IN SITU IMMOBILIZATION OF ARSENIC AND LEAD IN
SMELTER CONTAMINATED SOIL

A Dissertation

by

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ABSTRACT

The efficacy of in situ fixing of arsenic (As) and lead (Pb) in a highly contaminated soil was examined using chemical extractions for lability, bioavailability, and bioaccessibility accompanied by spectroscopic verification. Soil Samples from a former smelting site in Stockton, Utah, contained 7,520 mg kg\(^{-1}\) total As and 66,400 mg kg\(^{-1}\) total Pb, more than 100 times background levels. The high total Pb and As concentrations coupled with high bioaccessibility (Physiologically Based Extraction Test: 246 mg kg\(^{-1}\) As; 20,900 mg kg\(^{-1}\) Pb) raise concerns of environmental and human health effects. Goethite, ferrihydrite, and high-iron water treatment residuals (Fe-WTR) were tested as amendments. The Fe-WTR applied at a 10:1 Fe:As mole ratio was the most effective, reducing water soluble As and Pb by 95% and 72%, respectively. However, when soluble P was added to the soil to immobilize Pb, As lability significantly increased due to the similar chemistries of phosphate and arsenate. When soluble P and Fe-WTR were added in sequence, 90% reduction of bioaccessible As and 60% reduction in plant available As (uptake by Pteris quadriaurita) were observed. Speculation that the efficacy of Fe-WTR as an in situ immobilizing agent was due to the presence of high surface area and highly reactive, poorly crystalline Fe oxides was supported by μ-XRF and μ-XANES analyses. Unamended, contaminated soil was observed to be a mixture of As(III) and As(V) oxides whereas amendment with Fe-WTR resulted in a shift to As(V) solid phases dominated by As(V) oxides and sulfates, all containing Fe(III). Identified minerals included ferric arsenate sulfate...
[Fe$_5$(AsO$_4$)$_3$(SO$_4$)$_3$], yukonite [Ca$_{7}$Fe$_{11}$(AsO$_4$)$_9$O$_{10}$·24.3H$_2$O], and scorodite (FeAsO$_4$·2H$_2$O). When soluble phosphate was added as a single amendment, As mineralogy included significant concentrations of As(V) oxide, As$_2$O$_5$. For Pb, addition of soluble P increased hydropyromorphite [Pb$_5$(PO$_4$)$_3$OH] content to 70%, but when Fe-WTR was added after soluble P, hydropyromorphite never exceeded 40%. Just as the addition of soluble P interfered with in situ fixing of As, Fe-WTR partially prevented the conversion of Pb to pyromorphite minerals. The μ-XRF and μ-XANES analyses give physical evidence of the chemical shifts suggested in the bioaccessibility and chemical lability tests.
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CHAPTER I

INTRODUCTION

1.1 GENERAL BACKGROUND

The U.S. Environmental Protection Agency (US EPA) National Priority List (NPL), documents 1,341 contaminated sites in the United States as of March 22, 2018, that pose a health risk for humans, ecosystems, water, and other receptors [1]. Elevated arsenic has been found in at least 1,149 of current or former NPL sites [2]. According to the Agency of Toxic Substance and Disease Registry (ATSDR) [4], arsenic ranks number 1 out of the 275 contaminants on the Priority List of Hazardous Substances commonly found in Superfund sites [3]. Because arsenic is classified as a US EPA Group A carcinogen, elevated health risk is associated with long-term human exposure to arsenic contaminated water, food and soil.

The Jacobs Smelter Superfund Site is located adjacent to the town of Stockton, Tooele County, Utah. It is an abandoned smelting area which operated in early the 1860s until 1970 to produce silver and base metals. After a century of operation, the smelter was closed, but it left a legacy of mill tailings and smelter waste. Contamination occurred from several historic smelters including Jacobs Smelter, Chicago Smelter, Carson Buzzo Smelter, and Waterman Smelter. Nine former smelters with milling operations within the site boundaries have been documented. In 1997-1998, Utah
Department of Environmental quality performed preliminary assessments and identified elevated levels of arsenic and lead in the site, which resulted in its addition to the NPL on February 4, 2000. The greatest risk associated with the site is inhalation and ingestion of contaminated soil and dust particles. According to the risk assessment report from the US EPA, children under the age of seven are the most vulnerable because their central nervous system is rapidly developing. Animals are also at a risk from contaminated soil. Both arsenic and lead are present in elevated concentrations in residential as well as nonresidential areas [4].

The entire Superfund site is eight square miles and includes the town of Stockton. The topography is dominated by the Rush Valley, at an elevation of 5000 feet. Land use categories of this site include single family residential, rural residential, agricultural, grazing, industrial, commercial, open space undeveloped, and recreational. According to the Jacobs Smelter Remedial Assessment Report (2003) [5], human and environmental health risk was assessed and identified the importance of protecting ecosystem integrity by maintaining structural and functional groups such as endangered species, migrating birds, wetland and aquatic species as well as terrestrial wildlife population other than humans. The Utah Department of Environmental Quality (UDEQ), with the concurrence of the US EPA, presented a Record of Decision (ROD) emphasizing that “lead and arsenic are identified in concentrations that pose a significant risk to human health and environment” [5].
The area around Stockton is generally grassland and used primarily for grazing. Rush Lake is the dominant surface water body recharged primarily through ground water and several springs. The lake size can be variable, and in the spring of 2015, the lake was dry. Ground water consists of shallow aquifers that feed Rush Lake, perennial springs, and deep aquifers 200 feet below ground surface.

Due to the large geographic extent, the Superfund site was further divided into six divisions called Operable Units (OUs). Two of the units already have been cleaned. US EPA initiated a “time critical removal action” in March 1999 to reclaim the 29 most contaminated residential properties in Stockton. UDEQ cleaned an additional 126 residential properties; all these cleaned properties were deleted from the NPL list in 2001. Remedial investigations for OU2 began in 1999, and remediation actions included excavation of 15-45 cm of soil and placing the material in a covered repository in the subdivision. Cleanup target levels are <500 mg kg\(^{-1}\) Pb in residential areas, <3000 mg kg\(^{-1}\) for non-residential areas, and <10,000 mg kg\(^{-1}\) from all other soil. Contaminated soil was replaced with 30 cm of clean soil and 15 cm of top soil. The source of clean soil was from northern and central portion of the Tooele County Landfill property which certified that it did not contain hazardous waste or substances.

The primary soils in the area are gravelly loam and sandy loam in texture. Parent materials are lake deposits include well-bedded silt over older alluvial deposits. The climate is typical of high elevations in the Rock Mountains: dry, warm summers; cold winters with accumulations of snow; significant rainfall in spring and fall. The average
annual precipitation is 47 cm. The maximum daily temperature is 36 °F in December and 88 °F in July. Rush Valley formed from a closed drainage basin 50 km long and 29 km wide with all surface drainage directed to Rush Lake. The streams are short with high gradients and carry runoff immediately after precipitation. Approximately 32 acres within OU2 contain Pb and As with the highest Pb concentration of 150,000 mg kg⁻¹. Contamination is generally limited to the upper 45 cm of soil.

Based on US EPA standard protocols for assessing risk of cancer and non-cancerous diseases, an action level of 500 mg kg⁻¹ Pb and 100 mg kg⁻¹ As was used for residential surface soil; 800 mg kg⁻¹ Pb for residential subsurface soil; 3000 mg kg⁻¹ in both surface and subsurface soil for recreational areas; 2,200 mg kg⁻¹ of Pb for surface and subsurface soils in for commercial and industrial areas. To achieve these levels, the record of decision by the US EPA is to excavate the contaminated soil to a maximum of 45 cm and place the soil in an offsite land-fill. The projected time is 12 months at a cost of $9,647,000.

Conventional active remediation methods for metal contaminated soils include acid washing/acid extraction, flushing, vitrification, and immobilization using solidification/stabilization. Solidification/stabilizing is the most cost effective of these approaches and is heavily practiced in many parts of the world. Chemical immobilization through the use of soil amendments is geared to “fixing” the contaminants via adsorption or precipitation reactions. Use of soluble ferric or aluminum salts as amendments has been tested as a means to reduce the chemical lability of arsenic
in the soil by means of the formation of coprecipitates or inner sphere complexes with the resultant (hydr)oxides [6, 7]. Low cost and potentially effective substitutes for Fe/Al hydroxide are drinking water treatment residuals generated during the water treatment process. These materials primarily are composed of microcrystalline or amorphous Fe/Al hydroxides but also may contain some organic carbon.

Soil conditions such as pH, organic matter content, and competing cations impact the efficacy of immobilization of contaminant metals by Fe amendments. Therefore, the process needs to be optimized to avoid toxicity to plants and subsequent transfer of these toxic metals through food chain to animals and humans.

1.2 OBJECTIVES AND HYPOTHESES:

The overall goal of this research was to investigate the possible role of iron-based soil amendments to stabilize As and Pb in the highly contaminated soils from the Jacobs Smelter area.

1.2.1 SPECIFIC OBJECTIVES:

1. Characterize the chemical and mineralogical phases of Pb and As in the contaminated soil with particular emphasis on speciation.

2. Evaluate several sources of Fe in conjunction with soluble P amendments for in situ immobilization of As and Pb.

3. Use advanced spectroscopic techniques to examine the precipitation and transformation of secondary minerals in the amended soils.
These were the overarching objectives of the study that were established prior to beginning the research and were modified slightly as the experimental results unfolded. Additional sub objectives were added as the research progressed. Equally important were the hypotheses; as the experiments evolved, more hypotheses were added:

1.2.2 HYPOTHESES:

1. Iron oxides and poorly-crystalline, iron rich materials will significantly reduce labile, bioaccessible, and bioavailable As in soil.

2. Iron-rich water treatment products, being dominated by poorly crystalline oxides, will be effective in reducing arsenic chemical and biological lability.

3. Soluble P amendments will significantly reduce bioaccessible Pb content in the soil

4. Amending the soil with soluble P to stabilize Pb in contaminated soils will reduce Pb chemical and biological lability but will increase As lability.

5. Application iron-rich soil amendments simultaneously or in sequence with soluble P will be an effective in situ approach to controlling both Pb and As in contaminated soils.

6. Advanced spectroscopic techniques (XAS, XANES, μ-XRF) will demonstrate that amending contaminated soil with soluble orthophosphate and Fe-rich products results in the formation of identifiable Pb and As precipitates and/or surface complexes.
1.3 STRUCTURE OF THE DISSERTATION

This dissertation is written in six chapters. Chapter 2 will provide a detailed review of the literature. Chapter 3 is the chemical and mineralogical characterization of the Jacobs Smelter soil to establish the experimental baseline upon which to develop a suitable *in situ* remediation approach. Chapter 4 examines the use of several chemical amendment combinations to reduce chemical lability of As and Pb as well as determine the effects of these amendments on chemical extraction indices. Chapter 5 is a detailed spectroscopic investigation of the changes in Pb and As speciation resulting from soil amendments and provides physical evidence of the induced transformations. Chapter 6 provides overall conclusions of the project.
1.4 REFERENCES


2.1 ARSENIC

2.1.1 GENERAL INFORMATION

Arsenic (As) is the 20th most abundant element found in the natural environment. It is classified as a metalloid, exhibiting both metallic and nonmetallic properties. Arsenic has an atomic number of 33 and belongs to Group 15 (Pnictogens) of the periodic table with an electronic configuration of [Ar] 3d\(^{10}\) 4s\(^2\) 4p\(^3\) [1, 2]. Arsenic readily forms compounds in the aqueous systems in three major groups, inorganic, organic and gaseous, and exists in four oxidation states, +5, +3, 0 and -3 [3]. Inorganic solids and aqueous species of arsenic predominate over organic and gaseous forms. The most common inorganic forms are arsenate [As(V)] under oxidized conditions and arsenite [As(III)] under reduced conditions. Common As(V) species are arsenic pentoxide, arsenic acid, and arsenates; As(III) species includes arsenic trioxide, arsenites and arsenic trichloride [2].

Arsenic is widely distributed in the earth’s crust and found in more than 200 minerals. These minerals are classified into five groups: elemental, arsenide, arsenosulfide, arsenite, and arsenate [2]. Some of the common As rich minerals including realgar (As\(_4\)S\(_4\)), orpiment (As\(_2\)S\(_3\)), and arsenolite (As\(_2\)O\(_3\)) are used in a wide variety of products [4].
2.1.2 BACKGROUND LEVELS AND MAXIMUM ALLOWABLE CONCENTRATIONS

The distribution of arsenic in the soil depends upon parent material and type of soil [1]. In uncontaminated soils, arsenic concentrations range from 1 to 40 mg kg$^{-1}$, and the mean concentration is approximately 5 mg kg$^{-1}$ [5]. Regulations governing the remediation of As-contaminated soils are still under development and vary greatly based by country, state, and land use [6]. The United States Environmental Protection Agency (US EPA) established Ecological Soil Screening Levels (ESSL) for contaminants in soil that are protective of ecological receptors, such as plants and animals. For plants, the ESSL of arsenic is 18 mg kg$^{-1}$, and for wildlife mammalians, ESSL is 46 mg kg$^{-1}$ [7]. Based on the target cancer risk and toxicological guidance values from the Integrated Risk Information System, established regional screening levels for unrestricted soil (residential, recreational etc.) is as low as 0.39 mg kg$^{-1}$ [8]. Florida Department of Environmental Protection established a screening level for As in residential soils of 0.8 mg kg$^{-1}$ and 3.7 mg kg$^{-1}$ in industrial soils [9].

In 2001, the US EPA and many other countries followed World Health Organization (WHO) guidelines and changed the maximum allowable arsenic concentration in drinking water from 0.05 mg L$^{-1}$ to 0.01 mg L$^{-1}$. As a result, the number of drinking water sources found to exceed legal limits immediately increased. Countries such as Argentina, Bangladesh, China, Chile, Mexico and Nepal still maintain the maximum allowable concentration as 0.05 mg L$^{-1}$ due to technical and economic
difficulties associated in maintaining WHO recommendations [10]. More than 200 million people worldwide are exposed to As concentrations that exceed the 0.01 mg L\(^{-1}\) limit.

Arsenic is on the US EPA list of “high risk” air pollutants, and the air emissions are tightly regulated for glass manufacturing, copper ore and smelters, and phosphoric acid manufacturing [2]. The United States Occupational and Health Administration (OSHA) mandates permissible limits for As levels in air for occupational exposure to be no greater than 0.01 mg m\(^{3}\), averaged over any 8-hour period [5].

2.1.3 SOURCES OF ARSENIC CONTAMINATION

Arsenic contamination from natural geologic processes or human activities (anthropogenic sources) is a global issue [4]. The most common natural source for arsenic release into the environment is volcanic eruption, emitting on a yearly average 43,000 kg day\(^{-1}\)[11]. Weathering of arsenic rich igneous and sedimentary rocks is another natural process which slowly releases arsenic into the soil. Human activities such as mining, smelting, combustion of fossil fuels as well as commercial products including herbicides, pesticides, wood preservation chemicals (e.g., chromated copper arsenate, commonly known as CCA) and pharmaceuticals are some of the common anthropogenic sources of arsenic contamination [2, 12].

Mining and smelting of nonferrous metals and combustion of fossil fuels are among the major anthropogenic sources of arsenic contamination. Smelting is the largest
single anthropogenic source of air pollution [13]. Fine particles, tailings, and slag have the potential to contaminate nearby air, soils, and water bodies. Arsenic can be present at 2 to 3% (weight basis) in Cu and Pb ores, and 11% in gold ores [14]. Some of the arsenic compounds found in the mining sites are arsenopyrite (FeAsS), arsenical pyrite, scorodite (FeAsO₄·2H₂O), As(V) substituted jarosite (KFe₃(SO₄)₂(OH)₆), As in coprecipitated Ca and K bearing phases, and as As(V) sorbed to iron oxides [15]. In highly contaminated mining sites, total arsenic concentrations as high as 56,000 mg kg⁻¹ were recorded in South Korea [16]. Serious air pollution of arsenic in USA was recorded in Anaconda, Montana with the emission of arsenic trioxide 16,884 kg day⁻¹ and a gold smelter emitting 32,658 kg day⁻¹ [13].

Arsenic compounds are used in many products and processes and were once a major part of agricultural pesticides. Use of arsenical fungicides and insecticides in agriculture has caused extensive contamination in some older orchards. Accidental spills of preservative chemicals containing chromate, copper, and arsenate used by wood impregnation industries also have contributed to contamination [17]. US EPA restrictions essentially have eliminated the use of inorganic arsenic in wood preservation chemicals and pesticides.

2.1.4 ARSENIC TOXICITY

Exposure to As can result in a variety of health problems in humans including skin, neurological, and cardiovascular diseases and various forms of cancer [18]. Arsenic trioxide is the most toxic form of arsenic, and as little as 1 to 2.5 mg kg⁻¹ is fatal.
The International Agency for Research on Cancer classified arsenic as a Group I carcinogen that exhibits both acute and chronic toxicity [19]. The main routes of arsenic exposure in humans are ingestion (food or water) and inhalation [2].

Bangladesh and India (west Bengal area) have the highest populations exposed to arsenic from drinking groundwater, and the devastating impacts to human health are well documented [13, 20, 21]. The area had one of the highest rates of infant mortality resulting from ineffective sewage treatment contaminating the surface drinking water sources and poor water purification. United Nations International Children's Emergency Fund (UNICEF) and the World Bank sponsored the construction of millions of shallow wells to tap into cleaner groundwater. Although the groundwater initially tested clean, naturally occurring arsenic present in aquifer sediments released high concentrations of arsenic in 20% of the wells with severe health impacts [22, 23].

According to the Agency of Toxic Substances and Disease Registry’s (ASTDR) toxicological profile, the minimum risk level for acute oral exposure to inorganic arsenic is 0.005 mg kg\(^{-1}\) day\(^{-1}\) for 14 days [5]. Acute toxicity reactions includes gastrointestinal discomfort, vomiting, diarrhea, blood in urine, shock, convulsions, coma, and death [24].

Chronic exposure to As can cause skin lesions, which are characterized by hyper-pigmentation (skin become darker in color), hypo-pigmentation (loss of skin color) and hyperkeratosis (thickening of out layer of skin) [21]. A peripheral vascular disorder called “black foot disease” is commonly reported in the countries of extreme contamination such as Bangladesh. Chronic exposure can also cause non-cirrhotic portal
fibrosis [25]. The ASTDR determined minimal risk level for chronic exposure is 0.0003 mg kg\(^{-1}\) day\(^{-1}\) for a year or more [5]).

Both As(III) and As(V) oxidation states are capable of inhibiting energy-linked functions in mitochondria. As(III) can deactivate enzymes due to its high affinity to sulfhydryl groups. Arsenic(V) can replace phosphate in biochemical reactions due to its similarity in structure and properties and can uncouple oxidative phosphorylation [24, 26]. Mechanisms of arsenic toxicity and carcinogenicity involve oxidative stress, lipid peroxidation, DNA damage and tumor promotion and progression [18, 24]. Inorganic and organic trivalent forms are more toxic than the pentavalent form [2]. In the trivalent state, arsenic may react with critical thiols in protein and inhibit their activity [24].

2.1.5 FATE AND TRANSPORT OF ARSENIC IN SOIL

The form of As present in the soil is dependent upon pH and redox [27]; Ca, S, and Fe [3]; and microbial reactions [2]. Arsenic(III) and (V) tend to co-exist in the soil due to variation in the environmental conditions and slow transformation rates. Organic arsenic species such as methylarsonate (CH\(_3\)AsO\(_3\)) and dimethylarsinate ([CH\(_3\)]\(_2\)AsO\(_2\)) can be found in the soil in minor amounts as a result of microbial transformation of arsenate to arsenite [28, 29]. These compounds are highly volatile, and their conversion to the gas phase is dependent upon soil pH [18].

Partitioning of arsenic to the solid phase is mostly dependent upon oxidation state and pH. Arsenate tends to bind more extensively and strongly to most mineral
phases than arsenite [30], but this is not always the case. Sorption of arsenate onto ferrihydrite (Fe₂O₃·0.5H₂O) and goethite (α-FeOOH) was preferable only below pH 5 to 6; at pH above 6 to 7 arsenite has a greater absorption maximum [31]. Aluminum hydroxide and aluminosilicates also exhibit preference of arsenate over arsenite. Due to the absorption preferences, unless in highly alkaline conditions (pH greater than 8.5) arsenate is less mobile and has a limited impact on environmental quality [30]. Aqueous solubility of arsenic in soils reaches a maximum near neutral pH [27].

Oxides of Fe, Al, and Mn have high affinity for arsenic and readily absorb through surface complexation [30]. Using infrared and X-ray absorption, arsenate absorption has been determined to be is bimodal: a combination of bidentate, inner-sphere moieties and outer-sphere complexes [32]. Arsenite also forms bidentate complexes with iron (hydr)oxides and, to a smaller extent, produces monodentate complexes on the mineral surface [31, 33]. This process can be affected by temperature and the presence of competing ions [33]. Organic matter in soils and sediments also adsorbs arsenic. Maximum adsorption of arsenate and arsenite on humic acid occurs from pH 5.5 and 8.0, respectively [34, 35]. The presence of Fe, Al, and Mn enhances this process as these ions act as bridging complexes for arsenate on humic substances [36].

In highly contaminated soils, direct precipitation of arsenic solid phases is possible, but more common is surface precipitation after adsorbing to soil colloids. In calcareous soils, arsenic can precipitate with Ca and Mg cations; under acidic conditions, arsenic precipitates with Al and Fe(III) ions [30]. At elevated arsenic concentrations,
arsenic can precipitate as $\text{FeAsO}_4$. Arsenate is similar in size and charge to phosphate or sulfate and may replace these anions in certain minerals [37]. Arsenate also has the potential to precipitate with various heavy metals, such as Pb, and some alkaline earth metals, such as Ca, Mg, and Ba, but these compounds are relatively soluble in anaerobic environments [38].

Under reducing conditions, arsenite can be incorporated into sulfide solids by conversion of As-O coordination to As-S coordination forming a polynuclear arsenic sulfide complex [39]. In the presence of Fe in high concentrations in the soil, sulfide may co-precipitate with Fe and arsenic or adsorb arsenite into metal sulfide structure [39]. In mining and smelting areas, arsenopyrite (FeAsS) is one of the main sources of arsenic found in the soil (Fig. 2.1) [40]. If the Fe concentration in the soil is low, orpiment ($\text{As}_2\text{S}_3$) or realgar ($\text{As}_4\text{S}_4$) may form [39]. Under oxidizing conditions, arsenopyrite will weather into iron oxyhydroxides and scorodite ($\text{FeAsO}_4\cdot2\text{H}_2\text{O}$) [41]. At low pH, mobility and availability of arsenic in the soil will be restricted due to low solubility of scorodite and high affinity of As for iron oxyhydroxide [41].

Arsenic is a more potent human health and ecological threat when it partitions from the solid phase into the aqueous phase. Ion displacement, desorption, reduction of arsenate to arsenite, reductive dissolution of iron/manganese oxides or oxyhydroxides favor solubilization of arsenic [43]. High concentrations of dissolved arsenic in soil solution might lead to leaching of arsenic to ground water and increased availability for plant uptake, increasing the opportunity for food chain transfer.
Ion displacement of $H_n\text{AsO}_4^{3-n}$ and $H_n\text{AsO}_3^{3-n}$ by phosphate potentially could release arsenic from minerals and increase mobility [44, 45]. Dissolved silica and natural organic matter promote desorption of arsenic from minerals and compete with As for adsorption sites on mineral surfaces [34, 35]. Silica and sulfate are not as competitive for As adsorption sites as phosphate and bicarbonate [46].

Figure 2.1 Chemical structure of arsenopyrite, monoclinic, outline represents the repeating cell. (Reprinted with permission from the journal RSC advances [42])
Transitioning from oxidizing to reducing conditions can impact arsenic adsorption by several processes. When the soil undergoes flooding, consumption of $O_2$ by aerobic microbes force facultative anaerobic microbes to utilize alternative electron acceptors, such as arsenate (resulting in reduction to arsenite) [30]. Under reduced conditions, dissolution of iron and manganese oxides and hydroxides release arsenic to the aqueous environment [33].

Soil texture can influence arsenic mobility [47]. Arsenic is more mobile in coarse textured soils than fine textured soils due to lack of arsenic binding sites. Greater surface area, clay minerals, non-crystalline alumino silicate phases and iron phases in fine textured soil absorb HAsO$_4^{2-}$ and HAsO$_3^{2-}$ over the range in pH values in which mineral surfaces are positively charged [48]. Sorption of As to clay minerals depends mainly on the type of clay present in the soil [49, 50].

2.2 LEAD

2.2.1 GENERAL INFORMATION

Lead (Pb) is a naturally occurring element, found in association with sulfides, oxides, halides, carbonates, and sulfates [51]. Lead has an atomic number of 82 with an electronic configuration of [Xe] 4f$^{14}$ 5d$^{10}$ 6s$^2$ 6p$^3$. Lead(II) and (IV) are the two most common oxidation states found in the environment with Pb(II) being predominant [52]. Common Pb minerals in soils and sediments are galena (PbS), cerussite (PbCO$_3$), hydrocerussite (Pb$_5$(CO$_3$)$_2$(OH)$_2$), anglesite (PbSO$_4$), massicot (PbO), and minium (Pb$_3$O$_5$) [53]. Zinc, copper, arsenic, tin, antimony and bismuth can be found as common...
impurities in Pb minerals [53]. Uses of Pb include Pb acid storage batteries, construction (as sheets and pipes), radiation shielding, and pigments and paint additives, alloys, and ceramics [53].

2.2.2 SOURCES OF LEAD CONTAMINATION

Small amounts of Pb can be released during weathering of igneous rocks and radioactive decay [53]. However, the primary sources of Pb contamination are industrial activities such as mining, smelting, and manufacturing of products like paint, gasoline, and pesticides [54]. Chips and dust from peeling or cracking of leaded paint (especially in houses built before 1978) are potential sources of Pb exposure for both children and adults and account for as much as 90% of childhood Pb poisoning [55].

2.2.3 BACKGROUND LEVELS, MAXIMUM ALLOWABLE CONCENTRATIONS

Uncontaminated soil on average has less than 50 mg kg\(^{-1}\) of Pb, but many urban areas exceed more than 200 mg kg\(^{-1}\) [56]. Lead can be present in soil in very high concentrations in mining and smelting areas, commonly exceeding 10,000 mg kg\(^{-1}\) [57]. US EPA recommends that bare soil Pb concentrations in play areas are <400 mg kg\(^{-1}\) and <1200 mg kg\(^{-1}\) for non-play areas [56]. Targeted Pb concentration in the drinking water is 0 mg kg\(^{-1}\) but action is required if the Pb exceeds 0.015 mg kg\(^{-1}\). The permissible exposure limit of Pb in the workplace air is 0.05 mg m\(^{-3}\) average over an 8 hour workday. Individual states may have more rigid regulations. California, for example, has
set a cleanup level of 80 mg kg$^{-1}$ for the residential areas and 320 mg kg$^{-1}$ for industrial areas [58].

2.2.4 TOXICITY

Lead is a non-essential element for plant growth and can impede plant development [53]. The metal inhibits growth, reduces photosynthesis, interferes with cell activities such as division and respiration, water absorption and water translocation [52]. Very high plant tissue concentrations (>200 mg kg$^{-1}$) are required to observe toxic effects in plants. Availability of soil Pb to uptake by plants strongly depends on soil physical and chemical properties [53]. Low pH and low organic carbon content favors the uptake.

Children are especially sensitive to Pb exposure and can suffer adverse health effects such as neurocognitive impairment. Ingestion is the most common Pb exposure pathway for humans [59]. Ingested soil and dust are important contributors of elevated blood Pb levels in children exposed to Pb-contaminated environments [60]. Lead exposure has been reduced substantially after bans on the use of leaded gasoline in 1996 and Pb-based paint in 1978 [52].

2.2.5 FATE AND TRANSPORT IN SOIL

Lead present in the soil is relatively immobile and resistant to weathering, and only a small fraction is water soluble (0.2-1%) [51]. The mobility and solubility of Pb
usually is controlled by sparingly soluble compounds or adsorption by organic matter and clay minerals [61].

In mining- and smelting-area soils, Pb can be present as sorbed to humic acid, manganese oxides, and iron (hydr)oxides [57]. At near neutral or alkaline pH, 50% of total Pb was found to be adsorbed to iron (hydr)oxides, a fraction that increased with increasing pH and mineral surface area [57]. Lead-bearing jarosite or galena is the dominant Pb species at low pH and sulfate rich tailing [57]. In oxidation conditions, galena is readily transformed into anglesite, cerrussite, and pyromorphite [62]. Pyromorphite minerals are stable under a range of environmental conditions [54, 59, 60].

2.3 REMEDIATION OF METAL CONTAMINATED SOIL

Soil can act as a sink for As, Pb, and other hazardous materials but also has the capacity to transfer pollutants to plants, animals, and water. Remediation techniques used to treat metal contamination soil can be categorized into two major groups: a) in situ remediation in which the contaminants are treated on site, and b) ex situ or off-site remediation. Physical, chemical, and biological treatments can be used both in situ and ex situ. Common treatment techniques used for metal-contaminated soil include solidification/stabilization, excavation/offsite disposal, and acid extraction. Jacob’s Smelter in Utah (the site used for the research in this dissertation) is an example of a site with many challenges for remediation. The site is approximately eight square miles in area, including the town of Stockton and Rush Lake. The risks posed by the site are
derived from mining activity that occurred primarily in 1860’s. Unaltered mining waste is reported to exist in several places. Lead and arsenic are the primary contaminants of this site. Based on the US EPA sampling activities report, the average arsenic content in the surface soil is $3000 \text{ mg kg}^{-1}$, and the Pb content averages $5000 \text{ mg kg}^{-1}$. However, the concentrations are spatially variable, and much higher localized concentrations have been observed. The site already is under remediation by Utah Department of Environmental Quality (UDEQ) and US EPA Region 8 using excavating and offsite disposal to a landfill. The estimated cost for this project is $50 million [63].

Soil flushing treats contaminated soil by injecting an extraction solution into the soil that passes through the contaminated area and is drawn to a well where the fluid is pumped and collected. The injection fluid containing dissolved contaminants is treated further and discarded. This technique works best when a single contaminant is targeted [64-66].

Electrokinetic treatments induce the migration of charged species in response to a low-density current passed through a contaminated soil between two electrodes. Contaminants will be collected near the electrode by electroplating, electrodeposition, precipitation, complexing with ion exchange resins, or pumping fluids surrounding the electrode. Metals are removed as soluble ions bound to soils as oxides, hydroxides, and carbonates. This process can be used both in situ or ex situ; unlike soil flushing, electrokinetics is applicable to clay soils with low permeability and can be used to treat wide range of pollutants [66-69].
Phytoremediation, the use of plant species to remove, detoxify, or stabilize pollutants, is another common practice. In phytoextraction, plants are used to extract contaminants from the soil. Successful phytoextraction is achieved through high-biomass metal hyperaccumulators with the ability to assimilate high concentrations of metal contaminants (>1000 mg/kg) in their aboveground tissues [70]. Plants used for phytoextraction need to be discarded properly to avoid further contamination. Composting, compacting, and pyrolysis are the pretreatment steps to reduce the biomass, and incineration, direct disposal, ashing or liquid extraction are the final disposal techniques [71]. Plants belonging to the genera *Thlaspi*, *Urtica*, *Chenopodium* and *Alyssum* have been used to accumulate Cd, Cu, Pb, Ni and Zn [66, 72]. Phytostabilization is a process in which metals are made less labile by activities of the roots and associated rhizosphere microorganisms [66]. *Atriplex lentiformis* (quailbush) has been studied for the stabilization of Pb and Zn in mine tailings [73]. The applicability of phytoremediation is limited to shallow depths because it depends upon exploration by plant roots. Long treatment times, potential food chain transfer of pollutants, and the need for proper disposal of the plants are some of the disadvantages. On the other hand, low capital inputs and reduced operation costs are the major advantages. Additional benefits are reduced soil loss from erosion and conservation of the soil resources. Phytoremediation can be enhanced through improving the extraction by genetics and standard plant breeding [66].

Stabilization is a broad term associated with a range of remediation efforts with the common goal of reducing the availability of soil pollutants and decreasing the risk
associated with these contaminants [74]. In stabilization, total contaminant concentration remains the same but in a less toxic form. Agricultural limestone, rock phosphate, and diammonium phosphate have been found to effectively reduce Cd, Pb, and Zn lability in contaminated soil [75]. Hexavalent chromium can be stabilized by first reducing the hexavalent chromium to Cr(III) followed by precipitation of the trivalent oxide or through coprecipitation with iron hydr(oxides). Increasing soil pH with the application of fly ash can reduce copper mobility in contaminated soil [49]. Other forms of stabilization include adsorption onto mineral surfaces, formation of stable complexes, ion exchange, and co-precipitation as metal oxides [49, 76]. The cost effective and non-destructive nature makes stabilization an attractive strategy in remediation, and low cost byproducts such as slag from steel industry, red mud from aluminum production, and water treatment residuals can be used effectively.

2.4 REMEDIATION OF ARSENIC

Phytoremediation is a promising, eco-friendly technique to remediate arsenic in contaminated soil [19]. The first discovered arsenic hyperaccumulator, *Pteris vittata* (Chinese brake fern), is efficient in arsenic uptake due to its ability to solubilize soil arsenic from recalcitrant fractions [77]. Other species of *Pteris* genus are found to be hyperaccumulators including *P. biaurita*, *P. quadriaurita* and *P. ryukyuensis*.

Aluminum oxides have a high affinity for adsorbing As, but the use of Al as a soil amendment is rare. Maximum adsorption of As(V) to Al compounds occurs within a pH range of 3 to 4 and decreases with increasing pH [50]. If the soil is contaminated
only with As, additions of Mn oxide can significantly reduce As mobility and toxicity [49]. Manganese oxides have the ability to oxidize As(III) to As(V), reducing As toxicity. Stabilization mechanisms often involve co-precipitation as MnHAsO$_4$·8H$_2$O or Mn$_3$(AsO$_4$)$_2$·8H$_2$O [49, 78].

Formation of calcium-arsenic precipitates such as CaHAsO$_4$ and Ca$_3$(AsO$_4$)$_2$ under highly oxidizing, moderately alkaline conditions is the mechanism of arsenic stabilization when amending the soil with cement, lime, and fly ash [78]. Increasing soil pH without increasing soluble Ca$^{2+}$ may increase arsenic mobility [49, 79].

2.4.1 IRON AS AN AMENDMENT FOR *IN SITU* REMEDIATION OF ARSENIC

Iron minerals and iron industry byproducts are being used with greater frequency as amendments for *in situ* remediation [6, 34, 49, 80-82]. Chemical extractions and bioavailability tests have demonstrated the efficiency of Fe-based amendments [83, 84]. Iron (hydr)oxides commonly found in soil, such as goethite and ferrihydrite, influence the mobility and behavior of arsenic in the soil due to strong sorption affinity for both As(III) and As(V) species [6]. Iron oxides have been extensively studied in stabilization of As in contaminated soil, reducing the mobile, bioavailable, and bioaccessible As fractions in the soil [84, 85].

Two dominant processes occur during iron based arsenic remediation. First is the sorption of arsenic on the reactive surfaces amorphous or crystalline iron (hydr)oxides [44, 86, 87]. The second process is the co-precipitation of As with Fe oxides [82, 88].
The adsorption of As involves replacement of \(-\text{OH}_2\) and \(-\text{OH}^-\) with the anionic As species ($\text{AsO}_4^{3-}$ and $\text{AsO}_3^{3-}$) on surface structural Fe atoms [89] resulting in monodentate, mononuclear bidentate, or binuclear bidentate bridging complexes (Fig. 2.2) [6, 87].

![Figure 2.2 Different types of bonding mechanisms for arsenate on Fe oxide.](Reprinted with permission from the journal of Soil Science Society of America [90])

At low pH, the As(V) adsorbed to the Fe oxide surface remains protonated as Fe-O-As-OH and occurs as a monodentate bond, not bidentate [89]. In contrast, adsorption of As(III) preferably forms bidentate surface complexes with smaller amounts of edge sharing [91]. Another factor affecting As adsorption is the degree of crystallization of the Fe oxide because increased crystallization reduces the density of
adsorption sites. Poorly crystalline material is more effective in stabilizing arsenic in soil [92].

A typical approach to \textit{in situ} remediation of As in contaminated soil is to add soluble Fe$^{2+}$ (as ferrous sulfate) to form discreet Fe-As solid phases or adsorb As on the surface of the resulting Fe hydroxides. If the initial dissolved As(V)/Fe(III) molar ratio is greater than 0.2, amorphous As(V)/Fe(III) hydroxysulfate forms. From EXAFS data, As(V) forms inner-sphere, binuclear bidentate surface complexes by means of corner sharing between AsO$_4$ tetrahedra and FeO$_6$ octahedra [91]. If the initial dissolved As(V)/Fe(III) molar ratio is less than 0.2, As(V) will bond to more crystalline ferric hydroxysulfates (e.g., schwertmannite). Because the oxides are positively charged at pH<6 and negatively charged at pH>9, pH plays a role in adsorption phenomena [16]. Sorption of As(V) is more favorable when pH<5-6, and As(III) sorption is favorable when pH>7-8 [86]. As (III) forms inner sphere surface complexes on iron minerals in higher proportions at octahedral edges [91]. The pH at which both As(III) and As(V) equally sorb depends on factors such as solid-solution ratio, mineral type, specific surface area of the mineral, and the presence of competing ions such as phosphate [86].

When initially present in high soluble concentrations, As(V) will co-precipitate with iron forming highly insoluble Fe(III) minerals such as scorodite (FeAsO$_4$·2H$_2$O), pharamacosiderite (Fe$_4$(AsO$_4$)$_3$(OH)$_3$·6H$_2$O), parasimplesite (Fe$_3$(AsO$_4$)$_2$·8H$_2$O) and amorphous ferric arsenate [49, 89, 91]. Soil pH plays a major role in co-precipitation process. At low pH and under highly oxidized conditions, scorodite was observed. Under
reducing conditions and near pH 5, $\text{Fe}_3(\text{AsO}_4)_2$ formation is anticipated [78]. The oxidation state and presence of other cations such as Mn highly influence solid phase formation [82]. Arsenic(III) behavior was identical to As(V) with iron and manganese, except more arsenic bound to the precipitate and a small amount of As(III) remained in the solution [82].

Ferrous oxides and Fe(II)/(III) sulfate (commercially available byproducts) show promise in limiting As mobility and plant availability [16, 83, 93, 94]. Because the precipitation of ferric oxide after the addition of Fe(II) to soil can cause the release of acidity during the precipitation process, co-mixing with lime is recommended to avoid soil acidification. Iron(II)/(III) sulfate application combined with lime has been reported to be much more efficient than Fe(III) oxides (goethite) but should not be used if the soil is contaminated with other metals, such as Cu and Zn, due to increased mobility and plant uptake of those metals [83, 94].

In iron-based arsenic remediation, the molar ratio of Fe/As is important. The contamination level is different for different soils and different sites, but a Fe/As molar ratio of 2 or higher provided the best efficiencies [49, 95].

2.4.2 WATER TREATMENT RESIDUALS FOR ARSENIC STABILIZATION

Water treatment residuals (WTR) are the solids remaining after treatment to make the drinking water suitable for distribution for personal consumption. Some forms of treatment are standard, but individual treatment facilities may use different processes
due to conditions or state and local regulations. A coagulating agent (Fe or Al) often is used to remove suspended solids and common contaminants such as phosphate, and the WTR will be high in Al or Fe. Most water treatment facilities use KAl(SO$_4$)$_2$·12H$_2$O (alum) as the coagulant, thus generating Al oxide rich byproducts. Some water treatment facilities use ferric chloride or ferric sulfate as a coagulating material, and the resulting WTR will be rich in Fe oxides.

Disposal of WTR is a challenge faced by all treatment plants. The WTR and their disposal are not governed by federal regulations, but local and state requirements take precedent. However, US EPA regulations will come into play if the WTR are discharged into surface waters. As a result, water treatment plants often apply the WTR to soil or dispose of them in landfills. Alum-based WTR will be of little benefit to the soil and is used primarily as filler. Application to land used for food crops is often avoided because the high reactivity of WTR could be detrimental by acting as a sink for phosphate, depleting the soil of a critical nutrient. However, the presence of elevated organic matter could enrich the soil and increase the water holding capacity and cation exchange capacity [96]. In the USA, WTR are generally applied to land as either top dressing or incorporated into the soil [97]. Reuse of WTRs is an emerging approach applicable to agriculture and ecological reclamation projects. These byproducts also can be an alternative to more expensive iron amendments [97-99].

In an experiment to test the efficacy of WTRs in reducing As lability in contaminated soils, As was 100% sorbed to Fe-WTR and 98% sorbed to Al-WTR 48...
hours after application in a sandy soil [100]. Also, Fe-WTR are more effective than Al-WTR in resisting As re-release [99]. Application of WTR reduces bioaccessibility of As and decreases soluble concentrations in pore water [101]. Considering the potential phytotoxicity of Al originating from Al-WTR, Fe-WTP is a more suitable option. Fe-WTR can sorb up to 10,000 mg kg$^{-1}$ of As from contaminated solutions [99] and 13,500 mg kg$^{-1}$ of As from soil. The binding of As to Fe-WTR is strong enough to resist release even in the presence of P [99]. Spectroscopic evidence supports the hypothesis that strong As binding to Fe-WTR is the result of inner-sphere mononuclear bidentate complexes [102, 103]. Arsenate absorption is equally strong on Fe-WTR treated with lime [104].

2.5 REMEDIATION OF LEAD

Excavation and landfill disposal followed by replacement with clean soil is the most common remediation practice used for Pb contaminated soil. The process is expensive, removes the soil from its function as a resource, and requires replacement of the soil from another location [62]. Phytoextraction has been discussed as an effective alternative; however, low solubility of Pb in the soil generally makes Pb unavailable for plant uptake [105].

The possibility of using soluble phosphorous amendments for remediating Pb contaminated soil has been explored by several research groups. Both phosphorous and manganese oxide were found to be effective in reducing bioavailable Pb [54, 106]. Amending soils with phosphate will facilitate formation of sparingly soluble Pb minerals.
(pyromorphites) which remain sparingly soluble with limited bioaccessibility after accidental ingestion [60]. Phosphorous effectively reduces the Pb bioavailable fraction with or without other additives [54, 106].

2.6 REMEDIATION OF ARSENIC AND LEAD CONTAMINATED SOIL

Many contaminated soils contain high concentrations of more than one polluting metal [107]. This can be a complicating factor because a remediation strategy for controlling one metal may serve to increase the mobility or bioavailability of another. Adding diammonium phosphate at a 13:1 molar ratio of P:Pb reduced the leachability of Pb by 98.9% but increased As leached from the system from undetectable to 0.13 mg kg\(^{-1}\) [75]. In the same study, increasing the P application rate by nine-fold actually increased leachable Pb by a factor of ten and increased leachable As by a factor 37 [75]. After applying a mixture of portland cement and fly ash, the leachability of As initially decreased but increased over time [108]. The use of high-iron biosolid compost [109] had mixed results for Pb and As [103, 107, 110, 111].

2.7 TECHNIQUES TO ASSESS METAL BIOAVAILABILITY (NON-MAMMALIAN)

Bioavailability is defined as the degree to which a substance is absorbed by a living system or is made available at to a target organ or organism. Total metal in soil and water (e.g., US EPA Method 3051 [105]) is used routinely for risk assessment of metals in soils [112]. However total metal content is a poor indicator of bioavailability.
Fortunately, several tests are available to measure availability and bioavailability of metals in soil.

Evaluation of remediation efficiency must be assessed based on relevant pathways of exposure (e.g., direct ingestion, water contamination) and environmentally relevant endpoints (microbes, plants and humans) [113]. Various extraction procedures are used to test the soluble metal fraction which could potentially be available for plants, animals, and humans. Specific extraction techniques have been developed to target different pools of metals in soil [114]. Deionized water has been used to extract readily available/soluble metals, providing an indication of potential off-site transport in the aqueous phase [115-117]. Concentration of water-soluble As in soil varies from 0.01 mg kg\(^{-1}\) from uncontaminated soil to up to 109 mg kg\(^{-1}\) of highly contaminated soil [41, 115, 116]. Sodium bicarbonate has been used for decades to predict plant-available P in alkaline soils, and the extractant has been used with some success for plant-available As [114, 116].

The Toxicity Leaching Characterization Procedure (TCLP) is used to determine the mobility of both organic and inorganic analytes present in liquid, solid, or multiphase waste [118]. This process is heavily used in metal contaminated soil to measure the requirement of application of remediation techniques based on regulatory levels [108]. Different metals have different regulatory levels. For arsenic, Pb, and silver, the regulatory level is 5 mg L\(^{-1}\) in the leachate and for cadmium it is 1 mg L\(^{-1}\).
2.8 MAMMALIAN BIOACCESSIBILITY AND BIOAVAILABILITY OF ARSENIC

In the context of mammals, bioaccessibility and bioavailability are fundamental factors in predicting risk from the contaminants. The amount of contaminants available for systemic absorption in gastric or gastro intestinal solution is known as the *bioaccessible* fraction. The fraction ingested that crosses the GI epithelium and becomes available for distribution to internal tissues and organs is the *bioavailable* fraction [113].

Animal dosing trials (*in vivo* tests) traditionally have been used to assess the bioavailability of metals, especially Pb and As [119, 120]. Arsenic can be absorbed by the blood stream after ingestion or inhalation [113]. The resulting dose after ingesting arsenic contaminated soil is influenced by the mineralogy of arsenic. For example, As$_2$S$_3$ solubility in water is $0.0002$ g L$^{-1}$ while As$_2$O$_3$ solubility is $17$ g L$^{-1}$ making As$_2$O$_3$ far more bioavailable [113]. Arsenic bioavailability studies have been conducted with different ecoreceptors including juvenile swine, monkey, rabbit, dog and plants [119, 121]. Bioavailability was evaluated based on As concentration in urine, blood, feces, bone, skin, nail, and hair [113]. Due to similarities with respect to the human digestive tract, nutrient requirement, bone development, and mineral metabolism, monkey and swine are the animal models used most often in arsenic bioavailability studies in risk assessment at superfund sites [113, 122]. However, laboratory mice are an accepted alternative to swine and primates, and are far less expensive. The mouse assay is highly reproducible and yielded similar results to monkey and swine models [123].
Direct risk assessment using target organisms on all contaminated sites that might need remediation is not feasible. Therefore, chemical methods (*in vitro*) have been developed that simulate the gastrointestinal environment and quantify bioavailable metals with respect to soil ingestion pathways [117, 121, 124-126]. To validate *in vitro* methods, results should be highly correlated with *in vivo* studies. The physiological based extraction test (PBET) [121] and the *in vitro* gastrointestinal method (IVG) [124] are two of the most frequently used tests to estimate Pb and As bioaccessibility [121, 126]. Because oral ingestion of soil particles less than 250 µm is the main exposure route of metals to children, particles less than 250 µm are evaluated in all the procedures proposed in predicting and assessing the risk associated to human exposure. Arsenic bioaccessibility measured by Simplified Bioaccessibility Extraction Test (SBET) also is correlated with swine *in vivo* tests [119]. Ruby et al. (1996) [121] used PBET to measure bioaccessibility in three contaminated soils using rabbit and monkeys which shows a slight over-prediction based on the primate model (2-12%). PBET is a good bioaccessible measure for both arsenic and Pb and is accepted by state regulatory agencies for site specific assessment [113].

2.9 MAMMALIAN BIOACCESSIBILITY AND BIOAVAILABILITY OF LEAD

The hazard posed by Pb depends upon the exposure pathway and potential bioavailability. Ingestion by hand to mouth is the most common pathway of Pb exposure in children [113]. Contaminated airborne soil particles, interior dust, and paint dust can account for excessive Pb exposure. The chemical form of Pb present in the soil or dust
plays a major role in absorption into the blood stream. Some chemical forms are less favorable (PbS) while some are highly absorbable (PbCO$_3$) [113]. Elevated dietary Ca can inhibit Pb absorption [127]. Bioavailability of Pb in soil can be reduced by treating the soil with biosolids or soluble phosphate, as confirmed by various model ecoreceptors including rats, juvenile swine, and plants [113, 121, 128].

PBET emerged as being well-correlated with the results of feeding studies using Pb contaminated soil [121]. Another Pb bioaccessible test, leaching with a 0.4 M glycine solution adjusted to pH 1.5 with HCl to mimic a fasting stomach, correlated strongly ($R^2=0.9$) with relative bioavailability measured on animal models. The correlation was poorer ($R^2=0.7$) when a higher pH was used [129]. Extraction with the IVG test (pH 1.8) has shown a strong relation with the relative bioavailable results [130].

2.10 METAL SPECIATION IN SOIL

Toxicity, bioavailability, and fate and transport of As and Pb are dependent on the chemical speciation at a molecular level [131]. As an example, inorganic As(III) is more mobile and toxic than As(V) [109]. Chemical extraction methods provide indirect information about speciation, such as chemical partitioning into solid phases, but direct confirmation methods should be used to avoid over- or underestimation of metal concentrations or speciation in other fractions [132, 133]. For instance, sequential extraction of Pb contaminated soil that was amended with phosphorous (P) had the unintended consequence of pyromorphite (Pb$_5$(PO$_4$)$_3$Cl) formation during the extraction procedure which was confirmed via X-ray spectroscopies [134].
Instrumental methods are available to explore the chemistry of metals in the solid phase of soils and sediments. X-Ray diffraction (XRD) is a nondestructive technique that can be used to identify crystalline materials in simple mixtures [135-137]. Electron microprobe, scanning electron microscopy, and transmission electron microscopy create images at high resolution, and in conjunction with wavelength or energy dispersive spectroscopies (EDS), can provide elemental composition [138, 139].

During the past two decades, synchrotron-based techniques have been used in soil, plant, and environmental studies. These methods provide information at scales of measurement from angstrom ($10^{-10}$ m) to millimeters ($10^{-3}$ m) [140]. When electrons in an accelerator are brought to velocities near the speed of light (“relativistic electrons”) and are directed through a curved path by magnetic fields, the electrons emit intense electromagnetic radiation, called “synchrotron radiation”, that covers the spectral range from the infrared to the hard X-ray region [141]. Electromagnetic radiation from the synchrotron has the basic properties of typical instrumental sources (e.g., X-ray tubes) but is distinctly different: (i) very intense, several orders of magnitude brighter than conventional sources; (ii) covers a wide spectrum; (iii) highly polarized -- elliptical, linear, or circular; (iv) nanosecond, time-structured emissions [142].

X-ray absorption and fluorescence techniques are powerful tools in the synchrotron environment. X-rays directed at a solid engage in absorption in a systematic fashion that reveals information about the elements in the solid. If an X-ray has lower energy than the binding energy of the core electrons of the element of interest in a target
sample, this element will not participate in the X-ray absorption process. As the incident X-rays increase in energy to the point where the X-ray energy is approximately equal to the binding energy of the core level electrons, a defined increase is observed in absorption of the X-rays. Fluorescence occurs simultaneously when core electrons of the target element are ejected by the incident X-rays. An electron from a higher energy orbital fills the vacancy created by the ejected electron to return the atom to the ground state, and fluorescence occurs at a wavelength dictated by the difference in energy between the two electron levels. Fluorescence and absorption depend upon the specific energies of the incident X-rays and the characteristics of the electronic configuration of the target atoms [142]. The specific energies of the fluorescence and absorption are the foundation of XRF (X-ray fluorescence) and XAS (X-ray absorption), flexible techniques commonly used for metal(loid) speciation in soils [13]. Synchrotron based XRF determines elements in a wide variety of samples in a nondestructive manner, generating maps showing multielemental distribution and quantity.

Generation of high intensity of X-rays and the ability to “tune” are unique to synchrotrons. Generally, the XAS spectrum is consists of two energy regions: extended X-ray absorption fine structure (EXAFS) and X-ray absorption near edge spectroscopy (XANES). Although not explicitly defined, the XANES spectrum is understood to extend from 50 to 100 eV lower than the absorption edge to approximately 50 eV above the absorption edge. The part of the spectrum from the end of the XANES to about 350 eV above the absorption edge is the EXAFS spectrum (Fig. 2.3). The absorption edge will increase in energy by 1–3 eV for every valence electron removed (e.g., increasing
oxidation state) due to the increased attraction of the electrons for the nucleus in the core levels. The position of the absorption edge in the energy spectrum also depends upon the bonding environment of the target element in relation to the electronegativity of the ligand(s) to which it is bonded. [142]

![X-ray absorption spectrum of an As-rich region in contaminated soil from Jacob’s smelter, illustrating the XANES and EXAFS ranges.](image)

Figure 2.3 X-ray absorption spectrum of an As-rich region in contaminated soil from Jacob’s smelter, illustrating the XANES and EXAFS ranges.

Fluorescence-XANES (X-ray absorption near edge spectroscopy) is a recent development and demonstrates the complementary data that can be gained when employing XRF and XAS on the same samples. The XAS data are gathered by
repeatedly examining the same locations, selected from XRF maps, using a series of x-ray energies above and below the adsorption edge [143].

When more than one component (e.g., solid phase) of a given element is present in an XAS analysis, the spectrum will be the sum of the contributions of each component. The percentage of each component present in a sample can be determined using a linear combination fit (LCF) and principal component analysis (PCA) to match the unknown sample spectrum to known reference spectra [144]. Information obtained via XAS was used to identify the long term fate of the metals and potential bioavailability based on the known solubility products [145].

Most spectroscopic methods need relatively high concentrations of the target element, solid, dry samples, or high vacuum to complete a representative analysis. XAS has no such requirements. XAS is capable of distinguishing: adsorption from precipitation for many soil metals and metalloids; inner versus outer sphere surface complexes; mono- versus bidentate surface complexes; and provides specific chemical information including oxidation state, multinuclear species, and ternary complexation. For most of elements, XAS can determine coordination number and bond lengths to nearest neighboring elements. XAS can be used on wet samples, suspensions, and solutions under ambient conditions at absorber concentration down to 100 mg kg\(^{-1}\) or less [140].

XAS techniques and micrometer-scale XRF mapping are being employed frequently as nondestructive techniques for examining trace element associations,
distributions, speciation in a variety of samples [141]. The most recent developments in synchrotrons allow modification of the beam size, enabling elemental mapping with a spatial resolution well below 100 nm [17]. Karna et al. (2017) used synchrotron-based XAS technique to validate in vitro bioaccessibility test results on Pb and As, by examining how speciation and bioaccessibility change as a function of soil particle size [144].
2.11 REFERENCES


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CHAPTER III
CHEMICAL AND MINERALOGICAL CHARACTERIZATION OF AN ARSENIC
AND LEAD CONTAMINATED SUPERFUND SITE SOIL

3.1 INTRODUCTION

Mining and smelting are important industrial processes that extract minerals from ore. However, these activities release large amounts of heavy metals into the environment, including arsenic (As), chromium (Cr), copper (Cu), lead (Pb), cadmium (Cd), and zinc (Zn), thus creating a substantial pollution problem [1-4]. Due to their persistence and the risk of possible bio/geo-accumulation and biomagnification, these contaminants pose a threat to ecological and human health [1, 2]. Metals and metalloids such as Pb, Cd, and As do not have a beneficial effect for living organisms but may be harmful to plants, humans, and animals [5, 6].

Arsenic is a metalloid commonly found in Cu, Pb, and gold (Au) ores and is the second most common inorganic contaminant at Superfund sites [7]. The International Agency for Research on Cancer (IARC) classified arsenic as a Group I carcinogen [8]; the 120 agents in this group are known to cause cancer in humans and include benzo[a]pyrene, polychlorinated biphenyls (PCBs), and alpha emitting radiation. The mechanisms of arsenic-induced cancer include genotoxicity, alteration of DNA methylation, oxidative stress, altered cell proliferation, co-carcinogenesis, and tumor
promotion [9]. Nearly every organ in the body is at risk, but the lungs and skin are
highly vulnerable [7]. Chronic and acute exposure to arsenic can cause cardiovascular
disease (hypertension and atherosclerosis), neurological disorders, gastrointestinal
disturbances, liver disease and renal disease, reproductive health effects, dermal changes
and other health disorders in humans [10]. According to the Agency for Toxic
Substances and Disease Registry (ATSDR), the minimum risk level (MRL) for acute
oral exposure to inorganic As is 5 $\mu$g kg$^{-1}$ per day for up to 14 days, and chronic
exposure is 0.3 $\mu$g kg$^{-1}$ per day for a year or more [7]. Due to the nature of adverse
health effects from exposure to As even in minor concentrations, the World Health
Organization (WHO) and U.S. Environmental Protection Agency (US EPA) listed the
maximum allowable level of As in the drinking water as 10 $\mu$g L$^{-1}$ [11, 12].

Lead is the oldest known and most widely studied metal toxin associated with
mining and smelting industry; therefore, its health hazards are well documented [13-15].
Lead can pose significant hazards, especially in children, affecting the development of
brain and nervous system [14, 15]. The U.S. Center for Disease Control and Prevention
and WHO indicate that concentrations as low as 10 $\mu$g Pb/dL in the blood of children is
an elevated level [16]. Lower academic standing in high school, increased absenteeism,
lower vocabulary and grammatical-reasoning scores, poorer hand-eye coordination,
longer reaction times, and slower finger tapping are some of the problems resulting from
exposure to Pb in childhood [17]. Long term exposure to a low dose of Pb is associated
with deficit in central nervous system functioning and may cause weakness in fingers,
wrist, or ankle in children [18]. It can cause anemia, increased blood pressure and gastro
intestinal effects in adults [19]. Elevated blood lead concentrations leads to miscarriages and low infant birth rates in women exposed to lead [20]. High levels of Pb exposure severely damage kidneys and brains in both adults and children [18]. Though the evidence for direct carcinogenicity relationship is inadequate, large epidemiological studies of Pb workers found an association between Pb exposure and incidence of cancer [21]. Accidental ingestion of contaminated dust and soil particles are the main route of exposure of this toxin, especially to children [6, 22].

Chemical and mineralogical assessments are necessary to delineate the degree of contamination, determine the nature and extent of the pollution, and establish the foundation for quantifying ecological risk. A good assessment delivers information about primary and secondary sources, fate and transport, and pathways of possible migration of the contaminant. This information will be useful in assessing the best remediation strategy. When characterizing a contaminated site, the physical and chemical properties of the contaminant must be assessed in detail. Information about flora and fauna in the area is important in identifying the potential bio-transformation and bio-accumulation. Current activity, geography/demography, and the proximity of population at risk are helpful in decision making about remedial and mitigation processes [23].

When analyzing the risk posed by As, Pb, and other heavy metals, the total content of a given element is important, providing a snapshot of the degree and extent of contamination in the soil system [24]. However, the total metal content provides little if
any information regarding mobility, bioavailability, and potential toxicity [22]. Therefore total metal content alone is not enough in the characterization process. Metals in soil present themselves in several different physicochemical phases and in a variety of structural forms. For example, trivalent (As$^{3+}$) is more mobile and toxic than pentavalent the (As$^{5+}$) form [25]. Therefore, identifying and quantifying the readily available fraction of metals in the soil which can be easily accessible by plants, animals, and humans is necessary to gain a more precise understanding of its potential impacts and assess the best remediation strategies.

Sequential extraction is a widely used technique for operationally defining various forms of metals in the solid phase [26-29]. The major issue with this approach is that the detailed chemical nature of the material being extracted is not known. A lack of uniformity in the procedures, low selectivity of the extractants used, and quality control issues are some other problems [27]. Incomplete dissolution of certain phases may lead to re-adsorption or desorption of some of the metals [30]. Because the behavior of contaminants is driven by the nature of the inorganic and organic constituents with which the metals are associated, in practice the operationally-defined metal forms (from sequential extractions) may be much less specific than desired [27]. Due to these limitations, employing individual chemical extractions that access known chemical pools is more desirable than sequential extractions.

The choice of extraction technique should be based on the targeted metal fraction, such as water-soluble, exchangeable/plant available, and bioavailable [30-32].
The Physiologically-Based Extraction Test (PBET) is a widely used test to predict the bioavailability of metals from a solid matrix by extraction with a solution that mimics the chemistry of the human gastrointestinal tract [33]. Toxicity Characteristic Leaching Procedure (TCLP; US EPA 1992) is another standard method of toxic waste characterization, evaluating long-term environmental leachability [34]. In addition to these chemical extractions, direct methods of characterization such as electron microscopy, energy-dispersive X-ray spectroscopy, and X-ray diffraction should be used to obtain direct information regarding mineralogy and chemical bonding environment of the solid phase. Knowledge of mineralogy of metal bearing phases helps better understand stability, solubility, mobility, bioavailability and toxicity [35].

The goals of this study were to: a) characterize the general properties of soil from Jacob’s Smelter Superfund Site; b) determine the total concentrations of contaminant metals; c) use chemical extractants that are validated indices of bioavailability to provide an indication of potential risk posed by these metals. Information obtained from the study can be used to improve the efficiency of remediation strategies currently practiced at the site.

3.2 MATERIALS AND METHODS

3.2.1 SAMPLING

Soil was sampled from the vicinity of Jacobs Smelter on July 17, 2014. Surface soil (<30 cm) was collected from areas contaminated with As and Pb. A field portable X-ray fluorescence (XRF) analyzer (DP-6000 Delta Premium, featuring Rh X-ray tube)
[36] was used as a screening device to identify sampling areas with suitably high concentrations (>3000 mg Pb kg⁻¹; >1000 mg As kg⁻¹). The instrument was operated in “soil mode” at 15–40 keV, with scanning time of 90s per sample. Soil collected from each sampling location was mixed to produce a homogenous composite sample to be used for all investigations. Plant roots and other debris were removed in the laboratory and the remaining soil was air dried, crushed, and sieved (<2 mm) prior to analyses.

3.2.2 SOIL PROPERTIES

Basic soil properties were determined by the Soil, Water and Forage Testing Laboratory, at Texas A&M University, College Station. All chemicals were from Sigma Chemical Co. unless otherwise noted.

Particle size was analyzed by hydrometer method [37]. Conductivity and pH were determined in a 1:2 soil:water suspension. Organic matter content was measured by heating at 400 °C overnight [38]. Major elements P, K, Ca, Mg, Na, S were extracted using the Mehlich III extractant [39] and determined by inductively coupled plasma. Cation exchange capacity (CEC) of the soil was determined with a CaCl₂ method [40]. Soil was pretreated with sodium acetate buffer at pH 5 and heated to 90 °C to remove the carbonate material. The soil was saturated with Ca²⁺ ion which was then displaced with Mg²⁺ and quantified by atomic absorption spectrophotometer (AAS) to calculate the CEC of the soil.

The total iron content and “poorly crystalline iron” content in the soil were determined as follows: Total iron oxide content was quantified by citrate/bicarbonate/dithionite (CBD) [41]. Soil (0.5 g) was suspended in a solution of sodium citrate
bicarbonate and heated to 75 °C. Sodium dithionate was added, maintained at 75 °C for 15 min., and centrifuged. The Fe concentration in the supernatant was determined by AAS. Poorly crystalline iron content was determined using ammonium-oxalate-oxalic acid (pH 3) test in the dark [41]. Carbonate free soil (0.5 g) was added to 30 mL of ammonium oxalate-oxalic acid solution at pH 3 and shaken for 2 h on a reciprocating shaker at 50 rpm in a light proof container. The suspension was centrifuged, and the supernatant was analyzed for Fe by AAS.

Carbonate content was determined by titration method [42]. Five grams of fine crushed soil and 100 mL of 0.2 M HCl were added to a conical flask, reacted overnight, shaken for 2 hrs, and titrated against 0.1 M NaOH to the phenolphthalein endpoint.

3.2.3 EXTRACTION PROTOCOLS

Extraction procedures were conducted at the Soil Chemistry Laboratory at Texas A&M University, College Station, to test for the fractions that could potentially affect human and ecological health.

Deionized water was used to dissolve water soluble and readily available metals [30]. One gram of soil was extracted with 20 mL of deionized water for 2 hr at room temperature in a reciprocating benchtop shaker at 100 rpm. Extracts were filtered through 0.45 µm syringe filter and acidified to 1% with ultra-pure nitric acid for preservation until analysis. Plant-available As in soil was extracted using 0.5 M NaHCO₃ solution [43]. This test is very similar to the Olsen test used to estimate plant available levels of phosphorous in alkaline soil. One g of soil was extracted with 20 mL of 0.5 M
NaHCO$_3$ at pH 8 for 30 min in a reciprocal shaker at 100 rpm. The solution was filtered with 0.45 µm syringe filter and analyzed by ICP-MS.

The potentially bioaccessible metal fraction was assessed by the Physiologically Based Extraction Test (PBET) [33] to estimate gastrointestinal bioavailability though the ingestion of soil. One gram of air dried soil (<250 µm) was mixed with 100 mL 0.4 M glycine (at 37 °C and pH 2.00±0.05 adjusted with ultra-pure HCl) in a 125 mL HPDE plastic bottle. After extracting for 1 hr in a water bath shaker (100 rpm) at 37 °C, the solution was filtered through 0.45 µm syringe filter and analyzed by ICP-MS. Contaminated soil was tested to determine its hazardous waste disposal status using the Toxicity Characteristic Leaching Procedure (TCLP) [44]. The total metal content in the soil was determined by nitric acid digestion [45] at AgSource Cooperative Services, Stratford, WI.

3.2.4 ANALYTICAL METHODS

Metal concentrations (As, Pb, Cd, and Zn) in all extracts and digests were measured using Inductively Coupled Plasma Mass Spectrometry (ICP-MS, PerkinElmer NexION 300D). Calibration curves were determined from standards prepared using certified stock solutions. Sample blanks were analyzed to determine and correct for any matrix effects. Trace metal Standard Reference Materials (As and Pb plasma standard solution from Alfa Aesar) were used to assess instrument precision and accuracy and recoveries of 92-104% for As and 90-106% for Pb.
3.2.5 MINERALOGICAL ANALYSES

Bulk X-ray diffraction powder patterns were obtained using a PANanalytical X’Pert PRO X-ray diffraction system (PANalytical, Almelo, Netherlands). Soil samples were ground to pass a 140 μm sieve and placed in front-loading powder mount slides. Soil was pretreated to remove flocculating and cementing materials to enhance dispersion of and separation into three size fractions (sand, silt and clay). Size fractionation increases the XRD detection sensitivity of the minerals (some minerals tend to be more prevalent in specific size range) [46]. Soluble salts and carbonates were removed using 1 M sodium acetate adjusted to pH 5.5. Organic matter was removed by oxidizing with 30% hydrogen peroxide overnight. Soil was washed with deionized water to remove residual chemicals. The samples were separated with a 53 μm sieve with the sand particles remaining on the sieve. The particles passing through the sieve were centrifuged to separate silt particles (2-53 μm) from clay particles (<2 μm). The time required to settle silt particles was calculated based on Stoke’s Law [46].

Oven-dried (110 °C, overnight) sand and silt fractions were prepared for XRD analysis by the previously described powder mount. The clay fraction was dialyzed to remove excess electrolytes in the sample. The clay-sized sample was oven dried at 60 °C, ground to a powder, and saturated with either Mg or K before analysis. The clay dispersions were air dried on thin glass slides to create an oriented film. For the Mg-saturated sample, XRD peaks were recorded at 25 °C first and again after misting with 20% (v/v) glycerol solution. For the K-saturated sample, the XRD patterns were
recorded first at room temperature (25°C); after heating for 2 hours at 330 °C and cooling to room temperature; and after heating for 2 hrs at 550°C and cooling to room temperature. The XRD peaks of the samples were recorded on a Brucker Advance D8 X-ray diffractometer with Cu and Kα X-ray radiation, and analyzed with EVA software. A search and match method was employed to identify the minerals in the different fractions.

An FEI QUANTA 600F field emission scanning electron microscope-energy dispersive X-ray spectrometer (SEM-EDX) was used to examine the mineralogical properties of silt (2 to 53 μm) particles. Particles were coated with 4 nm-thick Pt/Pd alloy by sputter coating to ensure electrical conductivity. An accelerating voltage of 20 kV was used for chemical analysis using EDS during the count time of 100 s. Back-scattered electron (BSE) images were collected to locate the particles containing heavy metals.
3.3 RESULTS AND DISCUSSION

3.3.1 SITE INFORMATION

Figure 3.1 Site map and soil sampling locations.

The study area, known as “Jacob’s Smelter” is located within Rush Valley, Tooele County, Utah and immediately northeast of the small town of Stockton (Figure 3.1). The topography of the region is rolling hills and is 1524 m above sea level [47]. The climate of the area is semi-arid with warm, dry summers and cold winters. Average annual precipitation is 47 cm (18.5 in). The dominant vegetation is short to medium
grasses, shrubs, and herbaceous plants. Higher areas carry Douglas fir, yellow pine, scrub oak, and box elders. Lower areas bear considerable growth of juniper, pinon and scrub oak. Cliff rose, buck brush, June berry, and varieties of mountain shrubs and mahogany grow on mountain slopes. The host rock is a dolomitic limestone, and top soil is 10-20 cm deep. Bedrock is derived from quartzite, limestone and dolomite. Lead, silver, zinc copper deposits are associated with metamorphic lime-silicate rocks [48].

The Stockton area was a center of silver mining, base metal mining, and smelting from 1860 until 1970. A total of 9 smelters were documented, and the largest smelter was the Waterman Smelter, operated from 1871 until 1886. Some of the former property of the Waterman Smelter includes residential yards, vacant lots, unpaved streets and alleys. Non-residential land in the Stockton vicinity is used for agriculture (mostly grazing) and recreation [47]. The Jacob’s smelter site is considered a public health hazard due to high levels of lead and arsenic in the residential soil, as assessed by Utah Department of Environmental Quality (UDEQ) and US EPA. The site was added to the National Priority List in 2000 for long-term federal clean-up activities [49]. As the lead agency, UDEQ partnered with US EPA to address the unacceptable human health and environment at the site. Cleanup has been completed for several areas, including residential areas within the 1999 boundaries of the town of Stockton.

Investigations and evaluations for the clean-up of remaining areas are ongoing. In 2001, surface soil contaminated with 500mg kg\(^{-1}\) Pb and subsoil with 800 mg kg\(^{-1}\) lead were excavated to off-site landfill and replaced with clean soil for five planned but
undeveloped residential plots. An additional four residential subdivisions were cleaned up in 2011.

3.3.2 SOIL CLASSIFICATION AND ANALYSES

The soil in the sampled areas belongs to the Abela series: deep, well-drained Typic Calcixerolls formed from alluvial and lacustrine deposits. The Abela soils are derived from limestone, sandstone, and quartzite parent material. Basic soil properties are listed in Table 3.1. The textural class is clay loam with 25% sand, 38% silt, and 37% clay. The soil was slightly alkaline (pH of 8±0.2) and has low salinity (0.133 dS m\(^{-1}\)). No precipitate was observed when the saturated extract was treated with acetone, BaCl\(_2\), or AgNO\(_3\), indicating low concentrations of anions associated with evaporative minerals such as sulfate and chloride.

The average organic carbon content in the soil was 3.4% (w/w). The cation exchange capacity is 20 cmol kg\(^{-1}\), and with 93% of the exchange sites occupied by Ca and 5% base by K. High organic matter and CEC favor immobilization of Pb and, to a lesser extent, As. Lead has a high affinity for organic matter and forms strong complexes with organic ligands [50].

Total Fe content was 75,000 mg kg\(^{-1}\) as quantified by the citrate/bicarbonate/dithionite test. Only 850 mg Fe kg\(^{-1}\) soil was poorly-crystalline oxides as determined by the ammonium oxalate method. The average carbonate content in the soil was 9.7%.
Table 3.1 Basic soil properties of the contaminated soil used in this study

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH</td>
<td>8.0±0.2</td>
</tr>
<tr>
<td>EC (dS m(^{-1}))</td>
<td>0.13</td>
</tr>
<tr>
<td>Texture(^1)</td>
<td>Clay loam</td>
</tr>
<tr>
<td>clay (%)</td>
<td>37</td>
</tr>
<tr>
<td>silt (%)</td>
<td>38</td>
</tr>
<tr>
<td>sand (%)</td>
<td>25</td>
</tr>
<tr>
<td>Organic Matter (%, w/w)(^2)</td>
<td>3.4</td>
</tr>
<tr>
<td>CEC (cmol(_c) kg(^{-1}))(^3)</td>
<td>20</td>
</tr>
<tr>
<td>Extractable elements</td>
<td></td>
</tr>
<tr>
<td>Phosphorous (mg kg(^{-1}))(^4)</td>
<td>23</td>
</tr>
<tr>
<td>Calcium (mg kg(^{-1}))(^4)</td>
<td>3,700</td>
</tr>
<tr>
<td>Magnesium (mg kg(^{-1}))(^4)</td>
<td>735</td>
</tr>
<tr>
<td>Iron (total) (g kg(^{-1}))(^5)</td>
<td>75</td>
</tr>
</tbody>
</table>

\(^1\) Determined by hydrometer method; \(^2\) Mass loss by ignition; \(^3\) CaCl\(_2\) method; \(^4\) Mehlich(III) extraction; \(^5\) Citrate/bicarbonate/dithionite test

The metal concentrations were highest at the approximate location of the former Waterman smelter: 29,300 mg As kg\(^{-1}\) soil and 111,000 mg Pb kg\(^{-1}\) as determined in the field by XRF. These values decreased with distance from the smelter and were lowest (14 mg As kg\(^{-1}\) and 454 mg Pb kg\(^{-1}\)) next to the Superfund site boundary.
The metal concentrations extracted by different methods are summarized in Table 3.2. Total metal contents in the acid digests of contaminated soil were 7,520 mg As kg\(^{-1}\) and 66,440 mg Pb kg\(^{-1}\). Total metal content in the uncontaminated Abela soil were 10 mg As kg\(^{-1}\) and 51 mg Pb kg\(^{-1}\). According to the US EPA, the maximum allowable Pb content in residential soils is 300 mg Pb kg\(^{-1}\) [6, 51]. A similar value has not been developed for arsenic, but some standards for soil are emerging. US EPA Regional Screening Level (RSL) for unrestricted use (e.g., residential) is 0.39 mg As kg\(^{-1}\). The level is based on target cancer risk toxicological guidance values from the Integrated Risk Information System (IRIS), and standard assumptions for exposure assessment and risk assessment [52]. A regulated concentration of 0.39 mg kg\(^{-1}\) is problematic because the background concentrations of As in most soils exceed this value by at least a factor of ten [53]. This conundrum is being overcome in part by recommended Ecological Soil Screening Levels (ESSL) that account for reasonable paths of exposure. The ESSL values for As range from 43 to 170 mg As/(kg soil) for most birds and mammals and is 18 mg As/(kg soil) for plants [53].

3.3.3 EXTRACTION ANALYSES

The TCLP-extractable metal concentrations exceeded US EPA regulatory levels of 5 mg L\(^{-1}\) for both As and Pb (Table 3.2) [54]. In the literal application of TCLP, this result means that the soil could not be disposed in a standard, sanitary landfill but would require disposal in a RCRA Subtitle C landfill, licensed to accept hazardous waste. Extractions with water and 0.5 \(M\) NaHCO\(_3\) (Olsen method) removed relatively high
concentrations of the metals, meaning these metals are potential toxic to humans and other biological organisms. Water soluble As concentration in the soil was 1.83 mg As kg$^{-1}$. Water soluble As concentrations between 1.8 and 4.3 mg As kg$^{-1}$ have been found to inhibit seed germination for *Lactuca sativa* in ecotoxicity tests [55]. Arsenic water solubility from the soil is 0.09 mg As L$^{-1}$, which is 9 times higher than the WHO and US EPA maximum allowable concentration of 0.01 mg L$^{-1}$ in drinking [11, 12]. Concentrations of As in the soil extracted by NaHCO$_3$ are correlated with concentrations of As in plants growing in the same soils [32, 43, 56].

The Physiologically Based Extraction Test (PBET) simulates the chemical conditions found in the human gastrointestinal tract, and PBET-extractable As and Pb are strongly correlated metal assimilation by animal models [33]. For As, PBET removed 246 mg As kg$^{-1}$ soil or 3.3% of the total As present in the soil. For Pb, PBET removed 20,900 mg Pb kg$^{-1}$ soil, or 31% of the total Pb in the contaminated soil. These data indicate that the soil would be highly toxic if accidentally ingested.

### 3.3.4 MINERALOGICAL ANALYSES

Powder XRD patterns were obtained to identify the major minerals in the bulk soil. Quartz (SiO$_2$) and calcite (CaCO$_3$) were identified as the major components. The soil contained two crystalline Fe phases: jarosite [KFe[III]$_3$(OH)$_6$(SO$_4$)$_2$] and magnetite (Fe$_3$O$_4$). Kaolinite, montmorillonite, and illite, common clay minerals, also were identified. The suite of minerals varied among the size fractions. After removal of flocculating and cementing material, the sand fraction yielded only 2 minerals: quartz
Table 3.2 Metal content determined by different extraction techniques in the contaminated soil

<table>
<thead>
<tr>
<th>Method</th>
<th>As</th>
<th>Pb</th>
<th>Cd</th>
<th>Zn</th>
</tr>
</thead>
<tbody>
<tr>
<td>Total (mg kg(^{-1}) soil)</td>
<td>7,520</td>
<td>66,400</td>
<td>156</td>
<td>10,600</td>
</tr>
<tr>
<td>PBET (mg kg(^{-1}) soil)</td>
<td>246</td>
<td>20,900</td>
<td>138</td>
<td>4430</td>
</tr>
<tr>
<td>Water soluble (mg kg(^{-1}) soil)</td>
<td>1.83</td>
<td>17.5</td>
<td>0.11</td>
<td>7.44</td>
</tr>
<tr>
<td>Water soluble (mg L(^{-1}))</td>
<td>0.09</td>
<td>0.88</td>
<td>0.01</td>
<td>0.37</td>
</tr>
<tr>
<td>Sodium bicarbonate (mg kg(^{-1}) soil)</td>
<td>20.2</td>
<td>226</td>
<td>0.42</td>
<td>8.65</td>
</tr>
<tr>
<td>TCLP (mg L(^{-1}) extract)</td>
<td>5.67</td>
<td>6.36</td>
<td>1.83</td>
<td>8.83</td>
</tr>
</tbody>
</table>

and jarosite. In the silt fraction (Figure 3.2), quartz, magnetite and plumbojarosite were identified. Unlike in the sand fraction, the silt fraction contained minerals with the contaminant metals, indicating that the metal distribution favored the smaller size fractions and that the metals are being found in secondary minerals. Clay-sized fraction analysis by XRD revealed the presence of kaolinite, muscovite, smectite, quartz, and jarosite.
Additional mineral phases were identified in the silt fraction from the scanning electron microscope data, which was coupled with energy-dispersive X-ray elemental spectrometry [57]. The most commonly identified phase was jarosite, platy-shaped particles consisting of Fe, S, and K. Pyrite was another Fe phase identified by SEM, with an Fe:S molar ratio of 1:2. With a considerable amount of As in the spectrum (Figure 3.3a), some of the pyrite particles were identified as arseno-pyrite (FeAsS). Goethite (α-FeOOH) was present with a dominant Fe peak in the EDS data (Figure 3.3b). The EDS spectrum also indicated that Pb and As were present in the goethite structure, possibly through surface adsorption.
The chemical and mineralogical environment strongly influence bioavailability, and one must account for these factors in assessing the threat posed and in evaluating the remediation options for a contaminated soil. Total and plant available metals also are dependent upon physical interactions with the internal surfaces of soil aggregates which are directly influenced by the mineralogy [58]. Other critical factors to consider include pH, redox potential, soil texture, clay mineralogy, organic matter, reactive oxides,
surface area, and presence of competitive ions (cations and anions). The biotic environment also will have a strong impact: microbial activity, distribution of plant roots, and invertebrate activities can influence the bioavailability [59].

The contamination of the soil used in this study began over 100 years ago with a suite of potentially toxic metals being introduced by a smelting facility. Despite a legacy of extraordinarily high metal concentrations, the site is vegetated, mostly in the form of perennial grasses, indicating that the metals are not phytotoxic.

The soil is rich in quartz, limestone, and clay minerals. High clay content and the presence of organic carbon tend to reduce metal availability by various mechanisms of chemisorption, and the presence of carbonates can inhibit metal transfer from soil to plants [60]. Geochemical cycling of Fe plays an important role in metal biogeochemistry, particularly for oxyanions such as arsenate and arsenite. The average Fe content of soils ranges from 3% to 5% [61], but the contaminated Abela soil contains 7.5% total Fe, mostly as oxides including goethite, jarosite, and magnetite with a small fraction of non-crystalline oxides. In an oxidized, alkaline environment, arsenopyrite is unstable and oxidizes into arsenate and ferric iron [62]. The residual FeAsS (arsenopyrite) found in the contaminated Abela soil apparently has been protected to some degree from oxidation, but much of it has been oxidized to scorodite (FeAsO₄·2H₂O) [63]. The As oxyanions also can substitute similar oxyanions in secondary minerals such as jarosite, gypsum, and calcite. They also may form inner sphere complexes or localized precipitates on the surfaces of poorly crystalline iron
oxides [64]. These mechanisms are in play in the contaminated soils in this study, but substantial concentrations of bioaccessible arsenic and lead remain and require remediation measures to reduce the associated risks.

3.4 CONCLUSIONS

Several techniques were implemented to evaluate the chemical and mineralogical properties of metals contaminating the soil around Jacob’s Smelter. This is the first documentation of a) detailed soil physical and chemical characterization in the Jacob’s smelter superfund site and b) investigation of solubility and bio-availability of both As and Pb. Total arsenic and lead content and bioaccessible fractions are high, raising concerns of possible environmental and human health effects.

The mobility of the heavy metals in soils often is controlled by adsorption/desorption and co-precipitation with the metal oxides [7]. Therefore, the formation of oxides is a strong option for stabilizing these metals, potentially making the metals unavailable for plant uptake and translocation within the soil. Even though the soil in this study is enriched with iron oxides, most of these oxides are present in a crystalline form with lower surface area and fewer reactive binding sites than the poorly crystalline Fe oxides generally associated with in situ immobilization of contaminant metals. There is potential for using either non-crystalline Fe sources such as iron rich compost/biosolid or materials such as elemental sulfur to dissolve and re-precipitate the iron oxides in the soil, which would allow them to bind with the substantial amount of metals [8-10]. This avenue of research is pursued in the next chapter.
3.5 REFERENCES


CHAPTER IV

STABILIZATION OF ARSENIC IN ARSENIC-LEAD CONTAMINATED SOIL
USING IRON RICH WATER TREATMENT RESIDUALS (Fe-WTR)

4.1 INTRODUCTION

Arsenic (As) is a naturally-occurring element found in more than 245 minerals. Although arsenate [As(V)] is the predominant oxidation state, As can occur as +5, +3, 0 and -3 in the soil [1, 2]. Natural phenomena such as volcanic eruptions and mineralization of arsenic-bearing minerals, and anthropogenic activities such as mining, smelting, disposal of industrial waste, and burning of fossil fuels can result in elevated levels of arsenic concentrations in the environment [3]. According to the World Health Organization (WHO) and U.S. Environmental Protection Agency (US EPA), the maximum contaminant level for arsenic in drinking water is 10 µg L\(^{-1}\) [4, 5]. Although this drinking water standard is widely used, regulations for arsenic in the soil vary by region and have changed over time [6, 7].

Exposure to elevated arsenic concentrations may cause cancer in lungs, liver, bladder, kidneys, and skin. Acute and chronic poisoning includes respiratory, gastrointestinal, cardiovascular, nervous, and hematopoietic system failures [8, 9]. Arsenic release from mining and smelting sites is one of the major sources of contamination, but pollution is seldom limited to the immediate vicinity of the source and can be spread to
surrounding areas [10, 11]. Arsenic can migrate to residential and agricultural areas through dust particles, surface runoff, and leaching [11].

Use of iron compounds to limit As availability and mobility in polluted sites recently has been examined recently. Iron grit, a form of zero-valent iron, reduces As uptake by plants [12, 13]. Application of FeSO₄ can reduce As mobility and plant availability by formation of iron (hydr)oxide in soil [14]. In anoxic environments, application of sulfur-rich organic amendments, such as sewage sludge, can reduce the potential risk from arsenic contamination by precipitating immobile arsenic sulfide [15]. The solubility of As in the soil remained low under both aerobic and anaerobic conditions after amendment with sludge.

*In situ* stabilization of arsenic with Fe amendments can be achieved by the formation of amorphous iron arsenate or sparingly soluble secondary Fe minerals such as scorodite, FeAsO₄ [16], or adsorption by ligand exchange of As species for -OH₂ and -OH⁻ groups on Fe oxide/hydroxide surfaces [17, 18]. Spectroscopic analyses such as Extended X-ray Absorption Fine Structure (EXAFS) and Energy Dispersive Analysis of X-ray (EDAX) indicate that arsenic forms inner-sphere surface complexes with Fe compounds [19]. EXAFS analysis shows clear evidence of inner sphere bidentate arsenate complexes on the surface of ferrihydrite [20]. Ferrous sulfate also has been effective in reducing As mobility [14, 21] and phytoavailability [22, 23]. Application of steel shot to a contaminated soil at a rate of 10 g kg⁻¹ soil was effective in decreasing the
mobility of As in the soil [24] and reduction of As by vegetables grown in contaminated soil [25].

Water treatment residuals (WTR) often contain Al or Fe oxyhydroxides due to use of alum, \([\text{Al}_2(\text{SO}_4)_3 \cdot 14\text{H}_2\text{O}]\), ferric chloride [FeCl_3], or ferrous sulfate [FeSO_4] to remove particulates or co-precipitate dissolved constituents (e.g., orthophosphate) from the water [26]. These WTRs are nonhazardous and are generally buried in a landfill or used as soil amendments. In the USA, WTR are generally applied to land as either top dressing or incorporated into the soil [27]. Reuse of WTRs is an emerging approach applicable to agriculture and ecological reclamation projects. These byproducts also can be an alternative to more expensive iron amendments [27-29].

In an experiment to test the efficacy of WTRs in reducing As lability in contaminated soils, As was 100% sorbed to Fe-WTR and 98% sorbed to Al-WTR 48 hours after application in a sandy soil [30]. Also, Fe-WTR are more effective than Al-WTR in resisting As re-release [29]. Application of WTR reduces bioaccessibility of As and soluble concentrations in pore water [31]. Considering the potential phytotoxicity of Al originating from Al-WTR, Fe-WTP is a more suitable option. Fe-WTR can sorb up to 10,000 mg kg\(^{-1}\) of As [29] from contaminated solutions. Similarly, Fe-WTR can absorb 13,500 mg kg\(^{-1}\) of As from soil, and the sorption is strong enough to resist release even in the presence of P [29]. Spectroscopic evidence supports the hypothesis that strong As binding to Fe-WTR is the result of inner-sphere mononuclear bidentate complexes [32, 33]. Arsenate absorption is equally strong on Fe-WTR treated with lime [34].
Arsenic retention generally increases with increasing rates of Fe application, and a molar ratio of 2:1 Fe:As or higher is best for in situ remediation [14]. Interaction of As with Fe minerals, schwertmannite and ferrihydrite, at pH 3 resulted in As contents of 175 to 210 mg As kg\(^{-1}\) and degraded the host Fe mineral, possibly forming FeOHAs [16]. High-Fe, biosolid-based compost from a wastewater treatment facility and a low-Fe municipal solid waste compost were tested for their ability to decrease bioaccessibility of As and Pb in contaminated soil [35]. Low Fe composts were ineffective in reducing bioaccessibility, but the addition of high-Fe composts reduced Pb bioaccessibility from 48% in the untreated control to 35% in the Fe-WTR compost and reduced As bioaccessibility from 6.7% in the control to 5.0% in the Fe-WTR compost [35].

Lead is also a widespread environmental contaminant resulting from various human activities and natural phenomena. Lead and arsenic are the two most common inorganic contaminants in Superfund sites in the USA [31, 36]. Although various treatments are available for remediation of As and Pb in soils, finding a feasible treatment option for co-contaminated soils is a complex process [31, 37]. Phosphate, organic matter, and lime have been effectively used to remediate Pb-polluted soils [38, 39]; however, phosphate and organic matter are not only ineffective in As remediation, they increase the mobility and bioavailability of As in the soil due to the competition for adsorption sites between As oxyanion, phosphate, and organic ligands [40-43]. As a result, remediation of soil contaminated with both As and Pb is challenging because the most effective treatment for Pb increases the chemical lability and bioavailability of As.
After reviewing the literature, Fe-WTR was chosen over Al-WTR. Both WTR types have their advantages [44], but the key properties relevant to this research favored Fe-WTR. Although both Al-WTR and Fe-WTR strongly sorb As, Fe-WTR had greater As retention [30]. After amending both Fe-WTR and Al-WTR into contaminated soils, the Fe-WTR had greater resistance to re-release of the sorbed As when exposed to a bioaccessibility test that simulated the human stomach and intestinal phases [45]. A sample of Fe-WTR was found to have the capacity to adsorb 13,500 mg As kg\(^{-1}\) with little release upon exposure to soluble phosphate [32]. Application of Fe-WTR decreased As concentrations in pore water by 93% [46].

The objectives of this study were to determine: 1) The effect of adding goethite, ferrihydrite, and Fe-WTR to contaminated soil on the bioavailability and bioaccessibility of As; 2) The changes in PBET concentrations of As and Pb after simultaneous additions of P and Fe-WTR; 3) The optimum sequencing and rates of addition of P and Fe-WTR for reducing the bioaccessibility of Pb and As. 4) The impact of P and Fe-WTR additions on the uptake of As by the arsenic hyperaccumulator, *Pteris quadriaurita*.

4.2 MATERIALS AND METHODS

4.2.1 SOIL CHARACTERIZATION

The surface layer (<20 cm) of a soil highly contaminated with As and Pb was collected from a former smelting site in Stockton, Utah. The soil belongs to the Abela series: deep, well-drained Typic Calcixerolls formed from alluvial and lacustrine deposits. The Abela soils are derived from limestone, sandstone, and quartzite parent
material. The typical textural class is clay loam with 25% sand, 38% silt, and 37% clay. The soil sample was air dried and sieved (<2 mm) prior to use. Soil pH, electrical conductivity, organic matter content, total metal content, and particle size were determined using the standard protocols (Chapter 3). The contaminated soil was tested to determine its hazardous waste disposal status using Toxicity Characteristic Leaching Procedure [47].

The total Pb (66,400 mg Pb kg\(^{-1}\)) and total As (7,520 mg As kg\(^{-1}\)) concentrations in the original soil are at the high end of the spectrum for contaminated soils. These concentrations presented a number of practical challenges (such as the requirement for extreme concentrations of amendments); therefore, the soil was diluted for all experiments to make the metal concentrations more manageable: 1 part contaminated soil mixed with 4 parts uncontaminated soil of the same Abela soil series.

4.2.2 CHEMICAL EXTRACTION PROCEDURES

Water soluble Pb and As were extracted using de-ionized water [48]. One gram of soil was added to 20 mL of deionized H\(_2\)O shaken for 2 hrs at room temperature on a reciprocating benchtop shaker. The solution was filtered through 0.45 µm syringe filter and acidified to 1% using ultra-pure nitric acid until analyzed by inductively coupled plasma-mass spectrometry (ICP-MS).

Plant available arsenic in soil was extracted using 0.5 \(M\) NaHCO\(_3\) [49]. This extraction process is similar to Olsen test, which is used to estimate plant available levels
of phosphorous in alkaline soils and has been found to correlate with plant-available As in soil [50, 51]. One gram of soil was mixed with 20 mL of 0.5 M NaHCO$_3$ at pH 8.5 for 30 min on a reciprocal shaker. The solution was filtered using 0.45 µm syringe filter and acidified with enough ultra-pure nitric acid to neutralize the 0.5 M NaHCO$_3$ and provide a residual 1% HNO$_3$. The samples were analyzed by ICP-MS.

The Physiologically Based Extraction Test (PBET) [52] was used to quantify the bioaccessible fractions on Pb and As in the soil. The PBET estimates gastrointestinal bioavailability assuming ingestion of the soil. One gram of air dried soil (<250 µm) was mixed with 100 mL 0.4 M glycine (at 37 °C and pH 2.00 ± 0.05, adjusted with metal grade HCl) in a 125 mL HDPE plastic bottle. After extracting for 1 hr in a water bath shaker at 37 °C, the solution was filtered through 0.45 µm syringe filter and analyzed by ICP-MS.

4.2.3 INDUCTIVELY COUPLED PLASMA-MASS SPECTROMETRY

Arsenic and Pb concentrations were measured using ICP-MS (PerkinElmer NexION 300D). Sample blanks were analyzed to determine matrix effects and sources of contamination. To assess the accuracy of the methods, appropriate standard reference materials were used (As and Pb plasma standard solution from Alfa Aesar), and recoveries of 92-104% for As and 90-106% for Pb were observed.
4.2.4 IRON AMENDMENTS

Iron rich Fe-WTR, one of the chemical immobilizing treatments in this study, were collected from East Water Purification Plant, Houston, Texas (USA). Fe-WTR were air dried, crushed, and sieved into a uniform size of less than 0.2 mm. Mineralogy was characterized using X-ray diffraction techniques and electron microprobe. Total and poorly crystalline iron contents were characterized using citrate dithionate bicarbonate (buffered at pH 7) and ammonium oxalate oxalic acid (pH 3, dark) methods, respectively [53].

Goethite was used as a model iron compound and synthesized in the laboratory following the procedure presented in Cornell and Schwartzman (2003) [54]. In the procedure, 180 mL 5 M KOH was added to 100 mL 1 M Fe(NO$_3$_3)·9H$_2$O solution. An instant precipitation of red-brown ferric hydroxide was observed, assumed to be two-line ferrihydrite. The suspension was diluted to 2 L with deionized water and kept in a closed polypropylene bottle at 70 °C for 60 hours. During the heating stage, the voluminous, red-brown suspension of ferrihydrite was converted to a compact, yellow brown precipitate of goethite. The precipitate was washed three times with deionized water (to remove OH$^-$ and NO$_3^-$) and dried at 40 °C to avoid phase transformations before grinding into a fine powder. The solid product was verified as goethite by X-ray diffraction.

Two line ferrihydrite (FH) was used as another model compound synthesized following the procedure reported in Schwertmann and Cornell (1991) [55]. Three
hundred mL of 1 M KOH was added to the 500 mL of solution containing 40 g of Fe(NO\(_3\))\(_3\)·9H\(_2\)O, during vigorous mixing with a magnetic stirrer. The pH of the suspension was adjusted to 8.0±0.2, dewatered, and washed three times with deionized water. The resulting compound was centrifuged, freeze dried, and ground to a powder. The solid product was further verified by X-ray diffractometry.

4.2.5 REDUCING ARSENIC AND LEAD BIOACCESSIBILITY WITH IRON AMENDMENTS

Samples of the diluted soil were mixed thoroughly with Fe-WTR, goethite, or ferrihydrite at 2:1, 5:1, 10:1 Fe:As molar ratio. The contaminated soil without amendments was used as the control. All treatments were applied in triplicate in a completely randomized design. Soils treated with amendments were allowed to incubate in open air for 3 months at room temperature. At the end of the incubation, the soils were air dried and extracted with deionized water, 0.5 M NaHCO\(_3\), and PBET as described previously.

4.2.6 SIMULTANEOUS ADDITION OF IRON AND PHOSPHORUS

The impact of adding both Fe-WTR and orthophosphate on PBET-extractable Pb and As was tested. When used as an amendment, Fe-WTR was added at a molar ratio of 10:1 Fe:As. The treatments were Fe-WTR alone, Fe-WTR plus P at a 0.2:1 P:Pb molar ratio, Fe-WTR plus 0.5:1 P:Pb, Fe-WTR plus 1:1 P:Pb, Fe-WTR plus 5:1 P:Pb, and an untreated control. The treated soils were incubated in open air for 1 week. All treatments
were applied in triplicate in a completely randomized design. At the end of the incubation, the soils were air dried and extracted with deionized water, $0.5\ M\ \text{NaHCO}_3$, and PBET as described below.

4.2.7 SEQUENCING IRON AND PHOSPHORUS AMENDMENTS

Initial experiments confirmed that amending Pb/As contaminated soil with orthophosphate diminished Pb bioaccessibility but increased As bioaccessibility; however, adding Fe-containing amendments reduced As bioaccessibility but had little impact on Pb. Therefore, a combined, sequenced approach was taken. Two sequences were tested:

1) **P followed by Fe.** Orthophosphate was added first at a molar ratio of 0.2:1 P:Pb and 5:1 P:Pb. The soils were incubated for one week followed by Fe-WTR additions of 0, 4:1, and 10:1 Fe:As molar ratios.

2) **Fe followed by P.** Fe-WTR were added to the soil at 4:1 and 10:1 Fe:As molar ratios, incubated for one week, and then amended with P:Pb molar ratios of 0, 0.2:1, 0.5:1, and 5:1.

After incubating for an additional week, bioaccessibility of As and Pb was evaluated by PBET. All treatments were applied in triplicate in a completely randomized design.
4.2.8 PLANT UPTAKE AS AFFECTED BY IRON AND PHOSPHORUS AMENDMENTS

A species of the arsenic hyperaccumulating Chinese brake fern, *Pteris quadriaurita*, was selected as a bioindicator to test the efficiency of the amendments in reducing bioavailability of As [56]. Three month old plants were purchased (Edenspace, Purcellville, Virginia) and transferred to 2 L pots filled with 1 kg of treated soil. This experiment was conducted in a controlled environment with 8 hours of light at an intensity of 350 μmol m⁻² s⁻¹, 25 °C daytime temperature, 20 °C night temperature, and 60–70% relative humidity. A completely randomized design was employed for eight Fe treatments: 1) ferrihydrite at a 4:1 molar ratio of Fe:As, 2) ferrihydrite at a 10:1 ratio, 3) goethite at a 4:1 molar ratio of Fe:As, 4) goethite at a 10:1 ratio, 5) Fe-WTR at a 4:1 molar ratio of Fe:As, 6) Fe-WTR at a 10:1 ratio, and 7) contaminated soil with no Fe added, 8) uncontaminated soil with no Fe added. These eight treatments were amended with orthophosphate at a 1:1 P:Pb molar ratio or received no P. All combinations were imposed in triplicate: eight treatments x two P levels x 3 replicates for 48 pots. After a 90 day growth period, the fronds of the ferns were harvested and washed with de-ionized water. The harvested fronds were dried at 60 °C for 48 h, and the dry weights were recorded.

Ground plant materials (0.5 g) were digested with nitric acid and hydrogen peroxide on a temperature controlled digestion block (Environmental Express, Mt.
Pleasant, S.C.) using US EPA Method 3050A for metal analysis (As and Pb) using ICP-MS [57].

4.2.9 STATISTICAL ANALYSES

All data were statistically analyzed using CoHort Software (Berkeley, CA). Analysis of variance (ANOVA) for complete randomization was applied for each experiment with 1-way, 2-way, or 3-way ANOVA, as appropriate. Significance was determined with a Tukey’s test (P<0.05).

4.3 RESULTS AND DISCUSSION

4.3.1 SOIL AND Fe-WTR PROPERTIES

Total lead and arsenic contents of the contaminated soil samples are 66,440 mg kg\(^{-1}\) and 7,520 mg kg\(^{-1}\), respectively. As reported in Chapter 3, bioaccessible (PBET) concentrations of Pb and As are high in the soil (20,900 mg Pb kg\(^{-1}\) and 246 mg As kg\(^{-1}\)); 30% of the Pb and 3% of the As are readily bioaccessible. These values are similar to those of Brown et al. (2012) who found 48% bioaccessible Pb and 6.7% As in a near-neutral soil.

The goethite synthesized in this experiment contained 63% Fe, ferrihydrite is 66% Fe, and Fe-WTR is 12% Fe. Arsenic and Pb were not detected in these amendments. X-ray diffraction analysis of the Fe-WTR detected quartz and some minor quantities of magnesian calcite, but no iron-containing materials were detected by this method. Nearly all of the Fe in Fe-WTR is non-crystalline as determined by the ammonium oxalate
method; non-crystalline, oxalate extractable Fe generally has a high surface area and is highly reactive. The organic matter content in Fe-WTR is 14%.

4.3.2 REDUCING ARSENIC AND LEAD LABILITY WITH IRON AMENDMENTS

**Water Soluble As and Pb:** Reduction in the potentially mobile fraction of As and Pb in the soil in response to Fe amendments was assessed by measuring the water soluble fraction. Water extractable As concentrations (Figure 4.1) are significantly reduced in all three amended soils compared to the control. Application of goethite at a 2:1 Fe:As molar ratio reduced the As water solubility by 40%; 65% reduction in the 5:1 treatment, 79% in the 10:1 treatment. The same application rates of ferrihydrite reduced water soluble As by 59%, 80% and 86%, respectively; reductions in water soluble As concentrations in response to ferrihydrite were significantly greater than the corresponding Fe:As ratios of goethite. Application of Fe-WTR at Fe:As a ratio of 2:1 reduced water soluble As by 65%; by 82% in the 5:1, and 95% in the 10:1. These reductions were greater than those of ferrihydrite and goethite for all ratios with the exception of the 10:1 in which Fe-WTR and ferrihydrite were statistically equivalent.

Water soluble Pb responded similarly to As. Even the lowest molar ratios of Fe:As decreased Pb solubility, and Pb solubility decreased with increasing Fe:As ratios. The degree to which Pb solubility declined (5 to 72%) was somewhat less than for As (40 to 86% decrease).
The strong impact of Fe additions on As solubility is likely due to surface interactions between As and the Fe oxides. The ferrihydrite and Fe-WTR have higher surface area and are more reactive than goethite, and the presence of organic matter also likely played a role in immobilizing the As [35].

![Figure 4.1](image)

**Figure 4.1** Water soluble As and Pb as affected by Fe as goethite (GOE), ferrihydrite (FH), and Fe-WTR (WTR) at various molar ratios. The dashed line is water soluble contaminant in the unamended, contaminated soil. Error bars represent one standard deviation. Mean values associated with the same letter are not statistically different.

**Bicarbonate-Extractable Arsenic and Lead:** Arsenic can be mobilized in geologic media by bicarbonate ions [58], and extraction of As from the soil using the Olsen method (0.5 $M$ NaHCO$_3$, pH 8.5) provides an index of As readily available for plant uptake [49-51]. Bicarbonate-extractable As (Figure 4.2) responded to Fe additions in a manner similar to
water soluble As. The control has the highest bicarbonate extractable As, while amendment with goethite, FH and Fe-WTR reduced As extractability significantly.

![Figure 4.2 Bicarbonate (0.5 M, pH 8.5) extractable As and Pb as affected by Fe amendments as goethite (GOE), ferrihydrite (FH), and Fe-WTR (WTR) at various molar ratios. The dashed line is bicarbonate extractable concentrations in the unamended, contaminated soil. Error bars represent one standard deviation. Mean values associated with the same letter are not statistically different.](image)

Application of goethite with molar ratios of 2:1, 5:1 and 10:1 Fe:As reduced bicarbonate extractable As by 20%, 31% and 45%, respectively; ferrihydrite reductions were 17%, 22% and 33%; and Fe-WTR reductions were 39%, 52% and 60%. For 2:1 and 5:1 rates, goethite and ferrihydrite are statistically equivalent, and goethite is more effective than ferrihydrite in reducing bicarbonate-As at a molar ratio of 10:1. At all
molar ratios, Fe-WTR is more effective in reducing bicarbonate-As than goethite and ferrihydrite. Additions of Fe-WTR at molar ratios of 5:1 and 10:1 are the only applications that reduced the bicarbonate-As by more than 50%.

Extraction of Pb with bicarbonate has not been given any biological or environmental significance, and the solution and solid phase chemistry of Pb in a 0.5 \( M \) \( \text{HCO}_3^- \) is complicated by the tendency to precipitate carbonate solids and form strong carbonate solution complexes [e.g., \( \text{Pb} (\text{CO}_3)_2^{2-} \)]. Therefore, although the bicarbonate-Pb data are interesting, they do not have any particular physical meaning. In response to goethite additions, bicarbonate-Pb significantly increased. Ferrihydrite had no impact on bicarbonate-Pb. Fe-WTR addition at a ratio of 10:1 Fe:As decreased bicarbonate-Pb, but amendment with lower ratios did not impact extractable Pb concentrations.

**Bioaccessible As and Pb:** The physiologically based extraction test (PBET) predicts the bioavailability of arsenic from soil by simulating the chemical conditions found in the human gastrointestinal tract [52]. Because the area from which the soil was collected is located next to a residential area, characterizing the potential effects of accidental ingestion and inhalation of the contaminated soil is relevant.

The means of PBET-As concentrations (Figure 4.3) in response to all treatments are less than the control, but the differences between the PBET-As for the untreated control and the goethite 2:1 and ferrihydrite 5:1 treatments are not significant. Application of goethite reduced PBET-As by 9%, 20% and 21% for 2:1, 5:1 and 10:1 Fe:As amendments, respectively; reductions of 16%, 11% and 45% for ferrihydrite
additions; and 73%, 94% and 96% for Fe-WTR. Goethite and ferrihydrite amendments at a given molar ratio resulted in PBET-As concentrations that are statistically equivalent with the exception of 10:1 in which ferrihydrite had a lower concentration. All PBET-As concentrations associated with Fe-WTR amendments are significantly lower than the goethite and ferrihydrite treatments. Within Fe-WTR treatments, increasing the Fe:As ratio significantly decreased the PBET-As concentration.

**Figure 4.3** PBET extractable As and Pb as affected by Fe as goethite (GOE), ferrihydrite (FH), and Fe-WTR (WTR) at various molar ratios. The dashed line is PBET extractable concentrations in the unamended, contaminated soil. Error bars represent one standard deviation. Mean values associated with the same letter are not statistically different.
Lead concentrations extracted by PBET were generally unimpacted by Fe additions. Although some of the treatments were significantly different from each other, only the Fe-WTR at 10:1 Fe:As resulted in PBET-Pb concentrations that were significantly lower than the unamended control. This agrees with previously observed trends [35] and suggests that Fe amendments would not be a reasonable alternative to soluble P for reducing Pb bioaccessibility.

For the three extractions tested, Fe-WTR is the best option for reducing the extractable/available As in the contaminated soil. Within the Fe-WTR treatments, increasing the Fe:As ratio resulted in significantly lower extractable As concentrations (with the exception of the bicarbonate extract in which the 5:1 and 10:1 were statistically equivalent). This is an encouraging resulting in going forward to find treatments that effectively reduce both Pb and As bioavailability.

The addition of Fe had consistent impacts only on water soluble extractable Pb concentrations with water soluble Pb decreased with increasing Fe treatments. For bicarbonate and PBET, only Fe-WTR consistently decreased Pb concentrations with increasing Fe additions.

4.3.3 MANAGING CONTAMINATED SOIL WITH Fe-WTR AND PHOSPHORUS

A major difficulty in reducing simultaneously the bioavailability of Pb and As in contaminated soil is their contrasting chemistries. Lead bioaccessibility is efficiently controlled by added orthophosphate to form the sparingly soluble pyromorphites [59].
Unfortunately, the addition of orthophosphate to an As contaminated soil tends to mobilize the As [24, 59, 60]. However, a combination of P and Fe added together has the potential to immobilize both Pb and As [59, 61].

In this study, Fe-WTR was added at a 10:1 Fe:As mole ratio simultaneously with soluble P (KH$_2$PO$_4$) added at 0, 0.2:1, 0.5:1, 1:1, and 5:1 P:Pb mole ratios. An untreated soil served as the control, and the impact of PBET-Pb and PBET-As was observed after a 1 week incubation period. The most effective treatment for reducing PBET-As was Fe-WTR (reducing PBET-As by 72%) followed by Fe-WTR + 0.2:1 P:Pb (Fig. 4.4). The 0.5:1 and 1:1 P:Pb treatments were not significantly different than the control, and adding 5:1 P:Pb actually doubled the PBET-As. For PBET-Pb, each treatment resulted in significant decreases in extractable concentrations, with 5:1 P:Pb being the most effective.

The results of this experiment are consistent with observations published previously. The addition of phosphate decreased As(V) sorption to WTR, but the trends were dependent on pH, WTR type, amendment application rates, and phosphate concentration [28]. In another study [29], application of soluble P after adding Fe-WTR caused 50% desorption of As regardless of the application rate. Yuan et al. (2017) [61] added a synthesized “iron hydroxyl phosphate” to a Pb and As contaminated, calcareous soil and found excellent immobilization efficiency of both Pb and As as determined by DPTA for Pb and NaHCO$_3$ for As (the authors did not measure bioaccessibility).
Figure 4.4 As (upper) and Pb (lower) concentrations extracted by PBET 1 week after treatment with soluble P and Fe-WTR. Fe-WTR at 10:1 Fe:As molar ratio; 0.2P - 0.2:1 P:Pb molar ratio; 0.5P – 0.5:1 P:Pb; 1P – 1:1 P:Pb; 5P – 5:1 P:Pb.

Error bars represent 1 standard deviation.
In this experiment, as more orthophosphate is added, more As becomes available. At the higher P:Pb ratios, PBET-As exceeds the control. In an attempt to overcome this tendency, the next strategy was to add the P and Fe in different sequences.

We were particularly interested in knowing if adding P alone followed by Fe-WTR would be a solution: the P creates a stable pyromorphite phase to immobilize the Pb, and the iron adsorbs all labile As.

4.3.4 SEQUENCING IRON AND PHOSPHORUS AMENDMENTS

In this experiment, two sequencing strategies were used: 1) adding soluble P, incubating for one week, adding Fe-WTR, and incubating an additional week. 2) adding Fe-WTR, incubating for one week, adding soluble P, and incubating an additional week. At the end of the final incubation period, PBET bioaccessible Pb and As were determined.

The patterns of PBET-As concentrations in response to the treatments (Figure 4.5) are dependent on the amendment sequence. If P is added first, PBET-As initially is high but decreases with increasing Fe:As as provided by the Fe-WTR amendment. If Fe-WTR is added first, PBET-As concentrations are low but increase with increasing P:Pb ratio.

The response of Pb to the treatments is complex and depends upon both sequencing and levels of amendment applications. When P was added first, PBET-Pb was approximately 50% of the value in the control. For the 5:1 P:Pb molar ratio, PBET-Pb concentration
remained constant across all subsequent Fe treatments. For the 0.2:1 P:Pb treatment, increasing Fe-WTR additions increased the PBET-Pb concentrations. The reason for this pattern could be one or both of the following: a) the Fe from the Fe-WTR solubilized pyromorphite by precipitating a ferric phosphate solid phase, such as strengite; b) the organic matter content of the Fe-WTR solubilized the Pb from the matrix. The consistently low values of PBET-Pb at the 5:1 P:Pb are the result of the excessive quantities of soluble P overcoming the tendencies of the Fe-WTR to solubilize the Pb. When Fe-WTR was added first, all PBET-Pb concentrations were significantly higher than the control except for the 5:1 P:Pb treatments. Again, the Fe-WTR treatment was interfering with the reaction between the P and the Pb, preventing pyromorphite from forming until an excessive concentration of soluble was added.
Figure 4.5 The effect of P and Fe sequencing on PBET-As and PBET-Pb. The initial amendment is represented as the second line below the horizontal axis; the second treatment is represented in a small font and in the line immediately below the horizontal axis. Initial treatments: 0.2P – 0.2:1 molar ratio of P:Pb; 5P – 5:1 P:Pb; 4Fe – 4:1 Fe:As; 10Fe – 10:1 Fe:As. Secondary treatments: Ctrl – no amendments; 0Fe – no Fe-WTR added; 4Fe and 10Fe – same as initial treatments; 0P – no P added; 0.2P – 0.2:1 P:Pb; 2P – 0.2:1 P:Pb; 5P – 0.2:1 P:Pb. Error bars are 1 standard deviation.
Of the two sequences tested, adding P first at the lower rate holds the most promise. When Fe-WTR was the first amendment added, very high levels of P were needed to overcome the solubilizing action of the Fe-WTR. Examining the data for both PBET-As and PBET-Pb in Figure 4.5, three treatment combinations were able to decrease both Pb and As concentrations by more than 20%: 0.2P+4Fe decreased As by 42% and Pb by 31%; 0.2P+10P decreased As by 64% and Pb by 20%; and 5P+10Fe decreased As by 37% and Pb by 57%. The 5P+10Fe treatment is the most effective. However, from a practical perspective, the 0.2+4Fe treatment might be preferred because it would require fewer inputs.

4.3.5 PLANT GROWTH TEST

Plant availability of As in contaminated soil is an important component of ecotoxicity. If As is readily available to plants, then transfer of As throughout the terrestrial food chain is possible, but this transfer becomes less likely if bioavailability can be suppressed by soil amendments. Extraction of As with 0.5 M NaHCO$_3$ at pH 8.5 has been used as an index of plant uptake of As [49, 50, 51], and additions of Fe to the contaminated soil significantly reduced HCO$_3$-As (Fig. 4.3). Perhaps the ultimate test of the efficacy of Fe amendments for restricting As plant availability is to evaluate arsenic uptake by an As hyperaccumulator, a plant with exceptional capability to remove As from soil. In this experiment, *Pteris quadriaurita* was employed in this role.

The contaminated soil collected from Jacobs Smelter was diluted by a factor of five with clean soil (4 parts clean soil to 1 part contaminated soil) from the same Abela
soil series collected near the smelter. Dilution was necessary to avoid the many problems from the extreme contamination of the original soil and from the high levels of amendments needed to meet the required P:Pb and Fe:As ratios. For example, an amendment of 1:1 molar ratio of P:Pb in the undiluted soil would require 43.6 g KH$_2$PO$_4$ kg$^{-1}$ soil and would generate an electrolytic conductivity of approximately 60 dS/m. *Pteris quadriaurita* is sensitive to soil salinity, and this level of amendment would be toxic. Applied on a field basis, this amount of P (43,600 mg kg$^{-1}$ or 87,200 lb P/ac) would likely have serious environmental consequences.

The amendments had little visual impact on the growing plants (Figure 4.6). The plants generally were healthy and added several new fronds during the experiment (new fronds emerge red in color). However, plants grown in FH 4:1+P and FH 10:1+P treated soils were observed to have necrotic leaf tips and curling fronds, which was not observed with any other treatments. These symptoms are typical of salt stress in the ferns.

The oven-dry biomass of the ferns is shown in Figure 4.7. The dashed line is the biomass of the ferns grown in the uncontaminated Abela soil with no amendments, serving as the benchmark for healthy growth. Several of the treatments had significantly less growth than the uncontaminated control including the contaminated control with or without soluble P amendments; all goethite treatments except 4:1 Fe:As with no P; all ferrihydrite treatments. However, all Fe-WTR treatments, both with and without P, had biomass that was equivalent to the uncontaminated control. The level of contamination was high enough to reduce plant growth, but adding Fe-WTR overcame the inhibition.
Even though the addition of P reduced biomass, in the Fe-WTR treatments, the biomass was not significantly less than the uncontaminated control.

Figure 4.6 Pteris quadriaurita grown in A) contaminated untreated soil, B) uncontaminated soil, C) 5:1 Fe:As goethite treated soil, D) 5:1 Fe:As ferricydrite treated soil, E) 5:1 Fe:As Fe-WTR treated soil 12 weeks after transplanting.
Figure 4.7 Biomass of *Pteris quadriaurita* grown in various treatments Ctrl: Contaminated/ untreated soil; G – goethite; FH – ferrihydrite; WT – Fe-WTR; 4 – 4:1 Fe:As molar ratio; 10 – 10:1 Fe:As molar ratio. Error bars represent one standard deviation, and the dashed line is the biomass of the *P. quadriaurita* grown in uncontaminated, untreated soil.

*P. quadriaurita* grown in uncontaminated soil had a mean As content of 7.6 mg kg$^{-1}$, the lowest among all the treatments (Fig. 4.8). Plants in the contaminated soil with no Fe but 1:1 mole ratio of Pb:P had the highest As content of 142 mg As kg$^{-1}$ soil followed by the 0 Fe, 0 P treatment with 137 mg kg$^{-1}$. None of the goethite treatments reduced the As concentrations significantly below these concentrations. All ferrihydrite
treatments resulted in plant As concentrations significantly below the untreated contaminated soil. The 10:1 Fe:As 0P ferrihydrite treatment and both 10:1 Fe-WTR treatments resulted in significantly lower plant As concentrations than all goethite treatments and were statistically equivalent to the As concentrations in the plants in the uncontaminated soils.

Figure 4.8 Arsenic in *P. quadriaurita* fronds in response to Fe and P treatments. UnCtrl – uncontaminated control soil; ConCtrl – contaminated soil without Fe treatments; all other labels are defined in Figure 4.7. Error bars represent one standard deviation.
The trend in Figure 4.8 was the trend predicted from Fig. 4.2 for Fe-WTR treatments, but ferrihydrite was more effective in reducing As than predicted. Phosphorus treatments were absent in the data from Figure 4.2; therefore, the contaminated soils from the *P. quadriaurita* experiment were extracted with 0.5 M NaHCO₃ to determine the ability of the Olsen test to predict plant As uptake (Fig. 4.9). A significant, positive correlation resulted, agreeing with previous observations that a HCO₃ extraction provides a good index of plant availability for As [49-51].

The addition of Fe was effective in reducing As uptake by the highly efficient As hyperaccumulator. All Fe-WTR and the ferrihydrite 10:1 Fe:As treatments reduced As uptake more efficiently than all goethite treatments. The high surface area of the amorphous/microcrystalline Fe oxides in these treatments apparently provided the best opportunity for strong adsorption and immobilization of As. Although the addition of P increased As uptake, the impact was not significant within any Fe treatment. These results are in contrast with the PBET bioaccessibility results in which the impact of P additions always were significant (Fig. 4.5). This is probably due to the more aggressive nature of the PBET compared to rhizosphere/bicarbonate extractant.
Figure 4.9 Relationship between As concentrations in *P. quadriaurita* fronds and bicarbonate-extractable soil As. Only the contaminated soil was included in this analysis.

4.3.6 FUTURE RESEARCH

Three important questions remain from this study: 1) What is the long-term stability of As sorbed to Fe-WTR? Arsenic can be released from Fe-WTR amended soil under water logged conditions because of the solubilization of the Fe oxides under...
anoxic conditions. Under oxidizing conditions, this was not observed [68]. Further study of the long-term stability of this surface complex is warranted. 2) What is the mechanism of As adsorption to Fe-WTR? Many chemical and mineralogical pathways are possible, but direct evidence is needed. Examining the microstructure and mineralogy along with chemistry, speciation, and biogeochemistry is required. Synchrotron based x-ray analysis techniques such as X-ray Absorption Spectroscopy and μX-ray diffraction could provide the answers. This approach is pursued in Chapter 5. 3) Would alternative approaches to the sequencing of Fe and P addition prove to be more efficient? The current research is hopeful, but much greater reductions in bioaccessibility of Pb and As are needed.
4.4 REFERENCES


CHAPTER V

µ-XANES AND µ-XRF INVESTIGATION OF ARSENIC AND LEAD STABILIZATION BY IRON RICH DRINKING WATER TREATMENT RESIDUALS IN CONTAMINATED SOIL

5.1 INTRODUCTION

Human activities such as mining, manufacturing, and agricultural frequently add metal(loid)s to the earth’s surface, creating air, water, and land pollution [1]. Lead (Pb) and arsenic (As) are common contaminants associated with mining and smelting activities [2, 3], and they are toxic and potentially harmful to humans, microbes, and animals [4-6]. The health risks posed by metal(loid) contaminants are magnified when the contaminants are found in proximity to human activities due to exposure through drinking water, food, and inhalation of airborne particles [7]. In many cases, these contaminants are heterogeneously dispersed at the micrometer scale, and this small size helps facilitate accidental ingestion and inhalation. The toxicity, bioavailability, and environmental fate/transport of contaminants are also dependent on the chemical speciation at the molecular level [8].

Assessment of speciation includes contaminant identification; oxidation state; physical phase; association with retention as surface-bound or adsorbed species; empirical formula; and detailed molecular structure [9, 10]. Spatially resolved
characterization of elemental abundance and speciation provides a better understanding of the mechanisms by which these metal contaminants are bound and transported in the environment [11]. Chemical extractions, such as sequential, partial, or simple methods, provide indirect information about speciation and should be confirmed by other methods. Chemical species may be altered during or after the extraction process, generating over- or underestimation of metal concentrations in the various pools [12, 13]. For example, X-ray spectroscopic analyses discovered that a sequential extraction procedure for a Pb contaminated, phosphorous (P) amended soil resulted in the formation of pyromorphite [Pb$_5$(PO$_4$)$_3$Cl] [14].

Many physical instrumental methods are available to explore the chemistry of solid phase metals in soils and sediments. Mass spectrometry has high sensitivity and the ability to handle complex mixtures but lacks the ability for speciation, and the destructive nature of the technique results in lost details of surface structure [13]. Raman spectroscopy, X-ray diffraction (XRD), and Fourier transform infrared spectroscopy (FTIR) are nondestructive techniques that can be used to identify the known compounds in simple mixtures [15-17]. FTIR is limited to compounds with IR-active bonds, absorbing electromagnetic radiation in the IR range or emitting IR radiation [18]. XRD can identify crystalline material, but microcrystalline or non-crystalline solids are not detected [17]. Instrumental methods such as electron microprobe, scanning electron microscopy, and transmission electron microscopy create images at high resolution and, if combined with wavelength or energy dispersive spectroscopies, can determine the elemental composition of the material/mineral [19, 20]. A common problem associated
with some of these instruments is that the high vacuum used by these techniques may alter elemental speciation [21, 22].

During the last two decades, synchrotron-based techniques have been used in soil, plant and environmental studies. These methods provide information at scales of measurement from angstrom ($10^{-10}$ m) to millimeters ($10^{-3}$ m) [23]. When electrons in an accelerator are brought to velocities near the speed of light (“relativistic electrons”) and are directed through a curved path by magnetic fields, the electrons emit intense electromagnetic radiation, called “synchrotron radiation”, that covers the spectral range from the infrared to the hard X-ray region [24]. The light from a synchrotron has the basic properties of typical instrumental sources (e.g., X-ray tubes) but is distinctly different: (i) very intense, several orders of magnitude brighter than conventional sources; (ii) covers a wide spectrum; (iii) highly polarized (elliptical, linear, or circular); (iv) nanosecond, time-structured emissions [25].

X-ray absorption and X-ray fluorescence are powerful tools in the synchrotron environment [24, 26]. X-rays directed at a solid engage in absorption in a systematic fashion that reveals information about the elements in the solid [27]. If an X-ray reaching a sample is of lower energy than the binding energy of the core electrons of the element of interest, this element will not participate in the X-ray absorption process [25]. As the incident X-rays increase in energy to the point where the X-ray energy is equal to the binding energy of the core level electrons, a defined increase in absorption of the X-rays is observed [25]. Fluorescence occurs simultaneously when core electrons of the
target element are ejected by the incident X-rays. An electron from a higher energy orbital fills the vacancy created by the ejected electron to return the atom to the ground state, and fluorescence occurs at a wavelength defined by the difference in energy between the two electron levels [27]. Fluorescence and absorption depend upon the specific energies of the incident X-rays and the quantum characteristics of the electronic configuration of the target atoms [25]. The specific energies of fluorescence and absorption are the foundation of XRF (X-ray fluorescence) and XAS (X-ray absorption), powerful techniques commonly used for metal(loid) speciation in soils [17]. Synchrotron-based XRF identifies and quantifies elements in a wide variety of samples in a nondestructive manner and generates multielemental maps [28]. The XAS data are gathered by repeatedly examining the same locations, selected from XRF maps, using a series of x-ray energies above and below the adsorption edge [29].

High intensity synchrotron X-rays and the ability to “tune” them is the basis for splitting the XAS spectrum into two energy regions: extended X-ray absorption fine structure (EXAFS) and X-ray absorption near edge spectroscopy (XANES) [25]. The XANES spectrum is generally understood to extend from 50 to 100 eV lower than the absorption edge to approximately 50 eV above the absorption edge [25] (Fig. 5.1). The remaining portion of the XAS spectrum, from the end of the XANES to about 350 eV above the absorption edge, is the EXAFS spectrum [25]. The oxidation state of an element can be determined by XANES because the absorption edge will increase in energy by 1–3 eV for every valence electron removed (e.g., increasing oxidation state) due to the increased attraction of the electrons for the nucleus in the core levels. The
position of the absorption edge in the energy spectrum also depends upon the bonding environment of the target element in relation to the electronegativity of the ligand(s) to which it is bonded [25]. Fluorescence-XANES generates complementary data when employing XRF and XAS on the same samples [29].

![X-ray absorption spectrum of an As-rich region in contaminated soil from Jacob’s smelter, illustrating the XANES and EXAFS ranges.](image)

**Figure 5.1** X-ray absorption spectrum of an As-rich region in contaminated soil from Jacob’s smelter, illustrating the XANES and EXAFS ranges.

When more than one component of a given element is present in an XAS analysis, the spectrum will be the sum of the contributions of each component. The percentage of each component present in a sample can be determined using a linear
combination fit (LCF) and principal component analysis (PCA) to match the unknown sample spectrum to known reference spectra [30].

Many spectroscopic methods require relatively high concentrations of the target element/solid, dry samples, and high vacuum [23]. XAS has no such requirements. XAS is capable of distinguishing between adsorption from precipitation for many soil metals and metalloids; inner versus outer sphere surface complexes; mono- versus bidentate surface complexes; and provides specific chemical information including oxidation state, multinuclear species, and ternary complexation [23]. For most of elements, XAS can determine coordination number and bond lengths to nearest neighboring element. XAS can be used on wet samples, suspensions, and solutions under ambient conditions at absorber concentration down to 100 mg kg$^{-1}$ or less [23].

XAS techniques and µm-scale XRF mapping are frequently employed as nondestructive techniques for examining trace element associations, distributions, speciation in a variety of samples [24]. Recent developments in synchrotrons have modified the beam size, enabling elemental mapping with a spatial resolution well below 100 nm [20]. Synchrotron-based XAS has been used to validate in vitro bioaccessibility test results for Pb and As by examining changes in speciation and bioaccessibility as a function of soil particle size [30].

Iron-based amendments for in situ remediation of arsenic-contaminated soil have been used increasingly over the past decade [31]. Application of iron grit, industrial byproducts high in Fe, and Fe/Al-based water treatment residues (WTR) to contaminated
soils diminishes As bioavailability and toxicity [32, 33]. The experiments in Chapter 4 and other published studies [32, 34, 35] demonstrated that iron-rich drinking water treatment residuals (Fe-WTR) show promise in reducing soluble and bioaccessible fractions of As in a soil also contaminated with Pb. Water soluble, plant available, and bioavailable fractions of As decreased immediately after amending with Fe-WTR. Efficiency in reducing bioaccessible Pb fraction can be increased by combining soluble P with the Fe-WTR, but additions of orthophosphate can increase As desorption [36].

Goethite and ferrihydrite were used in Chapter 4 as model, Fe-based amendments to be added to contaminated soil for in situ immobilization of As. Goethite is crystalline with less surface area [37] than the microcrystalline, high surface area, and highly reactive ferrihydrite [38-40]. Additions of goethite and ferrihydrite to the Jacobs Smelter soil and an untreated control were compared to Fe-WTR amendments for efficiency of As fixation. After laboratory incubation, the soils were evaluated by a suite of wet chemical extractions, and As extractability followed the trend: untreated soil > goethite > ferrihydrite > Fe-WTR amended soil. The trends in extractability of both Pb and As were clear, but chemical and mineralogical explanations were lacking.

The overall goal of this study is to understand the processes by which As and Pb are stabilized through the addition of Fe-WTR and soluble P. Synchrotron techniques, μ-XRF and μ-XANES, were employed to determine the oxidation states of As and Fe; identify As and Pb minerals in the original sampled soils; and identify and quantify changes induced by amending the contaminated soils with Fe-WTR and/or soluble P.
5.2 MATERIALS AND METHODS

5.2.1 SOIL SAMPLES

The samples used in this experiment came from soil treatments in the previous experiment:

1) Contaminated soil. The soil is from the Jacobs Smelter site near Stockton, Utah, and contained 66,400 mg Pb kg\(^{-1}\) and 7,520 mg As kg\(^{-1}\). The soil belongs to the Abela series: deep, well-drained Typic Calcixerolls formed from alluvial and lacustrine deposits. For all treatments, the contaminated soil was diluted 1:4 with uncontaminated Abela soil to reduce the total contaminant levels.

2) Iron-rich water treatment residuals (Fe-WTR). The Fe-WTR were collected from the East Water Purification Plant, Houston, Texas (USA). Fe-WTR were air dried, crushed, and sieved into a uniform size of less than 0.2 mm. The Fe-WTR contains 12% Fe (mass basis) in the form of poorly crystalline Fe(III) oxides.

3) Contaminated soil + Fe-WTR. The Fe-WTR treatment used for this study was 10:1 Fe:As molar ratio. This required adding approximately 10% (mass basis) Fe-WTR to the soil. The Fe-WTR-soil mixture was homogenized, incubated for one week at approximately field moisture, further homogenized, and air dried.

4) Contaminated soil + P. The contaminated soil was amended with orthophosphate (as KH\(_2\)PO\(_4\)) as P:Pb molar ratio of 1:1. The mixture was homogenized, incubated for one week at field moisture, further homogenized, and air dried.

5) Contaminated soil + P + Fe-WTR. The contaminated soil was amended with KH\(_2\)PO\(_4\) at a 1:1 P:Pb molar ratio, homogenized, and incubated for one week at
approximately field moisture. Fe-WTR was then added at a 10:1 Fe:As molar ratio, homogenized, incubated for one week at approximately field moisture, again homogenized, and air-dried.

5.2.2 μ-XRF AND μ-XANES

The micro-scale spatial distribution of As, Pb, and Fe in the unamended and amended contaminated soil samples was mapped by μ-XRF, and speciation of these elements was determined by μ-XANES. The analysis was conducted at Beamline Sector 13-IDE (GeoSoilEnviro Consortium of Advanced Radiation Sources) at the Advanced Photon Source at Argonne National Laboratory, Argonne, Illinois. The μ-XRF mapping and μ-XANES spectra were collected in fluorescence mode with a solid-state 13-element detector at ambient temperature. Sieved soil samples (<250 µm) were placed on 5-by-5 cm slide mounts by sandwiching several milligrams of the sample between two pieces of Kapton tape that spanned the aperture in the slide mount. The slides were mounted on the rotation axis of an x-y-θ stepping-motor stage. Fluorescence data were collected at 16,000 eV after the X-ray beam was focused to 2 µm step size, and μ-XRF maps were generated for each sample to identify the distribution of As, Pb and Fe in the sample.

Using μ-XRF, a 300 µm by 300 µm map was developed for the control (untreated) contaminated soil and a sample of the Fe-WTR. A 400 µm by 400 µm map was developed for Fe-WTR amended soil, Fe-WTR + phosphate amended soil, and phosphate amended soil.
5.2.3 DATA ANALYSIS

After creation of μ-XRF maps, As-rich locations (points of interest where As was relatively highly concentrated) were identified in each map and μ-XANES data were obtained for the As-K edge at 11,867 eV at 50 μm step size. Spectra were successfully collected for seven As locations in contaminated soil, six locations in Fe-WTR amended soil, four locations for phosphate amended soil, and four locations for Fe-WTR + phosphate treated soil. Three XANES spectra were collected for each As location and averaged to increase spectral quality. The edge energy was calibrated, the pre-edge was subtracted, and the spectrum was normalized [41]. These As spectra were compared to the spectra of a set of 25 As minerals, used as standards, employing linear combination fitting (LCF) to understand the range and combination of As species present. Linear-combination fitting (LCF) of the μ-XANES spectra of samples with those of various model compounds (standards) was performed using the Athena software [42]. The LCF procedure reconstructs the experimental spectra using combinations of the standard spectra. The combination with the lowest reduced $\chi^2$ was chosen as the most likely set of components for μ-XANES fitting [41].

Lead and Fe μ-XANES data were collected and analyzed by LCF using Athena software, IFEFFIT software [42] as described above. Spectra were collected from five Pb locations in contaminated/untreated soil, five locations in Fe-WTR treated soil, three locations in phosphate treated soil, and three locations in Fe-WTR + phosphate treated soil. For Fe, μ-XANES spectra were collected for five locations in
contaminated/untreated soil, four locations in Fe-WTR amended soil, five locations for Fe-WTR. Due to time constraints at the Argonne facility, Fe XANES data were not collected for Fe-WTR + phosphate treated soil.

Only well-characterized minerals were included as standards in LCF fitting. µ-XANES spectra for standard minerals were collected at the time of the sample analyses using standards were provided by Ganga Hettiarachchi and her research group at Kansas State University. Ferric arsenate sulphate (FAS) spectra were obtained from Dogan Paktunc at Canada Centre for Mineral and Energy Technology. Spectra for standard materials collected at the beamline included loellingite (FeAs$_2$), scorodite (FeAsO$_4$·2H$_2$O), schneiderhonite [Fe(II)Fe(III)$_3$As$_5$O$_{13}$], cerussite (PbCO$_3$), and magnetite (Fe$_3$O$_4$).

5.3 RESULTS AND DISCUSSION

Physical and chemical properties of the contaminated soil are given in Table 5.1. The soil is slightly alkaline (pH 8), and amending with Fe-WTR did not change the soil pH. The high pH is due to the calcic bedrock in the area and the semi-arid climate. Despite extremely high metal concentrations found in the soil, typical densities of native grasses are observed in the abandoned mine, and moderate organic matter content is present in the soil.
5.3.1 ARSENIC AND LEAD BIOACCESSIBILITY

Using the physiological based extraction test (PBET), 1 to 3% of As and 25 to 30% of lead is bioaccessible (Chapter 4). Application of Fe-WTR at a 10:1 Fe:As molar

<table>
<thead>
<tr>
<th>Table 5.1 Basic chemical properties of the contaminated soil and Fe-WTR</th>
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<td>pH</td>
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<td>EC (dS m(^{-1}))</td>
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<td>Texture(^1)</td>
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<td>clay (%)</td>
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<tr>
<td>silt (%)</td>
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<tr>
<td>sand (%)</td>
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<tr>
<td>Organic Matter (%, w/w)(^3)</td>
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<tr>
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<td>Extractable elements</td>
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<tr>
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<td>Calcium (mg kg(^{-1}))(^5)</td>
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<tr>
<td>Magnesium (mg kg(^{-1}))(^5)</td>
</tr>
<tr>
<td>Iron (mg kg(^{-1}))(^6)</td>
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<tr>
<td>Total metals(^7)</td>
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<tr>
<td>As (mg kg(^{-1}))</td>
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<tr>
<td>Pb (mg kg(^{-1}))</td>
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<tr>
<td>Fe (% w/w)</td>
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\(^1\) Determined by hydrometer method; \(^2\) not determined; \(^3\) Mass loss by ignition; \(^4\) CaCl\(_2\) method; \(^5\) Mehlich(III) extractant; \(^6\) DTPA extractant; \(^7\) nitric acid/peroxide digest.
ratio decreased As bioaccessibility by 71% and bioaccessible Pb by 14%. When soluble phosphate (5:1 P:Pb molar ratio) was added first, incubated for one week, followed by Fe-WTR (10:1 Fe:As), As bioaccessibility decreased by 43% and Pb decreased by 63%. The amendments can change As and Pb bioaccessibility by providing additional adsorption sites or incorporate the As and Pb into stable minerals through coprecipitation [43]. Iron (hydr)oxides have received some attention for As stabilization, while soluble P and biosolids have been studied extensively for lead stabilization in the soil [26, 44-46]. Organic C and iron oxides provide additional sorption sites for metal adsorption; solubleFe promotes formation of stable minerals such as scorodite, FeAsO$_4$·2H$_2$O; and soluble P promotes formation of stable Pb minerals such as the pyromorphites [1]. The synchrotron-based techniques used in this study can identify changes in chemical associations induced by the addition of Fe-WTR and soluble P to As and Pb contaminated soils.

5.3.2 CHARACTERIZATION OF THE Fe-WTR MATERIAL

Chemical and physical properties of the Fe-WTR are given in Table 5.1. Fe-WTR has a slightly alkaline pH and is enriched with calcium and organic matter (14% by weight). Fe-WTR consist of 12% Fe (weight basis) mainly as non-crystalline form as determined by NH$_4$-oxalate-oxalic acid (pH 3, in the dark) extraction. Quartz was the predominant crystalline mineral identified from XRD in addition to minor amounts of magnesian calcite. Consistent with the oxalate extraction data, XRD analysis was unable
to identify crystalline Fe minerals. The major component of Fe identified in the Fe-WTR by μ-XANES analysis is ferrihydrite.

5.3.3 ARSENIC SPECIATION

The arsenic K-edge XANES absorption spectrum covers a 5 eV interval, beginning at 11,865 eV for As(0) and approximately 11,870 eV for As(V) compounds. With the increasing oxidation state, the absorption edge increases in height. Each compound for each treatment type was compared separately to identify the As oxidation state.

Figure 5.2 is a series of μ-XRF generated maps for the various treatments. Figure 5.3 gives, for each treatment, an example XANES spectrum with the measured spectrum in blue and the LCF result in red. The mineral composition for each treatment was averaged over several locations, and the resulting mean composition is given in Table 5.2. In the uncontaminated soil, the LCF matches well with the measured spectrum when it was assumed that 73.6% of the As was found in arsenolite and 25.3% in yukonite (Fig 5.3). When averaged over all locations used from Fig. 5.2a, the mineral composition is 60% arsenolite, 20% yukonite with lesser amounts of beudantite, scorodite, and loellingite. In the Fe-WTR treated soil (Figs. 5.2b, 5.3b), the average predominant solid phases were sorbed As(V) (27%), arsenolite (25%), scorodite (22%), and yukonite (18%) (Table 5.2).
Figure 5.2 μ-XRF maps generated for a) control soil (300 μm X 300 μm); b) Fe-WTR amended soil (400 μm X 400 μm); c) P + Fe-WTR amended soil (400 μm X 400 μm); d) KH₂PO₄ amended soil (400 μm X 400 μm).
Figure 5.3 μ-XANES analysis for As in different treatments. Blue lines are the measured XANES spectra. Red lines are LCF best fit. a) Location As-5 in Fig 5.2a; b) Location As-1 in Fig 5.2b; c) Location As-2 in Fig 5.2c; d) Location As-2 in Fig 5.2d. Mineral compositions for the LCF models are given in Table 5.2
Table 5.2 speciation of As, Pb and Fe identified by μ-XANES on selected points of interest located on μ-XRF elemental maps of contaminated and amended soil samples

<table>
<thead>
<tr>
<th>Treatment</th>
<th>As Minerals/Solids</th>
<th>%</th>
<th>Pb Minerals/Solids</th>
<th>%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Untreated</td>
<td>Arsenolite As₄O₆</td>
<td>60</td>
<td>Plomboferrite Pb₂Mn(II)₀.₂Mg₀.₁Fe(III)₁₀.₆O₁₈.₄</td>
<td>30</td>
</tr>
<tr>
<td></td>
<td>Yukonite Ca₇Fe₁₁(AsO₄)₃O₁₀·24.₃H₂O</td>
<td>20</td>
<td>Pb sorbed to hydroxyl apatite</td>
<td>15</td>
</tr>
<tr>
<td></td>
<td>Beudantite PbFe₃(AsO₄)SO₄(OH)₆</td>
<td>10</td>
<td>Hydroxyypyromorphite Pb₅(PO₄)₃OH</td>
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<tr>
<td></td>
<td>Scorodite FeAsO₄·2H₂O</td>
<td>8</td>
<td>Leadhillite Pb₄SO₄(CO₃)₂(OH)₂</td>
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</tr>
<tr>
<td></td>
<td>Loellingite FeAs₂</td>
<td>2</td>
<td>Cerussite PbCO₃</td>
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<tr>
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<td></td>
<td>Chloropyromorphite Pb₅(PO₄)₃Cl</td>
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<td></td>
<td></td>
<td></td>
<td>Galena PbS</td>
<td>5</td>
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<tr>
<td></td>
<td></td>
<td></td>
<td>Anglesite PbSO₄,</td>
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<tr>
<td></td>
<td></td>
<td></td>
<td>Plombonacrite Pb₁₀(CO₃)₆O(OH)₆</td>
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<tr>
<td>Fe-WTR</td>
<td>Sorbed As(V)</td>
<td>27</td>
<td>Leadhillite</td>
<td>40</td>
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<tr>
<td></td>
<td>Arsenolite</td>
<td>25</td>
<td>Sorbed Pb</td>
<td>40</td>
</tr>
<tr>
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<td>Scorodite</td>
<td>22</td>
<td>Chloropyromorphite</td>
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<tr>
<td></td>
<td>Yukonite</td>
<td>18</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Ferric arsenate sulfate (FAS)</td>
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Table 5.2 continued

<table>
<thead>
<tr>
<th>Treatment</th>
<th>As Minerals/Solids</th>
<th>%</th>
<th>Pb Minerals/Solids</th>
<th>%</th>
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<tr>
<td>P + Fe-WTR</td>
<td>FAS</td>
<td>39</td>
<td>Hydroxy pyromorphite</td>
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<tr>
<td>Arsenolite</td>
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<td>24</td>
<td>Sorbed Pb</td>
<td>30</td>
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<td>Scorodite</td>
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<td>Cerussite</td>
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<td>Yukonite</td>
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<td>12</td>
<td>Plumboferrite</td>
<td>10</td>
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<td>Parascorodite</td>
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<td>3</td>
<td>Hydrocerussite Pb₃(CO₃)₂(OH)₂,</td>
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<td></td>
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<td>Hinsdalite PbAl₃(PO₄)(SO₄)(OH)₆</td>
<td>5</td>
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<tr>
<td>Phosphate</td>
<td>Sorbed As(V)</td>
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<td>Hydroxy pyromorphite</td>
<td>70</td>
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<tr>
<td>Yukonite</td>
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<td>20</td>
<td>Leadhillite</td>
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<tr>
<td>As₂O₅</td>
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<td>20</td>
<td>Cerussite</td>
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<td>Beudantite</td>
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<td>Plumboferrite</td>
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<tr>
<td>FAS</td>
<td></td>
<td>5</td>
<td>Sorbed Pb</td>
<td>5</td>
</tr>
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</table>
Adding Fe-WTR oxidized much of the As(III) in the unamended soil increasing adsorbed As(V) and the fraction of scorodite. This is consistent with what we know about the chemistry of As in soils in the presence of poorly crystalline Fe oxides [33, 34, 36, 48].

When soluble phosphate was added alone (Fig. 5.3d), As$_2$O$_5$ was 74% of the total, yukonite was 18%, and 5% sorbed As. When averaged over all measured locations (Table 5.2), the dominant minerals were the same but the percentages shifted. Adding soluble P to soil will release As from previous binding sites, making it more soluble ([37] and Chapter 4 Fig. 4.7). The high content of As$_2$O$_5$ (Fig. 5.3c), one of the more soluble forms of As(V), is consistent with this information. The presence of beudantite is consistent with findings from the investigation of mineralogy from mine tailings in Mexico [49].

When soluble P was added to the contaminated soil first followed one week later by Fe-WTR amendment (Figs. 5.2d and 5.3d), the dominant solid phases were ferric arsenate sulfate (39%), arsenolite (24%), scorodite (22%), and yukonite (12%). These results are similar to those of the adding Fe-WTR alone with significant decreases in the As(III) mineral, arsenolite, and increases in ferric arsenolate sulfate. In both treatments with added Fe-WTR, the formation of Fe-bearing As minerals was observed, a result consistent with the previous observations (Chapter 4).
153 plumboferrite 56%
Pb-goethite 27%
Galena 17%

leadhillite 42%
sorbed Pb 33%
chloropyromorphite 25%

Sorbed Pb 49%
Hydroxypyromorphite 32%
plumboferrite 17%

Cerussite 52%
Hydroxypyromorphite 28%
sorbed Pb 21%

Figure 5.4 µ-XANES analysis for Pb in different treatments. Blue lines are the measured XANES spectra. Red lines are LCF best fit. a) Location Pb-1 in Fig 5.2a; b) Location Pb-4 in Fig 5.2b; c) Location Pb-2 in Fig 5.2c; d) Location Pb-2 in Fig 5.2d. Mineral compositions for the LCF models are given in Table 5.2

5.3.4 LEAD SPECIATION

X-ray absorption measurements were performed at the Pb L_{III} edge (13,055 eV) for air-dried soils (<250 μm). After generating µ-XRF maps, µ-XANES spectra were collected
for five different Pb-rich locations in the contaminated/control soil, three locations in phosphate treated soil, five locations in Fe-WTR amended soil, and four locations in Fe-WTR+P amended soil.

Lead in the unamended soil (Fig. 5.2a) was found as plumboferrite (30%), sorbed to hydroxyapatite (15%), pyromorphites (20%), leadhillite (10%), cerussite (10%), and minor amounts of galena, anglesite, and plumboacrite (Fig. 5.4a, Table 5.2). These are the types of minerals one would expect for Pb to form in a calcareous soil with a high Fe content. The predominant minerals changed very little when Fe-WTR was added as an amendment (Fig 5.2b and 5.4b; Table 5.2). Leadhillite, sorbed Pb, and chloropyromorphite were the dominant minerals. Plumboferrite, important in the untreated control, was not dominant in the Fe-WTR treatements.

With the addition of soluble P alone, the mineral composition shifted toward hydroxypomorphite (70%) with smaller amounts of leadhillite and cerussite (10% each) (Table 5.2, Fig. 5.4c). This is not a surprising outcome; adding soluble P to a Pb contaminated soil is known to form the sparingly soluble pyromorphite minerals [31, 47]. Adding P followed by Fe-WTR resulted in 40% hydroxypomorphite, 30 sorbed Pb, and 10% each of cerussite and plumboferrite (Table 5.2, Fig. 5.3d). These results are consistent with the observations in Chapter 4 in which adding Fe-WTR after soluble resulted in slightly more bioaccessible Pb. The negative impact of Fe-WTR on soluble P in situ remediation of soil Pb soil can be attributed the interaction of the highly reactive Fe oxide surfaces with the P. Keeping in mind that Fe-WTR was added at a 10:1 Fe:As molar ratio,
enough Fe oxides were added to potentially draw at least some of the P from the pyromorphites, thus negating some of the impact of adding soluble P.

Application of Fe-WTR has the potential to reduce bioaccessible Pb content due to increased sites of Pb adsorption on the ferrihydrite and organic matter found in the Fe-WTR. Molecular and macroscopic scale investigation accompanied with surface complexation model predicted that Pb(II) sorption onto 2-line ferrihydrite as bidentate-monomonuclear/monodentate-monomonuclear species pairs [47]. The formation of inner-sphere sorption complexes depends on morphology, temperature and time [48]. In Chapter 4, additions of Fe-WTR at a ratio 10:1 Fe:As slightly, but significantly, increased PBET-Pb compared to the control soil. LCF analysis of the XANES spectra of the identified locations in Fig. 5.2b yielded 87% sorbed Pb in Pb-2, 50% sorbed Pb in Pb-1, and 33% sorbed Pb in Pb-4 (Fig 5.4b). Those Pb locations were adjacent to Fe particles. Although sorbed Pb increased in the Fe-WTR amended soils, the increased PBET-Pb in these soils suggests that the sorbed Pb was still bioaccessible. Other minerals identified in the Fe-WTR treated soils included leadhillite \([\text{Pb}_4\text{SO}_4(\text{CO}_3)_2]\) 42% in Pb-4 and chloropyromorphite 25% (Fig 5.4b).

With the application of only P to contaminated soils (Fig. 5.2d), Pb mobility is restricted due to formation of low soluble secondary Pb minerals such as chloropyromorphite \([\text{Pb}_5(\text{PO}_4)_3\text{Cl}]\). Pyromorphites are the most thermodynamically stable and least soluble Pb minerals over a large pH range [50]. Pyromorphite mineral content increased 50% compared to the untreated soil. Sorbed Pb was identified in the phosphate treated soil as was an increased leadhillite content. Formation of sparingly soluble secondary Pb minerals is a primary reason for decreased bioaccessibility when Pb-
contaminated soils are treated with soluble P. The efficacy of this approach depends upon soil pH, ancillary amendments (e.g., Mn oxides), incubation time and etc. [26]. Addition of soluble P to highly contaminated soils must be managed carefully to avoid offsite movement of the P, which will promote eutrophication in aquatic ecosystems [51].

When the contaminated soils were amended with soluble P followed on week later with Fe-WTR (Fig. 5.2c), bioaccessible Pb was lower than in the control but not as low as in the absence of Fe-WTR (Chapter 4, Figure 4.5). Other minerals identified in the Fe-WTR+P amended soil include sorbed Pb, hydroxypyromorphite, hinsdalite, plumboferrite, cerussite, and hydrocerussite. As an example, Pb-4 (Fig 5.2c) consists of 50% sorbed lead, 32.5% hydroxypyromorphite and 17.5% plumboferrite (Fig 5.4c).

Neutral and alkaline soils have the potential to support the presence of cerussite, hydrocerussite, hydroxypyromorphite, Pb(OH)₂, Pb₅(PO₄)₂, and Pb₄O(PO₄)₂. The lead phosphate minerals, particularly the pyromorphites, are sparingly soluble and predicted to control Pb²⁺ in soil solution under the Eh and pH conditions commonly found in natural systems [52].

Because the soil in Jacob’s smelter is slightly alkaline (pH 8), in an oxidative environment pyromorphite is the most stable Pb solid phase (Fig. 5.5). The LCF analysis suggested that the uncontaminated soil has 20% pyromorphites prior to amendments, but the addition of soluble P favors the formation of more pyromorphite (Fig. 5.4).
5.3.5 IRON SPECIATION

One of the most useful characteristics of the Fe-K pre-edge is determining the oxidation state [53]. Pre-edge position and shape of the spectra indicate that the Fe in the unamended contaminated soil is present as a mixture of Fe(II) and Fe(III), but Fe(III) predominates in the Fe-WTR and Fe-WTR amended soil. Figure 5.6 illustrates Fe(II) being present in the contaminated soil in the Fe location Fe-control 1 (Fig. 5.2a) and Fe(III) present in the contaminated soil at location Fe-control-3. The Fe-WTR and Fe-WTR amended soil were totally Fe(III) oxidation state.
Figure 5.6 Pre-edge position of Fe location in contaminated soil (Fe-control positions 1 and 3 in Fig. 5.2a), Fe-WTR material (Fe-WTR) and Fe-WTR amended soil (Fe-WTR-50).

LCF fitting of the Fe-XANES spectra was not of the same quality as for As and Pb. Rather than mineral identification with poor fits, only the oxidation state of the Fe in the mineral was identified.

5.4 CONCLUSIONS

The goal of this project was to use advanced spectroscopic techniques to explain observed trends in chemical and biological lability of Pb and As in a contaminated soil in response to amendments. The synchrotron analyses, particularly XANES, provide at least partial explanation of the observed trends in lability.
1) When iron-rich water treatment solids (Fe-WTR) were added to the soil, water soluble, bicarbonate extractable, and PBET As all decreased dramatically. However, although water soluble and bicarbonate extractable Pb decreased with Fe-WTR additions, the effect on PBET-Pb was far less dramatic. These observations are readily explained by the XANES analyses: As(III) was oxidized to As(V), Fe-sorbed As increased, and sorbed Pb increased.

2) When soluble P was added in the absence of other amendments, bioaccessible Pb decreased by at least 50%, but bioaccessible As concentrations increased. XANES analyses of contaminated soil samples amended with only P revealed the formation of large quantities of pyromorphite minerals (sparingly soluble, P-containing solids) and a decrease in clearly defined complex soil minerals and an increase in As$_2$O$_5$. Both of these are consistent with trends in PBET extractions.

3) When P was added to the soil first, incubated, treated with Fe-WTR, and incubated another week, PBET-Pb increase slightly compared to P-only treatments, and PBET-As was much lower than in the P-only treatment. For Pb, XANES analyses found more pyromorphite than in the Fe-WTR treatment but less than in the P-only treatment. Ferric arsenate sulfate and scorodite minerals dominated the As solid phases but were not as prevalent as in the Fe-WTR treatment.

Overall, the XANES analyses explained the changes in lability of Pb and As. Time on the synchrotron is very difficult to schedule, requiring the approval of a competitive grant, and more time at this powerful facility could have greatly improved our results.
5.5 REFERENCES


CHAPTER VI

CONCLUSIONS

This dissertation presents results from a series of experiments conducted on a highly contaminated soil that was sampled in July 2014 from the Jacobs Smelter Superfund Site. The area is the former site of several smelters that began operations in the 1860s and ran for nearly 100 years. The soils from this site are contaminated with As and Pb with concentrations that pose a significant risk to human health and environment. In this dissertation, chemical stabilization of As and Pb using iron-based amendments in conjunction with soluble P was investigated. The Fe treatments were ferrihydrite, goethite, and Fe-rich water treatment residuals (Fe-WTR). The Fe-WTR are a byproduct of a water treatment process in which ferric chloride was used as a coagulant to remove particles in the water. Fe-WTR is composed mainly of quartz, non-crystalline Fe rich oxides, 20% organic matter, and small amounts of magnesian calcite. Total Fe content of Fe-WTR is 12% by weight, all in the Fe(III) oxidation state.

In a laboratory in situ evaluation of the efficacy of the Fe amendments, an inverse relationship was observed between available As fraction, measured by several extraction procedures, and the Fe:As ratio application rate. For example, application of Fe-WTR reduced water soluble As fraction by 40 to 86%, plant available As fraction by 40 to 60%, and the bio-accessible As fraction by 73% to 93%, depending upon the Fe:As molar ratio. Based on the EPA’s toxicity leaching characteristic process (TCLP), application of Fe-
WTR decreased leachable As concentrations to less than 5 mg L$^{-1}$, the guideline to identify hazardous solid waste. Iron-based amendments were generally not as effective in reducing Pb bioavailability. For example, only the Fe-WTR at 10:1 Fe:As resulted in reduced PBET-Pb concentrations that were significantly lower than the unamended control. Based on these experiments and previously published data, Fe-WTR is an efficient stabilizing agent for As, but Fe alone is not a reasonable amendment for Pb. Application of Fe-WTR combined with a orthophosphate increased the efficiency of Pb stabilizing in the soil.

Plant availability of As is an important component in eco-toxicity because it facilitates food chain transfer. The arsenic hyperaccumulating fern, _Pteris vitata_, was used to quantify changes in phytoavailability in response to amending the contaminated with Fe and P. Application of Fe-WTR reduced As accumulation in plant shoot tissues, and these responses were highly correlated with bicarbonate extractable As in the treated soils.

Based on advanced X-ray techniques employed at a synchrotron facility, the untreated contaminated soil was consists of arsenate and arsenite in $\text{As}_2\text{O}_5$, arsenolite ($\text{As}_4\text{O}_6$), yukonite $[\text{Ca}_7\text{Fe}_{11}(\text{AsO}_4)_9\text{O}_{10} \cdot 24.3(\text{H}_2\text{O})]$, beudantite, and minor amounts of scorodite $[\text{FeAsO}_4 \cdot 2\text{H}_2\text{O}]$ and loellingite $[\text{FeAs}_2]$. When the soil was treated with Fe-WTR, the arsenolite content declined and secondary arsenic compounds such as scorodite content increased. Some other arsenic iron products found more in amended soil are ferric arsenate sulfate (FAS) and sorbed As. When treated with orthophosphate followed by Fe-WTR, more sorbed As and FAS were observed. X-ray absorption near edge structure confirmed that As is stabilized due to surface complexation with the iron (hydr)oxides. In addition to the Pb sorption by Fe minerals, soluble phosphorous amendments promote the formation of stable Pb phosphates such as chloropyromorphite and hydroxypayromorphite. The
composition of the minerals identified in the P and Fe-WTR amended soils includes sorbed Pb, hydroxypyromorphite \([\text{Pb}_5(\text{PO}_4)_3(\text{OH})]\), hinsdalite \([\text{PbAl}_3(\text{PO}_4)(\text{SO}_4)(\text{OH})_6]\), plumboferrite \([\text{Pb}_2(\text{Fe}^{3+}, \text{Mn}^{2+}, \text{Mg})_{11}\text{O}_{19}]\), cerussite \([\text{PbCO}_3]\) and hydrocerussite \([\text{Pb}_3(\text{CO}_3)_2(\text{OH})_2]\).

The Fe-WTR collected from a drinking water treatment plant is odorless and does not contain heavy metals in significant concentrations. Pathogenic contamination is minimal. Therefore, there is no restriction to the mixing the Fe-WTR with the soil. Large scale distribution and mixing can be accomplished by rotary screening bucket without any problem for the 0-5 m of soil depth. If used as an amendment, the Fe-WTR will be recycled in a beneficial manner and will avoid being landfilled. Cost for the \textit{in situ} stabilization includes amendment application, mixing with soil, and transportation. Average estimated cost for the selected area is $40-$60 per cubic yard [1], depending on transportation costs.

The need for alternative methods for treatment of As and Pb polluted soil calls for continued research to find the most economical and efficient technologies. Arsenic and lead stabilization with the use of phosphate and Fe-WTR may work for many different sources of contamination, not only mining and smelting contaminated soil including soil contaminated with excess use of pesticides, wood preservation process as well as soil contaminated surrounded in industrial manufacturing plants.
6.1 FUTURE RESEARCH NEEDS

- A large scale field application is needed for validation of experimental results.
- The approach needs to be tested on a wide variety of soils to investigate the influence of different soil properties: structure, organic matter, and pH (which all may influence the sorption process).
- Soil was tested for As availability based on single extraction procedures and plant endpoint. Adding microbial indicators as end point will provide more information.
- The stability of Fe-WTR induced arsenic immobilization needs to be checked under a spectrum of pH and redox values and with competing ions over an extended period of time.
- The negative interaction between As and soluble P has not been completely solved. Use of different ratios of P and Fe-WTR as well as extended sequencing (continuation) studies are required to find the most effective treatment to stabilize both As and Pb.

6.2 REFERENCES