POTENTIAL NEGATIVE EFFECTS OF ADDING PHOSPHATE-BASED FERTILIZERS TO LEAD IN METAL-CONTAMINATED SOILS

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THESIS ABSTRACT

POTENTIAL NEGATIVE EFFECTS OF ADDING PHOSPHATE-BASED FERTILIZERS TO LEAD IN METAL-CONTAMINATED SOILS

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The potential negative effects of adding phosphate amendments for lead (Pb) remediation in Pb-contaminated soils were studied using column and batch experiments. Soils contaminated with high levels of lead as well as moderate levels of arsenic (As) and antimony (Sb) were amended with triple superphosphate (TSP) and tested to determine the effects of P on Sb and As. It is generally known that P amendments can increase As mobility availability, and that As and Sb tend to behave similarly, chemically. In addition, tests were employed to determine if a correlation between Sb and Pb existed at small-arms firing range sites due to the corrosion of Sb-Pb ammunition.

Multiple column studies were performed to assess mobility changes in soil bound Sb and As, as well as Pb, with the addition of TSP. These tests showed elevated concentrations of Sb and As in column effluents for the P-amended contaminated soil, indicating an increase in Sb and As mobility as a result of the TSP addition. Minimal As and Sb leaching was observed during column tests performed on non-amended soil samples. Pb leaching was minimal in TSP amended and non-amended column tests, indicating no significant difference in soil-Pb mobility with and without the presence of TSP.

Batch experiments were performed to assess the changes in bioaccessibility for Pb, Sb and As with varying amounts of TSP addition, by using a streamlined version of the physiologically based extraction test (PBET). Minimal changes in both As and Sb bioaccessibility were observed with TSP additions. As was expected, Pb bioaccessibility was lowered with increasing amounts of TSP addition.

Strong correlations between Sb and Pb were detected for multiple soil samples collected from three small-arms firing ranges ($R^2 > 0.90$; p-value < 0.05 for all three tested sites). Laser ablation was also performed on several bullets collected from one of the sites in question, detecting a higher concentration of Sb in the bullet core compared to all other elements, excluding lead. Arsenic was also measured in one of the sites in question; however, no correlation between As and Pb was detected suggesting the presence of As to be naturally occurring or background As.

These experiments concluded that while phosphate amendments decrease bioavailability of Pb and slightly decrease the mobility of Pb, competition between P, As and Sb drives the release of Sb and As from soils, increasing their mobility and potentially their bioavailability as well.

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CHAPTER ONE

INTRODUCTION

1.1 Problem Statement

The U.S. Department of Defense (DoD) is currently responsible for thousands of contaminated sites, and a majority of these sites are contaminated with various toxic metals. Determining which of these sites require more immediate attention is based on the soil-metal concentrations present at these sites as well as other parameters, such as the type of metal present and the amount of metal in the soil that could potentially be absorbed into the human bloodstream (Salatas, Lowney et al. 2004). In a recent study, three of the top five metals most frequently exceeding human health criteria included lead (Pb), arsenic (As) and antimony (Sb), while Pb and As also were in the top five list for metals exceeding ecological criteria. Pb was the number one metal exceeding human and ecological criteria (Salatas, Lowney et al. 2004).

While Pb contamination has been linked to multiple sources, a significant source of highly concentrated lead in certain surface soils is due to the corrosion of Pb bullets at small arms shooting ranges, where Pb concentrations in the topsoil around butt stops can reach as high as 50,000 $mg.kg^{-1}$ (Rooney, McLaren et al. 1999). Pb mobilization in these firing range surface soils has also led to elevated concentrations in subsurface soils as well, further complicating the contaminant issue (Murray, Bazzi et al. 1997). At Pb-contaminated firing range sites where future commercial or residential growth may occur, ingestion of contaminated soil by children is typically the driving factor for site remediation, due to the fact that high Pb-blood levels in children have been linked to cognitive development problems (Ryan, Scheckel et al. 2004). Nonetheless, Pb remains the primary choice of ammunition in small-arms weapons, creating a growing need to expand our knowledge of Pb contamination and remediation to minimize the adverse impacts of Pb at shooting ranges as well as other sites (Cao, Ma et al. 2003).

Due to the high costs and other problems with current remediation techniques at metal contaminated sites, *in situ* remediation practices have been widely studied to provide more efficient means of site remediation (Hettiarachchi and Pierzynski 2004; Tang, Zhu et al. 2004; Lin, Lian et al. 2005; Chen, Zhu et al. 2006). These *in situ* techniques are not only predicted to cost less than one-tenth of off-site treatment techniques, but also provide a much easier remediation approach (Cunningham 2000). One method of *in situ* remediation in Pb-contaminated soils receiving recent attention is chemical stabilization with phosphorous (P) amendments. This method can lower both the mobility and toxicity of Pb, which would be preferred at larger sites where metal stabilization is needed, such as shooting ranges (Wilson, Brigmon et al. 2006). Highly soluble phosphate fertilizers, such as triple superphosphate [TSP; $Ca(H_2PO_4)_2$], have been shown to be effective in Pb remediation where immediate site remediation is needed (Stanforth and Qiu 2001). By applying phosphate amendments as a means of *in situ* remediation, Pb is immobilized through the formation of insoluble Pb-phosphate complexes, namely pyromorphites [$Pb_5(PO_4)_3X$, X=OH^-, Cl^-, F^-, etc.], which provide a highly insoluble species of Pb over a wide range of environmental scenarios (Ma, Traina et al. 1993; CotterHowells and Caporn 1996; Hettiarachchi, Pierzynski et al. 2000; Cao, Ma et al. 2003; Lin, Lian et al. 2005). Not only are pyromorphite solids less mobile forms of Pb, other recent research has shown that pyromorphites may also be less bioavailable as well, which has become more of a driving factor in determining the degree of importance in site remediation (Salatas, Lowney et al. 2004; Tang, Zhu et al. 2004).

Phosphorous amendments may be useful for quick and effective immobilization and bioavailability reduction of Pb in contaminated soils; however, there are several potential drawbacks. Relatively high P:Pb molar ratios have repeatedly been suggested when applying phosphate amendments to soils in order to significantly immobilize Pb, and using high molar ratios can leave an excess of soluble P (Stanforth and Qiu 2001; Tang, Zhu et al. 2004; Chen, Zhu et al. 2006). In addition, many DoD contaminated soils where P amendments could be applied contain not only Pb, but multiple metal contaminants. Arsenic and antimony, respectively, are the second and fifth most frequently occurring metals that exceed human health criteria at DoD sites (Davis, Sherwin et al. 2001; Salatas, Lowney et al. 2004). Antimony is also a common alloy in Pb ammunition, potentially creating higher concentrations of Sb at firing ranges. Competitive reactions between P and other contaminants such as Sb and As could potentially release these contaminants and increase their availability.

Phosphorous, arsenic, and antimony fall in the same group of elements, and both Sb and As tend to display similar chemical and toxic behavior (Wilson, Craw et al. 2004; Gal 2006). When present together, these elements compete for reaction sites. In oxic soil conditions such as metal contaminated sites, Sb and As are commonly present in the inorganic pentavalent (+V) oxyanions, arsenate (AsO_4^{3-}) and antimonate (SbO_4^{3-}) (Smedley and Kinniburgh 2002; Yang, Barnett et al. 2002; Mitsunobu, Harada et al. 2005; Radu, Subacz et al. 2005; Zhang and Selim 2005). Multiple studies have shown strong reaction site competition between As and P, where P has been shown to increase the mobility as well as availability of As (Hongshao and Stanforth 2001; Cao, Ma et al. 2003; Fayiga and Ma 2006; Tao, Zhang et al. 2006).

1.2 Hypotheses and Objectives

The hypothesis of this study is that phosphate use immobilize Pb in contaminated soils will increase the mobility and bioaccessibility of Sb and As.

The objectives of this study were to observe and quantify a potential increase in Sb and As mobility upon addition of a phosphate amendment to a Pb-contaminated soil through the use of column tests. Batch experiments were also conducted to assess bioavailability changes in soil As and Sb with various phosphate additions. Furthermore, studies were conducted on a small-arm firing range soil to determine if any correlations existed between Sb and Pb.

1.4 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 column and batch studies are shown in Chapter 3. Chapter 3 is a draft manuscript, which will later be submitted for publication in a peer-reviewed scientific journal.

CHAPTER TWO

LITERATURE REVIEW

2.1 Heavy Metal Soil Contamination

Heavy metal soil contamination is a growing environmental concern because of the adverse health and ecological effects that are associated with metal poisoning. The U.S. Department of Defense (DoD) is currently responsible for thousands of contaminated sites, where a majority of these sites are contaminated with various toxic heavy metals (Salatas, Lowney et al. 2004). Determining which of these sites require more immediate attention is based on the metal-soil concentrations present at these sites as well as other parameters, such as the amount of metal in the soil that could potentially be absorbed into the human bloodstream if ingested (Salatas, Lowney et al. 2004). Both human health criteria and ecological health criteria dealing with metal absorption were recently studied to conclude which metals actually exceed these criteria most frequently at random DoD sites (Salatas, Lowney et al. 2004). The top five metals most frequently exceeding human health criteria included lead (Pb), arsenic (As) and antimony (Sb), while Pb and As also were in the top five list for metals exceeding ecological.

2.2 General Lead Chemistry and Mineralogy

Lead (Pb) in its metallic state (Pb^0) is dense, malleable, blue to blue-grey in color, and is known to be a potent neurotoxin. In most compounds, Pb is present in either its +II or +IV oxidation state. Pb in the environment can be found in ores such as galena (PbS), cerussite ($PbCO_3$), anglesite ($PbSO_4$), minim (Pb_3O_4) as well as other minerals (Winter 2007). Lead mobility in surface and subsurface soils is strongly dependent on its chemical state as well as the solubility of the particular Pb-bearing mineral (Hettiarachchi and Pierzynski 2004):

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

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

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

Galena, the most common Pb ore mineral (87% Pb by weight), is found mainly in reduced systems where reduced sulfur is present. In oxidizing environments, however, galena can transform into other common forms of Pb, such as cerussite and anglesite (Hettiarachchi and Pierzynski 2004). Of the Pb minerals, galena is the most commonly used ore for Pb use. Lead oxides such as litharge and minim are commonly found on the surface of metallic Pb upon exposure to atmospheric conditions (Winter 2007).

2.3 Lead Contamination

Lead contamination sources have been widely documented, which include but are not limited to: mining and smelting of ores, recycling and corrosion of Pb batteries, and previous use of leaded gasoline. Another significant source of highly concentrated lead in surface soils is due to the corrosion of Pb bullets at shooting ranges, where soil Pb concentrations can reach as high as 50,000 mg.kg^{-1} (Rooney, McLaren et al. 1999). The weathering of Pb bullets generally occurs when bullets are exposed to water and oxidizing conditions in surface soils. The weathering rate of metallic Pb bullets depends on a variety of factors, both physical and chemical (Cao, Ma et al. 2003). Pb mobilization in firing range surface soils have also led to elevated concentrations in subsurface soils as well, further complicating the Pb contamination issue (Murray, Bazzi et al. 1997).

At Pb-contaminated sites in the United States where future commercial or residential growth may occur, child ingestion of contaminated soil is typically the driving factor for the degree of site remediation. This is due to the fact that high Pb-blood levels in children have been linked to cognitive development problems (Ryan, Scheckel et al. 2004). In the past decade, reductions of Pb in paint, drinking water, and especially gasoline have helped in lowering blood-Pb levels in children (Ryan, Scheckel et al. 2004). Lead, however, remains the metal of choice for ammunition because of its density, malleability, cost and ready availability (Hurley 2004). In the US, three million metric tons of Pb has been used as munitions for recreational activities such as hunting in the past century alone (Craig, Rimstidt et al. 1999). This figure does not include government expenditures of lead for weapons training and other firing range exercises. Industrial activities also continue to increase concentrations of Pb into the environment. The continued release of Pb into the environment due to industrial and military activities, along with the numerous sites that are currently Pb-contaminated, has furthermore created a need to expand our knowledge of Pb contamination and remediation to minimize the adverse impacts of Pb at shooting ranges as well as other sites (Cao, Ma et al. 2003; Wilson, Brigmon et al. 2006).

2.4 Treatment of Lead-Contaminated Soils

Current remediation techniques at metal contaminated sites include soil excavation and off-site soil contaminant removal. However, these methods of soil remediation may not completely remove all contaminants from contaminated soil and can be ineffective in restoring the soil to its original productive state (Hodson, Valsami-Jones et al. 2000). In addition to its inefficiencies, off-site remediation can be dangerous and is very costly. As a result of the disruptive nature as well as high costs of soil excavation as a means of site remediation, *in situ* remediation practices have widely been studied to provide more efficient means of site remediation (Hettiarachchi and Pierzynski 2004; Tang, Zhu et al. 2004; Lin, Lian et al. 2005; Chen, Zhu et al. 2006). *In situ* techniques used to treat metal-contaminated sites involve changing the chemical state of the target metal in the soil itself, rather than removing the metal from the contaminated soil. These *in situ* techniques, are not only projected to cost less than one-tenth of what off-site treatment techniques cost, but also provide a much easier remediation approach

(Cunningham 2000). By altering the species of Pb in the soil through chemical immobilization, reductions in Pb mobility and availability is achieved; as a result its toxicity and hazardous nature may be lessened (Ma, Traina et al. 1993). This method of species adjustment that decreases toxicity would be especially preferred at larger sites where metal stabilization is needed, such as shooting ranges (Wilson, Brigmon et al. 2006).

2.5 Lead Bioavailability

Soil contaminant bioavailability, that is the availability of a contaminant to a biological organism, is an important aspect of site remediation risk assessment that has received growing attention due to expensive costs and the need to determine an efficient method of remediation at metal contaminated sites. Previous standard procedures that were recommended by the U.S. Environmental Protection Agency (EPA) for evaluating risk assessments assumed “set” bioavailability values of metals in soil, that were highly inaccurate (Ruby, Davis et al. 1996). Recent research has led to a better understanding of varying bioavailability values for various metals existing in different environments such as soil types (ie. clay, silt, sand). Furthermore, the chemical state or mineral form that a particular metal exists in also affects how bioavailable a heavy metal may be. The concept behind reducing soil metal bioavailability as a means of site remediation is to alter the metal’s chemical form in order to reduce its availability to plants, animals, and most importantly, humans. *In situ* remediation techniques are ideal for reducing bioavailability.

Oral bioavailability, is referred to as the portion of an ingested contaminant that is absorbed into the bloodstream from the gastrointestinal tract (Ruby, Schoof et al. 1999; Hettiarachchi and Pierzynski 2004). While the human stomach dissolves a percentage of ingested minerals into soluble species, the fraction of these soluble species that enters the bloodstream via absorption through epithelial cells is the bioavailable portion. *In vivo* (animal) tests have previously been used as a means of modeling human bioavailability by equating bioavailability values found in animals such as swine and rats to bioavailability values expected to be found in humans (Graziano, Blum et al. 1996; Ellickson, Gallo et al. 1999). *In vivo* tests provide the capability to measure absolute bioavailability and specific toxicity (Furman, Strawn et al. 2006); however, the difficulty and expensive costs associated with *in vivo* models have led to the extensive development of *in vitro* models.

Bioavailability values from *in vitro* (e.g. laboratory extraction tests) models are referred to as bioaccessibility. Bioaccessibility is the soluble portion of a substance that is available for absorption into the bloodstream (Ruby, Schoof et al. 1999). Therefore, ideally the bioaccessible fraction of a contaminant will be slightly larger than the bioavailable fraction of a contaminant due to incomplete absorption with *in vitro* studies (Ruby, Davis et al. 1996). *In vitro* methods were originally used to determine the bioavailability of iron (Fe) in food for nutritional studies (Miller and Schricker 1981). More recently, however, *in vitro* studies are becoming more popular as extraction tests for contaminated media because of their cost-advantages as compared to *in vivo* tests.

One of the more widely used *in vitro* extraction models, the physiologically based extraction test (PBET), was designed to mimic the GI tract of a 2-3 year old, fasting child (Ruby, Davis et al. 1996). The factors controlled during the original PBET extraction included pH, temperature, soil-to-solution ratio, as well stomach mixing. Parameters for children were chosen based on the assumption that children are at a higher risk for ingesting contaminated soil, which is a more conservative approach (Ruby, Davis et al. 1996). Furthermore, a fasting stomach would result in higher absorption, which is also conservative. While the original PBET model involved several stages of the gastric pathway, including the addition of several organic chemicals and acids as well as pH changes, (Ruby, Davis et al. 1996) more current models provide a simpler strategy for measuring bioaccessibility. Equally important is that these easier methods allow for more studies to be conducted, helping to determine which amendments may be more effective for metal immobilization and bioavailability reduction.

2.6 Lead Amendments

Phosphorous amendments applied to Pb-contaminated soils have been widely studied as a possible means of *in situ* remediation, by immobilizing Pb through the formation of solid Pb-phosphate complexes (Ma, Traina et al. 1993; CotterHowells and Caporn 1996; Hettiarachchi, Pierzynski et al. 2000; Cao, Ma et al. 2003; Lin, Lian et al. 2005). These Pb-phosphate complexes have the potential to provide a less soluble, less bioavailable species of Pb as compared to naturally-occurring Pb species over a wide range of environmental scenarios (Cao, Ma et al. 2003). Of the Pb-phosphate complexes, possibly the most studied over the past decade in regards to Pb remediation is pyromorphite ($Pb_5(PO_4)_3X$, $X=OH^-$, Cl^-, F^-, etc.), which has been deemed as being much more insoluble than most other Pb minerals in oxidizing conditions, potentially reducing Pb mobility and toxicity. Of the pyromorphite minerals, chloropyromorphite (CPM) is the least soluble:

$$Pb_5(PO_4)_3Cl\,(s) + 6H^+ \leftrightarrow 5Pb^{2+} + 3H_2PO_4^- + Cl^- \qquad K_{sp} = 10^{-84.4} \qquad (2.4)$$

A comparison in solubility between pyromorphite and naturally occurring Pb species including litharge (PbO), cerussite ($PbCO_3$), and anglesite ($PbSO_4$) was performed with a geochemical computer model (Ruby, Davis et al. 1994). The study suggested that at pH conditions representing the human stomach, pyromorphite was the least soluble of the species considered (Tang, Zhu et al. 2004). Tang's study indicates that pyromorphite complexes may not only be less soluble, but less bioavailable as well, due to the fact that the tested parameters involved conditions representing the human gastric system. The reduced bioaccessibility in pyromorphite minerals could potentially become very important, since bioavailability has become more of a driving factor in determining the degree of importance in site remediation, rather than soil Pb concentrations alone (Ruby, Davis et al. 1996; Salatas, Lowney et al. 2004).

While P amendments in general have been accepted as an effective means of reducing Pb bioavailability and mobility in contaminated soils, determining which P amendments result in the most effective remediation (and in essence maximum pyromorphite formation) has been an ongoing challenge. Phosphate rocks (Frost and Kloprogge), hydroxyapatite [$Ca_5(PO_4)_3OH(s)$; HA], phosphoric acid (H_3PO_4), phosphate-containing fish bone, and water-soluble phosphate fertilizers have all been studied for their respective effects on Pb immobilization (Arnich, Lanhers et al. 2003; Melamed, Cao et al. 2003; Cao, Ma et al. 2004; Lin, Lian et al. 2005; Chen, Zhu et al. 2006; Wilson, Brigmon et al. 2006). Multiple studies involving various P amendments have shown that the nature of these amendments can greatly vary; some amendments have been more effective in Pb immobilization and bioavailability reduction than others. Phosphorous content, solubility, and pH effect on soils are all different. For example, HA and PR provide little change in soil pH and release soluble phosphate at a slower rate than water-soluble P amendments. The addition of phosphoric acid to Pb contaminated soils, on the other hand, provides a soluble source of phosphate as well as the ability to lower soil pH. By lowering soil pH, naturally occurring Pb complexes at Pb contaminated sites can potentially dissolve and release soluble Pb. This dissolution process may be beneficial for overall Pb immobilization by promoting the kinetics of pyromorphite formation (Zhang and Ryan 1999). At neutral soil pH conditions the solubility of Pb complexes is minimal, inhibiting the formation of pyromorphite. A previous study has shown that between pH values 5-8, the dissolution of the initial Pb mineral is the rate-limiting factor in the formation of hydroxypyromorphite [$Pb_5(PO_4)_3OH(s)$]. Furthermore, pH values closer to 5 resulted in faster hydroxypyromorphite formation (Laperche, Traina et al. 1996), which indicates that P amendments providing both soluble phosphate and the ability to slightly lower natural soil pH levels may be more effective in the remediation of Pb contaminated sites.

Triple superphosphate (TSP) is a common agricultural fertilizer containing calcium dihydrogen phosphate [$Ca(H_2PO_4)_2$], made by adding orthophosphoric acid to PR (Hettiarachchi, Pierzynski et al. 2001). TSP provides a source of soluble phosphate and the ability to slightly lower soil pH, potentially dissolving the natural Pb complex. TSP and other "water soluble" forms of phosphate are generally used as treatment techniques at hazardous waste sites to quickly achieve Pb immobilization in order for the sites to be considered non-hazardous (Stanforth and Qiu 2001). As compared to TSP, amendments such as HA and PR dissolve slower and as a result Pb uptake and immobilization can occur at a much slower rate. Previous research within our research group has shown TSP to be more effective in the reduction of Pb bioaccessibility than other rock phosphates in both contaminated soils as well as Pb-spiked soils.

2.7 Concerns with Phosphate Amendments

While highly soluble forms of phosphate amendments (i.e. phosphate fertilizers) may be useful in quick and effective immobilization of Pb in contaminated soils, several drawbacks may apply. Relatively high P:Pb molar ratios have repeatedly been suggested when applying phosphate amendments to soils in order to significantly immobilize Pb, leaving an excess of soluble phosphate (Stanforth and Qiu 2001; Tang, Zhu et al. 2004; Chen, Zhu et al. 2006). However, many DoD contaminated soils contain multiple toxic metals. The behavior between phosphate and toxic metals (other than Pb) should be analyzed prior to P additions because of potential negative effects.

As stated earlier, Pb is the metal that most frequently exceeds risk-based screening criteria for human health concerns at DoD sites, while arsenic and antimony, respectively, are the second and fifth most frequently occurring metals that exceed human health criteria at DoD sites (Davis, Sherwin et al. 2001; Salatas, Lowney et al. 2004). According to Salatas' (2004) study, arsenic exceeded human health criteria at about 20% of DoD sites containing some type of metal contamination, while antimony exceeded human health criteria at almost 10% of metal contaminated sites. Both of these metals commonly exist at sites where Pb contamination occurs too. Phosphate interaction between antimony and arsenic could potentially create problems. Phosphate strongly competes with As for adsorption sites, increasing its mobility as well as its bioavailability. Therefore, adding phosphate to Pb contaminated soil could increase the bioavailability of As. Furthermore, because Sb tends to display similar chemical behavior as As, phosphate could increase the bioavailability and toxicity of Sb as well.

2.8 Arsenic and Antimony Contamination

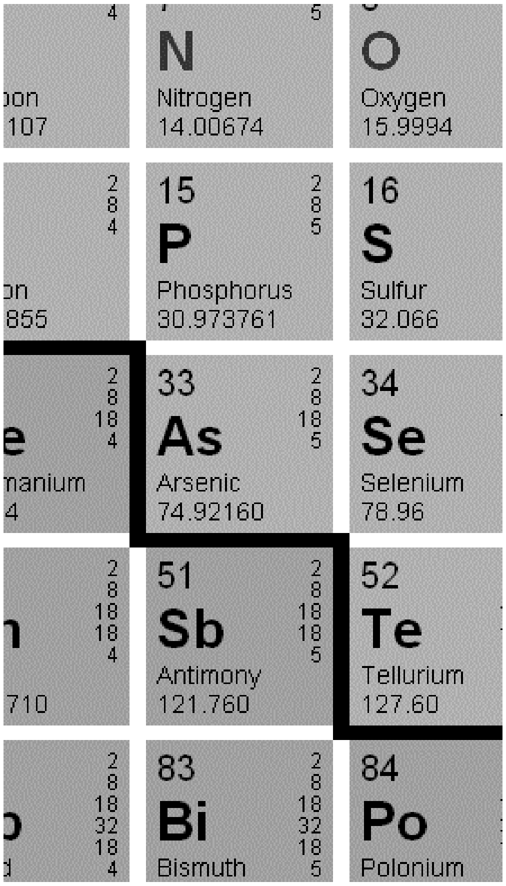
Arsenic is a widely-occurring contaminant due to previous uses of pesticides and wood treatment processes (Carbonell, Aarabi et al. 1998; Hingston, Collins et al. 2001), as well as current uses in other anthropogenic processes (Smith, Naidu et al. 1998). Naturally-occurring As in the United States has also sparked interest due to soil As concentrations reaching almost 1.25 $mmol.kg^{-1}$ in some areas (Beak, Basta et al. 2006).

As contamination in drinking water has become a concern in many aquifers systems around the world as well as US potable waters. In Bangladesh, many shallow tube wells exceed the country's maximum allowed concentration (5 $\mu g.L^{-1}$). In US potable water supply systems, the maximum contaminant level for As has been lowered from 50 $\mu g.L^{-1}$ to 10 $\mu g.L^{-1}$ (Parks 2003). Arsenic is a carcinogen and has been linked to health problems including cardiovascular disease and skin cancer (EPA 2007).

The primary industrial use of antimony (Sb) has been for flame retardants (Carlin 2005); however, Sb is also a common alloy in Pb batteries and bullets, providing increased concentrations of Sb at many DoD sites as well as small arms firing ranges. Natural soil concentrations of Sb are relatively low (<1.0 $mg.kg^{-1}$) but elevated concentrations of Sb have been observed in both soil and water due to human industrial activities. Elevated Sb concentrations at small arms firing ranges have been linked to increased corrosion rates associated with Pb-Sb bullets, releasing high Sb quantities into the surface soils of firing ranges (Hurley 2004). Studies within our research group have also shown strong correlations between Pb and Sb concentrations at several small arms firing range sites (Mosely 2006), further indicating an evenly proportioned release of both Pb and Sb due to bullet corrosion. Like As, Sb is carcinogenic and human health issues associated with these elements remains a concern (Gebel 1997; Mitsunobu, Harada et al. 2006).

2.9 Arsenic and Antimony Chemical Behavior

Arsenic and antimony (Kabata-Pendias) fall in the same group of elements, referred to as pnictogens, and both elements tend to display similar chemical and toxic behavior (Wilson, Craw et al. 2004; Gal 2006):



While both As and Sb can exist in four oxidations states (-III, 0, III, and V), the two most common oxidation states are +III and +V. Under aerobic conditions As(V) and Sb(V) are nominally present and in anaerobic conditions As(III) and Sb(III) commonly exist (Mitsunobu, Harada et al. 2006). Sb(III) and As(III) are considered to be more mobile and more toxic that the +V species. In oxic soil conditions, Sb and As are commonly present in the inorganic pentavalent versions, arsenate (AsO_4^{3-}) and antimonate (SbO_4^{3-})

(Smedley and Kinniburgh 2002; Yang, Barnett et al. 2002; Mitsunobu, Harada et al. 2005; Radu, Subacz et al. 2005; Zhang and Selim 2005). Arsenic is a triprotic acid (pK_a 2.20, 6.97, 11.5), commonly occurring as an oxyanion in normal soil pH conditions as either $H_2AsO_4^-$ (pH < 6.97) or $HAsO_4^{2-}$ (pH > 6.97) (Williams, Barnett et al. 2003). Little is known about the mobility of Sb in the environment (Wilson, Craw et al. 2004).

While oxic soils are normally the favored environment for Sb(V) and As(V), the slow redox reactions between the two can result in the +III or +V forms in soils (Zhang and Selim 2005). On the other hand, Sb(V) and As(V) can be found in reduced environments. One study observing Sb speciation in soils suggested that under reduced soil conditions Sb(V) was still the dominant species, despite the fact that Sb(III) is the nominally prevalent species in reduced conditions (Mitsunobu, Harada et al. 2005). Of the two elements, As has a greater potential to be reduced from As(V) to As(III) when exposed to reduced conditions. A recent study by Mitsunobu et al. (Mitsunobu, Harada et al. 2006) exposed As and Sb to reduced and oxic environments to observe the redox behavior between the two. Their findings suggested that Sb(V) remained very stable even in reduced conditions while As(V) was less stable, becoming reduced at a much more positive E_H than Sb. Due to the fact that the +III oxidation states of the two elements are both more toxic and more mobile, reduced environments could potentially cause problems with As and Sb leaching into groundwaters. Understanding the behavior between As and Sb and factors controlling their mobility and speciation is vital when dealing with both contaminants at a single site.

Multiple studies have been conducted on As mobility, solubility and bioavailability in both solutions and soils, but these types of studies on Sb are fewer. Furthermore, there have been more studies involving As uptake in solutions than As remediation experiments in soils, which has ultimately led to contradictory information involving As sorption in soils (Zhang and Selim 2005). Iron and aluminum content, pH, and microbial presence all been shown to have an effect on As speciation and mobility reduction (Yang, Barnett et al. 2002; Zhang and Selim 2005; Gal 2006; Shaw 2006). Phosphorous, on the other hand, resides in the same chemical group as As and Sb, and can compete directly for sorption sites on adsorbents such as soil particle surfaces, potentially increasing mobility through anion exchange. The effect of various chemical and physical parameters on As and Sb reactions in soils as compared to solutions, however, can vary greatly.

2.12 Arsenic Remediation Techniques

Iron (Fe) oxides and hydroxides have been shown to have a high affinity toward As. Soils containing higher amounts of Fe oxides generally have greater As uptake via adsorption (Yang, Barnett et al. 2002). Fe oxides such as goethite and ferrihydrite have been added to solutions in numerous studies to assess their As uptake abilities. As(V) and As(III) adsorption characteristics onto Fe oxides has been widely studied via extended X-ray absorption fine structure spectroscopy (EXAFS), showing that inner-sphere surface complexes are formed (Waychunas, Rea et al. 1993; Sun and Doner 1996; Fendorf, Eick et al. 1997; Ladeira, Ciminelli et al. 2001; Sherman and Randall 2003).

Furthermore these surface complexes may either be monodentate or bidentate configurations, with bidentate configurations generally being considered the dominant of the two configurations. Surface complexation, however, may not been the only method of removal by Fe hydroxides. Ferrihydrite ($Fe_5O_3(OH)_9$), an iron oxy-hydroxide, has been shown to remove As more effectively by coprecipitation than by surface complexation when high concentrations of Fe(III) and As(V) are present at low pH values (Richmond, Loan et al. 2004). On the other hand, Fuller et al. performed a study involving the adsorption of As(V) onto synthesized ferrihydrite, where spectroscopic investigations revealed no surface precipitate formation (Fuller, Davis et al. 1993). Arsenic adsorption-desorption, rather than precipitation, however, has been deemed the primary factor that impacts As uptake in soils (Zhang and Selim 2005).

Arsenic uptake by aluminum (Al) oxides and hydroxides has been found to be similar to Fe (hydr)oxides, but these studies are slightly fewer (Hering and Dixit 2005). One study involving a simulated gastrointestinal extraction test revealed that the bioaccessibility of As was rather minimal (0 to 16%) following As adsorption onto corundum (α-Al_2O_3), an aluminum oxide (Beak, Basta et al. 2006). Beak et al. (Beak, Basta et al. 2006) further suggested that corundum could effectively reduce As(V) bioaccessibility and risk in contaminated soils and also treat As(V) contaminated water.

Adsorption of As on either metal (hydr)oxides or geomedia at varying pH values has been extensively studied. Multiple studies have revealed that lower pH values promote a higher As uptake rate, where this rate slows significantly at near-neutral and higher pH values. One particular study found at a pH of 4.5, As(V) adsorption on Al oxide took about 3 days to complete, while at a pH of 7.8, complete adsorption took over a year (Arai and Sparks 2002). In As contaminated soils, increasing soil pH has resulted in the desorption of As into the soil solution (Gal 2006).

In regards to As bioavailability, it is often estimated that As present in soils is 100% bioavailable, which may be accurate for soluble As in solution, but not for soils. Soils have the potential to strongly sequester many metals, such as As, which can significantly reduce bioavailability (Yang, Barnett et al. 2002). Yang et al. (Yang, Barnett et al. 2002) suggested that during a six month aging process, the Fe oxide content in soils plays the greatest role in As adsorption, while pH was the most important, "and only statistically significant" soil property in reducing As bioaccessibility for their particular study. The aging time for As-spiked soils also showed the potential to reduce bioavailability, where half of the tested soils exhibited a significant reduction in bioaccessibility over the course of 6 months (Yang, Barnett et al. 2002). A study involving As(V) adsorption to ferrihydrite determined that As bioaccessibility is a function of both As(V) concentration and As adsorption maxima (Beak, Basta et al. 2006). Another study by Beak et al. showed only 0-16 % of As sorbed to corundum became bioaccessible in a simulated gastrointestinal tract indicating the presence of Al oxides to be important in As bioavailability reductions (Beak, Basta et al. 2006).

Although phosphates can increase the mobility and availability of As in contaminated soils, several studies have shown that this may actually be beneficial in the overall remediation of As. Phytoavailability studies have shown great potential as a means of As remediation. In one particular phytoavailability experiment, higher amounts of phosphate mobilized As(V) as well as As(III) in soils. This increase in As mobility resulted in a much higher As uptake by wheat plants. Phosphate additions ultimately increased As uptake by the plants as much as 4.2 times more than non-amended samples (Tao, Zhang et al. 2006). Similar results in As uptake by plants in conjunction with phosphate additions were observed with the Chinese brake fern (Pteris vittata L.), an As accumulator (Cao, Ma et al. 2003).

The additions of phosphate to contaminated soils containing both As and other heavy metals, in addition to using As hyperaccumulators, could result in simultaneous metal remediation. Greenhouse experiments showed a decrease in Pb, Zn, and Cd uptake by Chinese brake fern as well as an increase in As uptake upon phosphate rock additions (Fayiga and Ma 2006). Although phytoextraction studies involving As hyperaccumulators can take several months to complete, this method of heavy metal remediation may prove to be an effective strategy upon additional studies. For immediate remediation, however, other remediation methods need to be used.

CHAPTER THREE

POTENTIAL EFFECTS OF ADDING PHOSPHATE AMENDMENTS TO LEAD CONTAMINATED SOILS

(MANUSCRIPT)

ABSTRACT. An observational study of the potential negative effects of adding phosphate-containing fertilizers as amendments for lead immobilization in contaminated soils was performed using column and batch experiments. Soils contaminated with high levels of lead and antimony, as well as arsenic, were amended with triple superphosphate (TSP) rock and tested for effects of P on Sb and As. While it is generally known that P has the potential to increase As mobility and availability, studies assessing Sb behavior with P additions are fewer. Column studies found elevated concentrations of Sb and As in column effluents in TSP amended soils, indicating an increase in Sb and As mobility as a result of P addition. Minimal As and Sb leaching was observed during column tests performed on non-amended soils. Pb leaching was minimal in both amended and non-amended samples. *In vitro* extractions tests were performed to assess bioavailability changes in Pb, As, and Sb as a function of TSP addition. These experiments showed minimal changes As and Sb bioaccessibility with increasing P additions. As was expected, Pb bioaccessibility was lowered with increasing amounts of P. Our experiments conclude that while phosphate amendments aid in lowering the bioavailability of soil-bound Pb, it may also produce a significant release of Sb and As from soils, increasing their mobility and bioavailability as well.

INTRODUCTION

The U.S. Department of Defense (DoD) is currently responsible for thousands of contaminated sites a majority of which are contaminated with various toxic metals (Salatas, Lowney et al. 2004). Determining which of these sites require more immediate attention is based on the metal-soil concentrations present at these sites as well as other factors, such as the type of metal present, and the amount of metal in the soil that could potentially be absorbed into the human bloodstream. In a recent study, three of the top five metals most frequently exceeding human health criteria were lead (Pb), arsenic (As) and antimony (Sb). Additionally, Pb and As also were in the top five list for metals exceeding ecological criteria. Pb was the number one metal exceeding human and ecological criteria (Salatas, Lowney et al. 2004).

While Pb contamination has been linked to multiple sources, a significant source of highly concentrated lead in certain surface soils is due to the corrosion of Pb bullets at small arms shooting ranges. Pb concentrations in the topsoil at shooting ranges can reach as high as 50,000 $mg.kg^{-1}$ (Rooney, McLaren et al. 1999). Pb mobilization in these firing range surface soils has also led to elevated concentrations in subsurface soils, further complicating the contaminant issue (Murray, Bazzi et al. 1997). At Pb-contaminated firing range sites where future commercial or residential growth may occur, ingestion of contaminated soil by children is typically the risk driver, due to the fact that high Pb-blood levels in children have been linked to cognitive development problems (Ryan, Scheckel et al. 2004). Nonetheless, Pb remains the primary choice of ammunition in small-arms weapons, creating a growing need to expand our knowledge of Pb contamination and remediation to minimize the adverse impacts of Pb at shooting ranges as well as other sites (Cao, Ma et al. 2003).

Due to high costs of soil excavation and off-site remediation, *in situ* remediation practices have been proposed to provide more efficient means of site treatment (Hettiarachchi and Pierzynski 2004; Tang, Zhu et al. 2004; Lin, Lian et al. 2005; Chen, Zhu et al. 2006). *In situ* techniques are not only projected to cost less than one-tenth of off-site treatment techniques, they also provide a much easier to implement remediation approach (Cunningham 2000; Hettiarachchi and Pierzynski 2004). One method of *in situ* remediation for Pb-contaminated soils that has been extensively studied is chemical stabilization with phosphorous (P) amendments. This method can lower both the mobility and toxicity of Pb, which is preferred at larger sites where metal stabilization is needed, such as shooting ranges (Wilson, Brigmon et al. 2006). Highly soluble phosphate fertilizers, such as triple superphosphate [TSP; $Ca(H_2PO_4)_2$], have been shown to be greatly effective in Pb remediation, especially where immediate site remediation is needed (Stanforth and Qiu 2001). By applying phosphate amendments to Pb-contaminated soils, insoluble Pb-phosphate complexes such as pyromorphites [$Pb_5(PO_4)_3X$, X=OH^-, Cl^-, F^-, etc.] are formed. Pyromorphites provide a highly insoluble species of Pb over a wide range of environmental conditions(Ma, Traina et al. 1993; CotterHowells and Caporn 1996; Hettiarachchi, Pierzynski et al. 2000; Cao, Ma et al. 2003; Lin, Lian et al. 2005). Furthermore, this may reduce the bioavailability of Pb in soils, which is typically the driving factor in risk assessments at metal-contaminated sites (Salatas, Lowney et al. 2004; Tang, Zhu et al. 2004).

Oral bioavailability is the fraction of an ingested contaminant that is absorbed into the bloodstream from the gastrointestinal tract (Ruby, Schoof et al. 1999; Hettiarachchi and Pierzynski 2004). Animal models have been used to assess bioavailability values for Pb and As; however, the difficulty and expenses associated with *in vivo* models have led to the extensive development of *in vitro* models. Bioaccessibility is the soluble fraction of a substance, such as Pb in an in vitro extraction test, that is available for absorption into the bloodstream (Ruby, Schoof et al. 1999). The original physiologically based extraction test (PBET) was designed to mimic the GI tract of a 2-3 year old, fasting child (Ruby, Davis et al. 1996). While the original PBET modeled several stages of the gastric pathway, current extraction tests provide a simpler approach. A streamlined version of the original PBET considers only the percentage of dissolved metal in the stomach phase at a single pH (pH 2.3 for Pb), while remaining accurate in determining Pb bioaccessibility (Kelley 2002).

Phosphorous amendments may be useful in quick and effective immobilization and bioavailability reduction of Pb in contaminated soils; however, there are several potential drawbacks. Relatively high P:Pb molar ratios have been suggested when applying phosphate amendments to soils to immobilize Pb, which can leave an excess of phosphate (Stanforth and Qiu 2001; Tang, Zhu et al. 2004; Chen, Zhu et al. 2006). In addition, many Pb-contaminated soils also contain multiple toxic metals. As and Sb are the second and fifth most frequently occurring metals that exceed human health criteria at DoD sites, respectively (Davis, Sherwin et al. 2001; Salatas, Lowney et al. 2004). According to Salatas' 2004 study, As exceeded human health criteria at about 20% of DoD metal-contaminated sites, while Sb exceeded human health criteria at almost 10% of metal-contaminated sites. Furthermore, Sb is a common alloy in Pb ammunition, potentially creating higher concentrations of Sb at firing ranges. Competitive reactions between P and other contaminants such as Sb and As could potentially release these contaminants and increase their availability.

Phosphorous, arsenic and antimony fall in the same group of elements, and both tend to display similar chemical and toxic behavior (Wilson, Craw et al. 2004; Gal 2006). In oxic soil conditions such as metal contaminated sites, Sb and As are commonly present in the inorganic pentavalent (+V) versions, arsenate (AsO_4^{3-}) and antimonate (SbO_4^{3-}) (Smedley and Kinniburgh 2002; Yang, Barnett et al. 2002; Mitsunobu, Harada et al.

2005; Radu, Subacz et al. 2005; Zhang and Selim 2005). Studies have shown strong reaction site competition between As and P, increasing the availability and mobility of As (Hongshao and Stanforth 2001; Cao, Ma et al. 2003; Fayiga and Ma 2006; Tao, Zhang et al. 2006). An abundance of soluble phosphate at metal-contaminated sites could ultimately create problems such as increased mobility and bioavailability of As and Sb.

The objectives of this study were to determine if correlations between Sb and Pb existed at small-arms firing ranges, due to bullet corrosion. Column tests were employed to observe and quantify a potential increase in Sb and As mobility upon TSP addition to a Pb-contaminated soil. Batch experiments were also conducted to assess Sb and As bioaccessibility changes with various TSP additions.

MATERIALS AND METHODS

Bulk samples of metal-contaminated surface soils were acquired from four locations in the eastern United States: 1) an inactive firing range located in Roane County, Tennessee; 2) an active small-arms firing range used for military training located in south-central Alabama; 3) a recreational small-arms firing range used by police in east-central Alabama; 4) a DoD contaminated site in Maryland. These soils will be referred to as Soils 1-4, respectively. All soils were known to have high concentrations of Pb prior to testing and the particle size distribution of the soils was relatively different. Chemicals used in this research were all trace-metal chemical grade, and solutions were prepared with double-deionized water prepared with a Milli-Q system. Triple superphosphate [TSP – $Ca(H_2PO_4)_2$] used in these experiments was obtained from a local gardening store. Total soil metal concentrations were measured by EPA Method 3050B, a harsh acid soil digestion procedure.

Laser Ablation Analysis

Several bullets were collected from Site 3, split vertically with an industrial saw and then analyzed for correlations between Pb and other metals present, especially Sb. Both the bullet cores and jackets were analyzed. Chemical analysis of the bullet was performed using a New Wave UP 213 laser ablation system coupled with a Perkin Elmer Elan DRC ICPMS, using an Ar plasma. Laser ablation products collected along a 3 mm line at a rate of 20 $\mu m.s^{-1}$ over a swath of 80 µm were swept into the plasma with Ar gas. The ICP-MS operated in a simple mass scanning mode from 9 (F) to 80 (Hg) amu, and results are not quantitative. Rather, they provide a summary of elements present in different parts of the bullet, and enable chemical comparisons among these parts. Pb was not included in the scan because it is known to be present in high concentration and analysis would swamp the detector.

Scans were performed on the bullet core and exterior jacket both before and after a pre-ablation step. The exterior scan without pre-ablation preferentially samples the oxidized crust coating the bullet jacket, and the scan after pre-ablation samples the bullet jacket.

Sb-Pb Correlations

Sb-Pb correlation studies were performed on soils from Sites 1-3. Soil samples were collected from three locations at Site 1, three locations at Site 2 and ten locations at Site 3. Samples were taken from various areas at each firing range, but primarily around butt stops. Soil samples from all 3 sites were collected from the upper 12" portion of the surface. Soils were sieved to <2 mm on site in order to remove bullet fragments, gravel, and organic debris.

Each soil sample was homogenized using a mortar and pestle, disaggregated, air dried, and sieved to <250 μm, which is deemed adequate for approximating the particle size ingested by children (Hettiarachchi and Pierzynski 2004). Samples were stored dry prior to use. EPA Method 3050B was used to digest samples in order to determine their soil-metal concentrations.

Column Tests

Column tests were conducted in one cm-diameter glass columns at room temperature (22°C +/- 2°C) on soil from Site 4 (Soil 4). Four grams of contaminated soil was dry packed to a depth of 3.6 cm (+/- 0.1 cm). Amended samples also received a 1.0 g addition of TSP (5% P addition by weight) for a total packed mass of 5.0 grams, which increased the packing depth by approximately 25%. The TSP and soil were dry mixed prior to column packing. The columns were slowly flushed from the bottom using 10^{-3} M $CaCl_2$. Various amendment methods and flow rates for the column tests are described in Table 2. Effluent samples were collected with a fraction collector and analyzed for pH, Sb, As, Pb and PO_4. Column hydrodynamics were measured following column testing by adding a step-feed input of bromide-containing solution to the columns and measuring the effluent bromide concentration by ion chromatography. A non-amended (soil only) column on which a tracer test was performed (infiltration rate of 6.02 in hr^{-1}) had a porosity of 0.47, a dispersion coefficient of 0.021 $cm^2 \cdot min^{-1}$ (Column Peclet number 44.1), and a bulk density of 1.41 $g.cm^{-3}$. CXTFIT was used to model this data.

Mass balance checks on leached metals were performed to ensure data accuracy. Recovery of metals in terms of percentage was calculated by dividing the total amount of contaminant originally in the pre-tested soil by the amount of contaminant leached plus the amount of contaminant remaining in the soil at the conclusion of the experiment. EPA Method 3050B was used to determine the amount of metal in soils while graphical integration was used to determine the total amount of metal in the column effluent.

Batch Experiments

Batch amendment experiments were conducted in 20 mL HDPE vials at room temperature (22°C +/- 2°C) on soils from Sites 3 and 4. One gram samples of contaminated soil, along with 0, 1, 2.5, and 5% P additions by weight (via triple superphosphate) were added with 100% water to mass ratio (1.0 g water per 1.0 g soil plus amendment additions). Samples were then shaken for approximately 30 seconds on a Vortex shaking apparatus. The aging process of the samples consisted of 24 hours shaking at 250 rpm, followed by the samples being open to atmosphere and placed in a 100% humidity aging apparatus for 7 days at approximately 100% moisture. Following the aging procedure, samples were air dried prior to their *in vitro* extraction testing.

Extractions

A streamlined version (Kelley 2002) of the physiologically based extraction test (PBET) originally developed by Ruby et al. (1996) was used to determine the bioaccessibility of As, Pb, and Sb in the soil with and without amendment additions. The PBET extraction was designed to simulate a fasting child's gastrointestinal tract at a pH of 2.3 ± 0.01 for Pb and 1.5 ± 0.01 for As at 37^{o}C ± 2. This method has shown strong correlation with *in vivo* Pb bioavailability and is currently being validated for As. Due to its similarity in chemical behavior with As, Sb bioaccessibility was also assessed via the streamlined PBET. Samples from the batch experiments (0.1 g) were added to 15 mL polypropylene centrifuge tubes along with 10 mL of PBET solution for a 1:100 soil to solution ratio. PBET solution was added at a temperature of 37°C ± 2 then samples were immediately immersed in a rotating water bath at a temperature of 37°C ± 2 for one hour. Following the one hour water bath extraction duration, samples were centrifuged for five minutes at 2000 rpm, and filtered into 20 mL HDPE vials with a 0.45 μm disk filter and syringe. The As, Sb and Pb concentrations in the filtrates represented the bioaccessibility values for each respective metal. Samples not immediately analyzed were stored at 4°C until analysis.

Stock PBET solution was made using a 0.4 M Glycine (*Fisher Scientific, G48*) solution adjusted to a pH of 1.5 ± 0.01 for As and Sb and 2.3 ± 0.01 for Pb using trace metal grade, 12.1 M concentrated hydrochloric acid. The solution pH was adjusted at a temperature of 37 ± 2°C using a pH meter calibrated with buffer solutions adjusted to a temperature of 37 ± 2 °C.

Analytical Methods

A Perkin-Elmer HGA-600 graphite furnace and 3110 Perkin-Elmer atomic absorption spectrometer was used to analyze As and Sb concentrations in all aqueous samples. A SpectrAA atomic absorption spectrometer was used to analyze Pb concentrations in all aqueous samples. Phosphate concentrations in column effluents were measured with a Dionex DX-120 Ion Chromatograph. Both column and batch aqueous samples not immediately analyzed following experimentation were stored at 4°C until analysis.

RESULTS AND DISCUSSION

Lead-Antimony Correlations

One of the objectives of this study was to examine the relationship between Sb and Pb at small-arm firing range sites, due to the fact that Sb has been known to be a common alloy in Pb bullets. P additions at these sites for Pb remediation could potentially increase the mobility of Sb. Soil-metal concentrations for Sb and Pb were determined via EPA Method 3050B from various surface soils taken from Sites 1-3. Strong linear correlations ($r^2 > 0.9$; $P < 0.05$ for all three sites) between Pb and Sb were detected at all of the tested sites (Figure 1). Soil concentrations of As were also measured at Site 3 to detect any relationship between Pb and As at firing ranges. No linear correlation ($r^2 > 0.104$; $P > 0.05$) was detected at this site, indicating that the presence of As was not associated with Pb.

To further examine the relationship between Pb and Sb at firing ranges, bullets from Site 3 were collected, split with an industrial saw and analyzed by laser ablation. The bullet jacket showed different elemental signatures than the bullet core. A few elements were detected in higher concentrations in the bullet core compared with the jacket; Se, Sb, Ag, Te, and Au showed the greatest difference. The bullet jacket and the jacket crust exhibited similar concentrations of most elements; however, Se was greatly enriched in the crust relative to the jacket. Na, Mg, Si, Al, K, Ca, Ti and Fe were also preferentially associated with the crust, presumably originating from the soil from which the bullet was collected. Light rare earth elements and Hg were higher in the bullet jacket than the crust. Furthermore, Sb was the highest detected element in the bullet interior, other than Pb, while significant concentrations of As were not detected in either the bullet jacket or core.

Column Experiments

While no particular method of phosphate application to lead-contaminated soils in real-world scenarios has yet been deemed to be the most efficient or most effective, the column studies employed in this research represented dry-mixing phosphate fertilizer with contaminated soil, then adding water to promote Pb-immobilization reactions via phosphate. The mobility of Sb and As was observed by measuring the concentrations of Sb and As in collected effluents. Unlike batch experiments, this experimental method allows observation of how these contaminants could potentially enter groundwater through the leaching processes.

As stated earlier, three column tests were employed with soil from Site 4 to cover various amendment addition and water addition scenarios: TSP mixed and packed dry with soil at 15.3 $cm.hour^{-1}$ infiltration rate (1), TSP mixed and packed dry with soil at 1.53 $cm.hour^{-1}$ infiltration rate (2), and TSP mixed with soil wet, aged for one week, then packed dry at 15.3 $cm.hour^{-1}$ infiltration rate (3). The aging procedure for the third column test was done to promote $Pb\text{-}PO_4$ reaction prior to testing. Column test (1) was performed twice to assess experimental repeatability. Control tests were performed in the same manner, but without TSP addition. The mobility of antimony and arsenic were initially expected to increase upon TSP addition, due to the excess of soluble phosphate.

The mobility of antimony increased greatly with the addition of TSP to the contaminated soil. Among the three column tests, an average of 27.5% of total antimony leached from the TSP-amended samples. Most antimony leaching occurred during the initial 5 inches of infiltration and gradually decreased during the duration of the experiment (Figure 3.2a). Control samples leached an average of 2.1% of total antimony from the soil, a much smaller percentage than what leached during the phosphate-amended experiments. An average of over 13 times more Sb leached during the TSP-amended experiments versus the control experiments. The greatest amount of antimony leaching occurred during the amended, slow column test (2), where almost 38% of total antimony leached from the soil (Table 3.2). The initial collected effluent for this column test had an Sb concentration of 2180 µg L^{-1}. Longer phosphate retention in the column during the slow test increased the amount of desorbed Sb, potentially indicating the desorption reactions of the soil-bound Sb to be rate-limited.

The mobility of arsenic also increased greatly when TSP was applied to the contaminated soil columns (Figure 3.2b). An average of 17.9% of total As leached from the amended samples, while only 1.8% leached from samples with no amendment addition (Table 3.2). On average, almost ten times more As leached during TSP-amended column tests than controlled column tests. Like Sb, most As leaching occurred in the initial collected effluents; however, arsenic leaching reached a steady-state effluent concentration after twenty inches of infiltration rather than gradually decreasing as was observed in Sb leaching (Figure 3.2b). The As concentrations measured in the effluents exceeded the US drinking water maximum contaminant level (10 µg L^{-1}) during the first 20 inches of infiltration.

The total amount of Pb that leached for the duration of the experiments in both the control and amended samples were similar. On average, only 0.48% of total lead leached from the amended samples, while an average 0.58% of total lead leached from control samples slightly favoring TSP-amended samples. However, a spike in Pb effluent concentrations were observed in amended samples, where no spike occurred in controlled samples (Figure 3.2c). This is due to a slight drop in pH as a result of dihydrogen phosphate addition from TSP dissolution. Natural Pb solids are possibly dissolving during this process, increasing the amount of soluble Pb. This dissolution process may be beneficial for overall Pb immobilization by promoting the kinetics of pyromorphite formation (Zhang and Ryan 1999). The slow column test revealed less Pb leaching (~0.1% total Pb leached) than normal flow rate column tests.

The column tests where TSP was aged for seven days with the soil prior to experimentation (3) revealed interesting results in regards to the other column tests. The greatest amount of As leaching was observed during this test (28.7% of total As), while the opposite was true for Sb (19% of total Sb leached). These results indicate that the aging process favored the adsorption of Sb more so than As. Only 0.01% of lead leached during this column tests, suggesting that Pb-phosphate reactions are rate limited and the 7-day aging process provided more time for Pb-phosphate solids (i.e. pyromorphites) to form. Nonetheless, a higher initial Pb spike was observed in the initial collected effluent in the amended sample, as was observed in all amended column tests.

Due to the composition of TSP containing dihydrogen phosphate, it was expected that the TSP addition would decrease the pH in the amended effluents. On average, the initial 2.5 inches of infiltration had a pH of 5.03 for amended samples, while the initial pH of the non-amended samples had an average of 7.22. The pH in both control and amended samples gradually moved toward a steady-state pH of about 6.6-6.8, depending on the particular column test. The drop in pH for amended samples created a spike in Pb effluent concentrations in initial effluents; however, overall Pb immobilization may be enhanced as a result from this. At neutral soil pH conditions the dissolution of natural Pb complexes is minimal, inhibiting the formation of pyromorphite. Between pH values 5-8, the dissolution of the initial Pb mineral is the rate-limiting factor in the formation of hydroxypyromorphite ($Pb_{10}(PO_4)_6OH_2$) (Laperche, Traina et al. 1996). Furthermore, pH values closer to 5 results in faster hydroxypyromorphite formation. This indicates that P amendments providing both soluble phosphate and the ability to slightly lower natural soil pH levels (i.e. TSP) may be more effective in the remediation of Pb contaminated sites. In regards to phosphate leaching from TSP dissolution, most phosphate from the

TSP (60-80 %, depending on the particular column test) leached during the first 2.5 inches of infiltration (Figure 3.2d).

Saturation indices of chloropyromorphite (CPM) were calculated via Visual Minteq version 2.40 by using effluent pH values and concentrations of PO_4, Pb, Ca and Cl. Effluent pH values used for modeling CPM reactions were taken during the column experiments, but were then acidified (1% nitric acid) to determine phosphate and Pb concentrations. This was done to prevent further Pb-phosphate precipitation. The average saturation index (SI) of CPM for the first column test was 24.04 ± 2.72, while the average SI for the duplicate, first column experiment was 22.93 ± 2.13. The average SI for CPM in the effluents for the duration of the slow column experiment was 21.63 ± 1.11. Therefore, pyromorphite formation is likely occurring in the effluents as a result of soluble lead and phosphate. Saturation indices of CPM were not averaged for the aging column test due to undetectable Pb concentrations in sample effluents after 15 infiltration inches. However, the SI of CPM was modeled on the initial samples with detectable lead, and similar SI values were seen. Also, one-half of the effluent for the first 2.5 inches of infiltration (2.5 mL) for the aged column test was filtered prior to testing. The filtered sample had approximately one-tenth the amount of lead and 78% less phosphate than the non-filtered effluent, and as a result, the SI was slightly smaller (19.25-acidified only; 15.28-filtered). This is further indication that a Pb-PO_4 precipitate such as CPM is forming in the column effluents.

Batch Bioavailability Experiments

In order to assess changes in As and Sb bioavailability upon TSP addition to contaminated soils, batch experiments were conducted using various amounts of TSP additions to Site 3 and Site 4 soils. The Site 4 soil had average initial PBET bioaccessibility values of 37.5, 34.6, and 60.7% for Sb, As, and Pb, respectively (Figure 4a). Upon TSP additions, both the bioaccessibility of Pb and As decreased, while the bioaccessibility of Sb increased. At the maximum TSP addition (5% P by soil weight), final bioaccessibility values were 52.7, 23.8, and 33.1% for Sb, As, and Pb, respectively. The pH in these samples decreased with increasing TSP additions from 7.71 (no TSP) to 5.54 (5% P addition by TSP).

The Site 3 soil revealed opposite trends in As and Sb bioavailability change as compared to the other soil. Initial average bioaccessibility values for Sb, As, and Pb, respectively, were 41.7, 3.7, and 61.5% (Figure 4b). Upon maximum TSP addition, these values changed to 21.1, 12.0, and 13.6% (Sb, As, and Pb). The pH of these samples changed from an initial pH of 6.21 (0% P addition) to a final pH of 5.71 (5% P addition).

Major differences in the bioaccessibility batch tests between Site 3 and Site 4 soils were changes in pH and changes in Sb and As bioaccessibility. The pH of soils can have a great effect on As and Sb speciation and mobility, which could in turn affect their bioaccessibility (Gal 2006). The pH of Site 3 soil changed only slightly, even at the highest TSP additions (6.21 to 5.71), and as a result, the bioaccessibility of As in the Site 3 soil slightly increased (3.7% to 12.0%). The pH of the Site 4 soil was lowered more significantly than Site 3 at the highest TSP addition (7.71 to 5.54) and the bioaccessibility of As slightly decreased (23.8% to 12.0%). This trend in bioaccessibility versus pH is consistent with recent research suggesting that As bioaccessibility decreases with decreasing pH (Yang, Barnett et al. 2002). Regarding Sb bioaccessibility, values changed in an opposite manner from As bioaccessibility, where Sb bioaccessibility increased in Site 4 soil (37.5% to 52.7%) and decreased in Site 3 soil (41.7% to 21.1%).

Environmental Implications

Strong linear correlations were observed between antimony and lead in soils samples collected from Sites 1 through 3. Although As contamination is often present with other heavy metals, due to being released as a by-product of other metals, such as Pb (Fayiga and Ma 2006), no linear correlations were observed between As and Pb at these sites, suggesting the presence of As could be naturally occurring. High amounts of Sb were also detected in bullets collected from one of the sites in question using laser ablation analysis. Pb-Sb correlations at Pb-contaminated sites should be investigated prior to phosphate amendment addition due to potential Sb leaching caused by phosphate.

Adding P amendments to Pb contaminated soils may decrease both the mobility and the bioavailability of Pb, limiting its negative health impacts on humans. However, the use of phosphate as a Pb amendment can have a significant impact on the mobility and bioavailability of Sb and As. TSP additions to lead contaminated soil containing Sb and As greatly increased the mobility of Sb and As in soil column tests due to adsorption site competition between P, Sb and As. In regards to Pb mobility, column studies showed no major changes in controlled and amended samples. However, Pb spikes observed in the initial 2.5 infiltration inches in amended samples suggest the potential for Pb to initially become mobile and leach further into the soil profile. This increase in Pb mobility was likely caused by the decrease in soil pH due to TSP addition. It is possible that natural soil-Pb minerals were dissolved, releasing soluble Pb into the effluent. The dissolution of natural Pb-bearing minerals may be beneficial in overall Pb immobilization, however, by increasing the kinetics of pyromorphite formation (Zhang and Ryan 1999).

Batch experiments revealed bioavailability changes in both Sb and As, though these changes were not always negative. A particular increase/decrease in Sb and/or As bioaccessibility may be linked to soil pH. The pH of Soil 4 decreased with increasing TSP additions, resulting in decreased As bioaccessibility values and increased Sb bioaccessibility values. Soil 3 pH changed slightly, however, and as a result the bioaccessibility change of Sb and As was minimal, with As bioaccessibility slightly increasing and Sb bioaccessibility slightly decreasing. This data supports conclusions from Yang et al. (2002), that low soil pH is the most important soil property in reducing As bioaccessibility. These results indicate varying bioavailability behavior between As and Sb at varying sites, depending on soil properties such as the buffering abilities of the soil. More bioavailability studies involving various phosphate amendments and multiple contaminated soils should be conducted in order to fully assess their interaction with As and Sb.

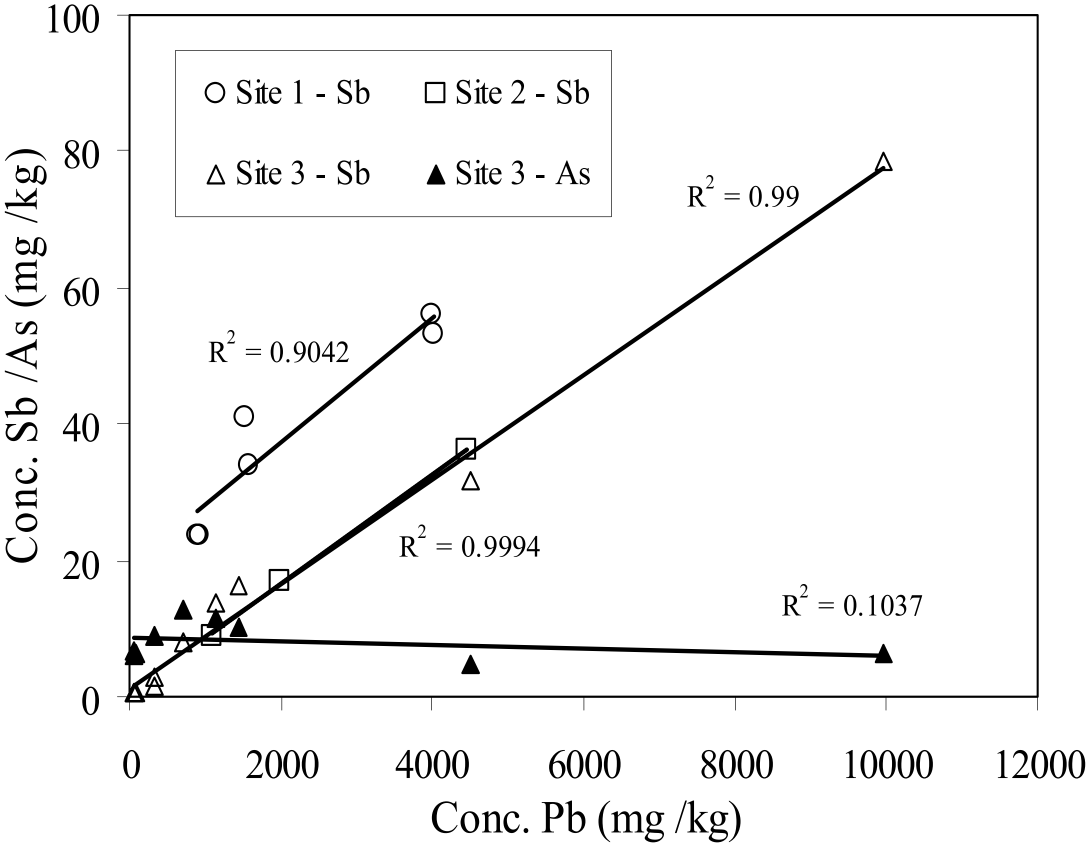


Figure 3.1. Correlations between Sb and Pb at Sites 1-3 and As and Pb at Site 3. Strong correlations were observed between Sb and Pb at all three sites ($r^2 > 0.9$; $P<0.05$), while no correlation was observed between As and Pb at Site 3 ($r^2 = 0.1037$; $P>0.05$).

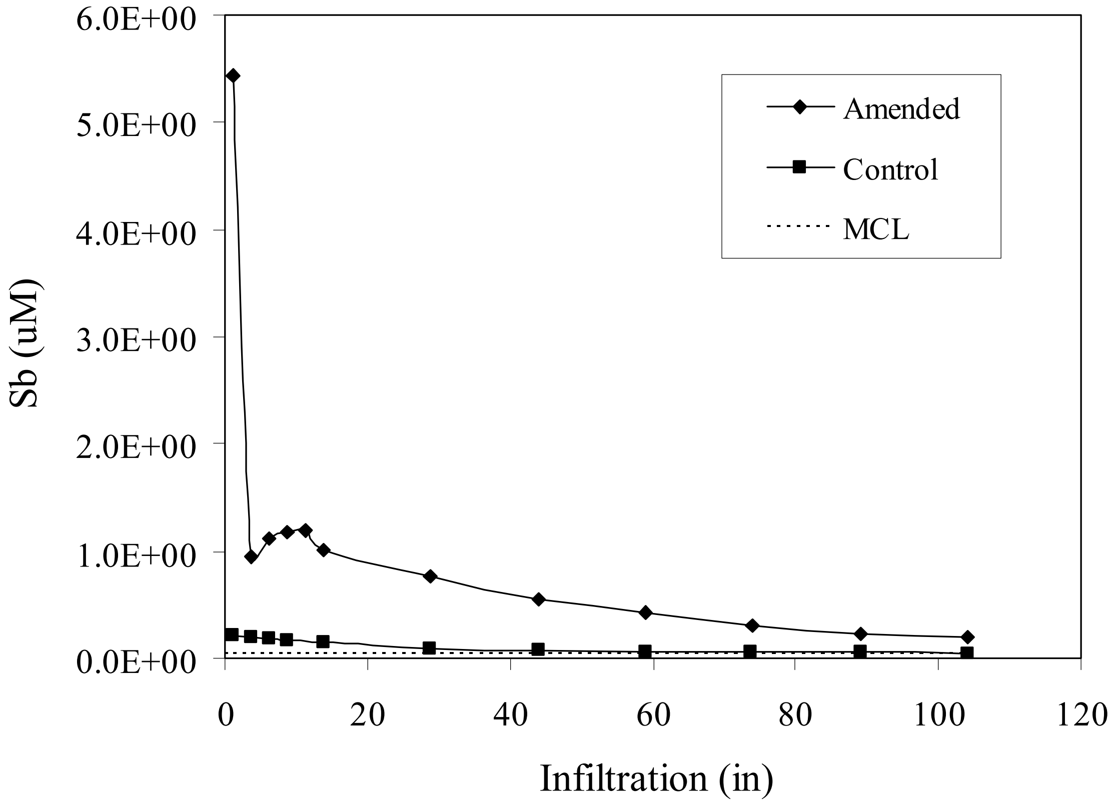


Figure 3.2a. Antimony leachate concentrations versus infiltration through the amended and control columns for the third column test. The Sb maximum contaminant level (6 $\mu g.L^{-1}$) is shown for comparison. A total of 105.3 inches of infiltration were pumped through the column; ~50 pore volumes. Amended indicates soil column with TSP addition; control indicates soil column without TSP.

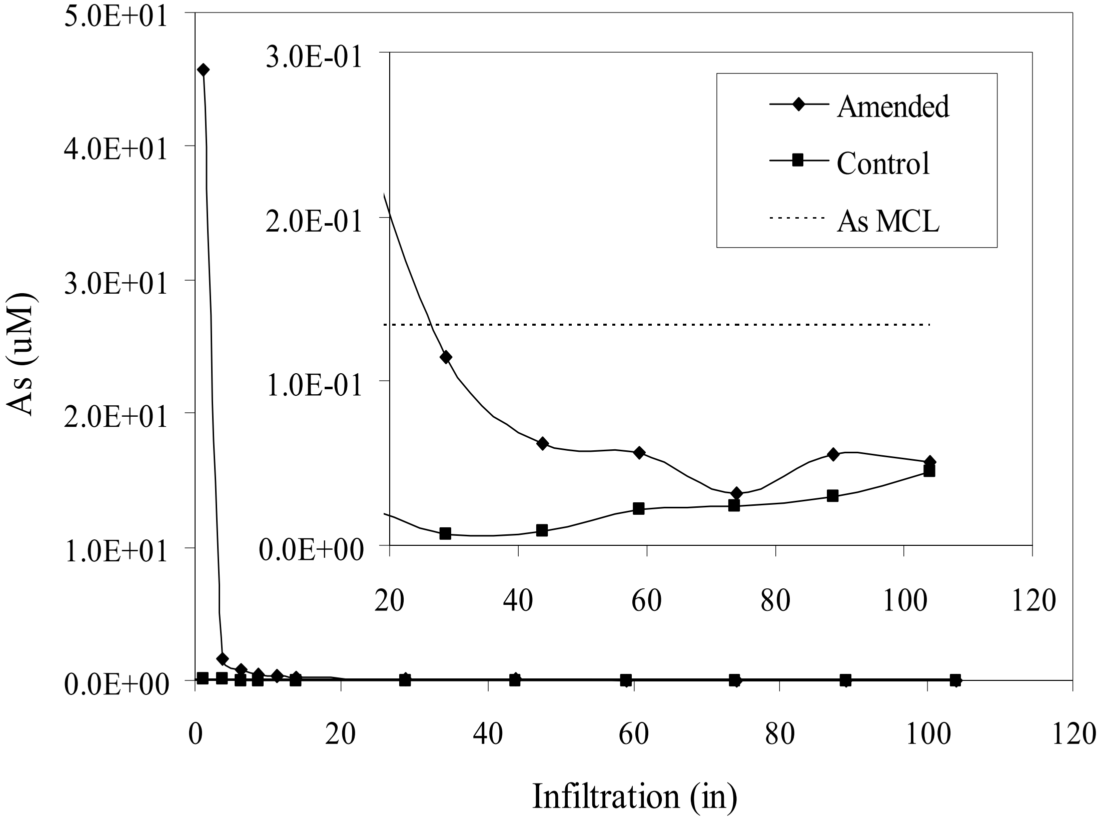


Figure 3.2b. Arsenic leachate concentrations versus infiltration through the amended and control columns for the third column test. The As maximum contaminant level (10 µg.L^{-1}) is shown for comparison. Amended indicates soil column with TSP addition; control indicates soil column without TSP.

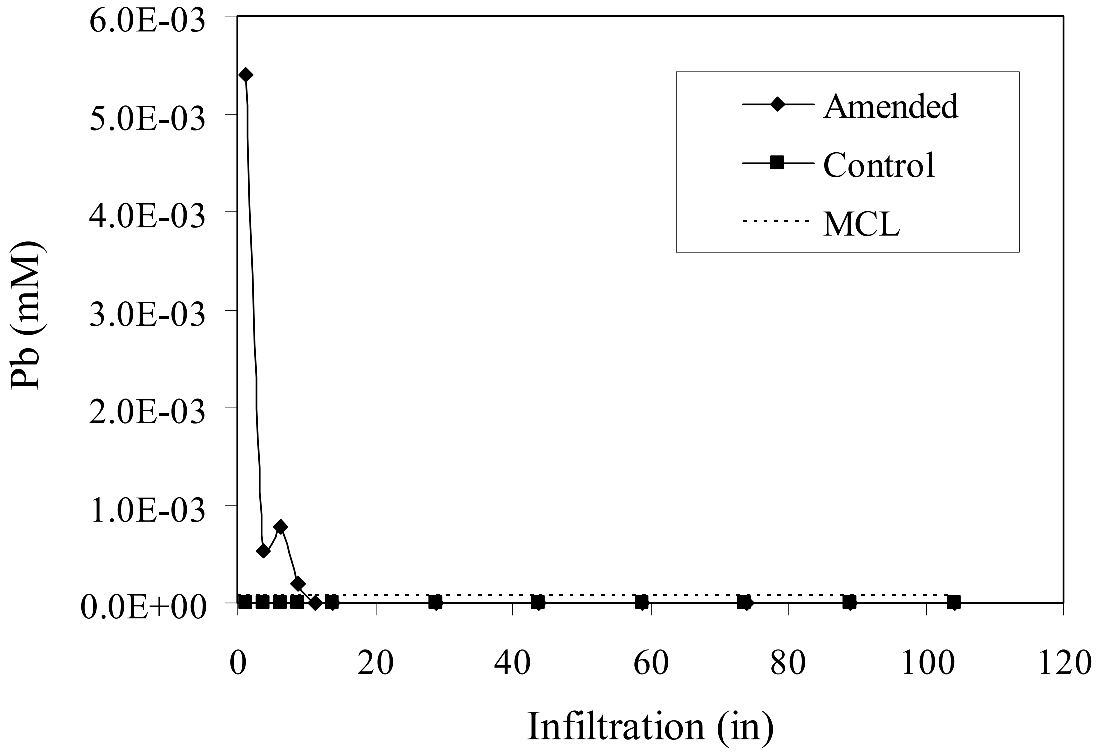


Figure 3.2c. Lead leachate concentrations versus infiltration through the amended and control columns for the third column test. The Pb maximum contaminant level

(15 µg.L^{-1}) is shown for comparison. Amended indicates soil column with TSP addition; control indicates soil column without TSP.

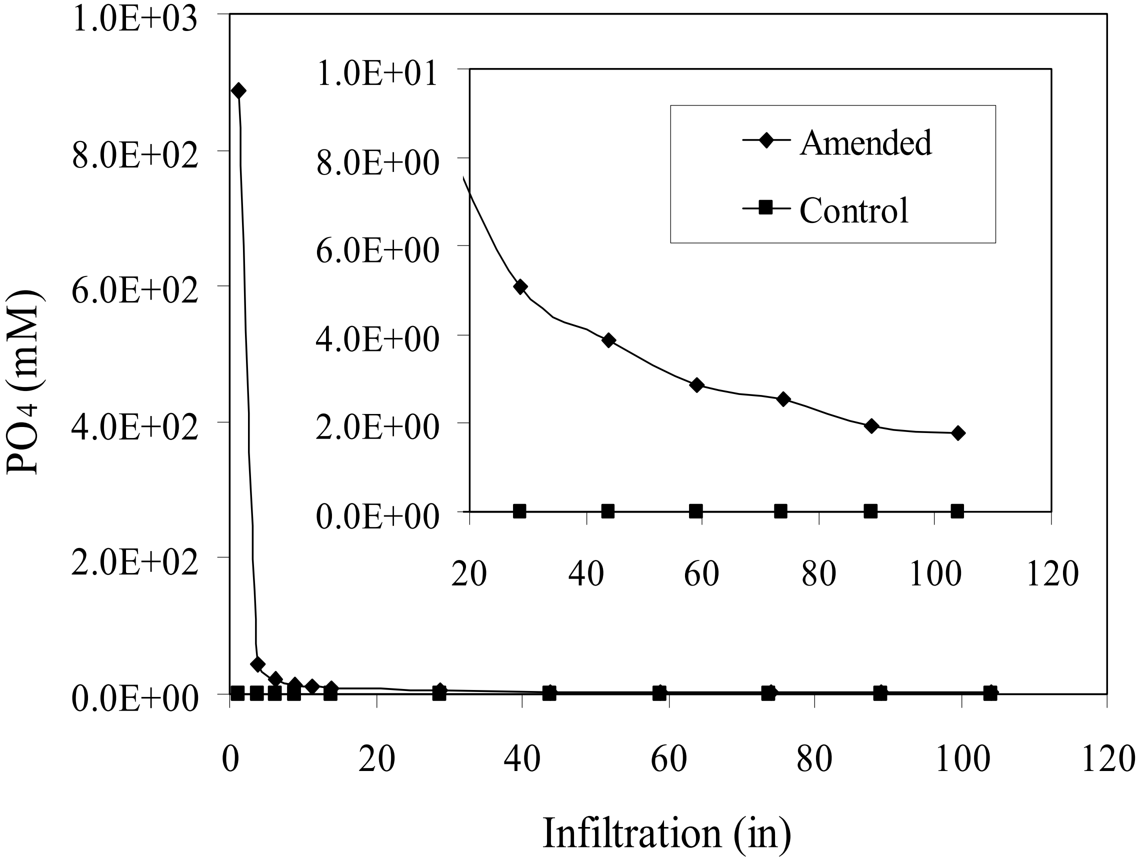


Figure 3.2d. Phosphate leachate concentrations versus infiltration through the amended and control columns for the third column test. Amended indicates soil column with TSP addition; control indicates soil column without TSP.

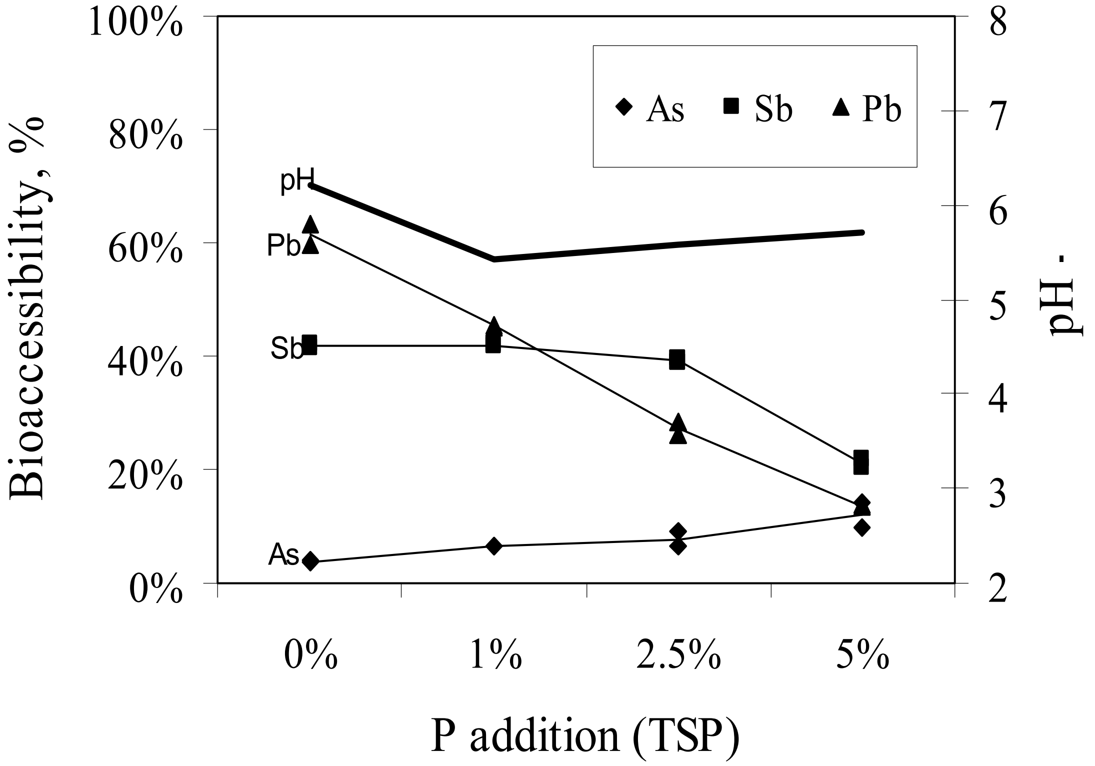


Figure 3.3a. Bioaccessibility values for arsenic, antimony, and lead versus phosphate addition by soil weight for soil from Site 3. Batch tests were performed in duplicate for each soil (As a, As b, etc.). The bold line indicates soil pH values at each amendment addition. (Bioaccessibility = PBET quantity leached / total quantity in soil).

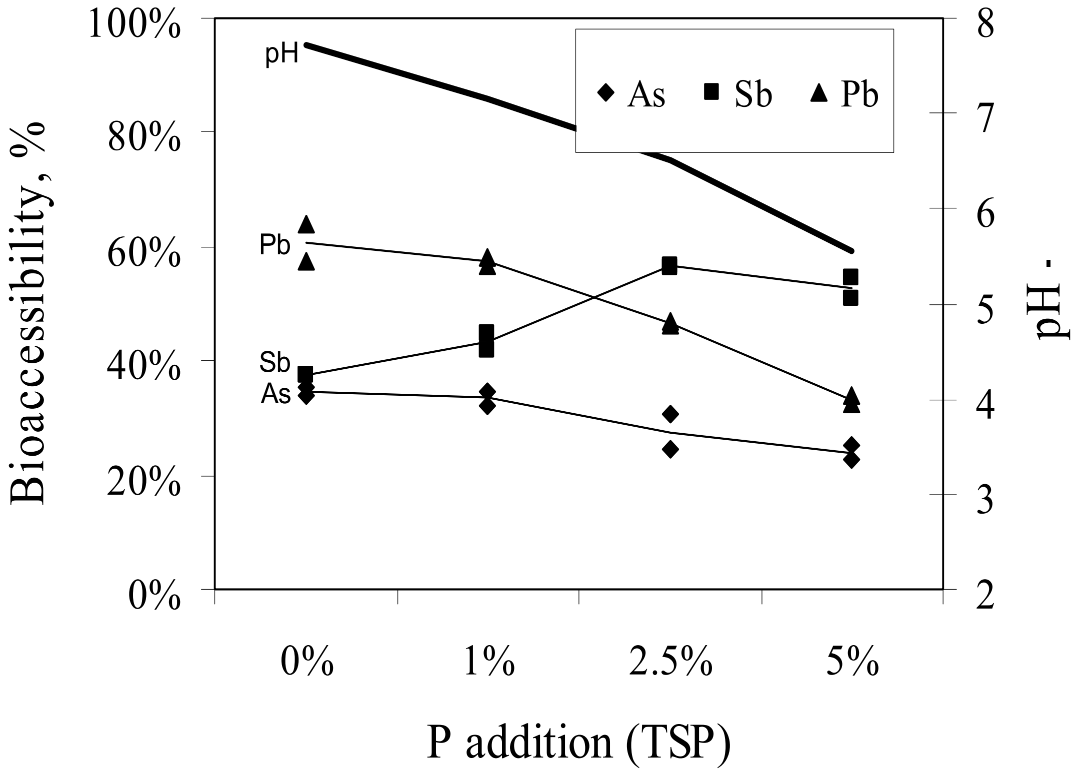


Figure 3.3b. Bioaccessibility values for arsenic, antimony, and lead versus phosphate addition by soil weight for soil from Site 4. Batch tests were performed in duplicate for each soil (As a, As b, etc.). The bold line indicates soil pH values at each amendment addition. (Bioaccessibility = PBET quantity leached / total quantity in soil).

Table 3.1. Soil properties and metal concentrations for tested soils from Sites 3 and 4.

Soil	**pH** **DDI**	**pH** **5mM $CaCl_2$**	**TC** **%**	**Pb** **(mg/kg)**	**As** **(mg/kg)**	**Sb** **(mg/kg)**	**Fe** **(g/kg)**	**Clay** **%**	**Silt** **%**	**Sand** **%**
Site 3	5.48	5.14	0.26	5080 ± 280	10.3	16.4	12.2	27.7	21.8	50.5
Site 4	7.47	6.99	1.49	8980 ± 680	17.0 ± 0.7	22.3 ± 0.3	11.3	6.20	30.6	63.2

*Standard error of multiple measurements for soil-metal concentrations

Table 3.2. Quantitative analysis of column experiments

Soil 4	infiltration rate	soil addition	TSP addition	initial effluent pH	% As leached	% As recovered**	% Sb leached	% Sb recovered**	% Pb leached	% Pb recovered**
	cm.hour^{-1}	g (a)*	g (a)*	-	%	%	%	%	%	%
Trial 1 a (contr)	15.3	4	0	7.01	3.3	97.9 ± 2.7	2.2	86.6	1.5	102.0
Trial 1 a (P)	15.3	4	1	4.82	18.8	100.6 ± 5.6	26.3	100.4	1.1	109.2
Trial 1 b (contr)	15.3	4	0	6.98	2.0	95.0 ± 4.6	0.8	94.9 ± 6.9	0.7	97.9 ± 0.6
Trial 1 b (P)	15.3	4	1	4.88	13.3	97.6 ± 1.5	26.0	92.8 ± 1.6	0.7	94.7 ± 7.4
Trial 2 (contr)	1.53	4	0	7.48	1.3	96.5 ± 4.5	3.0	106.4 ± 6.2	0.1	102.0 ± 2.8
Trial 2 (P)	1.53	4	1	5.00	10.8	62.0 ± 2.3	37.9	155.2 ± 0.6	0.1	95.1 ± 4.2
Trial 3 (contr)	15.3	4 (a)	0	7.19	0.6	97.8 ± 8.0	2.4	84.9 ± 1.0	0.0	98.1 ± 2.3
Trial 3 (P)	15.3	4 (a)	1 (a)	5.20	28.7	89.9 ± 3.6	19.6	110.0 ± 6.3	0.0	97.0 ± 1.1

*a: samples aged prior to column packing and testing; all other samples were packed dry without aging.

**Initial quantity in pre-tested soils / quantity in effluent + quantity remaining in post-tested soil. ± vales are the standard errors ($s \cdot n^{-1/2}$) of multiple measurements of post-tested soil-contaminant quantities.

CHAPTER FOUR

CONCLUSIONS AND RECOMMENDATIONS FOR FUTURE WORK

Conclusions

Strong linear correlations were observed between antimony and lead in soils samples collected from three lead-contaminated small arms firing ranges. Although As contamination is often present with other heavy metals, due to being released as a by-product of other metals, such as Pb (Fayiga and Ma 2006), no linear correlations were observed between As and Pb at these sites, suggesting the presence of As could be naturally occurring. High amounts of Sb were also detected in bullets collected from one of the sites in question using laser ablation analysis. Pb-Sb correlations at Pb-contaminated sites should be investigated prior to phosphate amendment addition due to potential Sb leaching caused by phosphate.

Adding P amendments to Pb contaminated soils may decrease both the mobility and the bioavailability of Pb, limiting its negative health impacts on humans. However, the use of phosphate as a Pb amendment can have a significant impact on the mobility and bioavailability of Sb and As. TSP additions to lead contaminated soil containing Sb and As greatly increased the mobility of Sb and As in soil column tests due to site competition between P, Sb and As. Controlled experiments with no phosphate additions revealed minimal Sb or As leaching. In regards to Pb mobility, column studies showed no major changes in controlled and amended samples. However, Pb spikes observed in the initial 2.5 infiltration inches in amended samples suggest the potential for Pb to initially become mobile and leach further into the soil profile. This increase in Pb mobility was likely caused by the decrease in soil pH due to TSP addition. It is possible that natural soil-Pb minerals were dissolved, releasing soluble Pb into the effluent. The dissolution of natural Pb-bearing minerals may be beneficial in overall Pb immobilization, however, by increasing the kinetics of pyromorphite formation (Zhang and Ryan 1999).

Batch experiments revealed bioavailability changes in both Sb and As, though these changes were not always negative. A particular increase/decrease in Sb and/or As bioaccessibility may be linked to soil pH. The pH of Soil 4 decreased with increasing TSP additions, resulting in decreased As bioaccessibility values and increased Sb bioaccessibility values. Soil 3 pH changed slightly, however, and as a result the bioaccessibility change of Sb and As was minimal, with As bioaccessibility slightly increasing and Sb bioaccessibility slightly decreasing. This data supports conclusions from Yang et al. (2002), that low soil pH is the most important soil property in reducing As bioaccessibility. These results indicate varying bioavailability behavior between As and Sb at varying sites, depending on soil properties such as the buffering abilities of the soil. More bioavailability studies involving various phosphate amendments and multiple contaminated soils should be conducted in order to fully assess their interaction with As and Sb. TSP significantly reduced the bioavailability of Pb, which was seen incrementally at each dose of amendment addition.

Future Work

This research has shown potential negative effects of adding phosphate amendments to lead contaminated soils that also contain antimony and arsenic. This research employed triple superphosphate as a source for phosphate addition. Other phosphate amendments should be tested to assess their effects on Pb, Sb, and As mobility and bioavailability effects. Longer aging times for amended samples should also be tested to observe a possible decrease in mobility and/or bioavailability for Sb and As.

Furthermore, column studies on a larger scale need to be employed to better model a real world situation where mobilized Pb, Sb, and As could possibly adsorb to lower surface soils rather than leaching into the column effluent. One study used larger scaled column tests involving multiple amendment strategies and various phosphorus amendments, but no assessments were made on the leaching of Sb or As (Yoon, Cao et al. 2007).

Phytoavailability studies have given us an alternate approach to soil-bound metal remediation, and may prove to be an effective strategy for the remediation of multiple-contaminant sites. Studies have observed the effectiveness of using hyperaccumulators for As uptake, where phosphate amendments increase the availability of As to the plants for more effective removal (Cao, Ma et al. 2003; Tao, Zhang et al. 2006). This strategy of using phosphate in conjunction with hyperaccumulators could aid in the removal of As and the immobilization of Pb simultaneously. While phytoavailability studies can require several months in order for successful remediation to occur, a further investigation of these types of studies could prove to be the most effective remediation approach for multiple metal contaminants.

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APPENDICES

Appendix A

EFFECTS OF VARYING FERRIC CHLORIDE DOSES ON ARSENIC BIOAVAILABILITY IN ARSENIC-SPIKED SOILS

Introduction

Arsenic (As) is a commonly occurring contaminant at US EPA Superfund sites primarily due to past uses of pesticides and wood treatment processes (Carbonell, Aarabi et al. 1998; Hingston, Collins et al. 2001), as well as current uses in other anthropogenic processes (Smith, Naidu et al. 1998). In addition, naturally-occurring As in the United States has been deemed a concern due to soil-As concentrations reaching as high as 1.25 $\mathrm{mmol \cdot kg^{-1}}$ in some areas (Beak, Basta et al. 2006). Arsenic contamination in drinking water has received attention in many aquifers around the world due to high As concentrations. In regards to US water distribution systems, the maximum contaminant level for As in drinking water has been lowered from 50 $\mu g \cdot L^{-1}$ to 10 $\mu g \cdot L^{-1}$ (Parks 2003). Arsenic is a known carcinogen and has been linked to health problems including skin cancer (EPA 2007).

While lead (Pb) is the metal that most frequently exceeds risk-based screening criteria for human health concerns at DoD sites, As is second (Davis, Sherwin et al. 2001; Salatas, Lowney et al. 2004). According to Salatas' 2004 study, As exceeded human health criteria at about 20% of DoD sites containing some type of metal contamination. Arsenic contamination often co-exists in Pb-contaminated soils due to the fact that it is commonly released into the environment as a by-product of Pb smelters (Bagga 2001).

As can exist in four oxidations states (-III, 0, III, and V), though the two most common oxidation states are +III and +V. Under aerobic conditions As(V) is typically present while in anaerobic conditions As(III) normally exists (Mitsunobu, Harada et al. 2006), and is considered both more mobile and more toxic than As(V).

In oxic soil conditions, As is commonly present in the inorganic pentavalent oxyanion, arsenate (AsO_4^{3-}) (Smedley and Kinniburgh 2002; Yang, Barnett et al. 2002; Mitsunobu, Harada et al. 2005; Radu, Subacz et al. 2005; Zhang and Selim 2005), although the slow redox reactions can leave either the +III or +V forms in soils (Zhang and Selim 2005). Arsenic also has the potential to be reduced from As(V) to As(III) when exposed to reducing conditions in soil subsurfaces. A recent study by Mitsunobu et al. (2006) exposed As and antimony (Sb) to reduced and oxic environments to observe the redox behavior between the two. Their findings suggested that Sb(V) remained very stable even in reduced conditions while As(V) was less stable, becoming reduced at a much more positive E_H than Sb (Mitsunobu, Harada et al. 2006). Due to the fact that As(III) is both more toxic and more mobile than As(V), reduced environments could potentially cause problems with As leaching into groundwater.

Multiple studies have been conducted on As mobility, solubility and bioavailability in both solutions and soils, however, information regarding As presence in soils remains somewhat contradictory (Zhang and Selim 2005). While the bioavailability of As in drinking water is approximately 100% (US EPA 1992), this value is considerably less for soil bound As. This is due to different As species as well as the particular soil properties decreasing As solubility. Iron and aluminum content, pH, and microbial presence all have an effect on As speciation and mobility (Yang, Barnett et al. 2002; Zhang and Selim 2005; Gal 2006; Shaw 2006).

Iron (III) (Fe) oxides and hydroxides, such as goethite and ferrihydrite have shown a high affinity toward As, and as a result have been widely used in As remediation studies. As(V) and As(III) adsorption characteristics onto Fe oxides have been widely studied via extended X-ray absorption fine structure spectroscopy (EXAFS), showing that inner-sphere surface complexes are formed (Waychunas, Rea et al. 1993; Sun and Doner 1996; Fendorf, Eick et al. 1997; Ladeira, Ciminelli et al. 2001; Sherman and Randall 2003). Furthermore, these surface complexes may either be mono- or bidentate configurations, with bidentate configurations generally being considered the dominant of the two configurations. Surface complexation, however, may not be the only method of removal by Fe (III) hydroxides. Ferrihydrite, an iron oxy-hydroxide, has been shown to remove As more effectively by coprecipitation than by surface complexation when high concentrations of Fe(III) and As(V) are present at low pH values (Richmond, Loan et al. 2004). On the other hand, Fuller et al. (1993) performed a study involving the adsorption of As(V) onto synthesized ferrihydrite, where spectroscopic investigations revealed no surface precipitate formation. In regards to soil-bound As, soils containing higher amounts of Fe oxides generally have greater As uptake via adsorption (Yang, Barnett et al. 2002), where adsorption-desorption reactions, rather than precipitation, has been deemed the primary factor that impacts As uptake (Zhang and Selim 2005).

The adsorption of As on either metal (hydr)oxides or geomedia at varying pH values has been extensively studied. Arsenic (V) adsorption is greater at a slightly acidic pH values, due to the fact that it is a triprotic acid (pK_a 2.20, 6.97, 11.5), commonly occurring as an oxyanion in normal soil pH conditions [$H_2AsO_4^-$ (pH < 6.97); $HAsO_4^{2-}$ (pH > 6.97)] (Williams, Barnett et al. 2003). Multiple studies observing As uptake under varying pH conditions have come to the conclusion that lower pH values promote higher As(V) uptake. Furthermore, the rate at which As is sorbed is greatly increased at lower pH values; this rate slows significantly at near-neutral and higher pH values. One particular study found at a pH of 4.5, As(V) adsorption on Al oxide took about 3 days to complete, while at a pH of 7.8, complete adsorption took over a year (Arai and Sparks 2002). Both a low pH and greater iron content have also been proven to lower the bioavailability of As (Yang, Barnett et al. 2002).

Methods and Materials

Soil Spiking Experiments

Thirty-four non-contaminated soils from various locations throughout the United States were spiked with enough As to yield 100 $mg \cdot kg^{-1}$ As. Table A.1 lists the properties of the soils. 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, 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, which is deemed adequate for approximating the particle size ingested by children (Hettiarachchi and Pierzynski 2004).. 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. A 200 mg/L As solution was prepared by adding 0.307 g of As_2O_5 to 1 L of DI water. Each of the 34 soil slurries were spiked with 5 mL of the As solution, which was sufficient to obtain a 100 mg/kg As soil concentration. The pH of each spiked soil slurry was measured while a neutralizing solution (10^{-3} *M* HNO_3) was added drop-wise to neutralize the basic nature of the added As 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 As 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 As standards. The As concentration in the filtrate was analyzed using an atomic absorption spectrophotometer (AAS) equipped with a electrode-less discharge lamp. The difference between the amount of As added and that remaining in the filtrate was used to calculate the initial spiked soil As 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 As remaining on the soils was analyzed by EPA Method 3050B (U.S. EPA, 1994) to verify a mass balance recovery of ± 10 – 20%.

Amendment Addition and Aging

Amendment addition and aging experiments were performed on the 34 As-spiked soils. Each air dried and sieved soil was weighed, divided into 4 equal portions (2.0 grams each), and placed into 20 mL polypropylene sample vials. A solution of 1.33 M

$FeCl_3$ was prepared and appropriate volumes were added to the As-spiked soils to achieve correct amendment additions. To each soil, 0 (control), 100, 200, and 500 mol Fe: mol As molar ratios were achieved, based on a nominal 100 mg As$\cdot$kg^{-1} for each soil. After the $FeCl_3$ solution was added, deionized water was added to achieve 100% moisture. These samples were shaken for approximately 12 hours at 250 rpm, and then centrifuged for 5 minutes at 2000 rpm. The supernatant was then decanted, and the residue was then rinsed two times in 0.001 M $CaCl_2$. After rinsing, the samples were aged for 35 days in an aging apparatus at 100% moisture content. Equation A.1 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.

$$\%\ \text{Moisture} = \frac{wet - dry}{dry} \cdot 100 \tag{A.1}$$

The sample vials were partially covered with parafilm during the aging process to minimize evaporation while remaining open to the atmosphere. The aging apparatus, shown in Appendix C, 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. After aging for 35 days, the soils were air dried until all moisture was completely removed. Duplicate subsamples of 0.1 gram weight were removed and analyzed as described below.

Physiologically Based Extraction Test (PBET)

A streamlined version (Kelley 2002) of the physiologically based extraction test (PBET) originally developed by Ruby et al. (1996) was used to determine the bioaccessibility of As in the soil with and without amendment additions. 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.

Stock PBET solution was made using a 0.4 M Glycine (*Fisher Scientific, G48*) solution adjusted to a pH of 1.5 ± 0.01 using trace metal grade, 12.1 M concentrated hydrochloric acid. The solution pH was adjusted to 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 heated water bath (Appendix C) 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 1.5. The streamlined procedure was originally designed for 1 g of each soil immersed in 100 mL of PBET solution. However, the procedure was modified for 0.1 g soil and 10 mL of PBET solution, maintaining the same soil-to-solution ratio (Yang, Barnett et al. 2005). During the 1 hour extraction period, the water temperature in the bath was maintained at 37 ± 2^{o}C. After extraction, the samples were removed from the water bath and centrifuged at approximately 2000 rpm for five minutes to aid with filtration. The supernatant was then decanted and filtered through a 0.45 µm nylon media syringe disk filter (Fisher-Scientific), mimicking the 0.5 µm particle cutoff for absorption of the epithelial cells in the small intestine. The filtrates were then placed in 20 mL polyethylene vials and preserved at 4^{o} C until analysis, when they 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 As with each PBET extraction performed for quality assurance/quality control. Approximately one-quarter of the remaining PBET residues were digested by EPA Method 3050B (U.S. EPA, 1994) and analyzed for As to verify a mass balance of ±10%.

As bioaccessibility was calculated as a percentage according to Equation A.2. (See example calculations in Appendix C)

$$\%\text{As Bioaccess.} = \left(\frac{\text{As in PBET supernatant (mg/L)} * \text{Volume of PBET solution (L)}}{\text{Wt. of dry soil (kg)} * \text{Total As from Method 3050B (mg/kg)}} \right) * 100 \qquad \text{(A.2)}$$

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 As using a Perkin Elmer 3110 graphite furnace atomic adsorption spectrometer (GFAA). Equipment calibration was performed using matrix-matched standards with a range of 20 to 100 $\mu g \cdot L^{-1}$ As concentrations.

Results

Ferric Chloride Amendment

34 As-Spiked soil samples were divided into four equal portions, amended with $FeCl_3$ (0, 100, 250, 500 mol Fe: mol As) and aged for approximately one month. Samples that received no $FeCl_3$ had an average bioaccessibility of 33.4 %. Ten soils had a non-amended bioaccessibility equal to or greater than 50.0% (high: 76.0 %), while four samples had an initial bioaccessibility less than 5.0% (low: 1.3 %). The average pH of the control soils after the aging process was 5.85. Eight soils had a pH higher than 7.0 (high: 7.89) and eight soils had a pH of less than 5.0 (low: 4.31).

As a result of adding increasing amounts of ferric chloride to the As-spiked soil samples, average bioaccessibility decreased at each stage of amendment addition. For amendment additions of 100, 250, and 500 (mol Fe: mol As), bioaccessibility on average was 17.4, 12.6, and 10.6 %, respectively (Figure A.1). Most bioaccessibility reduction was observed at 100:1, where all 34 samples showed a decrease in bioaccessibility. From the 100:1 amendment addition to the 250 and 500:1 Fe:As additions, average bioaccessibility was reduced; some samples showed minimal to no decrease in bioaccessibility (Figure A.1).

The pH of the amended samples was lower than control samples, due to the addition of $FeCl_3$, a Lewis Acid. At the minimum amendment addition, average pH decreased from 5.85 (control samples) to 3.31 (100:1 amended samples). The pH continued to decrease up to the 500:1 amendment addition, but only slightly (2.66). Five samples showed resistance to pH change upon amendment addition. These soils had a relatively higher TIC content (0.67 % average) which likely acted as a pH buffer. The drastic change in soil pH for these experiments led to the use of calcium hydroxide as a co-amendment with $FeCl_3$, to keep the pH stable.

Calcium Hydroxide and Ferric Chloride Amendment

Thirty-four As spiked samples were amended with 100:1 mol Fe: mol As via ferric chloride as well as an amount of $Ca(OH)_2$ that was stoichiometrically (3 moles $Ca(OH)_2$ per 2 moles $FeCl_3$) equal to the $FeCl_3$ added. Remaining arsenic-spiked samples that were not used in the $FeCl_3$ experiments were used for these experiments. Additions of $Ca(OH)_2$ were to prevent a reduction in pH, in order to keep the soil close to its natural pH. The results from this test were compared to the results from the previously described 100:1 Fe: As test. The results from this test showed not only minimal change in pH of the amended soil samples, but bioaccessibility was decreased even more so than when $FeCl_3$ was added alone (Figure A.2). While the average pH of the samples for 100:1 Fe:As was reduced from 5.85 to 3.31, samples with the $Ca(OH)_2$ additions had an average pH of 5.46, much less of a change. Average bioaccessibility was reduced from 34.21% to 8.69% with $Ca(OH)_2$ additions with $FeCl_3$, where average bioaccessibility with $FeCl_3$ alone was 17.23% (Figure A.2). These results are consistent with recent research revealing that Ca can help to immobilize As that is sorbed to $Fe(OH)_3(s)$ (Parks 2003). Parks (2003) further suggested that Ca helps to neutralize the negative surface charges on $Fe(OH)_3(s)$ solids, keeping commonly occurring anionic As (arsenate and arsenite) sorbed on Fe hydroxides (Parks 2003). No Ca-As precipitant was discovered, suggesting only sorption of As onto the $Fe(OH)_3$ (Parks 2003). Therefore, by adding a pH buffer, such as $Ca(OH)_2$, soil pH is kept stable even with $FeCl_3$ additions. In addition, Ca also keeps As bioaccessibility low due to the divalent cation effect and strong As retention of $Fe(OH)_3$.

Table A.1. Soil Properties for As-Spiked Soils #1-35

				pH				Particle Size (%)		
Sample #	Sample Name	DCB-Fe (avg) (mg/kg)	DCB-Mn (avg) (mg/kg)	DDI	5mM $CaCl_2$	TOC (%)	TIC (%)	Clay	Silt	Sand
1	Oricto Bt	6009	201.55	9.05	8.10	0.15	0.51	13	21	66
2	Norfolk A	3531	22.55	7.41	7.21	0.35	0.23	7	14	79
3	Norfolk B	22338	5.00	7.35	6.65	0.26	0.03	41	16	43
4	Towaliga B	19306	23.35	6.25	4.64	0.25	0.08	33	22	45
5	Sibley A	9780	477.45	6.36	5.89	1.45	0.04	23	55	22
6	Sibley B	10566	452.65	6.58	6.03	1.06	0.16	29	53	18
8	Oricto A1	4403	235.85	8.67	7.93	0.19	0.30	6	23	71
9	San Ysidro A	6133	264.75	7.05	6.67	1.07	0.00	25	30	45
10	Doakum Bf	5856	131.05	7.93	7.67	0.26	0.08	17	17	66
11	Crider A	10167	1201.5	7.38	7.05	1.10	0.19	16	74	10
12	Stoneham B	3389	83.95	N/D	6.8	0.88	0.06	27	25	48
13	Cecil Bt	54220	81.25	6.66	6.45	0.32	0.06	50	18	32
14	Wakeland A1	9317	449.55	6.24	5.88	0.83	0.06	25	58	17
15	Towaligz Ap	5427	75.05	5.44	4.47	0.72	0.01	15	20	65
16	Wakeland A2	9576	532.4	5.91	5.36	0.69	0.06	24	50	26
17	Angola B	11797	27.55	5.04	4.42	0.18	0.04	33	60	7
18	San Ysidro B	5881	224.9	7.58	6.87	0.42	0.03	31	27	42
19	Angola Ap	15590	632.5	5.63	5.27	2.29	0.38	23	59	18
20	Oricto A2	4378	230.5	8.83	8.11	0.12	0.66	12	34	54
21	Kzin B	4489	233.6	8.29	7.87	1.18	1.04	20	44	36
22	Crider B	15220	470.2	6.34	5.90	0.69	0.14	21	62	17
23	Decatur A	29510	2940	6.12	5.39	0.50	0.07	35	45	20
24	Lenberg B	11053	419.1	4.88	4.28	2.12	0.11	24	49	27
25	Kzin A	5362	316.9	8.25	7.83	1.04	0.86	25	43	32
26	Robertsville A	10912	442.8	5.44	5.02	2.31	0.21	25	50	25
27	Wakeland A3	9224	432.25	5.70	5.23	0.47	0.00	21	49	30
28	Stoneham A	3073	98.9	N/D	6.42	1.08	0.00	14	23	63
29	Doakum A	3482	147.5	6.99	6.27	0.43	0.07	8	19	73
30	Lenberg A	10534	1063	5.16	4.67	1.88	0.36	19	52	29
31	Rocky Mtn. Arsenal-clean	N/D	N/D	N/D	N/D	N/D	N/D	N/D	N/D	N/D
32	Melton Valley A	10680	1420	7.18	6.91	3.55	0.62	13.8	30	56.2
33	Melton Valley B	22070	170	4.87	4.23	0.42	0.26	18.8	50.4	30.8
34	Walker Branch A	7710	1510	6.61	6.01	1.89	0.99	6.2	58.9	34.9
35	Walker Branch B	19550	160	5.17	4.3	0.1	0.07	23.6	44.2	32.2

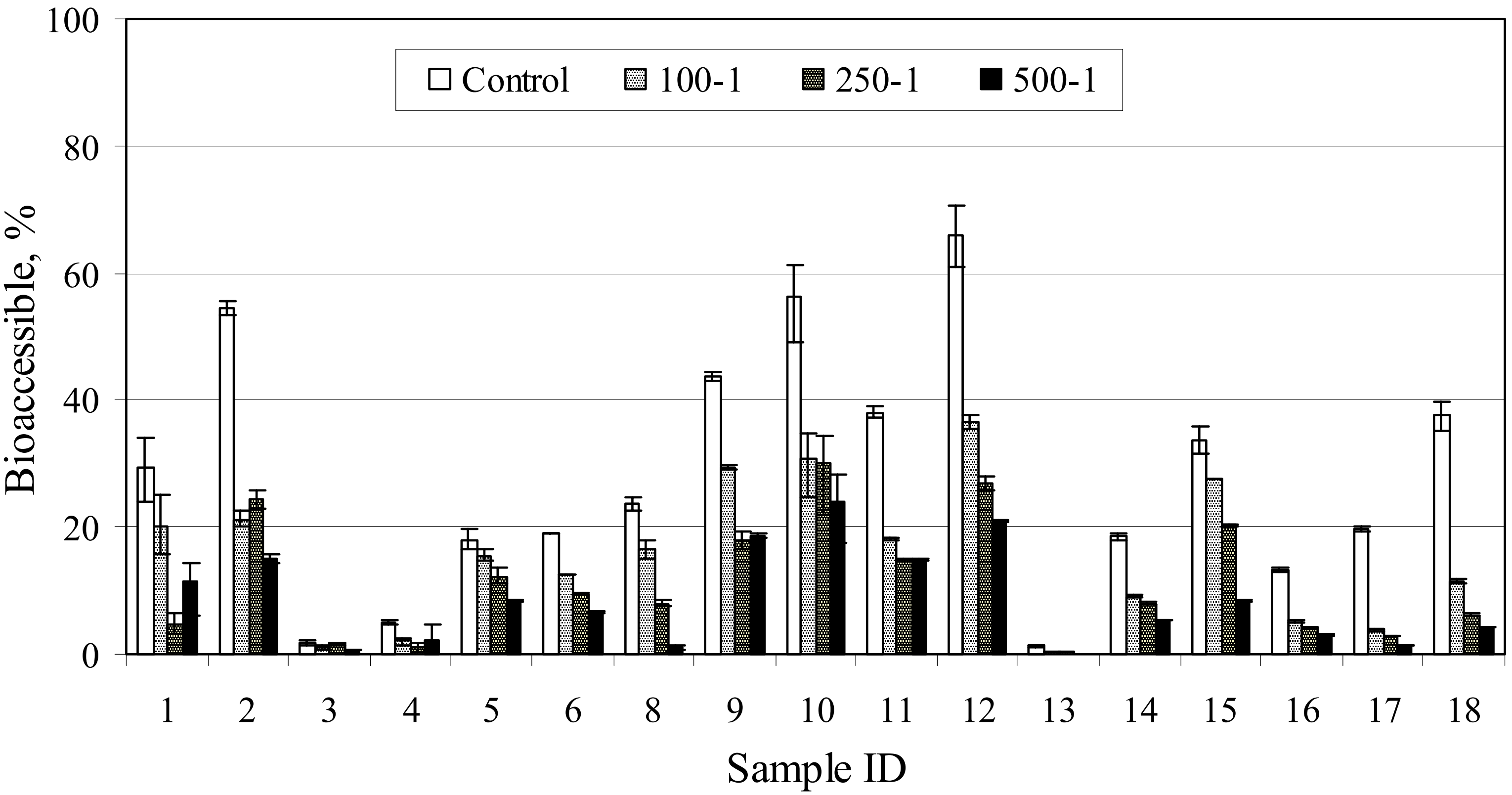

Figure A.1.a. Arsenic bioaccessibility values for As-spiked soil samples 1-18 for various Fe-As molar ratios (0, 100, 250, and 500) via $FeCl_3$ addition. Error bars indicate the range of bioaccessibility values recorded in duplicate PBET tests.

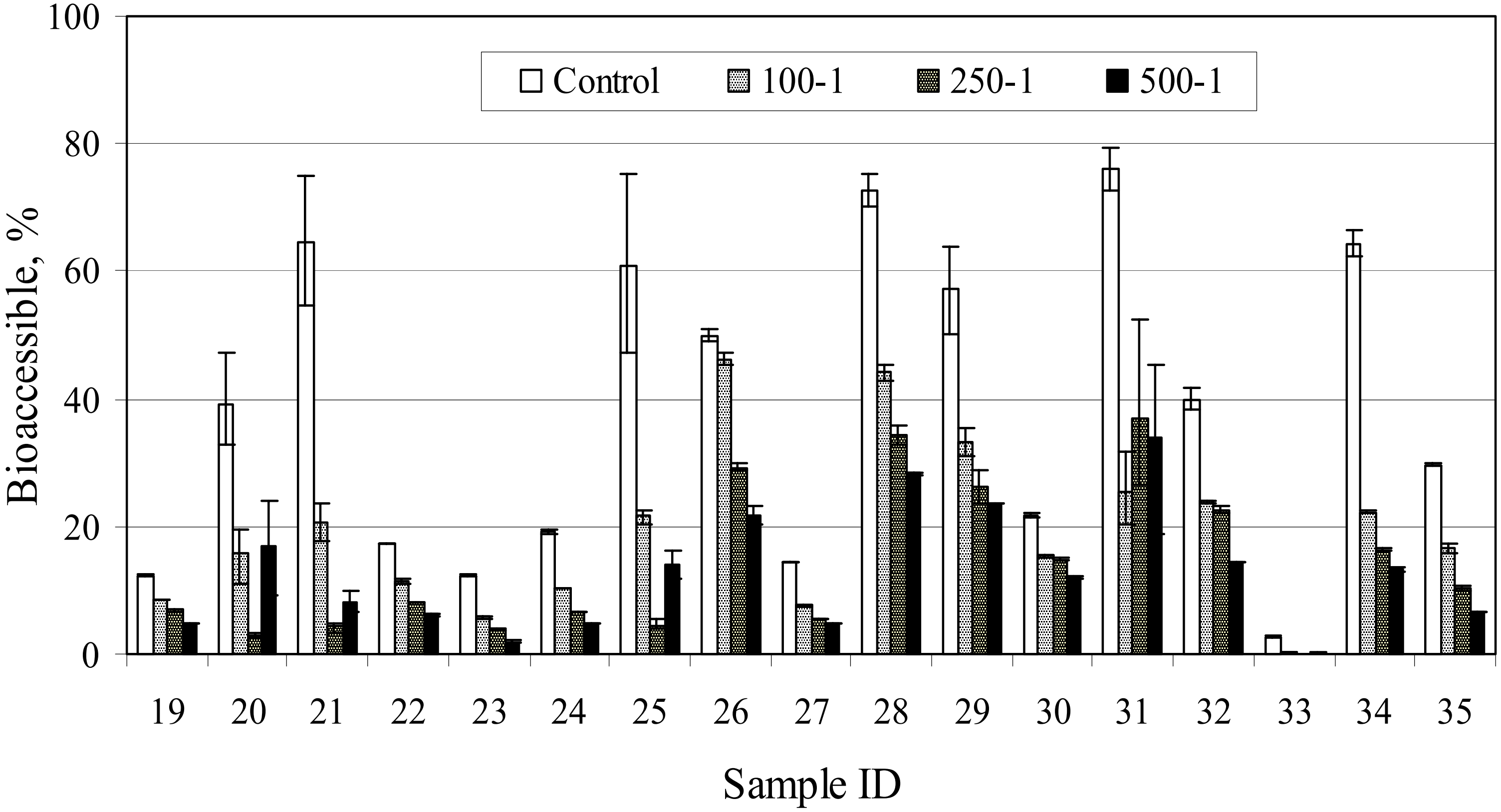

Figure A.1.b. Arsenic bioaccessibility values for As-spiked soil samples 19-35 for various Fe-As molar ratios (0, 100, 250, and 500) via $FeCl_3$ addition. Error bars indicate the range of bioaccessibility values recorded in duplicate PBET tests.

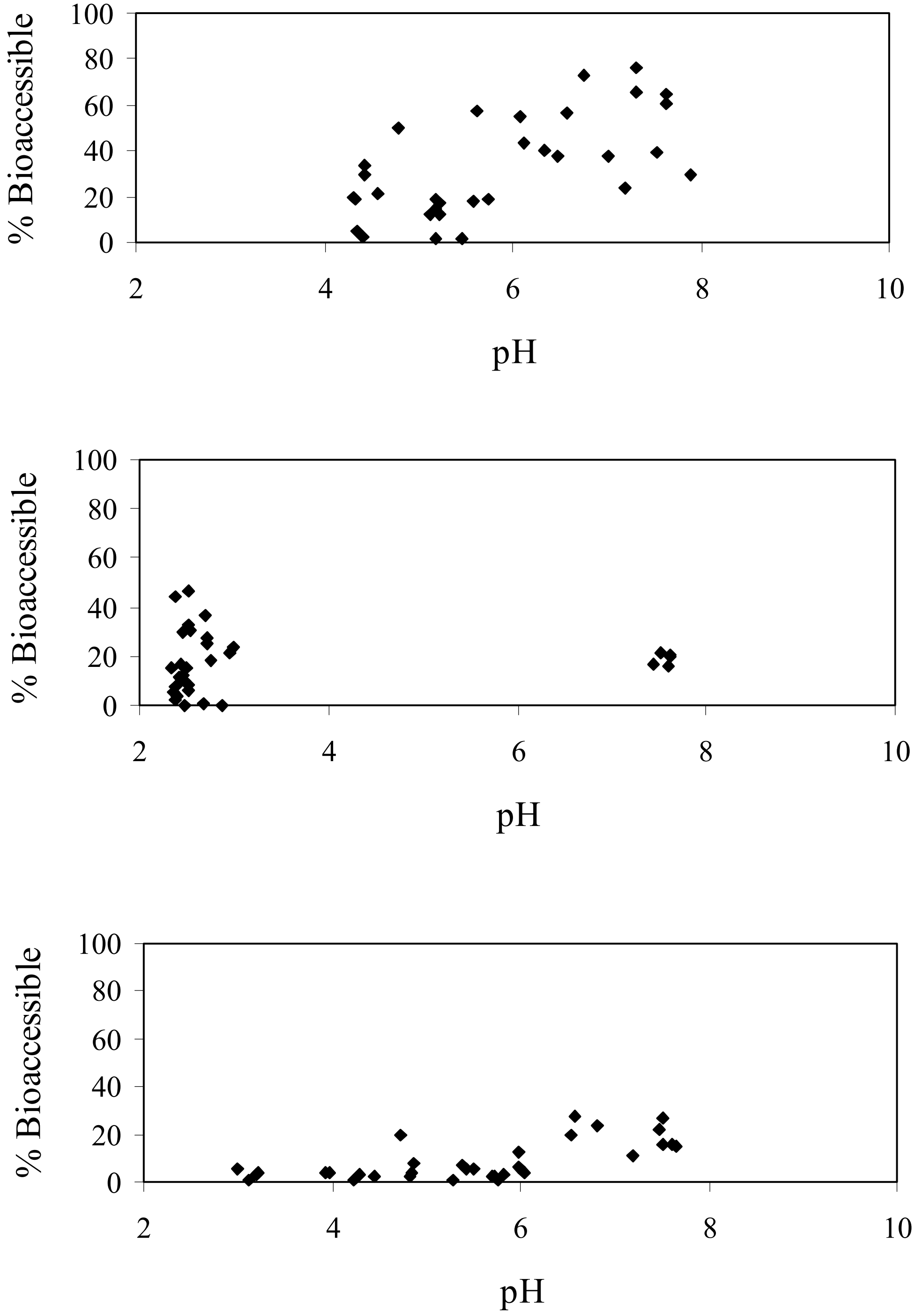

Figure A.2. Bioaccessibility vs. pH for control samples (A.2a); samples amended with 100:1 Fe:As via $FeCl_3$ (A.2b); samples amended with 100:1 Fe:As via $FeCl_3$ and $Ca(OH)_2$ (A.2c).

Table A.2. Bioaccessibility values (%) for soil samples.

Sample ID	Control	100:1	250:1	500:1	100:1 & $Ca(OH)_2$
	(%)	(%)	(%)	(%)	(%)
1	29.2	19.9	4.6	11.3	21.8
2	54.5	21.3	24.5	15.1	6.5
3	1.8	1.0	1.6	0.6	0.7
4	5.0	2.0	1.2	2.1	1.0
5	18.1	15.5	12.4	8.5	2.2
6	19.1	12.5	9.5	6.6	3.2
8	23.8	16.5	8.1	1.0	14.7
9	43.8	29.4	17.9	18.5	5.6
10	56.4	30.7	30.3	23.9	12.4
11	38.1	18.2	14.9	14.9	11.0
12	65.8	36.6	27.0	21.0	23.3
13	1.3	0.3	0.2	0.1	0.6
14	18.5	9.1	8.0	5.3	3.9
15	33.8	27.6	20.3	8.4	3.8
16	13.3	5.2	4.2	3.1	2.7
17	19.8	3.8	2.9	1.3	3.6
18	37.5	11.4	6.3	4.3	7.0
19	12.3	8.5	6.9	4.7	2.6
20	38.9	16.0	2.9	17.1	16.1
21	64.7	20.7	4.3	8.3	15.9
22	17.4	11.5	8.2	6.2	3.9
23	12.3	5.8	3.9	1.9	3.3
24	19.1	10.2	6.6	4.7	2.8
25	61.1	21.7	4.6	14.1	26.5
26	50.0	46.3	29.2	21.8	19.6
27	14.6	7.6	5.7	4.8	2.5
28	72.8	44.2	34.4	28.3	27.2
29	57.0	33.2	26.3	23.7	7.6
30	21.6	15.4	14.9	12.0	3.6
31	76.0	25.4	36.8	34.0	19.7
32	40.0	23.9	22.6	14.4	5.2
33	2.6	0.4	0.1	0.2	0.8
34	64.3	22.2	16.4	13.2	n/m
35	29.6	16.7	10.4	6.5	5.5

Data is shown for amendment additions of 0, 100, 250, and 500 moles of Fe to moles of As, as well as data for 100:1 Fe to As amendment addition with a stoichiometric amount of $Ca(OH)_2$ to neutralize pH change.

Appendix B

Supporting Data for Chapter 3

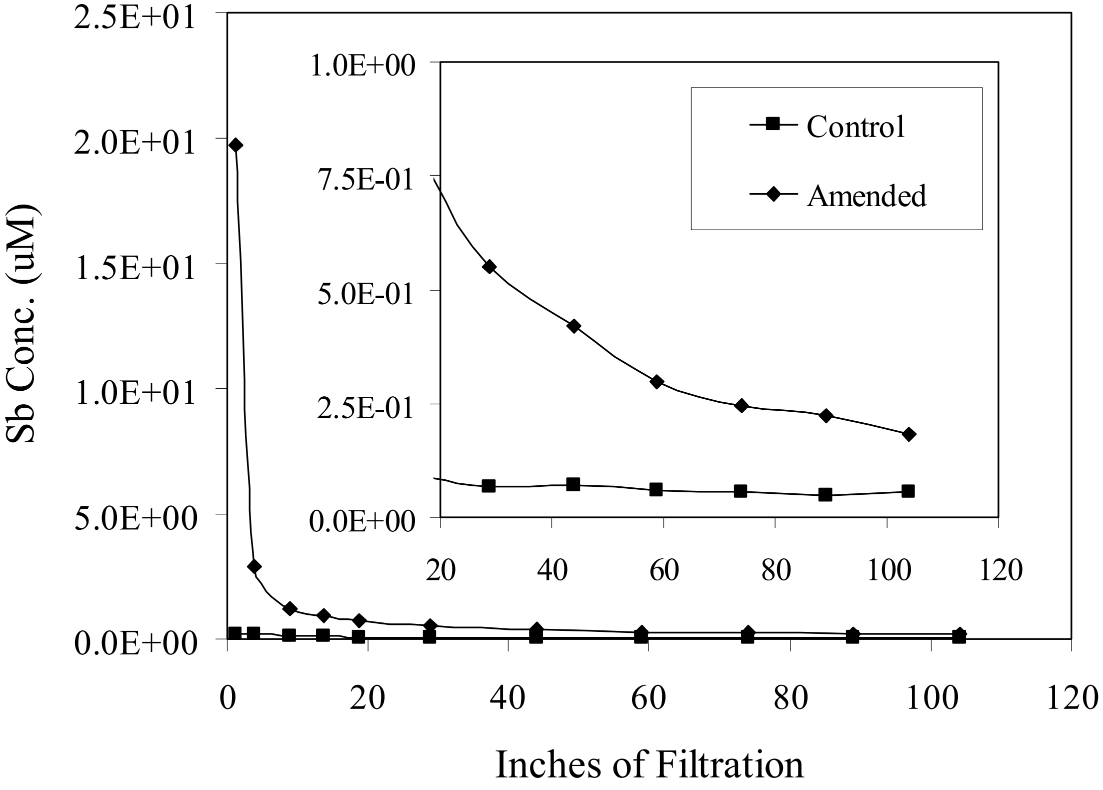

Figure B.1.a. Antimony leachate concentrations versus infiltration through the amended and control columns for the first column test; Soil 4 (15.3 cm.hour^{-1}; 5 % P addition via TSP). Amended indicates soil column with TSP addition; control indicates soil column without TSP.

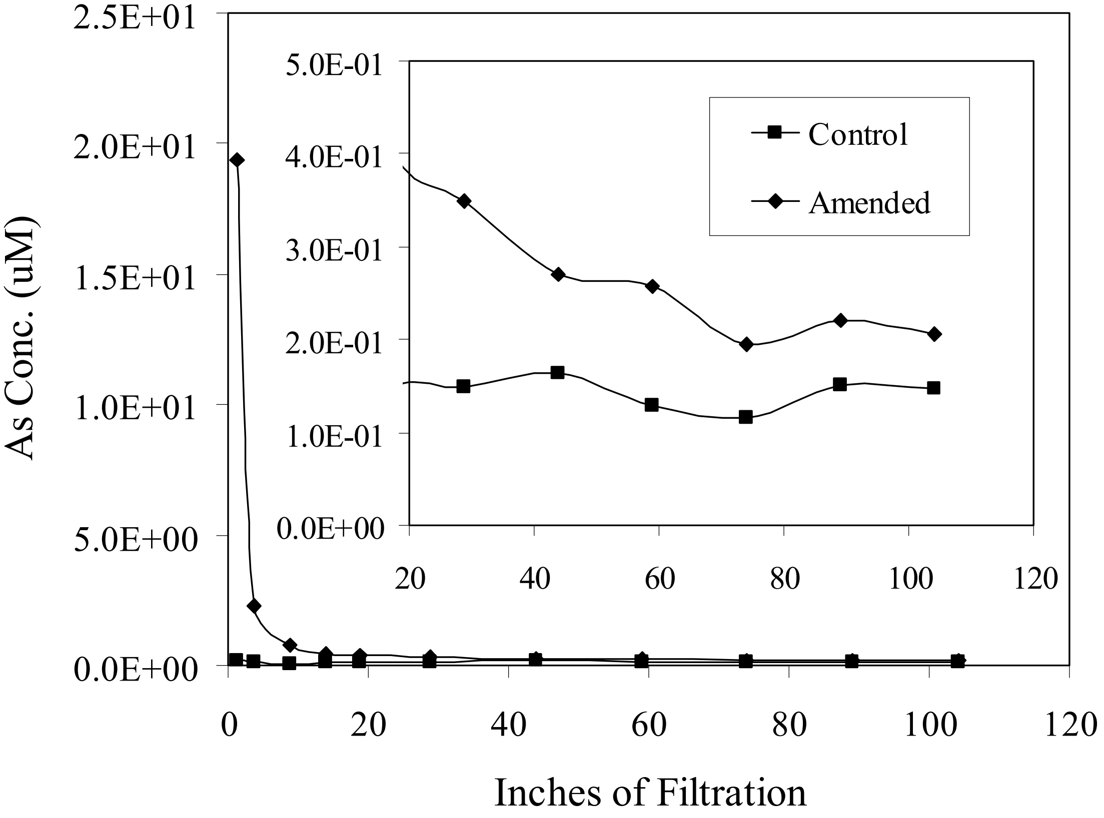

Figure B.1.b. Arsenic leachate concentrations versus infiltration through the amended and control columns for the first column test; Soil 4 (15.3 cm.hour^{-1}; 5 % P addition via TSP). Amended indicates soil column with TSP addition; control indicates soil column without TSP.

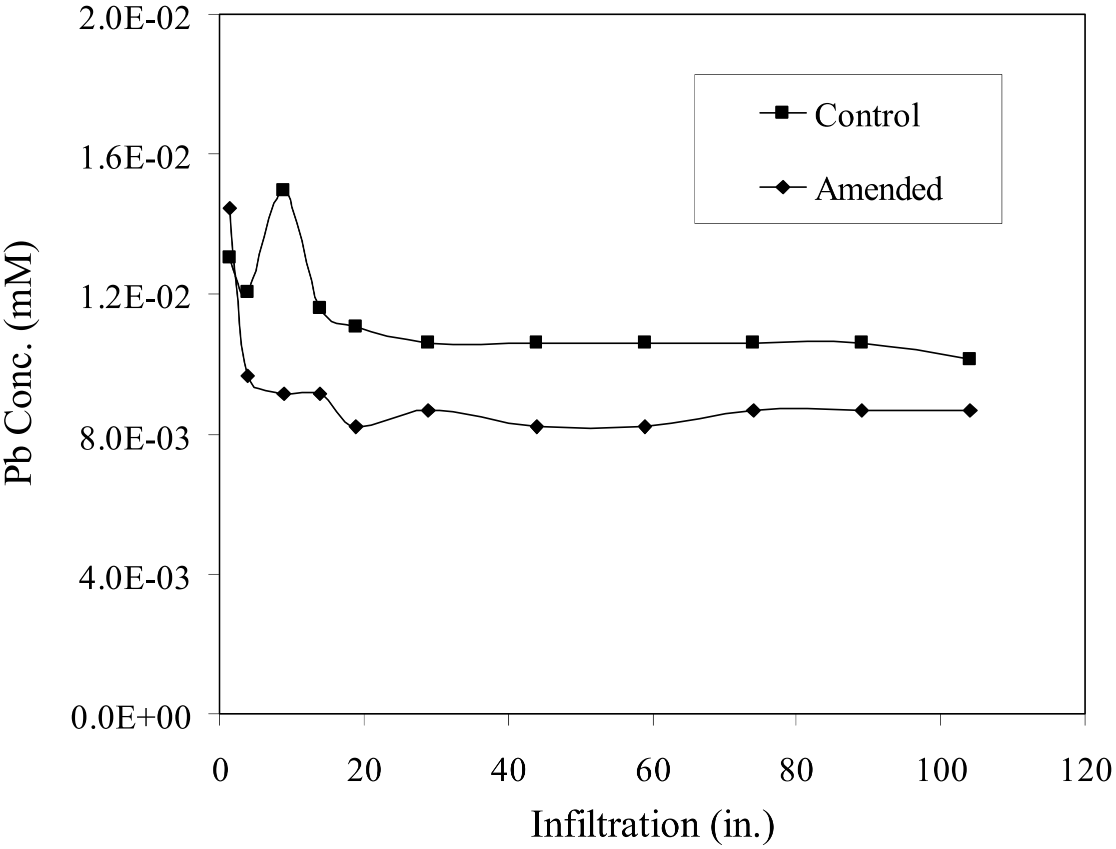

Figure B.1.c. Lead leachate concentrations versus infiltration through the amended and control columns for the first column test; Soil 4 (15.3 cm.hour^{-1}; 5 % P addition via TSP). Amended indicates soil column with TSP addition; control indicates soil column without TSP.

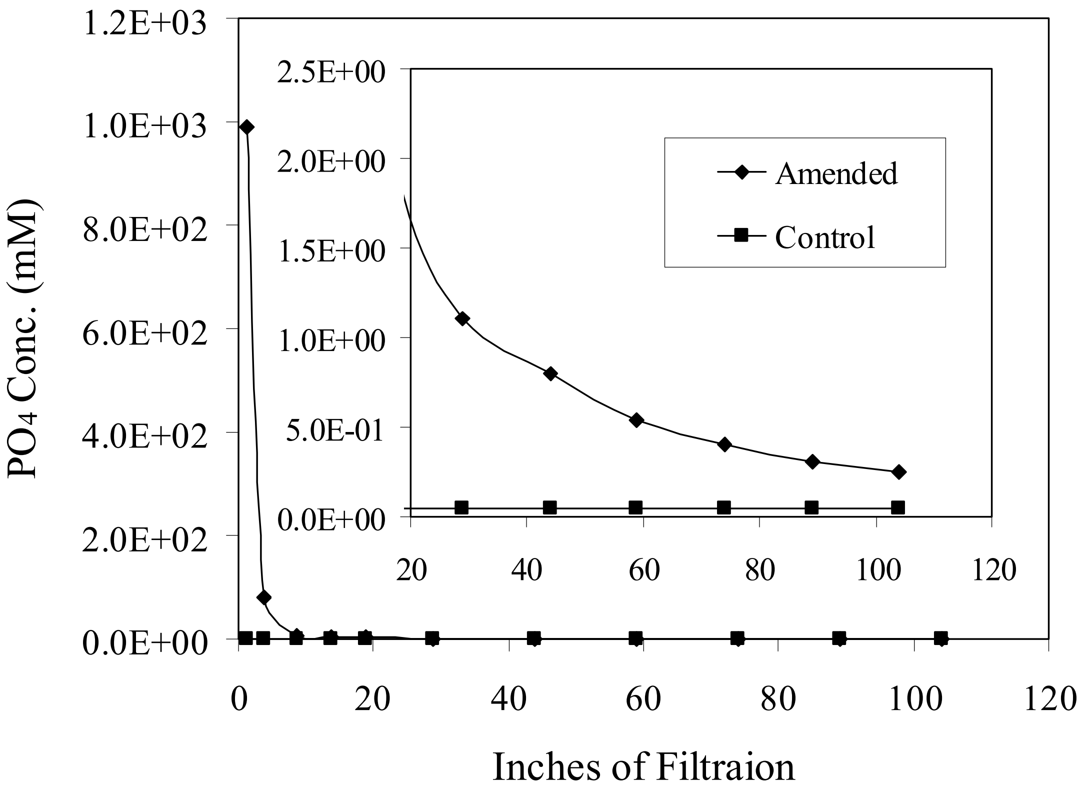

Figure B.1.d. Phosphate leachate concentrations versus infiltration through the amended and control columns for the first column test; Soil 4 (15.3 cm.hour^{-1}; 5 % P addition via TSP). Amended indicates soil column with TSP addition; control indicates soil column without TSP.

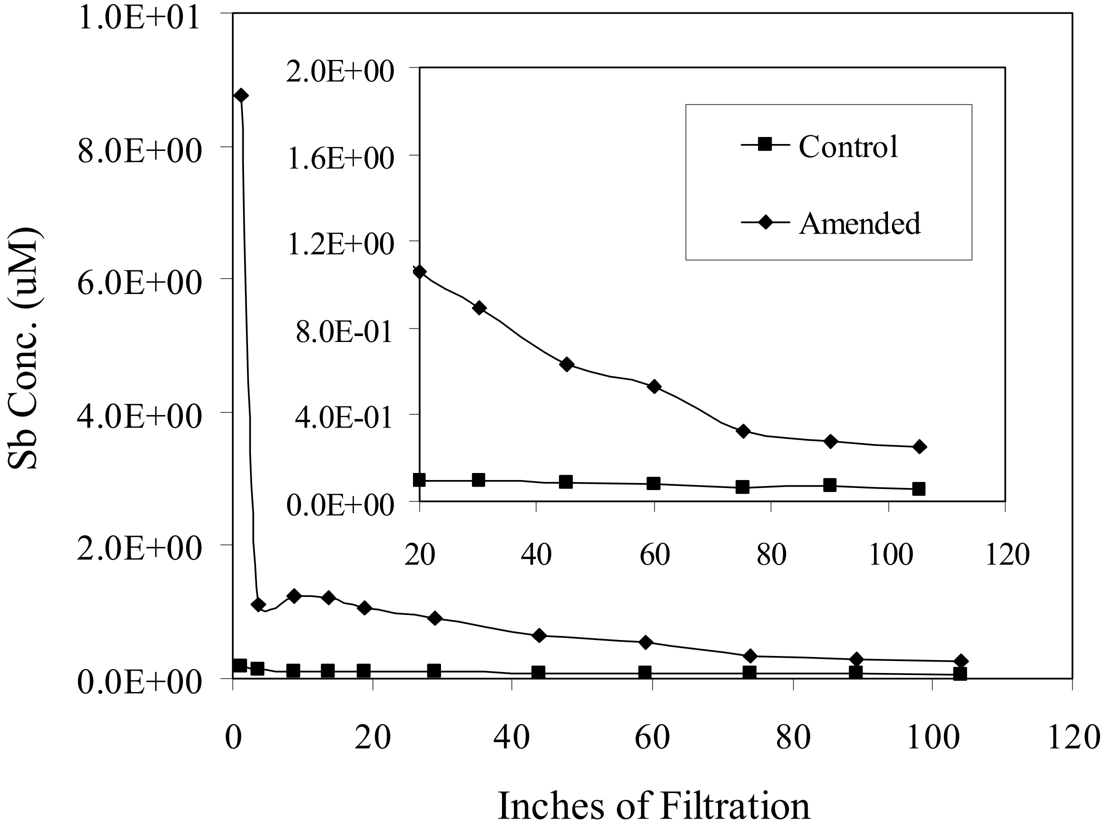

Figure B.2.a. Antimony leachate concentrations versus infiltration through the amended and control columns for the first column test; Soil 3 (15.3 cm.hour^{-1}; 5 % P addition via TSP). Amended indicates soil column with TSP addition; control indicates soil column without TSP.

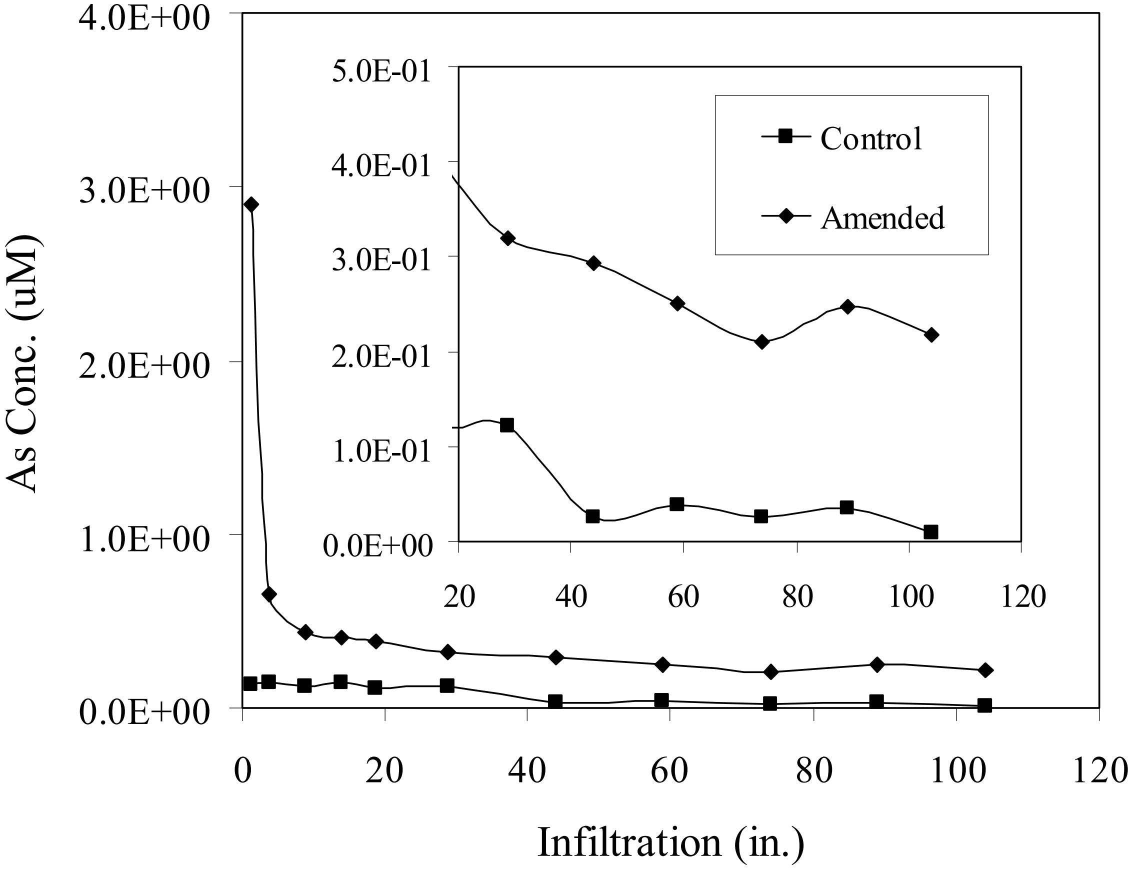

Figure B.2.b. Arsenic leachate concentrations versus infiltration through the amended and control columns for the first column test; Soil 3 (15.3 cm.hour^{-1}; 5 % P addition via TSP). Amended indicates soil column with TSP addition; control indicates soil column without TSP.

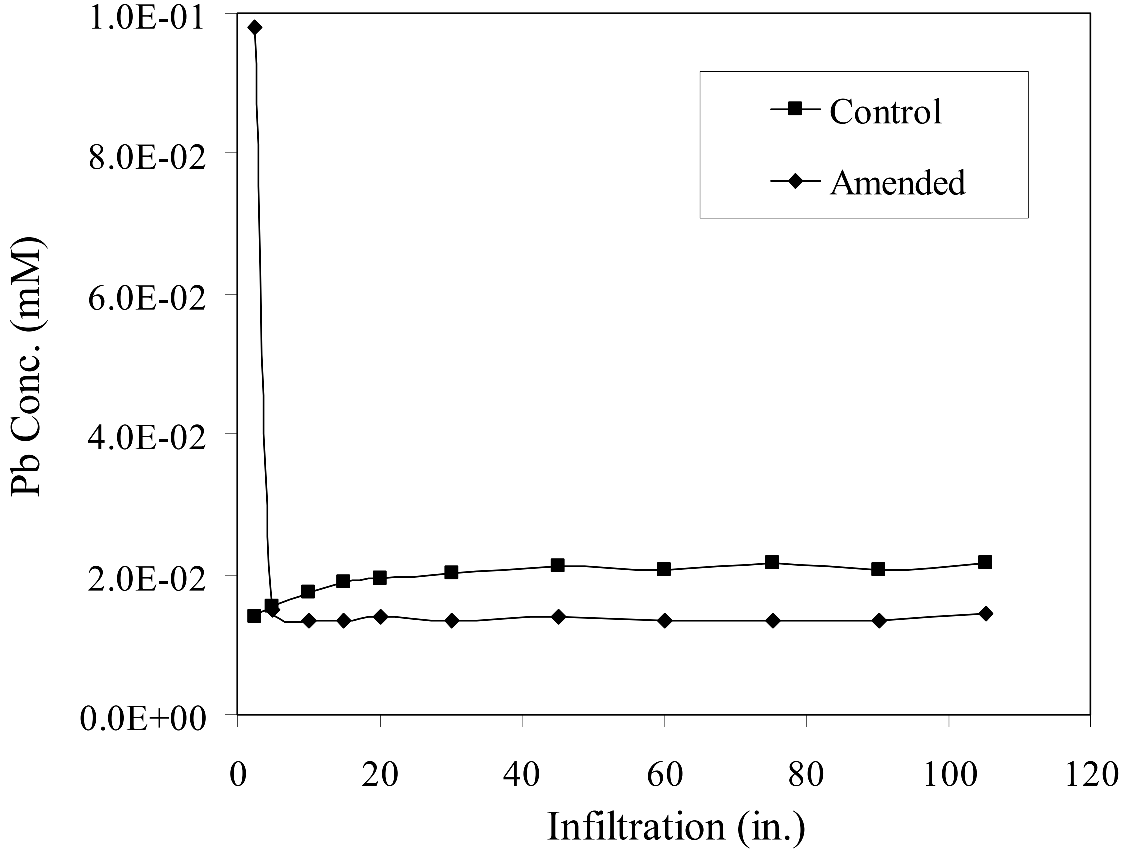

Figure B.2.c. Lead leachate concentrations versus infiltration through the amended and control columns for the first column test; Soil 3 (15.3 cm.hour^{-1}; 5 % P addition via TSP). Amended indicates soil column with TSP addition; control indicates soil column without TSP.

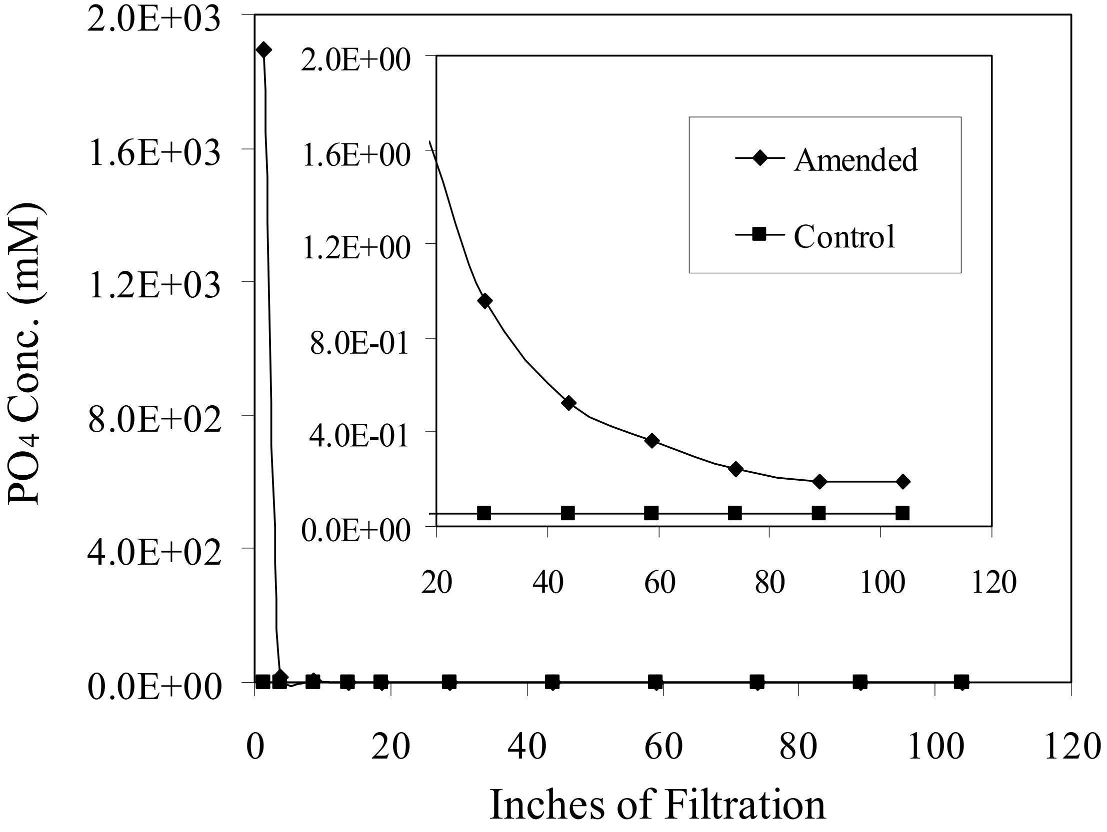

Figure B.2.d. Phosphate leachate concentrations versus infiltration through the amended and control columns for the first column test; Soil 3 (15.3 cm.hour^{-1}; 5 % P addition via TSP). Amended indicates soil column with TSP addition; control indicates soil column without TSP.

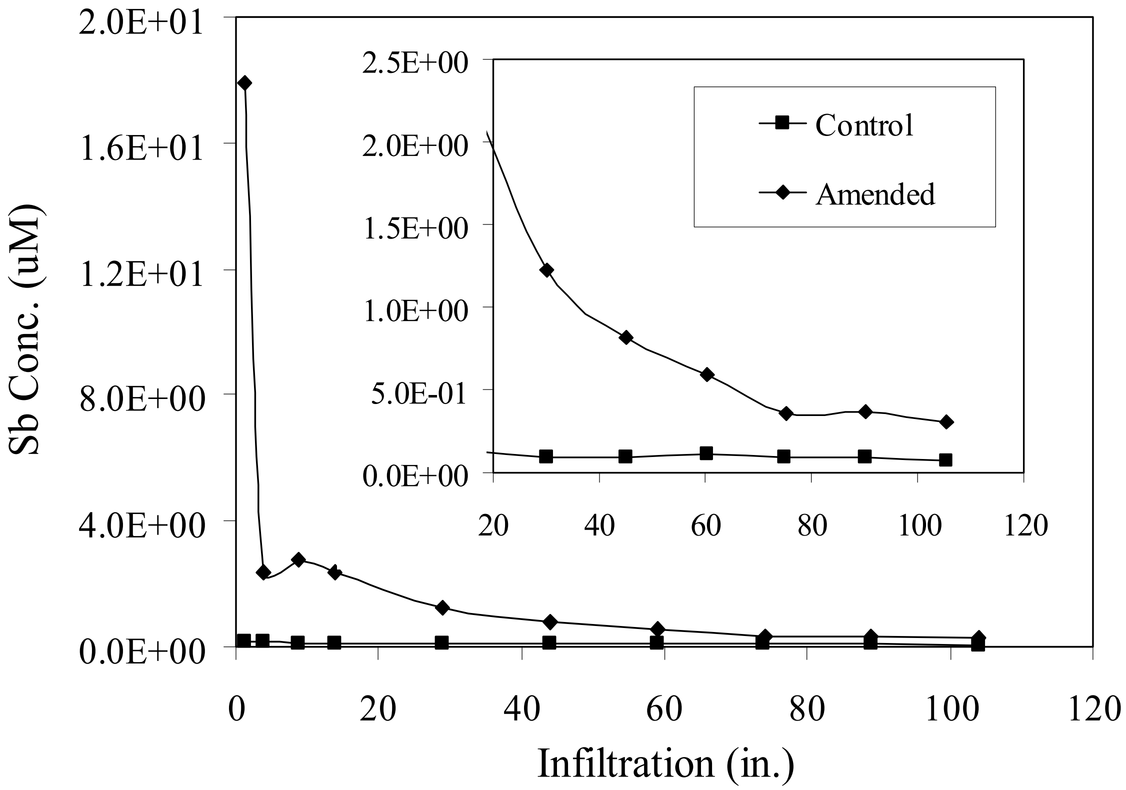

Figure B.3.a. Antimony leachate concentrations versus infiltration through the amended and control columns for the second column test; Soil 4 (1.53 cm.hour^{-1}; 5 % P addition via TSP). Amended indicates soil column with TSP addition; control indicates soil column without TSP.

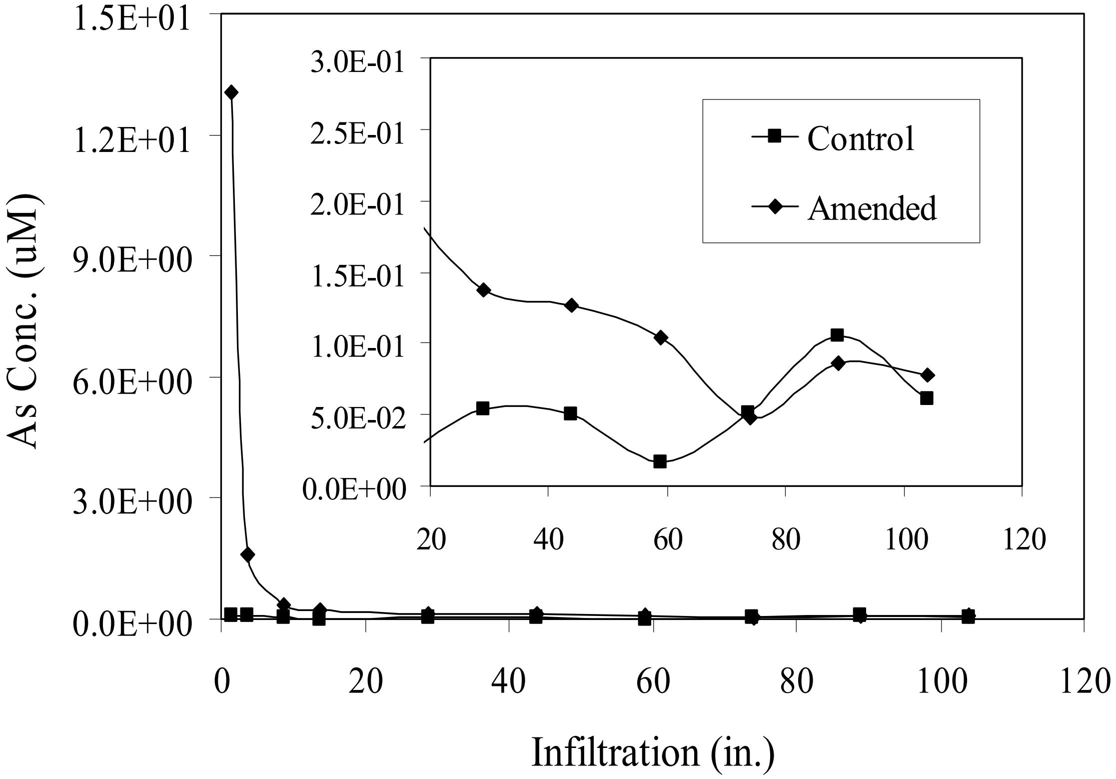

Figure B.3.b. Arsenic leachate concentrations versus infiltration through the amended and control columns for the second column test; Soil 4 (1.53 cm.hour^{-1}; 5 % P addition via TSP). Amended indicates soil column with TSP addition; control indicates soil column without TSP.

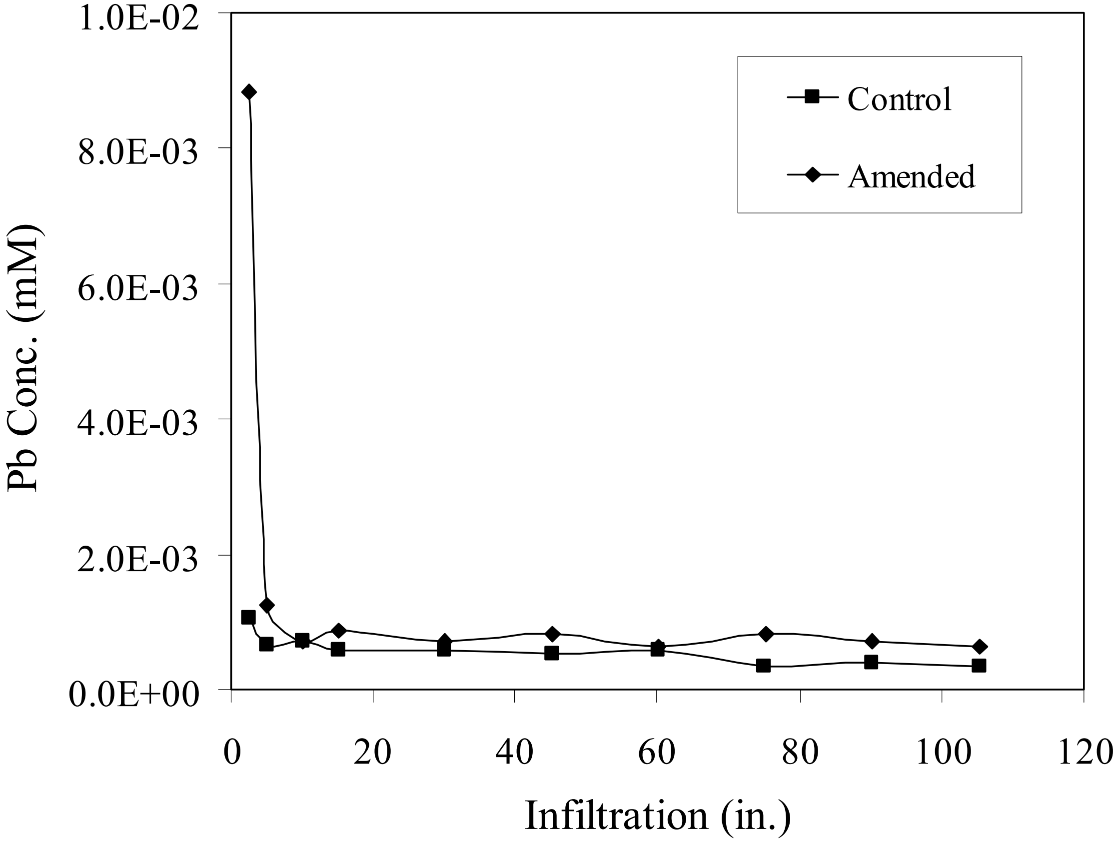

Figure B.3.c. Lead leachate concentrations versus infiltration through the amended and control columns for the second column test; Soil 4 (1.53 cm.hour^{-1}; 5 % P addition via TSP). Amended indicates soil column with TSP addition; control indicates soil column without TSP.

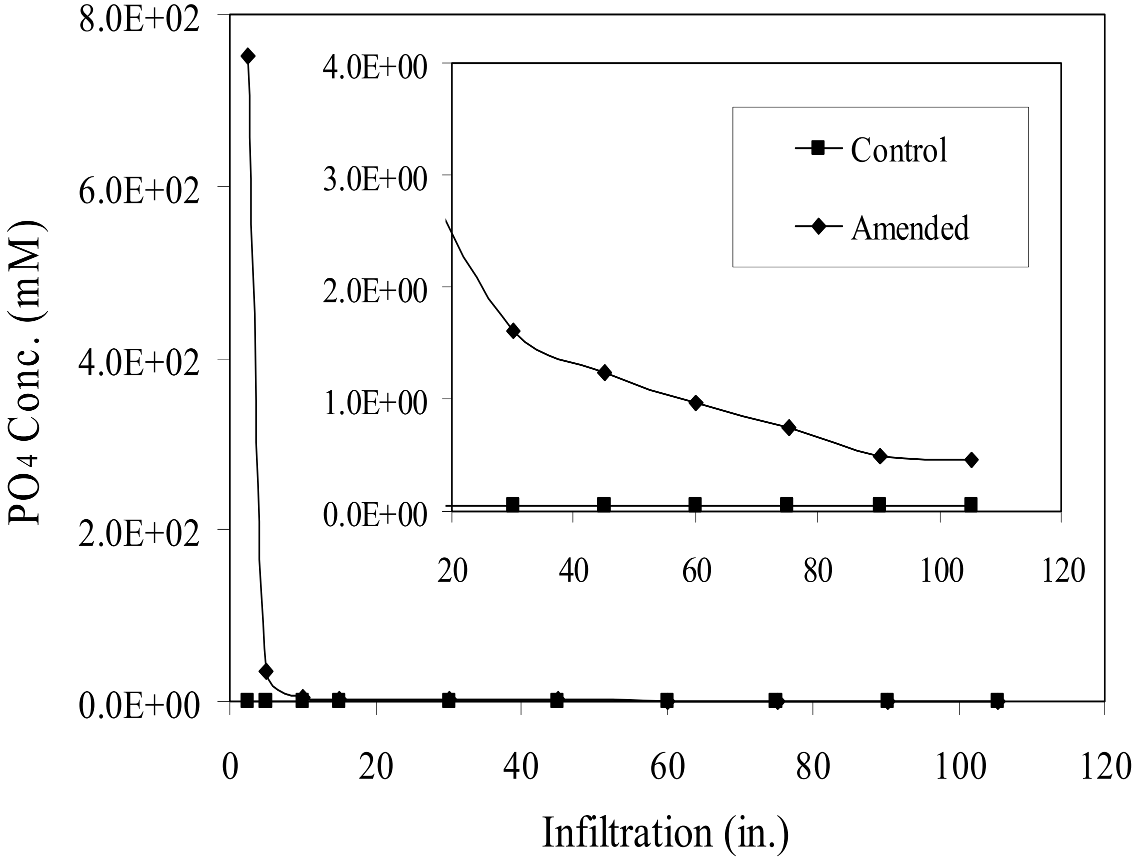

Figure B.3.d. Phosphate leachate concentrations versus infiltration through the amended and control columns for the second column test; Soil 4 (1.53 cm.hour^{-1}; 5 % P addition via TSP). Amended indicates soil column with TSP addition; control indicates soil column without TSP.

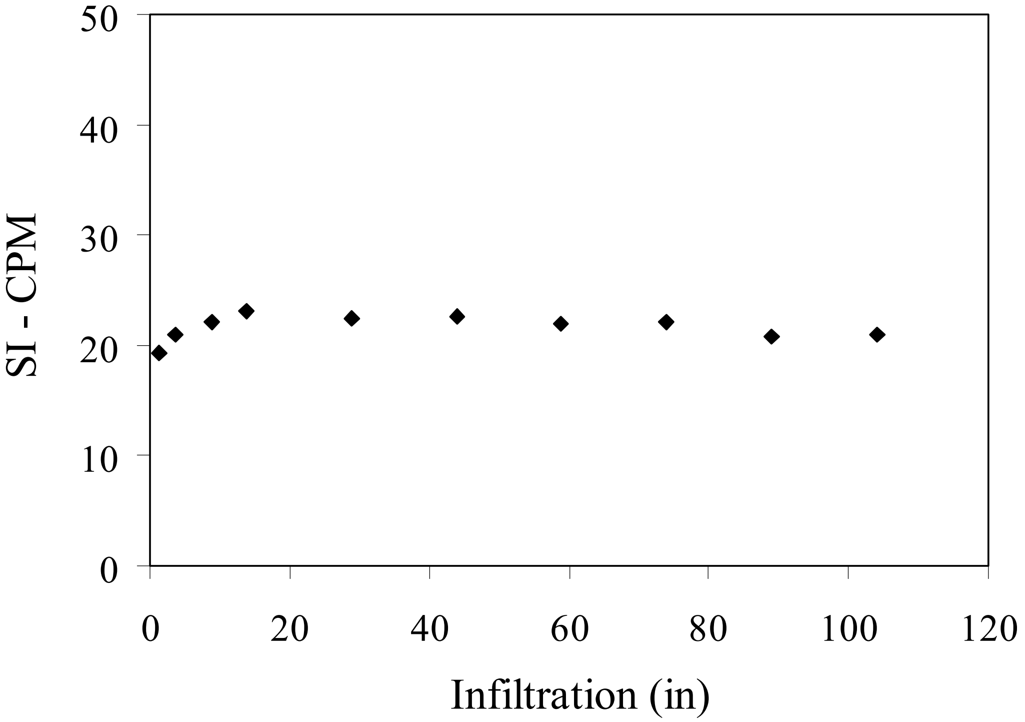

Figure B.4. Saturation indexes for chloropyromorphite versus infiltration for Soil 4, second column tests (TSP amended column effluents only). SI was modeled in Visual Minteq.

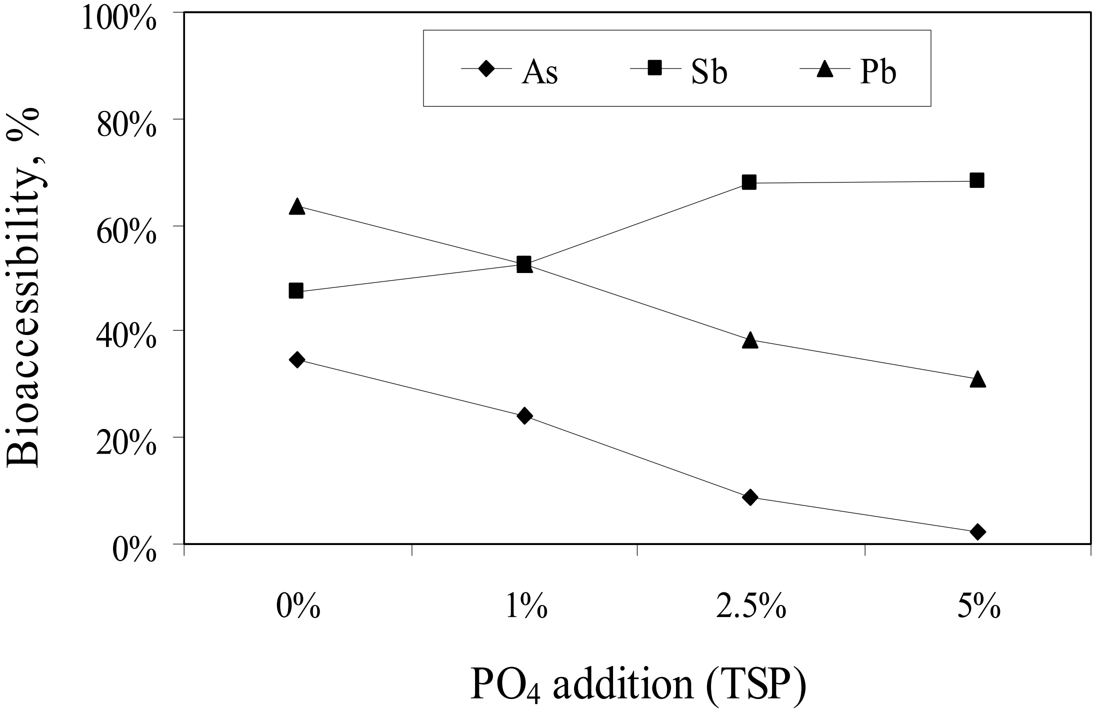

Figure B.5.a. Bioaccessibility values for arsenic, antimony, and lead versus phosphate addition by soil weight for Soil 4, trial 2.

(Bioaccessibility = PBET quantity leached / total quantity in soil).

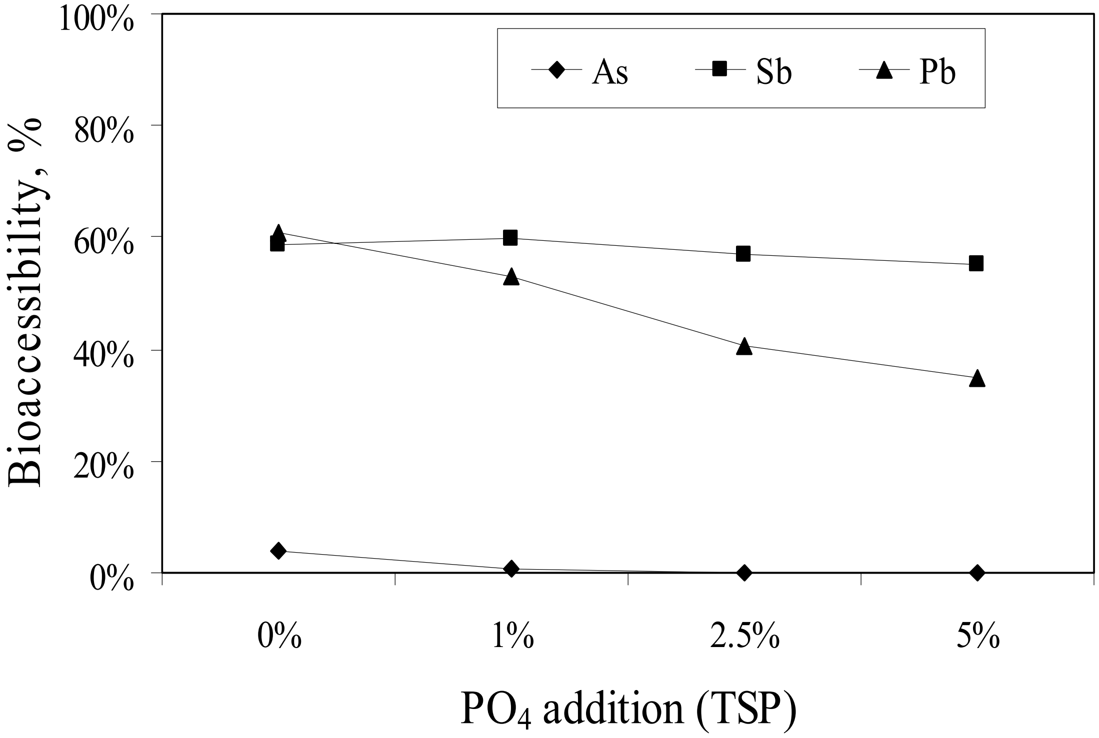

Figure B.5.a. Bioaccessibility values for arsenic, antimony, and lead versus phosphate addition by soil weight for Soil 3, trial 2.

(Bioaccessibility = PBET quantity leached / total quantity in soil).

Appendix C

Example calculations for the addition of TSP amendment for 5% P addition. (chapter three)

Given: 4.00 g of dry soil, 5% P added from TSP; TSP = 45% P_2O_5 = 19.8% P

From Equation 3.1:

$$\text{Amend. Added (g)} = \frac{(4.00\text{ g}) * 5\%\text{ P}}{19.8\%\text{ P}} = 1.01\text{ g}$$

Example calculations for the addition of $FeCl_3$ amendment in doses of 100, 250, and 500 mol Fe: mol As to 2.00 g of dry soil with assumed 100 mg/kg As.

100 mg As / kg soil * 2 g soil = 0.2 mg As (each vial of soil)

0.2 mg As * 1 mmol / 75 mg = 0.00267 mmol As (each vial of soil)

<u>For 100:1 addition</u>:

0.00267 mmol As * 100 mmol $FeCl_3$ = 0.267 mmol $FeCl_3$ (add to each vial)

0.267 mmol $FeCl_3$ * 162.2 mg / mmol = 43.31 mg $FeCl_3$ (add to each vial)

0.0433 g $FeCl_3$ / (1.33 M FeC_{l3} * 162.2 g / mol) = 0.0002 L or 0.2 mL

Add 0.2 mL of 1.33 M $FeCl_3$ solution to each vial for 100:1 addition

Appendix C (cont.)

Example calculations for % Pb Bioaccessibility for Soil 4 calculated from batch tests in Chapter 3.

Example 1 – 0%P added

Given: Pb in PBET supernatant (mg/L) = 54.5

Vol. of PBET solution (L) = 0.01

Wt. of dry soil only (kg) = 1.00 E-4

Total Pb for soil #6 from Method 3050B (mg/kg) = 8975

$$\% \text{ Pb Bioaccess.} = \frac{(54.5 \text{ mg/L}) * (0.010 \text{ L})}{(1.00 \text{ E-4 kg}) * (8975 \text{ mg/kg})} *100 = 60.7\%$$

Example 2 – 2.5%P added via TSP

Given: Pb in PBET supernatant (mg/L) = 37.1

Vol. of PBET solution (L) = 0.010

Wt. of dry soil only (kg) = 1.00 E-4 - (1.00 E-4 * 0.125) = 8.75 E-5

Total Pb for soil #6 from Method 3050B (mg/kg) = 8975

$$\% \text{ Pb Bioaccess.} = \frac{(37.1 \text{ mg/L}) * (0.010 \text{ L})}{(8.75\text{E-5 kg}) * (8975 \text{ mg/kg})} *100 = 47.2\%$$

Appendix E.1. Visual Minteq Saturation Index Data Sheet for 7-day Aged Column Test Effluents. (0-2.5 Inches Infiltration)

Mineral	log IAP	Sat. Index	Stoichiometry						
Arsenolite	-8.565	-7.185	2	H3AsO3	-3	H2O			
Ca3(PO4)2 (beta)	-31.96	-3.04	3	Ca+2	2	PO4-3			
Ca4H(PO4)3:3H2O	-50.958	-3.878	4	Ca+2	1	H+1	3	PO4-3	H2O
CaHPO4	-18.978	0.297	1	Ca+2	1	H+1	1	PO4-3	
CaHPO4:2H2O	-18.991	0.004	1	Ca+2	1	H+1	1	PO4-3	H2O
Claudetite	-8.565	-7.225	2	H3AsO3	-3	H2O			
Cotunnite	-12.516	-7.736	1	Pb+2	2	Cl-1			
Hydroxyapatite	-44.949	-0.616	5	Ca+2	3	PO4-3	1	H2O	H+1
Hydroxylpyromorphite	-57.158	5.632	5	Pb+2	3	PO4-3	1	H2O	H+1
Laurionite	-4.488	-5.111	-1	H+1	1	Pb+2	1	Cl-1	H2O
Lime	5.989	-26.711	-2	H+1	1	Ca+2	1	H2O	
Litharge	3.547	-9.143	1	Pb+2	1	H2O	-2	H+1	
Massicot	3.547	-9.343	1	Pb+2	1	H2O	-2	H+1	
Pb(OH)2	3.54	-4.61	-2	H+1	1	Pb+2	2	H2O	
Pb2(OH)3Cl	-0.947	-9.74	-3	H+1	2	Pb+2	3	H2O	Cl-1
Pb2O(OH)2	7.087	-19.103	2	Pb+2	3	H2O	-4	H+1	
Pb3(PO4)2	-39.285	4.245	3	Pb+2	2	PO4-3			
PbHPO4	-21.419	2.386	1	Pb+2	1	H+1	1	PO4-3	
PbO:0.3H2O	3.545	-9.435	-2	H+1	1	Pb+2	1.3	H2O	
Portlandite	5.982	-16.722	1	Ca+2	2	H2O	-2	H+1	
Pyromorphite	-65.185	19.245	5	Pb+2	3	PO4-3	1	Cl-1	
Sb2O3(s)	-10.415	-1.935	2	Sb(OH)3	-3	H2O			
Sb4O6 (cubic)	-20.831	-2.271	4	Sb(OH)3		H+1	-6	H2O	
Sb4O6 (rhombic)	-20.831	-3.121	4	Sb(OH)3		H+1	-6	H2O	
SbCl3	-29.302	-29.873	1	Sb(OH)3	3	Cl-1	3	H+1	H2O
Senarmontite	-10.415	1.025	2	Sb(OH)3	-3	H2O			
Valentinite	-10.415	-0.415	2	Sb(OH)3	-3	H2O			