated that soil lead concentrations increased with proximity to smelters (Battelle Memorial Institute, 1998), the inverse distances were then determined. To account for downwind deposition patterns (CDC, 1997), the direction from all sampling locations to each smelter was determined and compared to the predominant wind direction. Wind direction was based on the bearing angle (θ) which determined using the ATAN2 function syntax in Microsoft Excel 2016 (Redlands, Washington). The ATAN2 function is based on the following equation:

$$\theta = \left(\frac{360^{\circ}}{2\pi}\right) \cdot \tan^{-1} \frac{\sin(Long_2 - Long_1) \cdot \cos(Lat_2)}{(\cos(Lat_1) \cdot \sin(Lat_2)) - (\sin(Lat_1) \cdot \cos(Lat_2) \cdot \cos(Long_2 - Long_1))} \qquad \text{Equation 2}$$

where the terms are the same as those defined for Equation 1. However, the denominator in Equation 2 could result in zero, producing an error. The ATAN2 function syntax in Excel allows avoids this error. As shown in Figure 4.2, when the bearing angle between the sampling location and smelter matched the wind direction within 45 degrees, then the study site was characterized in our study as downwind of the smelter.

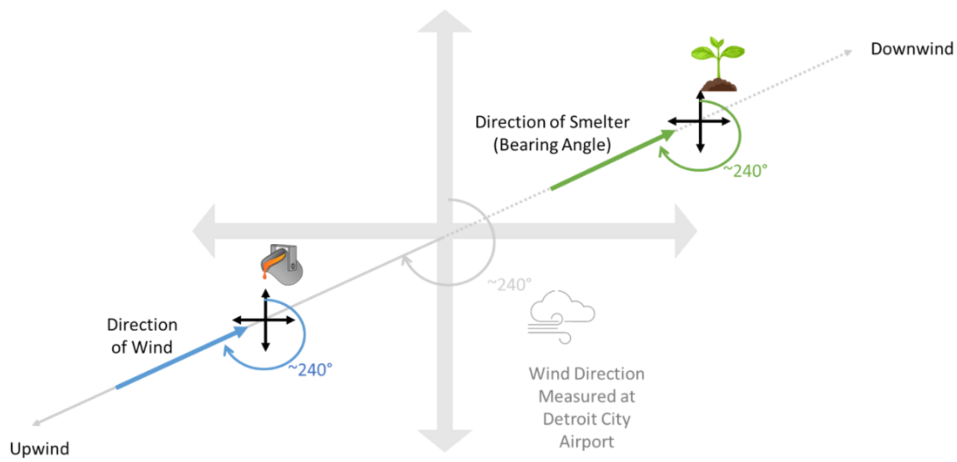

Figure 4.2. Alignment of the direction of wind and the bearing angle indicate the sampling location is directly downwind.

Therefore, 10 years of daily wind data from the Detroit City Airport weather station (USW00014822) from Jan. 1, 2010 to Dec. 31, 2019 was analyzed (Figure 4.3). Based on this analysis, the wind typically comes from the west-southwest (θ = 240º). The difference between the site bearing angle and 240º was then determined. Similar to the distance measure discussed previously, the smaller this difference, the stronger the anticipated influence of the smelter. Therefore, the inverse of the difference in angle was calculated. Because the distance and direction measurements have inconsistent units, a z-score of the inverse measures of these parameters were then calculated according to the following equation:

$$Zscore = \frac{x-\mu}{\sigma} \qquad \text{Equation 3}$$

where x is the observed value, μ is the mean of measurements for each sampling location, and σ is the standard deviation of measures for each sampling location. Finally, z-scores of the inverse direction and difference in angle were then multiplied together to characterize an overall measure of proximity, which will henceforth be referenced as a compound proximity.

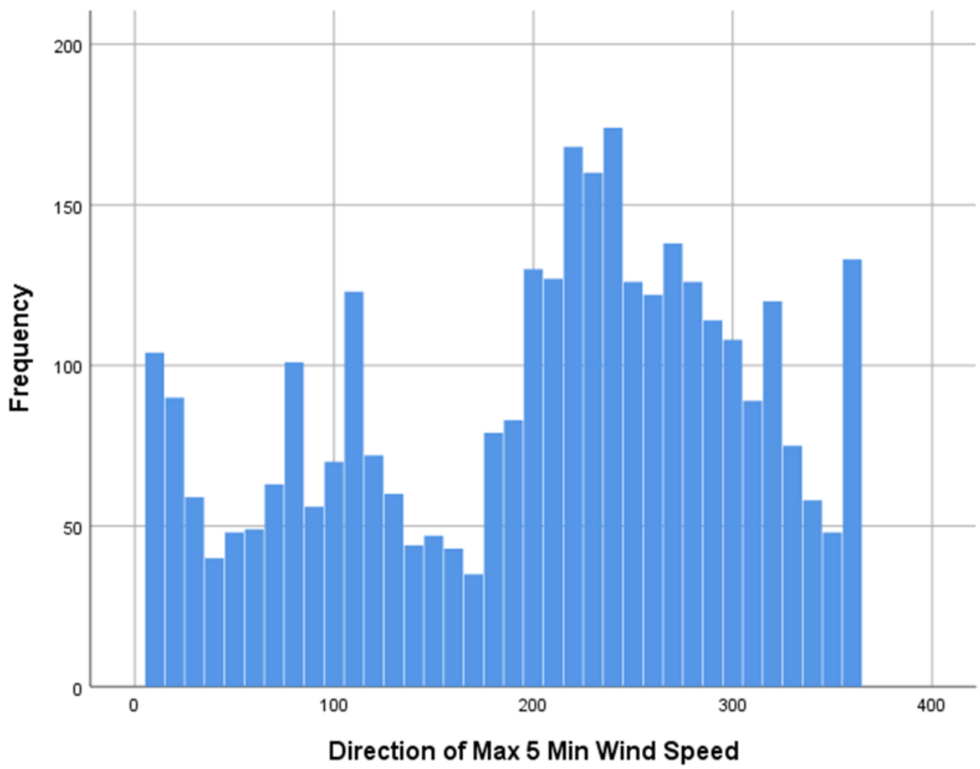

Figure 4.3. The direction (degrees from North) of the maximum 5-second wind speed (mph) observed at the Detroit City Airport weather station (USW00014822) from Jan. 1, 2010 to Dec. 31, 2019.

Statistical Analysis

All statistical analyses were performed using SPSS Version 26 (IBM, release 26.0.0.0). Data was analyzed using standard analysis of variance (ANOVA) and multiple linear regression procedures. Various models were tested to determine the impact of soil characteristics and chemical properties on *in vitro* bioaccessibility (Table 4.1). It is important to note that all statistical analysis in this chapter (Chapter 4) are conducted using only pre-treatment measurements, and that all results relating to the effectiveness of a soil amendment shall be discussed in Chapter 5. Prior to conducting analyses, all data were evaluated to determine if transformations were necessary (e.g. to ensure normality assumptions). When performing regression analyses, the following assumptions were verified (Pallant, 2010): (1) Linearity: each predictor/dependent variable has a linear relation with our outcome variable, (2) Independence: each predictor/dependent variable are not highly correlated ($r > 0.9$) and singularity was avoided, (3) Normality: the prediction errors (i.e. residuals) were normally distributed in the population, (4) Homoscedasticity: the variance of the errors was constant in the population, and (5) Outliers: no outliers were present within the dataset used for analysis – i.e. standardized residual values were less than ±3.3.

Table 4.1. Summary of pre-treatment environmental models and variables.

Model	Dependent Variable	Independent Variables
1	IVBA	Total Pb, OM, pH
2	IVBA	Total Pb, OM, pH, P
3	IVBA	Total Pb, OM, pH, CEC
4	IVBA	Total Pb, OM, pH, Fill Status
5	IVBA	Total Pb, OM, pH, K
6	IVBA	Total Pb, OM, pH, Ca
7	IVBA	Total Pb, OM, pH, S
8	IVBA	Total Pb, OM, pH, Mg

IEUBK Modeling

Characterizing the *in vitro* bioaccessibility of these soils is not enough to understand how lead contamination in Detroit would affect children's BLLs. For this reason, we utilized the EPA's IEUBKwin32 software (Version 1.1, build 11) to estimate resulting BLLs in children of different ages. Default parameters were assumed for IEUBK model runs with the exception of the *Outdoor Soil Lead Concentration (µg/g)* and the *Adsorption Fraction Percent for Soil and Dust* (assumed the same for all models). Note the default *Soil/Dust Ingestion Weighting Factor* of 45 (% soil) was used. Models were developed to estimate BLLs based on the mean, 10th percentile, and 90th percentile *in vitro* bioaccessibility results as well as the mean and 95th percentile total lead results.

Results

Soil Chemical Characteristics

Prior to any intervention, our initial characterization of the soil was as follows. Results from chemical analysis show a range of total lead values from 18.2 mg/kg to 1428 mg/kg with a mean value of 212 mg/kg ± 233 mg/kg. *In vitro* bioaccessibility (IVBA) values ranged from 5.9 mg/kg to 1044 mg/kg with a mean value of 93 mg/kg ± 135 mg/kg, with percent *in vitro* bioaccessibility ranging from 4.5% to 81% with a mean of 39% ± 13%. Phosphorus levels ranged from 0.5 mg/kg to 936 mg/kg with a mean value of 39 mg/kg ± 87 mg/kg. Sulfur levels showed a range from 4.5 mg/kg to 181 mg/kg with a mean value of 22 mg/kg ± 23 mg/kg. Soil pH ranged from 5.7 to 9.4, with a mean pH of 7.8 ± 0.5. Organic matter ranged from 1.10% to 20.6% with a mean of 5.5% ± 2.5%. Descriptive statistics for these soil characteristics are outlined in Table 4.2.

Table 4.2. Summary of pre-treatment descriptive statistics.

	Total Lead (mg/kg)	IVBA (mg/kg)	IVBA (%)	Phosphorus (mg/kg)	Sulfur (mg/kg)	Soil pH	Organic matter (%)
N	142	142	142	142	142	142	142
Minimum	18.2	5.9	4.5	0.5	4.5	5.7	1.10
Maximum	1428	1044	81	936	181	9.4	20.6
Mean	212	93	39	39	22	7.8	5.5
Median	130	46	40	17	15	7.9	5.1
95th percentile	808	369	60	147	65	8.5	9.8
Std. Deviation	233	135	13	87	23	0.5	2.5

Cation exchange capacity ranged from 9.6 meq/100g to 56.3 meq/100g with a mean of 21.2 meq/100g ± 7.2 meq/100g. Calcium levels ranged from 1584 mg/kg to 10,606 mg/kg with a mean value of 3623 mg/kg ± 1380 mg/kg; potassium ranged from 13.5 mg/kg to 451 mg/kg with a mean of 172 mg/kg ± 92 mg/kg; magnesium ranged from 150 mg/kg to 694 mg/kg with a mean of 313 mg/kg ± 83 mg/kg; and sodium ranged from 0 mg/kg to 149 mg/kg with a mean of 5.7 mg/kg ± 16 mg/kg. Descriptive statistics for cations are outlined in Table 4.3.

Table 4.3. Summary of pre-treatment cation descriptive statistics.

	Calcium (mg/kg)	Potassium (mg/kg)	Magnesium (mg/kg)	Sodium (mg/kg)	Cation Exchange Capacity (meq/100g)
N	142	142	142	142	142
Minimum	1584	13.5	150.0	0.0	9.6
Maximum	10606	451	694	149	56.3
Mean	3623	172	313	5.7	21.2
Median	3443	173	299	0.1	20.2
95th percentile	6525	330	456	25.0	35.8
Std. Deviation	1380	92	83	16	7.2

Physical Characteristics

Based on the NSRC *Texture by Feel Method*, the majority of soils included in this study had a sandy clay loam texture, complete results from this analysis are presented in Appendix B. We compared results of these two independent methods of determining soil textural class. Results were disjoint, as only one of the 22 samples sent to Dairyland Labs, Inc were consistent with results determined by using the NSRC *Texture by Feel Method* (Table 4.4).

Table 4.4. Comparison of soil texture methods and NRCS Soil Texture by Feel (Burt, 2014).

Sample ID	Sand (%)	Silt (%)	Clay (%)	Soil Texture	
				Particle size	NRCS Method
8	52.0	24.0	24.0	sandy clay loam	sandy clay
11	78.0	14.0	8.0	loamy sand	silty clay loam
16	84.0	14.0	2.0	loamy sand	loam
18	51.6	32.4	16.0	loam	clay
19	88.0	8.0	4.0	sand	sandy loam
22	63.6	28.4	8.0	sandy loam	clay loam
24	31.6	40.4	28.0	loam	clay
28	65.6	30.4	4.0	sandy loam	sandy clay loam
29	67.6	30.4	2.0	sandy loam	sandy loam
33	73.6	26.4	0.0	loamy sand	loam
71	60.8	21.2	18.0	sandy loam	sandy clay
72	42.8	33.2	24.0	loam	sandy clay loam
73	40.8	33.2	26.0	clay loam	sandy clay
80	46.8	29.2	24.0	loam	sandy clay
85	63.6	30.4	6.0	sandy loam	clay loam
115	72.8	21.2	6.0	sandy loam	silty loam
116	48.8	33.2	18.0	loam	clay loam
120	56.8	27.2	16.0	sandy loam	sandy clay loam
132	60.4	20.4	19.2	sandy loam	silty clay loam
138	70.8	17.2	12.0	loamy sand	loam
142	59.6	18.8	21.6	sandy clay loam	sand

Bioaccessibility Characteristics

Effect of PBET pH on bioaccessibility was tested on the 18 soils at pH 1.5, 2.0, and 2.5. Total lead levels for the selected soils ranged from 17 mg/kg to 1218 mg/kg. As shown in Table 1, the mean IVBA measured using the modified PBET method (extraction solution pH of 2.0 ± 0.2) was 93 mg/kg, or 39%. The IVBA concentration increased when the pH was lower (1.5) and decreased when the pH was higher (2.5) (Figure 4.4). Post-hoc analysis found significant differences between the IVBA (%) for all pH extraction solutions (LSD, $p<0.0005$)

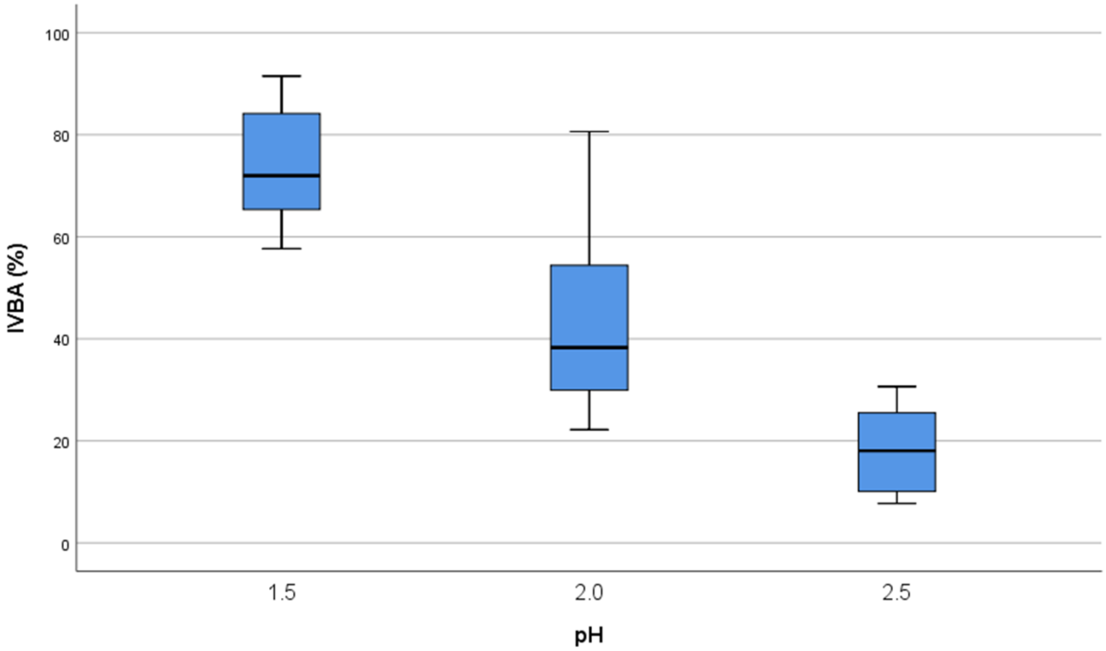

Figure 4.4. Effect of extraction pH on *In vitro* bioaccessibility (IVBA) determined by modified PBET (Ruby et al., 1996) for various soil samples (n=18).

Regression Analysis

The influence of soil properties (Tables 2 & 3) on IVBA was assessed using a series of multiple linear regression models based on the general equation:

$$y_i = \beta_0 + \beta_1 x_{1,i} + \cdots + \beta_k x_{k,i} + \epsilon_i \qquad \text{Equation 4}$$

where *y* is the $\log_{10}$ IVBA (mg/kg) , x are predictors variables, β are fitted coefficients, ϵ is the model error (i.e. residuals), *k* is the number of predictors, *i* is the sample, and $\epsilon_i \sim N(0, \sigma^2)$. Descriptive statistics for model variables are shown in Table 4.5.

Table 4.5. Descriptive statistics of pre-treatment model variables.

Variable	N	Minimum	Maximum	Mean	Standard Deviation	Skewness
Log_{10} CEC (meq/100g)	142	0.98	1.75	1.30	0.137	0.28
Log_{10} IVBA (mg/kg)	142	0.77	3.02	1.71	0.446	0.45
Log_{10} OM (%)	142	0.04	1.31	0.70	0.178	-0.29
Log_{10} P (mg/kg)	142	-0.30	2.97	1.22	0.554	0.23
Log_{10} Pb (mg/kg)	142	1.26	3.15	2.15	0.373	0.29
pH	142	5.70	9.40	7.81	0.540	-0.37

Tables 4.6a and 4.6b show regression analysis results for each of the eight models. A total of 141 samples were included in regression analysis, with one sample (Sample 113) being censored since the regression standardized residual was greater than 3. Ultimately, the parameters found to best predict IVBA concentrations included the concentrations of total lead, organic matter, and the soil pH (Model 1). This model explains 93.9% of the pre-treatment IVBA variability and is highly significant ($p<0.0005$). Of the predictors, the total lead concentration has the greatest influence with a high positive bivariate correlation with IVBA (Pearson coefficient, $r = 0.936$; $p<0.0005$; both log-transformed).

Table 4.6a. Pre-treatment model results.

	Model 4.1	Model 4.2	Model 4.3	Model 4.4
Model Fit				
Adjusted r^2	0.939	0.939	0.939	0.941
F-statistic	720.993	536.905	539.448	539.591
p-value	<0.0005	<0.0005	<0.0005	<0.0005
N	141	141	141	141
Parameters				
Constant				
β-value estimate	-1.227	-1.226	-1.188	-1.171
β-value 95% CI	(-1.593, -0.861)	(-1.593, -0.859)	(-1.567, -0.81)	(-1.561, -0.78)
p-value	<0.0005	<0.0005	<0.0005	<0.0005
Log_{10} Pb (mg/kg)				
β-value estimate	1.176	1.175	1.175	1.173
β-value 95% CI	(1.126, 1.226)	(1.123, 1.227)	(1.124, 1.225)	(1.122, 1.224)
p-value	<0.0005	<0.0005	<0.0005	<0.0005
Log_{10} OM (%)				
β-value estimate	-0.498	-0.501	-0.505	-0.515
β-value 95% CI	(-0.608, -0.388)	(-0.616, -0.386)	(-0.616, -0.394)	(-0.632, -0.398)
p-value	<0.0005	<0.0005	<0.0005	<0.0005
pH				
β-value estimate	0.098	0.098	0.080	0.093
β-value 95% CI	(0.059, 0.136)	(0.059, 0.136)	(0.021, 0.139)	(0.054, 0.133)
p-value	<0.0005	<0.0005	0.008	<0.0005
Log_{10} P (mg/kg)				
β-value estimate		0.003		
β-value 95% CI		(-0.033, 0.039)		
p-value		0.873		
Log_{10} CEC (meq/100g)				
β-value estimate			0.083	
β-value 95% CI			(-0.124, 0.291)	
p-value			0.428	
Fill Status				
β-value estimate				-0.011
β-value 95% CI				(-0.039, 0.016)
p-value				0.416

Phosphorus concentration (model 2), cation exchange capacity (model 3), and fill status (model 4) were not significant predictors for our analysis (p-values > 0.4). Cations including potassium, calcium, sulfur, and magnesium were assessed to determine their impact on model fit. Calcium, magnesium, and sulfur were not significant predictors (p-value > 0.1), and potassium was a slightly significant predictor (p-value = 0.029).

Table 4.6b. Pre-treatment model results continued.

	Model 4.5	Model 4.6	Model 4.7	Model 4.8
Model Fit				
Adjusted r^2	0.941	0.939	0.939	0.940
F-statistic	557.266	540.538	537.189	547.083
p-value	<0.005	<0.005	<0.0005	<0.0005
N	141	141	141	141
Parameters				
Constant				
β-value estimate	-1.091	-1.379	-1.240	-0.970
β-value 95% CI	(-1.471, -0.710)	(-1.863, -0.894)	(-1.616, -0.864)	(-1.458, -0.482)
p-value	<0.0005	<0.0005	<0.0005	<0.0005
Log_{10} Pb (mg/kg)				
β-value estimate	1.158	1.175	1.176	1.179
β-value 95% CI	(1.106, 1.210)	(1.124, 1.225)	(1.126, 1.227)	(1.129, 1.229)
p-value	<0.0005	<0.0005	<0.0005	<0.0005
Log_{10} OM (%)				
β-value estimate	-0.562	-0.501	-0.499	-0.455
β-value 95% CI	(-0.684, -0.440)	(-0.611, -0.392)	(-0.609, -0.389)	(-0.577, -0.333)
p-value	<0.0005	<0.0005	<0.0005	<0.0005
pH				
β-value estimate	0.066	0.076	0.101	0.108
β-value 95% CI	(0.018, 0.113)	(0.016, 0.136)	(0.056, 0.147)	(0.068, 0.149)
p-value	0.007	0.013	<0.0005	<0.0005
Log_{10} K (mg/kg)				
β-value estimate	0.092			
β-value 95% CI	(0.010, 0.175)			
p-value	0.029			
Log_{10} Ca (mg/kg)				
β-value estimate		0.093		
β-value 95% CI		(-0.101, 0.287)		
p-value		0.347		
Log_{10} S (mg/kg)				
β-value estimate			-0.013	
β-value 95% CI			(-0.095, 0.069)	
p-value			0.761	
Log_{10} Mg (mg/kg)				
β-value estimate				-0.152
β-value 95% CI				(-0.343, 0.040)
p-value				0.120

Resulting β-coefficients from Model 4.1 were used to develop further models that estimated the impact of increasing or decreasing organic matter content and pH on bioaccessibility. Holding all predictor variables constant, a 1% increase in OM content, from 5% to 6%, shows an expected 8.6% decrease in *in vitro* bioaccessible lead, on average (95% CI: -25% to +11%). An increase of one standard deviation, or 2.5% OM increase, from 5% to 7.5%, shows an expected 18.2% decrease in *in vitro* bioaccessible lead (95% CI: -35% to +2%). Similarly, decreasing the soil pH 0.1 units, from 7.8 to 7.7, a 2.2% decrease in *in-vitro* bioaccessible lead, on average (95% CI: -51% to +75%) can be expected, while decreasing soil pH one standard deviation, or 0.5 pH units, from 7.8 to 7.3, shows an expected 10.7% decrease in *in vitro* bioaccessible lead (95% CI: -54% to +69%). Table 4.7 shows resulting *in-vitro* bioaccessible lead concentrations and percentages.

Table 4.7. Influence of organic matter and pH (pre-treatment) on in-vitro lead bioaccessibility for (a) mean total lead concentrations and (b) 95th percentile total lead concentrations.

(a)

Variables	Estimated IVBA [mg/kg]	Estimated IVBA [%]	% Change IVBA
mean	52.7	36.9	
mean pH, +2.5% OM	43.1	30.2	-18.2
mean pH, +1% OM	48.1	33.7	-8.6
mean pH, -1% OM	58.8	41.2	11.7
mean pH, -2.5%	74.1	52.0	40.8
mean OM, -0.5 pH	47.0	33.0	-10.7
mean OM, -0.1 pH	51.5	36.1	-2.2
mean OM, +0.1 pH	53.9	37.8	2.3
mean OM, +0.5 pH	59.0	41.3	11.9

(b)

Variables	Estimated IVBA [mg/kg]	Estimated IVBA [%]	% Change IVBA
mean	403.9	50.1	
mean pH, +2.5% OM	330.4	41.0	-18.2
mean pH, +1% OM	369.1	45.8	-8.6
mean pH, -1% OM	451.0	55.9	11.7
mean pH, -2.5% OM	568.5	70.5	40.8
mean OM, -0.5 pH	360.8	44.7	-10.7
mean OM, -0.1 pH	394.9	49.0	-2.2
mean OM, +0.1 pH	413.1	51.2	2.3
mean OM, +0.5 pH	452.2	56.1	11.9

Proximity to Smelters

There is a significant, albeit weak, correlation between the total (Pearson coefficient, r = 0.239; N=141, p = 0.004) and IVBA (Pearson coefficient, r = 0.271; N=141, p = 0.001) concentration in soil and the downwind proximity to smelters (maximum compound proximity). The log transformed maximum compound proximity was incorporated as a fourth predictor term into Model 1, resulted in the following equation:

$$y_i = \beta_0 + \beta_1 x_{1,\,i} + \beta_2 x_{2,\,i} + \beta_3 x_{3,\,i} + \beta_4 x_{4,\,i} + \epsilon_i \qquad \text{Equation 5}$$

where y is the $\log_{10}$ IVBA (mg/kg) , x_1 and β_1 represent $\log_{10}$ total lead, x_2 and β_2 represent $\log_{10}$ organic matter, x_3 and β_3 represent pH, and x_4 and β_4 represent the $\log_{10}$ composite max Z-score. The resulting model was similar in predictive ability (r^2=0.942, N=141) however, the estimate of the predictor coefficient for the maximum compound proximity (β_4 = 0.038; 95% CI = -0.006, 0.083) was only marginally significant (p = 0.086). Nonetheless, the revised model (r^2 = 0.942, F = 549.336, p < 0.0005), suggests that the bioaccessibility increases with increasing proximity to smelters.

IEUBK Model Results

To predict how bioaccessibility results, total lead, and increasing or decreasing soil organic matter may affect children's BLLs, twenty-one IEUBK models were developed. IEUBK software considers soil lead and fraction bioaccessibility. For models 1-3, we identified samples that were closest to the 10th, 50th, and 90th percentile log transformed IVBA (mg/kg) values to provide a realistic framework. Using these values, total lead and percent bioaccessibility were matched for: 10th percentile (64.04 mg/kg, 25.37%), 50th percentile (121.97 mg/kg, 41.81%), and 90th percentile (261.98 mg/kg, 80.89%). Model results for predicted BLLs are shown in Figure 4.5.

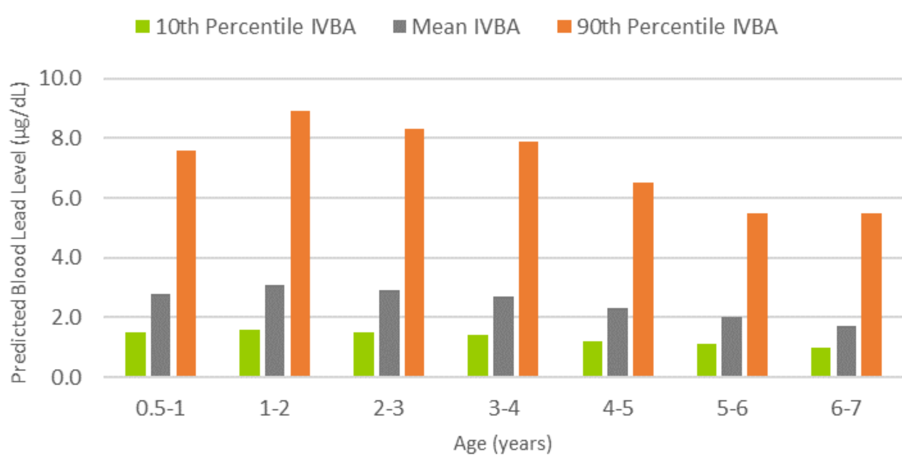

Figure 4.5. IEUBK predicted children's BLLs from 10th percentile, mean, and 90th percentile IVBA measurements (mg/kg) from Detroit soils.

Model 4.4 shows baseline predicted BLLs based on mean total lead, pH, and organic matter content. Models 4.5 - 4.8 adjusted pH by 0.1 and 0.5 pH units while maintaining mean total lead and organic matter. Models 4.9 - 4.12 adjusted organic matter by 1% and 2.5% while maintaining mean total lead and pH. Models 4.13 – 4.21 modeled the same changes as models 4.4 – 4.12 while using 95th percentile total lead results. Model descriptions, variable changes, input values, and output values are outlined in Appendix B. Figure 4.6 shows resulting BLL estimates.

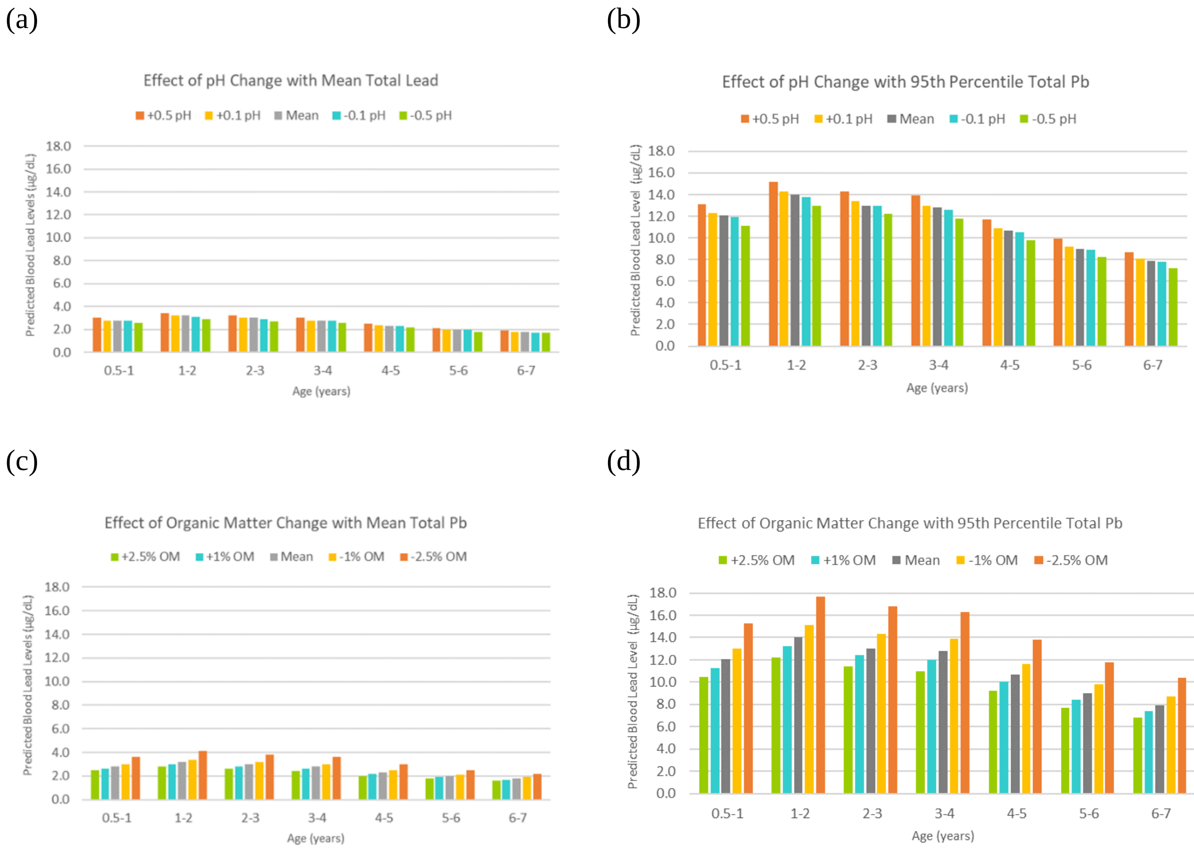

Figure 4.6. IEUBK model results for increasing and decreasing soil pH (a) for mean total lead and (b) 95th percentile total lead and for increasing and decreasing soil organic matter (c) for mean total lead and (d) 95th percentile total lead.

Based on mean total lead (143 mg/kg), pH, and organic matter observed in this study (n = 142), and the mean bioaccessible lead predicted using Model 4.1, the geometric mean BLL is estimated to be 2.52 µg/dL. Fixing the organic matter and total lead values at their mean (Table 4.6), decreasing the soil pH 0.1 units is predicted to decrease the geometric mean BLL 1.4% to 2.48 µg/dL. Decreasing the pH by one standard deviation, or 0.5 pH units, is predicted to decrease the geometric mean BLL 7.1% to 2.34 µg/dL. When the soil pH increases 0.1 and 0.5 units, BLLs are predicted to increase by 1.6% and 7.9%, to 2.56 µg/dL and 2.72 µg/dL, respectively. Geometric mean BLLs when considering 95th percentile total lead (806 mg/kg), mean pH, and mean organic matter are predicted to be 11.17 µg/dL. Based on the 95th percentile total lead and maintaining mean organic matter, an decrease in pH of 0.1 units results in a 1.6% reduction of geometric mean BLLs to 10.98 µg/dL, while decreasing the pH 0.5 units is predicted to reduce the geometric mean BLLs 8.1% to 10.26 µg/dL. An increase in pH by 0.1 units gives a predicted increase in geometric mean BLLs of 1.6% to 11.34 µg/dL, and a 0.5 pH unit increase results in an 8.6% increase in BLL to 12.12 µg/dL.

When maintaining the mean pH and total lead, increasing the organic matter by 1% results in a predicted geometric mean BLL decrease of 5.8% to 2.37 µg/dL, while increasing organic matter 2.5%, or one standard deviation, shows a 12.2% decrease to 2.21 µg/dL. Models predict a 1% organic matter decrease results in a 7.7% increase of BLLs to 2.71 µg/dL, and a 2.5% organic matter decrease results in a 26.8% increase to 3.20 µg/dL. When maintaining mean pH and 95th percentile total lead, a 1% increase in organic matter is predicted to decrease geometric mean BLLs by 6.4% to 10.45 µg/dL, and a 2.5% increase shows a predicted 13.8% decrease in BLLs to 9.62 µg/dL. Decreasing organic matter by 1% on the 95th percentile soils results in a predicted 8.3% increase in BLLs to 12.09 µg/dL, while decreasing the organic matter by 2.5% shows an expected increase of 27.8% to 14.27 µg/dL.

Discussion

Consistent with the findings of Roussel et al. (2010), there was a strong positive correlation between the total lead concentration in the soil and bioaccessibility. After total lead, the next most significant predictor for bioaccessibility was soil organic matter content. Statistical analysis shows an inverse relationship between soil organic matter and *in vitro* bioaccessibility for lead. An incremental increase in soil organic matter from 5% to 6%, reduces bioaccessibility by 8.6%, and increasing organic matter by 2.5%, from 5% to 7.5%, results in a reduction of 18.2%. These findings are consistent with our hypothesis that increased soil organic matter will decrease lead IVBA. In addition to other soil chemical changes, increased levels of soil organic matter offer additional binding sites for available lead ions to sorb. We did not analyze our soils for the types of organic matter they contained. To better understand the relationship between organic matter and soil lead, different types of organic matter (i.e. fulvic or humic) and sources of organic matter (i.e. peat moss, compost) should be assessed for their ability to trap and immobilize lead.

However, it is important to note that as organic matter decomposes over time, its effectiveness at adsorbing lead may decrease. Additions of soil organic matter in the range of roughly 1% to 2.5% could be feasible, yet further studies are needed to determine which types of organic matter and which doses could result in reductions of IVBA like those found in our study.

We hypothesized that increasing soil pH would result in decreased lead bioaccessibility, as acidic conditions promote lead solubility. Results showed the opposite of our hypothesis, with decreasing pH resulting in decreased bioaccessibility. A decrease in soil pH by 0.1 pH units from 7.8 to 7.7 showed a 2.2% decrease in lead bioaccessibility, while decreasing the soil pH by 0.5 units, from 7.8 to 7.3, resulted in a 10.7% decrease in bioaccessibility. These results are consistent with the premise that near neutral pH, organic matter can form durable complexes with lead which remain insoluble under lower-pH gastric conditions.

Generally, as soil pH decreases, lead bioaccessibility is expected to increase as Pb^{2+} ions compete for adsorption sites on organic matter. However, our statistical analysis shows a decrease in bioaccessibility when pH decreases from 7.8 to 7.7. These pH values are generally neutral. The reduction in *in-vitro* bioaccessibility within these neutral pH values support the claim that under neutral pH conditions, complexation of cations with organic matter can effectively immobilize lead in the soil. Out of all sample sites, the lowest pH observed was 5.7, and the highest was 9.4. It is also possible that lower pH values could promote the formation of stable lead-phosphates such as pyromorphite through increasing lead solubility (Scheckel et al., 2013).

There was no relationship between soil lead bioaccessibility and calcium, magnesium, or sulfur. However, there was a weak positive relationship between soil lead bioaccessibility and potassium. This relationship showed that lead bioaccessibility would increase minimally with increasing potassium content. This relationship may be due to the interaction of potassium on the soil surface, where it may exchange for lead ions or potentially take up sites that could otherwise, we filled with lead ions (He et al., 2018). Another possible explanation relates to the interaction between plant material and potassium, as potassium is vital for the regulation and uptake of water and nutrients in plant tissue (Malvi, 2011). It is possible that adequate or increased levels of potassium in soil enhance a plant's ability to uptake phosphorus, effectively removing phosphorus from the soil and into plant tissue, inhibiting the formation of insoluble minerals like pyromorphite.

Significant correlations were not observed between soil phosphorus levels or CEC and soil lead bioaccessibility. The lack of correlation between CEC and lead bioaccessibility may be attributed to the pH dependence of CEC (Rieuwerts et al., 1998). Lack of correlation between soil phosphorus and soil lead bioaccessibility may be attributed to the formation of lead-phosphate minerals, since soil phosphorus concentrations are based on extractable phosphorus, they do not represent phosphorus that is mineral bound (e.g. pyromorphite). Mineralogical analysis is needed to determine if pyromorphite minerals exist within the soil. Further tests are also needed to determine the relationship between soil pyromorphite formation and phosphorus concentrations measured by the Mehlich 3 extraction in the soil environment.

The data showed a weak, yet significant correlation between distance and direction from smelters and *in-vitro* bioaccessible lead. This weak correlation was observed despite this not being a primary objective of the experimental design. The weak correlation may be attributed to a distance greater than 0.2 miles from smelter location. The increase in bioaccessible lead with proximity to smelters is consistent previous studies (CDC, 1997).

Conclusions

Soil pH and soil organic matter have a significant effect on the *in-vitro* bioaccessibility of lead. Optimization of soil properties such as pH and organic matter may help to decrease the bioaccessibility of lead in urban soils. Further studies are needed to determine which types and sources of organic matter are most effective at decreasing lead bioaccessibility, as complexation of lead by organic matter is pH dependent (McLean and Bledsoe, 1992). Phosphate content in the soil could also relate to these decreases in lead bioaccessibility, although our models showed no significant relationship between phosphorus levels and lead bioaccessibility. It is possible that the relationship between phosphorus and lead bioaccessibility was not significant because lead and phosphorus were already bound in insoluble minerals, such as pyromorphite. If this was the case, its reasonable to assume that the Mehlich 3 extraction conducted by Dairyland Labs may not have measured phosphorus which was already bound by lead in a stable mineral form.

Results imply decreasing the pH and increasing the organic content of urban soils in Detroit may reduce child BLLs. Additionally, significant (albeit weak) correlations between the historic location of smelters and lead bioaccessibility suggest the bioavailability of lead near these sites may disproportionately increase child BLLs. Further research is required to better understand this relationship. A comparison of childhood BLLs throughout the years in which smelters were active and current BLLs in the same locations could provide insight into these relationships. Developing an experimental design which takes samples from more consistent distances and directions from smelters and using census or health department BLLs for neighborhoods near smelters could be an option for future research to better understand the impact of proximity to smelters on childhood BLLs.

CHAPTER 5 "EVALUATION OF BONE MEAL AMENDMENT"

Introduction

As anthropogenic lead sources in the environment have been eliminated, the proportion of children under the age of 5 with elevated blood lead levels (EBLLs) over 10 µg/dL have dropped from 88% in the 1970's to 0.2% nationwide (Dignam et al., 2019). Despite this national decline, about 15% of urban children still have blood lead levels (BLLs) over 10 µg/dL (Filippelli et al., 2005). Some neighborhoods have up to 40% of children with BLLs over 5 µg/dL (Laidlaw et al., 2017), a much higher proportion than the national average of 1.3% exceeding 5 µg/dL (Dignam et al., 2019). Even with removal of sources, lead continues to be ubiquitous in the urban environment.

Soil contaminated with lead is a major source of exposure for children (Hettiarachchi and Pierzynski, 2004). Deposition of leaded gasoline emissions, chipping leaded paint, smelting emissions, and emissions from various industries have deposited soil lead in urban environments where low-income, minority communities are often living in older homes, near high-traffic roads and industrial sites (Laidlaw et al., 2017). These disadvantaged communities are subjected to over twice the level of traffic density as compared to other communities, with soils showing background levels of lead around 500 mg/kg; whereas soil lead concentration are often an order of magnitude lower in surrounding suburban communities (Leech et al., 2016). Studies in major cities across the United States and worldwide have shown that the spatial distribution of soil lead concentrations resemble a bullseye, with the highest concentrations in the city center and concentrations decreasing outward (Laidlaw et al., 2005).

Remediation of soil lead has shown drastic decreases in child BLLs. Common remediation techniques for lead contaminated soil include excavating contaminated soil or creating a barrier to highly contaminated soil (i.e. capping). Remediation by capping contaminated soil with a clean soil barrier of the Bunker Hill Superfund Site in Idaho showed decreases in soil lead from about 750 mg/kg to 175 mg/kg, resulting in children EBLLs (>10 µg/dL) decreasing from 76% in 1988 to 3% in 2001 (Laidlaw et al., 2017). After Hurricane Katrina hit the city of New Orleans, LA, when surface soils were covered with sediment from floodwaters, soil lead levels decreased from a median of 280 mg/kg to 132 mg/kg over 10 years, average BLLs in the region over the same period of time decreased from 5 µg/dL to 1.8 µg/dL (Laidlaw et al., 2017). Although Hurricane Katrina was not a remediation event, it shows the important link between soil lead and BLLs. These studies demonstrate that reducing exposure to lead contaminated soil can greatly decrease child BLLs.

Typical remediation strategies, capping and excavation are costly and resource intensive, particularly when remediating large plots of land. Excavation also requires the contaminated soil to be transported elsewhere, where it could potentially continue to cause harm (Hettiarachchi and Pierzynski, 2004). It is desirable to develop methods for soil remediation that are both low-cost and *in-situ*. One approach that has been investigated has been to alter the bioavailability of the soil lead so that the exposure dose decreases, rather than limiting exposure (Henry et al., 2015; Hettiarachchi and Pierzynski, 2004; Ryan et al., 2004; Scheckel et al., 2013). The use of phosphate-based soil amendments has shown great promise, as these are able to bind with lead and form highly insoluble minerals (i.e. pyromorphite, hydroxypyromorphite, chloropyromorphite) that are stable under a wide-range of pH conditions, and are able to remain insoluble within a child's gastrointestinal tract, effectively reducing the amount of lead that may be released into the bloodstream (Henry et al., 2015). To test the ability of phosphate amendments to reduce blood lead, Ryan et al. (2004) conducted tests on swine and found BLL were lower in pigs fed phosphate treated lead contaminated soils than untreated lead contaminated soils, showing that the soil amendment was effective in trapping soil lead in an insoluble form. Despite these promising results by others, it is unclear how transferable the results of previous studies are to Detroit soils.

In this study, we applied a phosphate-based bone meal soil amendment to evaluate changes in bioaccessibility. Bone meal is a type of apatite [$Ca_{10}(PO_4)_6OH_2$] which is poorly crystalline and readily available (Hodson and Valsami-Jones, 2000). There are a variety of factors which can affect the formation of pyromorphite *in-situ*. As described in Chapter 2, high levels of organic matter can prevent the precipitation of pyromorphite by binding metal ions, inhibiting phosphate-lead reactions (Lang and

Kaupenjohann, 2003). This would be expected to reduce the amount of pyromorphite formed and be associated with higher bioaccessibility. However, as reported in Chapter 4, soils with greater amounts of OM were associated with lower amounts of bioaccessible lead. Most cationic metals, including lead, are anticipated to be more labile in low pH soils, less labile in high pH soils (McLean and Bledsoe, 1992). This increase in soluble lead likely increases the relative proportion of lead available to react with phosphate and form pyromorphite. Low soil pH also influences phosphate chemistry, as pH levels below about 7.2 contain predominately $H_2PO_4^{1-}$ and $H_3PO_4^{0}$, the forms of phosphate which interact with lead and promote pyromorphite formation (Scheckel et al., 2013). Since phosphate and lead chemistry are compatible at low pH, the acidic nature of the bone meal amendment (Down to Earth Liquid Bone Meal, pH 5.0 - 5.5) is also likely to enhance pyromorphite formation. Therefore, in this chapter, hypothesize that phosphate treatment will reduce bioaccessibility of lead in Detroit soils. We also hypothesize that as phosphorus levels in the soil increase, the bioaccessibility of lead in the soil will decrease.

Experimental Design

Participants from Detroit, Highland Park, and Hamtramck were recruited by EcoWorks through Clear Corp's community health events, phone calls to known urban gardeners, and through the EcoWorks website, social media, and mailing list. A total of 69 participants responded to the study resulting in 208 initial sample locations, as some participants had multiple land plots. Sampling locations are shown in Figure 5.1. Prior to sampling, a reference stake was placed at each site that remained throughout the study to ensure follow up samples were collected in the same location. For Phase I of sampling, before remediation, a bulb planter was used to extract the top 4" of soil in the north, east, south, and west directions at a distance of 8" from the stake. Soil samples collected prior to remediation were characterized and reported in Chapter 4. Out of the 208 locations initially sampled, 66 sites were removed from the study due to site disturbance or a stake being removed or unfindable, resulting in 142 sampling locations that completed the study. Study sites received bone meal phosphate remediation (treatment) or a placebo remediation (control) between November 2018 and January 2018. Out of 142 sites, 86 (61%) received the treatment and 56 (39%) served as controls. Property owners were not notified if they received the treatment or control to prevent potential bias in how the soil was cared for during the study period. Approximately 9 months (Min: 240 days, Max: 288 days, Mean: 269 days) after remediation, soils were collected again from study sites and recharacterized. For Phase II of sampling, after amendment was aged in soil, the top 4" of soil were sampled in the northeast, northwest, southeast, and southwest directions. The study protocol (IRB# 045618B3X) was submitted to WSU IRB and IRB review was deemed unnecessary.

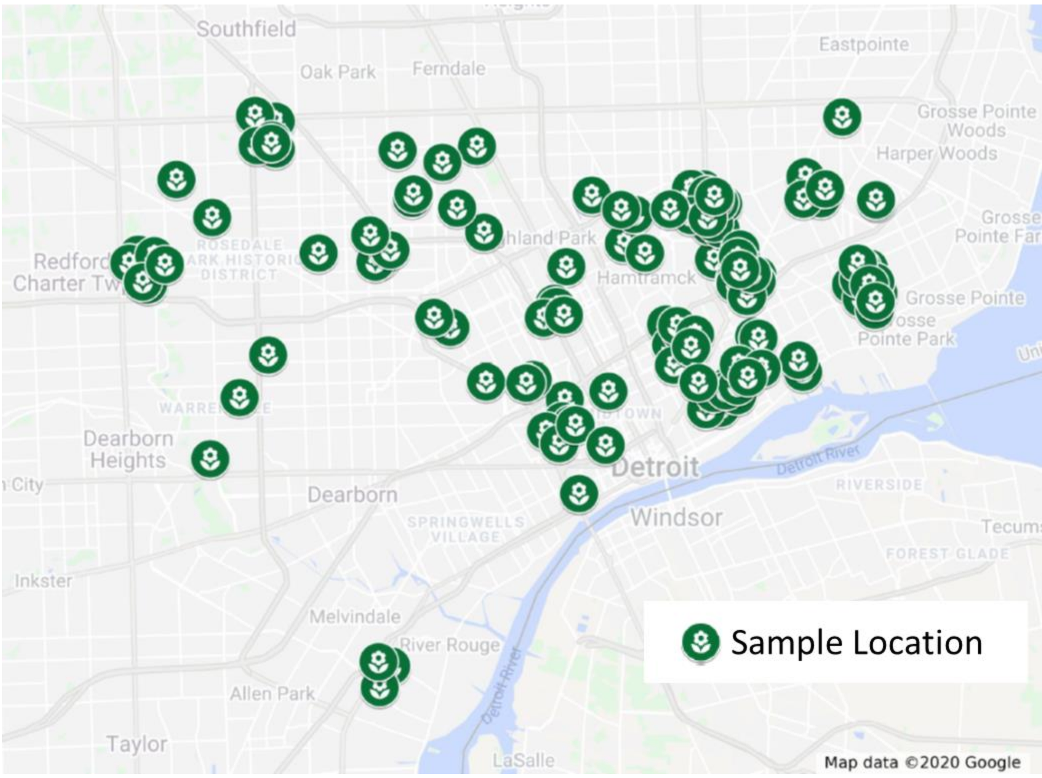

Figure 5.1. Map showing sampling site locations. Random offset was applied to sample site coordinates.

Choosing a Phosphate Source

A number of phosphate sources were considered for use in this study. Phosphoric acid can negatively affect surface waters, where runoff or groundwater intrusion may cause eutrophication of water bodies. The high acidity of phosphoric acid would also require pH neutralization in soil to ensure crops are able to grow. Calcium phosphates (e.g. hydroxyapatite) may be better suited for areas susceptible to runoff, such as urban properties, since they are less soluble and often sold in a solid state (Scheckel et al., 2013).

However, pyromorphite can form on the outside of solid phosphate, inhibiting the full capacity of the phosphate from reacting with lead in soil. As a result, smaller sized particles with increased surface area are recommended to maximize remediation (Scheckel et al., 2013). The reactivity of phosphate toward a variety of metals makes impurities a concern when selecting the ideal source of phosphate for remediation. Knox et al. (2006) reported that biogenic sources of apatite, such as bone meal, have levels of contaminants generally lower than non-biogenic sources, such as those from apatite mines. A liquified bone meal was selected for this study as it is less likely to result in nutrient runoff, will not have large impact on soil pH, and because it is less likely to contain impurities and contaminants than mined or non-biogenic apatite (Knox et al., 2006).

Amendment Application

The application of treatment solutions at each site was guided by a wooden 2'x2' board with holes spaced 2" apart in a grid pattern (Figure 5.2). After centering the board on the sampling location stake, a drill was used to aerate the soil, to a depth of 4", using the board as a guide. After removing the guide board, diluted bone meal soil amendment was poured as evenly as possible across the soil. Figure 2 shows the apparatus constructed for amendment application.

Figure 5.2. Construction of amendment application apparatus and resulting holes in soil where bone meal solution is applied.

The remediation treatment consisted of 100 mL of 12% P_2O_5 solution (Down to Earth Liquid Bone Meal 0-12-1; Eugene, OR) combined with 2,000 mL tap water. Therefore, each treatment site received 12g P_2O_5, or 5.2g P per area or 6g P_2O_5/ft^2, or 2.6 g P/ft^2. The treatment sites were selected randomly, and the same volume and concentration of amendment was added to each site, regardless of soil lead concentrations. Sites randomly selected to serve as controls received 2,000 mL of tap water. It was determined that the use of tap water did not input a measurable quantity of lead into the soil.

Chemical Characterization

Detailed description of all materials and methods are provided in Chapter 2. Briefly, approximately 1kg of soil was collected in plastic bags. Upon returning samples to the lab, soils were air dried and sieved to 150 µm. This size fraction was chosen according to EPA Method 1340 since it represents the particle size that may adhere to a child's hands (U.S. EPA, 2017). Total lead was measured according the EPA Method 3051a (U.S. EPA, 2007) via microwave assisted digestion (MARSXpress, CEM). After cooling, samples were diluted, to a 17% nitric acid solution, centrifuged and filtered through a 0.45 µm PTFE filter. *In-vitro* bioaccessible lead was measured according to a modified version of the Physiologically Based Extraction Test (Ruby et al., 1996) at pH = 2.0 ± 0.2. Soil pH, CEC, organic matter, cation concentrations, and phosphorus concentration were analyzed by Dairyland Labs, Inc. in Arcadia, WI.

Statistical Analysis

All statistical analyses were performed using SPSS Version 26 (IBM, release 26.0.0.0). Data was analyzed using standard analysis of variance (ANOVA) and multiple linear regression procedures. Prior to conducting analyses, all data were evaluated to determine if transformations were necessary (e.g. to ensure normality assumptions). When performing regression analyses, the following assumptions were verified (Pallant, 2010): (1) Linearity: each predictor/dependent variable has a linear relation with our outcome variable, (2) Independence: each predictor/dependent variable are not highly correlated ($r > 0.9$) and singularity was avoided, (3) Normality: the prediction errors (i.e. residuals) were normally distributed in the population, (4) Homoscedasticity: the variance of the errors was constant in the population, and (5) Outliers: no outliers were present within the dataset used for analysis – i.e. standard residual values were less than ±3.3.

IEUBK Modeling

The EPA's Integrated Exposure Uptake Biokinetic (IEUBK) model (IEUBKwin32, Version 1.1, Build 11) was used to determine how changes in bioavailability are expected to affect child BLLs. To conduct this sensitivity analysis, mean and 95th percentile total soil lead measurements, and *in-vitro* bioaccessible lead results from regression analyses were used to evaluate change in BLLs. Default parameters were assumed for IEUBK model runs except for the *Outdoor Soil Lead Concentration (µg/g)* and the *Adsorption Fraction Percent for Soil and Dust* (assumed the same for all models). Note the default

Soil/Dust Ingestion Weighting Factor of 45 (% soil) was used. The models report predicted BLLs among different age groups, geometric mean BLLs, and the percent of child BLLs expected to exceed 5 µg/dL.

Results

Chemical Characterization

Characterization of soils collected prior to remediation in Summer 2018 were reported in detail in Chapter 4 and are summarized in Table 1 below. The results are presented in Table 5.1. Log-transformed values were used for statistical analysis.

Table 5.1. Summary of descriptive statistics for soils pre- and post-treatment

Study Group	Measure		N	Minimum	Maximum	Mean	Standard Deviation	Skewness
Control	Total Lead (mg/kg)	Pre	56	20.7	1103.6	226.2	226.4	2.13
		Post	56	17.0	897.9	216.8	197.9	1.79
	IVBA (mg/kg)	Pre	56	7.4	511.8	94.7	110.9	2.10
		Post	56	5.8	470.4	98.8	107.5	1.85
	IVBA (%)	Pre	56	4.5	71.0	38.9	13.8	-0.43
		Post	56	11.4	72.5	42.0	14.7	-0.02
	pH	Pre	56	5.7	9.1	7.7	0.5	-1.06
		Post	56	5.9	8.6	7.6	0.5	-1.05
	Organic matter (%)	Pre	56	1.1	20.6	5.9	3.2	2.53
		Post	56	1.4	14.7	5.6	2.7	1.72
	CEC (meq/100g)	Pre	56	9.6	49	20.5	6.7	1.56
		Post	56	9.7	50.5	24.6	7.4	0.97
	Phosphorus (mg/kg)	Pre	56	5	198	38	49	1.83
		Post	56	0.0	200	46	45	1.66
	Calcium (mg/kg)	Pre	56	1584	9088	3486	1285	1.74
		Post	56	1521	6448	3506	977	0.32
	Magnesium (mg/kg)	Pre	56	179	591	307	75	1.04
		Post	56	146	665	308	85	1.51
	Sulfur (mg/kg)	Pre	56	5.5	87	19	17	2.78
		Post	56	7.0	55	18	9.26	2.25
	Potassium (mg/kg)	Pre	56	27	451	173	90	0.98
		Post	56	43	410	157	81.35	1.10
Treatement	Total Lead (mg/kg)	Pre	86	18.2	1428	202	238.8	3.15
		Post	86	14.1	1218	199	224.4	2.73
	IVBA (mg/kg)	Pre	86	5.9	1044.1	92	148.7	4.19
		Post	86	5.2	819.3	88	126.2	3.66
	IVBA (%)	Pre	86	14.2	80.9	39	13.2	0.61
		Post	86	15.8	86.7	40	13.1	0.45
	pH	Pre	86	6.5	9.4	7.9	0.5	0.11
		Post	86	6.4	8.5	7.6	0.5	-0.71
	Organic matter (%)	Pre	86	1.9	12.9	5.2	1.9	1.20
		Post	86	1.3	15.6	5.2	2.0	2.13
	CEC (meq/100g)	Pre	86	10.7	56.3	21.7	7.6	1.56
		Post	86	11.7	53.4	25.4	7.5	0.71
	Phosphorus (mg/kg)	Pre	86	0.5	935.5	40	105	7.58
		Post	86	5.5	957	84	106	6.94
	Calcium (mg/kg)	Pre	86	1782	10606	3711	1438	1.71
		Post	86	1838	8779	3729	1228	1.27
	Magnesium (mg/kg)	Pre	86	150	694	316	89	1.66
		Post	86	129	698	310	86	1.75
	Sulfur (mg/kg)	Pre	86	4.5	181	23	26	4.30
		Post	86	6.0	104	21	17	3.62
	Potassium (mg/kg)	Pre	86	14	434	171	94	0.33
		Post	86	38	416	163	93	0.66

Total lead changes are shown in Figure 5.3. There was a strong correlation (Pearson $r = 0.983$, $p < 0.0005$) observed for the concentration of total lead across all samples. No significant change was detected between sampling events in the total lead concentration (pre vs. post; t-test of log-transformed variables, $t=0.916$, $N=142$, $p = 0.361$). When the dataset was split into control and treatment groups and analyzed separately, the strong correlation (Pearson $r \geq 0.982$, $p < 0.0005$) and lack of a significant difference between pre and post measurements of soil total lead (t-test, $p > 0.346$) remained.

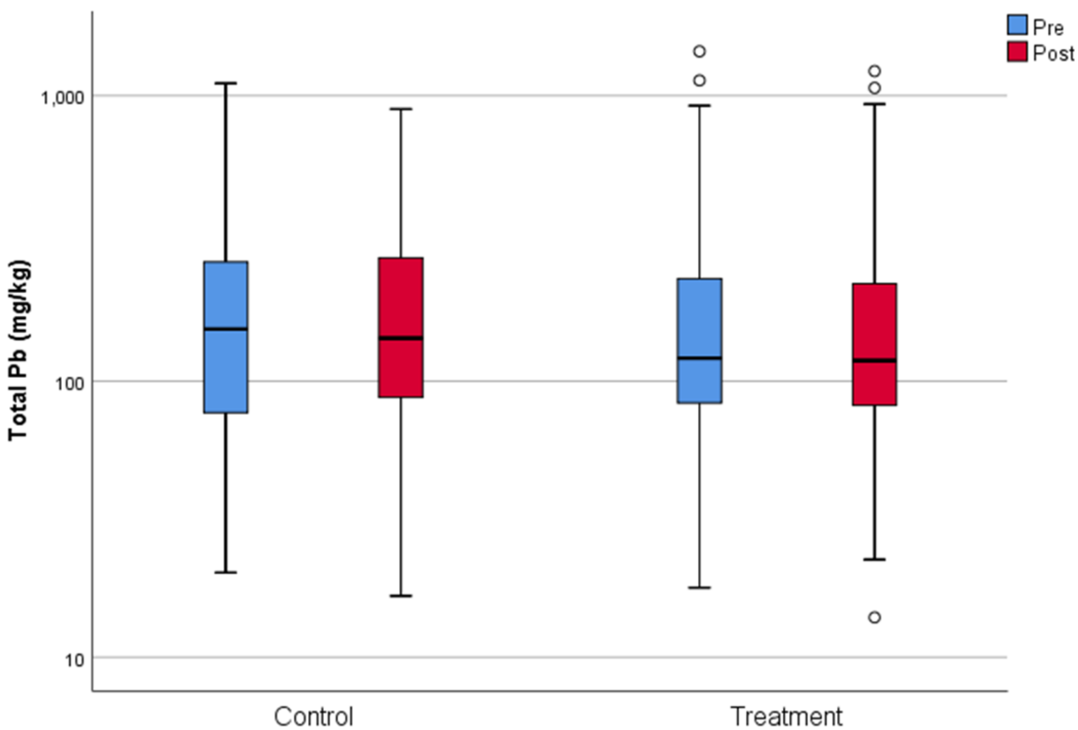

Figure 5.3. Total soil lead pre- and post-treatment for both controls and treatments. Note log-scale.

Results for changes in OM are shown in Figure 5.4. The amount of OM in pre and post samples were strongly correlated (Pearson $r = 0.828$, $p < 0.0005$). No significant change (pre vs. post) was observed in OM across all samples (t-test of log-transformed variables, $t=1.280$, $N=142$, $p = 0.203$). When the dataset was split into control and treatment groups and analyzed separately, the strong correlation (Pearson $r \geq 0.884$, $p < 0.0005$) and lack of a significant difference between pre and post measurements of soil OM (t-test, $p > 0.164$) remained.

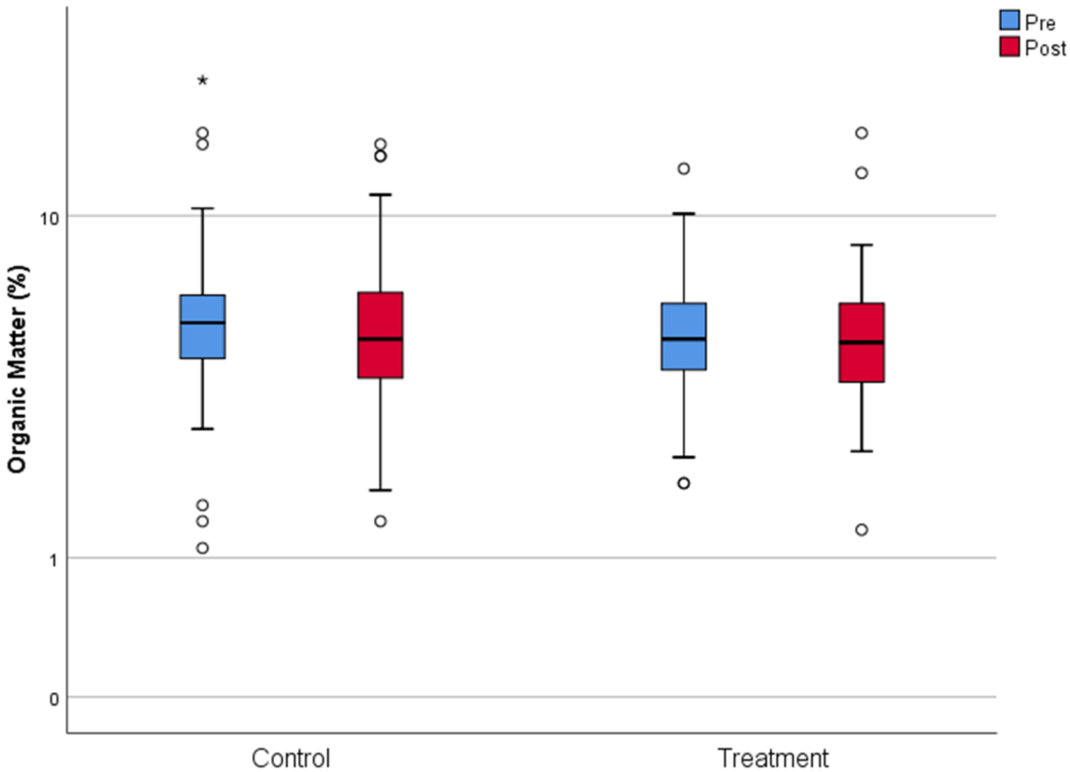

Figure 5.4. Soil organic matter pre- and post-treatment for both controls and treatments. Note log-scale.

Results for pH are shown in Figure 5.5. Like total lead and OM, there was a strong correlation (Pearson r = 0.837, p < 0.0005) between pre and post soil pH measurements. However, a significant change (pre vs. post) in the soil pH was detected across all samples (t-test, t=9.827, N=142, p < 0.0005). The strong correlation (Pearson r ≥ 0.798, p < 0.0005) and significant difference between pre and post measurements of soil pH (t-test, p < 0.0005) remained when splitting the dataset into control and treatment groups.

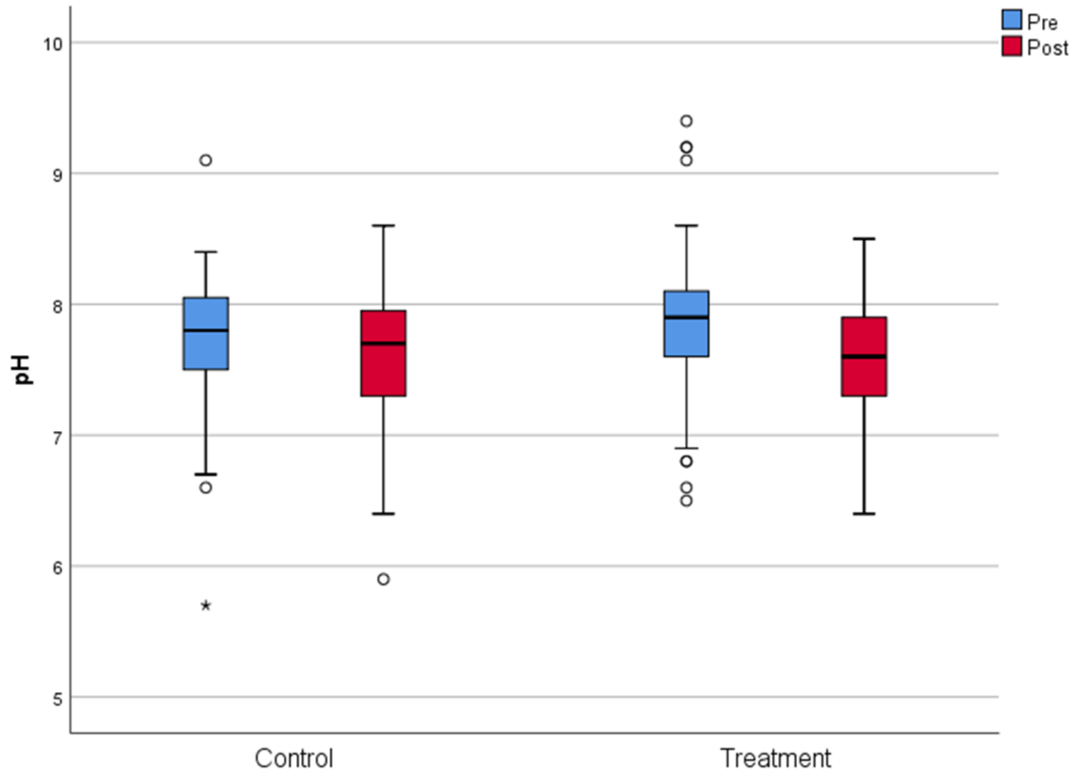

Figure 5.5. Soil pH pre- and post-treatment for both controls and treatments.

Results for phosphorus are shown in Figure 5.6. Like total lead, OM, and pH, there was a correlation (Pearson $r = 0.516$, $p < 0.0005$) between pre and post soil phosphorus measurements. However, a significant change (pre vs. post) in phosphorus was detected across all samples (t-test of log-transformed variables, $t = -11.852$, $N = 140$, $p < 0.0005$). The strong correlation (Pearson $r \geq 0.545$, $p < 0.0005$) and significant difference between pre and post measurements of phosphorus (t-test, $p < 0.0005$) remained when splitting the dataset into control and treatment groups. The average change across all samples in this study for phosphorus was +3.0 mg P/kg (with a standard deviation of 3 mg P/kg) and pH was -0.57 pH units.

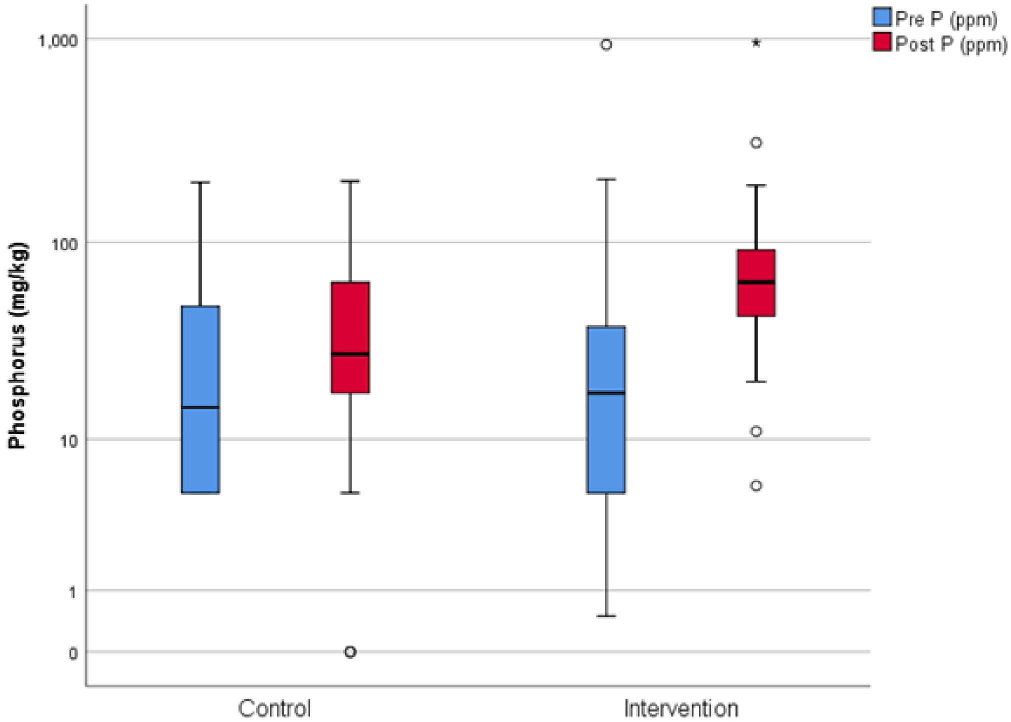

Figure 5.6. Soil phosphorus pre- and post-treatment for both controls and treatments. Note log-scale.

Regression Analysis

To determine how the bone meal soil amendment affected *in-vitro* bioaccessibility of lead in Detroit soils, a series of multiple linear regression models were developed based on the following equation:

$$y_i = \beta_0 + \beta_1 x_{1,i} + \cdots + \beta_k x_{k,\,i} + \epsilon_i \qquad \text{Equation 1}$$

where *y* is the post-treatment $\log_{10}$ IVBA (mg/kg) , x are predictors variables, β are model fit parameters, ϵ is the model error (i.e. residuals), k is the number of predictors, i is the sample, and $\epsilon_i \sim N(0, \sigma^2)$. All variables - with the exception of pH, change in pH, and change in phosphorus - were log-transformed. Descriptive statistics for these model variables are shown in Table 5.2.

Table 5.2. Descriptive statistics of model variables.

Study Group	Measure		N	Minimum	Maximum	Mean	Standard Deviation	Skewness
Control	Log_{10} CEC (meq/100g)	Pre	56	0.980	1.690	1.292	0.133	0.119
		Post	56	0.990	1.700	1.371	0.133	-0.503
	Log_{10} IVBA (mg/kg)	Pre	56	0.870	2.710	1.733	0.465	0.229
		Post	56	0.760	2.670	1.771	0.452	0.124
	Log_{10} Organic matter (%)	Pre	56	0.040	1.310	0.721	0.214	-0.443
		Post	56	0.150	1.170	0.702	0.196	0.005
	pH	Pre	56	5.7	9.1	7.73	0.55	-1.059
		Post	56	5.9	8.6	7.57	0.52	-1.052
	Log_{10} Total Phosphorus (mg/kg)	Pre	56	0.700	2.300	1.256	0.533	0.437
		Post	54	0.700	2.300	1.518	0.378	0.121
	Log_{10} Total Lead (mg/kg)	Pre	56	1.320	3.04	2.18	0.39	0.049
		Post	56	1.230	2.95	2.18	0.38	-0.128
	Log_{10} Phosphorus Change (mg/kg)		54	-0.530	1.270	0.272	0.399	0.117
	pH Change		56	-0.800	0.300	-0.154	0.227	-0.468
Treatement	Log_{10} CEC (meq/100g)	Pre	85	1.030	1.750	1.310	0.138	0.374
		Post	85	1.070	1.730	1.384	0.132	-0.319
	Log_{10} IVBA (mg/kg)	Pre	85	0.770	3.020	1.697	0.435	0.643
		Post	85	0.720	2.910	1.696	0.413	0.483
	Log_{10} Organic matter (%)	Pre	85	0.280	1.110	0.695	0.151	-0.244
		Post	85	0.110	1.190	0.688	0.157	-0.156
	pH	Pre	85	6.5	9.4	7.86	0.53	0.124
		Post	85	6.4	8.5	7.55	0.47	-0.692
	Log_{10} Total Phosphorus (mg/kg)	Pre	85	-0.300	2.970	1.202	0.571	0.126
		Post	85	0.740	2.980	1.809	0.298	0.065
	Log_{10} Total Lead (mg/kg)	Pre	85	1.260	3.150	2.133	0.362	0.493
		Post	85	1.150	3.090	2.122	0.363	0.437
	Log_{10} Phosphorus Change (mg/kg)		85	-0.360	1.810	0.607	0.480	0.414
	pH Change		85	-1.500	0.900	-0.306	0.324	-0.249

Previously, Chapter 4, we found that a regression model based on the total lead concentration, the amount of soil OM, and the pH of soil explained 94% of *in vitro* bioaccessibility of lead in soil (Table 4.7). To determine if bone meal amendments have a significant impact on bioaccessibility, we begin our statistical analysis using the same construct, but add a dummy variable to account for the treatment effect [1 if the sample received the bone meal amendment, 0 if no treatment was received (i.e. control)]. As described above, the difference in OM and total lead before and after treatment, for both treatment and control groups, was not significantly different. However, because we expect and observe changes in pH, we continue to use the pre-treatment measurements of total lead, OM, and pH (Model 1). Models which utilize pre-treatment variables are shown in Table 5.3.

Table 5.3. Model results describing lead *in vitro* bioaccessibility following bone meal remediation.

	Model 5.1	Model 5.2	Model 5.3	Model 5.4
Model Fit				
Adjusted r^2	0.918	0.920	0.927	0.929
F-statistic	392.461	398.731	446.104	364.553
p-value	<0.0005	<0.0005	<0.0005	<0.0005
N	141	139	141	139
Parameters				
Log_{10} OM (%)	**Pre**	**Pre**	**Pre**	**Pre**
β-value estimate	-0.432	-0.473	-0.435	-0.469
β-value 95% CI	(-0.556, -0.308)	(-0.599, -0.346)	(-0.552, -0.318)	(-0.587, -0.35)
p-value	<0.0005	<0.0005	<0.0005	<0.0005
Log_{10} P (mg/kg)				
β-value estimate				
β-value 95% CI				
p-value				
Log_{10} Pb (mg/kg)	**Pre**	**Pre**	**Pre**	**Pre**
β-value estimate	1.129	1.123	1.140	1.132
β-value 95% CI	(1.073, 1.186)	(1.067, 1.18)	(1.086, 1.193)	(1.079, 1.186)
p-value	<0.0005	<0.0005	<0.0005	<0.0005
pH	**Pre**	**Pre**	**Pre**	**Pre**
β-value estimate	0.113	0.105	0.153	0.146
β-value 95% CI	(0.072, 0.155)	(0.196, -0.024)	(0.11, 0.196)	(0.103, 0.189)
p-value	<0.0005	<0.0005	<0.0005	<0.0005
Treatment (Dummy)				
β-value estimate	-0.045			
β-value 95% CI	(-0.087, -0.002)			
p-value	0.039			
Log_{10} P Change (mg/kg)				
β-value estimate		-0.063		-0.050
β-value 95% CI		(-0.108, -0.019)		(-0.092, -0.008)
p-value		0.005		0.021
pH Change				
β-value estimate			0.173	0.160
β-value 95% CI			(0.1, 0.246)	(0.087, 0.233)
p-value			<0.0005	<0.0005
Constant				
β-value estimate	-1.256	0.201	-1.571	-1.460
β-value 95% CI	(-1.653, -0.859)	(-1.549, -0.748)	(-1.968, -1.175)	(-1.863, -1.057)
p-value	<0.0005	<0.0005	<0.0005	<0.0005

Model 5.1 finds a significant treatment effect ($\beta = -0.045 \pm 0.042$; $p = 0.039$) which indicates bioaccessibility is reduced by 0.045 mg/kg on average. It is important to note that regression coefficients

for the other variables (Table 5.3, Model 5.1) were similar to those reported previously (Table 4.7, Model 4.1), with the largest change being associated with pH (15% greater when including the treatment effect).

Because the primary mechanism responsible for reducing bioaccessibility is likely due to phosphorus enhanced mineral formation, the change in phosphorus was used as predictor variable (Model 5.2). Recall from Chapter 4 (Model 4.2), phosphate concentrations in soil prior to treatment were not significant predictors of bioaccessibility ($p=0.873$). The change in phosphorus best describes the impact of the bone meal amendment. This model was slightly better at predicting *in-vitro* bioaccessibility ($r^2 = 0.920$) than Model 5.1 ($r^2=0.918$). The result of this analysis finds the regression coefficients were within 7% of those obtained pre-treatment (Table 4.7, Model 4.1).

Since there was a significant change in pH (t-test, $t=9.827$, $N=142$, $p < 0.0005$) pre-treatment vs. post-treatment, Model 5.3 incorporates this change in pH and determine its impact on *in-vitro* bioaccessibility. The model fit was again improved slightly, predicting *in-vitro* bioaccessibility with an $r^2 = 0.927$. Based on this model, the regression coefficient for pH was 56% larger than those obtained in Models 5.1-5.2, while total lead and soil OM remained within 3% and 12%, respectively, of pre-treatment values (Table 4.7, Model 4.1).

To incorporate the changes in soil chemistry by addition of the bone meal soil amendment, both changes in pH and changes in phosphorus were used as predictor variables, while maintaining pre-treatment measurements for total lead, organic matter, and pH (Model 5.4). This model was better at predicting *in-vitro* bioaccessibility than either Model 5.1, 5.2, or 5.3 ($r^2 = 0.929$), although it changed the regression coefficient for pre-treatment pH by 49% compared to results found in Chapter 4, while the coefficients for total lead and organic matter were similar to those found previously, by 4% and 6%, respectively (Table 4.7, Model 4.1).

Due to the strong correlation between total and *in-vitro* bioaccessible lead (Pearson $r = 0.983$, $p < 0.0005$), Model 1 was revised to incorporate the post-treatment (for both control and treatment groups) total lead concentration (Model 5.5). All models which used post-treatment measurements as variables are shown in Table 5.4. While this model was slightly better at predicting the *in-vitro* bioaccessibility of lead (r^2 = 0.930), the treatment effect is similar (β = -0.034 ± 0.039; p = 0.089) and treatment was not found to be significant at the 0.05 level (p=0.089).

Table 5.4. Model results describing lead *in vitro* bioaccessibility following bone meal remediation (continued).

	Model 5.5	Model 5.6	Model 5.7	Model 5.8
Model Fit				
Adjusted r2	0.930	0.938	0.937	0.939
F-statistic	462.896	703.329	525.818	532.515
p-value	<0.0005	<0.0005	<0.0005	<0.0005
N	141	141	141	141
Parameters				
Log_{10} OM (%)	**Pre**	**Post**	**Post**	**Post**
β-value estimate	-0.429	-0.483	-0.485	-0.463
β-value 95% CI	(-0.544, -0.315)	(-0.598, -0.367)	(-0.6, -0.369)	(-0.58, -0.347)
p-value	<0.0005	<0.0005	<0.0005	<0.0005
Log_{10} P (mg/kg)				**Post**
β-value estimate				-0.054
β-value 95% CI				(-0.107, -0.001)
p-value				0.046
Log_{10} Pb (mg/kg)	**Post**	**Post**	**Post**	**Post**
β-value estimate	1.144	1.143	1.141	1.155
β-value 95% CI	(1.091, 1.197)	(1.093, 1.192)	(1.091, 1.191)	(1.104, 1.206)
p-value	<0.0005	<0.0005	<0.0005	<0.0005
pH	**Pre**	**Post**	**Post**	**Post**
β-value estimate	0.105	0.107	0.106	0.104
β-value 95% CI	(0.066, 0.143)	(0.066, 0.148)	(0.064, 0.148)	(0.063, 0.146)
p-value	<0.0005	<0.0005	<0.0005	<0.0005
Treatment (Dummy)				
β-value estimate	-0.034		-0.045	
β-value 95% CI	(-0.073, 0.005)		(-0.05, 0.023)	
p-value	0.089		0.468	
Constant				
β-value estimate	-1.223	-1.198	-1.179	-1.256
β-value 95% CI	(-1.59, -0.856)	(-1.58, -0.816)	(-1.565, -0.792)	(-1.653, -0.859)
p-value	<0.0005	<0.0005	<0.0005	<0.0005

Rather than evaluating the treatment effect using a dummy variable, another approach was to use the post-treatment (for both control and treatment groups) measures for the total lead concentration, the amount of soil OM, and the pH in the regression model (Model 5.6). If these parameters explain the *in-vitro* bioaccessible lead, they should be similar to those measured prior to treatment. Again, the result of this analysis finds the regression coefficients were like those obtained previously. All coefficient estimated were within 10% and 12% of those measured using values pre-treatment measurements with (Table 5.3, Model 5.1) and without (Table 4.7, Model 4.1) considering the treatment effect, respectively.

When attempting to measure the treatment effect using post-treatment measures of all predictors (Model 5.7), the treatment variable was not found to be significant ($p = 0.468$). However, all other predictors (total lead, OM, pH) in Model 5.7 were significant ($p < 0.0005$) and again similar to those measured prior to treatment (Model 5.1).

Because the primary mechanism responsible for reducing bioaccessibility is thought to be due to phosphorus enhanced mineral formation, it is reasonable that the treatment effect should be observed in the elevated phosphate concentrations in soils receiving bone meal (Model 5.4). Recall that the concentration of phosphorus in soil was not significant in the pre-treatment samples (Table 4.7, Model 4.3). When using post-treatment samples (control and treatment groups), phosphate concentrations were a significant predictor of IVBA ($\beta = -0.054 \pm 0.053$; $p = 0.046$). Importantly, the impact of soil phosphorus post-treatment on IVBA was similar to the treatment effect estimated previously, with other predictors remaining about the same (Model 5.1).

Effect of Bone Meal Amendment

The regression coefficients from Model 5.1 were used to estimate the change in bioaccessibility when the bone meal soil amendment was applied to soils. Mean concentrations of total lead and organic matter, and pH observed prior to treatment, *in-vitro* bioaccessible lead is estimated to be 56.4 mg/kg (39.7%). Post-treatment results estimate a 9.8% decrease in bioaccessible lead to 50.8 mg/kg (35.8%). Based on this same model (Model 5.1), when using 95th percentile total lead (806 mg/kg), and all other coefficients held at their mean, a decrease in bioaccessible lead from 400.5 mg/kg (49.7%), to 361 mg/kg (44.8%), is predicted (95% CI: +0.6% to +18.2%).

Model 5.4 was developed in an attempt to quantify how phosphorus dose alters lead bioaccessibility. When using mean values for all predictors, and no change in phosphorus, *in-vitro* bioaccessible lead is estimated to be 56.1 mg/kg (39.5%). When using mean values for all predictors, including the change in phosphorus, the *in-vitro* bioaccessible lead is predicted to be 53.1 mg/kg (37.4%), a decrease of 5.3% in bioaccessibility relative to no treatment (95% CI: -3.3% to +5.8%). If phosphorus levels were increased by 3.0 mg/kg (one standard deviation), bioaccessibility would decrease further to 50.3 mg/kg (35.4%); a 10.4% reduction in *in-vitro* bioaccessible lead relative to no treatment (95% CI: -14.2% to +5%). When using 95th percentile pre-treatment total lead, and holding all other predictors at their mean, *in-vitro* bioaccessible lead with no change in phosphorus is estimated to be 400.4 mg/kg (49.7%). When using mean values for all predictors, including the change in phosphorus, the *in-vitro* bioaccessible lead is predicted to be 379.1 mg/kg (47%), a decrease of 5.3% in bioaccessible lead relative to no treatment. If phosphorus change were increased by 3.0 mg/kg (one standard deviation), bioaccessible lead would decrease further to 358.9 mg/kg (44.5%); a 10.4% reduction in *in-vitro* bioaccessible lead relative to no treatment. Confidence intervals for 95th percentile total lead and mean total lead results are consistent with one another.

IEUBK Modeling

Results from the sensitivity analysis performed using the US EPA's IEUBK model to predict how treating soils with a bone meal soil amendment would affect children's blood lead levels are presented in Figure 5.7. For reference, a concentration of 5 µg/dL is considered an elevated blood lead level (CDC, 2020). Assuming an exposure to soils with 142 mg/kg total lead (mean observed in this study), the geometric mean BLL was estimated to be 2.64 µg/dL. Following treatment, the geometric mean BLL is estimated to be 2.46 µg/dL, a 6.7% reduction pre- to post-treatment. For 95th percentile total lead, models predicted a decrease from 9.39 µg/dL (pre-treatment) to 8.7 µg/dL (post-treatment) following treatment, a reduction of 6.6%. The percentages of children exceeding this guideline (>5 µg/dL) dropped from 8.7% to

6.6% for mean total soil lead, and from 95.5% to 93.7% in 95th percentile total soil lead. Distribution curves for geometric mean blood lead levels and percent exceeding 5 µg/dL are shown in Appendix C.

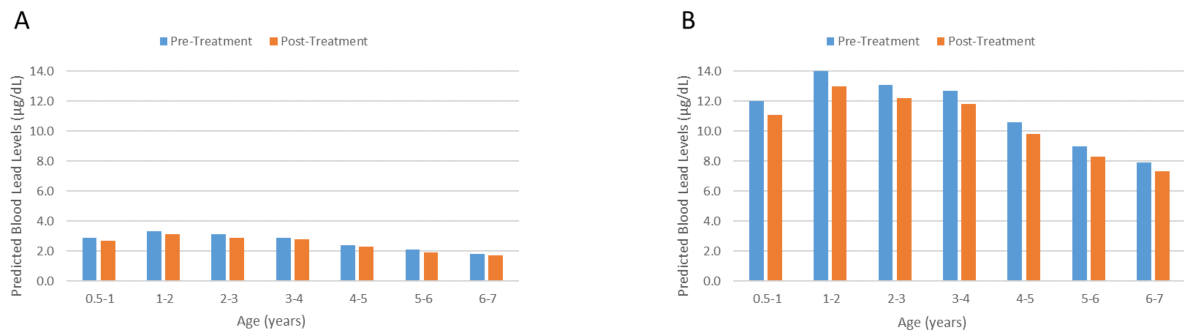

Figure 5.7. Predicted BLLs pre-treatment and post-treatment for (a) mean total lead and (b) 95th percentile total lead.

Figure 5.8 demonstrates how change in phosphorus content (pre vs. post) impact children's BLLs. For this is analysis, Model 4 (Table 5.3) regression parameters were used. Three scenarios were evaluated: 1) when *no change* in phosphorus concentrations pre- to post-treatment (0 mg P/kg); 2) when the soil phosphorus concentration increases by 3.0 mg P/kg, the mean change in soil phosphorus observed during this study; and 3) when the soil phosphate concentration increases by 6.0 mg/kg, the mean change in phosphorus observed in this study plus one standard deviation.

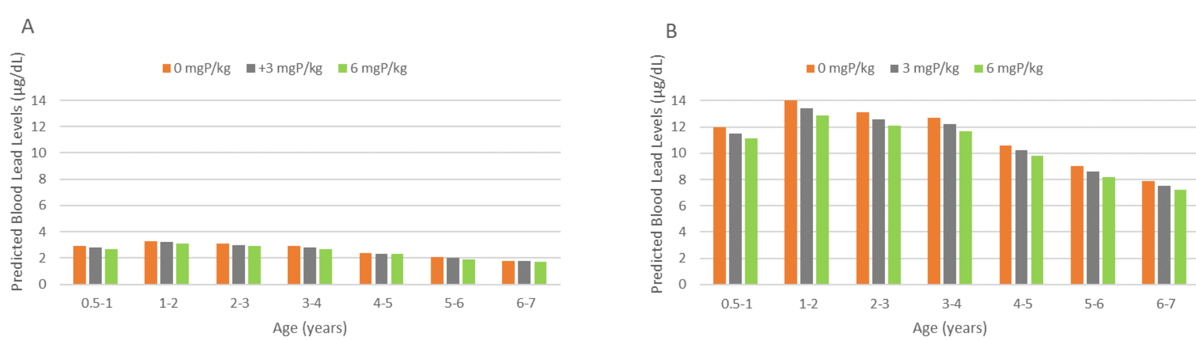

Figure 5.8. Impact on child BLLs resulting from a change in soil phosphate content assuming (a) mean total lead and (b) 95th percentile total lead.

For mean total lead, models showed an expected geometric mean BLL of 2.63 µg/dL when no phosphorus change occurs. This decreases to 2.54 µg/dL when accounting for our treatment (+3 mgP/kg), a decrease of 3.6%. When the phosphorus change is increased to 6 mg P/kg, geometric mean BLLs are predicted to be 2.44 μg/dL, a decrease of 7.1% from those with no treatment. For 95th percentile total lead, models predicted a decrease from 11.1 μg/dL with no treatment to 10.65 μg/dL post-treatment, a reduction of 4%. When increasing the change in phosphorus from 3 to 6 mg/kg, BLL predictions drop to 10.23 μg/dL, a decrease of 7.8% compared to if no phosphorus change occurs.

Assuming mean total lead concentrations, the percentages of children with EBLLs (>5 μg/dL) would be expected to drop from 8.6% to 7.4% following the treatment applied in this study (2.6 g P/ft^2). If the amount of phosphorus were to increase to 5.2 g P/ft^2 decreased to 6.9% when assuming an increase of one standard deviation in phosphorus change. For 95th percentile total lead, the percentages of children exceeding this guideline dropped from 95.5% to 94.6% when using our mean treatment (2.6 g P/ft^2) and decreased to 93.6% if the does increased to 5.2 g P/ft^2. Distribution curves for geometric mean blood lead levels and percent exceeding 5 μg/dL are shown in Appendix C.

Discussion

The lack of significant change in total lead concentrations pre- and post-treatment demonstrated no lead was added to or removed from the sample locations during this study. Similarly, no significant change in OM was observed pre- and post-treatment. Results for pH showed a significant correlation, and a significant change pre- and post-treatment, with pH decreasing slightly after treatment with the bone meal soil amendment. It is likely that this decrease in soil pH is due in part to the acidic nature of the liquified bone meal (pH 5.0 – 5.5).

We hypothesized that the application of a liquified bone meal soil amendment would result in reduced bioaccessibility of lead in soil. Our results (Model 1) are consistent with this hypothesis, finding that 2.6 g P/ft^2 bone meal applied to soil resulted in a 9.8% decrease in *in-vitro* bioaccessibility of lead. Based on IEUBK modeling, this decrease in lead bioavailability is predicted to decrease geometric mean

BLLs by 6.7% in typical Detroit soils (142 mg/kg) with mean total lead, and by 6.6% for soils with 95^{th} percentile total lead in soils (806 mg/kg).

Results were consistent with the hypothesis that as phosphorus levels in the soil increase, the bioaccessibility of lead in the soil will decrease. A significant relationship between phosphorus levels (mg/kg) and lead bioaccessibility (Model 8, $p = 0.046$) were observed. Similarly, the change in phosphorus resulted in a significant decrease in lead bioaccessibility (Model 4, $p = 0.021$). In this study, we added 2.6 g of phosphorus per square foot to sampling locations. The mean change in phosphorus was 3 mg/kg. This was estimated to decrease the *in-vitro* bioaccessibility 5.3%. If the phosphorus application rate increased to 5.2 g P/ft^2 would decrease *in-vitro* bioaccessibility of lead by 10.4%.

Lead is ubiquitous in the urban soil environment and poses a serious threat to the children of Detroit. In 2014, when the Michigan Department of Community Health (MDCH) tested 34.6% of the children under six in Detroit for BLLs, 10.6% of the children tested showed BLLs at or above 5 µg/dL (Moody et al., 2016). IEUBK modeling based on default parameter estimates and the mean soil lead concentrations (total and bioaccessible fraction) predicted 10.4% of children under the age of 6 (based on geometric mean) would have a BLL exceeding 5 µg/dL. The results of this study suggest it is reasonable that the number of children with EBLLs (>5 µg/dL) could be reduced by about 2% if the bone meal remediation used in this study was applied across the City of Detroit.

The bone meal amendment was aged in soil for approximately 9 months. It is possible that the bioaccessibility of lead in these soils could continue to decrease as the amendment ages in the soil. Ryan et al. (2004) reported reductions in the bioaccessibility of their soils of 29% when their 1% phosphorus amendment was aged for 3 months, with an increased reduction of 71% after 32 months, and decreases of 32% for 3 months and 52% at 32 months for their 0.5% phosphorus amendment. Further sampling and characterization should be conducted to determine the temporal effects of bone meal on lead bioaccessibility.

To determine if the decreases in bioaccessibility are attributed to lead-phosphate formation, mineralogical analysis would need to be conducted to identify the mineral species present before and after treatment with a bone meal soil amendment. It is important to reiterate that this study utilized an *in-vitro* methodology which estimates the amount of lead that would absorb into the bloodstream, and may not be perfectly representative of actual *in-vivo* bioavailability measurements, such as those studies which have assessed the effect of phosphate amendments on lead bioavailability on swine, rats, or humans (Scheckel et al., 2013).

Conclusions

Many remediation techniques for the removal of lead from soil are expensive, disruptive to the soil ecosystem, and require heavy machinery and expertise. There is urgent need for a low-cost, accessible treatment for lead in soils. In this study, we find a bone meal amendment to Detroit residential soils resulted in a 9.8% decrease in *in-vitro* bioaccessibility of lead. This reduction in *in-vitro* bioaccessibility is estimated to reduce the proportion of children under 6 years old with BLLs greater than 5 μg/dL by approximately 2%. Higher dosing of bone meal amendments to soils are likely to reduce this proportion further. Even low levels of exposure to lead can result in learning and behavioral issues, and there is no safe level of lead in the body (Zhang et al., 2013). Results of this study suggest soil amendments using liquid bone meal could enhance the wellbeing of Detroit children. Further trials are needed to determine to the accuracy of BLL reductions.

APPENDIX A: FORMS AND DIAGRAMS

SAMPLING DATA COLLECTION FORM

Name	**Date:**
Address:	
Phone: **Email:**	

1.	What is your preferred communication method?		
	☐ Phone call ☐ Text ☐ Email		
2.	Do you want to be included in the raffle/drawing?	☐ Yes	☐ No
3.	How is this soil being used?		
	☐ Vegetable garden ☐ Flower garden ☐ Farm ☐ Children's play area ☐ Grass area ☐ Orchard		
4.	Last lead(Pb) content measured (if available):		
	Units (ppm, mg/kg, etc.) ____________ Total or extracted (if known) ____________ Who tested? ____________ Date sampled:____________		
5.	General description of soil (choose all that apply)		
	☐ Clay ☐ Silty ☐ Sandy ☐ Backfill (construction debris) ☐ Dark brown ☐ Light brown ☐ Very light brown		
6.	**Please sketch a map of the garden area** Include ○ Orientation (north arrow) ○ Three landmarks and the distance to each ○ Soil sampling location		
7.	GPS Location of stake:		

Staff Name:

Figure A1. Data collection form.

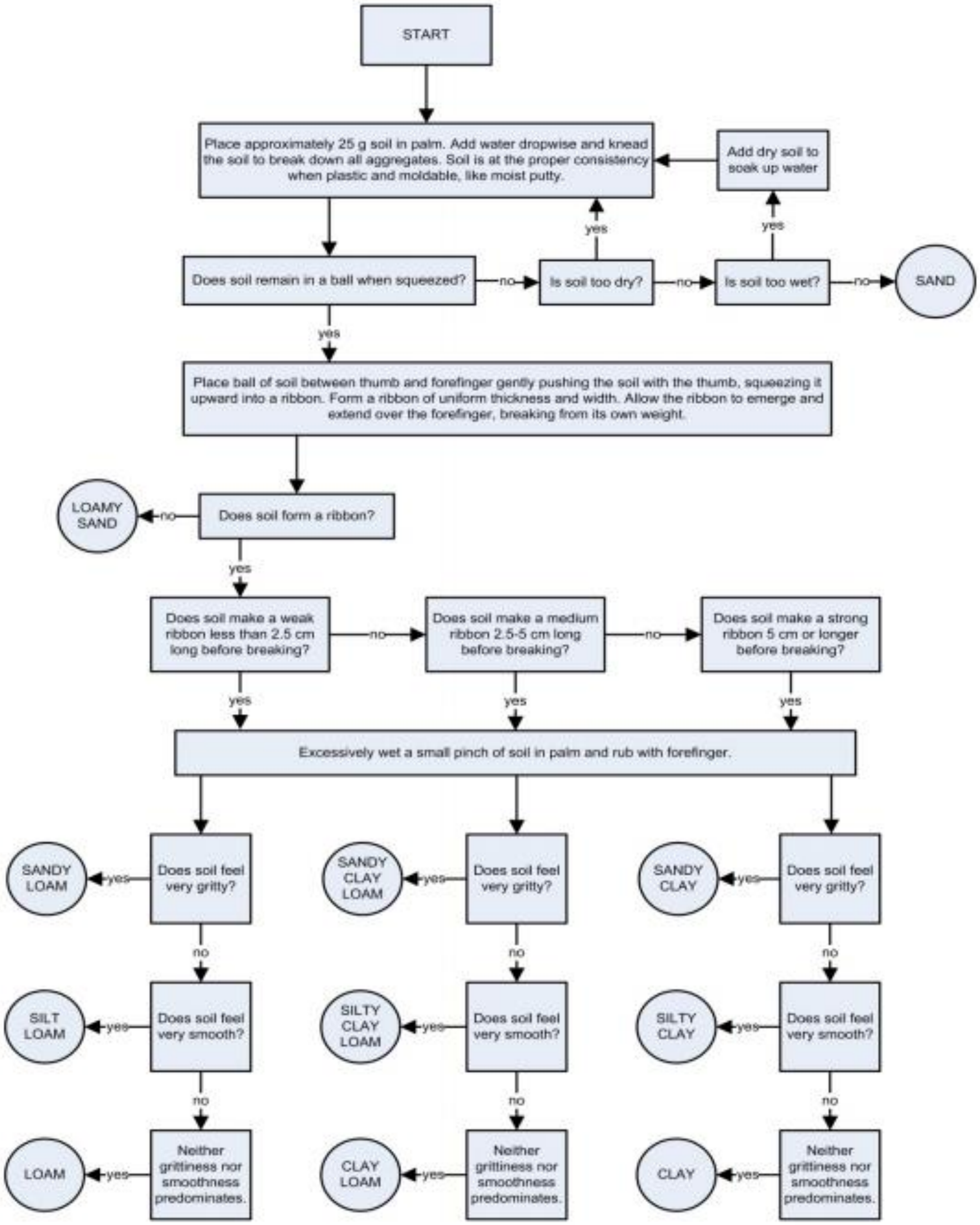

Figure A2. Flow chart for NRCS Texture by Feel Method (Burt, 2014).

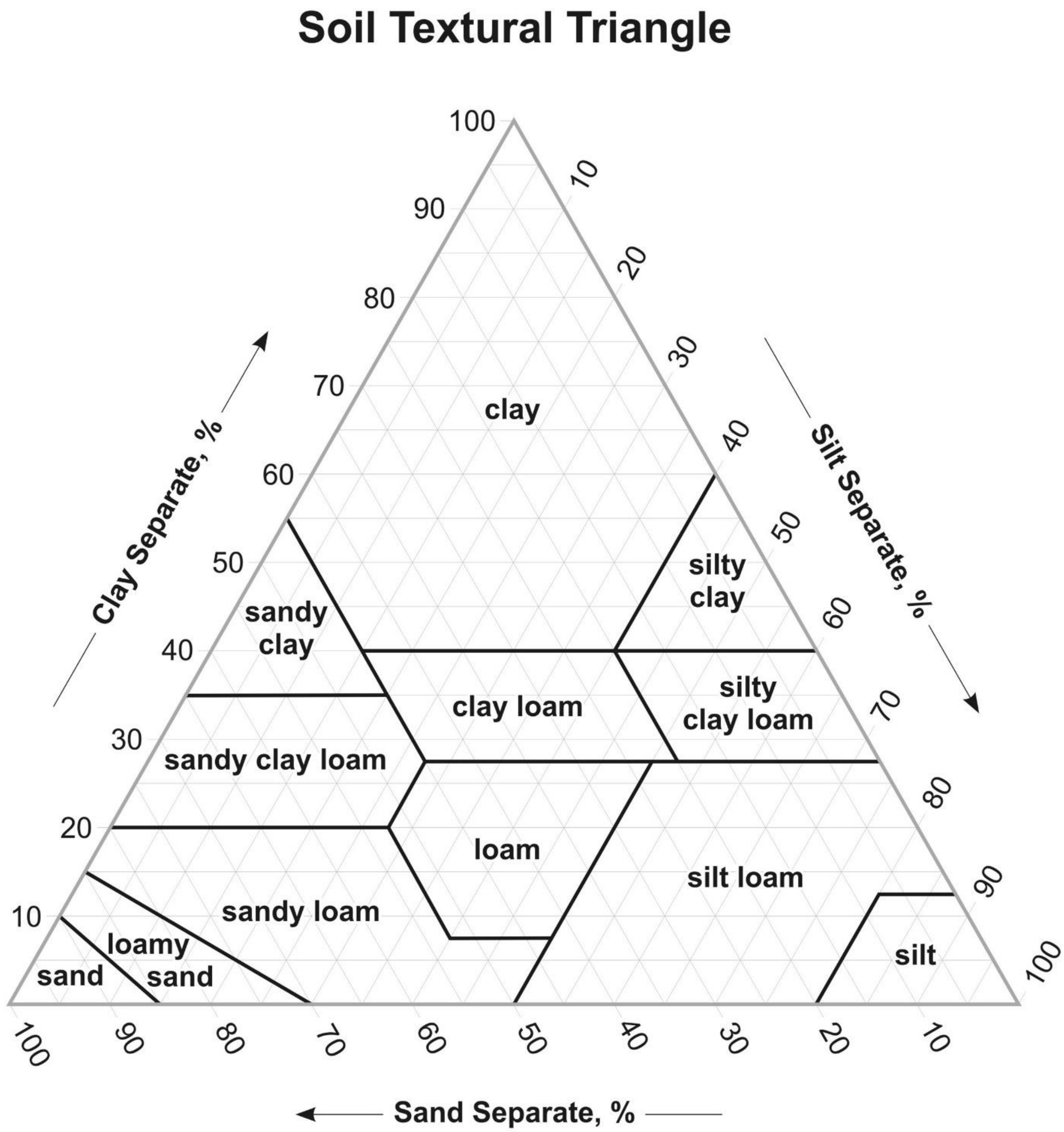

Figure A3. USDA Soil Textural Triangle (Burt, 2014).

APPENDIX B: DATASET

Table B1. Data dictionary.

Variable	Description
CompZmax	Maximum value for each smelter, multiple of z-scores of inverse distance and z-score of bearing angle
CompZmean	Mean value for each smelter, multiple of z-scores of inverse distance and z-score of bearing angle
DaysAged	Number of days that amendment aged in the field
DistSmelt	Distance to nearest smelter (miles)
DLclay	Fraction (%) clay (determined by Dairyland Labs)
DLsand	Fraction (%) sand (determined by Dairyland Labs)
DLsilt	Fraction (%) silt (determined by Dairyland Labs)
DLtexture	NRCS Soil Texture (determined by Dairyland Labs)
DWSmelter	Site was downwind (+/- 45 degrees)
DWSmelterSum	Number of smelters the sampling was downwind from (+/- 45 degrees)
FillStatus	Identification of non-native soils
Flag	Sample may be censored due to outlier (depends on analysis)
Group	Study site received intervention or control treatment
Notes	Notes
PostCappm	Post Ca (mg/kg)
PostCEC	Post CEC (meq/100g)
PostIVBAmgkg	Post IVBA (mg/kg)
PostIVBAperc	Post In Vitro Bioaccessible lead (%)
PostKppm	Post K (mg/kg)
PostMgppm	Post Mg (mg/kg)
PostModelFactors	Variables included or excluded in regression models describing post-treatment conditions
PostNappm	Post Na (mg/kg)
PostOM	Post Organic matter (%)
PostpH	Post pH
PostPppm	Post P (mg/kg)
PostRBA	Post Est. Relative Bioavailability (RBA)
PostSppm	Post S (mg/kg)
PostTotalPb	Post Total lead (mg/kg)
PreCappm	Pre Ca (mg/kg)
PreCEC	Pre CEC (meq/100g)
PreIVBAmgkg	Pre IVBA (mg/kg)
PreIVBAperc	Pre In Vitro Bioaccessible lead (%)
PreKppm	Pre K (mg/kg)
PreMgppm	Pre Mg (mg/kg)
PreModelFactors	Variables included or excluded in regression models describing pre-treatment conditions
PreNappm	Pre Na (mg/kg)

PreOM	Pre Organic matter (%)
PrepH	Pre pH
PrePppm	Pre P (mg/kg)
PreRBA	Pre Est. Relative Bioavailability (RBA)
PreSppm	Pre S (mg/kg)
PreTotalPb	Pre Total lead (mg/kg)
PubID	Unique Sample Identifier
SmelterModelFactors	Variables included or excluded in regression models describing relationship to smelters
SoilTexture	Soil Texture (based on NRCS Feel Method)

Table B2. Lead measurements.

PubID	PreTotalPb	PostTotalPb	PreIVBAperc	PostIVBAperc	PreIVBAmgkg	PostIVBAmgkg	PreRBA	PostRBA
1	256.46	339.49	54.47	53.16	139.70	180.47	0.45	0.44
2	355.65	363.74	48.00	48.82	170.70	177.59	0.39	0.40
3	232.73	280.05	50.95	41.12	118.58	115.16	0.42	0.33
4	49.55	58.51	41.54	40.44	20.58	23.66	0.34	0.33
5	96.37	83.16	31.09	40.02	29.96	33.28	0.24	0.32
6	64.05	62.38	25.37	25.84	16.25	16.12	0.19	0.20
7	118.33	107.49	25.22	29.15	29.84	31.33	0.19	0.23
8	685.16	657.19	54.34	59.87	372.33	393.48	0.45	0.50
9	21.62	23.11	59.52	72.21	12.87	16.69	0.49	0.61
10	29.50	32.20	35.95	45.32	10.60	14.59	0.29	0.37
11	108.69	120.93	27.19	41.32	29.56	49.97	0.21	0.33
12	64.78	63.59	16.51	17.25	10.69	10.97	0.12	0.12
13	60.32	67.33	47.54	52.89	28.68	35.61	0.39	0.44
14	27.12	31.72	35.16	40.58	9.54	12.87	0.28	0.33
15	101.51	109.86	23.86	24.15	24.23	26.53	0.18	0.18
16	81.06	81.06	34.15	22.61	27.68	18.33	0.27	0.17
17	102.48	90.07	28.58	26.89	29.29	24.22	0.22	0.21
18	1427.76	1217.83	73.13	67.27	1044.13	819.28	0.61	0.56
19	102.66	82.29	53.23	56.85	54.65	46.78	0.44	0.47
20	74.54	87.92	31.91	29.47	23.79	25.91	0.25	0.23
21	61.87	65.10	39.07	38.90	24.17	25.32	0.32	0.31
22	68.94	71.99	35.09	34.49	24.19	24.83	0.28	0.27
23	157.71	164.50	28.99	41.60	45.72	68.42	0.23	0.34
24	246.84	536.26	52.96	86.74	130.72	465.14	0.44	0.73
25	459.13	447.30	43.10	37.22	197.89	166.48	0.35	0.30
26	195.77	202.83	40.41	42.80	79.11	86.82	0.33	0.35
27	176.70	152.11	27.96	33.23	49.40	50.54	0.22	0.26
28	164.53	133.43	48.82	54.43	80.33	72.63	0.40	0.45
29	119.20	132.66	23.00	28.26	27.42	37.49	0.17	0.22
30	23.04	23.09	25.42	42.26	5.86	9.76	0.20	0.34
31	89.76	102.86	26.32	41.78	23.63	42.97	0.20	0.34
32	51.82	52.62	34.60	29.70	17.93	15.63	0.28	0.23
33	130.18	110.01	18.29	28.16	23.81	30.98	0.13	0.22
34	67.66	51.21	24.80	26.97	16.78	13.81	0.19	0.21
35	60.96	61.44	24.83	22.71	15.14	13.96	0.19	0.17
36	67.97	58.98	17.07	19.68	11.60	11.61	0.12	0.14
37	80.24	88.58	24.32	20.82	19.51	18.44	0.19	0.15
38	237.38	252.49	31.52	26.01	74.82	65.68	0.25	0.20
39	130.66	123.28	43.45	43.52	56.77	53.65	0.35	0.35
40	223.20	217.81	41.71	49.84	93.10	108.55	0.34	0.41

41	252.16	313.04	29.83	34.36	75.23	107.57	0.23	0.27
42	176.24	168.50	26.15	39.58	46.09	66.68	0.20	0.32
43	232.78	176.77	34.22	51.74	79.66	91.46	0.27	0.43
44	440.19	381.77	38.57	43.34	169.78	165.47	0.31	0.35
45	829.90	768.18	37.13	32.21	308.10	247.44	0.30	0.25
47	554.61	516.79	36.43	46.54	202.07	240.50	0.29	0.38
48	80.41	94.65	50.43	54.59	40.55	51.67	0.41	0.45
49	40.99	47.31	59.59	52.14	24.42	24.67	0.50	0.43
50	51.48	50.52	22.73	26.34	11.70	13.31	0.17	0.20
51	71.38	58.37	47.59	55.40	33.96	32.34	0.39	0.46
52	74.46	87.53	45.03	37.78	33.53	33.07	0.37	0.30
53	90.03	86.11	32.13	34.50	28.93	29.71	0.25	0.27
54	500.84	456.87	41.16	47.78	206.13	218.28	0.33	0.39
55	666.60	640.41	52.01	55.52	346.67	355.57	0.43	0.46
56	104.39	106.28	42.66	38.75	44.53	41.19	0.35	0.31
57	89.29	82.19	36.79	39.50	32.86	32.46	0.30	0.32
58	239.14	263.24	49.52	42.46	118.41	111.76	0.41	0.34
59	922.45	934.08	62.17	54.16	573.51	505.90	0.52	0.45
61	1103.57	897.90	46.37	52.39	511.78	470.43	0.38	0.43
62	396.31	484.07	70.03	32.44	277.54	157.03	0.59	0.26
63	121.97	144.97	41.81	53.42	51.00	77.44	0.34	0.44
64	73.63	104.73	12.00	17.06	8.84	17.87	0.08	0.12
65	74.11	72.99	30.88	35.35	22.89	25.81	0.24	0.28
66	172.06	211.48	17.53	25.50	30.16	53.93	0.13	0.20
67	53.45	59.23	41.02	38.65	21.93	22.89	0.33	0.31
68	91.36	85.24	51.80	65.02	47.32	55.43	0.43	0.54
69	61.43	64.08	49.54	37.03	30.43	23.73	0.41	0.30
70	73.02	76.13	41.53	46.02	30.33	35.04	0.34	0.38
71	84.84	110.66	49.51	55.16	42.01	61.04	0.41	0.46
72	123.68	109.04	35.86	50.84	44.35	55.44	0.29	0.42
73	113.61	123.77	37.67	44.15	42.80	54.65	0.30	0.36
74	93.77	98.56	43.87	46.38	41.14	45.72	0.36	0.38
75	143.02	153.94	46.62	44.49	66.67	68.48	0.38	0.36
76	161.83	152.53	30.03	37.19	48.60	56.72	0.24	0.30
77	89.57	76.26	14.19	20.65	12.71	15.75	0.10	0.15
78	109.97	104.45	48.83	19.41	53.70	20.27	0.40	0.14
79	145.50	135.25	27.55	40.62	40.09	54.94	0.21	0.33
80	46.31	48.24	40.32	29.94	18.67	14.44	0.33	0.23
81	99.67	92.02	22.15	19.91	22.08	18.32	0.17	0.15
82	1130.14	1063.96	42.90	23.65	484.80	251.63	0.35	0.18
83	615.78	606.20	46.06	54.40	283.62	329.77	0.38	0.45
84	188.08	164.04	56.61	57.76	106.47	94.76	0.47	0.48

85	224.23	170.99	48.33	33.21	108.36	56.78	0.40	0.26
86	102.33	101.30	25.01	25.50	25.59	25.83	0.19	0.20
87	103.93	85.83	31.54	31.02	32.78	26.62	0.25	0.24
88	79.29	83.17	46.32	30.51	36.72	25.38	0.38	0.24
89	142.14	129.89	24.89	25.48	35.38	33.10	0.19	0.20
90	323.55	274.89	57.71	59.34	186.73	163.13	0.48	0.49
91	142.24	139.57	12.00	11.44	17.07	15.96	0.08	0.07
92	205.85	250.76	38.91	40.37	80.10	101.25	0.31	0.33
93	663.73	581.41	41.75	41.70	277.10	242.45	0.34	0.34
94	229.17	219.93	40.96	46.04	93.87	101.26	0.33	0.38
95	59.22	49.55	48.05	51.38	28.46	25.46	0.39	0.42
96	180.01	153.96	35.45	40.91	63.82	62.99	0.28	0.33
97	147.13	125.56	42.35	50.58	62.30	63.51	0.34	0.42
98	148.36	137.41	36.49	45.32	54.13	62.28	0.29	0.37
99	276.00	202.15	49.41	63.61	136.38	128.59	0.41	0.53
100	151.29	171.59	43.94	52.07	66.49	89.34	0.36	0.43
101	240.83	191.17	45.59	53.67	109.80	102.59	0.37	0.44
102	29.74	24.68	70.96	72.54	21.10	17.90	0.60	0.61
103	167.92	127.74	46.10	38.72	77.41	49.46	0.38	0.31
104	301.86	294.11	39.77	45.66	120.04	134.28	0.32	0.37
105	139.00	143.64	20.87	26.54	29.01	38.12	0.16	0.21
106	242.90	275.29	41.00	42.41	99.58	116.75	0.33	0.34
107	129.43	210.66	53.05	62.39	68.66	131.42	0.44	0.52
108	139.96	167.08	42.53	47.74	59.52	79.76	0.35	0.39
109	110.80	93.46	53.11	58.55	58.85	54.73	0.44	0.49
110	46.40	44.32	50.14	59.91	23.27	26.55	0.41	0.50
111	236.17	247.15	44.60	47.26	105.34	116.81	0.36	0.39
112	210.72	250.18	56.38	56.54	118.80	141.44	0.47	0.47
113	163.85	114.96	4.53	16.44	7.43	18.90	0.01	0.12
114	20.73	16.99	41.76	34.10	8.66	5.79	0.34	0.27
115	206.08	200.63	18.96	27.85	39.06	55.88	0.14	0.22
116	832.35	800.27	65.49	65.92	545.11	527.55	0.55	0.55
117	96.84	109.47	24.75	35.65	23.97	39.02	0.19	0.28
118	123.58	106.30	27.50	32.10	33.98	34.12	0.21	0.25
119	83.86	82.18	49.78	53.80	41.75	44.21	0.41	0.44
120	334.59	355.14	39.82	37.60	133.25	133.54	0.32	0.30
121	368.11	315.89	48.94	47.67	180.14	150.58	0.40	0.39
122	496.66	484.14	45.59	48.59	226.43	235.26	0.37	0.40
123	103.75	68.93	50.36	57.76	52.25	39.81	0.41	0.48
124	111.54	92.56	22.02	37.14	34.38	34.38	0.17	0.30
125	304.83	316.06	23.21	26.78	70.76	84.63	0.18	0.21
126	76.39	78.70	23.18	21.46	17.71	16.89	0.18	0.16

127	316.43	284.03	38.42	41.68	121.58	118.37	0.31	0.34
128	208.35	208.79	46.26	45.09	96.39	94.14	0.38	0.37
129	253.37	260.73	46.46	51.29	117.73	133.72	0.38	0.42
130	213.21	217.02	34.74	40.40	74.07	87.68	0.28	0.33
131	280.16	286.41	56.76	56.10	159.01	160.67	0.47	0.46
132	114.69	127.65	20.76	22.69	23.81	28.97	0.15	0.17
133	95.32	92.05	17.60	15.77	16.78	14.51	0.13	0.11
134	88.18	93.50	57.78	38.36	50.95	35.86	0.48	0.31
135	261.98	242.03	80.89	52.41	211.92	126.84	0.68	0.43
136	118.86	92.34	42.34	56.99	50.32	52.62	0.34	0.47
137	46.36	54.33	37.97	33.48	17.60	18.19	0.31	0.27
138	97.06	115.61	35.05	26.55	34.02	30.70	0.28	0.21
139	120.29	117.89	32.84	23.70	39.50	27.94	0.26	0.18
140	971.46	816.41	45.07	45.84	437.79	374.28	0.37	0.37
141	268.42	266.89	16.97	18.53	45.55	49.45	0.12	0.13
142	18.21	14.14	37.58	36.85	6.84	5.21	0.30	0.30
143	210.73	207.84	35.86	47.62	75.57	98.97	0.29	0.39
144	196.79	210.52	32.60	22.20	64.16	46.73	0.26	0.17

Table B3. Phosphate concentrations, pH, organic matter content and cation exchange capacity of soils.

PubID	PrePppm	PostPppm	PrepH	PostpH	PreOM	PostOM	PreCEC	PostCEC
1	24.00	31.00	7.90	8.00	0.05	0.04	24.30	31.70
2	44.00	84.00	8.00	7.80	0.04	0.05	23.20	24.70
3	31.00	27.00	8.00	8.00	0.05	0.05	23.60	25.90
4	2.50	39.00	8.10	7.90	0.02	0.02	22.70	27.60
5	5.00	105.50	7.90	7.60	0.06	0.07	19.20	28.00
6	45.00	13.50	7.70	7.80	0.07	0.07	18.10	27.30
7	4.50	76.50	7.90	7.20	0.03	0.04	15.10	16.30
8	5.00	35.50	7.60	7.70	0.05	0.04	16.90	20.30
9	5.00	16.50	8.30	8.20	0.01	0.02	26.20	26.30
10	5.00	37.00	8.50	8.00	0.02	0.03	25.70	24.90
11	111.50	112.00	7.70	7.10	0.04	0.05	17.80	17.20
12	5.00	34.50	7.80	7.10	0.05	0.06	15.20	21.10
13	5.00	28.50	8.00	8.10	0.04	0.04	26.60	28.60
14	5.00	63.50	8.10	7.80	0.04	0.04	25.30	27.20
15	5.00	34.00	7.50	7.30	0.06	0.05	15.70	19.30
16	53.00	59.00	7.50	6.90	0.05	0.06	13.40	13.70
17	5.50	24.00	6.90	6.40	0.05	0.05	10.40	11.80
18	23.50	83.50	8.10	7.80	0.04	0.03	18.80	53.40
19	17.50	77.50	9.40	8.30	0.05	0.03	30.00	43.10
20	17.50	47.00	7.10	7.10	0.05	0.04	11.60	11.30
21	46.50	64.00	7.60	7.60	0.04	0.04	17.00	14.90
22	15.50	22.00	7.50	7.60	0.06	0.04	16.70	22.00
23	5.00	91.00	7.70	7.40	0.07	0.06	18.90	24.40
24	7.50	26.50	8.10	7.90	0.03	0.04	36.00	31.90
25	5.00	22.00	7.90	7.40	0.06	0.07	21.40	24.40
26	38.50	81.00	8.10	7.50	0.08	0.07	21.00	25.50
27	5.00	62.50	8.10	7.30	0.05	0.05	15.70	19.30
28	134.50	148.00	7.20	6.90	0.04	0.04	13.60	12.80
29	83.50	90.00	6.60	6.40	0.08	0.11	17.00	24.40
30	19.50	64.50	8.00	7.50	0.03	0.03	14.20	11.70
31	45.50	118.50	7.60	7.50	0.05	0.06	12.50	22.30
32	5.00	21.00	7.80	7.90	0.05	0.05	16.40	25.80
33	5.50	23.00	7.20	6.90	0.08	0.08	13.60	21.00
34	5.00	47.50	7.60	7.70	0.06	0.06	15.30	23.90
35	54.00	125.50	6.60	6.40	0.07	0.07	12.10	19.20
36	7.50	33.50	7.00	6.70	0.07	0.07	11.50	20.10
37	11.00	67.50	6.80	6.50	0.06	0.07	10.70	15.40
38	5.50	27.00	7.30	6.50	0.07	0.06	13.80	13.90
39	11.50	24.50	8.10	7.80	0.04	0.03	23.40	24.60
40	5.50	0.00	8.00	7.70	0.06	0.05	19.60	25.10

41	37.50	65.50	8.40	8.50	0.07	0.06	28.30	30.00
42	197.50	0.00	7.70	7.80	0.07	0.05	19.40	27.60
43	3.50	26.00	7.60	7.40	0.08	0.07	19.50	25.50
44	71.50	70.00	7.50	7.70	0.06	0.06	18.20	24.30
45	37.50	49.50	7.60	7.20	0.08	0.06	19.10	22.30
47	26.00	21.00	7.80	7.00	0.05	0.05	26.40	21.20
48	5.00	27.00	8.40	8.00	0.01	0.04	24.30	27.70
49	5.00	52.00	8.30	8.10	0.02	0.01	25.10	21.80
50	65.00	40.00	8.00	7.80	0.06	0.07	34.00	29.00
51	3.00	38.50	7.90	7.90	0.04	0.05	29.30	26.70
52	7.50	17.50	8.10	8.00	0.04	0.04	32.40	22.90
53	11.00	81.50	8.00	7.80	0.06	0.06	22.50	25.30
54	134.00	164.50	7.20	7.30	0.04	0.04	18.40	21.00
55	72.00	89.00	7.60	7.50	0.06	0.07	24.00	28.10
56	18.00	81.50	7.60	7.60	0.05	0.05	14.80	18.00
57	3.50	48.00	7.40	7.20	0.04	0.04	12.60	13.30
58	54.00	113.00	7.60	7.50	0.05	0.05	15.50	23.30
59	8.00	62.50	7.90	7.70	0.05	0.05	17.70	27.30
61	94.50	120.00	7.30	7.30	0.06	0.05	17.10	23.90
62	34.50	169.00	8.10	7.60	0.03	0.03	21.00	27.00
63	30.50	23.00	8.00	8.10	0.06	0.04	20.20	29.60
64	70.50	71.00	7.70	7.70	0.21	0.14	19.60	37.60
65	43.50	58.50	8.00	8.00	0.07	0.06	22.20	30.00
66	116.50	120.50	7.80	7.80	0.15	0.14	25.00	50.50
67	62.00	56.00	8.00	7.90	0.07	0.05	20.90	26.70
68	13.50	5.00	8.10	8.10	0.04	0.03	21.90	26.10
69	20.00	61.00	8.10	7.90	0.04	0.04	20.40	24.20
70	5.00	22.50	8.10	8.00	0.04	0.04	22.90	28.00
71	11.50	15.00	8.10	7.90	0.03	0.04	21.70	22.20
72	24.50	43.00	8.20	8.00	0.05	0.04	23.20	30.40
73	30.00	17.50	8.40	8.10	0.06	0.07	24.80	33.00
74	17.00	70.50	8.30	8.00	0.04	0.05	23.70	30.30
75	31.00	119.50	8.20	7.80	0.05	0.06	23.90	31.90
76	34.00	63.50	8.40	7.80	0.06	0.05	24.70	29.00
77	46.50	81.50	7.80	7.90	0.10	0.08	22.50	37.10
78	5.00	100.50	8.20	7.60	0.04	0.06	25.50	27.70
79	5.00	58.50	8.10	7.60	0.04	0.06	24.30	26.90
80	5.00	20.50	7.80	7.70	0.06	0.06	19.40	28.20
81	5.50	61.50	7.20	6.50	0.07	0.08	10.90	20.40
82	935.50	957.00	7.80	7.60	0.05	0.05	37.20	46.30
83	5.00	93.50	7.90	7.50	0.07	0.07	16.90	24.50
84	5.00	93.00	7.60	7.30	0.05	0.06	15.20	24.00

85	19.00	66.50	7.80	7.60	0.06	0.07	17.20	25.70
86	137.50	160.50	7.80	7.60	0.07	0.08	25.30	29.30
87	60.50	85.00	8.00	7.60	0.10	0.09	24.10	27.30
88	69.00	91.50	8.00	7.70	0.07	0.07	24.50	27.30
89	32.50	125.00	7.20	6.60	0.05	0.05	15.90	18.70
90	6.50	35.00	8.10	7.80	0.04	0.04	15.20	14.80
91	187.50	200.00	7.80	7.60	0.16	0.15	25.50	46.30
92	50.00	141.50	7.90	7.20	0.05	0.05	19.80	17.50
93	5.00	191.00	7.40	7.10	0.05	0.06	14.60	16.50
94	37.50	52.50	7.30	6.90	0.06	0.13	20.30	35.90
95	16.50	76.50	7.60	7.70	0.04	0.03	20.10	27.50
96	33.50	46.50	8.00	8.00	0.07	0.05	21.30	31.80
97	28.50	102.50	9.10	7.60	0.05	0.05	35.80	29.50
98	26.00	75.00	7.90	7.60	0.08	0.05	20.80	31.00
99	5.00	14.50	8.30	8.10	0.03	0.03	35.20	30.60
100	12.00	61.00	8.20	8.00	0.03	0.04	38.40	30.10
101	5.00	40.00	8.30	7.90	0.04	0.04	21.70	28.80
102	51.00	44.50	9.10	8.60	0.02	0.01	49.00	32.20
103	0.50	32.00	8.00	7.80	0.04	0.03	26.70	22.70
104	25.50	29.00	7.90	7.40	0.06	0.05	16.30	16.10
105	100.50	76.00	8.10	7.80	0.10	0.09	25.90	33.20
106	38.00	55.50	7.40	7.20	0.06	0.04	11.90	12.40
107	5.00	19.50	8.30	8.20	0.03	0.03	24.70	30.80
108	24.00	36.50	8.60	8.00	0.05	0.03	32.70	33.20
109	5.00	11.00	8.50	8.20	0.04	0.03	35.80	31.80
110	1.00	35.00	8.40	8.20	0.03	0.03	37.00	30.80
111	5.00	15.00	8.20	8.00	0.04	0.04	19.80	23.10
112	27.50	61.00	8.10	7.90	0.05	0.04	20.20	24.40
113	5.50	22.00	5.70	5.90	0.10	0.09	17.00	19.50
114	5.00	20.50	8.00	7.60	0.04	0.03	18.30	15.70
115	17.50	43.00	6.80	6.60	0.06	0.06	12.80	13.60
116	149.00	152.50	7.00	6.60	0.03	0.05	13.60	16.30
117	4.00	40.50	7.90	7.60	0.05	0.06	22.00	23.50
118	5.00	58.50	7.70	7.80	0.07	0.04	23.00	35.00
119	16.00	70.50	9.20	8.20	0.04	0.03	56.30	32.50
120	53.00	121.00	7.50	7.40	0.06	0.06	17.20	20.90
121	22.50	79.00	7.90	7.80	0.05	0.04	20.20	26.20
122	55.00	99.50	7.70	7.70	0.05	0.04	19.00	26.50
123	13.00	17.00	7.80	7.80	0.05	0.04	15.80	23.00
124	26.00	48.00	6.50	7.40	0.09	0.04	16.70	28.50
125	5.00	120.50	7.40	7.40	0.04	0.05	15.60	16.30
126	4.00	72.50	6.90	6.80	0.06	0.07	16.00	23.70

127	158.00	112.00	7.60	7.20	0.04	0.03	13.40	13.80
128	10.50	29.50	8.30	8.00	0.05	0.04	23.70	21.70
129	5.00	14.00	7.90	7.90	0.05	0.04	18.70	18.80
130	14.00	5.00	7.80	7.20	0.06	0.06	21.20	21.50
131	25.50	7.50	7.90	7.60	0.06	0.06	31.40	22.20
132	4.50	32.50	7.20	6.80	0.08	0.08	20.10	26.00
133	204.50	309.50	8.00	7.60	0.13	0.16	33.50	38.20
134	12.50	5.50	8.00	7.70	0.05	0.05	22.40	23.70
135	138.00	150.50	8.00	7.60	0.05	0.04	21.60	23.00
136	1.00	60.00	8.00	7.80	0.05	0.05	20.50	19.30
137	5.00	8.00	7.90	7.80	0.06	0.05	19.60	22.90
138	16.50	20.00	7.10	7.50	0.06	0.06	15.00	18.00
139	5.00	60.50	8.10	7.60	0.05	0.07	26.60	29.20
140	157.50	143.50	6.80	7.10	0.05	0.05	12.30	19.90
141	35.00	37.00	6.70	6.70	0.04	0.03	9.60	9.70
142	19.00	42.50	9.20	8.30	0.05	0.06	24.50	35.10
143	28.00	26.00	7.00	6.90	0.08	0.06	18.00	20.40
144	7.50	40.00	7.10	7.00	0.06	0.06	15.40	21.70

Table B4. Type of soils present at sampling locations.

PubID	FillStatus	SoilTexture	DLsand	DLsilt	DLclay	DLtexture
1	unknown	sandy clay loam				
2	unknown	clay loam				
3	unknown	clay loam				
4	unknown	sandy clay loam				
5	native	clay				
6	native	clay				
7	native	sandy clay				
8	native	sandy clay	52.00	24.00	24.00	Sandy Clay Loam
9	fill	silty clay				
10	fill	sandy clay loam				
11	native	silty clay loam	78.00	14.00	8.00	Loamy Sand
12	unknown	silty clay loam				
13	native	sandy clay				
14	native	sandy clay				
15	native	clay loam				
16	native	loam	84.00	14.00	2.00	Loamy Sand
17	unknown	sandy clay loam				
18	unknown	clay	51.60	32.40	16.00	Loam
19	unknown	sandy loam	88.00	8.00	4.00	Sand
20	unknown	sandy loam				
21	unknown	sandy clay loam				
22	unknown	clay loam	63.60	28.40	8.00	Sandy Loam
23	unknown	clay loam				
24	fill	clay	31.60	40.40	28.00	Loam
25	unknown	sandy clay loam				
26	unknown	sandy clay loam				
27	native	sandy clay loam				
28	native	sandy clay loam	65.60	30.40	4.00	Sandy Loam
29	native	sandy loam	67.60	30.40	2.00	Sandy Loam
30	native	sandy loam				
31	native	clay loam				
32	unknown	clay loam				
33	native	loam	73.60	26.40	0.00	Loamy Sand
34	native	clay loam				
35	native	sandy loam				
36	native	sandy loam				
37	native	sandy loam				
38	unknown	sandy clay loam				
39	unknown	sandy clay loam				
40	unknown	sandy clay				

41	unknown	sandy clay loam				
42	unknown	sandy clay loam				
43	unknown	sandy clay loam				
44	unknown	sandy clay loam				
45	native	sandy clay loam				
47	unknown	sandy clay				
48	unknown	sandy loam				
49	fill	sandy clay loam				
50	unknown	sandy clay loam				
51	unknown	sandy clay loam				
52	unknown	clay loam				
53	unknown	sandy clay loam				
54	former garden area	sandy loam				
55	unknown	sandy clay loam				
56	native	sandy clay loam				
57	native	loam				
58	native	sandy clay loam				
59	native	sandy clay loam				
61	native	sandy clay loam				
62	unknown -- probably fill	sandy clay loam				
63	unknown	silty clay				
64	unknown	sandy clay loam				
65	unknown	sandy clay loam				
66	unknown	sandy clay loam				
67	unknown	sandy clay loam				
68	unknown	sandy clay				
69	unknown	sandy clay loam				
70	unknown	sandy clay				
71	unknown	sandy clay	60.80	21.20	18.00	Sandy Loam
72	unknown	sandy clay loam	42.80	33.20	24.00	Loam
73	unknown	sandy clay	40.80	33.20	26.00	Clay Loam
74	unknown	clay				
75	unknown	sandy clay				
76	unknown	silty clay				
77	unknown	silty clay				
78	unknown	sandy clay loam				
79	unknown	sandy clay				
80	unknown	sandy clay	46.80	29.20	24.00	Loam
81	unknown	clay loam				
82	unknown	sandy loam				
83	unknown	sandy clay loam				

84	unknown	sandy clay loam				
85	unknown	clay loam	63.60	30.40	6.00	Sandy Loam
86	unknown	sandy clay loam				
87	unknown	sandy clay loam				
88	unknown	sandy clay loam				
89	native	clay loam				
90	native	sandy clay loam				
91	unknown	sandy clay loam				
92	unknown	sandy clay loam				
93	native	sandy loam				
94	unknown	clay loam				
95	unknown	clay loam				
96	unknown	sandy clay loam				
97	unknown	sandy clay loam				
98	unknown	clay loam				
99	unknown	sandy clay loam				
100	unknown	sandy loam				
101	unknown	sandy clay loam				
102	unknown	sandy loam				
103	unknown	sandy clay loam				
104	unknown	clay loam				
105	unknown	sandy clay loam				
106	unknown	sandy clay loam				
107	unknown	sandy clay loam				
108	unknown	sandy clay loam				
109	unknown	clay loam				
110	unknown	sandy clay				
111	unknown	sandy clay loam				
112	unknown	sandy clay loam				
113	garden bed	sandy loam				
114	native	sandy loam				
115	native	silt loam	72.80	21.20	6.00	Sandy Loam
116	native	clay loam	48.80	33.20	18.00	Loam
117	unknown	clay loam				
118	native	sandy clay				
119	native	sandy clay loam				
120	native	sandy clay loam	56.80	27.20	16.00	Sandy Loam
121	unknown	sandy clay loam				
122	unknown	sandy clay loam				
123	unknown	sandy clay loam				
124	native	sandy clay loam				
125	unknown	sandy loam				

126	native	clay loam				
127	unknown	sandy loam				
128	unknown	clay loam				
129	unknown	sandy clay loam				
130	unknown	sandy clay loam				
131	unknown	clay loam				
132	unknown	silty clay loam	60.40	20.40	19.20	Sandy Loam
133	unknown	sandy clay loam				
134	unknown	sandy clay loam				
135	unknown	sandy clay loam				
136	unknown	sandy clay loam				
137	unknown	silty clay loam				
138	native	loam	70.80	17.20	12.00	Loamy Sand
139	native	clay loam				
140	native	sandy clay loam				
141	native	loamy sand				
142	fill	sand	59.60	18.80	21.60	Sandy Clay Loam
143	native	sandy clay loam				
144	native	clay loam				

Table B5. Model specifications

PubID	PreModelFactors	PostModelFactors	SmelterModelFactors	Flag	Notes
1	Include	Include	Include		
2	Include	Include	Include		
3	Include	Include	Include		
4	Include	Include	Include		
5	Include	Include	Include		
6	Include	Include	Include		
7	Include	Include	Include		
8	Include	Include	Include		
9	Include	Include	Include		
10	Include	Include	Include		
11	Include	Include	Include		
12	Include	Include	Include		
13	Include	Include	Include		
14	Include	Include	Include		
15	Include	Include	Include		
16	Include	Include	Include		
17	Include	Include	Include		
18	Include	Include	Include		
19	Include	Include	Include		
20	Include	Include	Include		
21	Include	Include	Include		
22	Include	Include	Include		
23	Include	Include	Include		
24	Include	Exclude	Include	Yes	post-IVBAperc outlier
25	Include	Include	Include		
26	Include	Include	Include		
27	Include	Include	Include		
28	Include	Include	Include		
29	Include	Include	Include		
30	Include	Include	Include		
31	Include	Include	Include		
32	Include	Include	Include		
33	Include	Include	Include		
34	Include	Include	Include		
35	Include	Include	Include		
36	Include	Include	Include		
37	Include	Include	Include		
38	Include	Include	Include		
39	Include	Include	Include		

40	Include	Include	Include		
41	Include	Include	Include		
42	Include	Include	Include		
43	Include	Include	Include		
44	Include	Include	Include		
45	Include	Include	Include		
47	Include	Include	Include		
48	Include	Include	Include		
49	Include	Include	Include		
50	Include	Include	Include		
51	Include	Include	Include		
52	Include	Include	Include		
53	Include	Include	Include		
54	Include	Include	Include		
55	Include	Include	Include		
56	Include	Include	Include		
57	Include	Include	Include		
58	Include	Include	Include		
59	Include	Include	Include		
61	Include	Include	Include		
62	Include	Include	Include		
63	Include	Include	Include		
64	Include	Include	Include		
65	Include	Include	Include		
66	Include	Include	Include		
67	Include	Include	Include		
68	Include	Include	Include		
69	Include	Include	Include		
70	Include	Include	Include		
71	Include	Include	Include		
72	Include	Include	Include		
73	Include	Include	Include		
74	Include	Include	Include		
75	Include	Include	Include		
76	Include	Include	Include		
77	Include	Include	Include		
78	Include	Include	Include		
79	Include	Include	Include		
80	Include	Include	Include		
81	Include	Include	Include		
82	Include	Include	Include		hydrophobic, high OM?
83	Include	Include	Include		

84	Include	Include	Include		
85	Include	Include	Include		
86	Include	Include	Include		
87	Include	Include	Include		
88	Include	Include	Include		
89	Include	Include	Include		
90	Include	Include	Include		
91	Include	Include	Include		
92	Include	Include	Include		
93	Include	Include	Include		
94	Include	Include	Include		
95	Include	Include	Include		
96	Include	Include	Include		
97	Include	Include	Include		
98	Include	Include	Include		
99	Include	Include	Include		
100	Include	Include	Include		
101	Include	Include	Include		
102	Include	Include	Include		
103	Include	Include	Include		
104	Include	Include	Include		
105	Include	Include	Include		
106	Include	Include	Include		
107	Include	Include	Include		
108	Include	Include	Include		
109	Include	Include	Include		
110	Include	Include	Include		
111	Include	Include	Include		
112	Include	Include	Include		
113	Exclude	Include	Exclude	Yes	
114	Include	Include	Include		
115	Include	Include	Include		
116	Include	Include	Include		
117	Include	Include	Include		
118	Include	Include	Include		
119	Include	Include	Include		
120	Include	Include	Include		
121	Include	Include	Include		
122	Include	Include	Include		
123	Include	Include	Include		
124	Include	Include	Include		
125	Include	Include	Include		

126	Include	Include	Include		
127	Include	Include	Include		
128	Include	Include	Include		
129	Include	Include	Include		
130	Include	Include	Include		
131	Include	Include	Include		
132	Include	Include	Include		
133	Include	Include	Include		
134	Include	Include	Include		
135	Include	Include	Include	Yes	
136	Include	Include	Include		
137	Include	Include	Include		
138	Include	Include	Include		
139	Include	Include	Include		
140	Include	Include	Include		
141	Include	Include	Include		hydrophobic
142	Include	Include	Include		
143	Include	Include	Include		
144	Include	Include	Include		

Table B6. Relationship between sampling and historical smelters locations.

PubID	DistSmelt	DWSmelterSum	CompZmax	CompZmean	DWSmelter
1	0.0132	1	0.468	-0.221	Downwind
2	0.0133	1	0.471	-0.222	Downwind
3	0.0134	1	0.472	-0.222	Downwind
4	0.0168	1	1.725	0.093	Downwind
5	0.0836	0	0.626	-0.306	Not directly downwind
6	0.0481	12	0.620	-0.257	Downwind
7	0.0060	1	4.629	0.593	Downwind
8	0.0272	9	2.598	0.125	Downwind
9	0.0223	0	0.362	-0.262	Not directly downwind
10	0.0204	0	0.354	-0.263	Not directly downwind
11	0.0204	0	0.355	-0.263	Not directly downwind
12	0.0205	0	0.355	-0.264	Not directly downwind
13	0.0202	0	0.354	-0.264	Not directly downwind
14	0.0208	0	0.357	-0.264	Not directly downwind
15	0.0208	0	0.359	-0.266	Not directly downwind
16	0.1208	0	0.524	-0.275	Not directly downwind
17	0.1201	0	0.523	-0.275	Not directly downwind
18	0.0134	1	0.471	-0.223	Downwind
19	0.0136	1	0.477	-0.226	Downwind
20	0.1193	0	0.523	-0.275	Not directly downwind
21	0.1192	0	0.523	-0.275	Not directly downwind
22	0.1193	0	0.519	-0.275	Not directly downwind
23	0.0194	0	2.974	0.327	Not directly downwind
24	0.0195	0	2.967	0.326	Not directly downwind
25	0.0217	0	2.806	0.308	Not directly downwind
26	0.0219	0	2.795	0.305	Not directly downwind
27	0.0053	1	0.178	-0.098	Downwind
28	0.0223	9	1.271	0.256	Downwind
29	0.0463	1	1.854	-0.031	Downwind
30	0.0635	13	3.291	0.022	Downwind
31	0.0802	0	0.579	-0.324	Not directly downwind
32	0.0804	0	0.580	-0.325	Not directly downwind
33	0.0803	0	0.579	-0.324	Not directly downwind
34	0.0801	0	0.579	-0.324	Not directly downwind
35	0.0804	0	0.580	-0.325	Not directly downwind
36	0.0805	0	0.582	-0.325	Not directly downwind
37	0.0805	0	0.583	-0.325	Not directly downwind
38	0.9205	6	0.341	-0.029	Downwind
39	0.9242	6	0.340	-0.029	Downwind
40	0.9313	6	0.338	-0.030	Downwind

41	0.9349	6	0.337	-0.030	Downwind
42	0.9516	6	0.335	-0.028	Downwind
43	0.9487	6	0.330	-0.031	Downwind
44	0.9572	6	0.327	-0.031	Downwind
45	0.9653	6	0.335	-0.026	Downwind
47	0.9572	6	0.327	-0.031	Downwind
48	4.5113	0	0.743	-0.402	Not directly downwind
49	4.5118	0	0.743	-0.402	Not directly downwind
50	1.1337	11	1.573	-0.165	Downwind
51	1.0323	11	0.608	-0.310	Downwind
52	0.9893	11	0.584	-0.303	Downwind
53	1.0151	11	0.599	-0.306	Downwind
54	0.5644	4	1.256	0.091	Downwind
55	1.4522	11	1.233	-0.331	Downwind
56	2.5084	12	0.591	-0.360	Downwind
57	6.2210	0	0.523	-0.275	Not directly downwind
58	1.1883	1	0.997	0.015	Downwind
59	1.6505	0	1.248	-0.151	Not directly downwind
61	1.6435	0	1.236	-0.151	Not directly downwind
62	1.6354	0	1.243	-0.144	Not directly downwind
63	1.9895	12	0.343	0.004	Downwind
64	1.9857	12	0.338	0.005	Downwind
65	1.9837	12	0.333	0.005	Downwind
66	1.9810	12	0.334	0.006	Downwind
67	1.9765	12	0.335	0.007	Downwind
68	1.9628	12	0.342	0.012	Downwind
69	1.9667	12	0.336	0.009	Downwind
70	1.9592	12	0.343	0.013	Downwind
71	1.9565	12	0.344	0.014	Downwind
72	1.9575	12	0.344	0.014	Downwind
73	1.9524	12	0.346	0.016	Downwind
74	1.9490	12	0.346	0.017	Downwind
75	1.9476	12	0.346	0.018	Downwind
76	1.9423	12	0.345	0.019	Downwind
77	1.9367	12	0.333	0.013	Downwind
78	1.7725	12	0.401	-0.308	Downwind
79	1.7796	12	0.393	-0.307	Downwind
80	1.7843	12	0.386	-0.306	Downwind
81	1.7895	12	0.380	-0.304	Downwind
82	1.2713	6	9.615	0.627	Downwind
83	1.2759	6	9.699	0.629	Downwind
84	1.3195	7	9.706	0.631	Downwind

85	1.3209	7	9.759	0.631	Downwind
86	1.3103	7	9.936	0.630	Downwind
87	1.3576	7	9.968	0.585	Downwind
88	1.3664	7	9.891	0.573	Downwind
89	3.8834	0	0.574	-0.287	Not directly downwind
90	0.6133	6	0.724	0.078	Downwind
91	0.0325	2	0.117	-0.107	Downwind
92	0.5697	5	0.592	-0.202	Downwind
93	0.6805	3	8.742	0.528	Downwind
94	0.6124	10	0.420	-0.225	Downwind
95	0.6196	10	0.422	-0.225	Downwind
96	0.6576	10	0.428	-0.222	Downwind
97	0.6247	10	0.424	-0.225	Downwind
98	0.6501	10	0.433	-0.227	Downwind
99	0.6337	10	0.429	-0.228	Downwind
100	0.1809	8	0.141	-0.099	Downwind
101	0.6583	10	0.437	-0.228	Downwind
102	0.5962	10	0.407	-0.219	Downwind
103	0.6435	10	0.431	-0.227	Downwind
104	0.7236	11	0.376	-0.167	Downwind
105	0.6576	10	0.428	-0.222	Downwind
106	0.6576	10	0.428	-0.222	Downwind
107	0.6606	10	0.431	-0.223	Downwind
108	0.1783	8	0.133	-0.092	Downwind
109	0.1778	8	0.131	-0.090	Downwind
110	0.6603	10	0.431	-0.223	Downwind
111	0.6577	10	0.429	-0.223	Downwind
112	0.6603	10	0.431	-0.223	Downwind
113	1.4754	0	0.385	-0.261	Not directly downwind
114	5.9291	0	0.527	-0.275	Not directly downwind
115	1.4117	1	0.780	-0.085	Downwind
116	1.5003	7	3.225	0.161	Downwind
117	1.9230	12	0.321	0.008	Downwind
118	5.5630	0	0.692	-0.336	Not directly downwind
119	1.1327	9	1.689	0.267	Downwind
120	1.7850	0	0.411	-0.235	Not directly downwind
121	1.7808	7	7.220	0.415	Downwind
122	1.7943	7	7.320	0.433	Downwind
123	1.7384	7	6.851	0.406	Downwind
124	4.6096	0	0.475	-0.274	Not directly downwind
125	1.8887	0	0.709	-0.157	Not directly downwind
126	2.5476	0	0.443	-0.264	Not directly downwind

127	0.7957	6	1.087	0.056	Downwind
128	0.9701	12	0.574	-0.298	Downwind
129	0.9837	11	0.578	-0.306	Downwind
130	0.9905	11	0.581	-0.308	Downwind
131	0.9905	11	0.581	-0.308	Downwind
132	0.9905	11	0.581	-0.308	Downwind
133	1.0012	11	0.580	-0.317	Downwind
134	1.0199	12	1.487	-0.008	Downwind
135	1.0038	11	0.580	-0.319	Downwind
136	0.9888	11	0.582	-0.306	Downwind
137	0.9905	11	0.581	-0.308	Downwind
138	6.2992	0	0.508	-0.283	Not directly downwind
139	4.4821	0	0.741	-0.402	Not directly downwind
140	0.9702	1	0.364	-0.220	Downwind
141	1.5708	0	0.400	-0.289	Not directly downwind
142	0.8337	1	0.565	-0.203	Downwind
143	1.0094	0	0.488	-0.229	Not directly downwind
144	1.0059	0	0.487	-0.229	Not directly downwind

Table B7. Remediation treatments.

PubID	DaysAged	Group
1	278	Control
2	278	Intervention
3	278	Control
4	273	Intervention
5	272	Intervention
6	265	Control
7	279	Intervention
8	278	Control
9	278	Control
10	278	Intervention
11	278	Intervention
12	278	Intervention
13	278	Control
14	278	Intervention
15	263	Control
16	278	Intervention
17	278	Control
18	278	Intervention
19	278	Intervention
20	278	Control
21	278	Intervention
22	278	Control
23	279	Intervention
24	279	Intervention
25	279	Control
26	279	Intervention
27	278	Intervention
28	278	Control
29	267	Control
30	278	Intervention
31	269	Control
32	269	Control
33	269	Control
34	269	Intervention
35	269	Intervention
36	269	Control
37	269	Intervention
38	252	Intervention
39	252	Intervention
40	253	Control

41	252	Intervention
42	252	Control
43	252	Intervention
44	252	Control
45	253	Intervention
47	246	Control
48	277	Control
49	277	Intervention
50	259	Intervention
51	259	Intervention
52	259	Control
53	259	Intervention
54	273	Control
55	273	Control
56	265	Intervention
57	278	Intervention
58	272	Intervention
59	273	Intervention
61	273	Control
62	288	Intervention
63	259	Intervention
64	259	Control
65	259	Intervention
66	259	Control
67	259	Control
68	259	Control
69	259	Intervention
70	259	Intervention
71	259	Control
72	259	Intervention
73	264	Control
74	264	Intervention
75	263	Intervention
76	263	Intervention
77	263	Intervention
78	269	Intervention
79	270	Intervention
80	269	Control
81	270	Intervention
82	264	Intervention
83	264	Control
84	264	Intervention

85	264	Control
86	264	Intervention
87	264	Intervention
88	264	Intervention
89	279	Intervention
90	278	Control
91	273	Control
92	249	Intervention
93	273	Intervention
94	273	Intervention
95	273	Intervention
96	272	Control
97	273	Intervention
98	272	Intervention
99	273	Control
100	274	Intervention
101	273	Intervention
102	274	Control
103	274	Intervention
104	274	Control
105	273	Control
106	274	Intervention
107	274	Control
108	274	Intervention
109	274	Intervention
110	279	Intervention
111	279	Control
112	279	Intervention
113	272	Control
114	278	Control
115	272	Intervention
116	278	Intervention
117	258	Intervention
118	279	Intervention
119	278	Intervention
120	267	Intervention
121	278	Intervention
122	278	Intervention
123	278	Control
124	277	Intervention
125	273	Intervention
126	272	Intervention

127	273	Intervention
128	263	Control
129	263	Control
130	250	Control
131	250	Control
132	258	Intervention
133	250	Intervention
134	250	Intervention
135	259	Intervention
136	263	Intervention
137	263	Control
138	240	Intervention
139	277	Control
140	279	Control
141	278	Control
142	279	Intervention
143	273	Control
144	273	Intervention

Table B8. Soil cation concentrations.

Pub ID	PreCa ppm	PreK ppm	PreMg ppm	PreS ppm	PreNa ppm	PostCa ppm	PostK ppm	PostM gppm	PostS ppm	PostNa ppm
1	4256.0	176.5	303.5	15.5	7.4	4639.5	135.5	293.5	12.0	0.0
2	4063.0	135.5	288.5	18.0	19.5	3663.0	87.0	272.5	15.5	0.3
3	4101.0	191.5	305.0	14.0	9.4	3882.5	134.5	271.0	13.5	1.0
4	3961.5	89.5	310.5	61.0	28.1	4948.0	96.0	289.5	41.5	10.1
5	3342.0	55.5	282.5	6.5	0.0	3296.0	106.0	238.0	13.0	10.4
6	2882.5	106.5	404.5	9.0	0.0	3544.0	100.0	450.0	16.5	5.9
7	2350.5	81.0	351.5	7.0	37.3	2358.5	80.0	344.5	11.5	8.8
8	2723.5	102.5	350.5	6.0	20.7	2926.5	117.0	350.0	12.0	4.5
9	4641.0	43.0	298.0	82.5	96.1	4454.5	89.0	344.0	45.5	39.0
10	4628.5	47.0	273.5	24.5	28.7	4358.5	75.5	305.0	18.0	26.6
11	3055.0	47.0	283.5	11.5	0.6	2457.5	93.0	313.0	14.0	4.4
12	2532.5	31.5	299.0	4.5	0.0	2841.5	72.5	358.5	9.5	3.5
13	4600.5	162.0	377.5	32.0	0.1	4307.5	183.0	340.5	15.0	1.7
14	4526.5	65.5	296.5	12.0	0.0	3887.5	80.0	263.5	9.0	1.0
15	2636.5	101.5	270.5	15.0	7.6	2872.0	99.0	294.0	22.0	6.3
16	2235.5	30.5	258.5	13.0	0.0	2006.0	39.0	247.0	10.5	0.0
17	1685.5	26.5	228.0	8.0	0.0	1521.0	48.5	284.0	7.0	0.0
18	3251.0	133.5	253.0	19.0	19.4	8778.5	309.5	420.0	104.0	21.5
19	5111.0	242.5	443.0	181.0	21.2	8301.0	296.5	411.0	103.0	20.5
20	1896.5	70.0	233.0	9.5	0.0	1714.0	103.0	233.0	9.0	0.0
21	2990.5	66.0	224.5	13.5	0.0	2782.0	57.5	184.5	21.5	0.0
22	2843.0	93.0	269.0	14.5	0.0	3606.0	83.0	267.5	11.5	0.0
23	2955.0	433.5	343.5	17.0	25.0	3472.0	416.0	393.0	17.5	24.6
24	6341.0	157.5	458.0	14.0	22.1	4837.0	154.0	429.0	10.0	8.6
25	3617.5	158.0	348.5	14.5	4.7	3311.0	152.0	388.0	14.0	5.1
26	3410.5	322.0	367.0	18.5	4.4	3666.5	268.5	342.5	15.0	5.5
27	2493.5	97.5	356.5	14.5	2.6	2716.0	101.5	352.0	9.0	0.0
28	2231.5	109.5	260.5	13.0	0.0	1864.0	98.5	235.5	11.0	0.0
29	2738.5	141.5	353.0	16.5	0.0	2709.0	100.5	339.0	15.5	0.0
30	2535.0	94.0	149.5	9.5	0.0	2031.0	60.0	128.5	6.0	0.0
31	2012.5	59.0	264.5	8.0	16.4	2657.0	53.0	351.5	13.5	40.7
32	2671.5	81.0	335.0	6.5	2.7	3337.5	107.5	405.5	11.0	0.0
33	2166.5	174.0	283.5	5.5	0.0	2271.5	96.0	285.5	11.5	28.6
34	2471.5	45.0	344.5	14.0	0.0	3101.5	37.5	356.0	15.0	0.0
35	1972.5	37.0	259.0	10.5	0.0	2240.5	50.0	283.0	12.5	0.8
36	1896.0	31.5	227.0	11.0	0.0	2368.5	42.5	242.0	13.0	4.8
37	1818.5	13.5	192.5	14.0	0.0	1932.0	56.5	234.0	14.0	0.0
38	2203.5	69.0	304.0	12.0	15.7	1900.0	55.5	241.5	14.5	4.5
39	4115.5	254.0	262.0	16.0	7.3	3933.5	141.5	246.5	23.0	2.8

40	3240.5	191.0	345.0	11.5	2.4	3585.0	141.0	343.0	16.0	10.1
41	4771.5	298.5	444.5	38.0	2.9	4046.5	217.0	363.5	35.5	3.7
42	3198.0	197.5	344.0	11.0	1.7	3857.5	176.0	315.0	18.0	3.7
43	3105.5	193.0	411.0	12.0	16.9	3423.0	138.5	356.5	17.0	24.4
44	2994.0	275.5	300.0	13.0	0.6	3275.0	258.5	288.5	21.5	3.4
45	3092.5	145.0	392.0	13.0	6.7	2961.0	124.5	338.0	17.0	3.4
47	4828.0	124.5	223.0	13.5	11.5	3595.0	112.0	186.5	20.5	3.9
48	4424.0	238.5	280.0	30.5	0.6	4403.5	199.0	290.0	33.0	0.0
49	4339.5	73.0	274.5	24.5	35.7	4403.5	86.5	252.0	17.5	9.6
50	5951.0	278.5	419.5	23.5	1.6	4391.0	260.5	386.5	25.0	4.7
51	5151.5	230.0	354.0	41.0	3.8	4064.0	212.5	311.0	21.5	2.1
52	5728.0	208.5	379.5	62.5	3.3	3696.0	187.0	237.5	13.0	0.4
53	3927.5	190.5	286.5	18.5	0.0	3607.5	209.5	296.5	19.0	2.1
54	3197.5	152.0	244.5	25.0	0.5	3533.0	94.0	250.0	22.5	0.0
55	4017.5	451.0	335.5	22.0	0.3	3625.0	369.0	345.5	35.5	0.0
56	2252.0	69.5	397.5	13.5	13.5	2374.5	55.5	392.5	14.0	5.9
57	2048.0	39.5	272.5	15.5	0.0	1905.0	51.5	237.5	13.5	0.0
58	2606.0	167.0	239.5	12.0	0.0	3185.5	159.5	240.5	17.5	0.0
59	3087.0	73.0	255.0	12.5	0.0	4353.0	100.0	302.0	15.0	0.0
61	2703.0	169.5	374.0	11.5	1.4	3406.0	130.0	418.0	16.0	1.3
62	3733.5	151.0	228.5	15.5	0.0	4775.5	163.0	280.5	16.0	1.2
63	3406.0	240.5	307.5	14.0	0.0	4424.0	210.5	336.5	15.0	6.6
64	3329.5	285.5	270.5	9.5	0.0	3950.5	329.5	310.5	14.0	5.9
65	3768.5	173.0	352.0	14.5	0.1	4107.0	200.0	377.5	25.5	6.2
66	4134.0	183.5	462.5	35.0	1.9	5710.0	236.0	537.5	46.5	7.8
67	3579.0	188.5	300.0	16.5	0.0	3667.0	203.5	325.0	19.0	5.9
68	3946.5	142.0	220.5	11.0	0.0	4494.5	126.5	234.5	16.0	5.7
69	3621.5	184.5	213.0	11.0	0.0	3942.5	210.0	219.5	17.0	6.0
70	4039.0	189.5	262.5	18.0	0.0	4540.0	193.5	269.0	16.5	5.2
71	3886.5	202.5	209.5	10.0	0.0	3681.5	170.5	209.5	16.0	5.7
72	4032.5	270.5	276.5	17.5	0.0	4635.5	312.5	336.0	18.5	6.8
73	4084.5	428.5	398.5	54.5	1.4	4546.0	324.0	377.5	24.5	7.1
74	4095.0	246.5	308.5	16.0	0.0	4450.0	284.5	314.5	20.0	6.1
75	4081.5	256.0	341.0	39.0	0.0	4565.5	263.5	337.0	23.5	5.8
76	4006.5	323.0	460.0	35.0	0.0	4158.0	313.5	337.5	18.5	5.9
77	3693.5	330.0	384.0	16.5	0.0	4504.5	376.0	445.5	15.5	5.6
78	4568.5	154.5	239.5	21.0	0.6	3781.5	244.5	291.5	16.5	0.6
79	4310.0	204.0	268.5	11.0	0.0	3616.0	267.0	336.5	15.5	0.0
80	3327.5	212.0	270.0	9.5	0.0	3863.5	271.5	365.0	25.0	0.3
81	1782.0	130.0	198.0	6.0	0.0	2611.0	198.0	318.0	15.0	2.7
82	6228.0	204.0	661.0	34.5	6.9	5532.0	201.5	647.5	35.5	8.0
83	2847.5	186.5	267.5	15.5	0.0	3243.5	178.5	267.5	16.0	6.0

84	2416.0	203.0	316.0	10.5	3.5	3202.5	198.5	331.0	24.0	6.3
85	2840.5	167.0	303.0	13.5	0.0	3403.5	180.0	345.5	15.5	5.3
86	4232.0	284.5	396.5	29.0	20.7	4052.0	268.5	317.0	25.0	13.0
87	4192.0	225.5	307.0	15.0	0.9	3757.5	193.0	258.5	18.0	5.3
88	4223.5	379.0	285.0	19.5	0.0	3720.5	370.0	283.0	28.0	5.6
89	2528.0	185.0	339.0	10.0	0.0	2677.0	127.5	311.0	10.5	0.0
90	2578.5	116.5	246.5	13.0	0.0	2205.5	90.0	199.0	14.0	0.0
91	3920.0	382.0	590.5	21.5	7.7	4854.5	409.5	665.0	25.5	3.3
92	3337.0	236.5	298.5	18.0	0.0	3029.5	135.5	228.0	15.5	0.0
93	2483.5	89.5	239.0	9.5	0.0	2597.0	75.5	241.5	19.0	0.0
94	3253.0	349.0	376.5	17.5	0.0	2497.0	392.5	289.0	55.5	28.6
95	3613.5	158.5	192.5	19.5	0.0	4106.0	114.5	210.0	16.0	0.0
96	3574.0	312.0	310.5	16.0	2.7	4392.0	234.0	318.5	26.0	0.0
97	6558.0	211.0	294.5	65.0	0.0	3917.5	181.5	274.0	17.5	0.0
98	3488.5	330.0	302.0	15.5	0.0	4094.5	202.5	288.0	12.0	0.0
99	6562.5	172.0	238.0	33.0	0.0	4748.5	200.0	250.5	16.5	0.0
100	6776.5	269.0	459.0	64.0	2.8	5194.5	220.5	388.0	50.5	2.0
101	3867.5	262.0	204.5	21.0	0.0	4434.0	237.5	219.0	19.0	0.0
102	9087.5	106.5	393.5	87.0	4.9	6448.0	109.5	360.5	55.0	6.1
103	4836.0	182.5	244.5	22.5	0.0	3620.0	121.5	214.5	13.5	0.0
104	2487.5	244.0	383.0	11.0	16.7	2219.5	134.0	333.0	14.0	0.0
105	4400.5	259.0	385.5	17.5	1.9	4387.0	164.0	336.5	20.5	0.0
106	1904.5	93.5	258.5	10.5	0.7	1837.5	49.5	221.0	13.5	0.0
107	4403.5	160.5	268.5	15.5	1.8	5013.0	143.5	290.5	11.5	0.0
108	5803.5	293.5	356.5	78.0	0.0	4850.5	197.5	298.0	12.0	0.0
109	6560.5	217.0	298.5	26.5	0.0	4601.0	129.5	238.0	17.0	0.0
110	6765.0	186.5	319.0	14.5	0.1	4949.5	154.0	289.0	14.5	0.0
111	3493.0	117.0	245.5	15.0	0.0	3513.0	110.5	230.5	12.5	0.0
112	3476.0	240.5	266.0	22.5	0.0	3704.0	122.5	227.0	15.0	0.0
113	2167.0	62.0	295.0	21.0	17.4	2375.0	103.0	304.5	18.5	13.6
114	3298.0	78.0	192.5	7.0	0.0	2967.0	42.5	146.0	7.5	0.0
115	2051.5	69.5	287.0	19.0	0.0	1984.5	56.5	252.5	16.0	0.0
116	2235.5	96.0	262.5	12.0	0.2	2304.5	71.0	294.0	13.0	0.6
117	3768.5	235.5	306.5	21.5	0.0	3598.5	258.0	342.0	17.0	6.4
118	3993.0	119.5	328.0	11.5	0.0	5731.0	130.5	360.5	19.5	0.0
119	10606	218.0	316.0	149.0	8.4	5819.5	127.5	239.5	77.0	8.8
120	2757.0	52.0	387.0	15.5	9.2	2982.0	60.0	396.0	15.5	6.7
121	3518.0	210.5	250.5	13.0	0.0	4275.0	170.0	262.0	17.0	0.0
122	3249.5	205.0	262.5	15.0	0.0	4356.0	159.0	262.5	15.5	0.0
123	2588.0	166.0	288.5	6.5	0.0	3768.0	87.0	231.5	15.0	0.0
124	2509.5	91.5	288.0	18.0	0.0	4724.0	55.5	273.5	9.5	0.0
125	2585.0	43.0	308.0	16.5	0.0	2549.5	39.5	268.0	17.5	0.0

126	2465.5	76.5	411.0	18.0	10.5	2757.0	66.5	405.0	12.5	2.4
127	2279.0	52.0	223.5	12.0	0.0	2187.5	46.5	217.5	15.0	0.0
128	4136.5	249.0	284.5	31.0	0.0	3464.5	256.5	268.0	14.0	0.0
129	3197.0	173.0	269.0	11.0	0.0	2938.0	147.5	274.0	24.0	0.0
130	3523.5	274.5	347.5	16.5	1.8	3176.0	234.0	314.0	17.0	1.8
131	5504.5	176.5	407.0	25.5	5.5	3517.5	128.0	293.5	14.5	3.8
132	3175.0	206.5	447.0	18.5	1.5	3338.5	301.5	466.5	22.0	6.5
133	5374.5	301.5	693.5	19.0	10.2	4303.0	266.5	698.0	21.5	5.2
134	3965.5	179.5	251.5	14.0	2.9	3768.0	109.0	233.5	12.0	0.9
135	3819.0	196.5	242.0	10.0	0.0	3625.0	198.5	264.0	19.5	2.3
136	3629.5	185.0	227.0	10.0	0.0	3137.0	180.0	226.5	13.5	0.0
137	3284.5	253.0	297.5	11.5	0.0	3388.5	252.5	296.0	12.0	0.0
138	2304.5	91.0	383.0	16.0	4.8	2764.5	68.0	391.5	17.5	4.8
139	4622.5	217.5	353.0	14.0	5.8	4267.5	228.0	337.0	18.5	0.3
140	2054.0	149.0	198.5	10.5	2.1	2870.0	136.0	229.5	14.5	0.8
141	1584.0	55.5	179.0	15.0	0.0	1750.0	53.0	169.0	17.0	3.7
142	4103.5	189.5	340.0	65.5	149.4	5041.0	211.0	356.0	47.0	413.1
143	2840.5	138.5	404.5	18.5	4.8	2548.5	115.0	377.5	14.5	3.0
144	2420.0	148.5	354.5	10.0	0.8	2761.5	133.0	360.0	9.5	0.0

APPENDIX C: IEUBK RESULTS

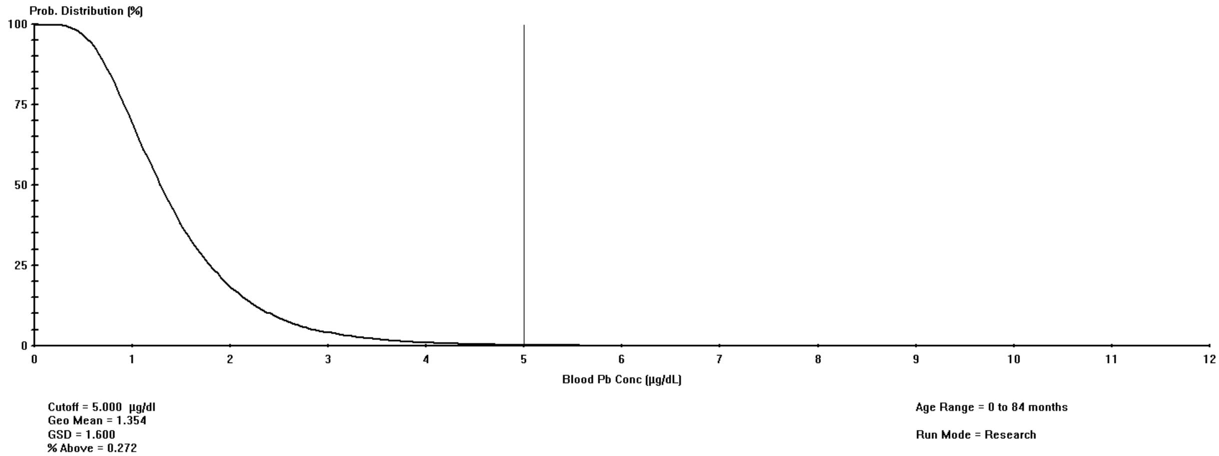

Figure C1. Distribution curve for IEUBK predicted blood lead levels for 10th percentile *in-vitro* bioaccessible lead.

Table C1. IEUBK predicted blood lead levels for ages 0-84 months for 10th percentile *in-vitro* bioaccessible lead.

Year	Soil+Dust (µg/day)	Total (µg/day)	Blood (µg/dL)
.5-1	1.233	2.738	1.5
1-2	1.953	3.902	1.6
2-3	1.961	4.067	1.5
3-4	1.970	4.065	1.4
4-5	1.468	3.571	1.2
5-6	1.324	3.566	1.1
6-7	1.252	3.600	1.0

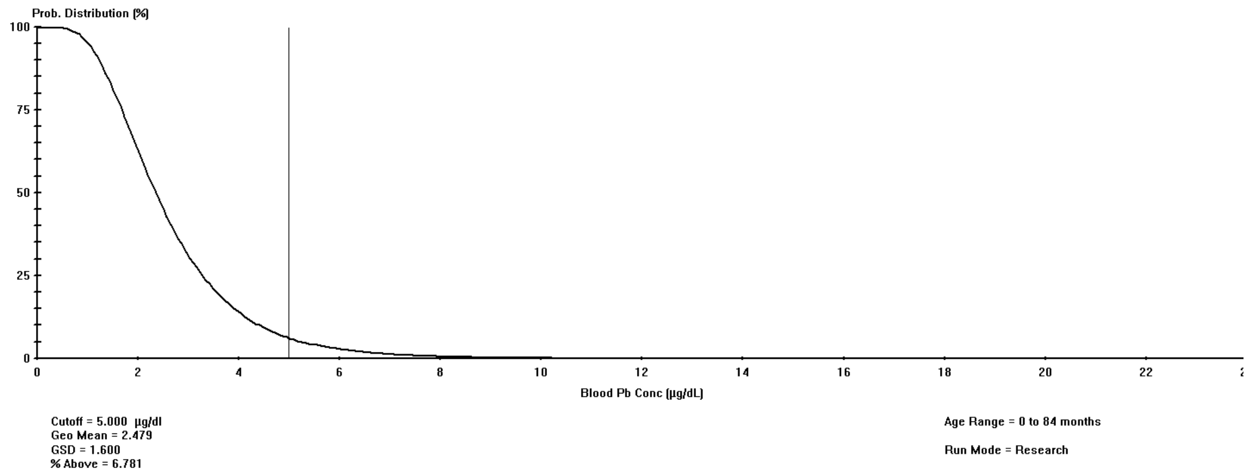

Figure C2. Distribution curve for IEUBK predicted blood lead levels for mean *in-vitro* bioaccessible lead.

Table C2. IEUBK predicted blood lead levels for ages 0-84 months for mean *in-vitro* bioaccessible lead.

Year	Soil+Dust (µg/day)	Total (µg/day)	Blood (µg/dL)
.5-1	3.602	5.068	2.8
1-2	5.672	7.560	3.1
2-3	5.721	7.771	2.9
3-4	5.768	7.815	2.7
4-5	4.335	6.406	2.3
5-6	3.923	6.138	2.0
6-7	3.715	6.039	1.7

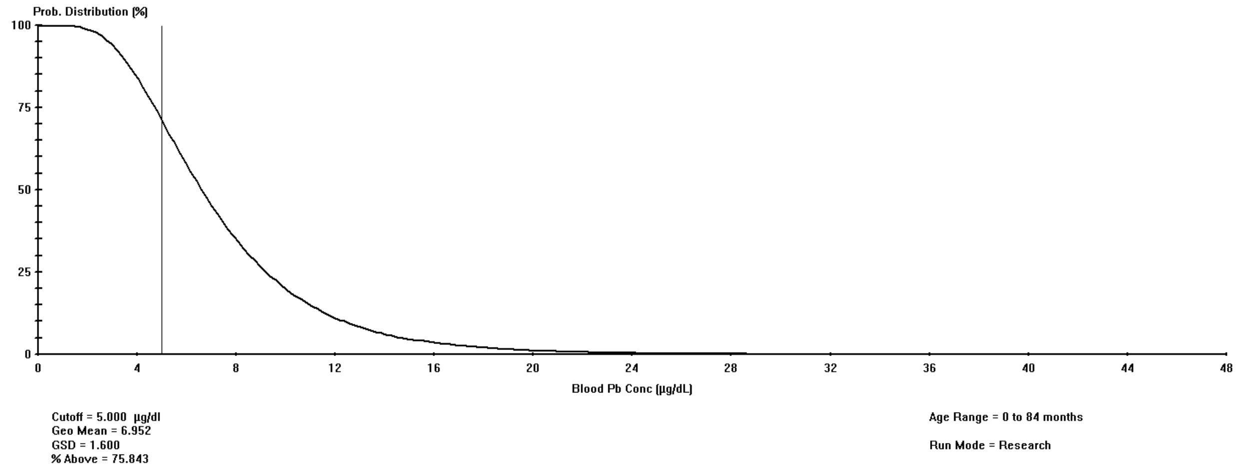

Figure C3. Distribution curve for IEUBK predicted blood lead levels for 90th percentile *in-vitro* bioaccessible lead.

Table C3. IEUBK predicted blood lead levels for ages 0-84 months for 90th percentile *in-vitro* bioaccessible lead.

Year	Soil+Dust (µg/day)	Total (µg/day)	Blood (µg/dL)
.5-1	13.052	14.368	7.6
1-2	20.137	21.800	8.9
2-3	20.647	22.484	8.3
3-4	21.111	22.971	7.9
4-5	16.393	18.335	6.5
5-6	15.018	17.122	5.5
6-7	14.321	16.542	4.8

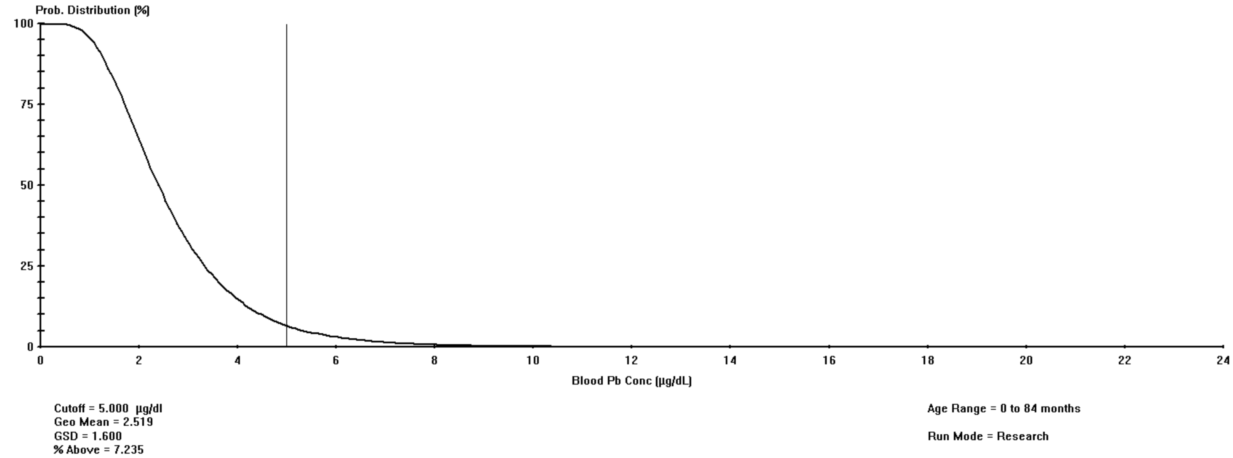

Figure C4. Distribution curve for IEUBK predicted blood lead levels for mean total lead, organic matter, and pH.

Table C4. IEUBK predicted blood lead levels for ages 0-84 months for mean total lead, organic matter, and pH.

Year	Soil+Dust (µg/day)	Total (µg/day)	Blood (µg/dL)
.5-1	3.686	5.150	2.8
1-2	5.803	7.688	3.2
2-3	5.854	7.901	3.0
3-4	5.903	7.948	2.8
4-5	4.438	6.508	2.3
5-6	4.016	6.230	2.0
6-7	3.804	6.127	1.8

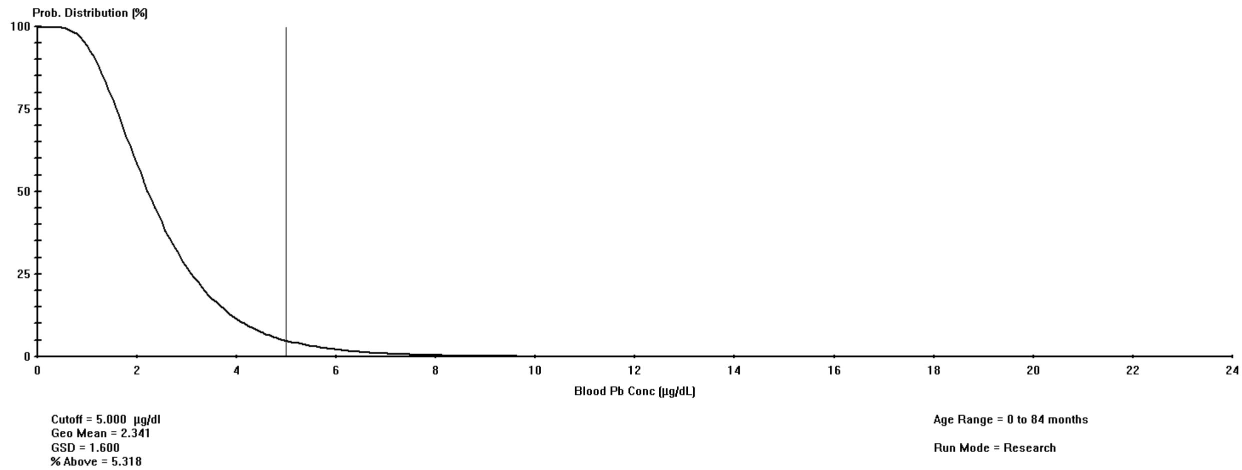

Figure C5. Distribution curve for IEUBK predicted blood lead levels for mean total lead and organic matter, and -0.5 pH units from mean pH.

Table C5. IEUBK predicted blood lead levels for ages 0-84 months for mean total lead and organic matter, and -0.5 pH units from mean pH.

Year	Soil+Dust (µg/day)	Total (µg/day)	Blood (µg/dL)
.5-1	3.310	4.781	2.6
1-2	5.216	7.111	2.9
2-3	5.258	7.315	2.7
3-4	5.299	7.352	2.6
4-5	3.979	6.054	2.2
5-6	3.599	5.817	1.8
6-7	3.408	5.734	1.7

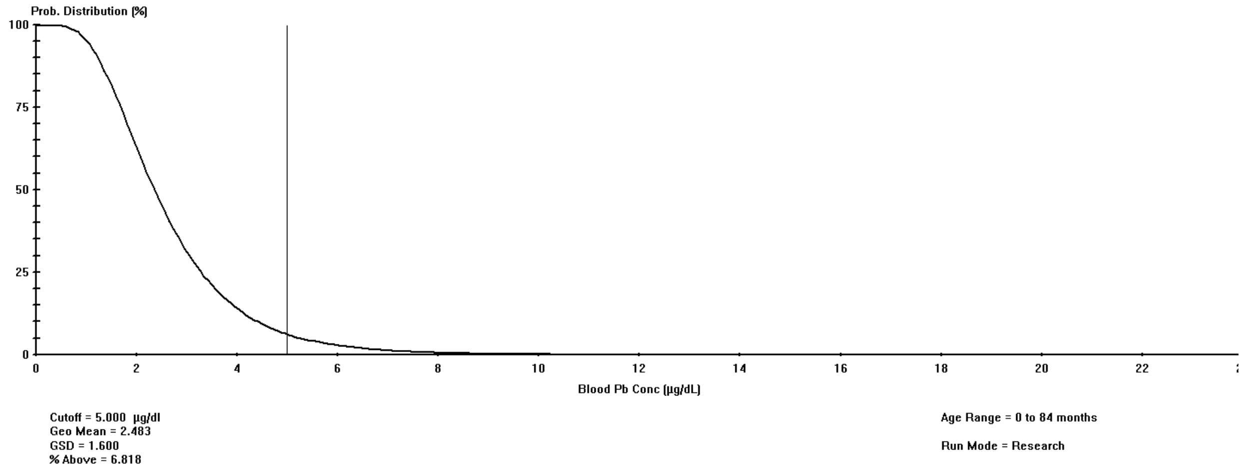

Figure C6. Distribution curve for IEUBK predicted blood lead levels for mean total lead and organic matter, and -0.1 pH units from mean.

Table C6. IEUBK predicted blood lead levels for ages 0-84 months for mean total lead and organic matter, and -0.1 pH units from mean.

Year	Soil+Dust (µg/day)	Total (µg/day)	Blood (µg/dL)
.5-1	3.609	5.074	2.8
1-2	5.683	7.570	3.1
2-3	5.732	7.782	2.9
3-4	5.779	7.826	2.8
4-5	4.344	6.415	2.3
5-6	3.930	6.146	2.0
6-7	3.723	6.046	1.7

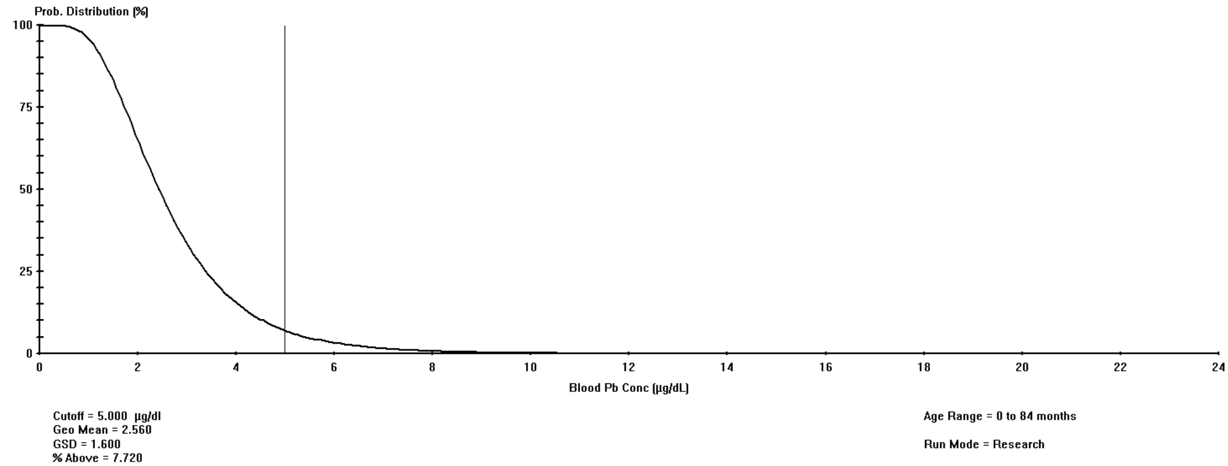

Figure C7. Distribution curve for IEUBK predicted blood lead levels for mean total lead and organic matter, and +0.1 pH units from mean.

Table C7. IEUBK predicted blood lead levels for ages 0-84 months for mean total lead and organic matter, and +0.1 pH units from mean

Year	Soil+Dust (µg/day)	Total (µg/day)	Blood (µg/dL)
.5-1	3.772	5.235	2.8
1-2	5.937	7.821	3.2
2-3	5.990	8.036	3.0
3-4	6.041	8.085	2.8
4-5	4.543	6.612	2.4
5-6	4.112	6.325	2.0
6-7	3.895	6.217	1.8

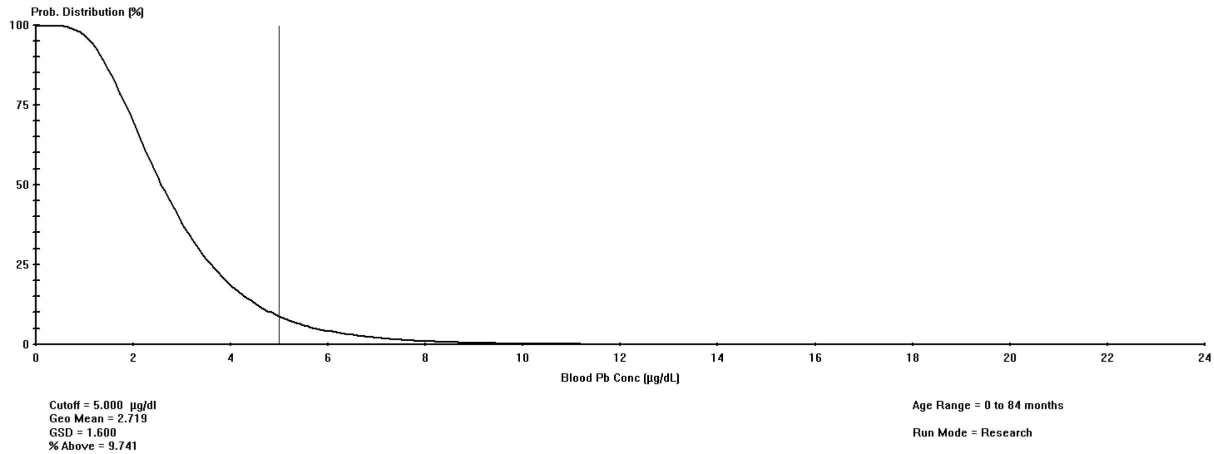

Figure C8. Distribution curve for IEUBK predicted blood lead levels for mean total lead and organic matter, and +0.5 pH units from mean.

Table C8. IEUBK predicted blood lead levels for ages 0-84 months for mean total lead and organic matter, and +0.5 pH units from mean.

Year	Soil+Dust (µg/day)	Total (µg/day)	Blood (µg/dL)
.5-1	4.106	5.563	3.0
1-2	6.457	8.332	3.4
2-3	6.519	8.557	3.2
3-4	6.578	8.615	3.0
4-5	4.953	7.017	2.5
5-6	4.485	6.694	2.1
6-7	4.249	6.567	1.9

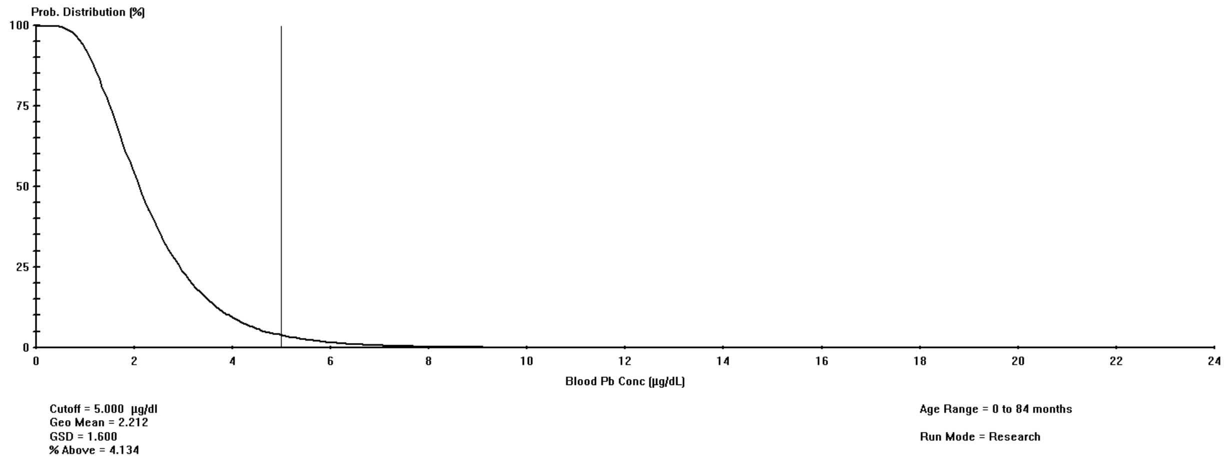

Figure C9. Distribution curve for IEUBK predicted blood lead levels for mean total lead and pH, and organic matter +2.5% from mean.

Table C9. IEUBK predicted blood lead levels for ages 0-84 months for mean total lead and pH, and organic matter +2.5% from mean.

Year	Soil+Dust (µg/day)	Total (µg/day)	Blood (µg/dL)
.5-1	3.039	4.514	2.5
1-2	4.791	6.693	2.8
2-3	4.828	6.890	2.6
3-4	4.863	6.921	2.4
4-5	3.648	5.726	2.0
5-6	3.298	5.520	1.8
6-7	3.123	5.452	1.6

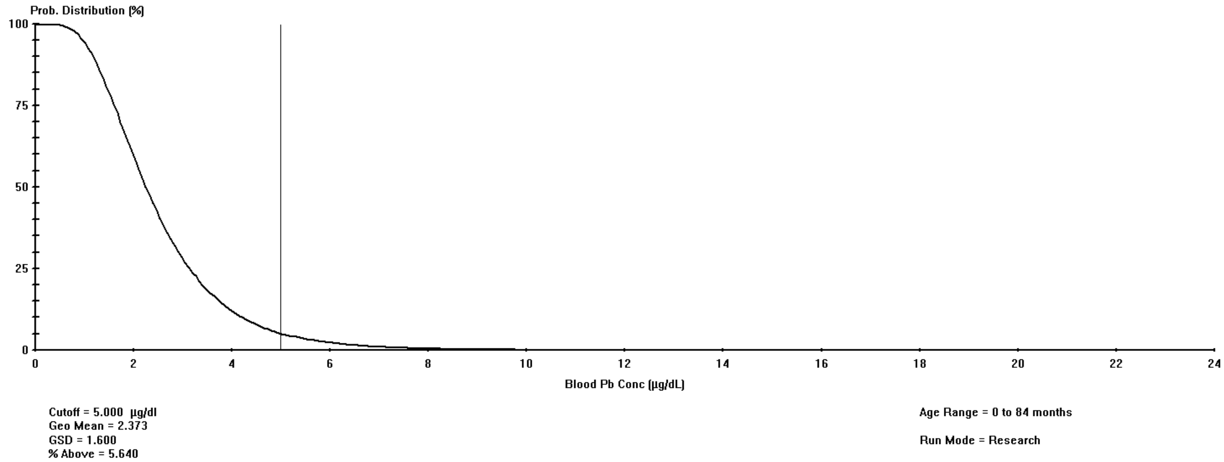

Figure C10. Distribution curve for IEUBK predicted blood lead levels for mean total lead and organic matter, and +1% from mean.

Table C10. IEUBK predicted blood lead levels for ages 0-84 months for mean total lead and organic matter, and +1% from mean

Year	Soil+Dust (µg/day)	Total (µg/day)	Blood (µg/dL)
.5-1	3.378	4.847	2.6
1-2	5.322	7.215	3.0
2-3	5.366	7.420	2.8
3-4	5.408	7.459	2.6
4-5	4.061	6.135	2.2
5-6	3.674	5.892	1.9
6-7	3.479	5.805	1.7

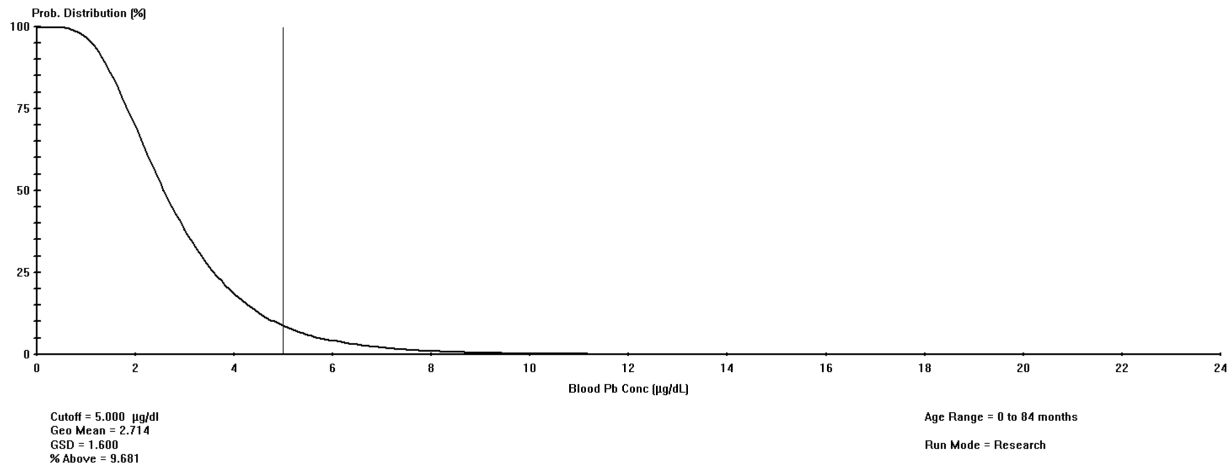

Figure C11. Distribution curve for IEUBK predicted blood lead levels for mean total lead and organic matter, and -1% from mean.

Table C11. IEUBK predicted blood lead levels for ages 0-84 months for mean total lead and organic matter, and -1% from mean.

Year	Soil+Dust (µg/day)	Total (µg/day)	Blood (µg/dL)
.5-1	4.096	5.554	3.0
1-2	6.442	8.318	3.4
2-3	6.504	8.542	3.2
3-4	6.563	8.600	3.0
4-5	4.941	7.006	2.5
5-6	4.474	6.684	2.1
6-7	4.239	6.557	1.9

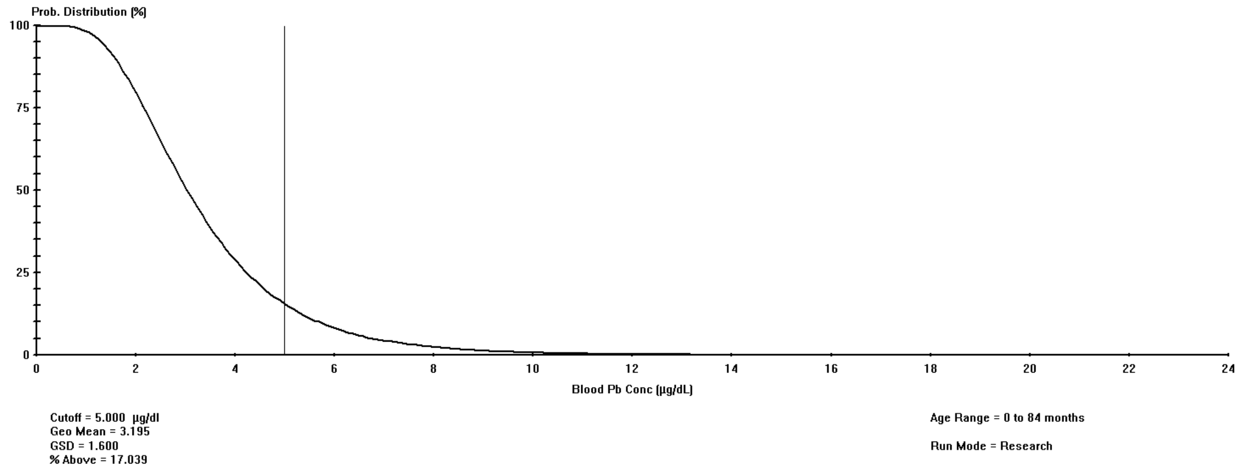

Figure C12. Distribution curve for IEUBK predicted blood lead levels for mean total lead and organic matter, and -2.5% from mean.

Table C12. IEUBK predicted blood lead levels for ages 0-84 months for mean total lead and organic matter, and -2.5% from mean.

Year	Soil+Dust (µg/day)	Total (µg/day)	Blood (µg/dL)
.5-1	5.110	6.551	3.6
1-2	8.019	9.869	4.1
2-3	8.111	10.126	3.8
3-4	8.198	10.214	3.6
4-5	6.194	8.245	3.0
5-6	5.616	7.814	2.5
6-7	5.324	7.632	2.2

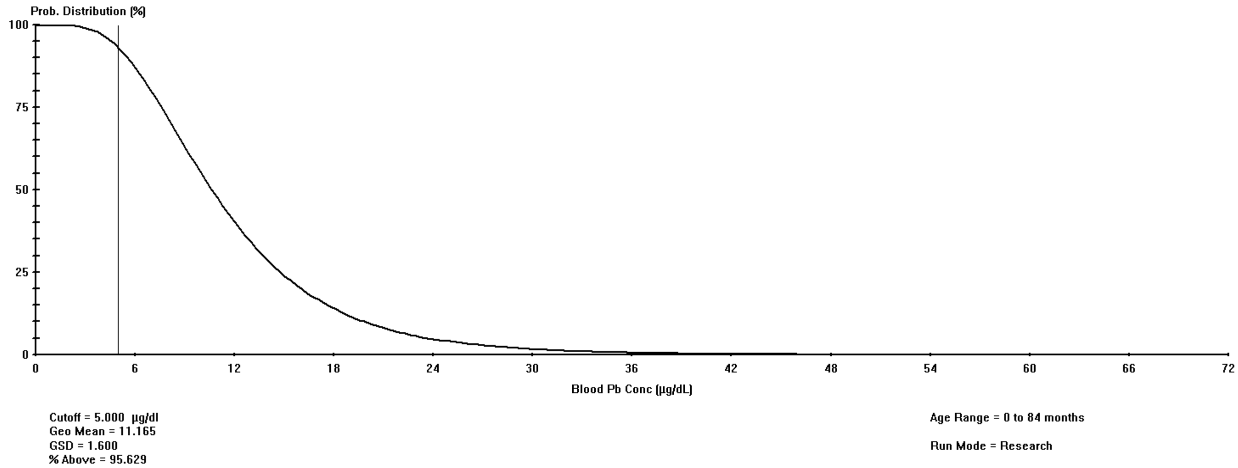

Figure C13. Distribution curve for IEUBK predicted blood lead levels for 95th percentile total lead, organic matter, and pH.

Table C13. IEUBK predicted blood lead levels for ages 0-84 months for 95th percentile total lead, organic matter, and pH.

Year	Soil+Dust (µg/day)	Total (µg/day)	Blood (µg/dL)
.5-1	21.998	23.184	12.1
1-2	33.401	34.875	14.0
2-3	34.680	36.332	13.2
3-4	35.869	37.561	12.8
4-5	28.665	30.481	10.7
5-6	26.575	28.566	9.0
6-7	25.511	27.625	7.9

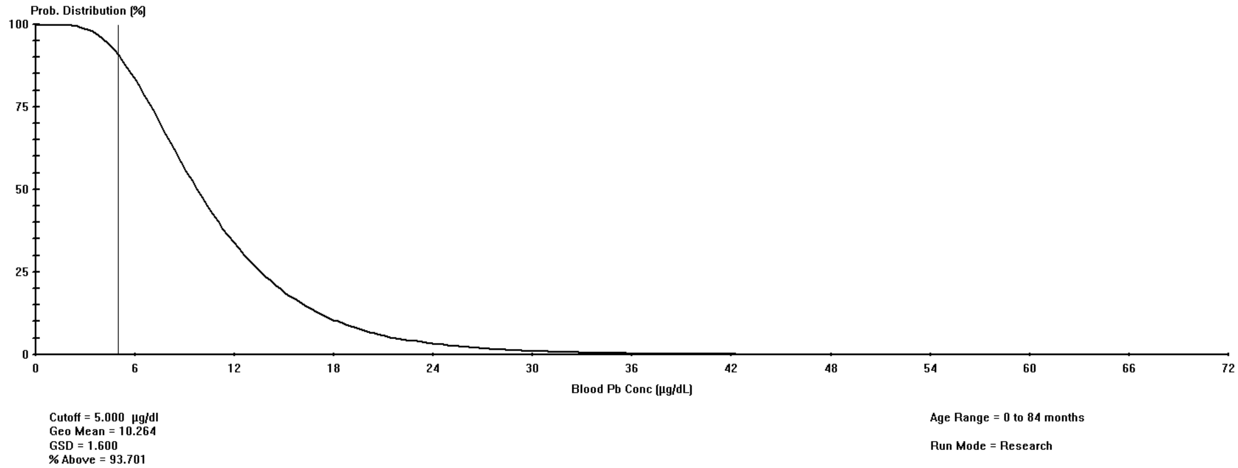

Figure C14. Distribution curve for IEUBK predicted blood lead levels for 95th percentile total lead and organic matter, and -0.5 pH units from mean pH.

Table C14. IEUBK predicted blood lead levels for ages 0-84 months for 95th percentile total lead and organic matter, and -0.5 pH units from mean pH.

Year	Soil+Dust (µg/day)	Total (µg/day)	Blood (µg/dL)
.5-1	20.083	21.295	11.1
1-2	30.588	32.101	13.0
2-3	31.682	33.372	12.2
3-4	32.693	34.420	11.8
4-5	25.972	27.815	9.8
5-6	24.018	26.033	8.2
6-7	23.023	25.161	7.2

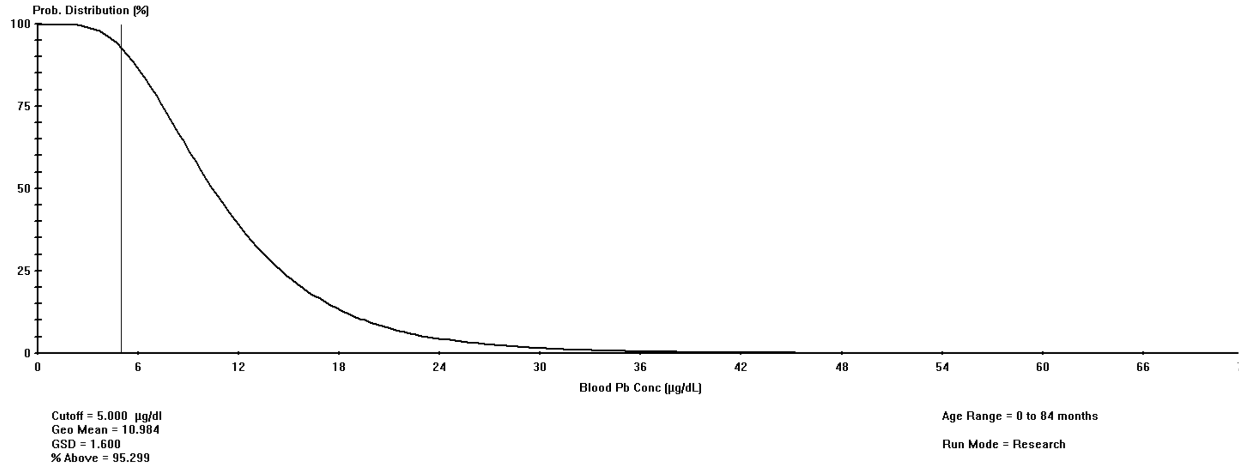

Figure C15. Distribution curve for IEUBK predicted blood lead levels for 95th percentile total lead and organic matter, and -0.1 pH units from mean.

Table C15. IEUBK predicted blood lead levels for ages 0-84 months for 95th percentile total lead and organic matter, and -0.1 pH units from mean.

Year	Soil+Dust (µg/day)	Total (µg/day)	Blood (µg/dL)
.5-1	21.614	22.805	11.9
1-2	32.838	34.321	13.8
2-3	34.080	35.739	13.0
3-4	35.232	36.931	12.6
4-5	28.123	29.944	10.5
5-6	26.059	28.055	8.9
6-7	25.008	27.128	7.8

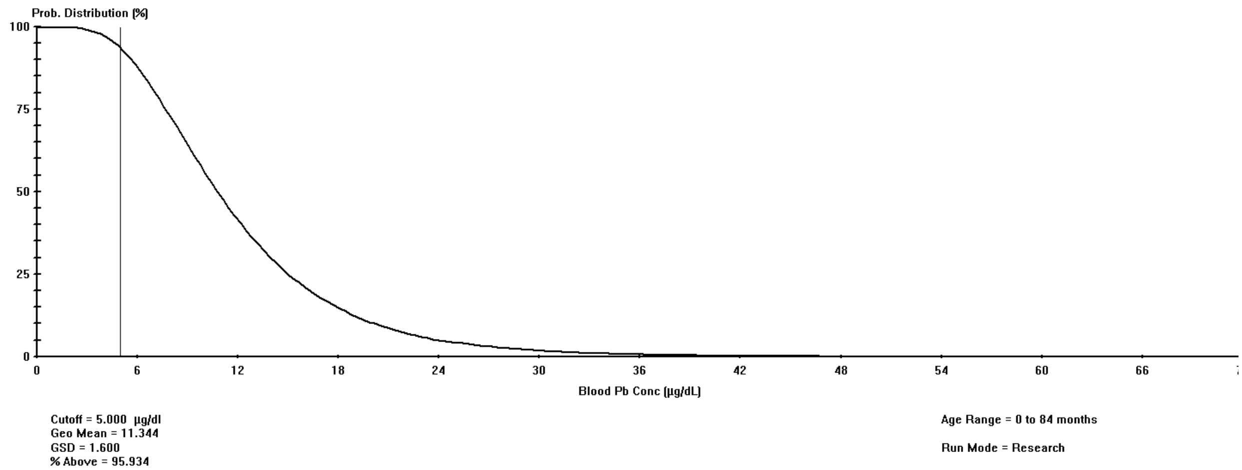

Figure C16. Distribution curve for IEUBK predicted blood lead levels for 95th percentile total lead and organic matter, and +0.1 pH units from mean.

Table C16. IEUBK predicted blood lead levels for ages 0-84 months for 95th percentile total lead and organic matter, and +0.1 pH units from mean.

Year	Soil+Dust (µg/day)	Total (µg/day)	Blood (µg/dL)
.5-1	22.379	23.559	12.3
1-2	33.958	35.425	14.3
2-3	35.275	36.920	13.4
3-4	36.501	38.186	13.0
4-5	29.204	31.015	10.9
5-6	27.088	29.074	9.2
6-7	26.011	28.121	8.1

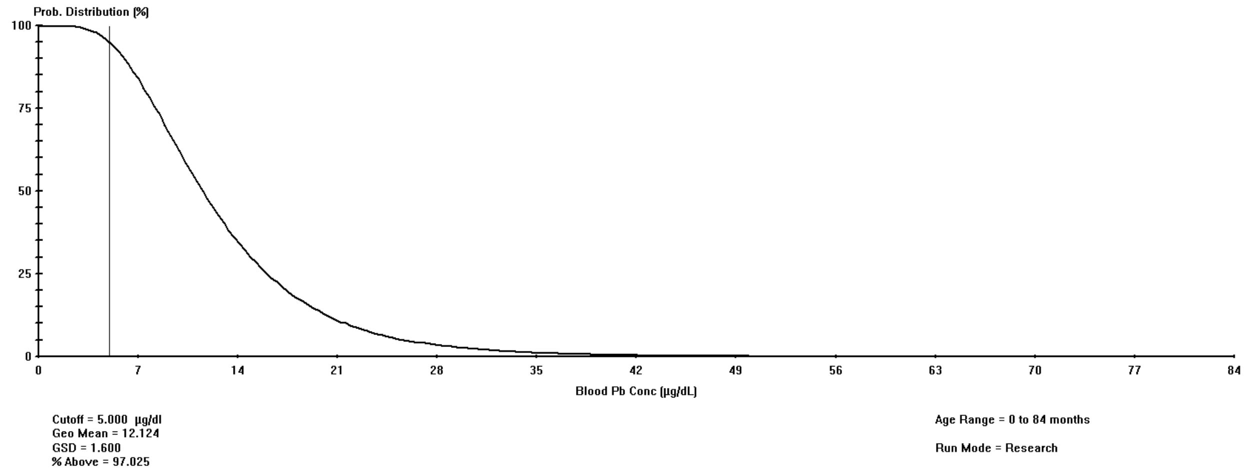

Figure C17. Distribution curve for IEUBK predicted blood lead levels for 95th percentile total lead and organic matter, and +0.5 pH units from mean.

Table C17. IEUBK predicted blood lead levels for ages 0-84 months for 95th percentile total lead and organic matter, and +0.5 pH units from mean.

Year	Soil+Dust (µg/day)	Total (µg/day)	Blood (µg/dL)
.5-1	24.038	25.195	13.1
1-2	36.381	37.816	15.2
2-3	37.868	39.481	14.3
3-4	39.258	40.913	13.9
4-5	31.568	33.354	11.7
5-6	29.344	31.308	9.9
6-7	28.212	30.301	8.7

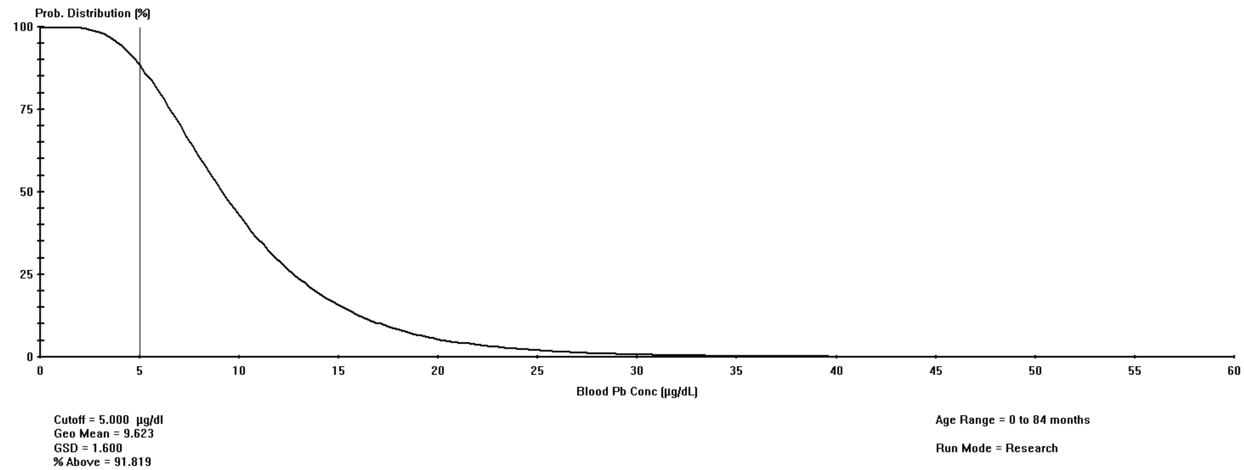

Figure C18. Distribution curve for IEUBK predicted blood lead levels for 95th percentile total lead and pH, and organic matter +2.5% from mean.

Table C2. IEUBK predicted blood lead levels for ages 0-84 months for 95th percentile total lead and pH, and organic matter +2.5% from mean.

Year	Soil+Dust (µg/day)	Total (µg/day)	Blood (µg/dL)
.5-1	18.722	19.954	10.5
1-2	28.582	30.123	12.2
2-3	29.550	31.268	11.4
3-4	30.443	32.195	11.0
4-5	24.081	25.943	9.2
5-6	22.228	24.261	7.7
6-7	21.286	23.440	6.8

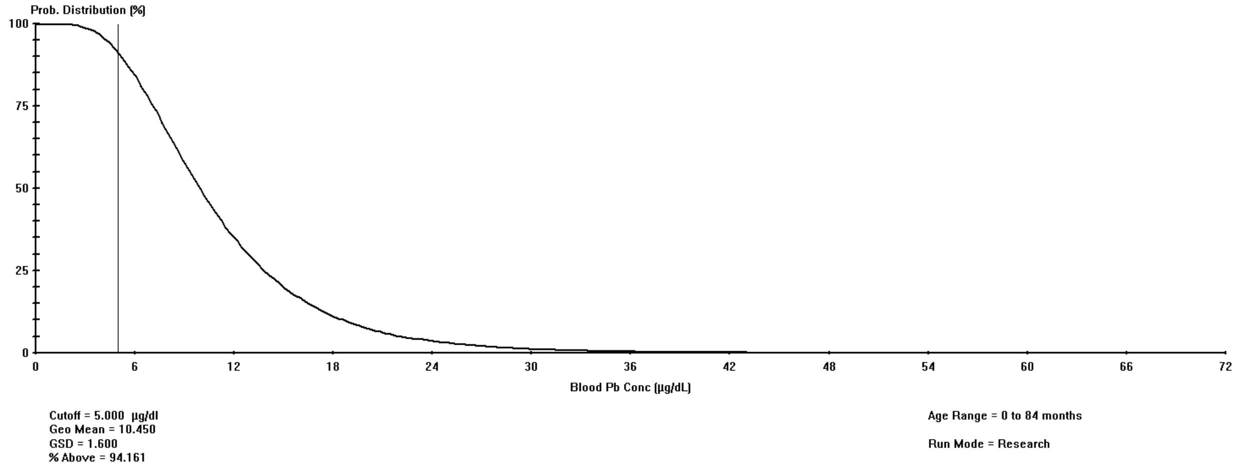

Figure C19. Distribution curve for IEUBK predicted blood lead levels for 95th percentile total lead and organic matter, and +1% from mean.

Table C19. IEUBK predicted blood lead levels for ages 0-84 months for 95th percentile total lead and organic matter, and +1% from mean.

Year	Soil+Dust (µg/day)	Total (µg/day)	Blood (µg/dL)
.5-1	20.479	21.686	11.3
1-2	31.172	32.677	13.2
2-3	32.303	33.985	12.4
3-4	33.351	35.070	12.0
4-5	26.527	28.365	10.0
5-6	24.544	26.554	8.4
6-7	23.534	25.667	7.4

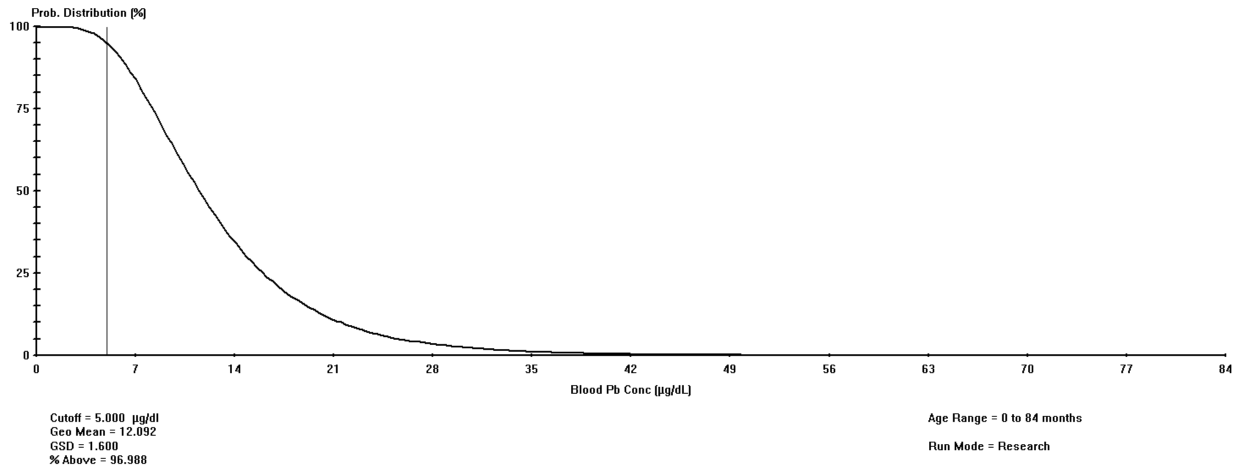

Figure C20. Distribution curve for IEUBK predicted blood lead levels for 95th percentile total lead and organic matter, and -1% from mean.

Table C20. IEUBK predicted blood lead levels for ages 0-84 months for 95th percentile total lead and organic matter, and -1% from mean.

Year	Soil+Dust (µg/day)	Total (µg/day)	Blood (µg/dL)
.5-1	23.971	25.129	13.0
1-2	36.284	37.721	15.1
2-3	37.764	39.378	14.3
3-4	39.147	40.804	13.9
4-5	31.472	33.260	11.6
5-6	29.253	31.218	9.8
6-7	28.123	30.213	8.7

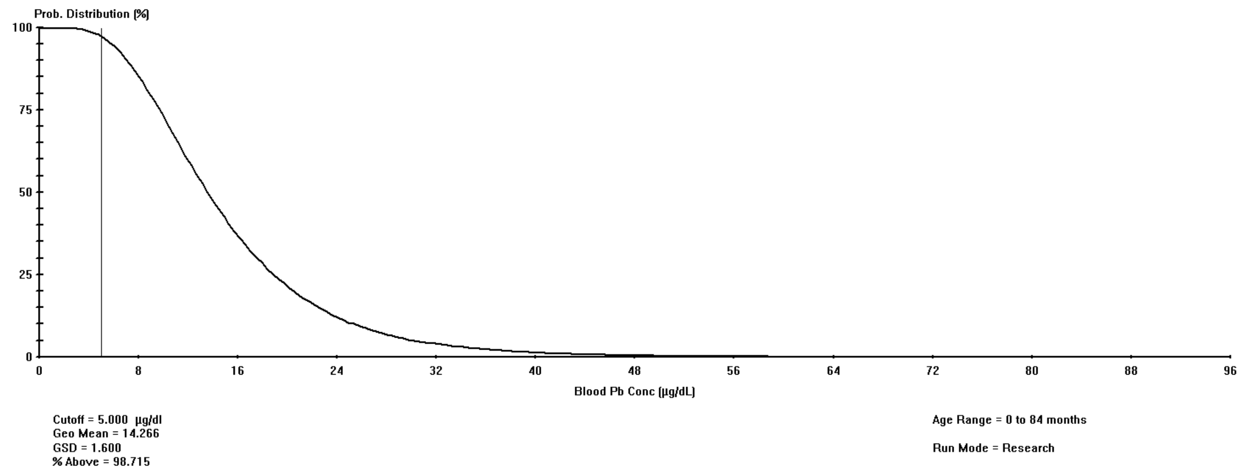

Figure C21. Distribution curve for IEUBK predicted blood lead levels for 95th percentile total lead and organic matter, and -2.5% from mean.

Table C21. IEUBK predicted blood lead levels for ages 0-84 months for 95th percentile total lead and organic matter, and -2.5% from mean.

Year	Soil+Dust (µg/day)	Total (µg/day)	Blood (µg/dL)
.5-1	28.599	29.696	15.3
1-2	43.005	44.357	17.7
2-3	44.986	46.514	16.8
3-4	46.862	48.438	16.3
4-5	38.182	39.905	13.8
5-6	35.701	37.606	11.8
6-7	34.442	36.474	10.4

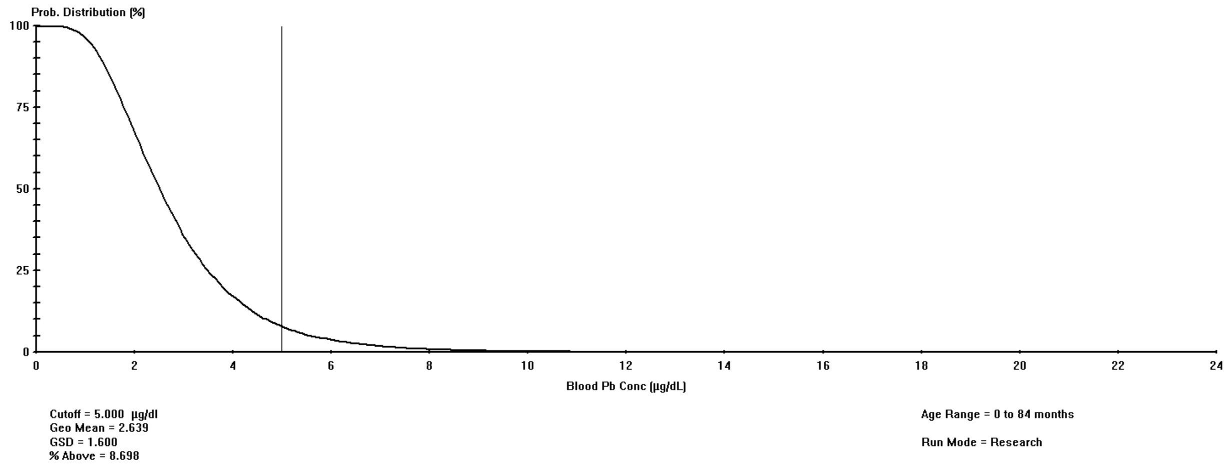

Figure C22. Distribution curve for IEUBK predicted blood lead levels for soils with mean total lead which did not receive treatment.

Table C22. IEUBK predicted blood lead levels for ages 0-84 months for soils with mean total lead which did not receive treatment.

Year	Soil+Dust (µg/day)	Total (µg/day)	Blood (µg/dL)
.5-1	3.938	5.398	2.9
1-2	6.196	8.076	3.3
2-3	6.254	8.296	3.1
3-4	6.309	8.349	2.9
4-5	4.747	6.814	2.4
5-6	4.297	6.509	2.1
6-7	4.071	6.391	1.8

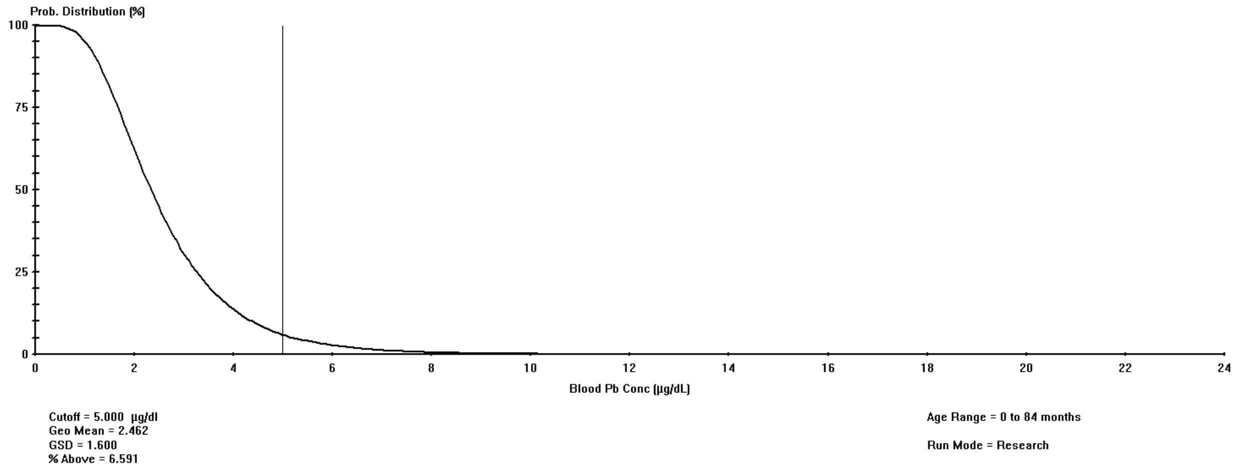

Figure C23. Distribution curve for IEUBK predicted blood lead levels for soils with mean total lead which received a bone meal soil amendment.

Table C23. IEUBK predicted blood lead levels for ages 0-84 months for with mean total lead which received a bone meal soil amendment.

Year	Soil+Dust (µg/day)	Total (µg/day)	Blood (µg/dL)
.5-1	3.566	5.032	2.7
1-2	5.616	7.505	3.1
2-3	5.664	7.715	2.9
3-4	5.711	7.758	2.7
4-5	4.292	6.363	2.3
5-6	3.883	6.099	1.9
6-7	3.678	6.002	1.7

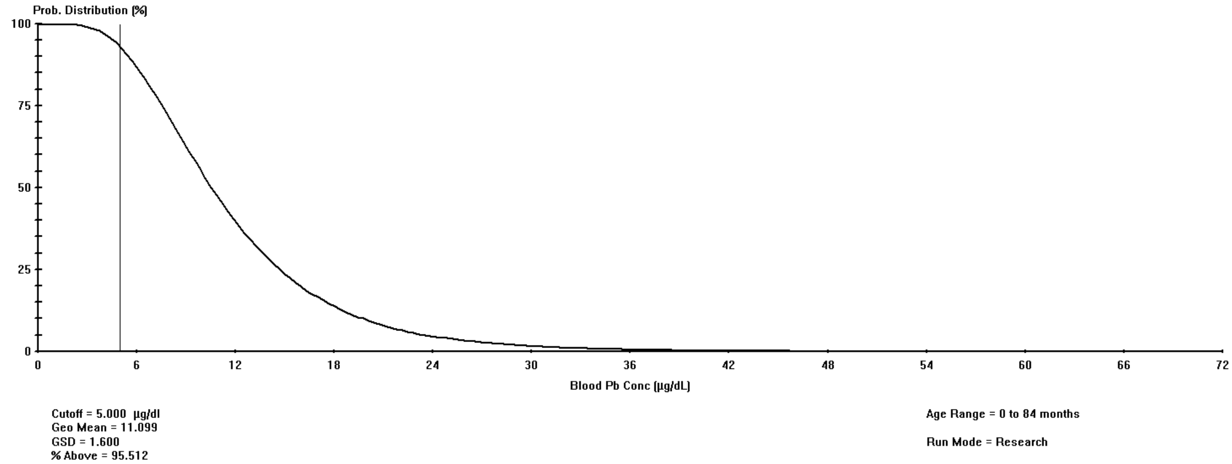

Figure C24. Distribution curve for IEUBK predicted blood lead levels for soils with 95th percentile total lead which did not receive treatment.

Table C24. IEUBK predicted blood lead levels for ages 0-84 months for 95th percentile total lead which did not receive treatment.

Year	Soil+Dust (µg/day)	Total (µg/day)	Blood (µg/dL)
.5-1	21.859	23.047	12.0
1-2	33.197	34.674	14.0
2-3	34.462	36.117	13.1
3-4	35.638	37.333	12.7
4-5	28.468	30.286	10.6
5-6	26.388	28.380	9.0
6-7	25.328	27.444	7.9

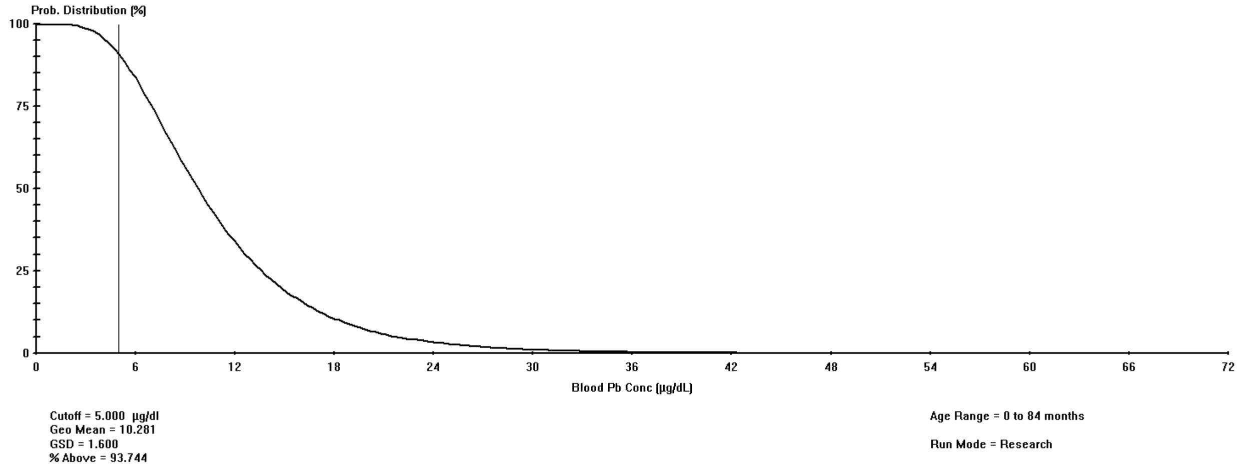

Figure C25. Distribution curve for IEUBK predicted blood lead levels for soils with 95th percentile total lead which received a bone meal soil amendment.

Table C25. IEUBK predicted blood lead levels for ages 0-84 months for 95th percentile total lead which received a bone meal soil amendment.

Year	Soil+Dust (µg/day)	Total (µg/day)	Blood (µg/dL)
.5-1	20.119	21.331	11.1
1-2	30.641	32.154	13.0
2-3	31.739	33.428	12.2
3-4	32.753	34.480	11.8
4-5	26.023	27.865	9.8
5-6	24.066	26.080	8.3
6-7	23.070	25.207	7.3

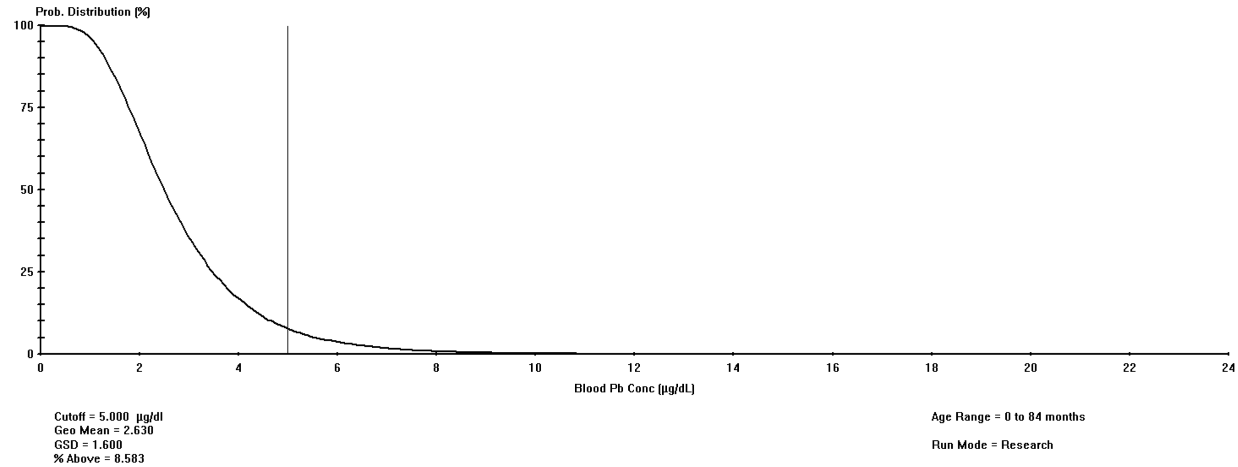

Figure C26. Distribution curve for IEUBK predicted blood lead levels for soils with mean total lead and no change in phosphorus (pre vs. post).

Table C26. IEUBK predicted blood lead levels for ages 0-84 months for soils with mean total lead and no change in phosphorus (pre vs. post).

Year	Soil+Dust (µg/day)	Total (µg/day)	Blood (µg/dL)
.5-1	3.919	5.380	2.9
1-2	6.167	8.047	3.3
2-3	6.224	8.266	3.1
3-4	6.278	8.319	2.9
4-5	4.724	6.791	2.4
5-6	4.276	6.488	2.1
6-7	4.051	6.371	1.8

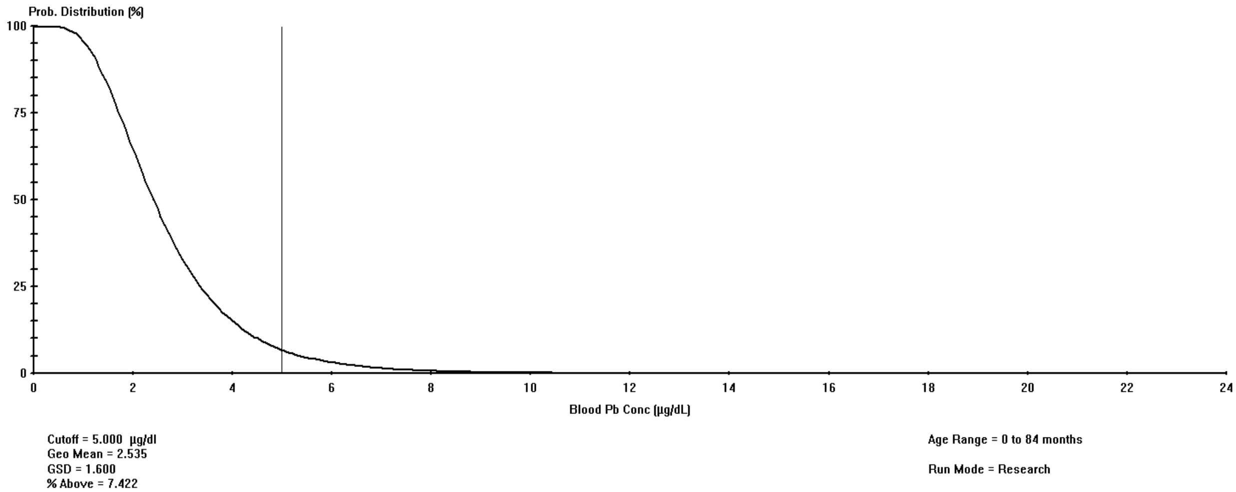

Figure C27. Distribution curve for IEUBK predicted blood lead levels for soils with mean total lead, and a change in phosphorus of 3 mg P/kg (pre vs. post).

Table C27. IEUBK predicted blood lead levels for ages 0-84 months for soils with mean total lead, and a change in phosphorus of 3 mg P/kg (pre vs. post).

Year	Soil+Dust (µg/day)	Total (µg/day)	Blood (µg/dL)
.5-1	3.719	5.183	2.8
1-2	5.855	7.740	3.2
2-3	5.907	7.954	3.0
3-4	5.957	8.001	2.8
4-5	4.479	6.548	2.3
5-6	4.053	6.267	2.0
6-7	3.839	6.162	1.8

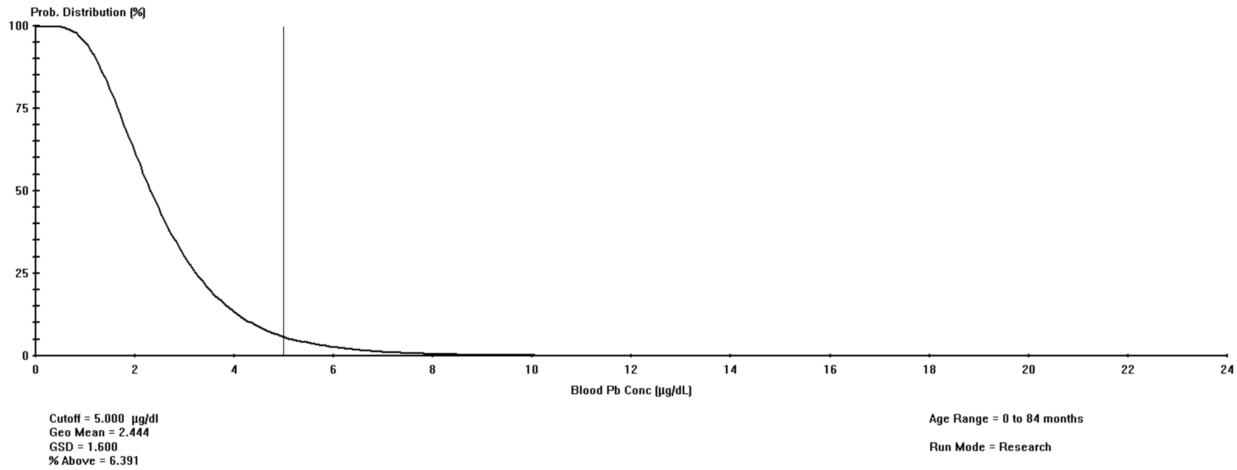

Figure C28. Distribution curve for IEUBK predicted blood lead levels for soils with mean total lead, and a change in phosphorus of 6 mg P/kg (pre vs. post).

Table C28. IEUBK predicted blood lead levels for ages 0-84 months for soils with mean total lead, and a change in phosphorus of 6 mg P/kg (pre vs. post).

Year	Soil+Dust (µg/day)	Total (µg/day)	Blood (µg/dL)
.5-1	3.528	4.995	2.7
1-2	5.556	7.446	3.1
2-3	5.604	7.655	2.9
3-4	5.649	7.697	2.7
4-5	4.245	6.317	2.3
5-6	3.840	6.057	1.9
6-7	3.637	5.962	1.7

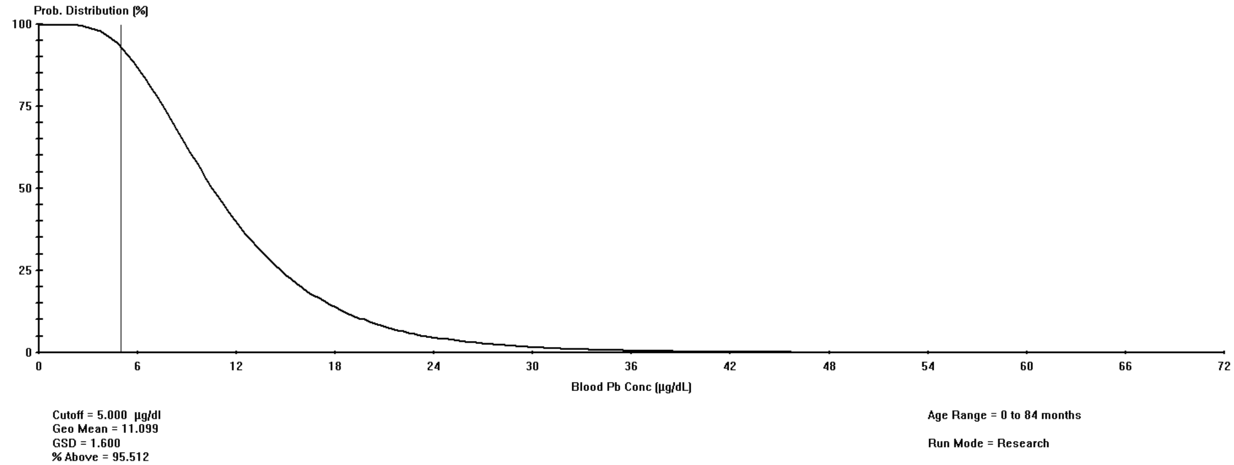

Figure C29. Distribution curve for IEUBK predicted blood lead levels for soils with 95th percentile total lead and no change in phosphorus (pre vs. post).

Table C29. IEUBK predicted blood lead levels for ages 0-84 months for soils with 95th percentile total lead and no change in phosphorus (pre vs. post).

Year	Soil+Dust (µg/day)	Total (µg/day)	Blood (µg/dL)
.5-1	21.859	23.047	12.0
1-2	33.197	34.674	14.0
2-3	34.462	36.117	13.1
3-4	35.638	37.333	12.7
4-5	28.468	30.286	10.6
5-6	26.388	28.380	9.0
6-7	25.328	27.444	7.9

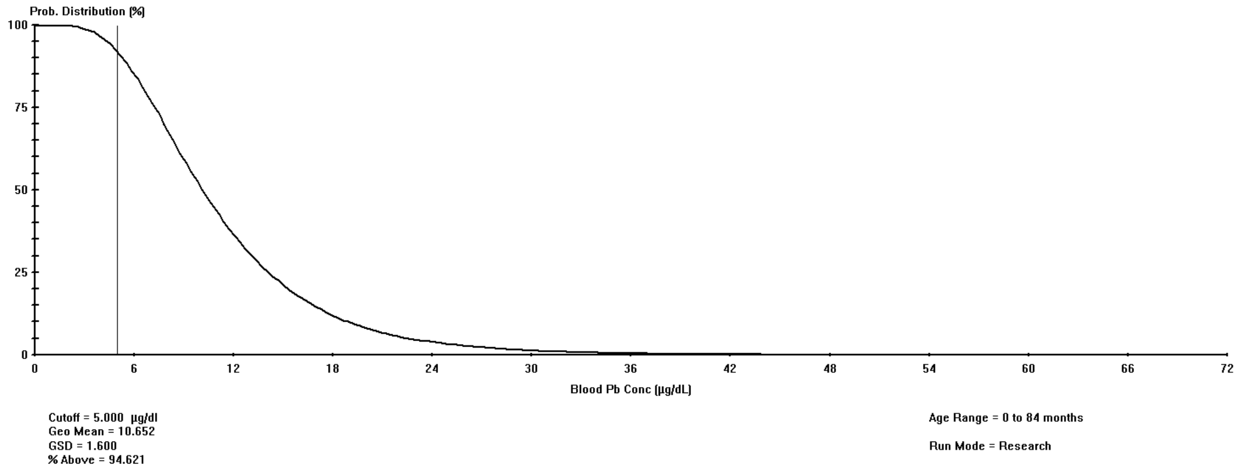

Figure C30. Distribution curve for IEUBK predicted blood lead levels for soils with 95th percentile total lead, and a change in phosphorus of 3 mg P/kg (pre vs. post).

Table C30. IEUBK predicted blood lead levels for ages 0-84 months for soils with 95th percentile total lead, and a change in phosphorus of 3 mg P/kg (pre vs. post).

Year	Soil+Dust (µg/day)	Total (µg/day)	Blood (µg/dL)
.5-1	20.908	22.109	11.5
1-2	31.802	33.298	13.4
2-3	32.975	34.648	12.6
3-4	34.061	35.773	12.2
4-5	27.129	28.960	10.2
5-6	25.115	27.119	8.6
6-7	24.089	26.217	7.5

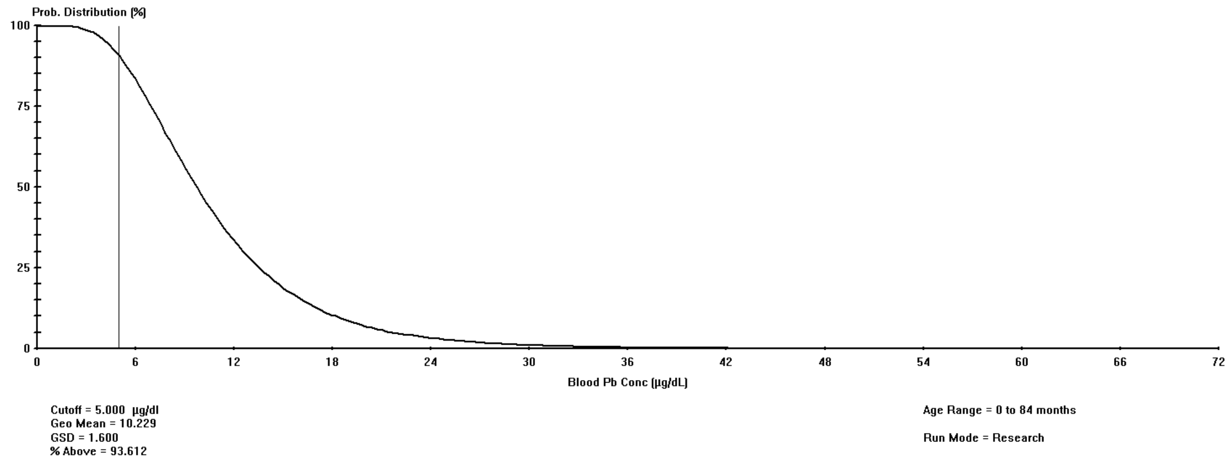

Figure C31. Distribution curve for IEUBK predicted blood lead levels for soils with 95th percentile total lead, and a change in phosphorus of 6 mg P/kg (pre vs. post).

Table C31. IEUBK predicted blood lead levels for ages 0-84 months for soils with 95th percentile total lead, and a change in phosphorus of 6 mg P/kg (pre vs. post).

Year	Soil+Dust (µg/day)	Total (µg/day)	Blood (µg/dL)
.5-1	20.010	21.224	11.1
1-2	30.481	31.996	12.9
2-3	31.568	33.260	12.1
3-4	32.573	34.302	11.7
4-5	25.871	27.715	9.8
5-6	23.922	25.938	8.2
6-7	22.930	25.068	7.2

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ABSTRACT

A FIELD STUDY OF BIOACCESSIBLE LEAD IN DETROIT SOILS: INSIGHT INTO THE EFFECTIVENESS OF PHOSPHATE-BASED LEAD SEQUESTRATION

by

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August 2020

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Historical and contemporary use of lead (Pb) in gasoline, paints, and industry have caused lead to be ubiquitous in the urban soil environment, disproportionately affecting low-income minority children. As soil is a major exposure pathway for children, an effective remediation technique for lead-contaminated soil is urgently needed. Common remediation techniques, such as excavation or soil capping, are expensive and environmentally destructive, especially on a city-wide residential basis. Decreasing the bioavailability of lead, or the fraction which is retained by the human body, may be a more economically and environmentally conscious option for remediating lead in urban environments.

Research has demonstrated that the addition of phosphates to lead-contaminated soil promotes the formation of insoluble minerals (i.e. pyromorphite) that can reduce bioavailability. Previous work typically focused on sites with high concentrations of lead, such as sites proximate to smelters or mining. It is unclear if urban residential properties, with relatively low levels of lead contamination, can be successfully remediated using phosphate amendments. Apatite, in the form of bone meal, may be an ideal phosphate amendment for lead-contaminated soils, as it is readily available, low-cost, contains significant amounts of phosphate, and it is suggested to be less likely to cause eutrophication compared to other phosphate sources.

In-vitro bioaccessibility (IVBA) tests, which simulate a child's digestive system, are often used to predict bioavailability of metals from soil.

In this study, a liquified bone meal soil amendment was applied to residential soils across Detroit, Michigan to determine if this treatment is effective at reducing IVBA. Soil characteristics were evaluated before and after treatment to determine their impact on IVBA. The initial mean Detroit soil IVBA was 39%. The total lead concentration (mg/kg), organic matter content (%) content and soil pH were the most important predictors of IVBA before treatment. Soils with organic matter (OM) 1% and 2.5% greater than the mean OM content (5%) had IVBA measurements 8.6% and 18.2%, respectively, greater than average soils. Soils with pH values 0.1 and 0.5 less than the mean (7.8) had IVBA measurements 2.2% and 10.7%, respectively, lower than the average soils. Overall, the application of bone meal amendment (5g P per 4 ft^2) resulted in a 9.8% decrease in IVBA. This reduction in IVBA was attributed to changes in soil pH and phosphate content. To assess the potential impact of this reduction, a sensitivity analysis was performed using the US EPA's Integrated Exposure Uptake Biokinetic (IEUBK) model. Based on default exposure assumptions in the IEUBK model, if the remediation were to be applied across all soils, the geometric mean of blood lead levels (BLLs) in children under the age of seven is expected to decrease 6.7%. The results of this study suggest bone meal may be a suitable remediation strategy for reducing lead bioavailability in Detroit.

AUTOBIOGRAPHICAL STATEMENT

Sabrina Good has a Bachelor of Science in Environmental Science and a Bachelor of Science in Geology from Wayne State University. She has conducted water quality and soil quality research in her undergraduate and graduate degrees, respectively. Her interests include remediation, environmental justice, sustainability, native plant biodiversity, community involvement, and all activities which promote the equality and well-being of her fellow humans and non-human animals.