DECREASING LEAD BIOACCESSIBILITY IN SOILS WITH

PHOSPHATE AMENDMENTS

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DECREASING LEAD BIOACCESSIBILITY IN SOILS WITH PHOSPHATE AMENDMENTS

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THESIS ABSTRACT

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PHOSPHATE AMENDMENTS

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Ingestion of Pb-contaminated soil has been proposed as a primary exposure pathway for elevated blood Pb levels in young children (Dudka and Miller, 1999). Children are often exposed to soils contaminated with toxic metals such as lead (Pb) through hand-to-mouth activity. Therefore, the ingestion of Pb-contaminated soils by children is typically the risk driver at Pb-contaminated sites (Dudka and Miller, 1999).

The subject of immobilizing Pb in Pb – contaminated soils has been frequently studied. In – situ stabilization using phosphorus (P) amendments, such as phosphate fertilizers and phosphate rock, were found to provide the most cost – effective and least disruptive alternative for stabilizing Pb in soils (Berti and Cunningham, 1997; Ma and Rao, 1999). However, few studies have examined the bioavailability of Pb –

contaminated soils amended with P using the physiologically based extraction test (PBET).

The primary objective of this research was to investigate the effects of aging time and P amendments on Pb bioaccessibility. Amendments were applied in situ to Pb – spiked (labile) soils and Pb – contaminated (non – labile) soils for comparison. Pb and Sb concentrations in small – arms firing range soils were also analyzed to determine whether the two are correlated.

Analysis of phosphate concentrations in PBET supernatants revealed that the PBET samples were well undersaturated (SI<0) with respect to chloropyromorphite. Therefore, chloropyromorphite did not form as an experimental artifact in the PBET.

The weathering and corrosion of Pb ammunition is a significant source of Pb in Pb - contaminated soils. The results from three small-arms firing ranges showed that Pb and Sb concentrations are linearly correlated (R^2>0.90). The data was consistent with the general composition of Sb in Pb bullets and the co-mobility of Pb and Sb due to the weathering and corrosion of ammunition.

Results from the two amendment studies revealed that large amounts (26.2% - 50.5% by weight) of P amendments must be applied in situ to achieve significant reductions in Pb bioaccessibility. Environmental implications for adding such large amounts of P to soil, such as increased leaching of oxyanions like Sb and As, should be considered. Thus, adding P amendments to soils may not be the most practical approach to reduce the bioaccessibility of Pb in Pb – contaminated soils.

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CHAPTER ONE

INTRODUCTION

1.1 Statement of the Problem

Children are often exposed to soils contaminated with toxic metals such as lead (Pb) through hand-to-mouth activity. Ingestion of Pb-contaminated soil has been proposed as a primary exposure pathway for elevated blood Pb levels in young children (Dudka and Miller, 1999). Research has shown that young children with high levels of Pb in their blood are more susceptible to slower cognitive development, leading to learning disabilities in addition to health problems (Dudka and Miller, 1999). As a result, billions of dollars are spent on medical treatment and special education (Ryan et al., 2004). Therefore, the ingestion of Pb-contaminated soils by children is typically the risk driver at Pb-contaminated sites (Dudka and Miller, 1999).

The subject of immobilizing Pb in Pb – contaminated soils has been studied extensively. In – situ stabilization using phosphorus (P) amendments, such as phosphate fertilizers and phosphate rock, were found to provide the most cost – effective and least disruptive alternative for stabilizing Pb in soils (Berti and Cunningham, 1997; Ma and Rao, 1999). Stanforth and Qiu (2001) showed that increasing the phosphate dose resulted in increasingly lower Pb solubility. However, few studies have examined the bioavailability of Pb – contaminated soils amended with P using the physiologically

based extraction test (PBET), a test developed to mimic the human digestive system that has been used to simulate *in vivo* results for Pb and As bioavailability (Ruby et al., 1996). In this study, the effects of aging time and P dose on Pb bioavailability in both labile (Pb – spiked) and non-labile (Pb – contaminated) soils was investigated using the PBET.

When P is present in the environment, very stable, insoluble forms of Pb phosphates called pyromorphites are formed. The most stable pyromorphite is chloropyromorphite ($Pb_5(PO_4)_3Cl$). Scheckel et al. (2003) found that chloropyromorphite was forming during a sequential extraction procedure itself rather than *in situ* and have expressed concern for the formation of chloropyromorphite during soil Pb contact with PBET extraction solution. Sequential extraction procedures have been previously used to determine solid-phase speciation of metals existing in soil and sediment matrices (Scheckel et al., 2003). An additional objective in this research is to determine whether chloropyromorphite is being formed as an experimental artifact in the PBET or *in situ*.

In many countries, the use of Pb – based ammunition is another significant source of Pb pollution. Annual deposition by hunting and recreational shooting reaches 55,000 tons of Pb in the U.S. alone (Jorgensen and Willems, 1987; Mellor and McCartney, 1994; Scheuhammer and Norris, 1996). Antimony (Sb) is used as a hardening agent in the manufacturing of Pb ammunition. Pb bullets are generally comprised of a Sb content of 2 – 5% by weight. The presence of P greatly decreases As (V) and As (III) sorption by soils (Smith et al., 2002). Because Sb has similar elemental properties to As (e.g. both are oxyanions), one concern is that Sb sorption may also be decreased when applying P to reduce Pb found in Pb – contaminated soils. A final goal

of this study was to determine whether or not a relationship exists between Sb and Pb in small – arms firing range soils and thus the potential for remediation strategies for Pb – contaminated soils to affect Sb mobility.

1.2 Objectives

The primary objective of this research was to investigate the effects of aging time and P amendments on Pb bioaccessibility. Amendments were applied *in situ* to Pb – spiked (labile) soils and Pb – contaminated (non – labile) soils for comparison. Total phosphate concentration was measured in the PBET to determine whether reductions in Pb bioaccessibility due to chloropyromorphite formation were occurring *in situ* (e.g., in the soil itself) or occurring as an experimental artifact in the PBET. Pb and Sb concentrations in small – arms firing range soils were also analyzed to determine whether the two are correlated.

1.3 Organization

The organization of this report follows the guidelines for a publication style thesis as outlined in the *Guide to Preparation and Submission of Theses and Dissertations* by the Auburn University Graduate School. Chapter 2 contains a literature review. The results of the Pb bioaccessibility study are divided into chapters 3 and 4. Chapter 3 contains the results from the Pb-contaminated soils, while Chapter 4 assesses the Pb-spiked soils. The results of the Pb and Sb pollution from firing range soils study are provided in Chapter 5 of this thesis. Chapters 3, 4, and 5 are prepared as draft manuscripts (with abbreviated introductions) for journal submission.

CHAPTER TWO

LITERATURE REVIEW

2.1 Risk Assessment

Lead (Pb) has been ranked as the second most hazardous substance in the U.S. by the Agency for Toxic Substances and Disease Registry (ATSDR) and the U.S. Environmental Protection Agency (U.S. EPA) (ATSDR, 1999). In 1999, Pb was identified as a major hazardous chemical at 47% of the 1219 Superfund sites on the U.S. EPA's National Priorities List (U.S. EPA, 1999). Pb is used in the manufacturing of ammunition, solders, metal alloys, ceramic glazes, antique-molded or casted ornaments, and storage batteries (U.S. CDC, 2005). In the past, Pb was added to paints and gasoline, and it has been used in plumbing for centuries. Small amounts of Pb also may be released from the burning of fossil fuels (U.S. CDC, 2005). Mining operations, smelter and industrial emissions, and applications of pesticides have all contributed to elevating Pb to harmful levels in soil (Ryan et al., 2004).

Water, soil, dust, and air are the major sources of exposure of Pb to humans (Hettiarachchi et al., 2004). The two main exposure pathways for intake of Pb – contaminated materials are ingestion via the gastrointestinal (GI) tract and inhalation by the lungs (Hettiarachchi et al., 2004). Children are often exposed to soils contaminated with toxic metals such as Pb through hand-to-mouth activity (such as biting nails,

sucking thumbs, and eating non-food items). Therefore, the ingestion of soils contaminated with toxic metals like Pb is of great concern because of their toxicity and threat to human health. As such, the ingestion of Pb-contaminated soils by children is typically the risk driver at Pb-contaminated sites (Dudka and Miller, 1999). In 1991, the Centers for Disease Control and Prevention (CDC) identified children less than six years of age as having a high risk of exposure to Pb because of their more frequent hand-to-mouth behavior (Ryan et al, 2004). Ingestion of Pb-contaminated soil has been proposed as a primary exposure pathway for elevated blood Pb (PbB) levels in young children (Dudka and Miller, 1999). Research has shown that young children with high levels of Pb in their blood are more susceptible to slower cognitive development, leading to learning disabilities in addition to health problems (Dudka and Miller, 1999). As a result, billions of dollars have been spent on medical treatment and special education (Ryan et al., 2004). Programs have been implemented to reduce children's exposure to Pb in paint and drinking water. Unfortunately, no program is in place for reducing children's exposure to Pb in soils beyond Superfund sites (Ryan et al., 2004).

Several studies have been conducted to investigate soil ingestion and Pb exposure, as summarized by Ruby et al. (1999). Experiments have been conducted with living animals (*in vivo*), and outside of a living organism in the laboratory (*in vitro*). The term "bioavailability" refers to the portion of a substance or element in soil that is available for absorption into living organisms, such as humans, animals, or plants (Hettiarachchi et al., 2004). In 2003, Hettiarachchi et al. defined relative bioavailability as "a comparative bioavailability of a substance from a particular exposure medium (e.g. soil) relative to a reference material (e.g. Pb acetate for Pb). Previously, the relative

bioavailability of metals in soil was determined by *in vivo* studies on laboratory animals (Ruby et al., 1999). In the past, the U.S. EPA typically relied on immature swine feeding studies to predict the bioavailability of Pb in humans. However, a drug absorption study done by Kararli (1995) revealed that although the right animal model can be selected for a specific purpose, no single animal can mimic the characteristics of the GI tract of humans.

One proposed alternative to expensive *in vivo* animal studies in assessing metal bioaccessibility in soils is the physiologically based extraction test (PBET). The PBET, developed to mimic the human digestive system, has been used to simulate *in vivo* results for Pb and As bioavailability (Ruby et al., 1996) and estimate changes in Pb bioavailability induced by soil amendments (Hettiarachchi et al., 2004). The soluble and dissolved Pb produced during this extraction procedure is available for absorption in the GI tract and is defined by Ruby et al. (1999) as "bioaccessibility." Ruby et al. (1996) compared the results of the PBET extraction with data from a Sprague-Dawley rat model and found that there is a linear correlation between *in vitro* estimated bioaccessibility and *in vivo* measured relative bioavailability. In January of 1997, the solubility/bioavailability research consortium (SBRC) was formed to further develop and verify an *in vitro* method for estimating the bioavailability of metals in soil (Ruby et al., 1999). The original PBET extraction method was designed to simulate the human GI tract by replicating conditions in the human stomach and the small intestine (Ruby et al., 1996). The factors controlled during the original PBET extraction included pH, temperature, soil-to-solution ratio, and stomach mixing and emptying rates (duration of contact). A modified, streamlined version of the PBET extraction has recently been

verified and published (Kelley et al., 2002). This procedure may be used to facilitate bioavailability/bioaccessibility research, where bioaccessibility is used as a surrogate for oral bioavailability. Two other alternatives to assess human health risks from Pb are the Adult Lead Methodology (ALM) and the Integrated Exposure Uptake and Biokinetic (IEUBK) Model (U.S. EPA, 2006). The ALM, developed in 2005, is a mathematical equation used to predict the Pb concentration in soil appropriate for non – residential areas where children are not likely to play (U.S. EPA, 2006). The IEUBK model is a computer program used to predict Pb concentrations in soil, water, and air in areas where children live and play (IEUBK, U.S. EPA, 1994).

2.2 General Chemistry and Mineralogy of Lead

Elemental Pb is a naturally occurring, malleable, dense, blue-gray metal found in soils and rocks. It can be combined to form inorganic and organic molecules and ions. In reduced systems and in the presence of sulfur, the most common, stable form of Pb is the mineral galena [PbS (s)]. Galena is composed of 87% Pb by weight (Hettiarachchi et al., 2004). In an oxidizing environment, [PbS (s)] can be converted into other forms of Pb such as anglesite ($PbSO_4$) and cerrusite ($PbCO_3$) via the oxidation of sulfide to sulfate (Hettiarachchi et al., 2004):

$$PbS\ (galena) \leftrightarrow Pb^{2+} + S^{2-} \qquad K_{sp} = 10^{-27.5} \qquad (2.1)$$

$$PbCO_3\ (cerrusite) + 2H^{+} \leftrightarrow Pb^{2+} + CO_2(g) + H_2O \qquad K_{sp} = 10^{-12.8} \qquad (2.2)$$

$$PbSO_4\ (anglesite) \leftrightarrow Pb^{2+} + SO_4^{2-} \qquad K_{sp} = 10^{-7.7} \qquad (2.3)$$

When ortho-phosphorus (P) is present in a similar environment, Pb phosphates such as pyromorphites ($Pb_5\ (PO_4)_3X$, where X = Cl^-, Br^-, F^-, OH^-) are formed. Davis et al.

(1993) reported that pyromorphites are a common weathering product of Pb compounds in mine spoils. Pyromorphites are the most stable forms of Pb in soil under a wide range of environmental conditions (Lindsay, 1979; Nriagu, 1972; Hem and Durum, 1973). The most stable pyromorphite is chloropyromorphite:

$$Pb_5(PO_4)_3Cl \text{ (chloropyromorphite)} + 6H^+ \leftrightarrow 5Pb^{2+} + 3H_2PO_4^- + Cl^-$$

$$K_{sp} = 10^{-84.4} \qquad (2.4)$$

As a result, P is sometimes added to soil to convert Pb to a more stable and less soluble form.

2.3 Lead-Phosphate Interactions

The primary objective of in situ immobilization of Pb-contaminated soil is to reduce the Pb bioavailability to environmentally acceptable levels (Ma and Rao, 1999). In the past, there have been several remediation strategies applied. Soil excavation was found to be both disruptive and costly as the total removal of all Pb-contaminated soils caused problems with landfill space (Rabinowitz, 1993). An alternative and more practical solution was developed to remediate soils highly contaminated with Pb, which used P-rich materials such as P - containing fertilizers and phosphate rock to immobilize Pb (Chen et al., 2003). An economic analysis of remediation alternatives was conducted by Berti and Cunningham (2000). The study showed that in-situ stabilization methods stabilize soils both chemically and physically and remain the lowest in net present cost over other alternatives. In-situ stabilization using P amendments provide the most cost-effective and least disruptive way of stabilizing Pb in soils (Ma and Rao, 1999; Berti and Cunningham, 1997).

Research has provided thermodynamic data for the bonds formed by Pb with phosphates in aqueous solutions. Ryan et al. (2004) have demonstrated that the addition of phosphate in the form of phosphate salt or a stable rock phosphate reduced aqueous Pb concentrations to low levels in Pb-contaminated soil solutions due to the rapid and exclusive formations of pyromorphites. Similarly, others have shown that apatite and other calcium phosphates can reduce the solubility of Pb in soils by forming Pb phosphates (Ma et al.,1993, 1995; Ruby et al., 1994; Berti and Cunningham, 1997). Stanforth and Qiu (2001) showed that increasing the phosphate dose resulted in increasingly lower Pb solubility. The formation of Pb phosphates was found to be responsible for immobilizing Pb in soils, thereby reducing the bioavailability of Pb in soils (Ruby et al., 1994; Hettiarachchi et al., 2000).

Previous studies have shown reductions in Pb bioaccessibility in soils amended with P. A study done by Hettiarachchi et al (2000) used triple super-phosphate (TSP) and rock phosphate (RP) as P amendments. TSP is a soluble form of P and a common agricultural fertilizer made by reacting RP with orthophosphoric acid (Hettiarachchi et al., 2001). Hettiarachchi et al (2000) found that the addition of P as TSP or RP to five Pb-contaminated soils or mine spoils decreased the Pb bioaccessibility in PBET extractions by 15 to 41%, relative to the control. However, these soils had only limited (18.3 – 36.6%) bioaccessibility initially. In a field study by Brown et al. (2004), several P treatments significantly reduced Pb bioaccessibility as measured by the PBET method (*in vitro*) and by Pb uptake by tall fescue. The addition of 1% P as rock phosphate (RP) reduced *in vitro* Pb, but it was not significantly different than the control (0% P). The addition of 1% P as TSP did not effectively reduce either *in vitro* Pb or Pb uptake by tall

fescue, but TSP at the highest dose (3.2% P) was found to be the only effective treatment. Most studies, however, observed very little variation in lead bioaccessibility over time (Hettiarachchi et al., 2000). For example, in a study conducted by Hettiarachchi et al. (2001), reductions in bioaccessible Pb occurred between 0 and 3 days after treatment and no further reductions occurred over 365 days of incubation. RP was equally or more effective than TSP or phosphoric acid (PA) at reducing Pb bioaccessibility in four out of five soils. Also, increasing the amount of P from 2500 mg/kg to 5000 mg/kg resulted in a significant reduction in bioaccessible Pb. Overall, a 25 – 38% reduction in bioaccessibility relative to the control was observed among all five soils (Hettiarachchi et al., 2001).

Scheckel et al. (2003) conducted research on the formation of chloropyromorphite ($Pb_5 (PO_4)_3Cl$) in P-amended, Pb – contaminated soils during sequential extraction procedures. Sequential extraction procedures have been previously used to determine solid-phase speciation of metals existing in soil and sediment matrixes (Scheckel et al., 2003). They found that chloropyromorphite was forming during a sequential extraction procedure itself rather than *in situ*. In 2005, Scheckel et al. postulated that Pb bioaccessibility reduction via formation of chloropyromorphite was probably occurring as an experimental artifact in the PBET rather than in the soils themselves.

In a study by Sonmez and Pierzynski (2005), relative bioaccessibility was defined as the percentage of Pb extracted in the PBET relative to the control sample. The objective of this study was to determine the effects of commercial and synthetic manganese (Mn) oxides, TSP, and RP on Pb bioaccessibility in five Pb – contaminated

soils or mine spoils (Sonmez and Pierzynski, 2005). Results from the PBET indicated that most amendments significantly decreased Pb bioaccessibility relative to the control, but treatment effects differed from soil to soil. The most effective amendments were TSP, RP, and birnessite (a synthetic Mn oxide), which reduced the relative % Pb bioaccessibility by 33%, 44%, and 81%, respectively in one soil. Combining RP or TSP with synthetic Mn oxides more effectively reduced the relative % Pb bioaccessibility (by 90% in one soil) than either of the amendments alone (Sonmez and Pierzynski, 2005). In contrast to Hettiarachchi et al. (2001), Pb bioaccessibility in the amended samples decreased with time.

2.4 Environmental Lead Pollution Caused By Firing Ranges

In many countries, the use of Pb-based ammunition is one of the most significant sources of Pb pollution. Annual deposition by hunting and recreational shooting varies between 200 and 6000 tons in the Netherlands, Denmark, Canada, and England and reaches 55,000 tons in the U.S. (Jorgensen and Willems, 1987; Mellor and McCartney, 1994; Scheuhammer and Norris, 1996). According to the Dept. of Environment in Switzerland, it is estimated that 400 – 500 tons of Pb and 10 – 25 tons of antimony (Sb) enter the soil environment every year as a result of shooting practice at over 2,000 ranges (Knechtenhofer et al., 2003). The contamination is the greatest in the top 20 – 30 cm of embankments that act as stop butts behind the targets. One soil column study showed an effluent concentration of 3400 $\mu g\ l^{-1}$ Pb from a firing range soil (Rooney and McLaren, 1999).

Bullets generally have cores made of a Pb-Sb alloy with a Sb content of 2-5% by weight. Other elements such as As, Bi, or Ag may be present in recycled Pb of secondary quality, and the bullet jacket may be of Cu or Ni alloy housing (Guy and Pate, 1973; Randich et al., 2002). Sb, a suspected human carcinogen (Gebel, 1997), has been found at concentrations of up to 155 $\mu g\ l^{-1}$ in soil solution (Farenhorst and Renger, 1990). A study done by Fahrenhorst (1993) showed that in neutral soils, aqueous concentrations of Sb exceeded those of Pb, despite the much higher solid phase Pb content. For acidic soils, the situation was reversed, and the aqueous Pb content exceeded the Sb content. This is consistent with the idea that the adsorption of metals and metalloids is pH dependent. At low pH, there was more Pb in solution because cations are less absorbed than oxyanions at lower pH values. As the pH increases, the situation is reversed. Cations (Pb) become more absorbed and oxyanions (Sb) less adsorbed.

Sb and its compounds have been listed as priority pollutants by the U.S. EPA and the European Union (Potin-Gautier et al., 2005). The Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) requires the U.S. EPA and the ATSDR to prioritize substances "which are deemed to pose the most significant potential threat to human health due to their known or suspected toxicity and potential for human exposure." Sb is ranked #241 out of 275 elements while Pb is ranked #2. The mobilization of Sb primarily depends on the corrosion of the bullets and on the oxidation of Sb (0) to Sb (III) and Sb (V) (Johnson et al, 2005). Sb has similar elemental properties to As. Both As and Sb are oxyanions. The presence of P greatly decreases As (V) and As (III) sorption by soils, indicating the competitive adsorption between P and

As for sorption sites (Smith et al., 2002). Similarly, Sb sorption may also be decreased when applying P to reduce Pb found in Pb-contaminated soils, particularly if bullets are the source of the Pb.

CHAPTER THREE

REDUCING THE BIOACCESSIBILITY OF LEAD IN LEAD-CONTAMINATED SOILS AMENDED WITH THREE PHOSPORUS AMENDMENTS

3.1 Introduction

The subject of immobilizing Pb in Pb – contaminated soils has been studied extensively. In – situ stabilization using phosphorus (P) amendments provides the most cost – effective and least disruptive alternative for stabilizing Pb in soils (Berti and Cunningham, 1997; Ma and Rao, 1999). However, few studies have examined the bioaccessibility of Pb – contaminated soils amended with P using the physiologically based extraction test (PBET). The objectives of this study were to examine the effects of PBET pH, aging time, P source, and P dose on Pb bioaccessibility in ten Pb - contaminated soils.

3.2 Materials & Methods

Ten lead-contaminated soils were collected from Department of Defense (DoD) sites throughout the United States, and their properties are described in Table 3.1. These soils had Pb concentrations of approximately 1000 – 6000 mg/kg. All soil samples were air dried and sieved to <250 μm. A particle size of <250 μm was used in determining all

Table 3.1. Soil Properties for 10 DoD Soils.

Soil #	Pb (mg/kg)	Fe (g/kg)	Mn (mg/kg)	% TC	% TOC	% TIC	pH 5mM CaCl2	pH DDI	% Clay	% Silt	% Sand
1	4880	11.3	299	1.49	1.23	0.260	6.99	7.47	6.20	30.6	63.2
2	1430	83.9	1160	22.2	36.8	0[a]	6.40	6.79	6.50	14.9	78.6
3	1890	10.2	372	2.59	1.55	1.05	7.52	7.82	11.5	16.5	72.0
4	4660	23.3	87.5	0.640	0.490	0.150	4.11	4.63	19.0	20.0	61.0
5	1060	12.3	458	13.3	15.8	0[a]	7.34	7.70	5.00	20.0	75.0
6	1220	7.90	764	7.68	8.02	0[a]	7.43	7.83	5.00	14.0	81.0
7	1070	19.2	605	1.64	1.44	0.201	6.08	6.52	23.0	33.0	44.0
8	1360	19.3	563	1.83	1.30	0.528	6.14	6.54	13.0	28.0	59.0
9	4020	19.3	490	1.41	1.20	0.204	6.27	6.71	26.0	34.0	40.0
10	5810	17.7	622	1.17	0.984	0.184	6.54	6.95	26.0	35.0	39.0

[a] % TIC is obtained by subtracting % TOC from % TC.

soil properties (with the exception of particle size) and was used throughout all experiments in this research. The particle size that normally adheres to the hands of a child is <100 μm. However, because it is difficult to collect large quantities of the <100 μm soil fraction, and the <250 μm fraction is deemed adequate for approximating the particle size ingested by children, the <250 μm particle size will be used for this research (Rodriguez et al., 1999; Hettiarachchi and Pierzynski, 2004). Samples were stored dry prior to use in polypropylene vials. Particle size analysis was measured using standard methodologies and was obtained from Oak Ridge National Laboratory (ORNL). Soil pH was determined using both double deionized (DDI) water and 5 mM $CaCl_2$ in a 2:1 solution to soil ratio. The pH of the clear supernatant was measured with a microprocessor ionalyzer/901 (Orion Research, Beverly, MA) using a combination glass and Calomel electrode (Beckman, Fullerton, CA). Total Pb concentrations in each soil were determined by a harsh acid digestion procedure (EPA Method 3050B) using the <250 μm particle size fraction.

3.2.1 Amendment Addition and Aging

Amendment addition and aging experiments were performed using the < 250 μm fraction for both soil and amendment. The air dried and sieved soil was weighed, divided into three equal portions, and placed into 20 mL polypropylene sample vials. Three P-rich fertilizers were used as soil amendments in this study. Triple-super-phosphate (TSP) and rock phosphate (RP) were obtained from a local garden center. VolCanaPhos™ (Vol) was obtained from an online source. RP is an insoluble, natural rock mined from P-rich deposits. There are over 300 phosphate minerals identified, and

each one reacts differently because of variations in pH, impurities, crystalline structure, and local weathering patterns associated with the location of the deposits (Nriagu, 1974). The rock is washed free from clay impurities and heated to remove moisture. It is then mechanically ground to a fine powder to be incorporated into P-deficient soils. RP naturally provides long-term, slow – release feeding to plants. TSP, a soluble form of P, is a common agricultural fertilizer made by reacting RP with orthophosphoric acid (Hettiarachchi et al., 2001). TSP is composed of 30% monocalcium phosphate ($Ca(HPO_4)_2 \cdot H_2O$), 45% gypsum by – product, 10% calcium biphosphate ($CaHPO_4$), 10% iron oxide, silica, and aluminum, and 5% water (Budavari, 1996). VolCanaPhos ™ is the registered trade name for the crystalline igneous apatite coming from a carbonatite deposit in northern Ontario in Canada. Carbonatites, most likely mined on a large scale in open pit mines, are carbonate-mineral-rich igneous rocks containing apatite, magnetite, baritite, fluorite, P, and irregular concentrations of rare earth elements (USGS, 1995). Like RP, VolCanaPhos ™ is an insoluble, natural rock that after pellitization, provides slow – release feeding to crops. Repeated analysis of VolCanaPhos ™ reveals a composition of 30% to 40% P_2O_5, 40% to 50% CaO, and 1.5% to 2.5% sulfates.

Phosphate amendments were weighed and placed into the appropriate sample vial resulting in a final calculated % P by weight. The P_2O_5 composition was included by the manufacturer for each amendment: TSP = 45% P_2O_5, Vol = 32.07% P_2O_5, RP = 32% P_2O_5. 1% P, 2.5% P, and 5% P by weight were added to each soil. The total P concentration in soils varies between 0.02 to 0.10% by weight. Therefore, the initial concentration of P in the soils was considered negligible. Similar to Hettiarachchi et al.

(2001), the calculations were made based on the % P contained in the amendment and the % P dose (Equation 3.1). (See Appendix A for an example calculation).

$$\text{Amendment Added (g)} = \frac{\text{Soil Wt.(g)} * \text{\% P dose}}{\text{\% P in amendment}} \tag{3.1}$$

The final P:Pb ratios were calculated for each soil for every % P dose. No matter which amendment was applied, the P:Pb ratio was the same for a given soil and a given dose. However, the P:Pb ratio increased with increasing % P dose and decreased with increasing total Pb conc. (Table 3.2).

The phosphate amendments were dry mixed into the soil samples using a vortex shaker for 1 minute. DI water was added to bring the samples to the experimental moisture content. A moisture content of 30% was used to approximate field capacity (Yang et al., 2003). Moisture content was calculated based on the total weight of the soil and amendment. Equation 3.2 shows the moisture content calculation, where *wet* refers to the wet weight (g) of soil + amendment and *dry* represents the dry weight of the soil (g) + amendment.

$$\text{\% Moisture} = \frac{wet - dry}{dry} \cdot 100 \tag{3.2}$$

The sample vials were partially covered with parafilm to allow air exchange and minimize evaporation (Hettiarachchi et al., 2001) and then placed into an aging apparatus receiving a continuous flow of air at 100% relative humidity. The aging apparatus, shown in Appendix C.1, was designed from an anaerobic gas-pak chamber,

Table 3.2. P:Pb Ratios for Each Soil Amended with 1% P, 2.5% P, and 5% P.

Soil #	Soil Name	%P	mg P/kg soil	mg Pb/kg soil	P:Pb ratio (mg:mg)	P:Pb ratio (mol:mol)
1	Aberdeen SS19	1	10000	4880	2.05	13.7
		2.5	25000	4880	5.12	34.3
		5	50000	4880	10.25	68.5
2	Aberdeen B116	1	10000	1430	6.99	46.8
		2.5	25000	1430	17.5	117
		5	50000	1430	35.0	234
3	Kansas AAP	1	10000	1890	5.29	35.4
		2.5	25000	1890	13.2	88.5
		5	50000	1890	26.5	177
4	Radford AAP	1	10000	4660	2.15	14.4
		2.5	25000	4660	5.36	35.9
		5	50000	4660	10.73	71.8
5	Hill AFB #4	1	10000	1060	9.43	63.1
		2.5	25000	1060	23.6	158
		5	50000	1060	47.2	316
6	Hill AFB #5	1	10000	1220	8.20	54.8
		2.5	25000	1220	20.5	137
		5	50000	1220	41.0	274
7	Travis AFB # 1	1	10000	1070	9.35	62.5
		2.5	25000	1070	23.4	156
		5	50000	1070	46.7	313
8	Travis AFB # 2	1	10000	1360	7.35	49.2
		2.5	25000	1360	18.4	123
		5	50000	1360	36.8	246
9	Travis AFB # 4	1	10000	4020	2.49	16.6
		2.5	25000	4020	6.22	41.6
		5	50000	4020	12.4	83.2
10	Travis AFB #5	1	10000	5810	1.72	11.5
		2.5	25000	5810	4.30	28.8
		5	50000	5810	8.61	57.6

which was modified to remain open to the atmosphere. Compressed air was bubbled through DI water and into the chamber, creating an environment with approximately 100% relative humidity. Samples were aged for 0, 60, 200, and 365 days. At the end of each aging period, the soils were removed from the aging apparatus and air dried for 24 hours. After the samples were completely dried and well mixed, 0.3 g subsamples were removed in duplicate for the PBET. After sub-sampling, the remaining samples were re-wetted to 30% moisture and placed in the aging apparatus until the next sampling time.

3.2.2 Physiologically Based Extraction Test (PBET)

A streamlined version (Kelley et al., 2002) of the Physiologically Based Extraction Test (PBET), originally developed by Ruby et al. (1996), was used in determining the relative bioaccessibility of Pb in the soil before and after amendment additions. This new version is a modification of the original PBET method in that the $NaHCO_3$ extraction step (mimicking the small intestine) has been eliminated, reflecting recent research that has shown that an acid gastric-like extraction is predictive of *in vivo* bioavailability for Pb and As (Ruby et al, 1999; Rodriguez et al, 1999). The PBET extraction was originally designed to simulate a fasting child's gastrointestinal tract at pH of 1.5 and a temperature of 37 ^{o}C (98.6 °F). However, Ruby et al. (1999) revealed that a pH of either 1.3 or 2.5 in the stomach phase of the *in vitro* test correlated equally well with the Relative Absorption Factors (RAFs) of the *in vivo* weanling rat model (r^2 = 0.93 at both pH values). Another recent Pb bioavailability study shows that an *in vitro* pH of 2.3 correlated well (r^2 = 0.90) with the *in vivo* rat bone results (Brown et al, 2003). Furthermore, the results from a swine *in vivo* study for predicting Pb bioavailability

reductions in phosphate amended soils correlated best with an *in vitro* pH of 2.3 (M. Ruby, 8 Dec, 2003, personal communication). Therefore, the initial Pb bioaccessibility and the Pb bioaccessibility at 365 days were measured using a PBET solution pH of 2.3 to compare the Pb bioaccessibility results from the PBET pH of 1.5.

Stock PBET solution was made using a 0.4 M Glycine (*Fisher Scientific, G48*) solution adjusted to a pH of 1.5 or 2.3 using trace metal grade, 12.1 M concentrated hydrochloric acid. The solution pH was adjusted at a temperature of 37 ± 2 ^{o}C using a pH meter calibrated with buffer solutions adjusted to a temperature of 37 ± 2 ^{o}C. The extraction test was performed in a TCLP-like extractor submerged in a heated water bath (Appendix C.2) connected to an external motor spinning the extractor at 30 ± 2 rpm. Duplicate 0.3 g dry weight samples were placed into 50 mL polyethylene tubes to which 30 mL of PBET stock solution heated to 37 ± 2 ^{o}C at a pH of 1.5 or 2.3 was added. The samples were rotated end-over-end at 30 ± 2 rpm for one hour. During the one hour extraction period, the water temperature in the bath was maintained at body temperature (37 ± 2 ^{o}C). After extraction, the samples were removed from the water bath and centrifuged at 2100 rpm for five minutes to aid with filtration. The supernatant was decanted and filtered through a 0.45 μm syringe disk filter, placed in 20 mL polyethylene vials, and stored at a refrigerated temperature of 4 ^{o}C until analysis.

Samples containing the dissolved Pb concentration in the filtrate were analyzed in duplicate, and bottle blanks of PBET solution were analyzed for quality assurance. A National Institute of Standards and Technology (NIST) 2711 standard reference material (SRM) was extracted along with the other samples and measured for Pb bioaccessibility

with each PBET extraction performed for quality assurance/quality control. Pb bioaccessibility was calculated according to Equation 3.3:

$$\%\text{Pb Bioaccess.} = \left(\frac{\text{Pb in PBET supernatant (mg/L)} * \text{Volume of PBET solution (L)}}{\text{Wt. of dry soil (kg)} * \text{Total Pb from Method 3050B (mg/kg)}} \right) * 100 \quad (3.3)$$

The dry soil wt. refers to the weight of the contaminated soil only. This weight can be calculated according to equation 3.4, where values for % amendment added can be found in Table 3.3:

Wt. of contaminated soil (g) = 0.3 g – (0.3g * % amendment added by wt.) (3.4)

The % amendment added to each soil was calculated based on the P_2O_5 composition of each amendment as previously described and the % P content desired in each sample. (See Appendix B for an example calculation).

3.2.3 Analytical Methods

All chemicals employed in this research were analytical grade or above, and solutions were prepared with DI water (18 MΩ·cm) from a Purelab ultra water/ion exchange apparatus (U.S. Filter system). The PBET supernatant was analyzed for Pb using a Varian SpectrAA 220FS flame atomic adsorption spectrometer (FLAA) or a Perkin Elmer ELAN 6100 (ICP-MS). Equipment calibration was performed using matrix-matched standards with a range of 2 to 6 mg L^{-1} Pb.

Table 3.3. % Amendment Added Based on Amendment Composition and % P Dose.

Amendment	%P	Wt. of Amendment Added (g)	Total Wt. of Soil + Amendment (g)	% Amendment Added
TSP	1	0.101	2.101	4.81%
	2.5	0.253	2.253	11.2%
	5	0.505	2.505	20.2%
Vol	1	0.142	2.142	6.63%
	2.5	0.354	2.354	15.0%
	5	0.709	2.709	26.2%
RP	1	0.142	2.142	6.63%
	2.5	0.355	2.355	15.1%
	5	0.711	2.711	26.2%

Samples were diluted with PBET stock solution, if needed, during analysis to within the concentration range of the standards.

3.3 Results and Discussion

3.3.1 Effect of Time on % Pb Bioaccessibility in P-Amended Soils

The % Pb bioaccessibility for all ten soil samples was calculated by equation 3.3. One objective of this study was to investigate the absolute % Pb bioaccessibility of P – amended, Pb – contaminated soils with respect to time. Figures 3.1, 3.2, and 3.3 compare the % Pb bioaccessibility data over time at the 5% P dose at a PBET pH of 1.5 for Vol, RP, and TSP amendments, respectively. A paired t-test was conducted to study the effect of time on average % Pb bioaccessibility at a pH of 1.5 at the 5% P dose for each amendment. For Vol. and TSP, there was a significant ($P<0.05$) decrease in Pb bioaccessibility between 0 days and 60 days, but RP showed no significant ($P<0.05$) difference in bioaccessibility. For Vol. and RP, there was no significant ($P<0.05$) difference in bioaccessibility between 60 days and 200 days. However, there was a significant ($P<0.05$) decrease in bioaccessibility between 200 days and 365 days. For RP, the bioaccessibility decreased slightly between 60 days and 200 days and decreased at a higher, more significant rate between 200 days and 365 days. For TSP at 5% P, there was a significant decrease in bioaccessibility between 60 days and 200 days, while there was no significant ($P<0.05$) decrease in bioaccessibility between 200 days and 365 days. These results indicate that stead-state bioaccessibility has not been reached. The rate of aging decreased after 200 days for soils amended with TSP and increased after

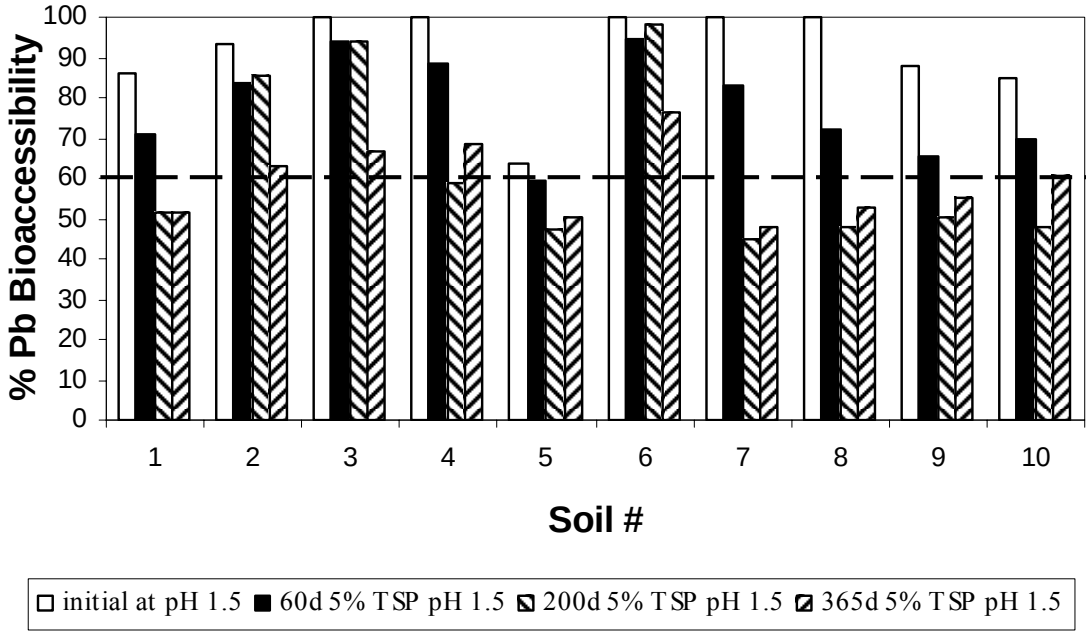

Figure 3.1. % Pb Bioaccessibility With Respect to Time with 5% P as TSP at a PBET pH of 1.5.

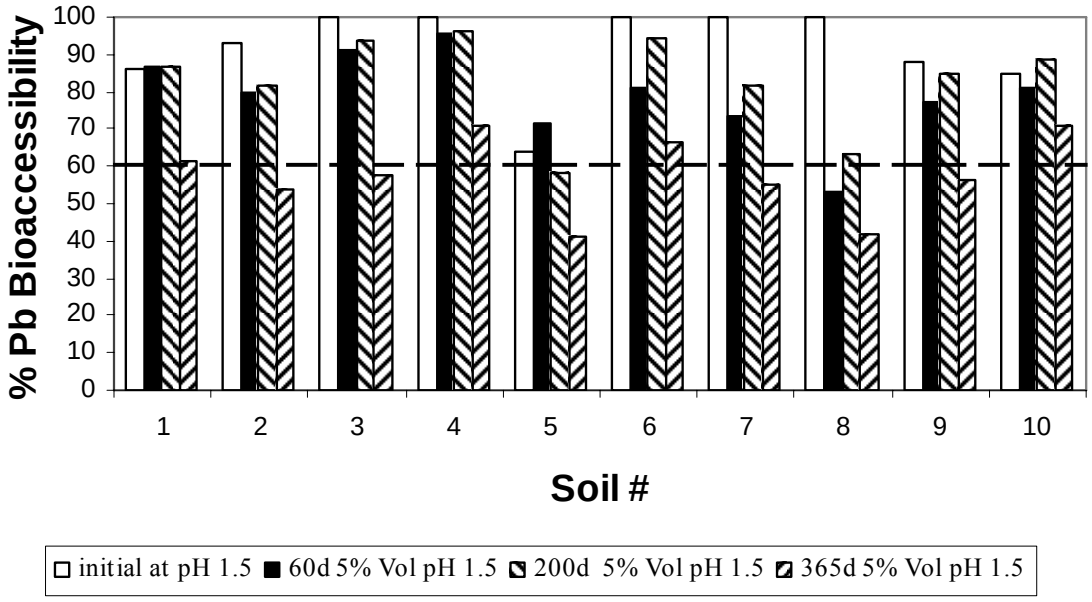

Figure 3.2. % Pb Bioaccessibility With Respect to Time with 5% P as Vol at a PBET pH of 1.5.

200 days for soils amended with Vol. and RP. These results were expected as TSP is a more soluble amendment by nature than RP and Vol. In contrast, the work done by Hettiarachchi et al. (2001) concluded that for soils amended with RP and TSP, reductions in bioavailable Pb occurred between 0 and 3 days after treatment and no further reductions occurred over 365 days of incubation. This trend was attributed to the possible formation of chloropyromorphite in the PBET rather than in situ (Hettiarachchi et al., 2001). However, because Pb bioaccessibility in this study changed significantly ($P<0.05$) over time, chloropyromorphite was not exclusively forming as an experimental artifact in the PBET.

3.3.2 Effect of P dose and PBET pH on % Pb Bioaccessibility

Figures 3.4, 3.5, and 3.6 compare % P dose at 365-day for PBET pH of 2.3 for TSP, Vol, and RP amendments, respectively. The effect of P dose was studied for each amendment on the 365-day data at two pH levels (1.5 and 2.3) by using a paired t-test. The data indicate significant ($P<0.05$) decreases in % Pb bioaccessibility for all % P doses for all three amendments in increasing the PBET pH from 1.5 to 2.3. However, results from the pH 2.3 data differ. Significant ($P<0.05$) decreases in average % Pb bioaccessibility were found between 1% P and 2.5% P and between 2.5% P and 5% P doses for TSP and RP amendments. However, for Vol., there was no significant difference in average % Pb bioaccessibility between all % P doses. Therefore, unlike at pH 1.5, at a pH of 2.3, Vol. did not significantly decrease Pb bioaccessibility.

The U.S. EPA currently assumes that the absolute bioavailability of Pb in diet and water is 50% and that the absolute bioavailability of Pb in soil is 30% for children

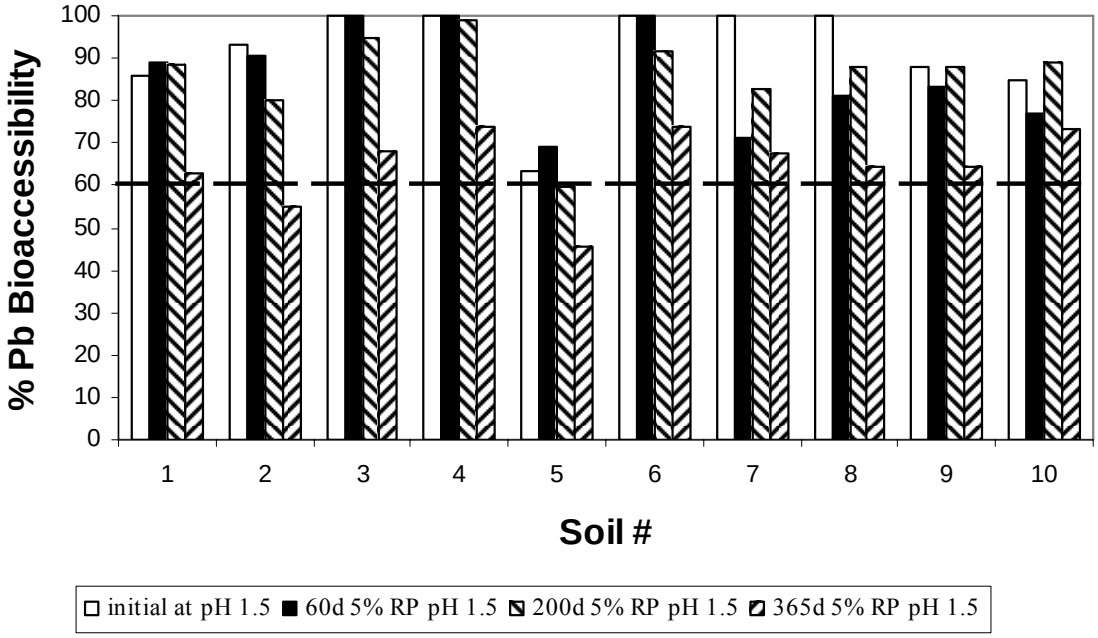

Figure 3.3. % Pb Bioaccessibility With Respect to Time with 5% P as RP at a PBET pH of 1.5.

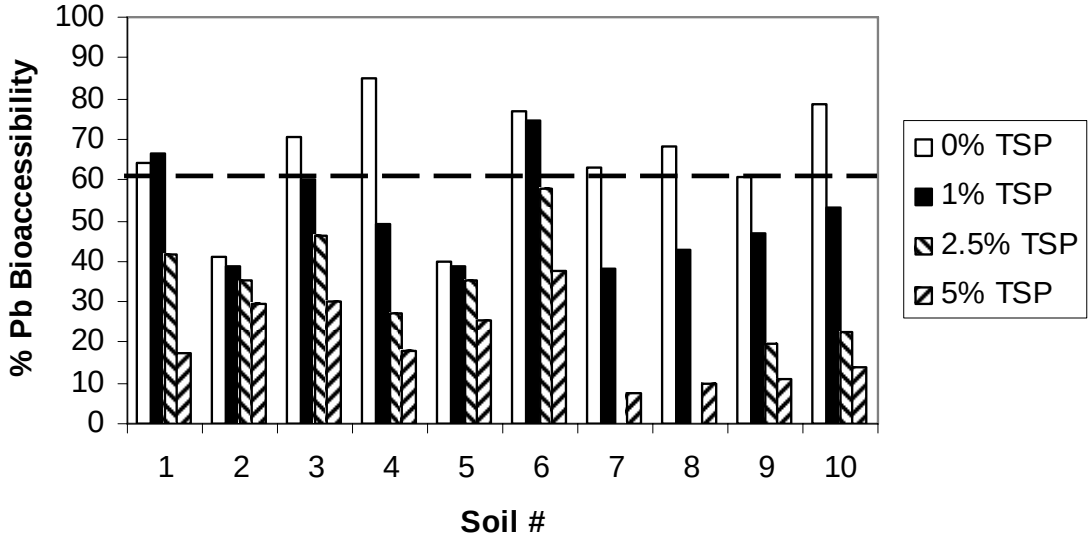

Figure 3.4. Pb Bioaccessibility Charts Comparing % P Dose as TSP for 365-Day Data at a PBET pH of 2.3.

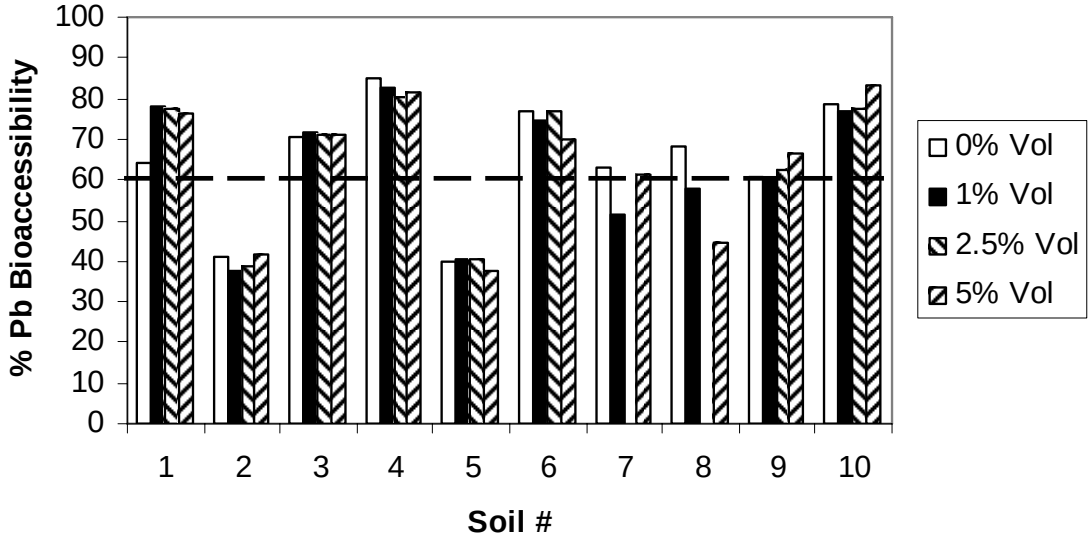

Figure 3.5. Pb Bioaccessibility Charts Comparing % P Dose as Vol for 365-Day Data at a PBET pH of 2.3.

(USEPA, 1994). This corresponds to a soil relative absorption factor (RAF) of 60% for the bioavailability of soil Pb relative to Pb in water (i.e., RAF = 0.3/0.5) (Ruby et al., 1999). The default RAF value for Pb (indicated by a dashed line) is included in all figures for comparison. The average relative % Pb bioaccessibility for all 10 soils (without P amendments added) at a pH of 1.5 was 96.3%, with a range of 63.6% to 100%, which is much greater than the RAF value of 60%. The average initial % Pb bioaccessibility at a pH of 2.3 is 64.8%, with a range of 40.1% to 85.2%. In Figure 3.7, the addition of 5% P over 365 days decreases the average % Pb bioaccessibility at a pH of 1.5 to below the RAF for 50% of soils amended with TSP, for 20% of soils amended with RP, and for 60% of soils amended with Vol. In Figure 3.8, the addition of 5% P over 365 days decreases the average % Pb bioaccessibility at a pH of 2.3 to below the RAF for all soils amended with TSP, for 80% of soils amended with RP, and for 30% of soils amended with Vol.

3.3.3 Amendment Comparison

When the effectiveness of each amendment was compared, TSP had the highest average reduction in % Pb bioaccessibility at a 44.9% difference from the initial bioaccessibility value at a pH of 2.3 (Figure 3.9). The results from a rank-order test agree with Figure 3.9 and show that the best combination of amendment, dose, and time to yield the highest reduction in average % Pb bioaccessibility is TSP, 5% P, and 365 days. The Kruskal-Wallis Test (Woolson, 1987) determined that there is no significant difference (K=1.67, 0.80, and 1.16; $x^2_{0.90}(2) < 4.61$) between the dose at the 10% level of significance. However, when comparing the same dose with respect to time, there is a

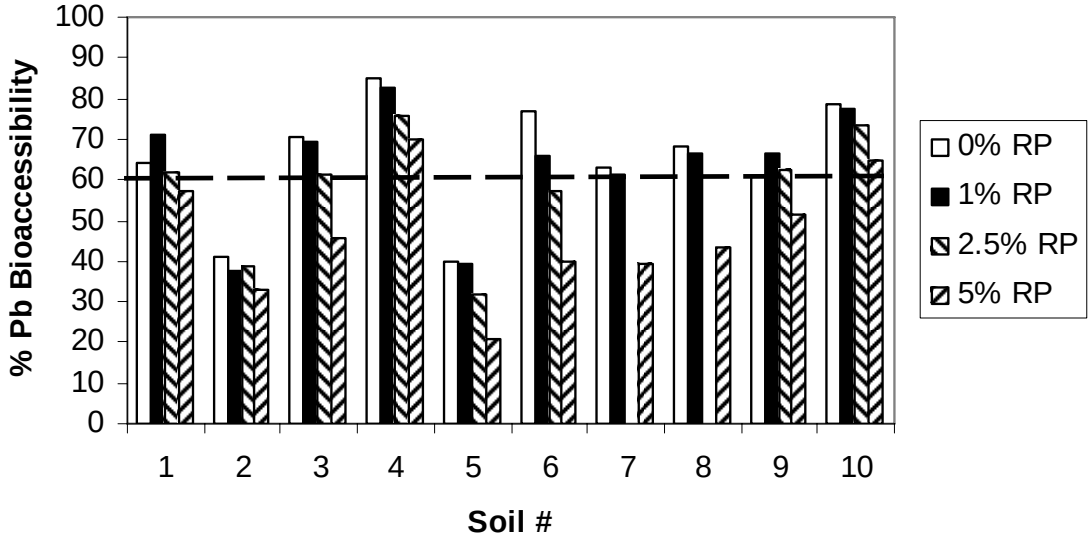

Figure 3.6. Pb Bioaccessibility Charts Comparing % P Dose as RP for 365-Day Data at a PBET pH of 2.3.

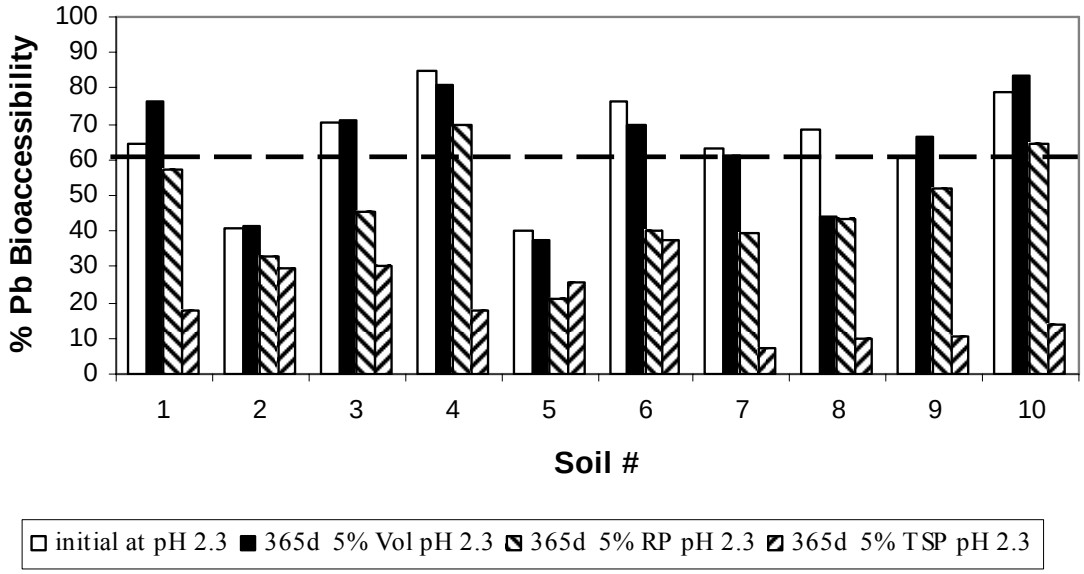

Figure 3.7. 365-Day Data Comparing the Efficiencies of Vol, RP, and TSP at the 5% P Dose at a PBET pH of 2.3.

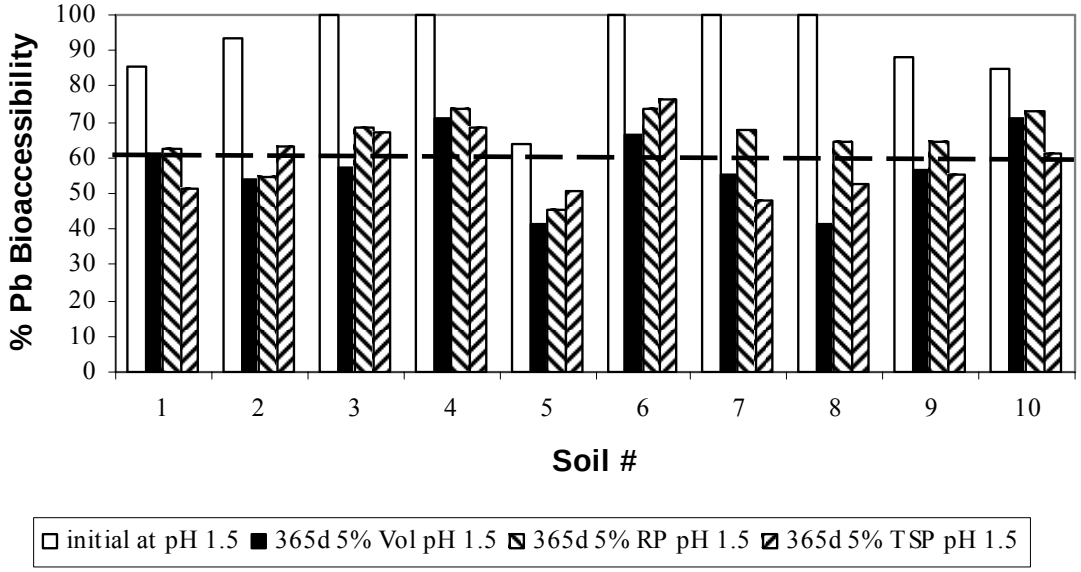

Figure 3.8. 365-Day Data Comparing the Efficiencies of Vol, RP, and TSP at the 5% P Dose at a PBET pH of 1.5.

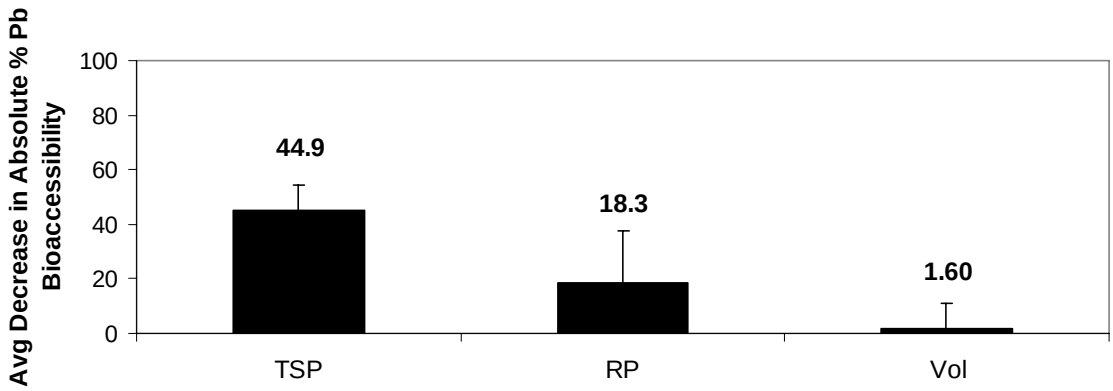

Figure 3.9. Comparison of the Average Decrease in % Pb Bioaccessibility for Each Amendment over 365 Days at 5% P.

significant difference (K=5.6, $x^2_{0.90}(2)>4.61$) at the 10% level of significance for the 1% P and 2.5% P doses. Results from the 5% P dose show that there is a significant difference (K=4.36, $x^2_{0.80}(2)>3.22$) at the 20% level. The RP addition decreased the Pb bioaccessibility by 18.3%, while Vol. decreased by only 1.60%. These results are comparable to those of Brown et al. (2004) who show a 50% reduction in % Pb bioaccessibility in soils treated with 2.5% Fe + 1%P as TSP. Therefore, TSP was overall the most effective amendment.

3.4 Conclusions

In this study, two pH values of PBET solution were compared: 1.5 and 2.3. At a pH of 1.5, % Pb bioaccessibility results were significantly greater than those at pH of 2.3. At a pH of 2.3, Vol. was not effective at reducing Pb bioaccessibility at any P dose. Another objective of this study was to compare the effect of time after the addition of the P amendments on Pb bioaccessibility. The effect of time was more important for the non – soluble amendments (RP and Vol), which showed a significant decrease in % Pb bioaccessibility at pH 1.5 between 60 and 365 days of aging. Overall, after 365 days of aging, at a PBET solution pH of 2.3, the greatest reduction in Pb bioaccessibility occurred in the following order: TSP>RP>Vol. However, because 20.2% - 26.2% of the sample weight was composed of the amendment only, a large amount would need to be applied *in situ* to achieve these results. Environmental implications for adding such large amounts of P to soil, such as the leaching of oxyanions like Sb and As, should be considered. Thus, adding P amendments to soils may not be the most practical approach to reduce the Pb bioavailability in Pb – contaminated soils.

CHAPTER FOUR

REDUCING THE BIOACCESSIBILITY OF LEAD IN LABILE, LEAD-SPIKED SOILS

4.1 Introduction

Most previous Pb bioaccessibility studies have involved the use of Pb-contaminated soils, typically from mining and smelting industries. However, Pb-spiked soils have not previously been used. The advantages of using Pb-spiked soils over Pb – contaminated soils are so that "the initial metal concentration and speciation can be controlled and changes in bioaccessibility from the initial labile metal can be followed with time" (Yang et al., 2003). In this study, the effects of aging time and P dose on Pb bioaccessibility in labile (Pb – spiked) soils in the PBET were investigated.

4.2 Materials & Methods

4.2.1 Soil Spiking Experiments

Thirty-four non-contaminated soils from various locations throughout the United States were spiked with enough Pb to yield 1000 mg/kg Pb. Appendix D lists the properties of each soil. Soil properties were measured as referenced in Stewart et al. (2003). Soil pH was determined using both 5 m*M* $CaCl_2$ and double deionized (DDI) water in a 2:1 solution to soil ratio. A microprocessor ionalyzer/901 (Orion Research,

Table 4.1. Soil Properties for Pb-Spiked Soils #1-34

Sample #	Sample Name	DCB-Fe (mg/kg)	DCB-Mn (mg/kg)	pH		TOC (%)	TIC (%)	Particle Size (%)		
				DDI	5mM $CaCl_2$			Clay	Silt	Sand
1	Oricto Bt	6010	202	9.05	8.10	0.15	0.51	13	21	66
2	Norfolk A	3530	22.6	7.41	7.21	0.35	0.23	7	14	79
3	Norfolk B	22300	5.00	7.35	6.65	0.26	0.03	41	16	43
4	Towaliga B	19300	23.4	6.25	4.64	0.25	0.08	33	22	45
5	Sibley A	9780	477	6.36	5.89	1.45	0.04	23	55	22
6	Sibley B	10600	453	6.58	6.03	1.06	0.16	29	53	18
7	Cecil A	20700	116	6.71	6.08	0.80	0.00	17	22	61
8	Oricto A1	4400	236	8.67	7.93	0.19	0.30	6	23	71
9	San Ysidro A	6130	265	7.05	6.67	1.07	0.00	25	30	45
10	Doakum Bf	5860	131	7.93	7.67	0.26	0.08	17	17	66
11	Crider A	10200	1200	7.38	7.05	1.10	0.19	16	74	10
12	Stoneham B	3390	83.9	N/D	6.8	0.88	0.06	27	25	48
13	Cecil Bt	54200	81.3	6.66	6.45	0.32	0.06	50	18	32
14	Wakeland A1	9320	450	6.24	5.88	0.83	0.06	25	58	17
15	Towaligz Ap	5430	75.1	5.44	4.47	0.72	0.01	15	20	65
16	Wakeland A2	9580	532	5.91	5.36	0.69	0.06	24	50	26
17	Angola B	11800	27.6	5.04	4.42	0.18	0.04	33	60	7
18	San Ysidro B	5880	225	7.58	6.87	0.42	0.03	31	27	42
19	Angola Ap	15600	633	5.63	5.27	2.29	0.38	23	59	18
20	Oricto A2	4380	231	8.83	8.11	0.12	0.66	12	34	54
21	Kzin B	4490	234	8.29	7.87	1.18	1.04	20	44	36
22	Crider B	15200	470	6.34	5.90	0.69	0.14	21	62	17
23	Decatur A	29500	2940	6.12	5.39	0.50	0.07	35	45	20
24	Lenberg B	11100	419	4.88	4.28	2.12	0.11	24	49	27
25	Kzin A	5360	317	8.25	7.83	1.04	0.86	25	43	32
26	Robertsville A	10900	442.8	5.44	5.02	2.31	0.21	25	50	25
27	Wakeland A3	9220	432.25	5.70	5.23	0.47	0.00	21	49	30
28	Stoneham A	3070	98.9	N/D	6.42	1.08	0.00	14	23	63
29	Doakum A	3480	147.5	6.99	6.27	0.43	0.07	8	19	73
30	Lenberg A	10500	1063	5.16	4.67	1.88	0.36	19	52	29
31	Melton Valley A	10700	1420	7.18	6.91	3.55	0.62	13.8	30	56.2
32	Melton Valley B	22100	170	4.87	4.23	0.42	0.26	18.8	50.4	30.8
33	Walker Branch A	7710	1510	6.61	6.01	1.89	0.99	6.20	58.9	34.9
34	Walker Branch B	19600	160	5.17	4.3	0.1	0.07	23.6	44.2	32.2

Beverly, MA) with a combination glass and Calomel electrode (Beckman, Fullerton, CA) was used to measure the natural pH of each soil. Extractable iron and manganese oxides were determined with dithionite-citrate-bicarbonate (DCB). Total organic carbon (TOC) and total inorganic carbon (TIC) were measured by combustion on a Perkin-Elmer 2400 Series II CHNS/O analyzer. Soil TOC was determined on pretreated samples to remove TIC, which involved a near-boiling 3 *M* HCl extraction method on agitated samples. Soil TIC was computed from the difference between total soil C (no pretreatment) and TOC. Particle size analysis was used to determine the sand, silt, and clay content of each soil. A particle size of <250 μm was used throughout all experiments in this research. The particle size that normally adheres to the hands of a child is <100 μm. However, because it is difficult to collect large quantities of the <100 μm soil fraction and the <250 μm fraction is deemed adequate for approximating the particle size ingested by children (Rodriguez et al., 1999), the <250 μm particle size was used for this research. Ten grams of each soil were weighed and placed into 125 mL HDPE wide-mouth bottles. A 10:1 soil suspension in 10^{-3} *M* $CaCl_2$ was prepared for each sample. The pH of the soil slurry was measured by an Orion combination electrode and pH meter. A 2,000 mg/L Pb solution was prepared by adding 3.201 g of Pb $(NO_3)_2$(s) to 1 L of DI water and then adding 10^{-3} *M* HNO_3 drop-wise to adjust the pH from 4.76 to 3.10. The soil slurry was spiked with 5 mL of the lead nitrate solution, which was sufficient to obtain a 1000 mg/kg Pb soil concentration. The pH of the spiked soil slurry was measured while a neutralizing solution (10^{-3} *M* NaOH) was added drop-wise to neutralize the acidity of the added Pb solution and maintain the soil's original pH.

Each soil slurry sample was mixed on an agitator for 48 hours, centrifuged at 2000 rpm for 20 minutes, and then the supernatant was decanted into a clean 125 mL HDPE wide-mouth bottle. The remaining soil was washed with 5 mL of DI water, centrifuged, and the supernatant decanted into the same bottle. The washing, centrifuging, and decanting were repeated once more to remove any traces of the original soluble Pb spike. The decanted supernatant and rinse water were filtered through a 0.45 μm membrane filter (Fisher-Scientific), and the pH of the filtrate was measured and adjusted to that of the Pb standards. The Pb concentration in the filtrate was analyzed using an atomic absorption spectrophotometer (AAS) equipped with a hollow cathode lamp. The difference between the amount of Pb added and that remaining in the filtrate was used to calculate the initial spiked soil Pb concentration.

The remaining wet soil was air-dried for at least 48 hours and then dried in the oven at 55 °C for at least 3 hours until the soil was completely free of moisture. After mixing thoroughly, 0.1 gram of soil was removed in duplicate for each sample. The Pb remaining on the soils was analyzed by EPA Method 3050B (U.S. EPA, 1994) to verify a mass balance recovery of ± 10 – 15%.

4.2.2 Amendment Addition and Aging

Amendment addition and aging experiments were performed on the 34 Pb-spiked soils. Each air dried and sieved soil was weighed, divided into 3 equal portions, and placed into 20 mL polypropylene sample vials. In Chapter 3, VolCanaPhos was used as a phosphate amendment and was found to reduce the bioaccessibility of Pb in Pb-contaminated soils. Because VolCanaPhos was no longer available, HumaPhos, a

replacement for VolCanaPhos, was used in this study. HumaPhos is a naturally occurring, insoluble, rock phosphate fertilizer obtained from *North Pacific Ag Products*© and was the only amendment used in this study. HumaPhos is composed of 20% Ca, 15% PO_4, 14% humic substances, 10% SiO_2, 4% S, 2% Fe, 80 ppm Zn, 100 ppm Mn, 50 ppm Co, 15 ppm Ni, 14 ppm Cu, and 2 ppm Mo. The amendment was weighed and placed into the appropriate sample vial resulting in a final calculated % P by weight (Equation 4.1). To each soil, 0% (control), 2.5%, and 5% P were added by weight. The total P concentration in soils varies between 0.02 to 0.10% by weight. Therefore, the initial concentration of P in the soils was considered negligible. The calculations were made based on the % P dose and the % PO_4 in the amendment. (See Appendix D.1 for example calculations.)

$$\text{Amendment Added (g)} = \frac{\text{Soil Wt.(g)} * \%\text{P desired} * \left(\frac{(94.97\text{g PO}_4\text{/mol PO}_4)}{(30.97\text{g P/mol P})} \right)}{15\%\,\text{PO}_4\text{ by weight}} \qquad (4.1)$$

The phosphate amendment was then dry mixed into the soil samples using a vortex shaker for 1 minute. DI water was added to bring the samples to a moisture content of 30% to approximate normal field capacity. Moisture content was calculated based on the total weight of the soil and amendment. Equation 4.2 shows the moisture content calculation, where *wet* refers to the combined wet weight (g) of the soil, amendment, and water, and *dry* represents the dry weight (g) of the soil and amendment.

$$\%\ \text{Moisture} = \frac{wet - dry}{dry} \cdot 100 \qquad (4.2)$$

The sample vials were partially covered with parafilm to minimize evaporation while remaining open to the atmosphere and then placed into an aging apparatus receiving a continuous flow of air at 100% relative humidity. The aging apparatus, shown in Appendix C.1, was adapted from an anaerobic gas-pak chamber that had been modified to remain open to the atmosphere. Compressed air was bubbled through deionized water and into the chamber, creating an environment with approximately 100% relative humidity. Samples were aged for 0 (initial), 30, 60, 90, and 120 days. At the end of each aging period, the soils were air dried for at least 24 hours and then dried in a 55 °C oven for at least 4 hours until all moisture was completely removed. Duplicate subsamples of 0.1 gram weight were removed for the Physiologically Based Extraction Test (PBET), an extraction procedure created by Ruby et al. (1996, 1999) and modified as described by Kelley et al. (2002). The remaining samples were then rewetted and returned to the aging apparatus until the next sampling period. After 120 days, a 1.0 gram subsample was removed to measure the final soil pH.

4.2.3 Physiologically Based Extraction Test (PBET)

A streamlined version (Kelley et al., 2002) of the Physiologically Based Extraction Test (PBET) originally developed by Ruby et al. (1996) was used to determine the relative bioaccessibility of Pb in the soil with and without amendment additions. This new version is a modification of the original PBET method in that the $NaHCO_3$ extraction step (mimicking the small intestine) has been eliminated, reflecting recent research that has shown that an acid gastric-like extraction is predictive of *in vivo* bioavailability for Pb and As (Ruby et al., 1999; Rodriguez et al., 1999). The PBET

extraction was designed to simulate a fasting child's gastrointestinal tract at a pH of 1.5 and a temperature of 37 ^{o}C (98.6 °F). However, Ruby et al. (1999) showed that a pH of either 1.3 or 2.5 in the stomach phase of the *in vitro* test correlated best with the Relative Absorption Factors (RAFs) of the *in vivo* weanling rat model (r^2 = 0.93 at both pH values). Another recent Pb bioavailability study shows that an *in vitro* pH of 2.3 correlated well (r^2 = 0.90) with the *in vivo* rat bone results (Brown et al., 2003). Furthermore, the results from a swine *in vivo* study for predicting Pb bioavailability reductions in phosphate amended soils correlated best with an *in vitro* pH of 2.3 (M. Ruby, 8 Dec, 2003, personal communication). Therefore, a pH of 2.3 was used for all PBET experiments in this study.

Stock PBET solution was made using a 0.4 M Glycine (*Fisher Scientific, G48*) solution adjusted to a pH of 2.3 ± 0.01 using trace metal grade, 12.1 M concentrated hydrochloric acid. The solution pH was adjusted at a temperature of 37 ± 2^{o}C using a pH meter calibrated with buffer solutions adjusted to a temperature of 37 ± 2 ^{o}C.

The extraction test was performed in a TCLP-like extractor submerged in a heated water bath (Appendix C.2) connected to an external motor spinning the extractor at 30 ± 2 rpm. Soil samples were placed into 15 mL polyethylene centrifuge tubes containing a 1:10 solid-to-solution ratio of PBET stock solution at pH 2.3. The streamlined procedure was originally designed for 1 g of each soil immersed in 100 mL of PBET solution. However, the procedure was modified (Yang et al., 2005) for 0.1 g soil and 10 mL of PBET solution to conserve soil samples while maintaining the same soil-to-solution ratio. Yang et al. (2005) reported that there was no significant difference ($P<0.05$) in extractable As between the 0.1 g and 1.0 g extractions. In this study, a

similar experiment for Pb soils was conducted and replicate analyses with both sample sizes (0.1 g and 1.0 g) also indicated no significant difference ($P<0.05$) between the two. Therefore, 0.1 g samples were used in all PBET measurements. The samples were rotated end-over-end at 30 ± 2 rpm for 1 hour. During the 1 hour extraction period, the water temperature in the bath was maintained at body temperature (37 ± 2^{o}C). After extraction, the samples were removed from the water bath and centrifuged at 2100 rpm for five minutes to aid with filtration. The supernatant was decanted and filtered through a 0.45 μm nylon media syringe disk filter (Fisher-Scientific), placed in 20 mL polyethylene vials, and preserved at a refrigerated temperature of 4 ^{o}C until analysis.

Samples containing the dissolved Pb concentration in the filtrate were analyzed in duplicate. A National Institute of Standards and Technology (NIST) 2711 standard reference material (SRM) was extracted along with the other samples and measured for Pb with each PBET extraction performed for quality assurance/quality control. Results indicate that conditions in the PBET were such that the Pb concentration in the SRM was consistently within 10% of the expected value. Approximately 25% of the remaining PBET residues were digested by EPA Method 3050B (U.S. EPA, 1994) and analyzed for Pb to verify a mass balance of ±10%.

Pb bioaccessibility was calculated as a percentage according to Equation 4.3. (See example calculations in Appendix D.2)

$$\%\text{Pb Bioaccess.} = \left(\frac{\text{Pb in PBET supernatant (mg/L)} * \text{Volume of PBET solution (L)}}{\text{Wt. of dry soil (kg)} * \text{Total Pb from Method 3050B (mg/kg)}} \right) * 100 \quad (4.3)$$

4.2.4 Analytical Methods

All chemicals employed in this research were analytical grade or above, and all solutions were prepared with DI water (18 MΩ·cm) from a Purelab ultra water/ion exchange apparatus (U.S. Filter system). The PBET supernatant was analyzed for Pb using a Varian SpectrAA 220FS flame atomic adsorption spectrometer (FLAA). Equipment calibration was performed using matrix-matched standards with a range of 2 to 6 mg L^{-1} Pb concentrations. Samples were diluted with PBET stock solution, if needed, during analysis to within the concentration range of the standards.

4.3 Results & Discussion

4.3.1 Effect of Time on % Pb Bioaccessibility in Control Soils

Over the length of the study, several hundred bioaccessibility measurements were conducted, and the average coefficient of variation for duplicate samples was <10%, indicating good repeatability. Throughout this study, control samples (0%P) were aged and extracted in the PBET along with the amended samples to see if a change was occurring in % Pb bioaccessibility over time simply due to the effects of moisture and aging (i.e., and not as a result of adding P). An average initial (t = 0) % Pb bioaccessibility was found to be 64.5% and ranged from 38.0% to 95.2% (Table 4.2). The U.S. EPA currently assumes that the absolute bioavailability of Pb in diet and water is 50% and that the absolute bioavailability of Pb in soil is 30% for children. This corresponds to a soil relative absorption factor (RAF) of 60% for the bioavailability of Pb in soil relative to Pb in water (i.e., RAF = 0.3/0.5) (Ruby et al., 1999). In this study, the average initial % Pb bioaccessibility was ≤60% in 13 of 24 (54.2%) soils and 24 of

34 (70.6%) soils were 60 ± 10% bioaccessible, initially. The default RAF for Pb (indicated by a dashed line) is included in all figures for comparison.

To quantify the reduction in Pb bioaccessibility over time (i.e., aging), the relative change in bioaccessibility over 120 days was calculated as the % sequestration as defined by Yang et al. (2005):

$$\%\ sequestration = \frac{B_0 - B_{120}}{B_0} \tag{4.4}$$

where B_0 and B_{120} represent the 0-day and 120-day bioaccessibility values, respectively. The average initial (t = 0) % Pb bioaccessibility was found to be 64.5% and ranged from 38.0% to 95.2% (Table 4.2). After 120 days of aging, the average % Pb bioaccessibility was 49.8% and ranged from 27.8% to 72.2% (Table 4.2). Therefore, aging at 30% moisture decreased the average % Pb bioaccessibility over 120 days by 14.6% with a relative sequestration of 22.2% (Table 4.2). From a paired t-test (Table 4.3), 25 out of 34 (73.5%) control soils showed a significantly ($P<0.05$) reduced bioaccessibility over 120 days, while only 10 soils (29.4%) further exhibited a significantly ($P<0.05$) reduced bioaccessibility from 90 to 120 days. For the majority of the control soils, aging was completed after 90 days. Therefore, time is an important factor in decreasing the bioaccessibility of Pb, at least in Pb-spiked soils.

From a multivariable linear regression analysis with backward elimination, three soil properties significantly ($P<0.05$) influenced the sequestration of Pb in the soils used in this study: Fe, Mn, and clay content. However, a poor correlation ($R^2 = 0.39$) was observed during this analysis, which indicated that a model to predict % Pb

Table 4.2. % Pb Bioaccessibility for Soils Amended with 0%P Over Time

Soil #	Initial Pb conc. (mg/kg)	0-day	30-day	60-day	90-day	120-day	Diff. (0-120)	% sequestration
1	968	59.9	65.3	60.1	52.6	45.3	14.6	24.3%
2	736	95.2	89.2	97.9	85.9	68.9	26.3	27.6%
3	880	68.9	80.3	72.1	59.3	58.0	10.9	15.9%
4	525	81.6	73.8	70.8	56.1	54.2	27.4	33.6%
5	914	63.1	79.1	71.3	59.3	56.3	6.81	10.8%
6	1000	61.9	69.7	67.8	58.2	56.3	5.62	9.08%
7	660	84.7	84.6	81.1	69.9	72.1	12.6	14.8%
8	816	79.6	77.6	72.8	66.8	72.2	7.34	9.22%
9	640	64.5	70.0	64.7	55.8	46.0	18.5	28.7%
10	800	71.1	78.4	68.9	65.2	49.7	21.4	30.1%
11	858	76.3	72.2	72.1	69.6	52.8	23.5	30.8%
12	870	67.7	60.4	61.5	57.5	45.5	22.1	32.7%
13	696	86.4	78.3	79.6	75.7	58.4	28.0	32.4%
14	912	67.2	62.9	60.2	58.9	48.0	19.2	28.6%
15	620	60.8	54.2	49.4	45.8	37.8	23.0	37.9%
16	920	57.5	59.4	64.5	56.5	48.4	9.03	15.7%
17	860	51.0	58.8	53.4	48.7	43.0	8.04	15.8%
18	920	45.8	52.6	58.6	48.9	47.1	-1.26	-2.75%
19	970	61.1	62.2	59.3	51.3	46.4	14.7	24.1%
20	920	68.6	67.8	57.8	53.1	49.9	18.7	27.3%
21	940	61.7	62.7	57.9	48.4	47.7	14.1	22.8%
22	930	60.1	74.4	72.1	52.6	48.6	11.5	19.2%
23	960	54.5	58.6	63.7	47.0	44.9	9.66	17.7%
24	870	38.0	39.0	41.2	32.0	27.8	10.2	26.9%
25	944	61.6	64.2	70.5	55.5	52.6	9.05	14.7%
26	924	52.6	53.8	53.6	44.6	38.2	14.4	27.4%
27	900	54.8	63.4	67.8	50.2	45.8	8.95	16.3%
28	924	46.2	50.3	51.7	40.1	40.4	5.84	12.6%
29	696	69.6	65.0	77.0	54.2	50.0	19.6	28.2%
30	884	59.9	57.6	54.9	51.1	45.6	14.3	23.8%
31	960	59.6	56.3	49.5	49.1	39.2	20.4	34.2%
32	892	57.8	53.5	48.3	47.2	42.5	15.3	26.4%
33	928	70.3	77.4	65.8	65.9	57.3	13.0	18.4%
34	768	71.8	76.8	62.4	62.7	57.9	14.0	19.5%
mean	853	64.5	66.2	64.1	55.8	49.8	14.6	22.2%
min	525	38.0	39.0	41.2	32.0	27.8	-1.26	-0.03
max	1000	95.2	89.2	97.9	85.9	72.2	28.0	0.38
std dev	117	12.1	11.2	11.2	10.4	9.46	6.92	0.09

Table 4.3. Paired t-test Results for Control Soils (0% P) over 120 Days

Soil #	Initial Pb conc. (mg/kg)	0-day	30-day	60-day	90-day	120-day	significant aging? over 120 days[b]	significant aging? between 90 and 120 days[c]
1	968	59.94 ± 0.44	65.31 ± 2.95	60.12 ± 0.05	52.60 ± 1.48	45.35 ± 0.21	yes	no
2	736	95.23 ± 6.74	89.17 ± 0.46	97.93 ± 0.02	85.93 ± 1.24	68.94 ± 1.31	yes	yes
3	880	68.92 ± 0.40	80.32 ± 1.05	72.09 ± 2.75	59.32	58.00	yes	yes
4	525	81.63 ± 2.18	73.82 ± 1.32	70.83 ± 1.05	56.07	54.18	yes	yes
5	914	63.14 ± 2.10	79.06 ± 2.50	71.27 ± 3.63	59.30 ± 1.41	56.33 ± 0.70	yes	no
6	1000	61.87 ± 1.92	69.71 ± 0.24	67.82 ± 0.34	58.16 ± 4.67	56.25 ± 1.26	yes	no
7	660	84.65 ± 6.65	84.56 ± 1.08	81.10 ± 2.62	69.89	72.09	no	yes
8	816	79.56 ± 0.66	77.60 ± 3.27	72.84 ± 0.58	66.84	72.22	yes	yes
9	640	64.46 ± 1.67	70.02 ± 0.64	64.65 ± 1.72	55.77 ± 3.55	45.96 ± 0.16	yes	no
10	800	71.12 ± 0.94	78.42 ± 5.40	68.94 ± 4.04	65.17 ± 1.02	49.69 ± 1.63	yes	yes
11	858	76.27 ± 0.71	72.23 ± 0.91	72.11 ± 0.95	69.62 ± 2.98	52.78 ± 2.03	yes	no
12	870	67.69 ± 5.22	60.41 ± 3.31	61.52 ± 0.04	57.51 ± 0.64	45.54 ± 2.01	yes	yes
13	696	86.38 ± 1.92	78.25 ± 0.15	79.63 ± 2.64	75.74	58.39	yes	yes
14	912	67.19 ± 1.18	62.90 ± 1.09	60.21 ± 1.39	58.95 ± 0.57	47.99 ± 0.33	yes	yes
15	620	60.79 ± 7.64	54.24 ± 0.32	49.42 ± 3.73	45.80 ± 0.61	37.75 ± 1.24	no	no
16	920	57.47 ± 0.32	59.41 ± 0.82	64.48 ± 0.53	56.45 ± 1.92	48.44 ± 1.36	yes	no
17	860	51.00 ± 1.07	58.81 ± 1.44	53.38 ± 2.49	48.73 ± 1.01	42.96 ± 0.52	yes	no
18	920	45.83 ± 0.31	52.56 ± 3.30	58.58 ± 3.86	48.85 ± 1.01	47.09 ± 1.96	no	no
19	970	61.13 ± 0.34	62.24 ± 1.43	59.34 ± 0.62	51.29 ± 0.76	46.38 ± 0.49	yes	no
20	920	68.64 ± 7.81	67.81 ± 2.50	57.83 ± 0.04	53.14 ± 1.72	49.89 ± 0.02	no	no
21	940	61.71 ± 1.10	62.66 ± 0.86	57.94 ± 0.75	48.36 ± 0.35	47.65 ± 0.99	yes	no
22	930	60.08 ± 4.55	74.38 ± 0.99	72.12 ± 1.92	52.56 ± 0.57	48.56 ± 1.14	no	no
23	960	54.54 ± 2.38	58.63 ± 1.29	63.73 ± 0.11	46.98 ± 1.26	44.87 ± 0.07	no	no
24	870	38.00 ± 0.50	38.97 ± 0.32	41.15 ± 1.29	32.02 ± 1.01	27.76 ± 0.29	yes	yes
25	944	61.62 ± 0.74	64.22 ± 1.34	70.54 ± 1.40	55.48 ± 1.52	52.57 ± 1.38	no	no
26	924	52.60 ± 0.89	53.81 ± 0.92	53.63 ± 2.17	44.58 ± 1.69	38.20 ± 0.26	yes	no
27	900	54.79 ± 0.21	63.35 ± 3.80	67.83 ± 0.11	50.24 ± 0.62	45.84 ± 0.91	yes	no
28	924	46.21 ± 13.04	50.33 ± 1.09	51.69 ± 0.13	40.12 ± 1.79	40.37 ± 0.23	no	no
29	696	69.59 ± 1.22	65.01 ± 6.13	77.02 ± 16.44	54.15 ± 2.14	49.97 ± 0.31	yes	no
30	884	59.88 ± 1.24	57.63 ± 1.91	54.88 ± 0.38	51.09 ± 0.91	45.60 ± 1.42	yes	no
31	960	59.63 ± 1.80	56.34 ± 0.59	49.50 ± 1.61	49.15 ± 1.42	39.24 ± 1.23	yes	yes
32	892	57.78 ± 2.27	53.47 ± 0.85	48.34 ± 0.81	47.16 ± 1.85	42.50 ± 3.22	no	no
33	928	70.32 ± 1.22	77.39 ± 2.19	65.78 ± 0.21	65.91 ± 2.17	57.35 ± 1.33	yes	no
34	768	71.85 ± 0.71	76.82 ± 0.99	62.36 ± 0.18	62.67 ± 0.63	57.87 ± 1.26	yes	no
mean	853	64.5	66.2	64.1	55.8	49.8		
min	525	38.0	39.0	41.2	32.0	27.8		
max	1000	95.2	89.2	97.9	85.9	72.2		
std dev	117	12.1	11.2	11.2	10.4	9.46		

[a] Errors represent standard deviation (n=2). Some data shown without errors were obtained by single measurements. [b]Pb measured by paired t-test results with 0 and 120 days bioaccessibility data. [c]Pb measured by paired t-test results with 90 and 120 days bioaccessibility data.

bioaccessibility from soil properties could not be obtained. Yang et al. (2003) found that such small reductions in bioaccessibility are due to metal – soil interactions rather than pre-existing solid phase speciation because soluble metals ($Pb(NO_3)_2$) were added to the soil initially. The use of Pb-spiked soils allowed us to study soils that were initially more bioavailable than Pb-contaminated soils and follow the changes in bioaccessibility over time. Regardless of amendment additions, a long-term reduction in bioaccessibility is implied as long as the soil properties governing sequestration do not change.

4.3.2 Effect of P Dose and Time on % Pb Bioaccessibility

Figures 4.1-4.4 compare the effects of three P doses with the average % Pb bioaccessibility, calculated by equation 4.3, for soils amended with HumaPhos. By comparing the data of the amended soil versus the control soil for each aging time point separately, the effect of P dose alone can be assessed. The 30-day data for all soils is presented in Figure 4.1. After 30 days of aging, soils #1-34 amended with 2.5% P showed an average decrease in % Pb bioaccessibility from the 0% P (control) of 6.30% (Table 4.4). A further decrease (15.8%) in average % Pb bioaccessibility was present in soils amended with 5% P (Table 4.4).

The 60-day Pb bioaccessibility data for all soils is presented in Figure 4.2. After 60 days of aging, soils #1-34, amended with 2.5% P, showed an average decrease in % Pb bioaccessibility from the control of 6.72% (Table 4.5), and an even further decrease (17.3%) in average % Pb bioaccessibility was seen with the 5% P dose.

The 90-day % Pb bioaccessibility data for all soils is presented in Figure 4.3. After 90 days of aging, average % Pb bioaccessibility data for soils #1-34 was consistent

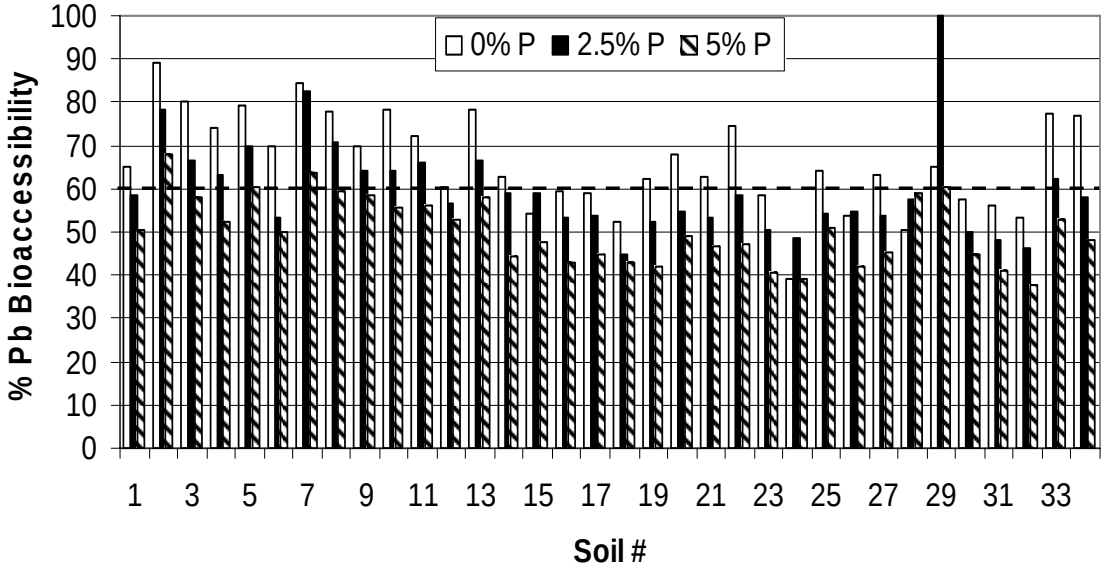

Figure 4.1. % Pb Bioaccessibility at 30 days for Soils #1-34

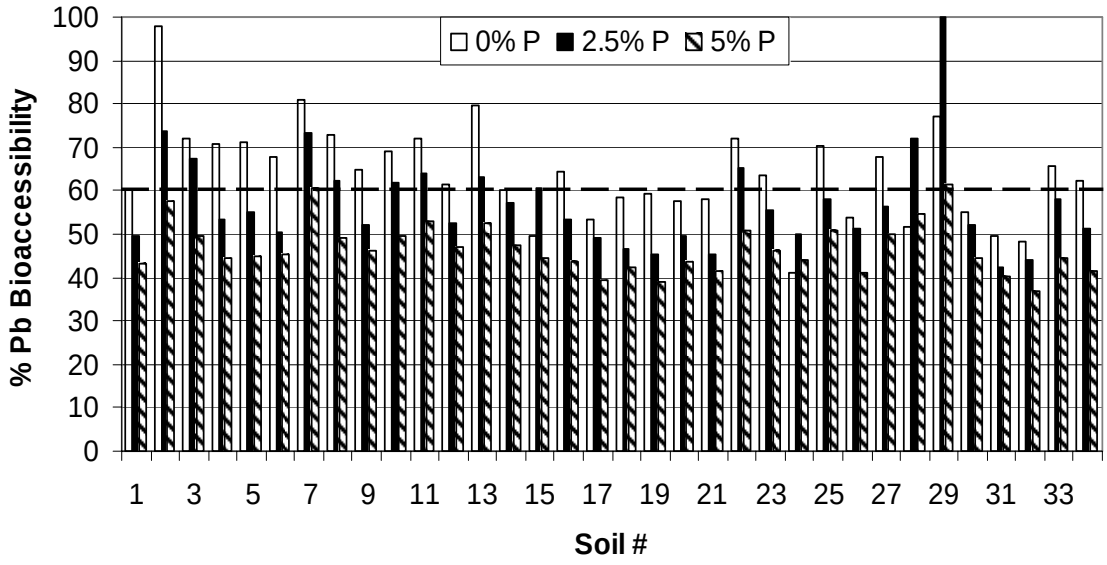

Figure 4.2. % Pb Bioaccessibility at 60 days for Soils #1-34

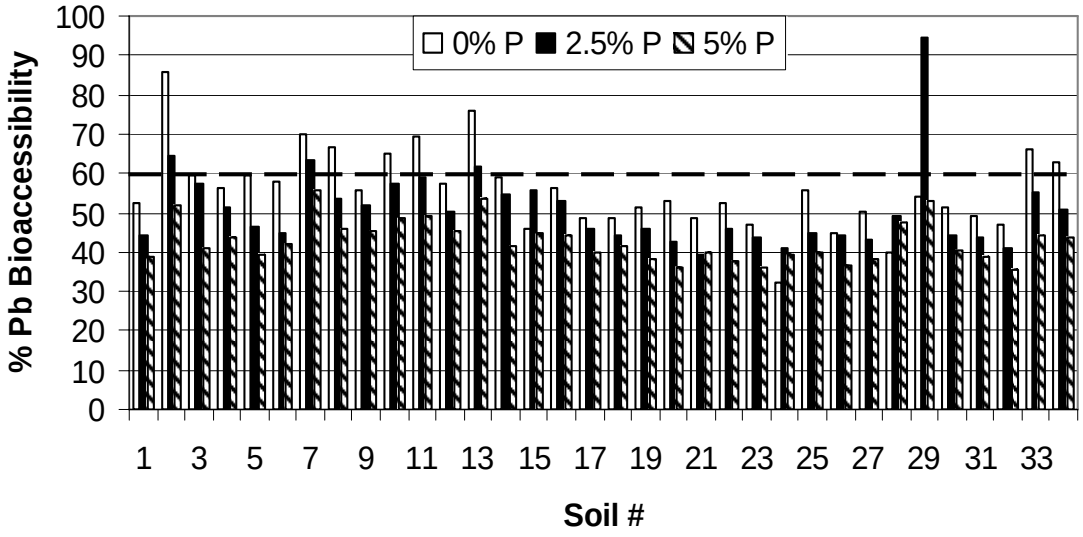

Figure 4.3. % Pb Bioaccessibility at 90 days for Soils #1-34

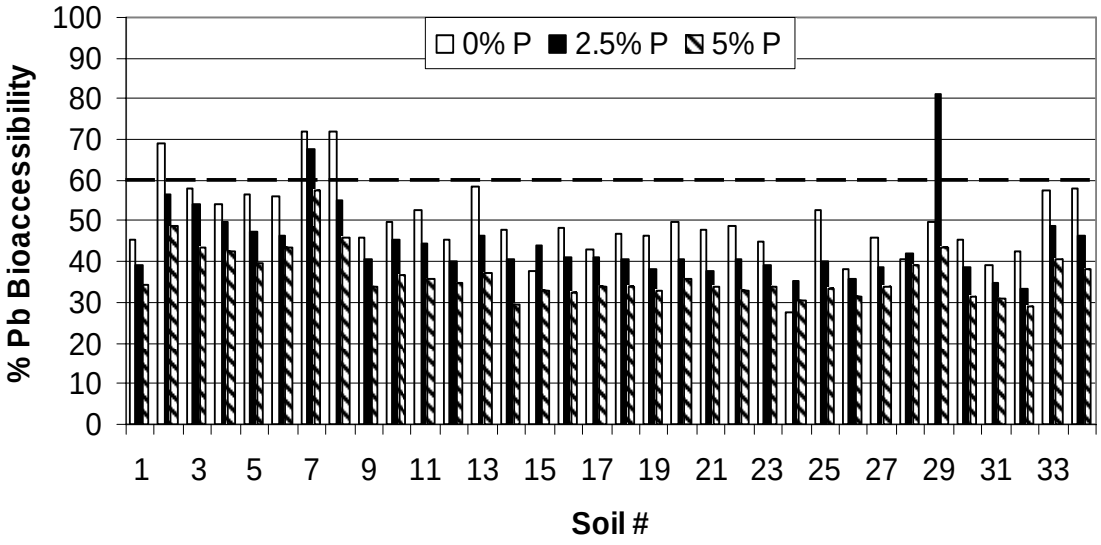

Figure 4.4. % Pb Bioaccessibility at 120 days for Soils #1-34

Table 4.4. % Pb Bioaccessibility for Soils Amended with 0% P, 2.5% P, and 5% P at 30 Days.

Soil #	0% P	2.5% P	5% P	Diff. (0-2.5%)	Diff. (0-5%)
1	65.3	58.3	50.5	7.00	14.8
2	89.2	78.3	68.1	10.9	21.1
3	80.3	66.6	57.9	13.7	22.4
4	73.8	63.0	52.5	10.8	21.3
5	79.1	69.9	60.4	9.21	18.6
6	69.7	53.3	50.2	16.4	19.5
7	84.6	82.6	63.8	1.99	20.8
8	77.6	70.6	59.3	6.95	18.3
9	70.0	64.3	58.4	5.68	11.6
10	78.4	64.4	55.5	14.0	23.0
11	72.2	66.3	56.3	5.98	15.9
12	60.4	56.5	53.0	3.93	7.42
13	78.3	66.7	58.2	11.6	20.1
14	62.9	59.1	44.2	3.78	18.7
15	54.2	58.9	47.8	-4.69	6.44
16	59.4	53.1	43.1	6.29	16.3
17	58.8	54.0	44.6	4.85	14.2
18	52.6	44.9	43.0	7.67	9.59
19	62.2	52.6	42.2	9.66	20.1
20	67.8	54.8	48.9	13.0	18.9
21	62.7	53.1	46.8	9.56	15.9
22	74.4	58.6	47.4	15.8	27.0
23	58.6	50.5	40.7	8.15	17.9
24	39.0	48.5	39.2	-9.52	-0.180
25	64.2	54.1	50.9	10.1	13.3
26	53.8	54.6	42.0	-0.785	11.8
27	63.4	53.6	45.2	9.75	18.2
28	50.3	57.3	58.9	-7.00	-8.56
29	65.0	100	60.2	-35.0	4.80
30	57.6	49.9	45.0	7.71	12.6
31	56.3	47.9	41.2	8.45	15.1
32	53.5	46.3	37.8	7.19	15.7
33	77.4	62.3	53.0	15.1	24.3
34	76.8	58.2	48.1	18.6	28.8
mean	66.2	59.9	50.4	6.30	15.8
min	39.0	44.9	37.8	-5.92	1.17
max	89.2	100	68.1	-10.8	21.1
std dev	11.2	11.2	7.73	0.03	3.46

Table 4.5. % Pb Bioaccessibility for Soils Amended with 0% P, 2.5% P, and 5% P at 60 Days.

Soil #	0% P	2.5% P	5% P	Diff. (0-2.5%)	Diff. (0-5%)
1	60.1	49.6	43.3	10.5	16.8
2	97.9	73.6	57.8	24.3	40.1
3	72.1	67.6	49.5	4.52	22.6
4	70.8	53.5	44.7	17.3	26.1
5	71.3	55.1	45.1	16.1	26.2
6	67.8	50.6	45.2	17.3	22.6
7	81.1	73.4	60.6	7.67	20.5
8	72.8	62.3	49.3	10.6	23.5
9	64.7	52.2	46.1	12.4	18.6
10	68.9	62.1	49.6	6.88	19.3
11	72.1	63.8	52.8	8.33	19.3
12	61.5	52.7	47.2	8.82	14.4
13	79.6	63.1	52.7	16.5	27.0
14	60.2	57.3	47.4	2.94	12.8
15	49.4	60.8	44.3	-11.4	5.09
16	64.5	53.4	43.8	11.0	20.7
17	53.4	49.0	39.5	4.39	13.9
18	58.6	46.4	42.6	12.2	16.0
19	59.3	45.2	38.8	14.1	20.5
20	57.8	49.8	43.8	8.05	14.1
21	57.9	45.3	41.4	12.7	16.6
22	72.1	65.2	50.7	6.92	21.4
23	63.7	55.4	46.2	8.34	17.5
24	41.2	50.1	43.9	-8.92	-2.78
25	70.5	58.1	50.7	12.4	19.9
26	53.6	51.1	41.2	2.54	12.5
27	67.8	56.3	49.8	11.5	18.0
28	51.7	72.0	54.7	-20.3	-2.99
29	77.0	100	61.3	-23.0	15.7
30	54.9	52.3	44.4	2.58	10.4
31	49.5	42.5	40.1	7.04	9.45
32	48.3	43.9	36.9	4.42	11.4
33	65.8	58.0	44.6	7.74	21.2
34	62.4	51.2	41.7	11.1	20.6
mean	64.1	57.4	46.8	6.72	17.3
min	41.2	42.5	36.9	-1.30	4.24
max	97.9	100	61.3	-2.07	36.6
std dev	11.2	11.2	5.90	-0.01	5.30

with that of the 30-day and 60-day data (Figure 4.3). The average % bioaccessibility decreased with the addition of 2.5% P by 4.89% and decreased further with the 5% P dose by 12.9% (Table 4.6).

The 120-day data for all soils (#1-34) is presented in Figure 4.4. The average % bioaccessibility decreased with the addition of 2.5% P by 5.30% and decreased further with the 5% P dose by 13.2% (Table 4.7). Like the 30-day, 60-day, and 90-day data, the 120-day data shows that 30 out of 34 soils (88.2%) decreased in % Pb bioaccessibility with increasing % P dose (Figure 4.4). These results are in agreement with others who have shown that increasing the P dose resulted in a significant reduction in Pb bioavailability in Pb-contaminated soils (Brown et al., 2004; Hettiarachchi et al., 2001). However, there were 4 soils (#15, #24, #28, and #29) that did not consistently follow this trend. Figure 4.5 compares the % Pb bioaccessibility of soil #15 and soil #24 at all three doses for each aging period. Both soils show consistent behavior in % Pb bioaccessibility among each aging period with an increase in % Pb bioaccessibility at 2.5% P and a decrease in % Pb bioaccessibility at 5% P to above or below the 0% P bioaccessibility value. Figure 4.6 compares % Pb bioaccessibility with respect to time for soil #28 and soil #29. Soil #28 shows inconsistent behavior among each aging period, while the data for soil #29 seems somewhat consistent (Figure 4.6) Similar to soil #24 (Figure 4.5), soil #28 increased slightly in % Pb bioaccessibility at 2.5% P and then, at 5% P, decreased to below the control (0%P) bioaccessibility value (Figure 4.6). Powder X-ray diffraction results for soils #28 and #29 at 0% P and 2.5% P indicate a strong presence of quartz compounds, but no Pb complexes were found to explain the odd % bioaccessibility results at 2.5% P in these soils. The reasons for the outlying

Table 4.6. % Pb Bioaccessibility for Soils Amended with 0% P, 2.5% P, and 5% P at 90 Days.

Soil #	0% P	2.5% P	5% P	Diff. (0-2.5%)	Diff. (0-5%)
1	52.6	44.1	38.8	8.51	13.8
2	85.9	64.5	52.1	21.4	33.8
3	59.3	57.4	41.2	1.92	18.1
4	56.1	51.4	43.5	4.65	12.5
5	59.3	46.4	39.1	12.9	20.2
6	58.2	44.6	42.1	13.6	16.1
7	69.9	63.5	55.7	6.43	14.2
8	66.8	53.5	45.6	13.3	21.2
9	55.8	51.8	45.1	3.97	10.7
10	65.2	57.5	48.4	7.63	16.8
11	69.6	59.1	49.3	10.5	20.4
12	57.5	50.0	45.4	7.46	12.1
13	75.7	61.6	53.4	14.1	22.3
14	58.9	54.7	41.6	4.23	17.4
15	45.8	55.9	44.7	-10.1	1.06
16	56.5	53.2	44.1	3.28	12.3
17	48.7	45.9	39.8	2.88	8.96
18	48.9	44.0	41.7	4.81	7.16
19	51.3	46.1	38.1	5.23	13.2
20	53.1	42.4	35.9	10.7	17.2
21	48.4	39.4	39.9	8.99	8.50
22	52.6	45.9	37.5	6.66	15.0
23	47.0	43.8	36.2	3.17	10.8
24	32.0	41.1	39.2	-9.10	-7.19
25	55.5	44.7	39.7	10.8	15.8
26	44.6	44.5	36.9	0.0580	7.72
27	50.2	43.0	38.0	7.29	12.3
28	40.1	49.3	47.7	-9.15	-7.53
29	54.2	94.5	52.9	-40.4	1.22
30	51.1	44.5	40.3	6.63	10.8
31	49.1	43.7	38.7	5.44	10.4
32	47.2	41.1	35.8	6.01	11.4
33	65.9	55.1	44.2	10.8	21.7
34	62.7	51.1	43.6	11.6	19.0
mean	55.8	50.9	42.8	4.89	12.9
min	32.0	39.4	35.8	-7.35	-3.76
max	85.9	94.5	55.7	-8.58	30.3
std dev	10.4	10.3	5.34	0.137	5.09

Table 4.7. % Pb Bioaccessibility for Soils Amended with 0% P, 2.5% P, and 5% P at 120 Days.

Soil #	0% P	2.5% P	5% P	Diff. (0-2.5%)	Diff. (0-5%)
1	45.3	38.9	34.2	6.45	11.1
2	68.9	56.6	48.8	12.4	20.2
3	58.0	54.2	43.5	3.81	14.5
4	54.2	50.0	42.3	4.22	11.9
5	56.3	47.6	39.5	8.78	16.8
6	56.3	46.5	43.6	9.76	12.6
7	72.1	67.4	57.5	4.66	14.6
8	72.2	55.2	45.7	17.0	26.5
9	46.0	40.3	33.6	5.61	12.4
10	49.7	45.6	36.7	4.04	12.9
11	52.8	44.7	35.8	8.12	16.9
12	45.5	40.1	34.6	5.45	11.0
13	58.4	46.4	37.1	12.0	21.3
14	48.0	40.7	29.5	7.34	18.5
15	37.8	43.8	32.8	-6.02	4.94
16	48.4	41.2	32.5	7.28	15.9
17	43.0	41.3	33.7	1.67	9.25
18	47.1	40.8	33.9	6.32	13.1
19	46.4	38.0	32.8	8.42	13.5
20	49.9	40.7	35.6	9.24	14.3
21	47.7	37.8	33.7	9.82	14.0
22	48.6	40.8	32.7	7.80	15.9
23	44.9	39.2	33.8	5.68	11.1
24	27.8	35.5	30.6	-7.74	-2.81
25	52.6	40.3	33.4	12.3	19.2
26	38.2	35.5	31.3	2.68	6.86
27	45.8	38.7	33.6	7.11	12.2
28	40.4	41.9	39.3	-1.53	1.11
29	50.0	81.0	43.6	-31.0	6.33
30	45.6	38.9	31.6	6.73	14.0
31	39.2	35.0	30.8	4.27	8.48
32	42.5	33.4	29.1	9.15	13.4
33	57.3	48.7	40.4	8.69	17.0
34	57.9	46.2	38.1	11.6	19.7
mean	49.8	44.5	36.6	5.36	13.2
min	27.8	33.4	29.1	-5.59	-1.35
max	72.2	81.0	57.5	-8.75	14.7
std dev	9.46	9.55	6.13	-0.08	3.33

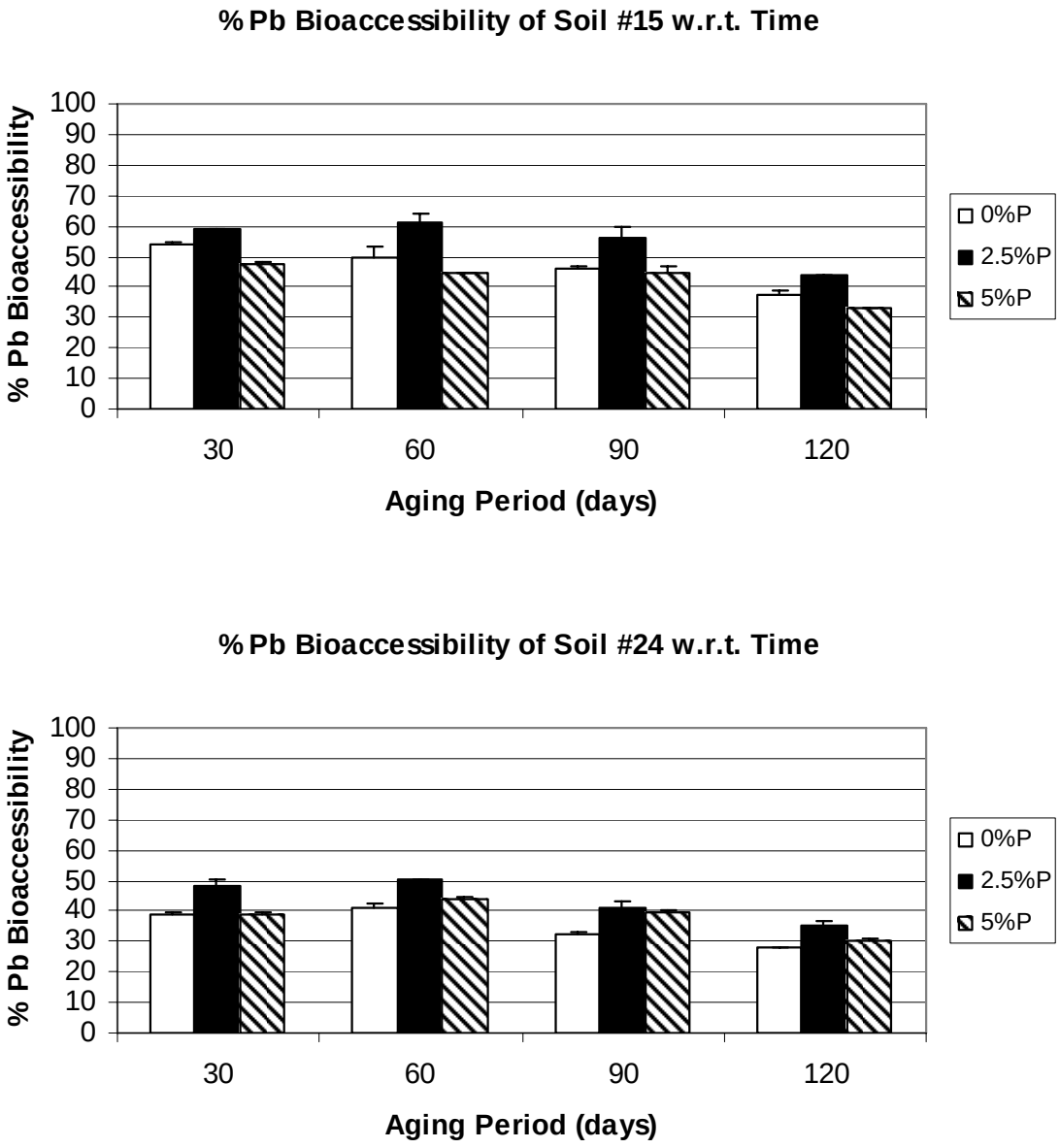

Figure 4.5. % Pb Bioaccessibility of Soil #15 and Soil #24 with respect to Time

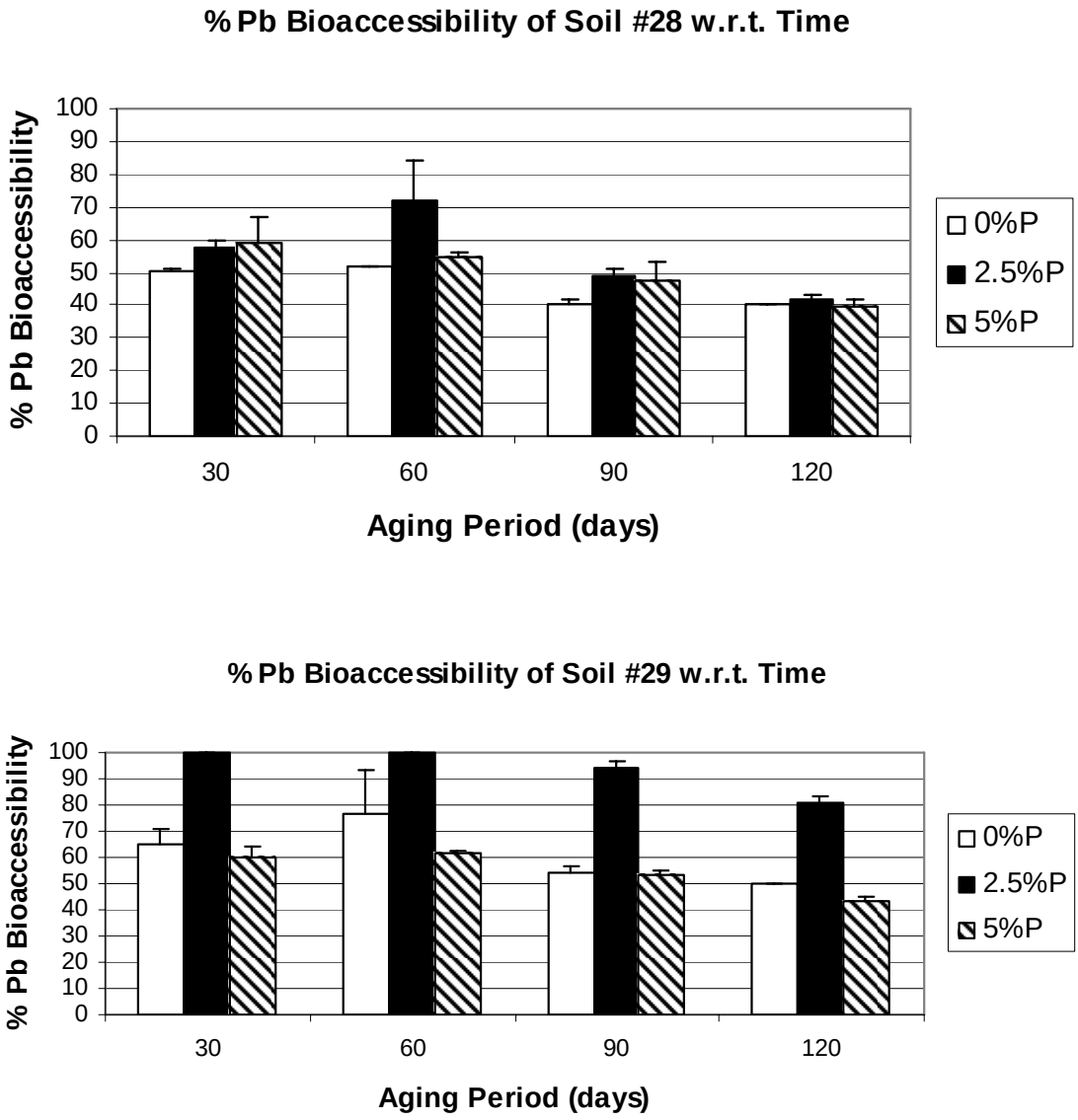

Figure 4.6. % Pb Bioaccessibility of Soil #28 and Soil #29 with respect to Time

behavior of soils #15, #24, #28, and #29 are uncertain. Soil properties (Appendix D) do not reveal any commonality to these soils separating them from other soils. Results from a paired t-test indicate there was no significant difference ($P<0.05$) in average % Pb bioaccessibility over time between the 0% P and 5% P doses for soils #24, #28, and #29. However, for soil #15, there were significant differences ($P<0.05$) in average % Pb bioaccessibility over time for all % P doses.

At the end of the 120-day aging period, the pH of each soil sample for each dose was measured and recorded (Table 4.8). The addition of 2.5% P and 5% P increased the soil pH from an average of 6.04 ± 1.30 to 7.48 ± 0.26 and 7.63 ± 0.18, respectively. As discussed above, a corresponding decrease in % Pb bioaccessibility occurred with increasing soil pH. The pH of only HumaPhos in a 2:1 $CaCl_2$ solution was measured to be 7.35. The small % coefficient of variation (COV) in pH with the phosphate additions indicates good buffering capacity of HumaPhos.

Scheckel et al. (2003) conducted research on the formation of chloropyromorphite ($Pb_5(PO_4)_3Cl$) in P – amended, Pb – contaminated soils during sequential extraction procedures. They found that chloropyromorphite was forming during the sequential extraction procedure itself rather than *in situ*. In 2005, Scheckel et al. speculated that Pb bioaccessibility reduction via formation of chloropyromorphite was probably occurring as an experimental artifact in the PBET rather than occurring in the soil itself. For this reason, approximately 25% of PBET supernatants amended with the largest % P dose (5% P) were analyzed for PO_4. Results from the PO_4 – PBET measurements and previous Pb – PBET measurements were tabulated (Table 4.9) and input in Visual MINTEQ, along with a fixed pH value of 2.3, a glycine concentration of

Table 4.8. pH Measurements at the Aging Endpoint (120 Days).

Soil #	0%P	2.5%P	5%P
1	7.58	7.85	7.89
2	6.24	7.23	7.45
3	5.18	7.40	7.57
4	4.30	7.45	7.64
5	6.47	7.55	7.59
6	6.33	7.56	7.69
7	4.99	7.33	7.57
8	7.60	7.92	8.03
9	6.04	7.41	7.56
10	7.04	7.46	7.57
11	7.76	7.65	7.69
12	7.82	7.70	7.76
13	5.22	7.58	7.67
14	6.09	7.45	7.65
15	4.30	7.39	7.63
16	5.83	7.51	7.71
17	4.39	7.34	7.63
18	6.67	7.65	7.75
19	5.26	7.21	7.44
20	8.01	7.93	8.01
21	7.94	7.97	7.97
22	5.76	7.48	7.61
23	5.39	7.46	7.55
24	4.14	7.17	7.44
25	8.02	8.01	8.00
26	5.29	7.07	7.37
27	4.76	7.35	7.55
28	7.26	7.57	7.63
29	5.45	7.42	7.66
30	4.74	7.09	7.40
31	6.98	7.36	7.46
32	4.05	6.96	7.39
33	6.61	7.26	7.40
34	4.11	7.45	7.69
mean	**5.99**	**7.48**	**7.64**
std dev	**1.29**	**0.26**	**0.18**
%COV	**21.5%**	**3.42%**	**2.36%**

Table 4.9. SI Calculations from Visual Minteq.

	Soil #	%P	PO4 (mg/L)	PO4 (mol/L)	Pb (mg/L)	Pb (mol/L)	Soil pH	SI (from VM)
	1	5	175	1.84E-03	1.60	7.72E-06	7.89	-3.43
	2	5	265	2.79E-03	1.76	8.49E-06	7.45	-2.69
	3	5	293	3.08E-03	1.78	8.59E-06	7.57	-2.53
	4	5	293	3.08E-03	1.05	5.07E-06	7.64	-3.68
	5	5	264	2.78E-03	1.78	8.59E-06	7.59	-2.66
120-day	6	5	276	2.91E-03	2.05	9.89E-06	7.69	-2.30
	7	5	257	2.71E-03	1.75	8.45E-06	7.57	-2.73
	8	5	236	2.48E-03	1.83	8.83E-06	8.03	-2.75
	mean		257	2.71E-03	1.70	8.20E-06	7.68	-2.85
	min		175	1.84E-03	1.05	5.07E-06	7.45	-3.68
	max		293	3.08E-03	2.05	9.89E-06	8.03	-2.30
	std dev		38.23	4.02E-04	0.29	1.40E-06	0.19	0.47

	Soil #	%P	PO4 (mg/L)	PO4 (mol/L)	Pb (mg/L)	Pb (mol/L)	Soil pH	SI (from VM)
	1	5	300	3.16E-03	2.33	1.12E-05	7.89	-1.92
	2	5	405	4.26E-03	2.34	1.13E-05	7.45	-1.52
	3	5	399	4.20E-03	2.48	1.20E-05	7.57	-1.40
	4	5	455	4.79E-03	1.35	6.52E-06	7.64	-2.56
	5	5	414	4.36E-03	2.42	1.17E-05	7.59	-1.41
30-day	6	5	370	3.89E-03	2.52	1.22E-05	7.69	-1.47
	7	5	391	4.12E-03	2.13	1.03E-05	7.57	-1.76
	8	5	369	3.89E-03	2.29	1.11E-05	8.03	-1.67
	mean		388	4.08E-03	2.23	1.08E-05	7.68	-1.71
	min		300	3.16E-03	1.35	6.52E-06	7.45	-2.56
	max		455	4.79E-03	2.52	1.22E-05	8.03	-1.40
	std dev		44.85	4.72E-04	0.38	1.82E-06	0.19	0.39

0.4 M, and a chloride concentration of 0.242 M. Results from output files reveal a saturation index (SI) range of -1.40 to -2.56 and -2.30 to -3.68 for 0-day and 120-day samples, respectively (Table 4.9). (See Appendix E for an example of a Minteq speciation output file for soil #1). Therefore, PBET supernatants were well undersaturated with respect to chloropyromorphite. Thus, chloropyromorphite did not form as an experimental artifact in the PBET as postulated by Scheckel et al. (2003).

4.4 Conclusions

For all 34 soils, the average % Pb bioaccessibility decreased with both longer aging time and increasing % P dose (Figure 4.7). Over 120 days, the addition of 2.5% P and 5% P decreased the average absolute % Pb bioaccessibility by 5.36% and 13.2%, respectively. A study done by Hettiarachchi et al (2000) found that the addition of P as triple super-phosphate fertilizer (TSP) or rock phosphate (RP) to five Pb-contaminated soils decreased the Pb bioaccessibility in PBET extractions by 15 to 41%, *relative to the control*. Because these soils had limited bioaccessibility initially (18.3 – 36.6%), it is confusing as to the actual reductions in Pb bioaccessibility. Sonmez and Pierzynski (2005) defined relative bioaccessibility as "the percentage of Pb extracted in the PBET relative to the control sample". In their study, the bioaccessibility of the control sample was scaled to 100%, and reductions in bioaccessibility were calculated as a percent reduction relative to the control sample. If the 120-day bioaccessibility results of this study were scaled relative to the control, the average % Pb bioaccessibility would decrease by 11% and 27% (versus absolute decreases of 5.36% and 13.2%) for soils amended with 2.5% P and 5% P, respectively.

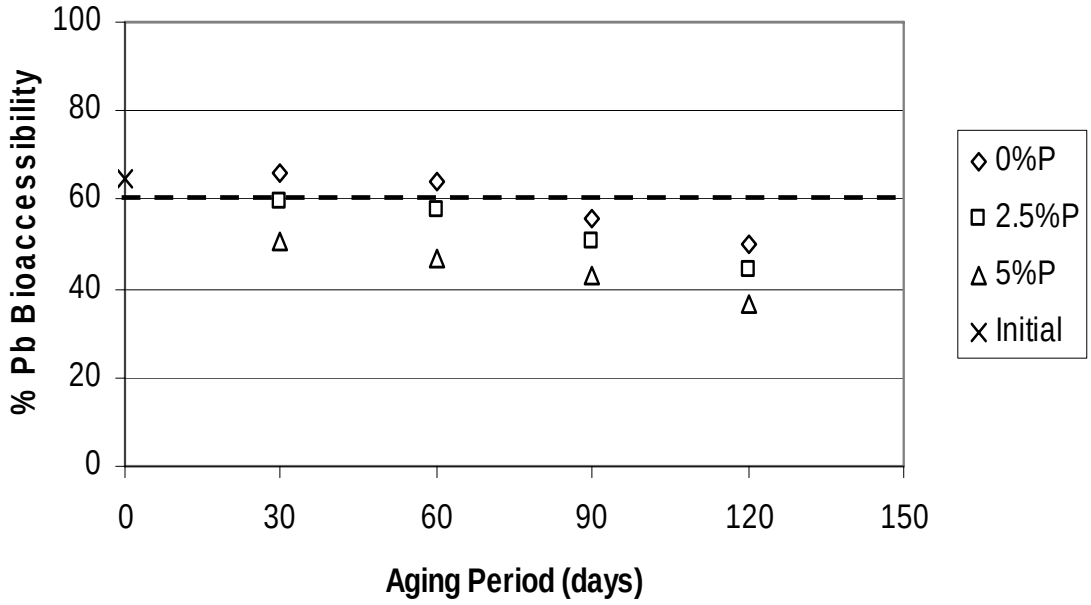

Figure 4.7. % Pb Bioaccessibility Averaged for All 34 Soils With Time for 0% P, 2.5% P, and 5% P Doses.

The addition of 2.5% P and 5% P decreased the average % Pb bioaccessibility to below the soil Pb RAF. However, in order to achieve a 2.5% P and a 5% P dose, 38.7% and 50.5% of the total amended soil weight was composed of only HumaPhos, respectively (Appendix D.1). Furthermore, time alone reduced the average absolute % Pb bioaccessibility by 14.6% (Table 4.2), which is a more significant reduction than either P dose. Therefore, the addition of P in the form of P amendments, while statistically significant, may not be a practical approach to decreasing the bioaccessibility of Pb in soils. Because the PBET supernatants were well undersaturated with respect to chloropyromorphite, chloropyromorphite did not form as an experimental artifact in the PBET.

CHAPTER FIVE

LEAD AND ANTIMONY POLLUTION CONCERNS IN FIRING RANGE SOILS

5.1 Introduction

In many countries, the use of Pb-based ammunition is one of the most significant sources of Pb pollution. Annual deposition by hunting and recreational shooting varies between 200 and 6000 tons in the Netherlands, Denmark, Canada, and England and reaches 55,000 tons in the U.S. (Jorgensen and Willems, 1987; Mellor and McCartney, 1994; Scheuhammer and Norris, 1996). According to the Dept. of Environment in Switzerland, it is estimated that 400 – 500 tons of Pb and 10 – 25 tons of antimony (Sb) enter the soil environment every year as a result of shooting practice at over 2000 ranges (Knechtenhofer et al., 2003). The contamination is the greatest in the top 20 – 30 cm of embankments that act as stop butts behind the targets. One soil column study showed an effluent concentration of 3400 $\mu g\ l^{-1}$ Pb from a firing range soil (Rooney and McLaren, 1999).

Bullets generally have cores made of a Pb-Sb alloy with a Sb content of 2-5% by weight. Sb is used as a hardening agent in the manufacturing of Pb ammunition. Other elements such as As, Bi, or Ag may be present in recycled Pb of secondary quality, and the bullet jacket may be of Cu or Ni alloy housing (Guy and Pate, 1973; Randich et al., 2002). Sb, a suspected human carcinogen (Gebel, 1997), has been

found at concentrations of up to 155 μg l^{-1} in soil solution (Farenhorst and Renger, 1990). A study done by Fahrenhorst (1993) showed that in neutral soils, aqueous concentrations of Sb exceeded those of Pb, despite the much higher solid phase Pb content. For acidic soils, the situation was reversed, and the aqueous Pb content exceeded the Sb content. This is consistent with the idea that the adsorption of metal(loid)s is pH dependent. At low pH, there was more Pb in solution because cations are less absorbed than oxyanions at lower pH values. As the pH increases, the situation is reversed. Cations become more absorbed and oxyanions (Sb) less adsorbed.

Sb and its compounds have been listed as priority pollutants by the U.S. EPA and the European Union (Potin-Gautier et al., 2005). The Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) requires the U.S. EPA and the ATSDR to prioritize substances "which are deemed to pose the most significant potential threat to human health due to their known or suspected toxicity and potential for human exposure". Sb is ranked #241 out of 275 elements while Pb is ranked #2. The mobilization of antimony primarily depends on the corrosion of the bullets and on the oxidation of Sb (0) to Sb (III) and Sb (V) (Johnson et al., 2005). Sb has similar elemental properties to As (e.g. both are oxyanions). The presence of P greatly decreases As (V) and As (III) sorption by soils, indicating the competitive adsorption between P and As for sorption sites (Smith et al., 2002). Similarly, Sb sorption may also be decreased when applying P to reduce Pb found in Pb-contaminated soils, particularly if bullets are the source of the Pb. Many studies have investigated the mobility of Pb in soils out of concern for human health. However, few studies have addressed the mobility and bioavailability of Sb and the threat it may be to human health. The goals of

this study are to determine whether Sb and Pb in small-arms firing range soils are correlated and to determine how remediation strategies for Pb-contaminated soils affect Sb mobility.

5.2 Materials & Methods

Pb-contaminated soils were collected from three active small arms firing range locations throughout the southeastern United States. Site 1 is a firing range located in Roane County, Tennessee. This firing range facility is an inactive range primarily used for their protective services organization. Site 2 is located in south-central Alabama. Site 2 contains an active small arms firing range used for military training purposes. Site 3 is a small arms firing range, located in east-central Alabama, and primarily used for target practice and recreational use by police.

Soil samples were collected from three locations at Site 1, and are listed in Table 5.1. Sample #1 was collected underneath the Pb bullets. Sample #2 was collected from the upper sump, while Sample #3 was sampled from the lower sump. Similarly to Site 1, soils were sampled from three different locations at Site 2. Site 2 has recently installed a new enclosed range which captures bullets and prevents their contact with soil, thus preventing soil contamination. Before the newly enclosed system was installed, an old stop butt was used for target practice. Sampling from the old stop butt was difficult because the new system provided limited access to the soil from the old stop butt. Soil samples were collected from the left/center (#3) and right (#2) sides of the old stop butt, and one sample was taken from the center of a heap pile (#1) that contained contaminated soil moved out from the old stop butt to make room for the new system.

Table 5.1. Sb and Pb in 3 Small Arms Firing Range Soils

	Sample ID	Sb (mg/kg)	Pb (mg/kg)
Site 1[a]	1A	53.34	4020
	1B	55.96	3980
	2A	33.94	1584
	2B	40.88	1520
	3A	23.81	920
	3B	23.83	892
Site 2	1	16.96	1994
	2	8.88	1073
	3	36.24	4460
Site 3	1	31.89	4510
	2	13.72	1148
	3	8.07	707
	4	16.40	1449
	5	2.84	326
	6	0.50	59.97
	7	78.44	9972
	8	0.50	82.93
	9	0.50	56.99
	10	1.48	331

[a]Results indicated by A and B represent analytical duplicates of the same soil sample.

Ten soil samples were collected from Site 3. Soil samples #1-10 were sampled sporadically throughout the stop butt. Soil sample #1 was taken approximately one year later near the sample #4 location. Samples #4 and #7 were collected in the middle of the stop butt, where the majority of bullets were fired. Soil samples from all 3 sites were collected from the upper 12" portion of the surface. On site, soils were sieved to <2 mm in order to remove bullet fragments, gravel, and organic debris.

Each soil sample was homogenized, disaggregated, air dried, and sieved to <250 μm. The particle size that normally adheres to the hands of a child is <100 μm. However, because it is difficult to collect large quantities of the <100 μm soil fraction and the <250 μm fraction is deemed adequate for approximating the particle size ingested by children (Rodriguez et al., 1999; Hettiarachchi and Pierzynski, 2004), the <250 μm particle size was used for this research. Samples were stored dry prior to use in polypropylene vials.

All chemicals employed in this research were analytical grade or above, and solutions were prepared with DI water (18 MΩ·cm) from a Purelab ultra water/ion exchange apparatus (U.S. Filter system). E.P.A. Method 3050B, a harsh acid digestion procedure, was used to determine total Pb and Sb concentrations in the soils (U.S. EPA, 1994). Soil samples (<250 μm) were digested in duplicates and blanks were included for quality assurance. Filtrates were analyzed for Pb using a Varian SpectrAA 220FS flame atomic absorption spectrometer (FLAA). Filtrates were analyzed for Sb using a Perkin-Elmer HGA-600 graphite furnace and Perkin-Elmer 3110 atomic absorption spectrophotometer (GFAA). Equipment calibration was performed using matrix matched standards with a range of 2 to 6 mg L^{-1} Pb concentrations and 20 to 100 μg L^{-1}

Sb concentrations. Samples were diluted, if needed, during analysis to within the concentration range of the standards. A National Institute of Standards and Technology (NIST) 2711 standard reference material (SRM) was digested and measured for Pb and Sb content with each acid digestion performed for quality assurance/quality control.

Modeled based on the threat to groundwater, the Toxicity Characteristic Leaching Procedure (TCLP) is a test often used to classify soils or wastes as hazardous or non-hazardous (Stanforth and Qiu, 2001). TCLP testing is used to determine whether a solid waste cannot be discarded in a landfill due to its leaching more than a pre-determined amount of a "toxic" element. The hazardous waste level for Pb in the TCLP leachate is 5.0 mg L^{-1}. If the Pb concentration falls above this level, the soil is deemed "hazardous". Otherwise, the soil is deemed "non-hazardous". Sb is not listed under TCLP regulations, and thus was not examined in this procedure. The TCLP was performed based on U.S. EPA's Method 1311 (U.S. EPA, 1992). Soil samples #4 and #7 from Site 3 were chosen due to their high soil Pb concentration. Method 1311 was conducted using duplicate samples and an NIST 2711 standard reference material (SRM) was extracted at the same time for quality assurance purposes.

5.3 Results & Discussion

The results from Method 3050B for Pb and Sb concentrations are listed in Table 5.1. The Sb and Pb data from each soil set was plotted to determine whether a linear relationship exists between the Pb concentration and the Sb concentration in the three firing range soils. Because Sb generally makes up 2-5% by weight of most Pb bullets (Guy and Pate, 1973; Randich et al., 2002), and if the main source of both Pb and Sb is

the soil due to the weathering of bullets over time (Johnson et al., 2005), a small (2-5%) concentration of Sb is expected to be found along with Pb in firing range soils where Pb-Sb alloy bullets are fired.

In Table 5.1, results shown are analytical duplicates of the same soil sample. Digest samples for Site 1 firing range soil #1 had the highest Pb and Sb concentrations at 3980-4020 mg Pb/kg soil and 53.34-55.96 mg Sb/kg soil (Table 5.1). This was expected as this portion was sampled under Pb bullets in the middle of the stop butt, where the majority of bullets are fired. In Figure 5.1, the Sb vs. Pb plot reveals a strong linear correlation ($R^2 = 0.9042$) between Sb and Pb for Site 1 firing range soils.

Results from Site 2 (Table 5.1) were similar to those of Site 1. The Pb concentration was the highest, 4460 mg Pb/kg soil, at the left/center sampling point of the old stop butt. The Sb concentration, 36.24 mg Sb/kg soil, was also higher at the left/ center side than the right side and the heap pile. Figure 5.1 shows a plot of Sb vs. Pb for the Site 2 soils. A very strong linear correlation ($R^2 = 0.9994$) exists among these soils.

Table 5.1 shows the sampling locations and results from Method 3050B for the Site 3 firing range soils. Samples #1, #4, and #7 had the highest concentrations of Pb and Sb. These soil samples were located in the middle of the firing range where the most bullets were found during sampling. A very strong linear correlation between Sb and Pb ($R^2 = 0.99$) was also found in the Site 3 soils, as shown in Figure 5.1. Results from the TCLP showed that sample #4 had Pb concentrations of 21.1 mg L^{-1} and 21.8 mg L^{-1} in the leachate, while sample #7 had 231 mg L^{-1} and 236 mg L^{-1} for duplicate samples. Because these results greatly exceed the regulatory limit of 5.0 mg L^{-1} for Pb, Site 3 may be deemed hazardous.

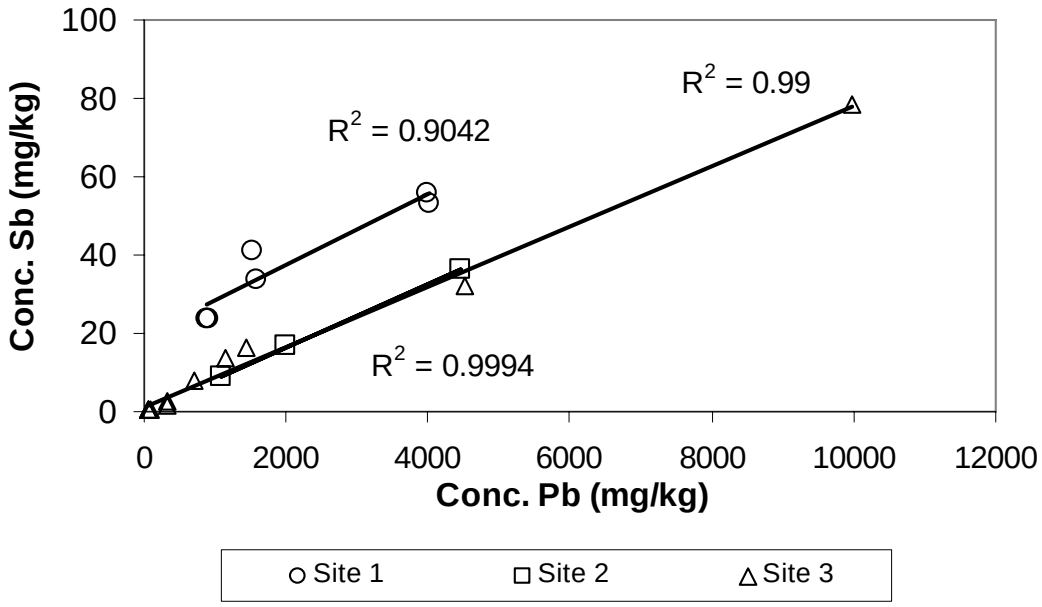

Figure 5.1. Comparison of Sb and Pb in Three Firing Range Soils.

The slope of Site 1 firing range soils increased, indicating a higher Sb content for the same Pb concentration in Site 2 and 3. The results from Figure 5.1 show that the slopes are nearly identical for Site 2 and 3. Since Sb makes up 2-5% of the total bullet weight, Site 1 bullets may have contained more Sb than Site 2 or 3.

5.4 Conclusions

The results from three small-arms firing ranges showed that all firing range soils, when compared both individually and collectively, show strong linear correlations ($R^2 > 0.90$) between Pb and Sb concentrations in the soil. These results were consistent with the general composition of Sb in Pb bullets and the co-mobility of Pb and Sb due to the weathering and corrosion of ammunition. The information found in this study may be useful to future research on Sb mobility and may be important when applying remediation strategies to reduce the bioaccessibility of Pb in soils.

CHAPTER SIX
CONCLUSIONS AND RECOMMENDATIONS FOR FUTURE WORK

In Chapter 3 of this study, the effect of PBET solution pH on % Pb bioaccessibility was compared. At a pH of 1.5, % Pb bioaccessibility results were significantly greater than those at pH of 2.3. At a pH of 2.3, VolCanaPhos was not effective at reducing Pb bioaccessibility at any P dose, whereas Vol. was the most effective amendment at a PBET pH of 1.5. Thus, the effect of PBET pH on bioaccessibility results was important.

The effect of time and P dose was important for both Pb – spiked and Pb – contaminated soils. In Chapter 3, the effect of time after the addition of the P amendments on Pb bioaccessibility was compared. The effect of time proved more important for the non – soluble amendments (Rock Phosphate and VolCanaPhos), which showed significant decreases in % Pb bioaccessibility in the Pb – contaminated soils between 60 and 365 days of aging. Overall, after 365 days of aging, at a PBET solution pH of 2.3, the greatest reduction in Pb bioaccessibility occurred in the following order: Triple Super Phosphate>Rock Phosphate>VolCanaPhos. For all Pb – spiked soils, the average % Pb bioaccessibility decreased with both longer aging time and increasing % P dose.

Scheckel et al. (2005) postulated that Pb bioaccessibility reduction via the formation of chloropyromorphite was occurring in the PBET rather than in situ.

Analysis of phosphate concentrations in PBET supernatants revealed that the PBET samples were well undersaturated (SI<0) with respect to chloropyromorphite. Therefore, chloropyromorphite did not form as an experimental artifact in the PBET.

The weathering and corrosion of Pb ammunition is a significant source of Pb in Pb - contaminated soils. The results from three small-arms firing ranges showed that Pb and Sb concentrations are linearly correlated ($R^2 > 0.90$). The data was consistent with the general composition of Sb in Pb bullets and the co-mobility of Pb and Sb due to the weathering and corrosion of ammunition. Results from the two amendment studies (Chapters 3 and 4) revealed that large amounts (26.2% - 50.5% by weight) of P amendments must be applied *in situ* to achieve significant reductions in Pb bioaccessibility. Environmental implications for adding such large amounts of P to soil, such as increased leaching of oxyanions like Sb and As, should be considered. Further investigation is needed to understand the magnitude of the effect of P on the mobilization of Sb in the environment. Thus, adding P amendments to soils may not be the most practical approach to reduce the bioaccessibility of Pb in Pb – contaminated soils.

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APPENDICES

Appendix A

Example Calculations based on equation 3.1 for the addition of TSP, Vol, and RP amendments in doses of 1% P, 2.5% P, and 5% P by weight.

Example 1
Given: 2.00 g of dry soil, 1% P added from TSP; TSP = 45% P_2O_5 = 19.8% P

From Equation 3.1:

$$\text{Amend. Added (g)} = \frac{(2.00\text{ g}) * 1\%\text{ P}}{19.8\%\text{ P}} = 0.101\text{ g}$$

Example 2
Given: 2.00 g of dry soil, 2.5% P added from Vol; Vol = 32.07% P_2O_5 = 14.11% P

From Equation 3.1:

$$\text{Amend. Added (g)} = \frac{(2.00\text{ g}) * 2.5\%\text{ P}}{14.11\%\text{ P}} = 0.354\text{ g}$$

Example 3
Given: 2.00 g of dry soil, 5% P added from RP; RP = 32% P_2O_5 = 14.08% P

From Equation 3.1:

$$\text{Amend. Added (g)} = \frac{(2.00\text{ g}) * 5\%\text{ P}}{14.08\%\text{ P}} = 0.711\text{ g}$$

Appendix B

Example Calculations based on equation 3.4 for the weight of contaminated soil given the % amendment added by weight (Table 3.3).

Example 1
Given: 0.3 g of dry soil, 1% P added from TSP; TSP = 45% P_2O_5 = 19.8% P
% Amendment Added = 4.81% (Table 3)

From Equation 3.4:

Wt. of contaminated soil only = 0.3 g – (0.3 g * 4.81%) = 0.2856 g

Example 2
Given: 0.3 g of dry soil, 2.5% P added from Vol; Vol = 32.07% P_2O_5 = 14.11% P
% Amendment Added = 15.04% (Table 3)

From Equation 3.4:

Wt. of contaminated soil only = 0.3 g – (0.3 g * 15.04%) = 0.2549 g

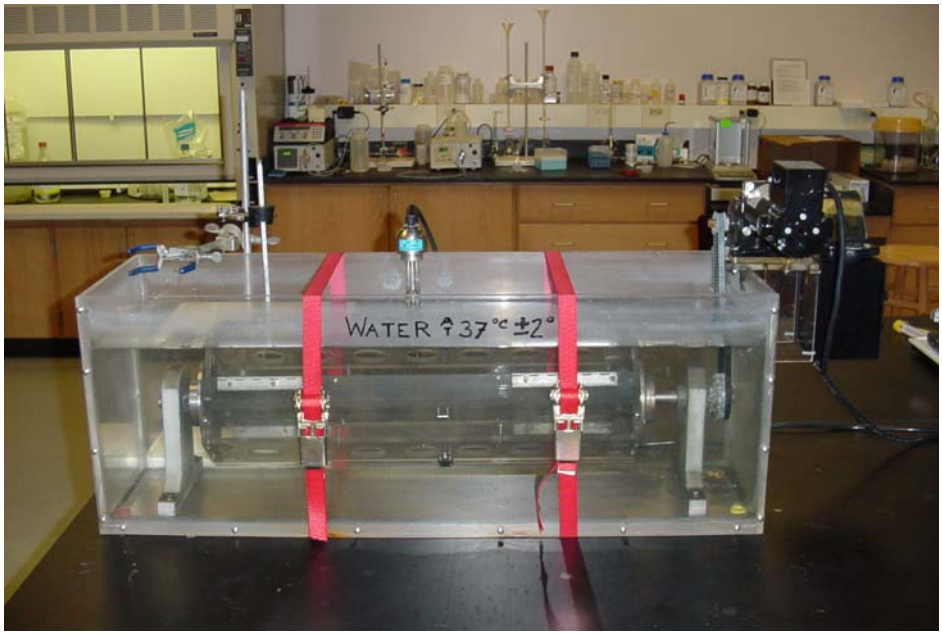
Example 3
Given: 0.3 g of dry soil, 5% P added from RP; RP = 32% P_2O_5 = 14.08% P
% Amendment Added = 26.23% (Table 3)

From Equation 3.4:

Wt. of contaminated soil only = 0.3 g – (0.3 g * 26.23%) = 0.2213 g

Appendix C.1. Aging Apparatus. Aging apparatus received continuous flow of air at 100% relative humidity to reduce evaporation for soil samples while aging.

Appendix C.2. Water Bath for PBET Extraction



Appendix D.1

Example Calculations based on Equation 4.1 for the addition of HumaPhos amendment in doses of 1%P, 2.5%P, and 5%P by weight.

Example 1
Given: 2.00 g of dry soil, 1%P added; HumaPhos = 15% PO_4

From Equation 4.1:

$$\text{Amend. Added (g)} = \frac{(2.00\text{ g}) * 1\%P * (94.97 / 30.97)}{15\%\ PO_4} = 0.409\text{ g}$$

Total Weight of Soil + Amend. Added = 2.409 g

% Amendment Added by weight = (0.409/2.409) *100 = 17.0%

Example 2
Given: 2.00 g of dry soil, 2.5%P added; HumaPhos = 15% PO_4

From Equation 4.1:

$$\text{Amend. Added (g)} = \frac{(2.00\text{ g}) * 2.5\%P * (94.97 / 30.97)}{15\%\ PO_4} = 1.022\text{ g}$$

Total Weight of Soil + Amend. Added = 3.022 g

% Amendment Added by weight = (1.022/3.022) *100 = 33.8%

Example 3
Given: 2.00 g of dry soil, 5%P added; HumaPhos = 15% PO_4

From Equation 4.1:

$$\text{Amend. Added (g)} = \frac{(2.00\text{ g}) * 5\%P * (94.97 / 30.97)}{15\%\ PO_4} = 2.044\text{ g}$$

Total Weight of Soil + Amend. Added = 4.044 g

% Amendment Added by weight = (2.044/4.044) *100 = 50.5%

Appendix D.2

Example calculations for % Pb Bioaccessibility based on Equation 4.3 for soil #6.

Example 1 – 0%P added

Given: Pb in PBET supernatant (mg/L) = 6.14

Vol. of PBET solution (L) = 0.01037

Wt. of dry soil only (kg) = $1.007*10^{-4}$

Total Pb for soil #6 from Method 3050B (mg/kg) = 1000

From Equation 4.3:

$$\% \text{ Pb Bioaccess.} = \frac{(6.14 \text{ mg/L}) * (0.01037 \text{ L})}{(1.007*10^{-4} \text{ kg}) * (1000 \text{ mg/kg})} * 100 = 63.23\%$$

Example 2 – 2.5%P added

Given: Pb in PBET supernatant (mg/L) = 3.50

Vol. of PBET solution (L) = 0.01040

Wt. of dry soil only (kg) = $1.005*10^{-4} – (1.005*10^{-4}*33.82\%) = 6.651*10^{-5}$

Total Pb for soil #6 from Method 3050B (mg/kg) = 1000

From Equation 4.3:

$$\% \text{ Pb Bioaccess.} = \frac{(3.50 \text{ mg/L}) * (0.01040 \text{ L})}{(6.651*10^{-5} \text{ kg}) * (1000 \text{ mg/kg})} * 100 = 54.73\%$$

Example 3 – 5%P added

Given: Pb in PBET supernatant (mg/L) = 2.30

Vol. of PBET solution (L) = 0.01032

Wt. of dry soil only (kg) = $1.001*10^{-4} – (1.001*10^{-4}*50.55\%) = 4.950*10^{-5}$

Total Pb for soil #6 from Method 3050B (mg/kg) = 1000

From Equation 4.3:

$$\% \text{ Pb Bioaccess.} = \frac{(2.30 \text{ mg/L}) * (0.01032 \text{ L})}{(4.950*10^{-5} \text{ kg}) * (1000 \text{ mg/kg})} * 100 = 47.95\%$$

Appendix E. Minteq Speciation Output File for Soil #1 at 120 Days

Mineral	log IAP	Sat. Index	Stoichiometry								
Cotunnite	-8.137	-3.357	1	Pb+2	2	Cl-1					
Hydroxylpyromorphite	-84.803	-22.013	5	Pb+2	3	PO4-3	1	H2O	-1	H+1	
Laurionite	-5.077	-5.7	-1	H+1	1	Pb+2	1	Cl-1	1	H2O	
Litharge	-2.008	-14.698	1	Pb+2	1	H2O	-2	H+1			
Massicot	-2.008	-14.898	1	Pb+2	1	H2O	-2	H+1			
Pb(OH)2	-2.018	-10.168	-2	H+1	1	Pb+2	2	H2O			
Pb2(OH)3Cl	-7.095	-15.888	-3	H+1	2	Pb+2	3	H2O	1	Cl-1	
Pb2O(OH)2	-4.026	-30.216	2	Pb+2	3	H2O	-4	H+1			
Pb3(PO4)2	-55.863	-12.333	3	Pb+2	2	PO4-3					
PbHPO4	-26.932	-3.127	1	Pb+2	1	H+1	1	PO4-3			
PbO:0.3H2O	-2.011	-14.991	-2	H+1	1	Pb+2	1.33	H2O			
Pyromorphite	-87.863	-3.433	5	Pb+2	3	PO4-3	1	Cl-1			

	Concentration	Activity	Log activity
Cl-1	0.242	0.18236	-0.739
Glycine-1	8.1728E-09	6.034E-09	-8.219
H+1	0.0063353	0.0046774	-2.33
H2-Glycine+	0.24009	0.17726	-0.751
H2PO4-	0.0012614	0.00093128	-3.031
H3PO4	0.00057856	0.00061246	-3.213
H-Glycine (aq)	0.15991	0.16928	-0.771
HPO4-2	4.2477E-08	1.2621E-08	-7.899
OH-	2.8514E-12	2.1052E-12	-11.677
Pb-(Glycine)2 (aq)	1.7302E-15	1.8316E-15	-14.737
Pb(OH)2 (aq)	7.3024E-20	7.7304E-20	-19.112
Pb(OH)3-	2.2043E-28	1.6274E-28	-27.789
Pb+2	7.3909E-07	2.1959E-07	-6.658
Pb2OH+3	6.201E-17	4.0414E-18	-17.393
Pb3(OH)4+2	8.8126E-35	2.6184E-35	-34.582
Pb4(OH)4+4	7.3784E-37	5.7498E-39	-38.24
PbCl+	1.9693E-06	1.4539E-06	-5.837
PbCl2 (aq)	5.4793E-07	5.8004E-07	-6.237
PbCl3-	1.138E-07	8.4019E-08	-7.076
PbCl4-2	1.9605E-08	5.825E-09	-8.235
Pb-Glycine+	2.5351E-10	1.8716E-10	-9.728
PbH-(Glycine)2+	9.2171E-11	6.805E-11	-10.167
PbH2-(Glycine)2+2	4.3642E-07	1.2967E-07	-6.887
PbH2PO4+	8.7593E-09	6.467E-09	-8.189
PbH-Glycine+2	3.8842E-06	0.000001154	-5.938
PbHPO4 (aq)	3.2958E-12	3.489E-12	-11.457
PbOH+	1.5728E-12	1.1612E-12	-11.935
PO4-3	1.7458E-17	1.1378E-18	-17.944