ABSTRACT:

Title of Thesis: CHARACTERIZATION AND MOBILIZATION OF ARSENIC IN VARIOUS CONTAMINATED MATERIALS

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Arsenic is a potentially toxic contaminant of concern even at relatively low concentrations in the environment. The complex chemistry of arsenic in the environment is influenced by a variety of chemical and physical factors. The presence of iron minerals is believed to be particularly important to arsenic mobility. Extraction methods were used to evaluate arsenic and iron in a variety of contaminated materials including mine tailings and soils. The contaminated materials were also evaluated for arsenic mobilization in batch experiments while pH and redox potential were monitored. A relationship between arsenic and iron was observed to occur in most, but not all, of the arsenic-contaminated samples. The most mobile fractions of arsenic were shown to be highly correlated with a simulated human oral bioavailable extraction method in the samples evaluated. The mobilization of arsenic by the simulated bioavailable extraction method was associated with a negligible mobilization of iron.

CHARACTERIZATION AND MOBILIZATION OF ARSENIC IN VARIOUS CONTAMINATED MATERIALS

by

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1.1 BACKGROUND

Arsenic, a metalloid that can be toxic to humans and other organisms, is present naturally and anthropogenically throughout the world at varying concentrations, including concentrations of concern in soil or groundwater (*1-3*). Arsenic toxicity to humans and other organisms in the environment depends on the possible pathways for exposure, concentration, mobility, and speciation. The United States Agency for Toxic Substances and Disease Registry in the *Toxicological Profile for Arsenic* (*4*) discusses three primary pathways for exposure in detail: inhalation; dermal; and oral . The other factors can vary significantly from place to place due to natural and anthropogenic conditions.

A variety of human activities, such as mining and agriculture, are believed to have mobilized and artificially elevated arsenic concentrations to levels of concern in some locations (*5-8*). Welch et al. (*1*) noted that out of the 1191 Superfund sites in the United States at the time, 30% had arsenic listed in Records of Decision (ROD) as a contaminant of concern. Determining concentrations of concern for arsenic is also complicated due to the wide variety of routine exposures, also called the background intake. In addition, depending on the pathway for exposure, the bioavailability of arsenic may vary. The bioavailable concentration of arsenic is the amount of arsenic that can enter an organism, depending on the exposure pathway. In the oral exposure pathway, for example, the oral bioavailable arsenic from a soil or other contaminated material is the amount of arsenic that becomes dissolved in the digestive system of an organism prior to excretion of the material. However, the amount of arsenic that is actually absorbed by an organism may be less than the oral bioavailable concentration.

The mobility of arsenic from a contaminated material to the aqueous phase is related to a variety of chemical processes including adsorption and precipitation. Varying conditions can vary the mobility of arsenic in a contaminated material. The oral bioavailable concentration of arsenic, for example, is representative of the mobility of arsenic under the conditions found in the digestive system. It is also possible for arsenic to become dissolved, or mobilized, by certain conditions and then transported through the flow of water to another location where it may be adsorbed, or fixed. This kind of transport of mobilized arsenic can result in arsenic sinks.

In the United States, regulations or policy identifying exposure thresholds for contaminants such as arsenic are based on toxicological data. Determination of risk associated with contaminants at different sites is based, in part, on these thresholds. Although data exist associated with effects of arsenic exposure at varying concentrations to humans, information on factors such as the oxidation state or speciation of arsenic exposure is not consistently available. However, arsenic as arsenite (As(III)) is known to be more toxic than the other arsenic species typically found in the environment. A conservative practice for considering potential deleterious impacts of arsenic from a contaminated site is to assume that total arsenic concentrations could potentially be entirely arsenite at the time exposure occurs.

1.1.1 Consideration of risk at arsenic contaminated sites

Arsenic cleanup levels for National Priority List sites vary in concentration and selection rationale (*9*). However, in the United States thresholds are developed based on health data to establish a baseline amount of contaminant ingestion below which an unacceptable level of risk is not expected. These thresholds are called reference doses. Typically, for determining the level of risk at contaminated sites, the reference dose is considered with respect to total arsenic concentrations rather than the oral or other bioavailable arsenic concentrations. Furthermore, total arsenic concentrations are typically derived by aqua regia (HCl and HNO_3) digestion or digestion by other strong acids.

Dudka and Miller (*10*) calculated that the critical threshold of total nitric acid digested-arsenic in contaminated materials with respect to a highly exposed child weighing 16 kg and ingesting 0.2 g/d of contaminated material was approximately 40 mg arsenic/kg material. The authors calculated this threshold using a reference dose of 0.8 µg arsenic/kg body weight/day. Currently, EPA lists a lower reference dose as 0.3 µg arsenic/kg body weight/day for chronic oral exposure (*11*), which is 37.5% of the reference dose used in the calculation by Dudka and Miller (*10*). The authors, however, also used a total background intake for the United States based in part on the previous drinking water maximum contaminant level for arsenic of 50 mg/L. The maximum contaminant level for arsenic will be 10 mg/L starting in January 2006. Both of these factors should influence the critical threshold.

The threshold of 40 mg/kg calculated by the authors exceeds the naturally occurring background concentrations at locations in the United States (*9*), but may be appropriate for residential sites with potential highly exposed individual receptors. This threshold can be used with respect to human oral bioavailable arsenic concentrations in different contaminated material in order to prioritize cleanup actions. Depending on the presence of receptors such as the highly exposed individual considered in the calculation by Dudka and Miller (*10*), it may be advisable to consider sites that have higher human oral bioavailable arsenic concentrations as a higher priority for more urgent removal or remedial actions regardless of total arsenic concentrations.

In comparison to the Dudka and Miller (*10*) calculation, with a few exceptions, the arsenic cleanup level was 20 mg/kg for the residential locations at the American University Experiment Station Formerly Used Defense Site (AUES FUDS) in the Spring Valley neighborhood of the District of Columbia (*8*). The arsenic cleanup level was determined by comparing the calculated non-cancer soil screening level of 23.5 mg/kg (assuming a child receptor) with the highest concentration of arsenic found in a “background” sample, which was 18 mg/kg. The selected cleanup method for AUES FUDS was excavation and landfill disposal of the material; and the removal actions at different locations within AUES FUDS were prioritized based on concentrations observed in soil.

Some of the variability in concentrations of arsenic that are considered acceptable based on the health-based reference dose and risk assessment paradigm is attributable to the limited understanding of the complexity of arsenic chemistry in soil and other materials, and subsequently variation in the selection of factors of safety to account for this limited understanding. The mobility of arsenic in these materials also depends on a variety of factors and chemical mechanisms that together create a complex puzzle. Adsorption of arsenic to different materials such as inorganic minerals, and to a much lesser extent organic matter, is one chemical mechanism that is known to occur (*12*). Varying physical and chemical conditions affecting pH and redox potential in soils can cause variability in arsenic speciation and solubility of arsenical minerals, can influence the dissolution or precipitation of different minerals that may provide sorption sites for arsenic, or can change the surface charge on different minerals by influence of hydroxyl ions (*12*). Arsenic can also be precipitated into or dissolved from minerals such as orpiment, arsenopyrite, realgar, and enargite (*13*).

1.1.2 Adsorption

Adsorption has been the focus of many studies regarding the mobility of arsenic in soils and other materials. Adsorption is a term representing various processes that involve ion interactions with surfaces of particles. Ions that become associated with sorption sites on these particles become unavailable in solution.

The oxidation state and speciation of arsenic has been shown to cause variability in the degree of adsorption to particular minerals. Arsenite (As(III)) has been shown repeatedly to be typically less likely to adsorb to particles consisting of minerals such as iron oxyhydroxides and clays when compared to arsenate (As(IV)) under different conditions (*14-17*). Arsenite is also more toxic than arsenate (4, *18*). Other arsenic oxidation states, As(O) and As(-III), have been observed less frequently in the environment (*13*), and the toxicity of these forms typically observed in the environment are less than arsenate and arsenite (*4*).

Studies have shown that in soils with iron oxyhydroxides, iron has an important role in adsorbing dissolved arsenic (*19*). Masscheleyn et al. (*19*) found that arsenate tended to form into negatively charged compounds that adsorbed to amorphous iron oxyhydroxide surfaces that were positively charged. Dissolution of iron oxyhydroxide by reduction released the adsorbed arsenate.

The presence of adsorption-competing ions has also been shown to affect the mobility of arsenic. Phosphates, in particular, have been well established as competitive with arsenic in sorption to iron oxyhydroxides (*20-24*). However, the nature of the interaction between arsenic and phosphates for sorption sites, as well as the actual reactions or mechanisms between these chemicals at the surface of particles, are not completely understood. Several different models have been suggested related to layering of arsenic and competing ions on sorption sites on known minerals.

Goldberg (*20*) found that a constant capacitance model described adsorption of arsenate on goethite, gibbsite, and amorphous aluminum hydroxide between pH 4.5 to 12 reasonably well, with and without competition of phosphate. The author found that desorption of arsenic may also be influenced by pH levels due to dissolution of minerals or changes in surface charge.

Low concentrations of phosphates, however, have less of an impact on adsorption of arsenic. Reynolds et al. (*21*) evaluated the effects of flooding on arsenic mobilization in arsenic and phosphate amended soils. The authors found limited effects from the addition of phosphate on arsenic mobilization in their study of oxygen-depleted conditions, but indicated that higher concentrations of phosphate may have had a more significant impact. However, the authors found through solid phase spectroscopy that phosphate decreased the fraction of arsenate in the solid phase. The authors did not suggest it, but phosphate may have had an indirect influence on the formation of sulfides and redox transformation to arsenite if biotic activity was limited without the presence of phosphate. The results indicated that arsenopyrite formation was enhanced with phosphate amendment in the soils. The desorption of arsenate by phosphate may have abiotically stimulated reduction to arsenite, formation of sulfides, and the formation of arsenopyrite.

Hongshao and Stanforth (*22*) found that adsorption of arsenic and phosphate is more complicated than can be described by a constant capacitance model, even when evaluated with a homogenous mineral (goethite). The authors suggested that at least two different reactions must be taking place to describe their observations of differences in the competitive adsorption of arsenic and phosphate depending on the sequence of adding chemicals. Differences in adsorption exchangeability were observed under the following scenarios: simultaneous addition of arsenic and phosphate; arsenic addition followed by phosphate addition; and phosphate addition followed by arsenic addition. When the two ions were added simultaneously, the ratio of adsorption was comparable to the ratio of the respective concentrations of the ions. However, for the first ion added in the sequential addition experiments, a higher level of adsorption was observed than compared to the ratio of concentrations. Additionally, the surface coverage of ions increased with time in all of the authors' experiments, however, a non-exchangeable fraction of the ion added first, under all of the conditions tested, remained relatively constant regardless of the equilibration time allowed prior to adding the second competitive ion. This suggests that more than one adsorption mechanism exists for phosphate and arsenic on goethite: at least one mechanism that is rapid and not exchangeable and at least one other mechanism that allows for exchange between competitive ions.

The practice of liming mine wastes to neutralize acidity and immobilize metals from the wastes and the practice of fertilizing locations with above-background arsenic concentrations with phosphate fertilizers has also been studied with respect to mobilization of arsenic (*23–25*). The mobilization of arsenic observed with liming has been attributed to desorption effects from the increase in pH – resulting in competition between hydroxyl ions and arsenic. Changes in pH can also cause the release of arsenic following reductive dissolution of iron oxides to which arsenate is known to adsorb. Jones et al. (*25*) studied the effects on mobility of liming soils contaminated with arsenic (ranging from 48 to 3421 mg/kg) by a copper smelter. Liming increased the concentration of soluble arsenic in the effluent that had leached through a column of contaminated soils. The study showed that for the tailings studied, increasing the soil pH by liming increased mobilization of arsenic by approximately one order of magnitude for a reprocessed tailing (pH increased from about 3.5 to about 8) and approximately two orders of magnitude for a pond tailing (pH increased from about 4.5 to about 9). The soluble arsenic levels determined in a sequential extraction process were not correlated with the total arsenic concentrations in tailings. However, the soluble arsenic concentrations were more highly correlated with soil pH. Based on an evaluation of the mineral content of tailing particles using SEM-EDAX, known arsenate metal compounds were determined to be undersaturated in saturated paste solutions indicating, according to the authors, that adsorption processes rather than precipitation/dissolution processes may control arsenic fixation in the tailings.

Frost and Griffin (*14*) found a pH dependence on the adsorption character of arsenite and arsenate on montmorillonite and kaolinite. For arsenate, maximum adsorption occurred in solutions with these clay materials at a pH of about 5.0, where predominance of $H_2AsO_4^-$ species is expected. For arsenite, the authors found that adsorption generally increased with increasing pH for solutions with these clay materials in the range of pH 3 to 9. However, a spike to a higher level of adsorption occurred at approximately pH 7.0 for reasons undetermined by the authors.

A study of pH and arsenic mobility under mild and unbuffered extraction conditions by Pantsar-Kallio and Manninen (*26*) on arsenic contaminated soils from two wood-preservative plants, observed the effects of extractants at set pH values between 1 to 11. The study showed that the maximum release of arsenic occurred at extremely high and extremely low pH levels. More arsenic was extracted from the sandy soils, compared with the humic and clay-dominated soils investigated. Since the extractants were not buffered, the buffering capacity of the soil altered the final pH of the extractants with pH levels ranging from 3 to 9. Studies on the extractant solutions showed that arsenate was stable at all pH levels in solution, and arsenite was not stable, but converted to arsenate at strongly basic and acidic pH levels. To a significant extent, the total dissolved arsenic concentration was highest at pH levels of 1.1 and 12.9.

The mobilization of arsenic by phosphate fertilizers has been attributed to exchange with phosphate at adsorption locations including on iron oxides and clays. Davenport and Peryea (*23*) reported that application and mixing in soil of monoammonium phosphate or monocalcium phosphate fertilizers mobilizes arsenic from soil historically polluted with acid lead arsenate ($PbHAsO_4$) under slightly acidic soil conditions (pH 5.9). Davenport and Peryea (*23*) noted the potential for phytotoxic and leaching ramifications related to the mobilization of arsenic by the competitive adsorption exchange with phosphate fertilizers, commonly used as starter fertilizers for newly planted fruit trees.

A leaching study (*24*) showed that arsenic was mobilized in contaminated soil when amended with phosphate. The phosphate-mobilized arsenic was also not re-adsorbed at lower uncontaminated soil depths. The authors concluded that the phosphate out-competed arsenic for sorption sites in the contaminated and in the uncontaminated zones, possibly because of higher sorption affinities of phosphate.

Robins (*27*) found that the presence of carbonate significantly increases solubility of calcium arsenate and magnesium arsenate. The author concluded that in a carbonate system, arsenate solubility is enhanced from calcium and magnesium minerals. Based on experiments and consideration of observations related to arsenic in groundwater in Michigan, Kim et al. (*28*) also theorized that carbonate mobilized arsenic in groundwater from Marshall Sandstone. The authors suggested mechanisms for the role of carbonate in dissolving arsenic sulfidic minerals and possible arsenic-carbonate and arsenic-carbonate-hydroxide complexes that may have a role in increasing mobilization of arsenic in Marshall Sandstone.

Appelo et al. (*29*) found their model predicted significant desorption of arsenate and arsenite when bicarbonate (HCO_3^-) sorption to weak sites on ferrihydrate was considered. Ferrous ion had a similar, but less significant, effect on arsenate and arsenate adsorption. The presence of both ions increased desorption further.

These studies show that arsenic adsorption processes are complex and are influenced by a variety of factors. The studies clearly show an affinity for arsenic to adsorb to sorption sites on metal oxyhydroxides and clays, in particular. Typically, more arsenate adsorbs to these minerals when compared to arsenite. It is also possible to predict isotherms for arsenic adsorption under controlled conditions with known mineral particles, but for exceedingly complex systems such as soils with a wide range of different minerals, isotherms cannot be easily developed.

However, the following generalizations can be made related to arsenic adsorption in soils and other materials. Adsorption of arsenic to metal oxyhydroxides and clays can be expected but not quantitatively predicted. Arsenite typically adsorbs to a lesser degree to these minerals than arsenate. Phosphates are known to compete with arsenic for sorption sites. Carbonate has been observed to desorp arsenic either by competition for sorption sites, or by forming complexes with arsenic. In addition, some arsenic desorption can be typically expected with increasing pH to levels of approximately 9.0 and above. Finally, arsenic is likely to also be mobilized at very low pH levels.

1.1.3 Influence of Redox Potential.

Redox potential, which is a representation of the transfer of electrons between constituents in a solution, can influence the chemistry of arsenic and other constituents in soils and other materials. The redox potential of systems in the environment is typically very complex especially since the kinetics of electron exchange can be very slow and equilibrium may not be reached before conditions change. Additionally, due to precipitation and dissolution reactions and buffer effects in systems in the environment, determination or prediction of possible changes in systems due to changes in redox potential is made even more complex. According to Grundl (*30*), while the measurement of pH is directly related to concentration of H^+ in solution, the measurement of pe is not related to concentration of electrons in solution (since free electrons do not exist in solution) but rather a measurement of the transfer of electrons across the redox electrode from "redox active solutes." Various microbes also use redox chemical reactions for energy and other purposes, and further complicate the understanding of natural systems.

The mobility of arsenic in a system is influenced by redox potential most fundamentally in the speciation or oxidation state. The amount of arsenic that can be adsorbed to a colloid is dependent on the oxidation state of arsenic, for example, which can be influenced by redox potential. It is possible for soil redox conditions in the environment to change due to reasons such as flooding, drying or through the addition of soil amendments such as biosolids. High redox potential in a system indicates different reactions are occurring when compared to a lower redox potential. Redox potential and pH (pe + pH) are related to the thermodynamics of reactions, and can be used to predict the occurance of different oxidation-reduction reactions. In complex systems with many constituents, the pe + pH can be also used to characterize the ranges for the types of reactions that may be expected to occur.

Variation in redox conditions can result in changes in speciation and mobility of arsenic. The two inorganic oxidation states of arsenic commonly observed are arsenate (As(V)) and arsenite (As(III)). Sadiq (*12*) indicated that based on thermodynamic data under idealized conditions, arsenate is the more abundant of the two states in soil solutions at $pe + pH > 9$ and arsenite is more abundant in soil solutions at $pe + pH < 7$.

Mok and Wai (*31*) in leaching experiments from contaminated sediments affected by mining activities, found that more arsenic was released in oxygen-free (reducing) conditions (under nitrogen compared with under air), in the form of arsenate. A relationship was apparent between increased dissolved iron and dissolved arsenic. The authors attributed the increase in dissolved arsenic to reduction of ferric arsenate and other ferric ions and concluded that free iron oxides inhibit mobility of arsenic. Similarly, Amrhein et al. (*32*) found a rapid increase of dissolved iron in their redox study of evaporation pond sediments from reduction of iron oxyhydroxides with electrons supplied by oxidation of organic matter, presumably with anaerobic microbial mediation. The alkalinity of the soil solutions increased under the reduced conditions (dried alfalfa shoots amendments and headspace sweeping with nitrogen), and promptly dropped upon reaeration. Arsenic appeared in solution at day 14 of the reducing condition experiment. Upon reaeration, arsenic was rapidly not detectable in the solution.

Several studies have evaluated changes in oxidation state for solid-phase arsenic in soils or sediment, due to changes in physical conditions resulting in changes in redox conditions (*33, 34*). Using x-ray absorption spectroscopy, McGeehan (*33*) found that, with time, flooding seemed to gradually increase the solid-phase arsenite concentration that initially was observed as entirely arsenate. Flooding may be expected to result in more reducing conditions as microbial activity is stimulated and oxygen depleted from biotic and abiotic chemical reactions.

Welch et al. (*1*) classified sedimentary deposits in the following categories: oxic (DO > 1mg/L); post-oxic (DO < 1 mg/L and no sulfide); sulfidic (DO < 1 mg/L and sulfidic); and methanic (methane present). Arsenite and arsenate species have been observed in groundwater under all redox conditions, but arsenite tends to dominate in sediment under sulfidic and methanic conditions, and arsenate tends to dominate in sediment under oxic conditions. The author also indicated that under a variety of redox conditions, microorganisms can influence the oxidation state and speciation of arsenic.

Welch et al. (*1*) suggest several important reactions that can occur under the different soil redox conditions that can affect mobility of arsenic. The important reactions or processes under oxic conditions include adsorption to iron oxyhydroxides as affected by pH and competing adsorbents, as well as precipitation of arsenic-containing minerals. For post-oxic conditions, where oxygen and sulfide are not present, oxidation state of arsenic and pH can affect adsorption to iron oxyhydroxides. In addition, biotic-driven dissolution of minerals can influence the mobility of arsenic in post-oxic conditions when organic substrates are present. Under sulfidic conditions, depending on the concentrations of iron, sulfide and arsenic, the mobility of arsenic is affected by mineral precipitation.

Gulens et al. (*35*) used a sand column, various types of groundwater with different redox qualities, and radioactive-labeled arsenic in experiments and determined that adsorption and retention of arsenite was less than of arsenate. Creating more reducing conditions narrowed the difference between arsenate and arsenite, presumably due to reduction of arsenate to arsenite. However, under reducing groundwater conditions, arsenite was not retained by the sand column while 20% of arsenate was retained. The authors pointed out that the sulfide concentrations in the reducing groundwater were too low to immobilize arsenic through precipitation of insoluble sulfidic minerals.

McCreadie et al. (*36*) studied the site of a goldmine in Canada. Pore water concentrations of various chemicals were measured at various depths in an area containing spoils and impounded water. Arsenite concentrations generally increased with depth with respect to arsenate concentrations. Overall arsenic concentrations peaked with overall iron concentrations, and quickly decreased with depth as sulfide concentrations increased, similarly to iron. A decrease in sulfate concentrations was coupled with an increase in sulfide at decreasing depths and the presence of organic carbon and an increase in alkalinity was coupled with a decrease in pH with depth, suggesting microbial activity. The authors believed that the most likely explanation for the distinct depth of arsenic mobilization was due to dissolution of iron oxide compounds via reductive biotic, abiotic, or a combination of processes. Additionally, the authors suggested that the most likely explanation for the distinct depth of arsenic removal (deeper than the mobilization zone) was due to the precipitation of insoluble arsenic sulfides. The authors theorized that organic carbon in tailings may induce microbial mobilization of arsenic, but depending on the overall hydrologic, chemical, and biological conditions, they could not predict the potential extent of arsenic transport beyond the location of the contaminated material.

Carbonell-Barrachina et al. (*37*) measured the effects of various pH levels and redox conditions in secondary sewage sludge (2.4% solids; 0.8 ppb As) spiked with 100 mg As kg^{-1} dry sludge under controlled redox and pH conditions. Their findings indicated that under oxidizing conditions, mobility of arsenic generally decreased and aqueous phase arsenic was dominated by the dimethylarsinic acid (DMAA) and arsenate species. Under highly anoxic conditions, the mobility of arsenic generally increased, but the aqueous phase arsenic was dominated by varying species at various Eh and pH levels. Total soluble arsenic levels, in the experiments, peaked at 0 mV at pH levels of 5, 6.5 and 8.

The study of Carbonell-Barrachina et al. (*37*) showed that increasing the pH from 5.0 to 6.5 evolved higher aqueous phase arsenic levels at most Eh levels, except for 100 mV. The authors suggested that due to increasing hydroxyl ions in solution, arsenic was replaced at various sorption sites. Additionally, the authors indicated that as the sludge surface charges increasingly become negative with increasing pH, desorption is increased.

Significant concentrations of arsenate under reducing conditions were observed by Carbonell-Barrachina et al. (*37*), indicating that the kinetics of arsenate reduction were slow, even under thermodynamically favorable conditions. The presence of organisms was indicated by the observed formation of DMAA, and may have influenced the slow arsenate reduction kinetics. The authors found that the findings of other researchers concerning the influence of arsenate reduction kinetics and the influence of iron oxyhydroxides on the mobility of arsenic were substantiated in their experiments (high correlation between aqueous iron and arsenic concentrations), but the influence of sulfide seemed to be important with respect to arsenic mobility in their experiments as well. Under reducing conditions, sulfate concentrations decreased significantly while sulfide concentrations increased significantly. The authors theorized that the decrease in aqueous arsenic concentrations from the Eh level of 0 mV to –250 mV may be attributed to the formation of insoluble arsenic sulfide minerals. A significant and positive correlation with aqueous arsenic was observed with soluble sulfide, and with organic matter and sulfide at -250 mV.

These findings were supported by the findings of Meng et al. (*38*). The authors studied arsenic and iron redox transformations in water treatment sludge from filter backwash. Redox potential was measured empirically by measuring voltage in solution with a platinum electrode. Filter backwash was collected in one experiment, and kept in a sealed container with little headspace over 80 days. A second experiment involved leaching tests of thickened water treatment residuals utilizing 0.10 M acetic acid and 0.064 M NaOH (pH 4.93), a leachate to sludge mass ratio of 20 to 1, and 18 h of mixing.

The authors found that after keeping the water treatment residuals in a closed flexible container with minimized air head gas for two days, arsenic and iron levels in the supernatant increased, but arsenate levels did not increase and DO dropped below 0.5 ppm – indicating that anoxic conditions had been achieved (*38*). After approximately 60 days, arsenite concentrations in the supernatant increased to approximately 700 ppb from 5.6 ppb (supernatant arsenite concentrations after two days of aging). The authors modeled the arsenic mobilization that they observed with respect to redox potential and identified three "redox zones:" reductive fixation (pe<-4.0, formation of reduced arsenic and iron minerals and reduction of sulfate to sulfide), mobilization (-4.0<pe<0, reduction of arsenate and amorphous iron oxyhydroxides), and adsorption (pe>0, stable arsenate and amorphous iron oxyhydroxide). The model considered adsorption of arsenic, reduction of arsenate to arsenite, sulfate reduction to sulfide, and the precipitation of orpiment, realgar, arsenopyrite, and pyrite. The authors believed that their observed data matched their redox zone model: sulfate concentrations dropped sharply with decreasing pe from approximately –3.0. However, the authors observed an apparent lag between the reduction of sulfate and the model predictions compared to the rate of decrease of redox potential. The difference between sulfate observed and predicted reduction indicates that the rate of other redox reactions may be slower than the rate of decrease of redox potential– possibly explaining why arsenate was observed in relatively high levels in the "mobilization" zone range of pe. The authors' model and their data suggested that pyrite formation might have reduced arsenite concentration in solution.

The authors suggest that complete reduction of Fe(III) to Fe(II) (complete dissolution of amorphous iron oxyhydroxides was expected at a pe level of 4.0) would release nearly all arsenic to solution (*38*). However, the authors observed that the amount of iron reduction, presumably from a slower rate of redox transformation, did not match the rate of change in pe.

The authors indicated that an arsenic release was observed at –4.0 < pe < 0 and that this range may shift due to environmental conditions. Additionally, in natural environments with high sulfur concentrations, arsenic may be immobilized due to formation of insoluble sulfur-arsenic-iron minerals.

O'Day et al. (*39*) used synchrotron x-ray absorption spectroscopy (XAS) as a non-destructive method for evaluation of preserved sediment cores from a site believed to be contaminated with arsenical pesticides. The analysis suggested that small particles of poorly crystalline realgar was the dominant arsenic species in the samples, not arsenopyrite. In addition, the analysis suggested that arsenic was not incorporated by adsorption or other means with the pyrite present in the samples.

The authors utilized a reaction-path model to evaluate possible mechanisms resulting in the observed mineralogy. Based on the model under the conditions considered with decreasing pe, sulfate reduction and reductive dissolution of ferric oxyhydroxides preceded formation of sulfidic precipitates. Similar to the suggestions of Meng et al. (*38*), the model predicted an arsenic mobilization zone with decreasing pe as reduction dissolution of iron oxyhydroxides released associated arsenic prior to formation of insoluble arsenic sulfide minerals. In the model, however, varying concentrations of sulfur and iron affected the types of sulfidic minerals formed which also affected the mobilization of arsenic. For systems with high iron concentrations, the model predicted the precipitation of realgar prior to any other arsenic sulfide minerals due to rapid precipitation of iron sulfide minerals. The model predicted precipitation of orpiment in systems with lower iron concentrations, but as concentrations of sulfide increased, dissolution of orpiment occurred due to formation of arsenic sulfide complexes. For systems with low sulfide and low arsenic concentrations, precipitation of iron sulfide minerals may preclude precipitation of arsenic.

There is some variability in observations by researchers related to arsenic speciation and mobilization under different redox conditions. This variability suggests that pe + pH cannot be used exclusively to predict arsenic chemistry in soils, which would not be expected due to the complexity of soil systems. There were some general tendencies observed, however, related to arsenic oxidation state and the types of reactions expected within different ranges of redox potential and pH.

Changes in the oxidation state of arsenic were observed to occur both in the aqueous and solid phases. The observed solid phase changes in oxidation state might be explained by a general dynamic interaction between the aqueous and adsorbed arsenic associated with the solid phase, or it could be related to more localized mineral dissolution and precipitation reactions. In the aqueous phase, arsenate reduction under reducing conditions and arsenite oxidation under oxidizing conditions is expected, although it may be limited by kinetics or complexation with other ions under certain conditions.

The redox reactions of constituents other than arsenic has also been shown to be important in controlling the mobility of arsenic. In particular, iron and sulfur redox reactions have been shown to influence the mobility of arsenic. The interaction between these constituents has been suggested to be caused by mechanisms such as dissolution of minerals, precipitation of arsenical minerals, or co-precipitation of arsenic with non-arsenical minerals.

As conditions become more reducing, dissolution of minerals such as iron oxyhydroxides that may be associated with adsorbed or otherwise fixed arsenic, may release the arsenic to solution. As conditions become more reducing, sulfate reduction to sulfide and ferric reduction to ferrous is expected to occur followed by the possible precipitation of minerals from these reduced irons. Depending on the relative concentrations of the iron, sulfide and arsenic ions, different minerals that may or may not include or co-precipitate arsenic may be expected. Additional research is necessary to test the different models proposed under reducing conditions with different iron, sulfide, and arsenic concentrations.

1.1.4. Microbial Influences of Arsenic.

Although arsenic is toxic to many microorganisms, some resistant species have been observed to influence the mobilization and speciation of arsenic in various ways. Bacteria that reduce iron and sulfur, as well as bacteria that respire arsenic have been observed to influence arsenic mobilization and speciation (*40-42*). Reductive dissolution of iron oxyhydroxides was observed by Ahmann et al (*40*). Sulfate reducing bacteria were believed by Stolz and Oremland (*41*) to reduce arsenate to arsenite, which was subsequently precipitated as orpiment. Bacteria can also influence the kinetics of reactions, including arsenate reduction to arsenite, under conditions that abiotically may have been thermodynamically favorable but normally would have occurred slowly. This can result in quicker mobilization or fixation processes than would be observed in the absence of microorganisms.

1.1.5. Methods for Characterizing Arsenic Mobility.

Due to the wide variety of potential mineralogical association with arsenic in the environment a wide variation of arsenic mobility has been documented in the literature between different sites and matrices. Total arsenic concentrations in soils and other materials loosely correlate with the degree of arsenic mobility by leaching at some sites (*6*), and poorly at others (*18*).

In one study of several sandy sites, the mobile iron fraction in samples was shown to correlate better with the mobile arsenic fraction between samples than total arsenic concentration correlated with the mobile arsenic fraction (*6*). Ullah et al. (*18*) found no correlation between total iron levels and total arsenic levels in Bangledesh groundwater samples, contrary to the theory that the decomposition of arsenopyrite is the primary source of dissolved arsenic.

Although measurements of total arsenic may not consistently relate to the mobile arsenic fraction in samples, total arsenic concentrations are important to consider while assessing potential risk associated with a given site. Various studies have identified the effects of various chemical and physical stimuli that can change the extent of arsenic mobility and speciation, and presumably cause transformations of arsenic mineralogical relationships. One study involving treatment of contaminated soils by solidification/stabilization found approximately one order of magnitude reduction in the mobility of arsenic as tested with the Toxic Contaminant Leaching Procedure (TCLP) (*43*).

TCLP, a method required for the determination of characteristic waste properties for solid waste under the Resource Conservation and Recovery Act (RCRA), has been used as a reference method in determining the mobility of arsenic in contaminated soils or other materials. Characterization of arsenic mobility in samples using TCLP may be limited. One study found a range of arsenic recovery of 0.19% to 0.97% with TCLP in comparison to total arsenic concentrations (*6*). The state of California uses a different leaching method called the waste extraction test (WET) which is used to determine a solid waste's soluble threshold limit concentrations (STLC). The regulatory threshold in California is the same as in RCRA: 5.0 mg/L arsenic in the leachate. The California WET method uses a longer extraction period and different extractants that TCLP; in the WET method, citrate is used rather than acetate because it is a more efficient chelating agent (*44*). Wellman et al. (*44*) reported on samples contaminated with arsenic from a former crude oil storage facility that were analyzed by both methods. The results showed that the California WET method yielded higher concentrations of arsenic in leachate than TCLP.

Ghosh et al. (45) compared the effect of different leachates (TCLP, the California WET, simulated landfill leachates, and actual collected landfill leachate) on arsenate desorption from activated alumina and granular ferric hydroxide. These sorbants are expected to be widely used in small water treatment facilities to comply with the modified Maximum Contaminant Limit (MCL) for arsenic. The TCLP method mobilized arsenic at significantly lower levels than the other methods. The

Calfornia WET method also mobilized arsenic at lower levels than the other methods, except for the TCLP method. For the leachates with oxidation reduction potential levels of 36.1 and -37 mV (corresponds to pe levels of 0.61 and -0.63, respectively), arsenite formation was observed. The TCLP method resulted in low levels of arsenite formation as well, however the ORP level was 103.5 mV (corresponds to pe level of 1.8). The authors indicated that for the activated alumina samples, dissolution of aluminum was not attributable to mobilization of arsenic. For the granular ferric hydroxide samples, the methods with lower redox levels mobilized more iron and arsenic than the methods with higher redox values. This may be attributable in part to reductive dissolution of the granular ferric hydroxide and reduction of arsenate to arsenite and subsequently lower overall arsenic adsorption. The overall implication of this study is that there is a potential for arsenic treatment residuals generated in some drinking water treatment processes to be classified as hazardous waste, which has significant disposal implications. This may be a significant issue if the toxicity characteristic limit for arsenic is lowered to correspond with the lowering of the MCL, or if an alternative method to the TCLP method be employed.

Sequential extraction methods have been used to illustrate approximate fractionation of arsenic and other contaminants in soils and other materials. A variety of sequential extraction methods have been used to characterize arsenic fixation (*46-48*) as well as fixation of similar metalloids (*49, 50*). Sequential extraction method characterization may help in predicting the mobility of arsenic from different materials. Changes in environmental conditions over extended periods may be mimicked by the conditions introduced in some sequential extraction methods.

Keon et al. (*46*) sought to verify extraction methods to isolate the mobilization of adsorbed or mineral phase arsenic. The researchers attempted to use standards of arsenical minerals or pure materials with arsenic adsorbed as spikes in natural sediment contaminated with arsenic. The procedure that the authors used involved the following steps: 1 M $MgCl_2$, pH 8, 2 h, 25 degrees C, two repetitions and one water wash (Mg); 1 M NaH_2PO_4, pH 5, 16 and 24 h, 25 degrees C, one repetition of each time duration and one water wash (PO_4); 1 N HCl, 1 h, 25 degrees C, one repetition and one water wash (HCl); 0.2 M ammonium oxalate/oxalic acid, pH 3, 2 h, 25 degrees C in dark, one repetition and one water wash (Ox); 0.05 M Ti(III)-citrate-EDTA-bicarbonate, pH 7, 2 h, 25 degree C, two repetitions and one water wash (Ti); 10 M HF, 1 and 24 h, 25 degrees C, added 5 g boric acid at 16 h, one repetition of each time duration and one boiling water wash (HF); 16 N HNO_3, 2 h, 25 degrees C, two repetitions and one water wash (HNO_3); 16 N HNO_3 + 30% H_2O_2 (hot HNO_3). The author found a high fraction of arsenic in their sediment samples in the PO_4 step (approximately 50%). Seemingly this would suggest that the majority of arsenic associated with the sediment were easily exchangeable with amorphous iron oxyhydroxides or other loosely binding sorbents. Due to the pH for the PO_4 step, there may have been some arsenic fractionation associated with carbonate minerals as well (see discussion in Chapters 3 and 4).

Spiking the sediment samples with arsenical minerals and arsenic laden goethite was employed to determine if fingerprints for these materials may be evident in using the sequential extraction method. The authors found significant mobilization of arsenic spiked on goethite by their PO_4 step, mobilization of arsenic from arsenic trioxide in the HF step, mobilization of arsenic from arsenopyrite by HNO_3, and mobilization of arsenic from orpiment by hot HNO_3. The mobilization of arsenic from a freeze-dried amorphous arsenic sulfide was observed in three steps to varying degrees: 9% by the HCl step; 43% by the Ti step; and 40% by the HNO_3 step.

McLaren et al. (*47*) evaluated a soil that was exposed to NaH_2AsO_3 as a cattle dip. The authors used a sequential extraction method with six steps (2 gram samples): Anion exchange membrane extractable arsenic (suspended with strip of anion exchange membrane (AEM) in 30 mL DI-H_2O, 24-hours; arsenic removed from AEM by 30 mL 0.1 N HCl, 1-hour); sodium bicarbonate extractable arsenic (30 mL $NaHCO_3$ (0.5 N, pH 8.5), 16-hours); sodium hydroxide extractable (30 mL 0.1 N NaOH, 16 hours); sonicated sodium hydroxide extractable (30 mL 0.1 N NaOH, 3-min sonication with probe, 16-hour); hydrochloric acid extractable(30 mL 1 N HCl, 16-hour); and residual arsenic (20 mL aqua regia (5:3 HCl/HNO_3), microwave digestion). In addition, the following extractants were used non-sequentially: Total (aqua regia 5:3 HCl:HNO_3); Water soluble (5g sample:25 mL DI H_2O 16 hours; and Acid oxalate soluble (g:100mL (0.2M NH_4oxalate, 0.2M oxalic acid, pH 3) 4 hours dark).

The authors found that typically 20% of arsenic was not mobilized by the sequential extraction method; they presumed that this fraction was not bioavailable. Generally, more arsenic was mobilized by the two NaOH steps than the other individual steps. The authors indicated that the first four steps of the sequential extraction method draw from the same "pool" of arsenic associated with iron and aluminum and capable of exchange into the aqueous phase.

A sequential extraction method that had been developed to characterize selenium fractionation in soils was selected for this study (*49, 50*). The sequential extraction method is presented in TABLE 1. Selenium can be fixed in soils by adsorption, organic, and other mineral associations, similarly to arsenic.

The "soluble" step utilizes a solution with known electrolyte to remove any soluble arsenic. For the "adsorbed" step, a phosphate solution is used at a high concentration (0.1 M). Phosphate is widely believed to be competitive with arsenic for sorption sites on minerals such as iron oxyhydroxides, and can cause some desorption of arsenic. The "carbonate" fraction will release arsenic fixed to carbonates by dissolution of the carbonates by the acetate buffer at pH 5. For the "soil organic matter" step, hypochlorite can oxidize organic matter that may fix some arsenic in soil. For the "easily reducible oxides" and "amorphous oxides" different concentrations of hydroxylamine are used. The half-reaction for hydroxylamine is shown below:

$$NH_2OH + 2H_2O \leftrightarrow NO_3^- + 7H^+ + 6e^- \qquad \log K^o = -67.69$$

TABLE 1. Sequential Extraction Method (*49*)

Step	Targeted fraction	Extraction procedure
a	Soluble arsenic	0.25M KCl (2hr)
b	Adsorbed arsenic	0.1M Na_2HPO_4 (pH 8, 20hr)
c + d	Carbonate associated arsenic	1M Na-acetate (pH 5, 1 + 4hr), then 0.1M Na_2HPO_4 (pH 8, 20hr)
e	Soil organic matter associated arsenic	NaOCl (pH 9.5, 0.5 hr boil, repeated once)
f	Easily reducible oxide associated arsenic	0.1M NH_2OH (pH 2, 0.5hr) followed by 0.1M KOH (20hr)
g	Amorphous oxide associated arsenic	0.25M NH_2OH/HCl (0.5 hr@50 ^oC) followed by 0.1M KOH (20hr)
h	Crystalline oxide associated arsenic	4M HCl (0.5 hr boil)
i	Amorphous aluminosilicate associated arsenic	0.5 M NaOH (0.2 hr boil)

The equation indicates an affinity for hydroxylamine degradation (oxidation of N) making electrons available for reductive dissolution of the targeted “easily reducible oxides” and “amorphous oxides” in steps f and g. The strong concentration of hydrochloric acid used in the "crystalline oxides" step is expected to effectively reduce and dissolve additional remaining oxides.

A slightly modified version of this method was used by Kim et al. (*48*). An aqua regia (HCl + HNO3 extraction) step was utilized instead of steps h and i. The authors used the method to characterize mine tailing samples collected from Korea. For these samples, a dominance of arsenic was extracted in the oxide reducing steps (f, g and the aqua regia steps). Less than one percent of the total iron extracted was extracted prior to these steps, indicating a strong association between iron mineral dissolution and mobilization of the majority of the arsenic contained in the samples. Treatment of the tailings with ferric sulfate and ferrous sulfate resulted in a shift of arsenic fractionation in the samples from steps a through e to the oxide reducing steps. With time, a further shift of arsenic fractionation was evidenced in the samples from steps a through e to the oxide reducing steps. The authors suggested a stabilization mechanism involving the formation of more thermodynamically stable anhydrous iron hydroxide minerals from amorphous forms, possibly enhancing the binding strength of sorbed arsenic or integrating arsenic into the mineral structures formed. The authors also found a similarity for the samples in extraction of arsenic using a 5% hypochlorite extractant and with steps a through e. The samples were also analyzed by the TCLP method, which resulted in mobilization of arsenic less than the sum of steps a and b. Based on other studies demonstrating the inadequacy of TCLP for demonstrating the potential for leaching of arsenic from landfilled materials, this suggests that the early steps are also more robust at extracting arsenic than TCLP.

Another type of extraction method has been used to simulate human oral bioavailable arsenic in the human digestion system (*51,52*). This type of method can be useful in understanding and characterizing risk associated with the ingestion pathway. Simulated human oral bioavailable extraction methods have been compared to in-vivo studies in pigs, which have similar digestive system characteristics to humans.

Many types of methods are used to characterize arsenic mobility and risk associated with arsenic in soils and other materials. The TCLP and WET extraction methods, which are designed to simulate landfill leaching conditions, have been shown to be inadequate at representing mobilization of arsenic in landfill conditions. A variety of sequential extraction methods have been used to characterize arsenic mobility from different materials. Some of the methods have shown moderate ability to identify known arsenic minerals or arsenic laden minerals within different extractant fractions. In addition, sequential extraction methods were successfully used to observe a shift in arsenic mobility related to addition of iron salts. Additionally, simulated human oral bioavailable extraction methods may provide useful information particularly related to risk associated with the ingestion of arsenic-contaminated soil or other materials. More extensive use of all of these methods with a wide variety of samples is necessary to determine the usefulness for characterizing arsenic mobility.

1.2 STUDY OBJECTIVES AND HYPOTHESES

Many factors have importance in influencing the mobility of arsenic in soils and other materials, which makes prediction of the mobility of arsenic in complex systems such as soils difficult. There is a need for understanding the mobility of arsenic in such systems due to the potential toxic effects of arsenic on humans and on other organisms in the environment. Different methods exist that may be used to characterize mobility of arsenic in contaminated materials under different conditions. Based on the findings of other researchers, and using different samples containing varying concentrations of arsenic and varying matrices, the following hypotheses were tested in this study:

- The human oral bioavailable component of arsenic in contaminated materials was expected to be much lower than total arsenic concentrations by microwave digestion in the same contaminated materials.
- Dissolution of iron was expected to be correlated with aqueous arsenic concentrations due to the known affinity of arsenic anions to adsorb to iron oxyhydroxides.

These hypotheses were tested using various characterization methods including a sequential extraction method, a simulated human oral bioavailable extraction method, and a microwave digestion method. Other soil parameters were determined for some of the samples. These arsenic-contaminated samples included some taken from and near a mine tailings pond system at a site in Mexico, contaminated sediment and soils from West Virginia, the District of Columbia, and Maryland, and poultry litter and associated soils from Maryland. Batch experiments with some of the samples were also used to also observe arsenic mobilization at different pH and redox potential levels.

Another objective in the study, beyond testing the aforementioned hypotheses, was to use the arsenic characterization methods on a wide variety of samples and matrices to evaluate the potential for use evaluating mobility of arsenic at contaminated sites. Depending on the matrix and source of arsenic contamination, different methods may or may not be appropriate in determining arsenic concentrations and potential mobility of arsenic from the contaminated material.

CHAPTER 2. MATERIALS AND METHODS

2.1 CHEMICAL REAGENTS

Potassium hydroxide (KOH), porcine pepsin (1:10,000), hydroxyl amine ($NH_2OH \bullet HCl$), Trizma® Hydrochloride ($C_4H_{11}NO_3 \bullet HCl$), CAPS ($C_9H_{19}NO_3S$), and MES ($C_6H_{13}NO_4S$) were obtained from Sigma (Louis, MO). Sodium acetate (CH_3COONa), trace metal grade hydrochloric acid, ferrous ammonium sulfate, 6-Hydrate ($Fe(NH_4)_2(SO_4) \bullet 6\ H_2O$), ferric ammonium sulfate, 12-Hydrate ($Fe(NH_4)(SO_4)_2 \bullet 12\ H_2O$), and sodium phosphate, monobasic ($NaH_2PO_4 \bullet H_2O$) were obtained from J.T. Baker (Philipsburg, NJ). Sodium hypochlorite solution (6% available chlorine) and certified arsenic standard (0.01 mg/mL) were purchased from VWR (Westchester, PA). OmniTrace nitric acid and potassium iodide (KI) were obtained from EM Science (Gibbstown, NJ). Sodium hydroxide pellets (NaOH), and sodium borohydride ($NaBH_4$) were obtained from Aldrich (Milwaukee, WI). Sulfuric acid was obtained from Fisher Scientific (Fairlawn, NJ). All chemicals used were ACS grade reagents or higher purity (98.0%). A NIST standard soil, SRM 2710, was used to calibrate the microwave digestion procedure.

2.2 SAMPLES

The samples used in this study include mine tailings and soil and sediment influenced by mine tailings (M1-M28), sediment from a stream in the vicinity of a smelter (WF), poultry waste and amended soils (PM), a soil sample from below a residential deck containing lumber treated with Copper Chromated Arsenate (RES), and soils obtained at the AUES FUDS site where Lewisite and other compounds containing arsenic were developed and tested to be used in weapons (AUS1-3). A description of each sample site follows.

Samples were air-dried in a vacuum hood at room temperature. Following air-drying, the soils were homogenized by grinding in a mortar and pestle and sieved through a No. 30 U.S.A. Standard Testing Sieve (Hogentogler & Co., Inc., Gaithersburg, MD). This sieve retains particles larger than 0.6 mm. Fragments that could not be ground to pass through the sieve were discarded. The materials were homogenized in order to provide relative continuity in batch and flow experiments. Since the bulk material was ground to small particles, the surface area of the material may have increased from the original natural condition. Therefore, the experimental results may not accurately represent natural conditions physically with respect to particle size and structure, and moisture content.

2.2.1 Samples from Site in Mexico

Samples of mine tailings and adjacent soils and sediments (M1-M28) were obtained in the vicinity of a silver mine tailings pond system for a mine (undisclosed name and specific location) in the state of Zacatecas, Mexico in 1999. A map of the mine tailings pond system from a study of cooperating researchers from the National University of Mexico (UNAM) is shown in FIGURE 1. The mine used a chemical flotation process to remove the desired metals. The waste from the chemical treatment process was pumped into a large mine tailings pond system. At the time of sampling, the process had been inactive for approximately five years.

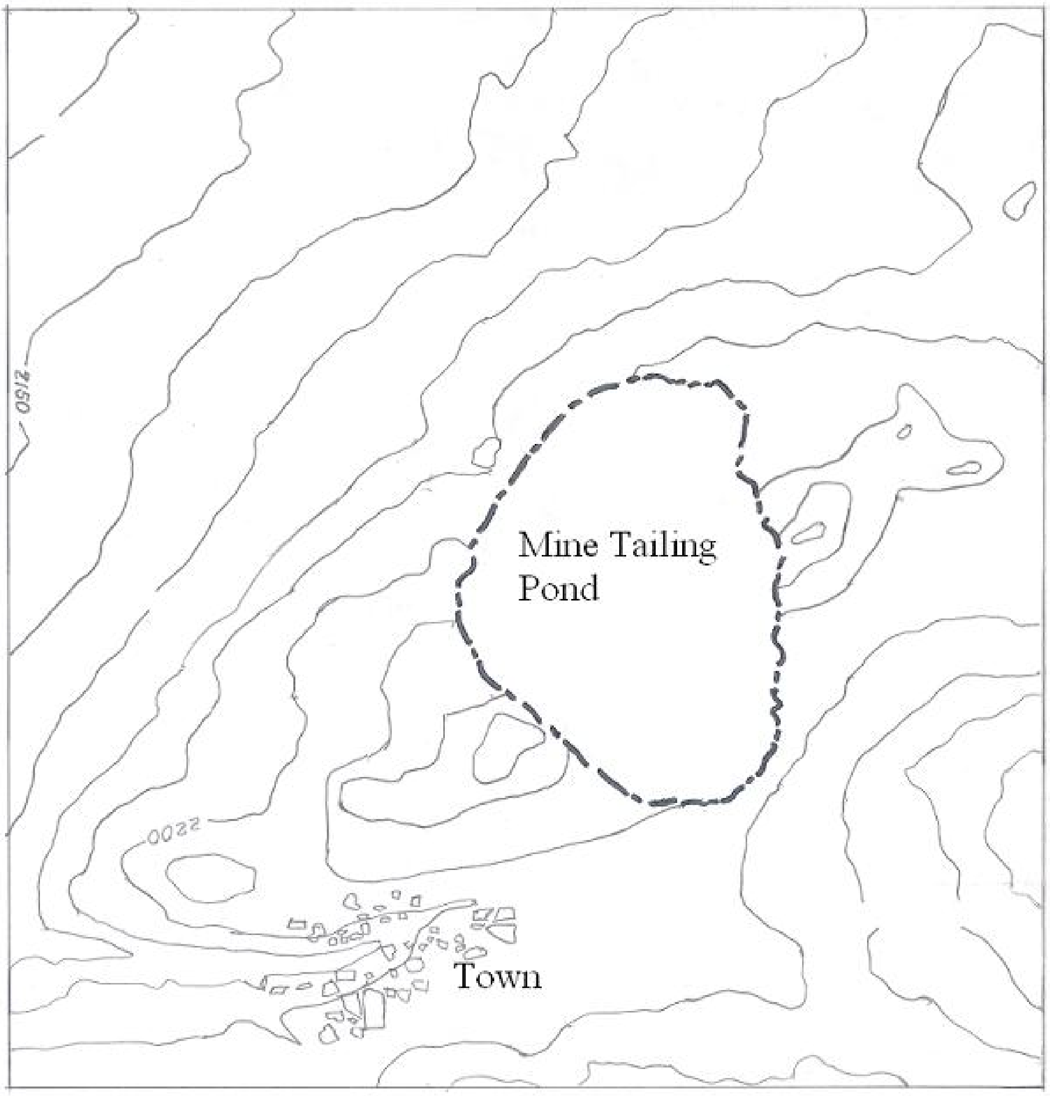

FIGURE 1. Site map from mine tailings pond system. No scale is shown and north is top of picture. Adapted from Gutiérez-Ruiz et al. (53).

The ponds are banked with berms composed of the waste material. The region is arid, and periodically experiences wind storms. In an effort to reduce wind erosion from the surface of the mine tailings ponds, trees and plants were planted around the ponds. According to the soil sampling team, the planted trees were not living during the summer of 1999, but some wetland vegetation was living.

Dr. Mazyar Zeinali (University of Maryland, College Park) and cooperating researchers at UNAM acquired 28 different samples from the mine tailings pond system area. A list of the samples with descriptions of the locations can be found in TABLE 2. Samples included mine tailings at different depths, and soils adjacent to the mine tailings ponds, including some sediment from an adjacent wetland. A spade was used to acquire the samples, and was cleaned using de-ionized water prior to the collection of each sample. The samples were double-bagged in plastic bags and were shipped to the University of Maryland. The samples were air-dried, homogenized, sieved, and stored double-bagged in plastic bags at room temperature.

Gutiérez-Ruiz et al. (*53*), the cooperating researchers from UNAM, evaluated soil samples taken from the surface and soil cores reaching depths up to 40 cm in the vicinity of the mine tailing pond. Total arsenic concentrations ranged from below 20 mg/kg to 1660 mg/kg. The arsenic in the soils generally increased in total concentration when in closer proximity to the mine tailings pond system. Additionally, higher concentrations of arsenic were observed in soils at a greater distance southward when compared to the samples evaluated to the north. This observation may suggest that there was a prevailing wind transport of arsenic laden

TABLE 2. Sample descriptions for Mexican mine tailings and associated samples.

Sample	Approximate Location (Site identification number)	Depth (cm)	Description
M1	Center of Tailings Pond (A1)	0-1	Light Gray, Dry
M2	Center of Tailings Pond (A2)	1-10	Dark Gray, Wet
M3	Center of Tailings Pond (A3)	>10	Dark Gray, Wet
M4	10 m East of Pond Center (B1)	0-1	Light Gray, Dry
M5	10 m East of Pond Center (B2)	1-10	Dark Gray, Wet
M6	10 m East of Pond Center (B3)	>10	Dark Gray, Wet
M7	20 m East of Pond Center (C1)	0-1	Light Gray, Dry
M8	20 m East of Pond Center (C2)	1-10	Dark Gray, Wet
M9	20 m East of Pond Center (C3)	>10	Dark Gray, Wet
M10	30 m East of Pond Center (D1)	0-1	Light Gray, dry
M11	30 m East of Pond Center (D2)	1-10	Dark Gray, wet
M12	30 m East of Pond Center (D3)	>10	Dark Gray, wet
M13	50 m from East Edge Center Point (E1)	0-5	Hard rock-like, dry
M14	50 m from East Edge Center Point (E2)	0-5	Hard rock-like, dry
M15	20 m from East Edge Center Point (F1)	0-5	Sand-like, dry
M16	20 m from East Edge Center Point (F2)	0-5	Sand-like, dry
M17	3 km NW of Tailing Pond (G1)	0-1	Very light brown, dry
M18	3 km NW of Tailing Pond (G2)	1-10	Very light brown, dry
M19	3 km NW of Tailing Pond (G3)	>10	Very light brown, dry
M20	2 km SW of Tailing Pond (H)	0-1	Light brown, dry
M21	50 m away from SW edge of Tailing Pond (I)	0-1	Soil, dry
M22	100 m away from SW edge of Tailing Pond (J)	0-1	Soil, dry
M23	50 m away from SW edge of Tailing Pond	0-1	Soil, dry
M24	50 m away from SW edge of Tailing Pond	0-1	Soil, dry
M25	SW wall of Tailings Pond	0-2	Soil/tailings/gravel mix
M26	SW wall of Tailings Pond	0-2	Soil/tailings/gravel mix
M27	Wetland sediment NW of Tailing Pond inside grid (K1)	0-0.5	
M28	Wetland sediment NW of Tailing Pond inside of grid (K2)	0.5-10	

particles southward. The soil cores showed decreasing arsenic concentrations with depth in six of eight samples.

Gutiérez-Ruiz et al. (*53*) also evaluated a mine tailings sample. The researchers found that the pH of the mine tailings was neutral and the samples contained carbonate, sulfuric, and oxide minerals. Inorganic arsenic was observed in the tailings primarily as arsenite. Higher concentrations of arsenic were found at more shallow depths. The researchers suggested that tailings directly from the chemical flotation process contained arsenic as arsenopyrite, which is oxidized and dissolved during the pumping process. The dissolved arsenic, the researchers suggested, subsequently precipitated with iron and lead to form colloidal particles.

2.2.2 Sediment Sample from West Fork River, West Virginia.

Dr. John Hando (West Virginia Department of the Environment) provided a sample of sediment (WF) from the West Fork River (West Virginia, USA) to the University of Maryland. The West Fork River may have been impacted by a zinc smelter, possibly increasing arsenic concentrations in sediment.

2.2.3 Samples from AUES FUDS.

Historical review indicates that chemical agents containing arsenic, including Lewisite, were developed, manufactured, and tested at the AUES FUDS which is now the Spring Valley neighborhood in the District of Columbia (*54*). Several soil samples were acquired by Mr. Michael Peterson from the Spring Valley site (American University, Washington, D.C.) on March 13, 2000 with Richard Albright (District of Columbia Government). The first sample (AUES1) is a composite sample, and was taken in several spots in an exposed apparent laboratory disposal pit of antiquity. A spring of water flowed through or adjacent to the disposal pit. The second soil sample (AUES2) was taken from the sediment of the stream owing a part or all of its flow to the spring.

Three additional soil samples were taken at residences in the vicinity of Spring Valley. A sample was taken at 4825 Glenbrook Road (AUES3), which is a residence adjacent to several munitions disposal locations discovered and excavated by various agencies. Some evidence exists to indicate that additional munitions and military-associated disposal locations have not been discovered and remain covered with earth in the vicinity. Two samples (AUES4 and AUES5) were taken on Sedgewick St., which is in an area formerly used as a munitions testing range.

All of the samples were taken from the surface of the soil (approximate depth of two centimeters) to represent soil most likely to be encountered by residents and stored in acid washed containers. The lids of the containers were used for excavating the soil so as to prevent contamination in the process of sampling. All samples were then prepared according to the soil homogenization procedure, and stored in the original collection containers. Material that could not be homogenized and sieved was discarded.

A project partnering system was established for managing the AUES FUDS between the Baltimore District of the United States Army Corps of Engineers (the agency responsible for performing the actual clean-up work), the District of Columbia Department of Health, and the Environmental Protection Agency Region

III. Under the project partnering system, these agencies make decisions by consensus.

In order to characterize the extent of potential arsenic contamination in the vicinity of the AUES FUDS arsenic was analyzed in an extensive systematic sampling process. According to the project Engineering Evaluation/Cost Analysis document (*8*), the average background concentration of arsenic in soil for this area was approximately 5 mg/kg. Concentrations of arsenic were observed to range in residential areas from background levels to 202 mg/kg. For locations exceeding arsenic concentrations of 20 mg/kg, removal of contaminated material was scheduled. Sites were prioritized by the project partners based in part on arsenic concentrations and work is currently on-going. Phytoremediation utilizing different species of ferns is also currently being tested at different locations within AUES FUDS to evaluate the technology efficiency. In 2005, approximately 9,900 ferns were planted on different properties throughout the area (*55*).

As part of the characterization of arsenic contamination at AUES FUDS, samples of contaminated material were analyzed for human oral bioavailable arsenic and association of arsenic with particles by electron microprobe (*8*). The five samples analyzed for arsenic particle association ranged in total arsenic concentration from 113 to 235 mg/kg. The arsenic particle association for all of the samples was dominated by iron oxyhydroxide particles. Other arsenic particle associations were observed at significantly lower levels in some of the samples to iron sulfate mineral particles, manganese oxyhydroxide particles, and clay particles. Using a simulated human oral bioavailable extraction procedure, extracted arsenic in samples was not correlated with total arsenic concentration. Of the five samples with total arsenic concentrations exceeding the 20 mg/kg cleanup threshold for AUES FUDS, only one sample was observed to have a simulated human oral bioavailable arsenic concentration (39 mg/kg) exceeding the threshold (this sample was the median for total arsenic concentration). However, the bioavailability information was not incorporated into the decision making process for AUES FUDS.

2.2.4 Samples Associated with Poultry Litter.

The poultry and swine feed additive called roxarsone ($C_6H_8O_6AsN$) is used in the watershed of the Chesapeake Bay for raising animals. Roxarsone is not absorbed into the biomass of the animal, but is excreted. Rutherford et al. (*56*) estimated that $2.5(10)^5$ kg of arsenic was present in poultry litter excreted by chickens fed roxarsone in the United States in 2000. The environmental fate of the arsenic in roxarsone, especially in the Delmarva Peninsula due to the high number of poultry farms, is currently under investigation.

Dr. Tracy Hancock (United States Geological Survey) provided samples associated with poultry litter. The samples include some poultry litter (PL), agricultural soil amended (in the field) with poultry litter (PL-TF), sediment from a ditch down-gradient from poultry raising activities (PL-AD), and soil from an area believed to be uninfluenced by poultry waste (PL-GB).

2.2.5 Sample from Residence in Maryland.

This composite sample (RES) was taken from the upper 2 cm at different spots beneath a residential deck in Maryland built with lumber treated with copper-chromated arsenate (CCA). At the time of the sampling, the deck was approximately seven years old, and had replaced an older deck that was built with lumber that may or may not have been pressure treated.

2.2.6 General Sample Characteristics

Many of the soils used in the study were analyzed by an agricultural soil lab (Maryland Cooperative Extension, University of Maryland, College Park – Eastern Shore) to evaluate the following characteristics: pH, % organic matter, % sand, % silt, % clay, cation exchange capacity, and soluble salts. The results are listed in TABLE 3.

All but three of the mine tailings and associated samples have soil pH levels that are neutral to slightly basic. The exceptions are M23, M27 and M28 which have acidic pH levels. Organic carbon in the mine tailings samples did not exceed 0.65% in any sample. The very low organic carbon component in these mine tailings is expected since the tailings are representative of rapidly processed rock in contrast to the naturally weathered rock found in soils and sediments. The other associated samples from soil, sediment, and mine tailing/soil matrices, had higher organic carbon percentages, ranging from 1.4 to 5.6%.

The particle distribution of the mine tailing samples varied considerably, even with respect to samples taken at common depths. This suggests that the mined rock

TABLE 3. Soil Characteristics for Selected Samples (values represent single replicate; units as indicated).

SAMPLE	pH	OM %	Sand %	Silt %	Clay %	CEC (meq/100 g)	Soluble Salts (ppm)
M1	7.8	0.53	22	70	8	49.26	3900
M2	7.4	0.1	41	54	5	45.64	1300
M3	7.4	0.15	43	40	17	44.53	1300
M4	8.1	0.55	19	72	9	50.14	3400
M5	7.6	0.09	45	35	20	45.79	1300
M6	7.5	0.2	34	49	17	50.19	1300
M7	8.3	0.65	43	48	9	61.67	6200
M8	7.8	0.54	25	72	3	50.4	2300
M9	7.6	0.01	43	35	22	46.16	1400
M10	8.3	0.27	61	30	9	67.6	9100
M11	8	0.1	31	57	12	47.27	1900
M12	7.8	0.01	30	63	7	45.81	1700
M13	7.9	0.13	44	35	21	50.02	2800
M14	8	0.01	16	80	4	53.18	3400
M15	8.1	0.07	96	1	3	50.65	2300
M16	8.1	0.01	94	3	3	49.95	2500
M20	7.2	5.63	49	41	10	18.93	240
M21	7.7	1.7	58	29	13	41.72	430
M22	8	2.87	50	34	16	34.16	110
M23	5.1	3.41	47	47	6	34.29	1700
M24	8	3.62	43	37	20	38.36	220
M26	7.2	1.4	65	22	13	44.61	550
M27	3.7	3.48	60	29	11	58.07	8000
M28	4.3	1.18	80	4	16	34.93	1800
WF	6.1	3.18	42	35	23	8.71	85
AUES1	7	4.15	47	32	21	14.6	190
AUES3	6.5	8.41	49	33	18	15.48	n/a
RES	6	6.52	46	39	15	11.77	220

or the flotation process itself is not uniform. All of the samples, including the other associated samples tended to have a predominance of sand-sized particles and/or silt-sized particles, except for M15, M16, and M28 (wetland sample). These exceptions consisted of almost entirely sand-sized particles (96, 94 and 80% respectively).

Soluble salts concentrations varied from location to location for the mine tailing samples, but were consistently highest at each location at the shallowest depth. This trend reinforces the Gutiérez-Ruiz et al. (*53*) suggestion that evaporation processes are expected to concentrate soluble minerals in the upper layer of the mine tailing pond. The other associated samples were generally much lower in soluble salts concentration except for the wetland samples (M27 and M28). The wetland samples were comparable in soluble salts concentrations to the mine tailings and also exhibited a higher concentration at the shallower depth. The higher concentrations at the shallower depths also suggest an importance on evaporation in the wetland area for the transport of soluble minerals upward in the soil column. The implication is that if arsenic in the contaminated material is soluble and is also transported upward, then higher concentrations of arsenic would be found in the layer that is most exposed and susceptible to wind erosion.

The high concentrations of soluble salts in the mine tailings compared to the other samples may suggest that the processing of the metal ore may have resulted in the breakdown on many of the amorphous and crystalline minerals and the formation of the more soluble ionic-bonded compounds. The formation of more stable minerals may be expected to occur with time and weathering of the mine tailings. The formation of these minerals may take a considerable amount of time particularly due to the limited rainfall in the area. Another explanation for the difference in soluble salts with depth for the mine tailings could be related to the formation of sulfidic minerals at the lower depths. The samples at lower depths were always wet while the shallowest samples were always dry. The wet conditions may have more reducing conditions where sulfides might be expected to form from sulfates. The reducing conditions may be a result of the depletion of oxygen from pore water that could occur due to chemical or biotic processes. Sulfates would be expected to be typically soluble salts while the sulfides would be expected to be relatively insoluble.

For the mine tailings samples, the cation exchange capacity was relatively high for the type of particle fractionation and percent organic matter. The level of cation exchange capacity in the mine tailings ranged from 44 to 67 meq/100 g. These levels may be expected for soils with higher clay and organic components that what was seen in the tailings. These high levels may be explained by the presence of magnesium, potassium and calcium salts rather than by the adsorption processes. The other associated samples tended to have similar or slightly lower levels of cation exchange capacity.

The other samples analyzed by the agricultural lab (WF, AUES1, AUES3, RES) were neutral to slightly acidic in pH levels. The percent organic carbon of these samples ranged from 3.18 to 8.41% and is not atypical of weathered soils or sediment. The particle distributions of these samples were all similar to each other: mostly sand-sized particles (42 - 49%), then silt-sized particles (32 – 39%), with the fewest particle being clay-sized (15 - 23%). The cation exchange capacity and concentration of soluble salts for these samples was much lower than the mine tailings samples. The level of cation exchange capacity for these samples was in the approximate range that might be expected for the amount of clay and organic material. The lower soluble salts concentration in these samples suggests that these materials are more weathered than the mine tailings. Transport of soluble salts from the material from rain or snow, or formation of more crystalline minerals may be expected in more weathered materials.

2.3 METHODS

2.3.1 Measurement of pH and Eh.

Determination of pH and redox potential (Eh) was performed using an Orion 91-57 triode pH probe and an Accumet 13-620-81 platinum Ag/AgCl combination electrode, respectively. Daily calibration of the pH probe was done using buffers at least three different points and at the pH levels: 3.00, 4.00, 7.00, 8.00, or 10.00. The redox probe calibration was verified daily using Light's solution (*57)*. The redox probe was used to provide an empirical approximation of redox potential relative to the samples used in this study.

2.3.2 Sequential Extraction Method.

Sequential extraction methods can be used as a tool to suggest fractionation of arsenic in soil. The sequential extraction method that we used was developed by Tokunuga et al. (*49*) and Lipton (*50*) and is summarized in TABLE 4. A slightly modified version of this method has been used in another study for characterizing arsenic in contaminated mine tailings from Korea (*48*). For each soil analyzed, approximately 2.5 g were measured into polystyrene centrifuge tubes with the actual mass recorded. For each step, except fraction "e", indicated in TABLE 2, 25 mL of solution were mixed with the soil samples and equilibrated via end-over-end shaker for the time period indicated in parentheses. For fraction "e", 10 mL of solution were mixed with the soil samples in both parts. For the fractions requiring boiling or temperature maintenance (as indicated in parentheses), samples and solutions were transferred to boiling flasks and were refluxed in a boiling water bath, or in a bath

TABLE 4. Sequential Extraction Method Used to Describe Arsenic Fractionation in Soil Samples (Adapted from Tokunaga et al. (*49*))

Step	Targeted fraction	Extraction procedure	Fraction grouping
a	Soluble arsenic	0.25M KCl (2hr)	Highly mobile fractions
b	Adsorbed arsenic	0.1M Na_2HPO_4 (pH 8, 20hr)	
c + d	Carbonate associated arsenic	1M Na-acetate (pH 5, 1 + 4hr), then 0.1M Na_2HPO_4 (pH 8, 20hr)	
e	Soil organic matter associated arsenic	NaOCl (pH 9.5, 0.5 hr boil, repeated once)	Oxidation mobile fraction
f	Easily reducible oxide associated arsenic	0.1M NH_2OH (pH 2, 0.5hr) followed by 0.1M KOH (20hr)	Reduction mobile fractions
g	Amorphous oxide associated arsenic	0.25M NH_2OH/HCl (0.5 hr@50 ^oC) followed by 0.1M KOH (20hr)	
h	Crystalline oxide associated arsenic	4M HCl (0.5 hr boil)	
i	Amorphous aluminosilicate associated arsenic	0.5 M NaOH (0.2 hr boil)	

maintained at the given temperature as indicated in TABLE 4. Upon completion of the temperature specific steps, soil and solution were transferred back into the original centrifuge tubes. After each step, the soil and solution mixture was centrifuged (4000 rpm, 10 min.), and the supernatant separated, then the soil was rinsed with 5mL of 0.25M KCl, centrifuged again, the supernatant separated, and added to original solution after which the combined solution was filtered (0.2 μm, Whatman Nuclepore). Each combined step and rinse solution was analyzed for arsenic and iron concentrations. All reagents used were ACS grade, and the pH levels were adjusted with trace-metal grade solutions of NaOH and HCl.

2.3.3 Microwave Digestion Method.

Total arsenic concentrations in the soil samples were determined via microwave digestion method, similar to several other published methods including those of Shepherd et al. (*58*), Deaker and Maher (*59*) and Niewenhuize et al. (*60*). Samples of approximately 1 g of soil were measured into polystyrene centrifuge tubes (the actual mass was recorded), and later transferred into Teflon microwave digestion liner vessels. The centrifuge tubes were rinsed twice with 5 mL trace metal grade nitric acid, which was subsequently transferred into the corresponding Teflon microwave digestion liner vessels. Each liner, containing soil and 10 mL nitric acid, were swirled and let stand for at least 15 min. to allow gases to be released. The liner caps had pressure release orifices that were sealed with disposable rupture membranes during the digestion process. After the gas formation had diminished, the liner vessels were sealed, and the microwave digester was run according to the power scheme as displayed in TABLE 5. The microwave used (MDS 2000, CEM Corp.) monitors the pressure in one reaction vessel. The maximum output for the microwave is 650 W. The system can run 12 samples per run. Upon completion of the digestion power scheme, the diminishing pressure was monitored until it reached atmospheric pressure, and samples were removed from the vessel liners into the original centrifuge tubes. The samples were centrifuged (4000 rpm, 10 min.), and the supernatant was diluted to an exact volume in a volumetric flask. The diluted solution was evaluated for arsenic concentration using with hydride generation atomic absorption spectrophotometric analysis (HG-AAS). This digestion procedure, coupled with HG-AAS, was found in an calibration study to detect greater than 91% of the total arsenic concentration in an arsenic-enriched standard soil (SRM 2710, US-NIST) in three replicates.

2.3.4 Arsenic Analysis via HG-AAS.

Arsenic was measured in the various methods via HG-AAS after reduction with 22 g/L potassium iodide (KI) in 3.0% hydrochloric acid. Measurements were taken after approximately 80 and 220 min. after the addition of KI. The highest readings were reported. Any dilutions necessary were done using a blank solution with 22 g/L KI and 3.0% hydrochloric acid. The KI was added to this blank at the same time as the samples. The hydride generator method uses a Perkin-Elmer FIAS 400 with AS-91 autosampler coupled to a Perkin-Elmer 5100 unit. The chemicals used in the hydride generation process were 0.2% $NaBH_4$ in 0.1 N high purity NaOH, 6 N trace metal

TABLE 5. Microwave digestion power scheme for arsenic analysis.

Stage	1	2	3	4	5
Power (%)	85	90	90	90	85
Pressure (psi)	20	40	80	120	160
Run Time (min.)	7	7	7	7	16
Min. Time @ Parameter (min.)	5	5	5	5	11

grade HCl, and argon as the carrier gas at ≈ 100 cm^3/min. Standards were prepared daily to evaluate the concentrations of arsenic in samples (R2>0.996).

2.3.5 Mobility Experiments.

A variety of pH and redox conditions were tested on several sample materials (M2, M5, M14, M15, M20, M27, WF, PM, AUS3). The samples were selected to represent some diversity in source, percent organic matter, soil pH, and type and extent of arsenic contamination. To maintain an approximate pH level, three "Good" buffers MES, CAPS, and Trizma-HCl were used at concentrations of 0.1 M. The experimental justification and rationale for using the "Good" buffers can be found in Appendix A. The buffered solutions contained 0.15 M $NaClO_4$ as background electrolyte, and pH was adjusted with trace metal grade HCl and NaOH. For each soil analyzed, approximately 2.5 g were measured into polystyrene centrifuge tubes with the actual mass recorded. The buffered solutions (25 mL)were added to the centrifuge tubes at pH levels of 10.0 (MES), 8.0 (Trizma-HCl), or 5.5 (CAPS). Reactors were either sparged with air or O_2-free nitrogen gas for approximately 10 min each. During sparging, the nitrogen-sparged reactors were partially sealed with Parafilm® to ensure reactor systems were under positive pressure to limit diffusion of atmospheric oxygen into the reactor system. The pH of the sample and buffer mixture in each reactor was measured and recorded. After approximately 24 h of end over end mixing, nitrogen sparged reactors were again sparged for approximately 10 m with O_2-free nitrogen gas while partially sealed with Parafilm®. During the sparging process, Eh was measured and recorded for each reactor. Additionally, the air-sparged reactors were sparged with air for approximately 10 min each, and the Eh level was measured and recorded. Within 72 h of the start of the experiment, both sets of reactors were sparged with the same gases a third time, and Eh levels were measured. After approximately 7 d of end over end shaking following the start of the experiment, pH and Eh were measured for each reactor, then the reactors were centrifuged (4000 rpm, 10 min) and the supernatant was filtered (0.2 μm, Whatman Nuclepore). The filtered supernatant samples were measured for arsenic and iron concentrations. Each different soil/pH/gas reactor experiment was performed in at least two replicates.

2.3.6 Simulated Human Oral Bioavailable Extraction of Arsenic.

Simulated human oral bioavailable extraction concentrations of arsenic was measured using a method similar to the published methods of Rodriguez et al. (*51*) and Ruby et al. (*52*). Seven samples were measured in duplicate for simulated human oral bioavailable arsenic concentrations (M2, M5, M14, M15, M20, M27, WF). A stomach acid simulated solution containing 1% porcine pepsin and 0.15 M $NaClO_4$ (as a background electrolyte) at pH 1.8 was created. The pH level was adjusted using trace metal grade HCl or NaOH solutions. A system was created using glass reactors with flow-through hollow walls and a heat pump maintaining temperature at 37 ± 1°C, mixing with magnetic stirrers, and sparging with O_2-free nitrogen gas. For each sample, approximately 0.5 g of material was measured and mass recorded, then combined with 75 mL of stomach acid simulated solution. The sample solution mixture pH was adjusted to 1.8 with trace metal grade HCl and

NaOH solutions. The mixture was then covered with Parafilm®, mixed, and sparged for 1 h. A 50 mL aliquot of the solution was then removed from the glass reactor system, centrifuged (4000 rpm, 10 min), and supernatant filtered. The filtered supernatant was measured for arsenic and iron concentrations. The simulated human oral bioavailable extraction method was performed in duplicate.

CHAPTER 3. RESULTS AND DISCUSSION (MEXICAN MINE TAILING AND ASSOCIATED SAMPLES)

3.1 MICROWAVE DIGESTION RESULTS

The measured concentrations of arsenic and iron from microwave digestion of the mine tailings and associated samples are presented in TABLE 6. Some of the samples that were collected were not evaluated by the sequential extraction method due to low arsenic concentrations from microwave digestion (M13, M17, M18, and M19).

For most of the samples, however, the microwave digestion method was reproducible in representing both arsenic and iron concentrations as shown by standard deviation levels typically below 10% of averages. For some samples, however, the reproducibility of the method for both arsenic and iron concentrations was not statistically acceptable. Some variability may be attributable to varying concentrations of iron and arsenic within subsamples despite homogenization.

The mine tailings (M1 – M16) and associated samples (M17 – M28) ranged in total arsenic concentration from very low (0.720 ± 0.11 mg/kg arsenic for M18) to very high (6,210 ± 508 mg/kg arsenic for M15). The mine tailing samples, however, were consistently very high in arsenic concentration by microwave digestion; the entire set had arsenic concentrations of 1,800 mg/kg or greater. The median mine tailing arsenic concentration was 2,800 mg/kg. These values are significantly higher than the risk-based site cleanup values typically used in residential areas in the United States (20 – 40 mg/kg). For high-risk individuals who might regularly ingest

TABLE 6. Average arsenic and iron concentrations via microwave digestion dnalysis in mine tailings and associated samples. Standard deviations represent duplicate or triplicate measurements. * Represents no duplicate measurements.

Sample	Average arsenic concentration (mg/kg)	Average iron concentration (mg/kg)
M1	2 880 ± 59.2	47 200 ± 328
M2	3 580 ± 431	59 200 ± 7 600
M3	2 770 ± 182	46 400 ± 1 270
M4	1 810 ± 28.8	44 500 ± 3 960
M5	2 440 ± 204	46 800 ± 1 090
M6	4 350 ± 108	51 500 ± 85.5
M7	2 780 ± 54.7	41 300 ± 635
M8	3 400 ± 131	47 900 ± 1 720
M9	3 120 ± 99.3	50 500 ± 899
M10	2 730 ± 18.5	39 300 ± 327
M11	3 430 ± 188	48 800 ± 2 580
M12	2 530 ± 1380	43 200 ± 1 820
M13	2 060 ± 25.5	47 100 ± 767
M14	2 330 ± 24.2	46 000 ± 2 160
M15	6 210 ± 508	38 000 ± 1 650
M16	5 480 ± 417	42 000 ± 2 210
M17	10.0 ± 0.79	21 000 ± 425
M18	0.720 ± 0.110	21 000 ± 380
M19	5.97 ± 1.37	21 800 ± 744
M20	132 ± 3.17	19 100 ± 814
M21	660 ± 15.1	22 600 ± 618
M22	206 ± 7.32	19 300 ± 528
M23	1 440 ± 135	36 500 *
M24	168 ±19.4	21 700 ± 77.7
M25	10.2 ± 0.28	44 400 ± 258
M26	373 ± 30.7	46 200 ± 813
M27	487 ± 52.5	22 400 ± 1 800
M28	676 ± 3.65	25 600 ± 9 790

small quantities of the material represented by the samples, based on consideration of total arsenic concentrations alone, chronic impacts may be expected.

Samples taken in the area beyond the perimeter of the tailings ponds included soil samples, wetland sediment, and material used in a perimeter berm around the tailings pond. The soil and wetland samples ranged in arsenic concentration by microwave digestion from below 1 to 1,400 mg/kg with a median value of 190 mg/kg. The samples taken from soils to the southwest of the ponds (M20, M21, M22, M23, and M24) exhibited elevated levels of arsenic (132 to 1,440 mg/kg) even at a distance of 2 km, suggesting that significant transport of arsenic may occur via wind erosion to the southwest. This observation is consistent with the findings of Gutiérez-Ruiz et al. (*53*) for the same site. All of the samples taken to the southwest exceeded the risk-based site cleanup values typically used in residential areas in the United States (20 – 40 mg/kg). Gutiérez-Ruiz et al. (*53*) cited health studies indicating possible impacts from arsenic exposure to residents in a village located to the southwest of the tailings pond.

The samples taken at approximately 3 km to the northwest of the ponds had much lower arsenic concentrations by microwave digestion (0.720, 5.97, and 10.0 mg/kg) than the samples taken to the southwest (132, 206, 660, and 1440 mg/kg). However, the samples of wetland sediment immediately to the northwest of the ponds (M27 and M28 at location K) exhibited moderately high levels of arsenic by microwave digestion (487 and 676 mg/kg, respectively). The two samples from the pond wall (M25 and M26) were significantly different in arsenic concentration by microwave digestion (10.2 and 373 mg/kg, respectively), possibly reflecting variable use of mine tailings materials in the construction of the berm.

For all of the samples, iron concentrations from microwave digestion correlated poorly with arsenic concentrations as shown in FIGURE 2 (R^2=0.449). For the mine tailings samples exclusively, iron concentrations from microwave digestion did not correlate with arsenic concentrations as shown in FIGURE 3 (R^2=0.0003). Although arsenic might be expected to be typically associated with iron by adsorption or as components in various minerals, because iron is more abundant than arsenic in the environment, overall iron levels may not be expected to correlate well with overall arsenic concentrations.

For the other associated soil samples, excluding the tailing/gravel/soil mix samples, microwave digested iron and arsenic concentrations were fairly well correlated (R^2=0.823, data not shown).

By removing the two outliers in the comparison of all samples for iron and arsenic concentrations, at the highest arsenic concentrations with relatively low iron concentrations, the correlation between arsenic and iron concentrations was improved (R^2=0.687). This suggests that total arsenic and iron levels are moderately correlated in most cases, but that arsenic may be associated with non-iron minerals under some conditions. Carbonates, clays, and sulfidic minerals may also be associated with solid-phase arsenic.

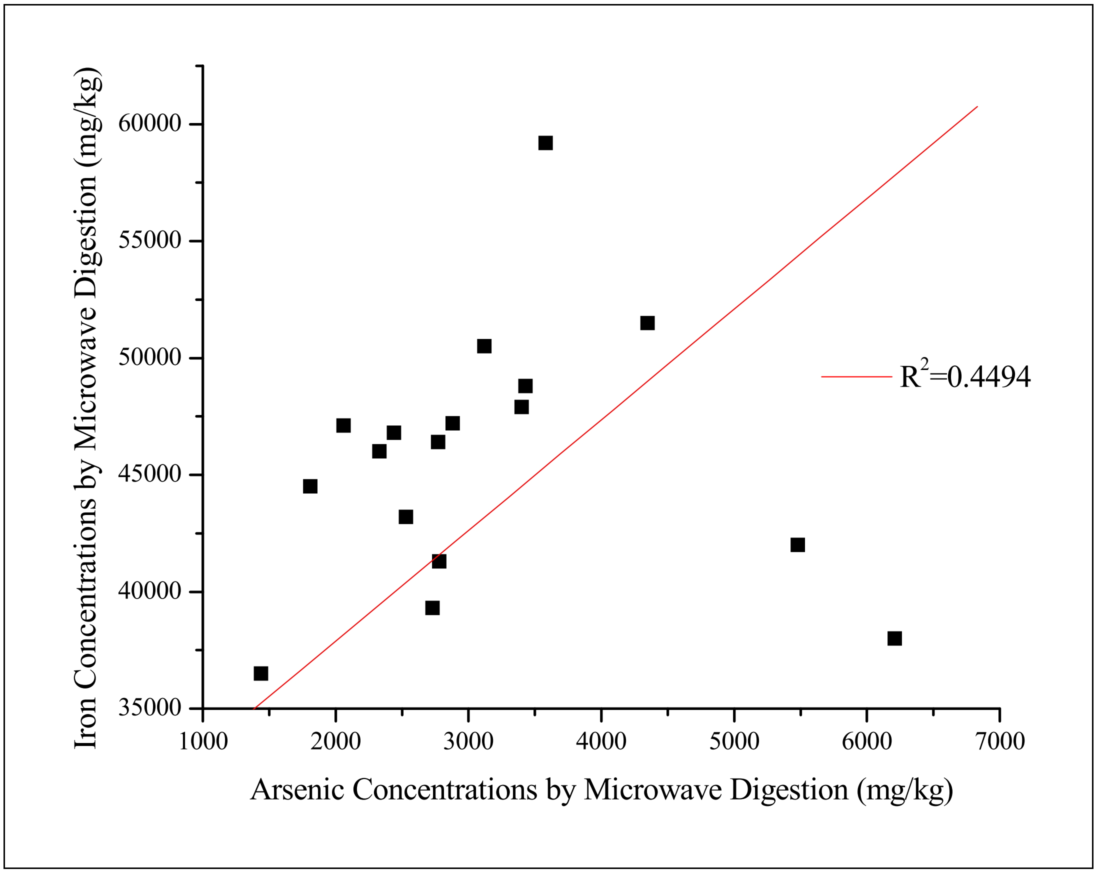

FIGURE 2. Comparison of arsenic and iron concentrations for different mine tailings and associated samples from microwave digestion.

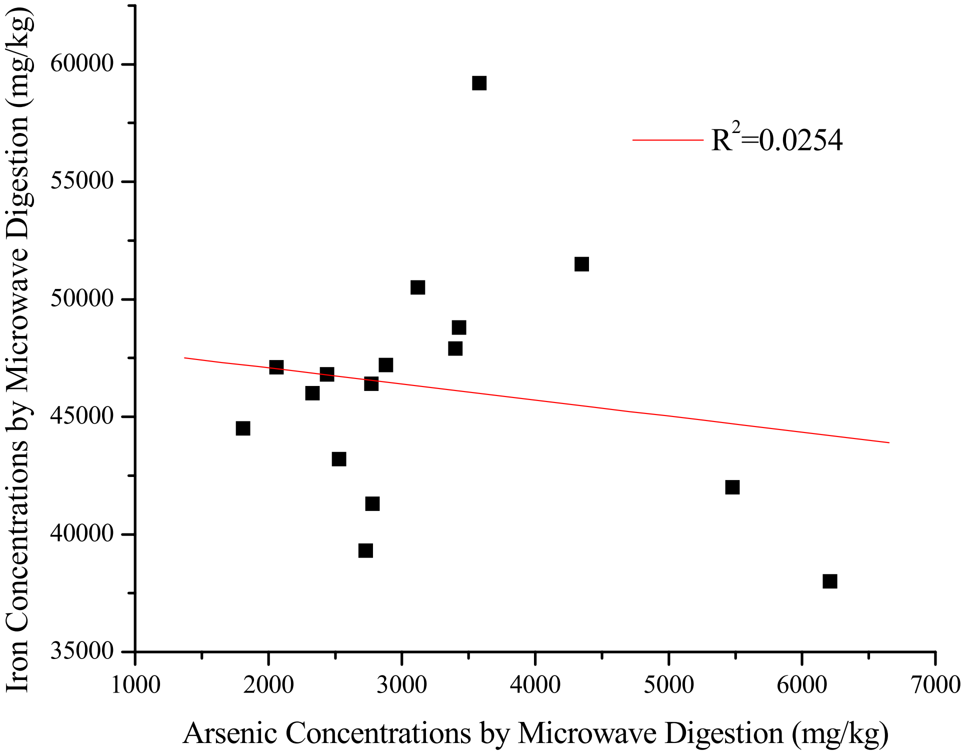

FIGURE 3. Comparison of arsenic and iron concentrations for mine tailing samples from microwave digestion.

3.2 SEQUENTIAL EXTRACTION METHOD RESULTS

The concentrations of arsenic mobilized by the sequential extraction method and the microwave digestion method for the mine tailings and associated samples are presented in FIGURE 4 through FIGURE 10. Four groups of fractions are evident in most of these samples based on the sequential extraction and microwave digestions methods: the highly mobile fractions (sequential extraction method steps a through d); the oxidation mobile fraction (step e); the reduction mobile fractions (steps f through i); and the fixed fraction (not extracted by sequential extraction). Concentrations of iron mobilized by the sequential extraction method and microwave digestion method were also analyzed for some of the samples and are shown with the corresponding cumulative arsenic concentrations in FIGURE 11 through FIGURE 15.

The arsenic concentration from microwave digestion for many of the samples was significantly higher than the cumulative amount of arsenic mobilized by all of the sequential extraction steps. In contrast, both of the "wetland" samples, M27 and M28 had significantly lower arsenic concentrations by microwave digestion than the cumulative sequential extraction arsenic concentration (FIGURE 10). This may have been caused by a loss of arsenic by volatilization of AsH_3 or another arsenical compound during the microwave digestion process. In many of the samples that underwent the microwave digestion extraction, regardless of allowing the temperature of the samples to cool to room temperature following digestion, a red vapor was observed upon opening the seal, which may have been related to nitric

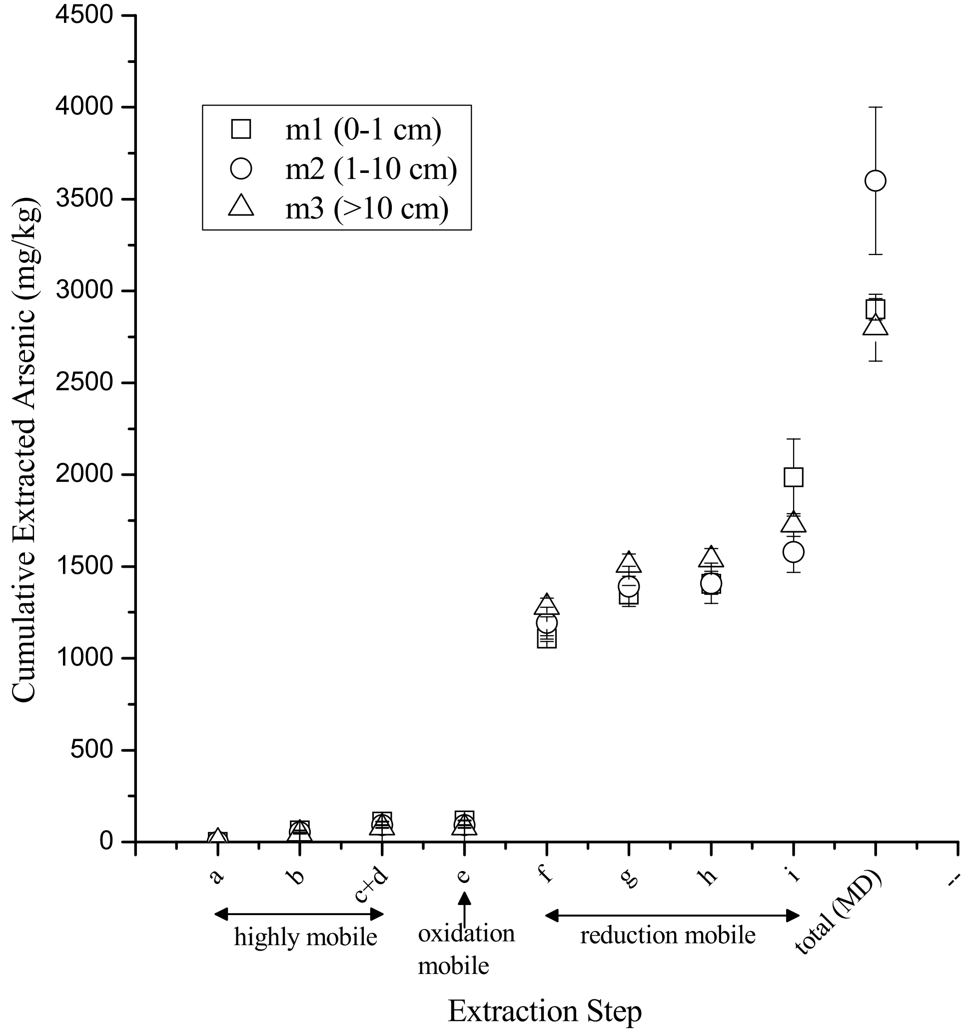

FIGURE 4. The cumulative averages of the sequential extraction method arsenic analysis (steps a through i) and averages of arsenic concentration from microwave digestion for mine tailing samples taken at Location A. The microwave digestion results are independent of the cumulative sequential extraction results. The error bars represent one standard deviation for the average of three replicates. The depth at which each sample was taken is indicated on the figure.

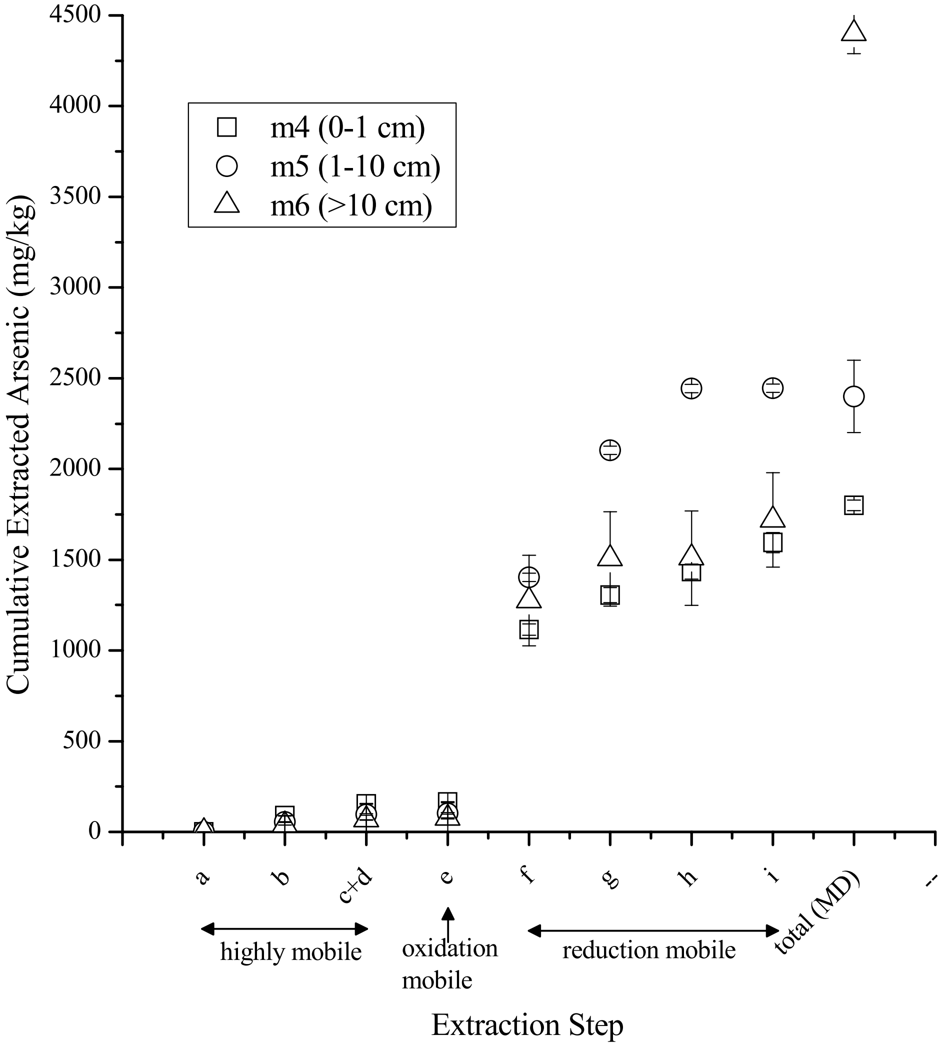

FIGURE 5. The cumulative averages of the sequential extraction method arsenic analysis (steps a through i) and averages of arsenic concentration from microwave digestion for mine tailing samples taken at Location B. The microwave digestion results are independent of the cumulative sequential extraction results. The error bars represent one standard deviation for the average of three replicates. The depth at which each sample was taken is indicated on the figure.

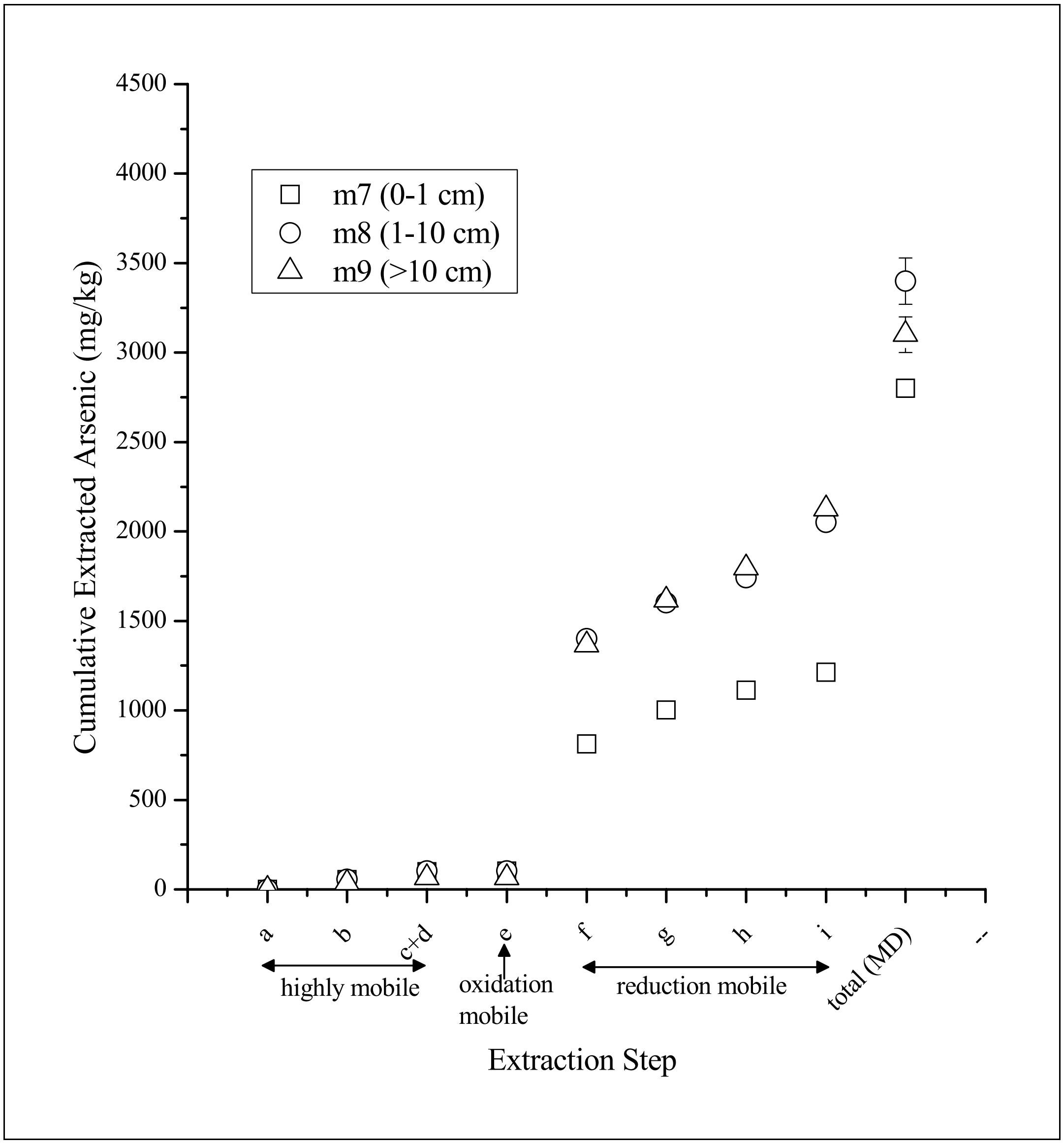

FIGURE 6. The cumulative averages of the sequential extraction method arsenic analysis (steps a through i) and averages of arsenic concentration from microwave digestion for mine tailing samples taken at Location C. The microwave digestion results are independent of the cumulative sequential extraction results. The error bars represent one standard deviation for the average of three replicates. The depth at which each sample was taken is indicated on the figure.

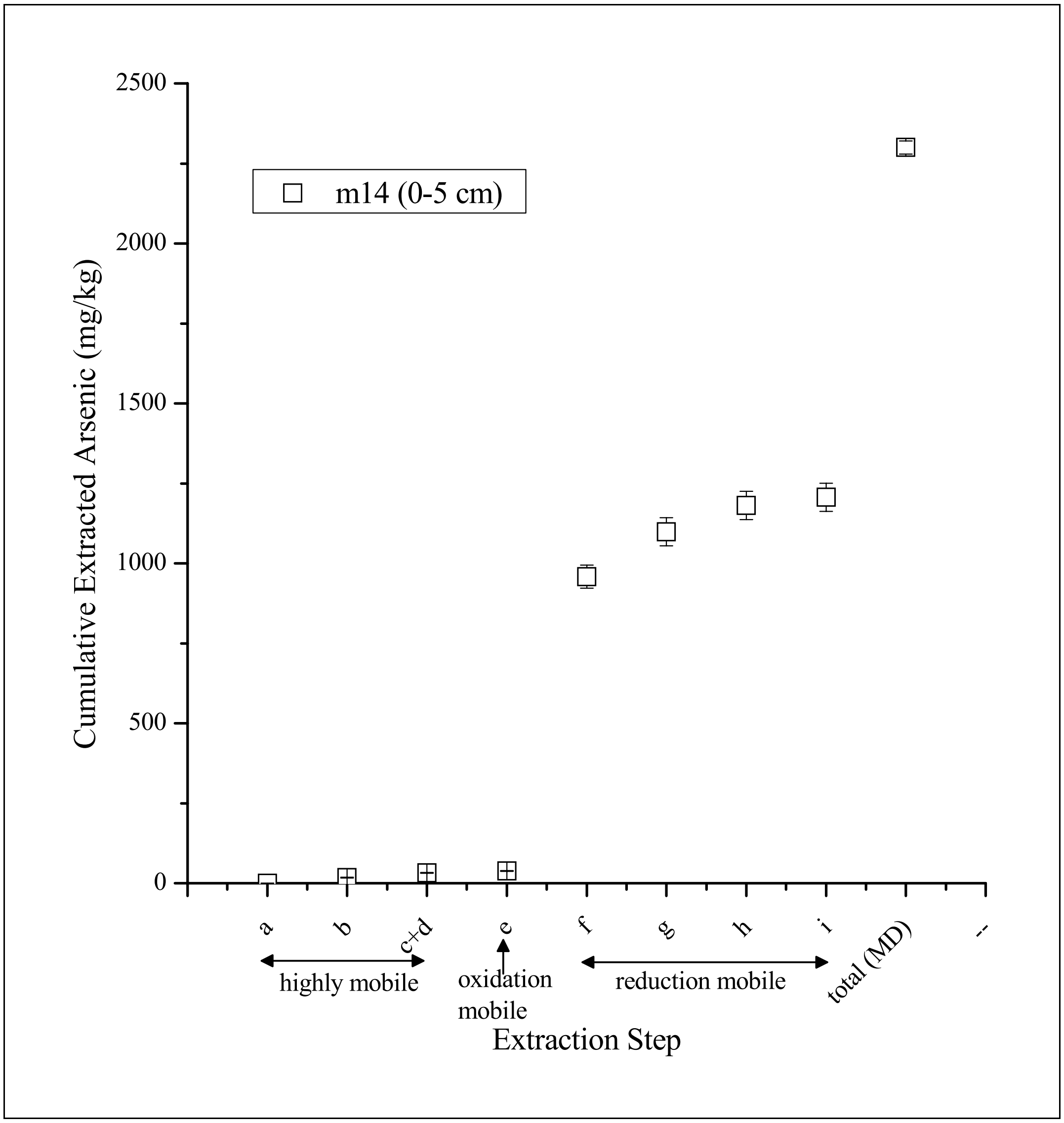

FIGURE 7. The cumulative averages of the sequential extraction method arsenic analysis (steps a through i) and averages of arsenic concentration from microwave digestion for mine tailing samples taken at Location E. The microwave digestion results are independent of the cumulative sequential extraction results. The error bars represent one standard deviation for the average of three replicates. The depth at which each sample was taken is indicated on the figure.

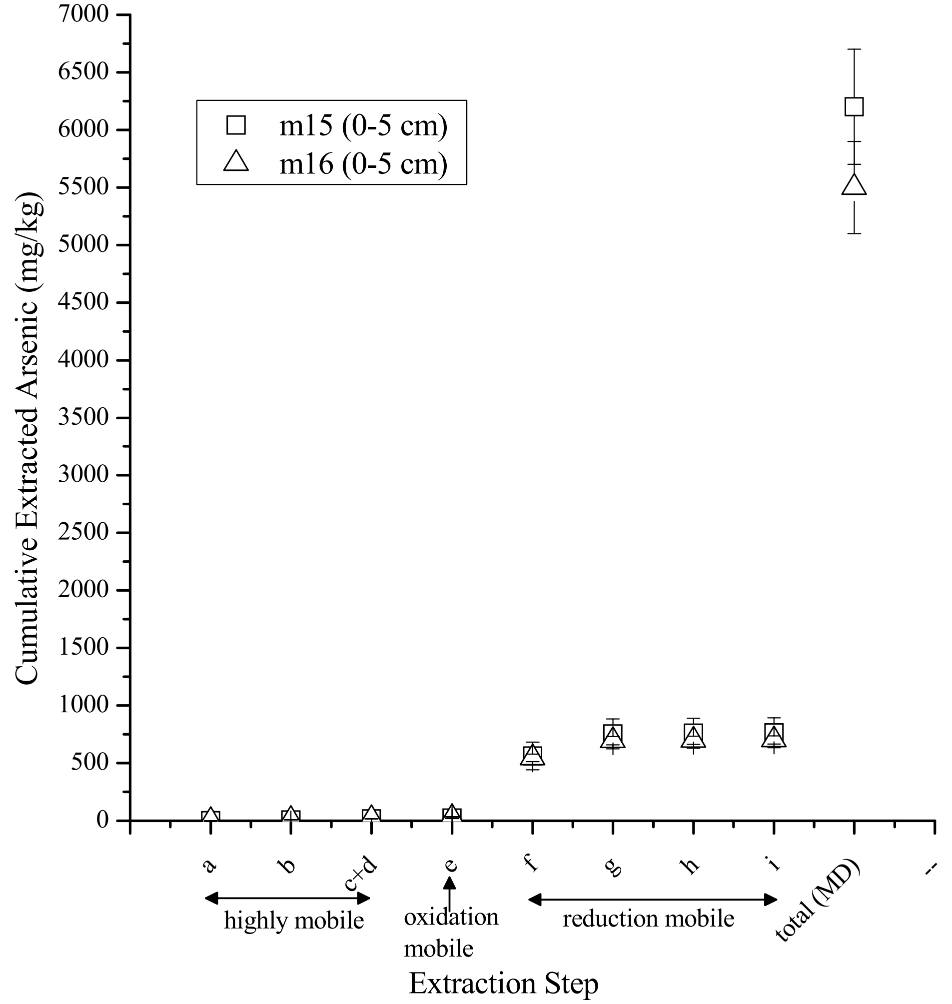

FIGURE 8. The cumulative averages of the sequential extraction method arsenic analysis (steps a through i) and averages of arsenic concentration from microwave digestion for mine tailing samples taken at Location F. The microwave digestion results are independent of the cumulative sequential extraction results. The error bars represent one standard deviation for the average of three replicates. The depth at which each sample was taken is indicated on the figure.

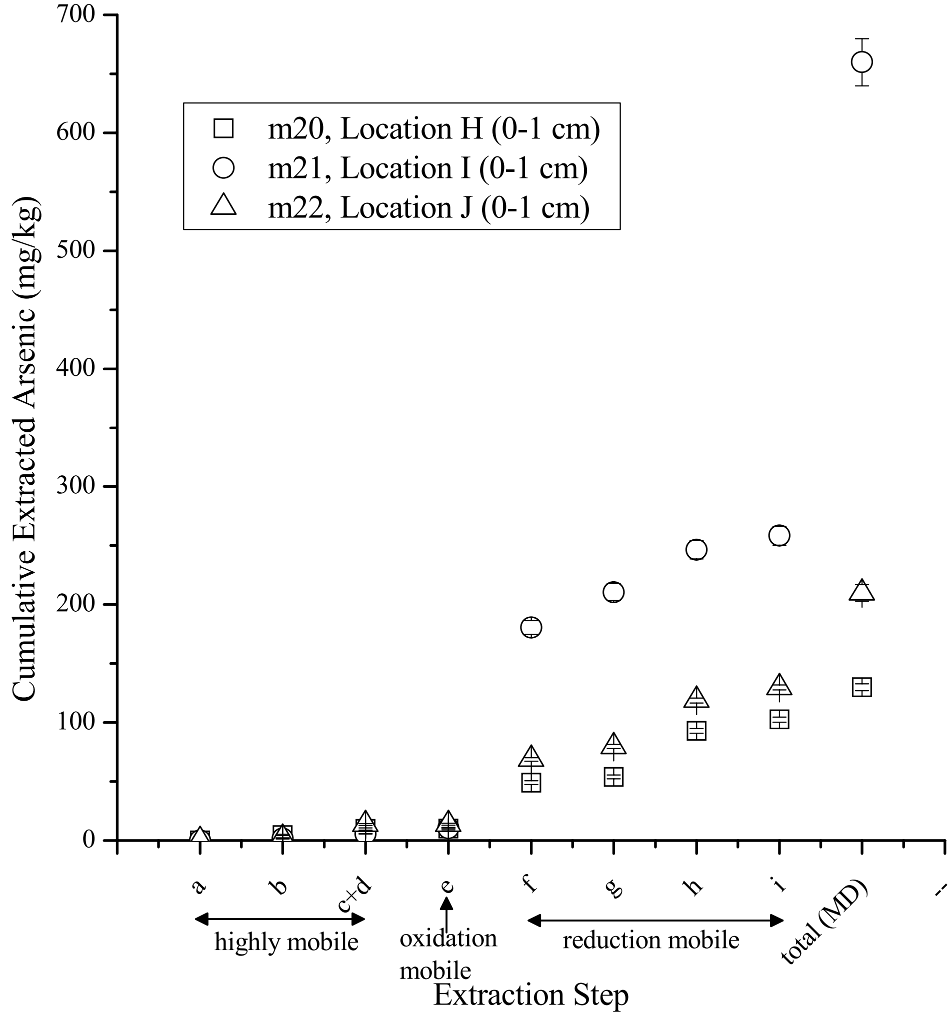

FIGURE 9. The cumulative averages of the sequential extraction method arsenic analysis (steps a through i) and averages of arsenic concentration from microwave digestion for mine tailing samples taken at Locations H, I, and J. The microwave digestion results are independent of the cumulative sequential extraction results. The error bars represent one standard deviation for the average of three replicates. The depth at which each sample was taken is indicated on the figure.

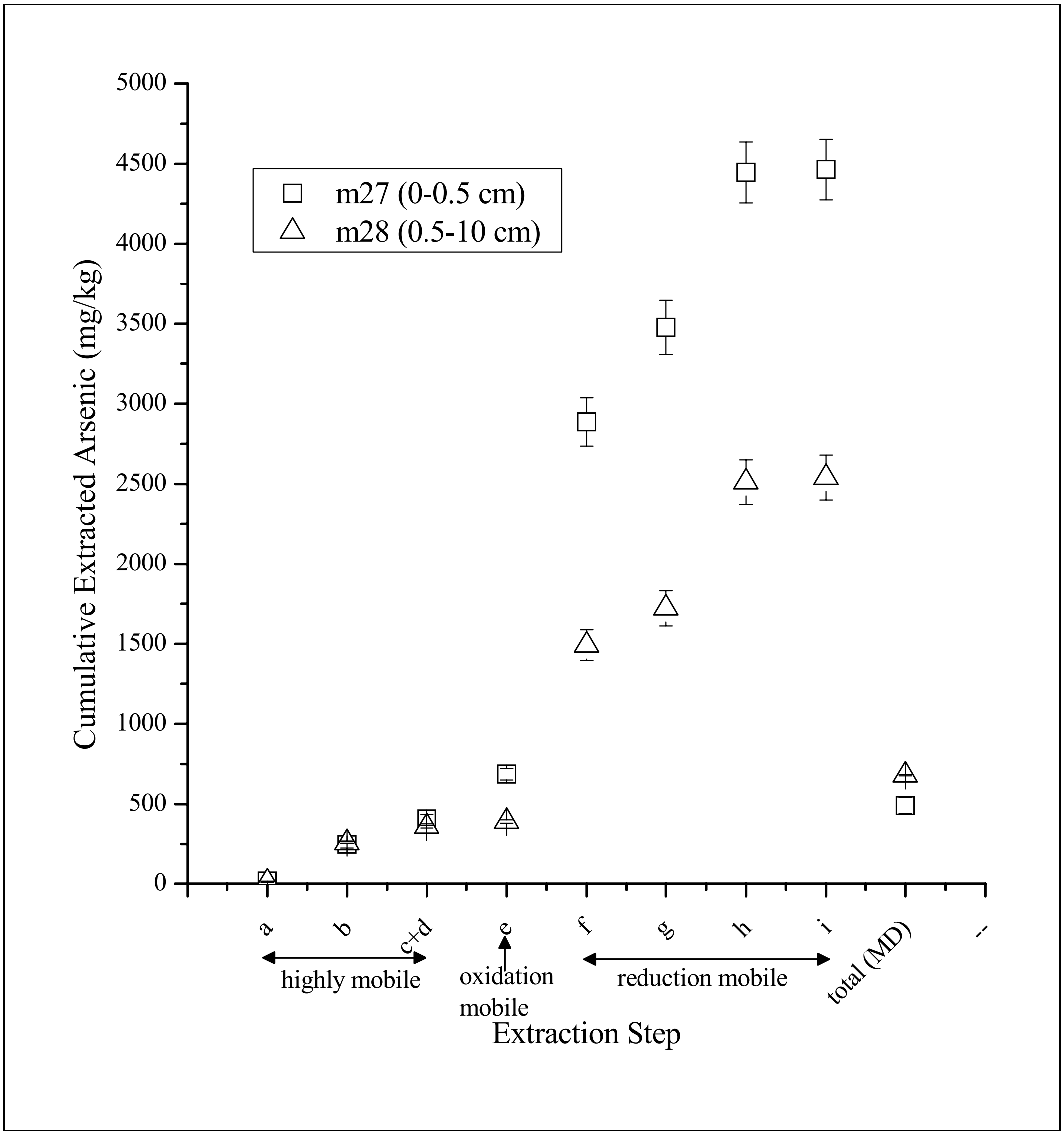

FIGURE 10. The cumulative averages of the sequential extraction method arsenic analysis (steps a through i) and averages of arsenic concentration from microwave digestion for mine tailing samples taken at Location K. The microwave digestion results are independent of the cumulative sequential extraction results. The error bars represent one standard deviation for the average of three replicates. The depth at which each sample was taken is indicated on the figure.

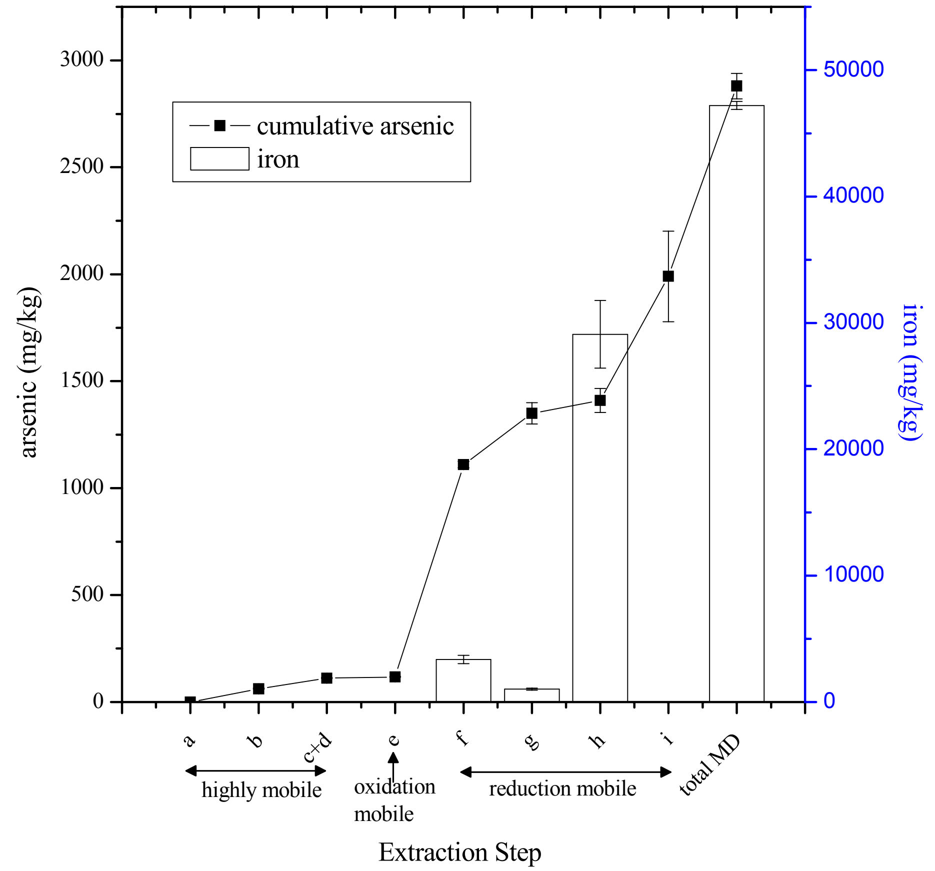

FIGURE 11. Iron and cumulative arsenic mobilization by sequential extraction method (steps a through i), and extraction of iron and arsenic by microwave digestion for mine tailing sample M1 at Location A. Error bars represent one standard deviation.

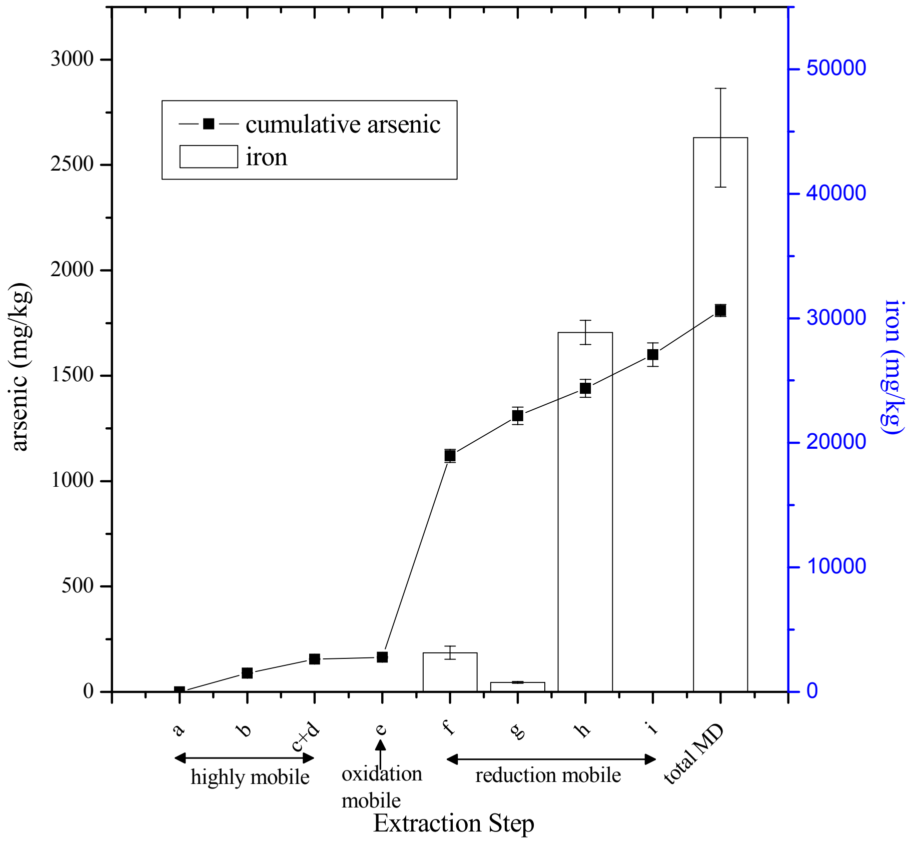

FIGURE 12. Iron and cumulative arsenic mobilization by sequential extraction method (steps a through i), and extraction of iron and arsenic by microwave digestion for mine tailing sample M4 at Location B. Error bars represent one standard deviation.

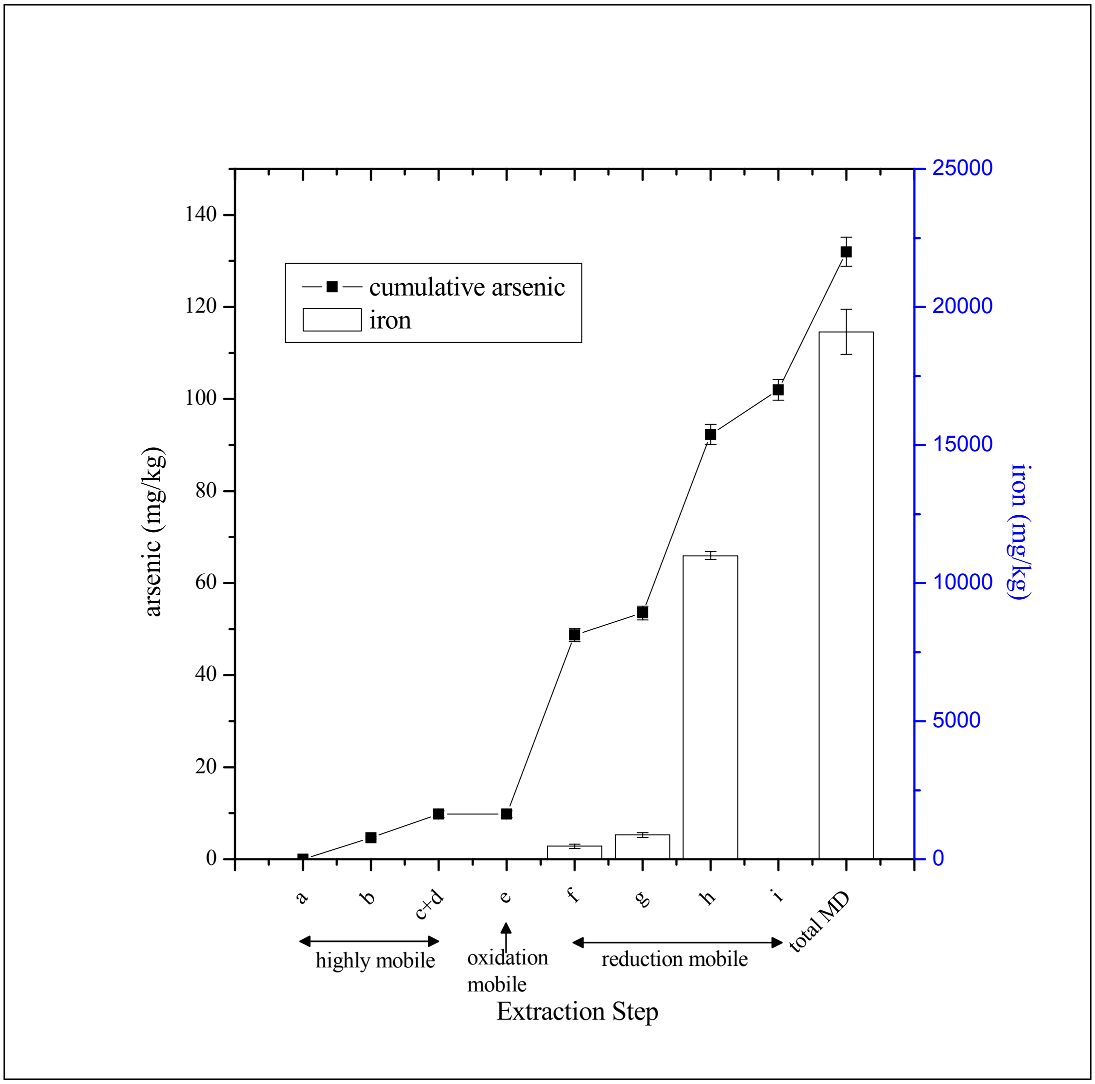

FIGURE 13. Iron and cumulative arsenic mobilization by sequential extraction method (steps a through i), and extraction of iron and arsenic by microwave digestion for the M20 sample at Location H, approximately 2 km southwest of mine tailing pond. Error bars represent one standard deviation.

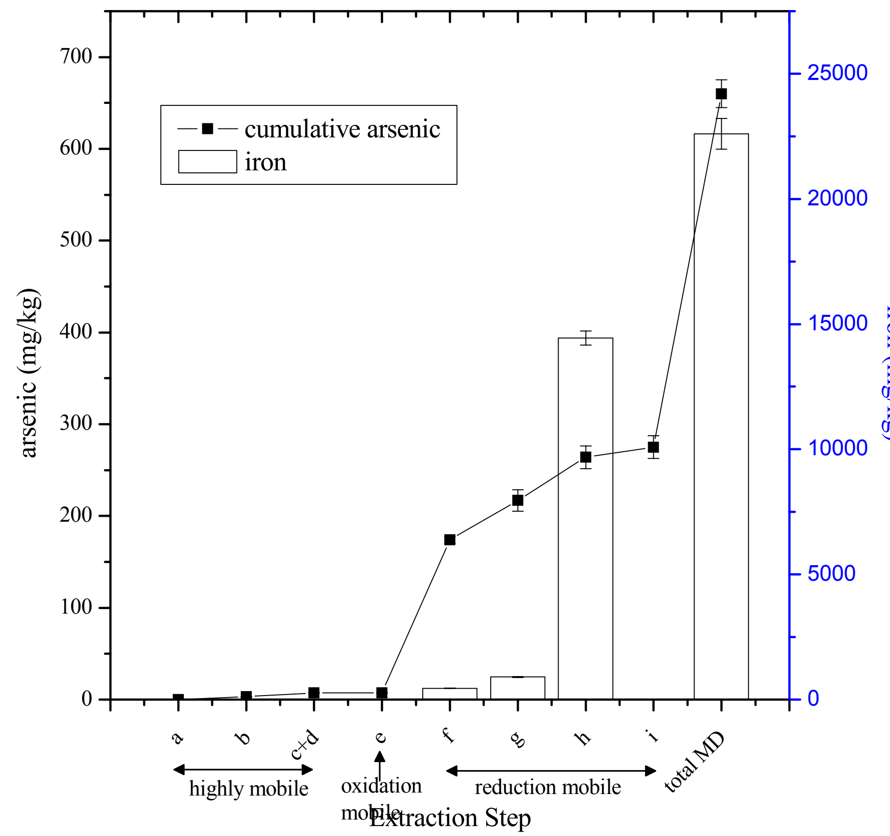

FIGURE 14. Iron and cumulative arsenic mobilization by sequential extraction method (steps a through i), and extraction of iron and arsenic by microwave digestion for the M21 sample at Location I, approximately 50 m southwest of mine tailing pond. Error bars represent one standard deviation.

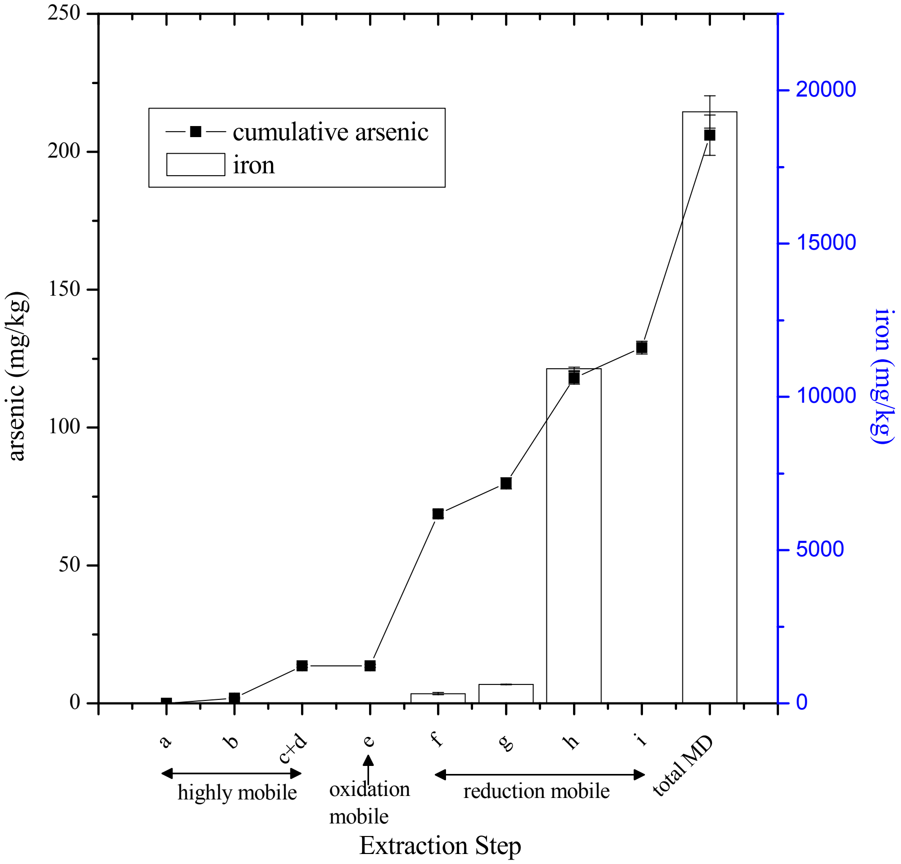

FIGURE 15. Iron and cumulative arsenic mobilization by sequential extraction method (steps a through i), and extraction of iron and arsenic by microwave digestion for the M22 sample at Location J, approximately 100 m southwest of mine tailing pond. Error bars represent one standard deviation.

acid vapors or another chemical. Pure arsine gas is reported as colorless, which would not be visually observable (*61*).

There are a variety of sample locations and matrices within this series of samples. In three of four cases at unique locations where samples were taken at different depths (FIGURE 4 through FIGURE 6), mine tailing samples taken from the middle depth (1 to 10 cm of the ground surface) had higher arsenic concentrations by microwave digestion than for samples taken between 0 cm and 1 cm or at depths greater than 10 cm. The soluble salt concentrations for each set of samples at unique locations suggested the evaporation process was possibly concentrating salts near the surface. The arsenic concentration at the different depths at these locations does not follow the trend of the soluble salts, suggesting that the arsenic is not readily soluble. The low amounts of arsenic extracted in the highly mobile fractions of the sequential extraction method also suggest arsenic is not readily soluble in the mine tailing samples. The arsenic concentration for these samples in the highly mobile fractions was also typically lower in the surface samples.

Gutiérez-Ruiz et al. (*53*) found typically higher concentrations of arsenic near the surface in soil cores outside of the mine tailings pond. These findings are consistent with the low arsenic solubility premise if the source of arsenic is related to wind deposition of tailings particles to the surface of the sampled cores. Low solubility in mine tailing particles deposited by wind to the adjacent areas would result in limited leaching of arsenic downward into the soil, even in the absence of the evaporation process.

Although arsenic in the mine tailings samples was generally mobilized to a relatively lesser extent from the highly mobile fractions and the oxidation mobile fraction than the reduction mobile fractions and the fixed fraction, the mass of arsenic mobilized in the initial steps (steps a through e) was still at levels of concern. As shown in FIGURE 4 through FIGURE 8, for the actual mine tailing samples (Locations A, B, C, E, and F), the sum of arsenic extracted in the highly mobile fraction group and the oxidation fraction ranged from 23 to 165 mg/kg with a median of 84 mg/kg, which is at or above the typical risk-based clean-up levels typically used for residential areas in the United States.

The sum of arsenic mass extracted in steps a through e for Location K (FIGURE 10), the wetland area, was very high: 690 and 390 mg/kg for samples M27 and M28, respectively. The difference between these values between samples M27 and M28 seemed to be exhibited by step e. In step e, 280 mg/kg arsenic was mobilized in M27 compared to 32 mg/kg in M28. The two samples (M27 and M28) were taken at the exact same location, at the top 0.5 cm and between 0.5 cm and 1.0 cm, respectively. Step e is an oxidizing step utilizing NaOCl (6%, pH 2) that would likely mobilize arsenic that is fixed in organic materials or sulfidic minerals that remained stable during the homogenization process and earlier steps. M27 showed evidence of transport of soluble salts by evaporation processes when compared to M28. In addition, M27 had more organic carbon than M28, to which arsenic may have been associated and extracted by oxidation.

Multiple distinct arsenic adsorption mechanisms on goethite were suggested by Hongshao and Stanforth (*22*). Desorption of some arsenic from minerals such as goethite may be expected from competition with phosphates in step b. Hongshao and Stanforth (*22*) showed that some of the arsenic that adsorbed to goethite was not exchangeable with phosphate. Complete desorption or release of arsenic from minerals such as goethite, therefore, may be expected to occur slowly or through dissolution of the mineral. The sequential extraction method steps that may extract non-exchangeable arsenic would be expected in steps f, g and h due to the dissolution of the sorbant minerals. Prior to these steps, desorption of exchangeable arsenic may be expected from competition with phosphate (steps b and c+d). Steps f, g and h might also be expected to dissolve arsenical minerals that were not adsorped.

The sequential extraction method, in all of these samples, exhibited high relative mobilization of arsenic in step f, as shown in FIGURE 4 through FIGURE 15. This particular fraction is likely dominated by the dissolution of some of the iron oxyhydroxides that have been shown to adsorb or be mineralized with arsenic. This fraction may contain some arsenic that is not exchangeable, as observed with goethite by Hongshao and Stanforth (*22*), due to the fact that the adsorbed arsenic that is exchangeable is likely to have been mobilized by earlier treatment with phosphate in steps b and c+d. Using an almost identical sequential extraction method, Kim et al. (*48*) found a dominance of arsenic extracted in the reduction mobile fractions in samples of mine tailings from Korea. The authors also found that the concentrations of iron extracted in steps a through e were very low relative to the cumulative mass of iron extracted by the sequential extraction method as a whole for the mine tailing samples.

With the mine tailing and associated samples from Mexico, arsenic and iron concentrations from step f were very well correlated, as shown in FIGURE 16 (R^2 = 0.990). Dissolution of more crystalline iron minerals, or mineral structures located deeper within individual particles, may be expected in the reducing steps subsequent to step f (namely steps g and h). In FIGURE 11 through FIGURE 15, the highest percent of iron dissolution relative to total arsenic concentrations occurred in step h. However, the cumulative sum of iron dissolved in all of the steps, as shown in these figures, was less than the microwave digested iron concentration for all of the samples. Interestingly, the iron dissolved in step h was associated with low or insignificant arsenic dissolution, as shown by the figures, except for M20 (FIGURE 13). These observations suggest a strong association in step f between non-exchangeable adsorbed arsenic with dissolution of iron minerals possibly as:

- non-exchangeable adsorbed arsenic on iron oxyhydroxide structures on particle surfaces,
- non-exchangeable adsorbed arsenic on less crystalline and more easily reducible iron oxyhydroxide minerals,
- or easily reducible arsenic-iron mineral structures.

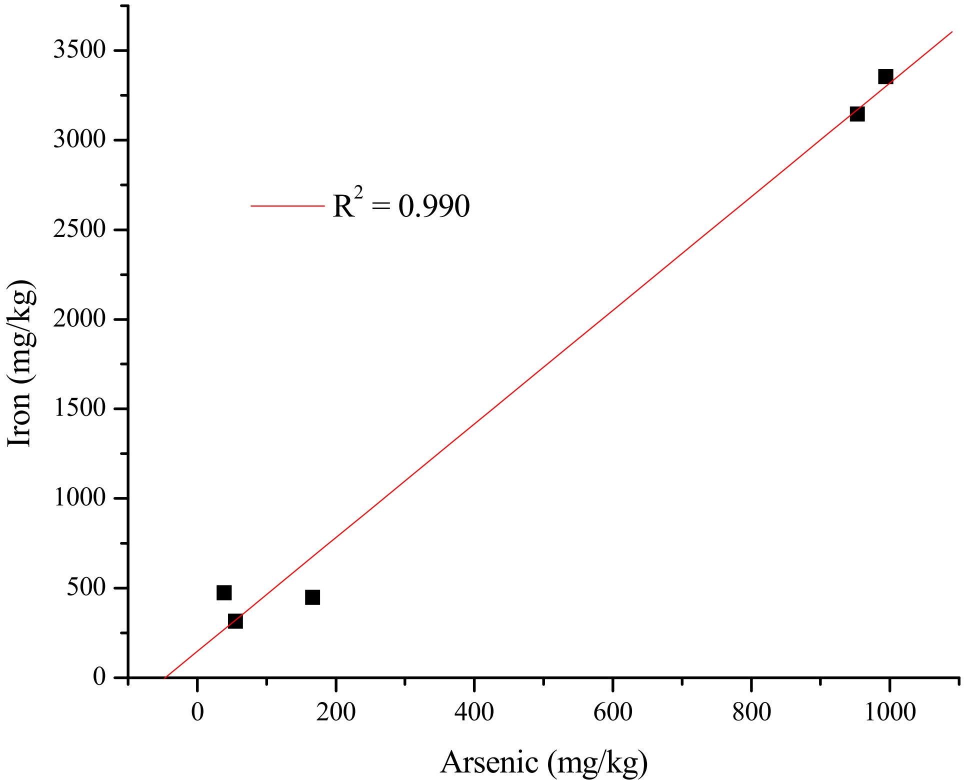

FIGURE 16. Comparison of iron and arsenic extracted in step f of the sequential extraction method for various mine tailings and associated samples.

3.3 SIMULATED HUMAN ORAL BIOAVAILABLE EXTRACTION RESULTS

The simulated human oral bioavailable extraction method may be useful, if oral exposure pathways exist at sites, in part for characterizing risk associated with different contaminated materials. The amount of arsenic that is dissolved by the simulated human oral bioavailable extraction method from a material is expected to be representative of arsenic levels that would be dissolved in the human digestive system if an equal mass of the material were ingested. The data from the simulated human oral bioavailable extraction method for selected soils is presented in **Error! Not a valid bookmark self-reference.**. Arsenic concentrations were at or above the typical risk-based clean-up levels typically used in residential areas in the United States (20 to 40 mg/kg) for all of the samples except for M20. The sites where these samples were taken may therefore be of concern if the ingestion pathway for exposure to individuals is also present.

As indicated in FIGURE 17, arsenic concentrations and iron concentrations extracted in the simulated human oral bioavailable extraction method were not correlated. However, as indicated in FIGURE 18 there is a strong positive correlation between the sum of arsenic extracted in the highly mobile fractions (steps a through d) in the sequential extraction method (TABLE 4) with the arsenic extracted in the simulated human oral bioavailable extraction method for these selected samples. Despite the fact that the low pH in the simulated human oral

TABLE 7. Simulated human oral bioavailable extraction method arsenic and iron concentrations for selected samples.

Sample	Average arsenic concentration (mg/kg)	Average iron concentration (mg/kg)	Percentage of simulated human oral bioavailable arsenic to total arsenic by microwave digestion (%)	Percentage of simulated human oral bioavailable iron to total iron by microwave digestion (%)
M2	128 ± 25	937 ± 255	3.6	2
M5	98.9 ± 1.3	853 ± 117	4.1	1.8
M14	54.1 ± 4.9	1080 ± 97.1	2.3	2.3
M15	23.0 ± 0.43	319 ± 3.97	0.37	0.8
M20	9.22 ± 4.04	89.5 ± 38.1	7.0	0.5
M27	319 ± 40	179 ± 7.68	66	0.8

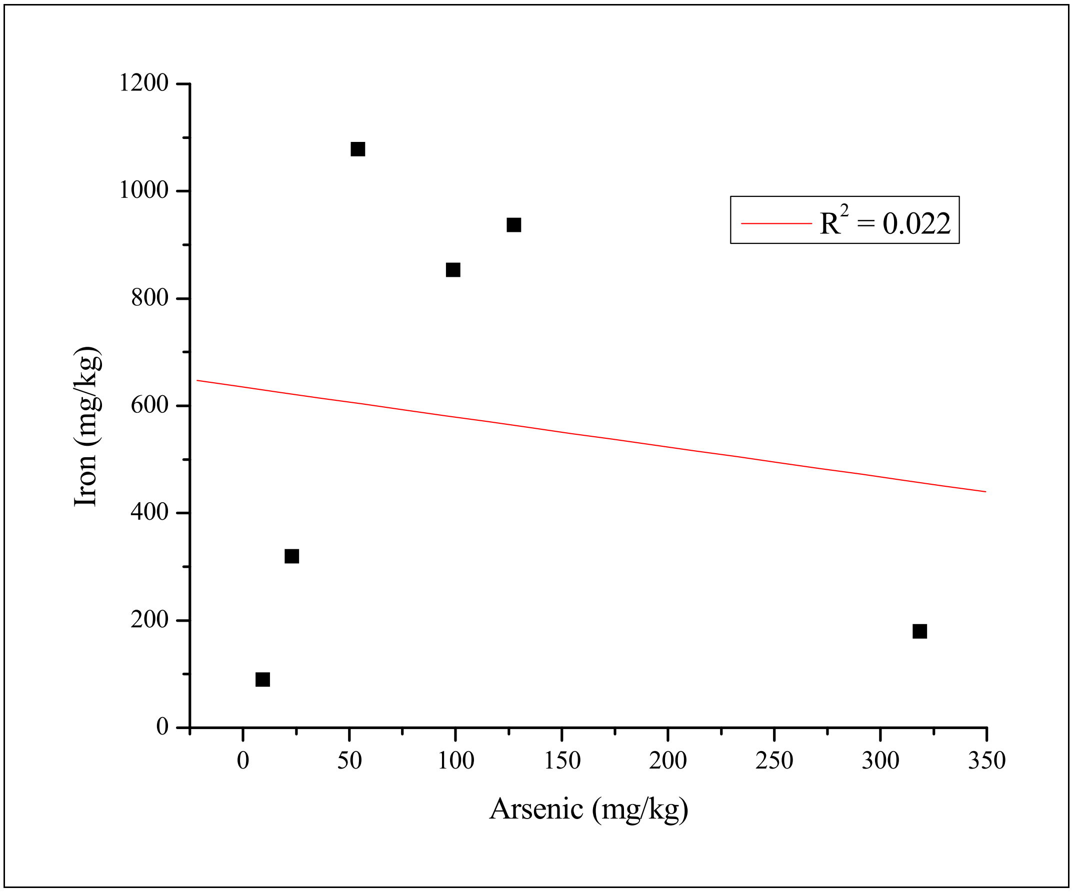

FIGURE 17. Iron measured in simulated human oral bioavailable extraction method with respect to arsenic measured by the same method for various samples.

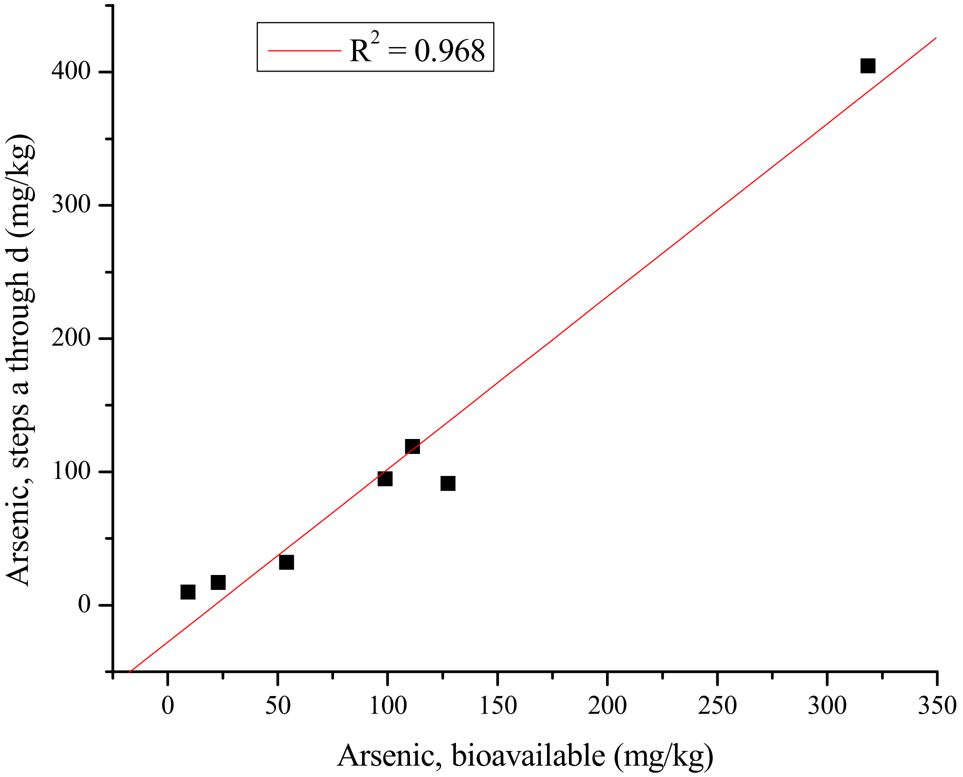

FIGURE 18. Sum of arsenic measured from the sequential extraction method steps a through d with respect to arsenic extracted by the simulated human oral bioavailable extraction method for various samples.

bioavailable extraction method might be expected to result in dissolution of a more significant amount of iron minerals, some proportionality exists with the early steps in the sequential extraction method and significant iron dissolution relative to total iron concentrations was not evident as shown in TABLE 7.

Arsenic concentrations from the microwave digestion method and arsenic concentrations from the simulated human oral bioavailable extraction method were also not correlated (not shown). The implication here is that utilizing “total” arsenic concentrations for determination of risk at a contaminated site may not be representative of actual risk. The sample that exhibited the highest concentration of arsenic from the simulated human oral bioavailable extraction method (S27) had lower arsenic concentrations from microwave digestion than some of the other samples. The same sample, however, had a significantly higher cumulative sequential extraction arsenic concentration than the total microwave digested arsenic concentration. One possibility for this is that the arsenic may have been in a species or mineral that was volatilized in the microwave digestion process. This same arsenic species or mineral may also be highly bioavailable in the human digestive system.

The findings of Kim et al. (*48*) provide some additional information useful to the analysis of the simulated human oral bioavailable extraction correlation with the sequential extraction steps a through d. The authors’ findings show that less than one percent of the total iron extracted was in steps a through d for two Korean mine tailing samples. Similarly low percentages of total iron (0.5 – 2.3%) were observed in the mine tailing and associated samples from Mexico when analyzed with the simulated human oral bioavailable extraction method in this study, despite the low pH of the simulated stomach acid. The low percentages of total arsenic extracted with the simulated human oral bioavailable extraction method is likely attributable to the absence of conditions sufficient to reductively dissolve iron oxyhydroxides.

3.4 MOBILIZATION EXPERIMENTS

Arsenic mobilizing effects of various pH-controlled solutions under varying redox conditions were evaluated for various samples contaminated with arsenic in order to identify if trends in arsenic mobility can be predicted by the characterization methods used.

3.4.1 Sample selection.

Samples were selected for the mobilization experiments for various reasons. The M2 and M5 samples represent typical characteristics of most of the other tailing samples including the overall order of magnitude of iron and arsenic concentrations by microwave digestion, however, they both were taken at a depth of between 2 cm and 5 cm of the surface of the tailing pond. The reason that these two samples were selected was that despite their similarities, they exhibit different sequential extraction curve characteristics. The M2 sample had a much more significant relative “fixed” fraction than the M5 sample. The M5 sample exhibited higher relative arsenic concentrations in steps g and h. This possibly suggests the presence in the M5 sample of more stable iron oxide or other minerals retaining arsenic compared to the M2 sample.

The M14 and M15 samples have similar sequential extraction curves with the exception of step f. Additional significant differences between the two samples include particle distribution (predominantly silt-sized particles and predominantly sand-sized particles, respectively) and arsenic concentrations by microwave digestion (2330 mg/kg and 6210 mg/kg). Geographically, these samples were separated by approximately 30 meters.

The M20 sample was taken from soil 2 km southwest of the tailings pond; it exhibited a similar sequential extraction curve to the AUES3 sample (Chapter 4). Due to the proximity of this sample location to developed residential areas, potential human exposure pathways may exist. The M27 sample was taken from sediment and was selected because of similar general characteristics with a few specific differences compared to the WF sample (Chapter 4). These two samples have similar percentages of organic matter and particle fractionation. However, the samples are strikingly different in pH, cation exchange capacity, and sequential extraction curves (see Chapter 4 for WF sequential extraction curve). The cumulative arsenic concentration for both samples was much higher than the arsenic concentration by microwave digestion. The M27 sample also had a much higher cumulative arsenic concentration from sequential extraction than the WF sample.

3.4.2 Mechanisms expected to influence arsenic mobilization.

The following types of processes are expected to influence arsenic mobility as redox potential and pH changes: arsenic oxidation-reduction reaction affecting speciation, adsorption/desorption processes relative to pH and arsenic speciation, dissolution of minerals, precipitation of arsenical minerals, or co-precipitation of arsenic with non-arsenical minerals.

More specifically, as the pe + pH decreases the following processes are expected to occur: arsenate reduction to arsenite and subsequent desorption from iron oxyhydroxide minerals; iron oxyhydroxide mineral reductive dissolution to ferrous iron, which will release associated arsenic; sulfate reduction to sulfide; precipitation of iron sulfide minerals such as pyrite; precipitation of arsenic sulfide and arsenic iron sulfide minerals. These processes, and the kinetics of the processes, are dependent on many variables besides pe + pH including iron concentrations, sulfide concentrations, and arsenic concentrations (*39*). O'Day et al. (*39*) suggested that under sulfidic conditions with high dissolved iron concentrations, for example, the formation of arsenic sulfide minerals may be precluded by the favored formation of pyrite, which offers fewer sorption sites than iron oxyhydroxide minerals.

3.4.3 Results and discussion.

The data from the mobility experiments for the Mexican mine tailings and associated samples are presented in FIGURE 19 through FIGURE 24. For these samples, the highest arsenic concentrations observed for individual samples in the mobilization experiments ranged from 2.77 mg/kg to 87.0 mg/kg. These peak

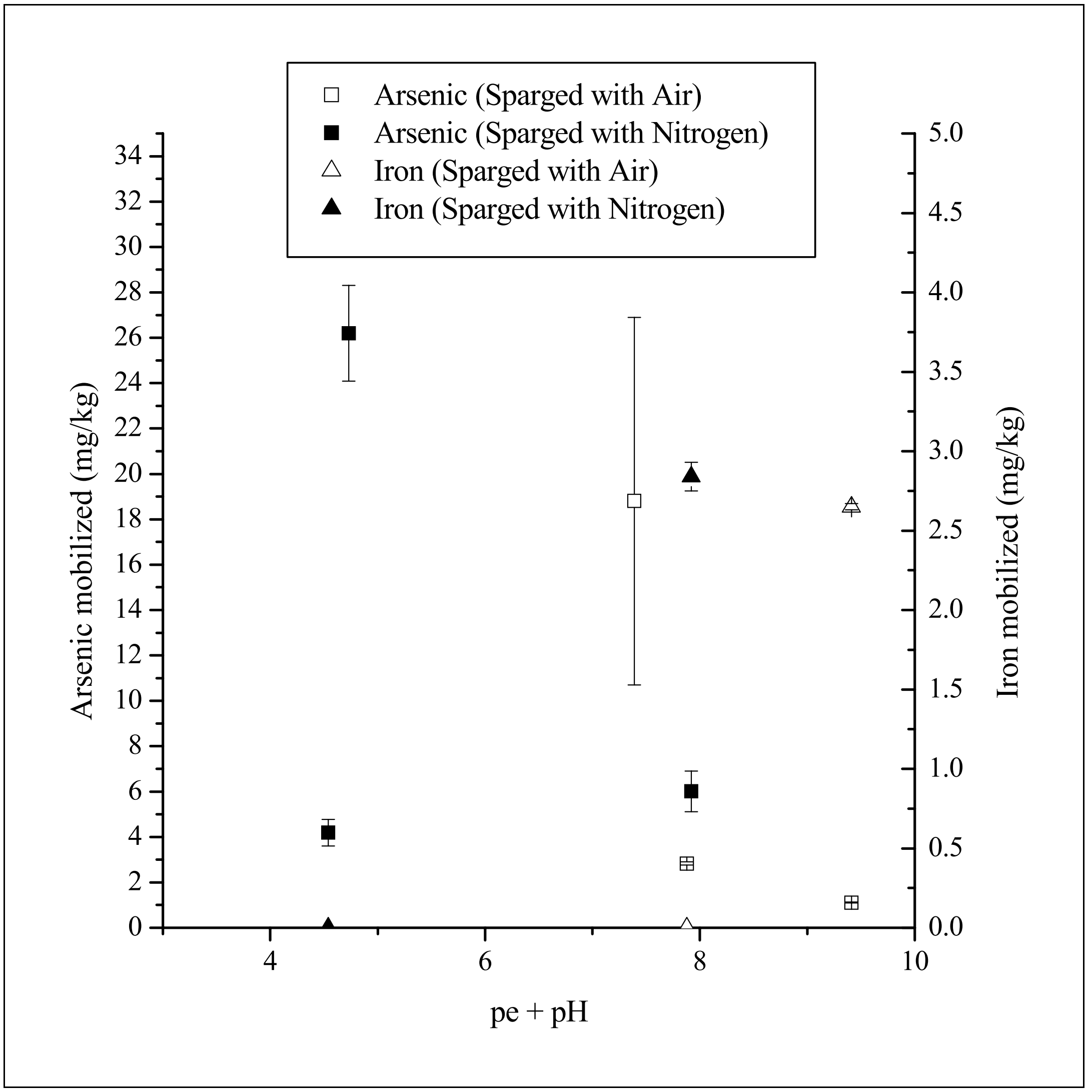

FIGURE 19. Arsenic mobilization from M2 with respect to measured pe + pH levels. The pH levels were controlled by using buffers and changes in pe were induced by sparging with air or nitrogen. The symbols represent average of duplicates and error bars represent one standard deviation.

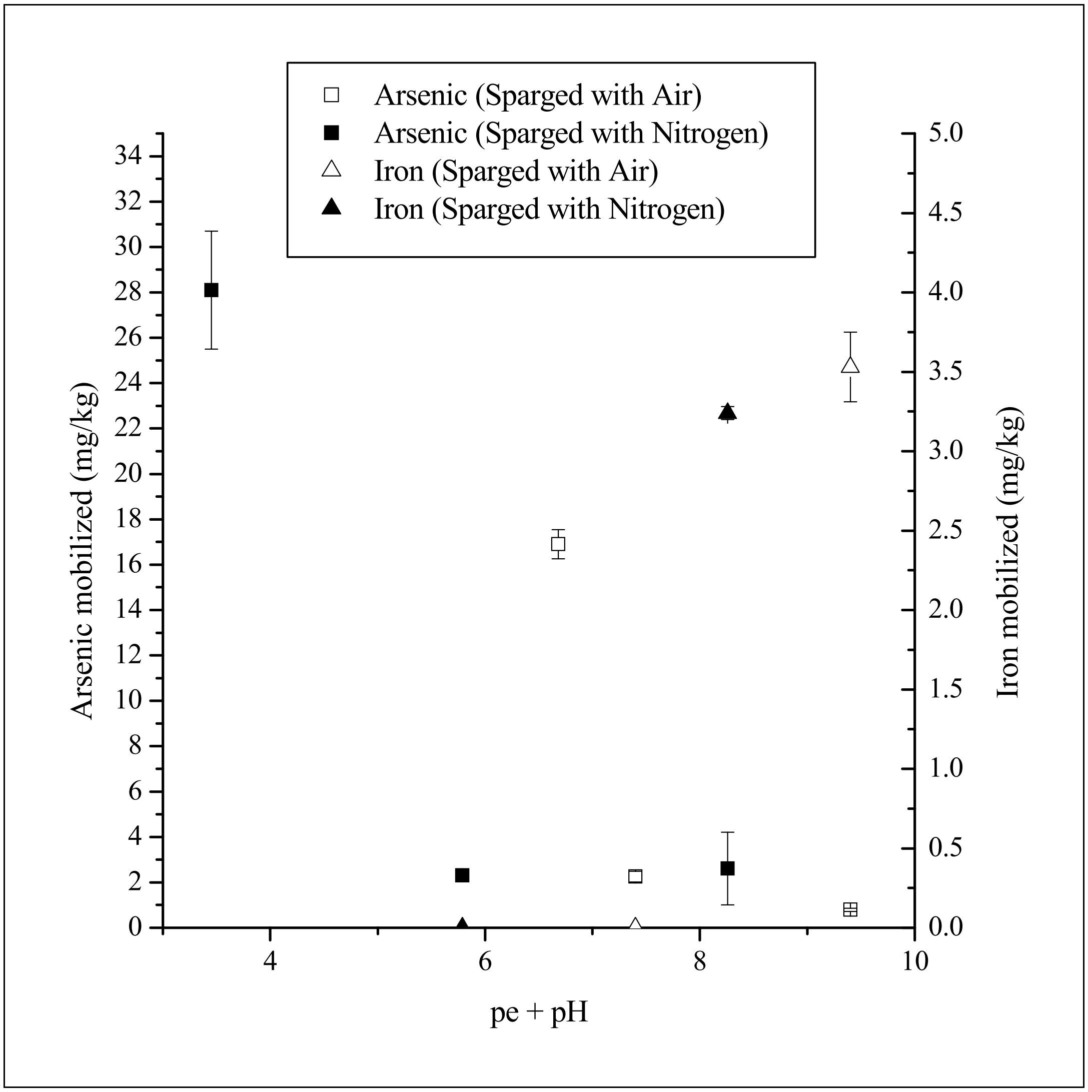

FIGURE 20. Arsenic mobilization from M5 with respect to measured pe + pH levels. The pH levels were controlled by using buffers and changes in pe were induced by sparging with air or nitrogen. The symbols represent average of duplicates and error bars represent one standard deviation.

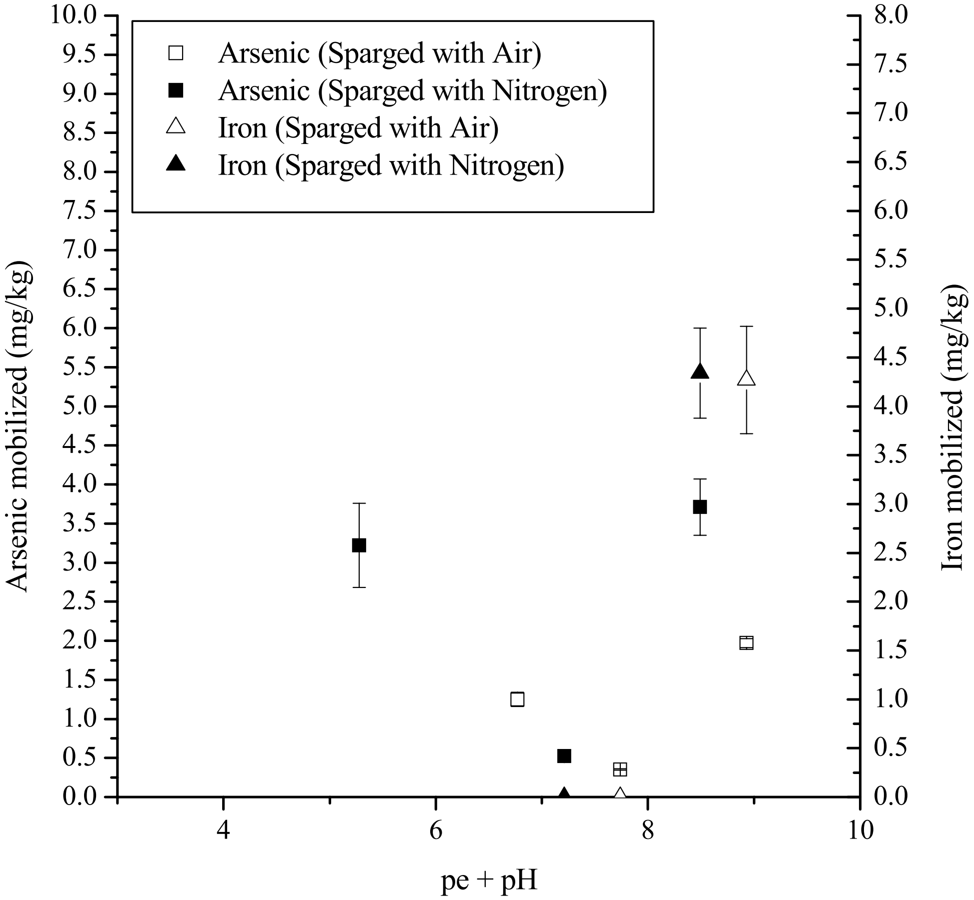

FIGURE 21. Arsenic mobilization from M14 with respect to measured pe + pH levels. The pH levels were controlled by using buffers and changes in pe were induced by sparging with air or nitrogen. The symbols represent average of duplicates and error bars represent one standard deviation.

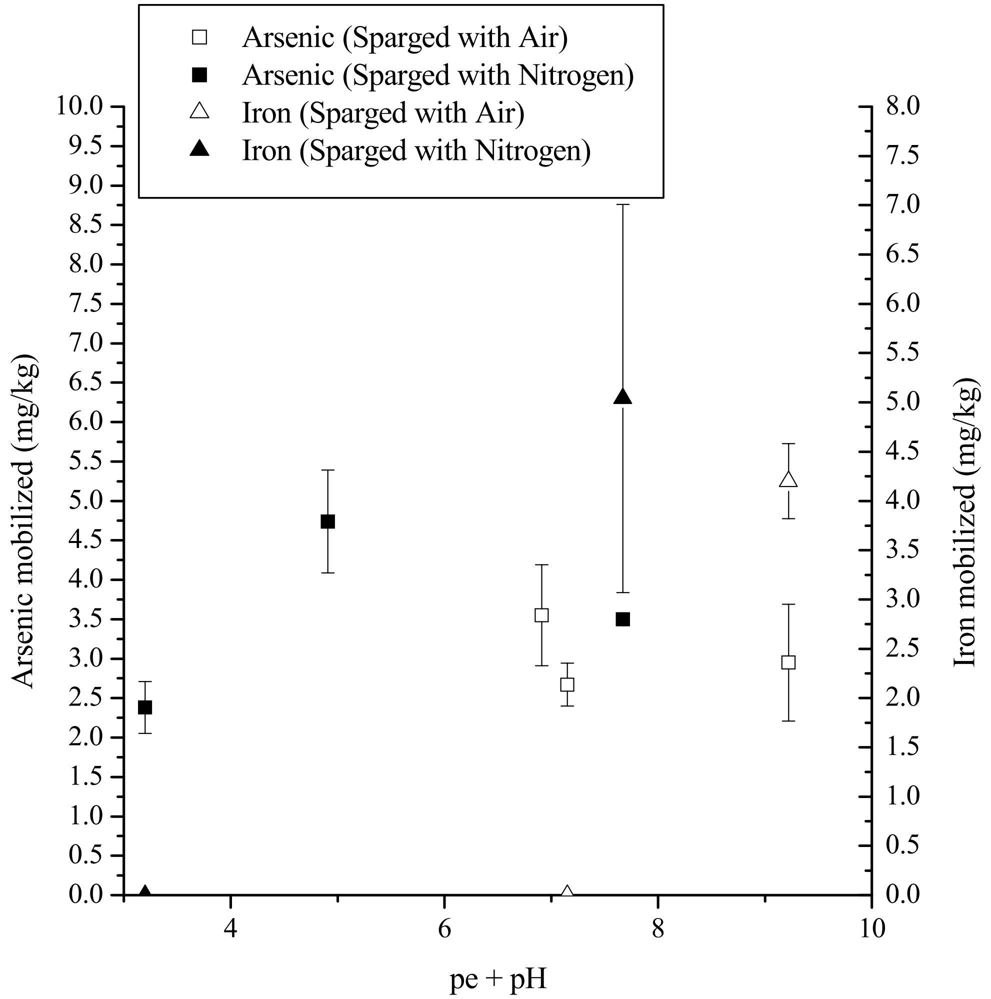

FIGURE 22. Arsenic mobilization from M15 with respect to measured pe + pH levels. The pH levels were controlled by using buffers and changes in pe were induced by sparging with air or nitrogen. The symbols represent average of duplicates and error bars represent one standard deviation.

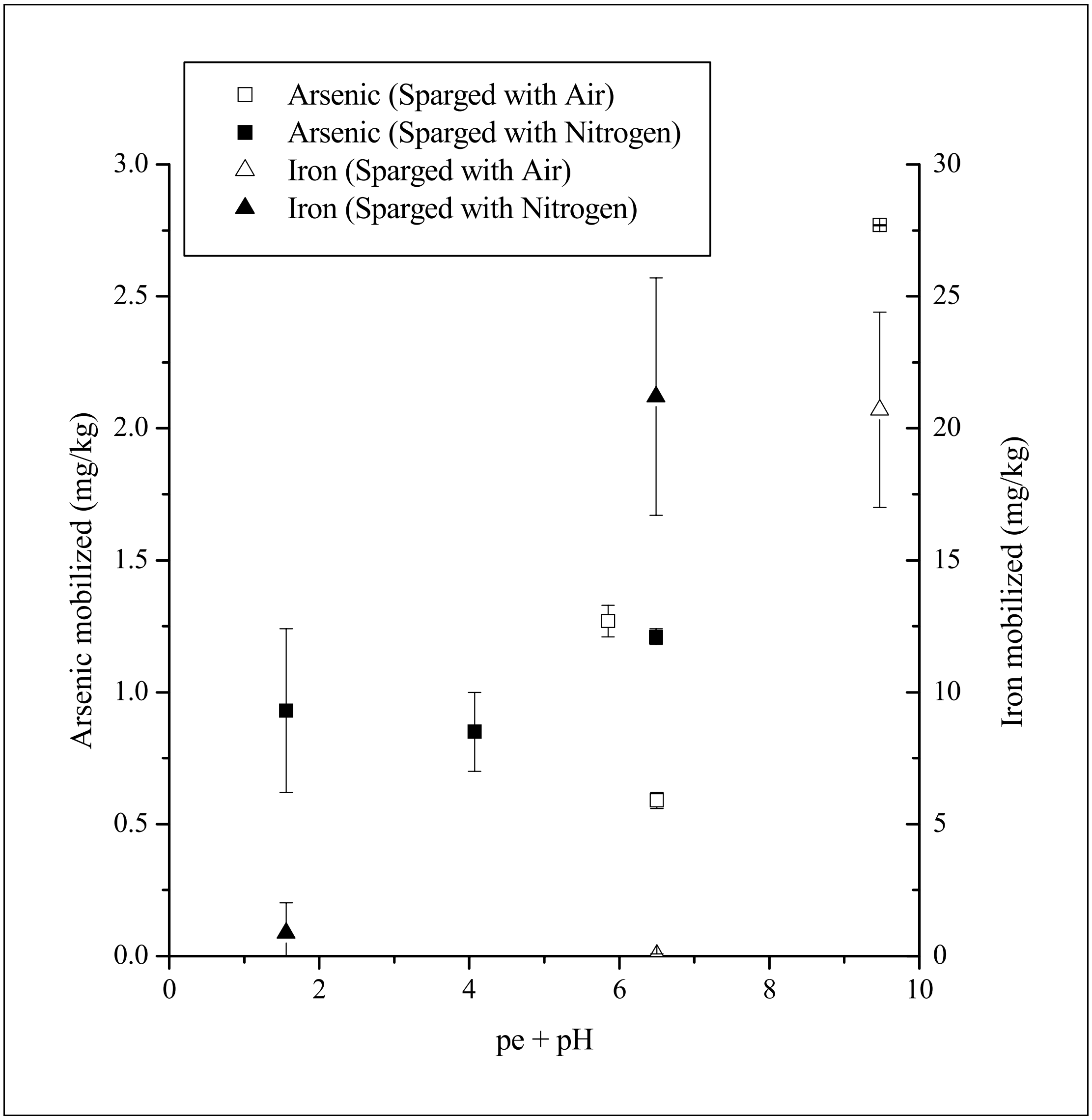

FIGURE 23. Arsenic mobilization from M20 with respect to measured pe + pH levels. The pH levels were controlled by using buffers and changes in pe were induced by sparging with air or nitrogen. The symbols represent average of duplicates and error bars represent one standard deviation.

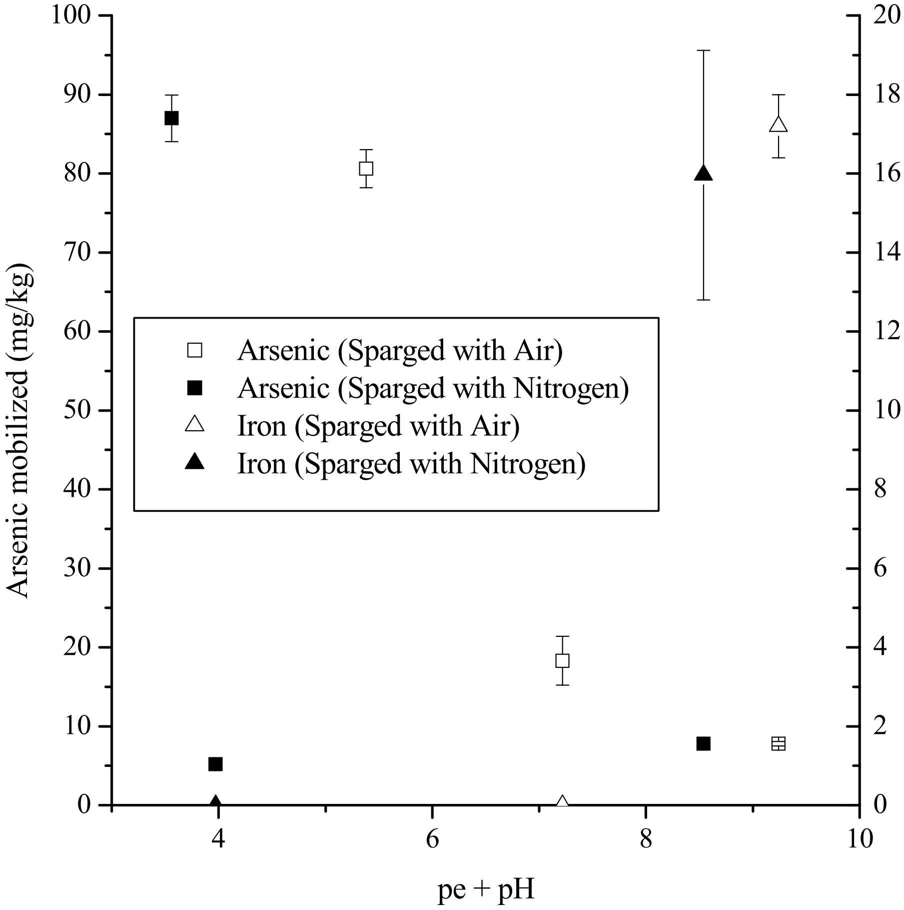

FIGURE 24. Arsenic mobilization from M27 with respect to measured pe + pH levels. The pH levels were controlled by using buffers and changes in pe were induced by sparging with air or nitrogen. The symbols represent average of duplicates and error bars represent one standard deviation.

concentrations were lower than the corresponding sums of highly mobile fractions in the sequential extraction method for all of the samples. These peak concentrations were also significantly lower than the overall cumulative arsenic concentration from the sequential extraction method and the total arsenic concentration from microwave digestion for all of the samples. TABLE 8 provides a comparison of the peak concentrations of arsenic mobilized in the experiments compared to the arsenic concentrations from microwave digestion and from the highly mobile fraction group from the sequential extraction method. Interestingly, the sample that had the highest mobilized arsenic concentration in these experiments (M27) had the second lowest concentration by microwave digestion of the six samples evaluated. The same M27 sample, however, had the highest cumulative arsenic concentration from the sequential extraction method and highest arsenic concentration from the simulated human oral bioavailable extraction.

The M2 and M5 samples exhibited similar mobilization of arsenic under the varying conditions with respect to changes in pe + pH. This may suggest that the mobilized arsenic was not representative of arsenic associated with the reducible oxides and fixed fractions that were distinct between the two samples.

M20 and M27 exhibited similar relative mobilization of arsenic trends as seem with M2 and M5 with respect to changing pe + pH. The relative arsenic concentrations for each sample were different, though. M20 had the lowest arsenic mobilization levels of all of the samples tested, and M27 had the highest arsenic mobilization levels. These corresponded to the relative arsenic concentrations from

TABLE 8. Peak concentrations of arsenic in mobilization experiments for individual samples.

Sample	Peak arsenic concentration (mg/kg)	Conditions at peak	Cumulative arsenic concentration for highly mobile fractions group (mg/kg)	Average simulated human oral bioavailable arsenic concentration (mg/kg)	Average total arsenic concentration by microwave digestion (mg/kg)
M2	26.2 ± 2.11	final pe + pH 4.73 ± 0.255 (nitrogen with pH 10 buffer)	91.37 ± 1.8	128 ± 25	3 580 ± 431
M5	28.1 ± 2.64	final pe + pH 3.45 ± 0.450 (nitrogen with pH 10 buffer)	95.48 ± 4.2	98.9 ± 1.3	2 440 ± 204
M14	3.71 ± 0.362	final pe + pH 8.49 ± 0.0582 (nitrogen with pH 5.5 buffer)	32.02 ± 1.2	54.1 ± 4.9	2 330 ± 24.2
M15	4.74 ± 0.651	final pe + pH 4.91 ± 0.770 (nitrogen with pH 10 buffer)	16.95 ± 0.04	23.0 ± 0.43	6 210 ± 508
M20	2.77 ± 0.002	final pe + pH 9.47 ± 0.132 (air with pH 5.5 buffer)	9.80 ± 0.99	9.22 ± 4.04	132 ± 3.17
M27	87.0 ± 2.94	final pe + pH 3.56 ± 0.874 (nitrogen with pH 10 buffer)	406 ± 29	319 ± 40	487 ± 52.5

the simulated human oral bioavailable extraction and the highly mobile fractions in the sequential extraction method.

M14 and M15 results were largely different in mobilization trends with respect to pe + pH. In addition, the peak mobilization of arsenic between the two samples was in the same order of magnitude, but M14 was lower than M15. M14, however, had higher arsenic concentrations from microwave digestion, simulated human oral bioavailable extraction, and highly mobile fractions from the sequential extraction method. In addition, due to the smaller typical particle size when compared to M15, particles in sample M14 may be expected to have more surface area. These factors may have suggested that M14 would exhibit typically higher mobilization than M15, contrary to what was observed.

3.4.4 Analysis of arsenic mobilization trends.

Slow kinetics of arsenate reduction to arsenite may provide part of the reason for the trends apparent for samples M2 and M5 (FIGURE 19 and FIGURE 20). The sets of air-sparged samples and nitrogen-sparged samples data seem to follow a rough trend with respect to pe + pH. However, at $7 < pe + pH < 8$ in FIGURE 19, for example, the arsenic concentrations mobilized in one of the air-sparged samples is significantly higher than the other air-sparged sample and the nitrogen-sparged sample. The air-sparged samples represent a higher pe and lower pH than the nitrogen-sparged samples at the similar pe + pH point. The air-sparged sample with higher dissolved arsenic represents the higher pH value of the two. If a distinct mass of arsenic should be mobilized for a given sample at a given pe + pH, then an arsenic mobilization driving force would presumably exist for the nitrogen sparged point and the lower air sparged point in FIGURE 19, and that kinetics of arsenate reduction or reductive dissolution of minerals are inhibiting the potential mobilization. Bartlett and James (*62*) suggested higher tendancy for reducing reactions in systems with a lower pH (and more available electrons as represented by the higher voltage) when compared to another system with a higher pH at the same pe + pH point. For the example in FIGURE 19 at $7 < pe + pH < 8$, the experimental results are contrary to this suggestion if considered only in terms of arsenate reduction and subsequent desorption. Interestingly, the highest mobilization of arsenic observed for four of six samples was with the buffer with the highest pH under nitrogen (TABLE 8). At least for these four samples in this experiment (M2, M5, M15, M27), it would clearly be incorrect to presume that arsenate reduction was the only process influencing the mobilization of arsenic.

High concentrations of iron and rapid precipitation of pyrite, may explain the high relative dissolved arsenic concentrations at low pe + pH in some of these samples. For other samples exhibiting decreasing concentrations of dissolved arsenic at low pe + pH, perhaps arsenic sulfide minerals or arsenic iron sulfide minerals were formed due to slower dissolution of iron oxyhydroxides. The precipitation of orpiment (As_2S_2) may be expected within the pe and pH values observed, depending on the concentrations of arsenic and sulfur (FIGURE 25). The concentration of arsenic used in the construction of FIGURE 25 was within the range of concentration observed in the mobilization experiments. The concentration of sulfur used may be

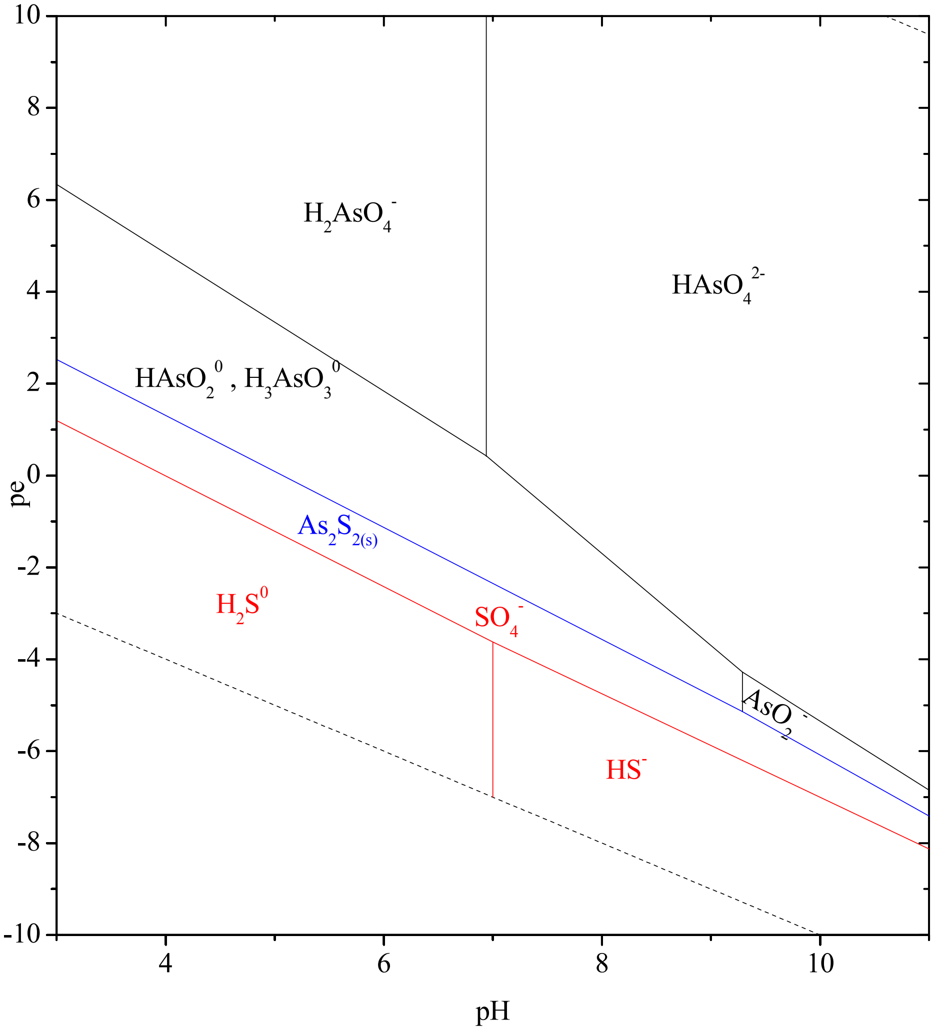

FIGURE 25. The pe-pH predominance area diagram for arsenic ($[As_T]$ = 1 mM) and sulfur ($[S_T]$ = 1 mM) species. Formulae used for construction of the diagram are in Appendix B.

representative of what might be found with a reactor containing the mine tailings samples. For 2.5 g of a sample with 1,000 mg/kg sulfate, 50% dissolution of sulfate in 25 mL of solution would result in a total sulfur concentration of 1 mM, assuming sulfate is the only source of sulfur in solution. Mine tailings samples from the site in Mexico were shown by other researchers to have sulfate concentrations of between 1,200 to 2,600 mg/kg (*53*). Therefore, the predominance diagram is representative of observed arsenic concentrations and conservatively low (with respect to the mine tailings samples) sulfur concentrations.

Carbonate may have also have influenced the mobilization of arsenic by enhancing desorption of both arsenate and arsenite. In the mobilization experiments, nitrogen sparging is likely to result in a reduction of dissolved carbon dioxide and possibly overall carbonate concentrations. Repeated air sparging, however, is likely to increasing carbon dioxide concentrations where carbonate has been consumed by adsorption processes. This is expected to decrease the sorption sites for arsenate and arsenite as suggested by Appelo et al. (*29*) This may also provide part of the explanation for variation in arsenic mobilization between nitrogen and air sparged samples at the same pe + pH level.

Dissolved iron levels were analyzed for the reactors with Trizma-HCl and CAPS buffers. For the samples sparged with nitrogen, as pe + pH decreased, both aqueous arsenic and iron concentrations decreased for the mine tailings and associated samples. This decrease in dissolved arsenic concentrations with decreasing pe + pH was significant for M14 and M15, but was insignificant in the other samples. In the nitrogen-sparged reactors in this experiment, therefore, decreases in aqueous iron concentrations occurred with varying degrees of decreases in aqueous arsenic concentrations.

For the reactors sparged with air, as pe + pH increased, aqueous iron concentrations increased. Aqueous arsenic concentrations, however, decreased slightly with increasing pe + pH in the air-sparged reactors for M2, M5, and M27, and increased slightly for M15. For the other samples (M14 and M20), aqueous arsenic concentrations increased more significantly with increasing pe + pH.

Arsenite oxidation to arsenate and subsequent increased adsorption may explain the drop in arsenic concentrations in solution for some of these samples, but does not explain the increase in iron concentrations with increasing pe + pH for the air-sparged samples. One possibility could be related to formation of unknown pH dependent iron complexes, or the influence of the buffer.

Compared to the CAPS buffered samples sparged with the same gas, the pe + pH was always lower for the Trizma-HCl buffered samples, despite the higher buffer pH. For sets of the mine tailings and associated samples sparged with the same gas, the lower pe + pH always exhibited lower iron concentrations to near or below the detection limit. Arsenic concentrations also decreased to differing degrees corresponding to the decrease in iron concentrations for sets of these samples sparged with the same gas.

One possible explanation for this could be due to the formation of iron sulfide precipitates. Sulfide formation has been suggested to occur at $pe < -4.0$ (*38*) and between pe -2 and 2 (*62*). Under nearly all conditions (varying buffers, varying gas sparging) pe approached (pe < 3.0), fell within (-2 < pe < 2), or was less than (pe < -2) the sulfidic range. Exceedence of pe 3.0 occurred only for M20 in one situation (air, CAPS buffer, final pH 5.7), M27 in two situations (air, CAPS buffer, final pH 5.3; nitrogen, CAPS buffer, final pH 5.3), WF in one situation (air, CAPS buffer, final pH 5.5), and AUES3 in one situation (air, CAPS buffer, final pH 5.6). For M20 and WF, these points exhibited higher arsenic mobilization, but this was not the case for M20 and AUES3.

For samples in situations with very low iron concentrations in solution, pe was always within or below the -2 to 2 range. However, there were samples with situations where pe levels were within the -2 to 2 range that had iron in solution. Other factors including slow kinetic precipitation, chelation of iron by unknown constituents, or pH related complexation of dissolved iron are possible reasons that formation of sulfidic iron minerals may have been minimized.

It is important to note a trend apparent when considering the measurement of iron for reactors buffered with TRIZMA-HCl when compared to reactors buffered with CAPS. For the Mexican mine tailings and associated samples, iron was very low or not detected for samples buffered with Trizma-HCl. The Mexican mine tailing samples buffered with CAPS typically exhibited higher iron concentrations. It is possible that the buffers may have influenced the mobilization of arsenic and iron.

The other samples analyzed exhibited entirely different trends with respect to iron mobilization (Chapter 4). With the other samples, iron levels did not diminish with decreasing pe as strikingly as with the Mexican mine tailings and associated samples. In addition, some of the situations where Trizma-HCl was used as the buffer, dissolved iron was observed.

For most of the samples (M2, M5, M15, M20, M27), characterization of arsenic mobility with the highly mobile fractions in the sequential extraction method and with the simulated human oral bioavailable extraction method corresponded with peak arsenic concentrations mobilized in the experiment. Prediction of mobilization of arsenic at a specific pe + pH level seems to be exceedingly complicated and is not likely possible using the extraction methods alone. The dissolution and precipitation of minerals such as iron oxyhydroxides as well as iron and arsenic sulfides seem to be important processes that may have occurred in this experiment. Several mechanisms may explain the wide variation in the mobilization of arsenic in this experiment. Some of the uncertainty in the results of this experiment might be reduced in similar future experiments by analyzing the reactor solutions for sulfate and sulfide, as well as distinguishing the speciation and oxidation state of iron and arsenic. Additional characterization of the samples with x-ray diffraction techniques to determine mineral and particle associations of arsenic prior to and following the experiment may also be useful in understanding the processes that are occurring.

CHAPTER 4. RESULTS AND DISCUSSION (AMERICAN UNIVERSITY EXPERIMENT STATION SAMPLES, POULTRY LITTER AND ASSOCIATED SAMPLES, RESIDENTIAL SAMPLE, AND WEST FORK RIVER SEDIMENT SAMPLE)

A variety of samples contaminated with arsenic were obtained to evaluate different extraction methods and whether these methods could be used to predict arsenic mobility from soils. Evaluation of a wide range of samples can help demonstrate the degree of universality a method may provide for characterizing arsenic contamination.

Samples were obtained from the American University Experimental Station Formerly Used Defense Site (AUES FUDS) in the District of Columbia, where testing of chemical weapons including materiel containing arsenic occurred during World War I. The AUES FUDS area is now a residential neighborhood and efforts are being undertaken to remove soil with elevated arsenic concentrations. Maryland poultry litter samples from animals fed roxarsone, an arsenical feed additive, were also obtained. The fate of the arsenic in the poultry litter is of concern due to the high concentration of poultry farms in Delaware and Maryland, and because the poultry litter is commonly amended to crop fields. Samples of CCA-treated lumber and soil from under a deck built with similarly treated lumber were collected. Due to the widespread use of CCA-treated lumber throughout the United States, the fate of arsenic potentially mobile from the lumber is of concern. A sediment sample was also collected from the West Fork River in West Virginia. The West Fork River is believed to have been impacted by the operations of a zinc smelter which may have increased arsenic concentrations in the sediment.

4.1 MICROWAVE DIGESTION RESULTS

The analyzed concentrations with standard deviations of arsenic and iron from microwave digestion of the AUES samples, poultry litter and associated samples, West Fork River sediment sample, CCA-treated wood chips sample, and the residential soil are presented in TABLE 9. Similar to the mine tailings samples, the reproducibility of the microwave digestion method for both arsenic and iron concentrations for some of the samples was limited. Some variability may be attributable to varying concentrations of iron and arsenic within subsamples despite homogenization.

4.2 SEQUENTIAL EXTRACTION METHOD RESULTS

The concentrations of arsenic mobilized by the sequential extraction method and the microwave digestion method for the mine tailings and associated samples are presented in FIGURE 26 through FIGURE 28. Similarly to the mine tailings samples from Mexico, four groups of fractions are evident in most of these samples based on the sequential extraction and microwave digestions methods: the highly mobile fractions (sequential extraction method steps a through d); the oxidation mobile fraction (step e); the reduction mobile fractions (steps f through i); and the fixed fraction (not extracted by sequential extraction). Concentrations of iron mobilized by

TABLE 9. Total Arsenic and Iron via Microwave Digestion for West Fork River sediment, AUES FUDS samples, poulty litter and associated samples, CCA-treated wood chips, and a residential soil.

Sample	Arsenic concentration by microwave digestion - average (mg/kg)	Iron concentration by microwave digestion - average (mg/kg)
WF	156 ± 21.1	12 400 ± 584
AUES1	3 360 ± 442	67 300 ± 13 400
AUES2	70.5 ± 7.29	75 800 ± 869
AUES3	165 ± 22.4	34 500 ± 2 530
AUES4	3.54 ±1.32	36 100 ± 7 550
AUES5	0.70 ± 0.62	39 600 ± 3 800
PL	27.2 ± 2.31	679 ± 200
PL-TF	<1 (ND)	n/a
PL-GB	<1 (NQ)	n/a
PL-AD	14.1 ± 0.97	n/a
CCA WOOD CHIPS	2 510 *	n/a
RES	39.9 ± 4.57	37 900 ± 4 770

the sequential extraction method and microwave digestion method were also analyzed for AUES1 and are shown with the corresponding cumulative arsenic concentrations in FIGURE 29.

The arsenic concentration from microwave digestion for the AUES1 sample was significantly higher than the cumulative amount of arsenic mobilized by all of the sequential extraction steps. In contrast, the WF sample had significantly lower arsenic concentrations by microwave digestion than the cumulative sequential extraction arsenic concentration. As discussed in Chapter 3, this may have been caused by a loss of arsenic by volatilization of AsH_3 or another arsenical compound during the microwave digestion process. The other samples had cumulative arsenic concentrations from the sequential extraction procedure similar to the arsenic concentration from microwave digestion.

The AUES1 sample exhibited significantly different sequential extraction characteristics compared to the AUES2 and AUES3 samples, as shown in FIGURE 26. The AUES1 sample was significantly higher in arsenic concentration by microwave digestion (3400 mg/kg) than the other samples (71 and 165 mg/kg for AUES2 and AUES3, respectively). Due to the topography of the sampling locations, it may be possible that AUES1 could represent a contamination source for AUES2; arsenic may have been transported downstream via very local shallow ground or surface water movement. Over time, arsenic from the original source may have chemically transformed and leached slowly, and may have subsequently become re-fixed by adsorption or another mechanism in soil or sediment. Arsenic transport

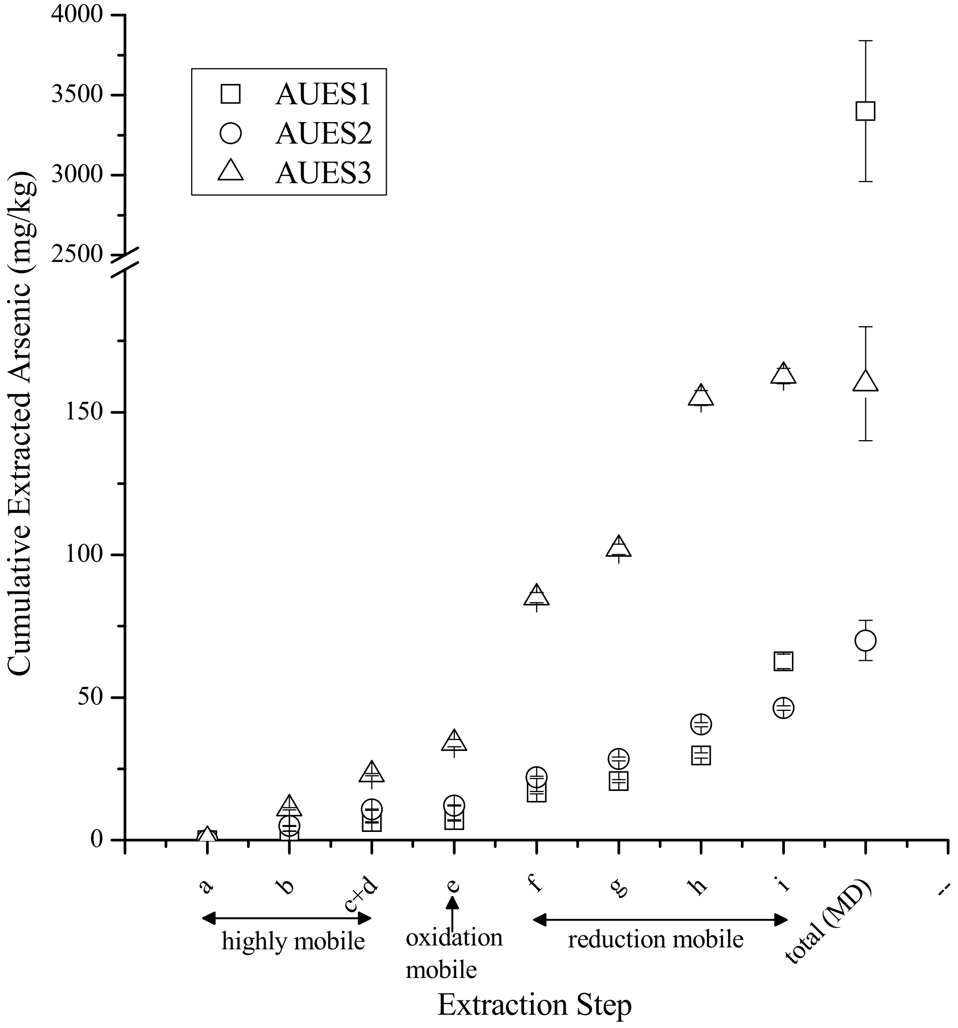

FIGURE 26. The cumulative averages of the sequential extraction method arsenic analysis (steps a through i) and averages for total microwave digestion method (MD) arsenic analysis for soil samples taken at the site of the former American University Experimental Station Formerly Used Defense Site in the District of Columbia. The MD results are independent of the cumulating of the sequential extraction results. The error bars represent one standard deviation for the average of three replicates.

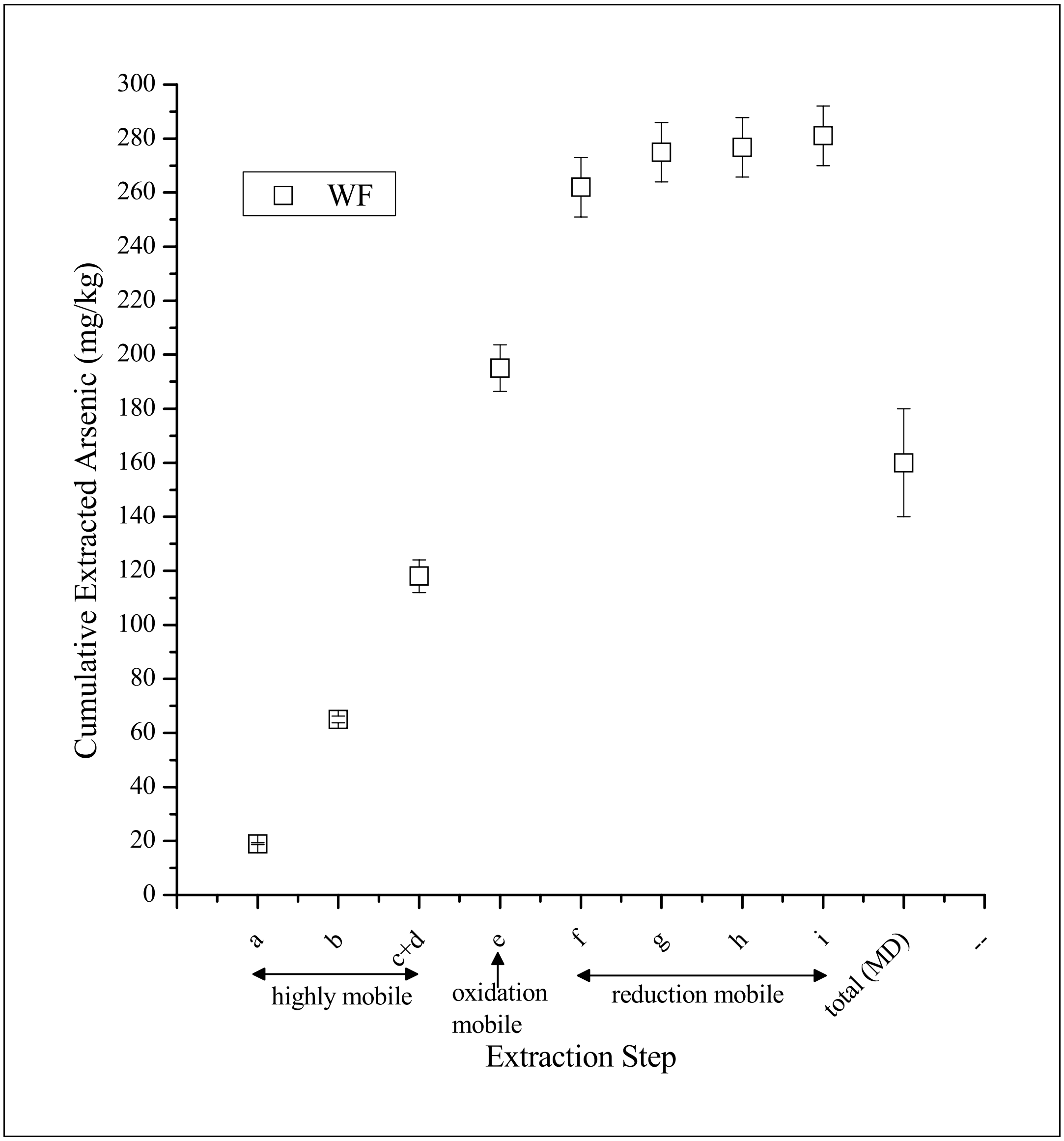

FIGURE 27. The cumulative averages of the sequential extraction method arsenic analysis (steps a through i) and averages for total microwave digestion method (MD) arsenic analysis for a sample of sediment taken from the West Fork River in West Virginia. The MD results are independent of the cumulating of the sequential extraction results. The error bars represent one standard deviation for the average of three replicates.

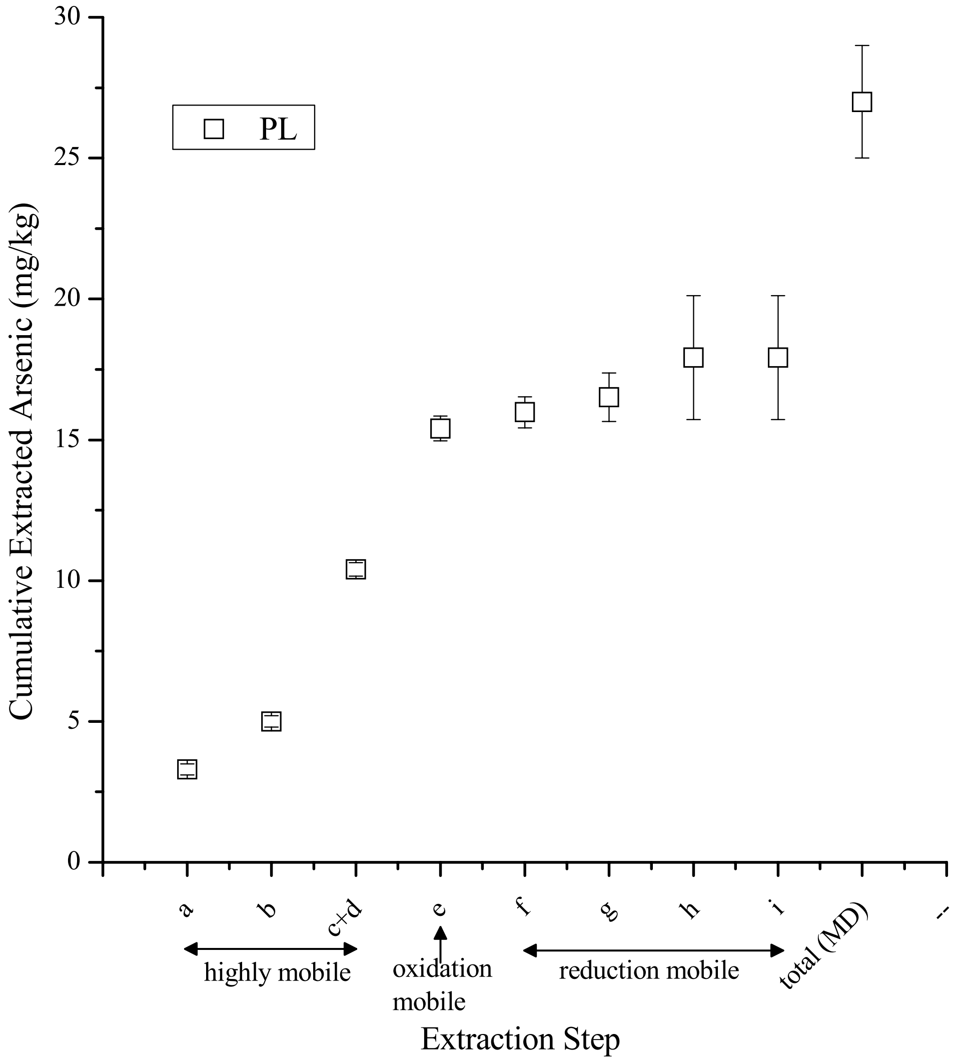

FIGURE 28. The cumulative averages of the sequential extraction method arsenic analysis (steps a through i) and averages for total microwave digestion method (MD) arsenic analysis for a sample of poultry litter from Maryland. The MD results are independent of the cumulating of the sequential extraction results. The error bars represent one standard deviation for the average of three replicates.

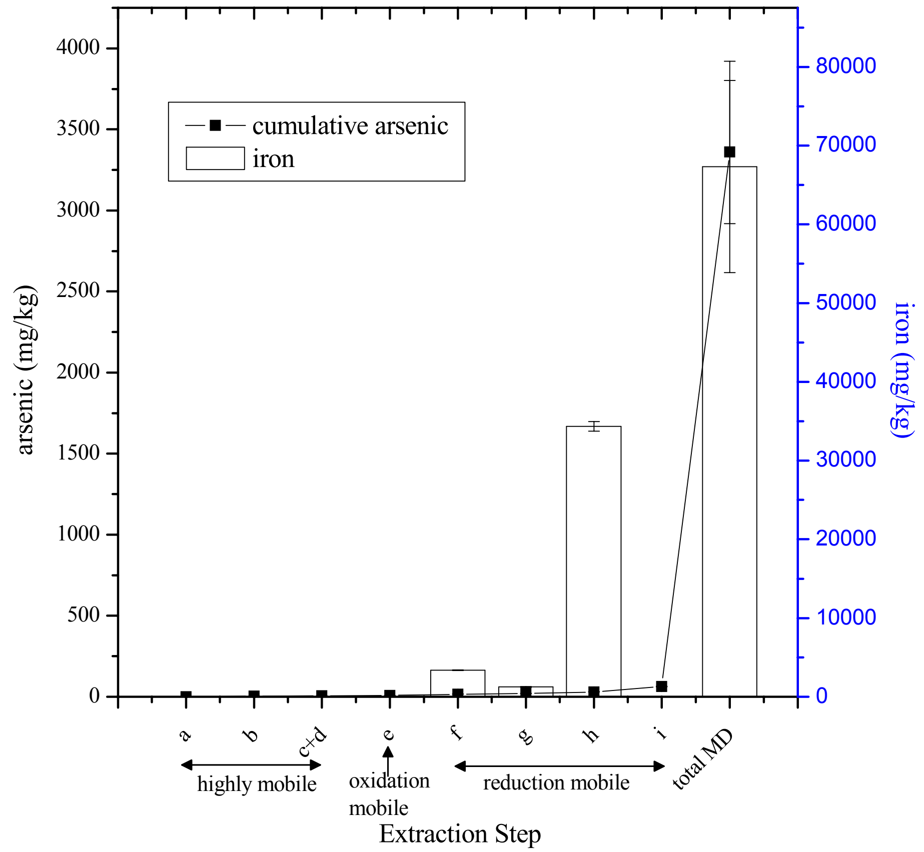

FIGURE 29. Iron and cumulative arsenic mobilization by sequential extraction method (steps a through i), and extraction of iron and arsenic by microwave digestion for a sample of soil (AUES1) taken from the AUES FUDS site. Error bars represent one standard deviation.

while incorporated in eroded sediment may be another possible origin of the contamination in AUES2. However, the latter possibility seems less likely due to the differences in the sequential extraction characteristics.

The fractionation of arsenic in the sequential extraction method for AUES2 and AUES3 are relatively similar despite the difference in total arsenic concentrations by microwave digestion. Iron concentrations in the three samples are in the same order of magnitude. AUES2 has the highest amount of iron extracted by microwave digestion, yet the lowest amount of arsenic extracted by microwave digestion. We were unable to evaluate the soil characteristics of sample 2 due to a limited amount of sample, but the observed characteristics of sample of samples 1 and 3, as shown in (Chapter 2), were very similar except for percent organic matter (4.2 and 8.4%, respectively). It may be expected that the difference in the sequential extraction characteristics for the samples lie in the different chemical form of arsenic, rather than due to differences in the soil makeup. Both AUES 2 and AUES3 had higher arsenic concentrations in the highly mobile fractions group than AUES1, despite the significantly lower arsenic concentration by microwave digestion. The highest arsenic concentrations were extracted in the reduction mobile fractions group, particular step f, for AUES2 and AUES3. Both of these samples, when compared to AUES1, had much lower relative arsenic concentrations observed in the fixed group.

The two other samples evaluated with the sequential extraction method were from the West Fork River and some poultry litter from chickens that were fed roxarsone. Both of these samples had high relative arsenic concentrations in the highly mobile fractions relative to the arsenic concentrations by microwave digestion compared to most of the other samples evaluated. Since WF was taken from saturated sediment, but subsequently air-dried and homogenized, some of the arsenic observed in the highly mobile fractions may be attributable to the oxidation of reduced arsenic minerals after sampling occurred. The poultry litter sample had very low relative amount of arsenic extracted in the reduction mobile fractions group, which is a unique characteristic not evidenced in any of the other samples. Other researchers have found that arsenic was readily soluble from similar poultry manure (*56, 63*).

Rutherford et al. (*56*) evaluated poultry litter from the Delmarva peninsula. The total arsenic concentration in the sample evaluated was 29 mg/kg. Water soluble extraction of arsenic was determined by mixing 1 g of sample with 20 mL of deionized water for 16 hours. One cycle of this extraction resulted in 22 ± 1.6 mg/kg arsenic mobilization. Repeating the water soluble extraction 13 times resulted in 95% mobilization of total arsenic. This suggests that arsenic in the poultry litter was highly mobile.

Soils from farms in Maryland and Oklahoma amended with poultry litter containing roxarsone waste were also evaluated by Rutherford et al. (*56*). Accumulation of arsenic was observed in soils amended with poultry litter. In one Oklahoma soil, water soluble arsenic concentrations decreased with increasing depth, but acid extracted arsenic concentrations increased with increasing depth. The water soluble arsenic concentrations in the amended Oklahoma field were 2.2 to 4.4 times higher than a nearby unamended field at the same depths. The acid extracted arsenic concentrations in the amended soil peaked at 5.6 mg/kg, and were approximately twice the concentrations observed in the unamended field at the same depths. These observations suggest that highly mobile arsenic in the poultry litter is mobilized and subsequently adsorped or precipitated in the soil as it percolates downward. Rutherford et al. point out that for a soil with a background arsenic concentration of 3.5 mg/kg, each application of poultry litter at 6 tons/acre would increase the concentration of arsenic by 3%.

Arai et al. (*63*) evaluated samples of poultry litter containing from chickens fed roxarsone from Delaware. Concentrations of arsenic up to 50 mg/kg were observed in samples. In batch pH controlled experiments (by buffered solutions) including sequential addition of identical extractants, higher mobilization of arsenic occurred at pH 7.0 (HEPES buffer) than at pH 4.5 (sodium acetate buffer). The peak mobilization of arsenic at pH 7.0 was only 6.01 mg/kg, which was 12.6% of total arsenic concentrations.

Keon et al. (*46*) sought to establish and standardize a sequential extraction method to potentially replace XRD and XAS in characterizing arsenic fractionation in soils and sediments. Some differences exist between the authors' method the method employed in this study. Keon et al. (*46*) used a much higher concentration of Na_2PO_4 (1.0 M compared with 0.1 M) at a lower pH (5.0 compared with 8.0) to represent the phosphate-exchangeable fraction. The higher concentration of Na_2PO_4 may enhance mobilization of easily exchangeable arsenic. However, the higher pH may also result in a change in the surface charge of sorption sites of metal oxyhydroxides (*12*) resulting in potential desorption of arsenic at these sorption sites. The authors found substantial recovery of arsenic from goethite using this step. Their finding would be contrary to the findings of Hongshao and Stanforth (*22*), except for the significant difference phosphate concentration (40 µM as P). The subsequent step in the sequential extraction method used in this study involved 1 M acetate buffer solution at pH 5.0, targeting dissolution of carbonate mineral-fixed arsenic. Generally, the findings of this study yielded far lower percent mobilization of arsenic in these two steps compared to the cumulative mass of arsenic mobilized than Keon et al. (*46*) observed in their single phosphate step. Variation in the samples alone between the two studies makes comparison difficult. However, the West Fork River sediment sample, albeit with a significantly lower total arsenic concentration, may be somewhat analogous to the sediment samples that were used by Keon et al. (*46*). The percentage of arsenic mobilized in the steps b and c+d, compared with the cumulative total of the entire sequential extraction method, was 19.0 and 16.5 percent, respectively. This suggests that carbonate minerals in the West Fork sediment, or another mineral that may dissolve at pH 5, may have been sequestering arsenic. The total between steps b and c+d in West Fork (35%) is moderately similar to the approximately 50% consistently observed by Keon et al. (*46*), in contrast to the rest of the samples. Another sample, M27, was taken in a marsh-like area near a mine tailings pond, may have been expected to have similar carbonate mineral except for its low pH (3.5).

The association of iron and arsenic in the sequential extraction method for the AUES1 sample was not similar to Mexican mine tailings and associated samples presented in Chapter 2. Iron was extracted in the steps similar to the other samples, but there was negligible arsenic associated with this iron as shown in FIGURE 29, most notably in step f. Only slightly more than half of the iron extracted by microwave digestion, however, was extracted by the sequential extraction method. The lack of arsenic extraction from the reduction mobile fractions suggests that the arsenic in this sample is more stable – due possibly to the source of contamination or the potential impacts of approximately 80 years of weathering if the arsenic enrichment was attributable to activities of the AUES FUDS. It may be possible that arsenic minerals were formed that were resistant to dissolution by the sequential extraction method. Additional characterization of this particular sample, possibly with x-ray diffraction techniques, may provide additional clues as to why it exhibits unique characteristics when compared to other samples.

4.3 SIMULATED BIOAVAILABILITY EXTRACTION

The WF sample was evaluated with the simulated human oral bioavailable extraction method, similar to the mine tailings and associated samples evaluated. The arsenic and iron concentrations from simulated human oral bioavailable extraction for WF were 111 ± 0.238 mg/kg and 207 ± 11.7 mg/kg, respectively. The percentage of iron extracted to the total iron by microwave digestion was 1.7%. For the mine tailings and associated samples evaluated (Chapter 3), a strong correlation was observed between arsenic concentrations from the simulated human oral bioavailable extraction and the highly mobile fractions from the sequential extraction method (FIGURE 18) represented by the following equation.

$$(As_{bioavailable}) = 24.3 + 0.74682 * (As_{a\ to\ d})$$

For WF, which had a cumulative arsenic concentration from steps a through d of 119 mg/kg, this curve would predict an arsenic concentration from simulated human oral bioavailable extraction of 113 mg/kg, which is within 2% of the actual measured value. This trend provides promising evidence that the initial sequential extraction method steps may provide a relatively simple and accurate surrogate method for predicting the simulated human oral bioavailable extraction method concentrations of arsenic in different samples. Less equipment is required for the sequential extraction method compared to the simulated human oral bioavailable extraction method (water bath and pump, flow-through reactor vessel, nitrogen sparging gas and equipment), but the latter method requires much less time.

4.4 MOBILIZATION EXPERIMENTS

Similarly as with the mine tailings and associated samples (Chapter 3), arsenic mobilizing effects of various pH-controlled solutions under varying redox conditions were evaluated for various samples contaminated with arsenic in order to identify if trends in arsenic mobility can be predicted by the characterization methods used.

4.4.1 Sample selection.

Samples were selected for the mobilization experiments for various reasons. The AUES3, WF, and PL samples were selected since they came from different sources, and allow for some diversity in the study. In addition to originating from different sources, these samples were enriched with arsenic by different routes, and they represent different mediums. Sample AUES3 was taken from a soil located in the Spring Valley neighborhood of the District of Columbia at the AUES FUDS. The WF sample is river sediment that originated in West Virginia, was impacted and presumably enriched with arsenic by local smelter operations. PL was a sample of poultry litter from livestock fed with roxarsone at an operation on Maryland's Eastern Shore.

4.4.2 Mechanisms expected to influence arsenic mobilization.

The following types of processes are expected to influence arsenic mobility as redox potential and pH changes: arsenic oxidation-reduction reaction affecting speciation, adsorption/desorption processes relative to pH and arsenic speciation, dissolution of minerals, precipitation of arsenical minerals, or co-precipitation of arsenic with non-arsenical minerals.

More specifically, as the pe + pH decreases the following processes are expected to occur: arsenate reduction to arsenite and subsequent desorption from iron oxyhydroxide minerals; iron oxyhydroxide mineral reductive dissolution to ferrous iron, which will release associated arsenic; sulfate reduction to sulfide; precipitation of iron sulfide minerals such as pyrite; precipitation of arsenic sulfide and arsenic iron sulfide minerals. These processes, and the kinetics of the processes, are dependent on many variables besides pe + pH including iron concentrations, sulfide concentrations, and arsenic concentrations (*39*). O'Day et al. (*39*) suggested that under sulfidic conditions with high dissolved iron concentrations, for example, the formation of arsenic sulfide minerals may be precluded by the favored formation of pyrite, which offers fewer sorption sites than iron oxyhydroxide minerals. In Chapter 3, orpiment (As_2S_2) formation was shown to be possible at around the pe and pH levels observed, dependant on arsenic and sulfur concentrations (FIGURE 25).

4.4.3 Results and discussion.

The results for the WF, AUES3, and PL samples are shown in FIGURE 30, FIGURE 31, and FIGURE 32, respectively. The results of the experiment for these samples were similar to the mine tailings samples in complexity (Chapter 3). The peak dissolved arsenic concentrations under all conditions for each sample is shown in TABLE 10. For the WF and AUES3 samples, the peak concentrations were low relative to the arsenic concentrations by microwave digestion and cumulative arsenic concentration by the sequential extraction method. In addition, the peak arsenic concentrations mobilized from these two samples were low relative to the highly mobile fractions group of the sequential extraction method for those samples. The peak arsenic concentration mobilized for both of these samples was in air-sparged reactors. The WF sample peak occurred in the pH 5.5 buffer reactor, which may be similar to step c+d conditions in the sequential extraction method. The AUES3 sample peak occurred in the pH 10 buffer reactor. Some desorption of arsenic may be expected at this high pH due to changes in the surface charge of particle sorption sites.

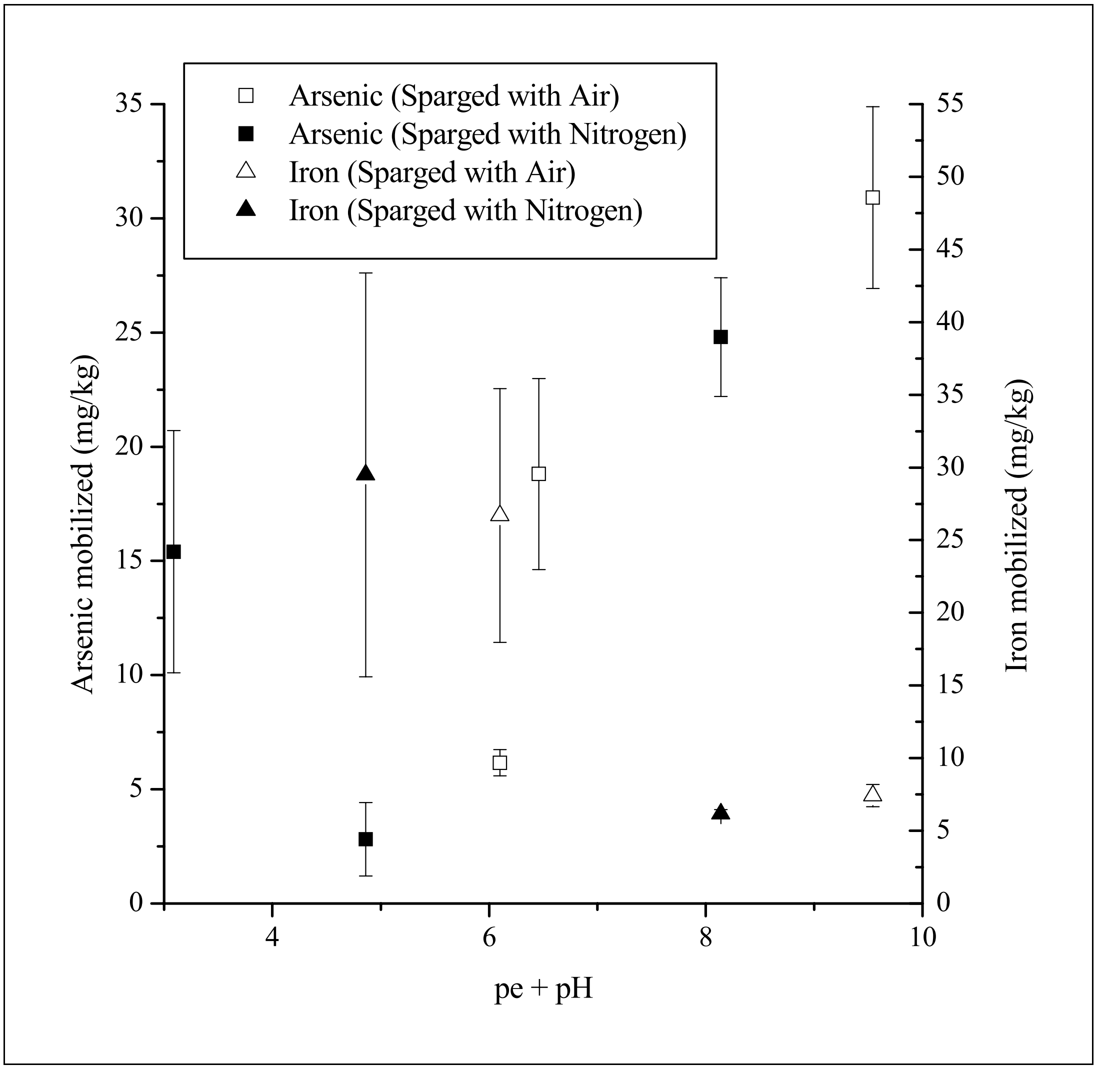

FIGURE 30. Arsenic mobilization from WF with respect to measured pe + pH levels. The pH levels were controlled by using buffers and changes in pe were induced by sparging with air or nitrogen. The symbols represent average of duplicates and error bars represent one standard deviation.

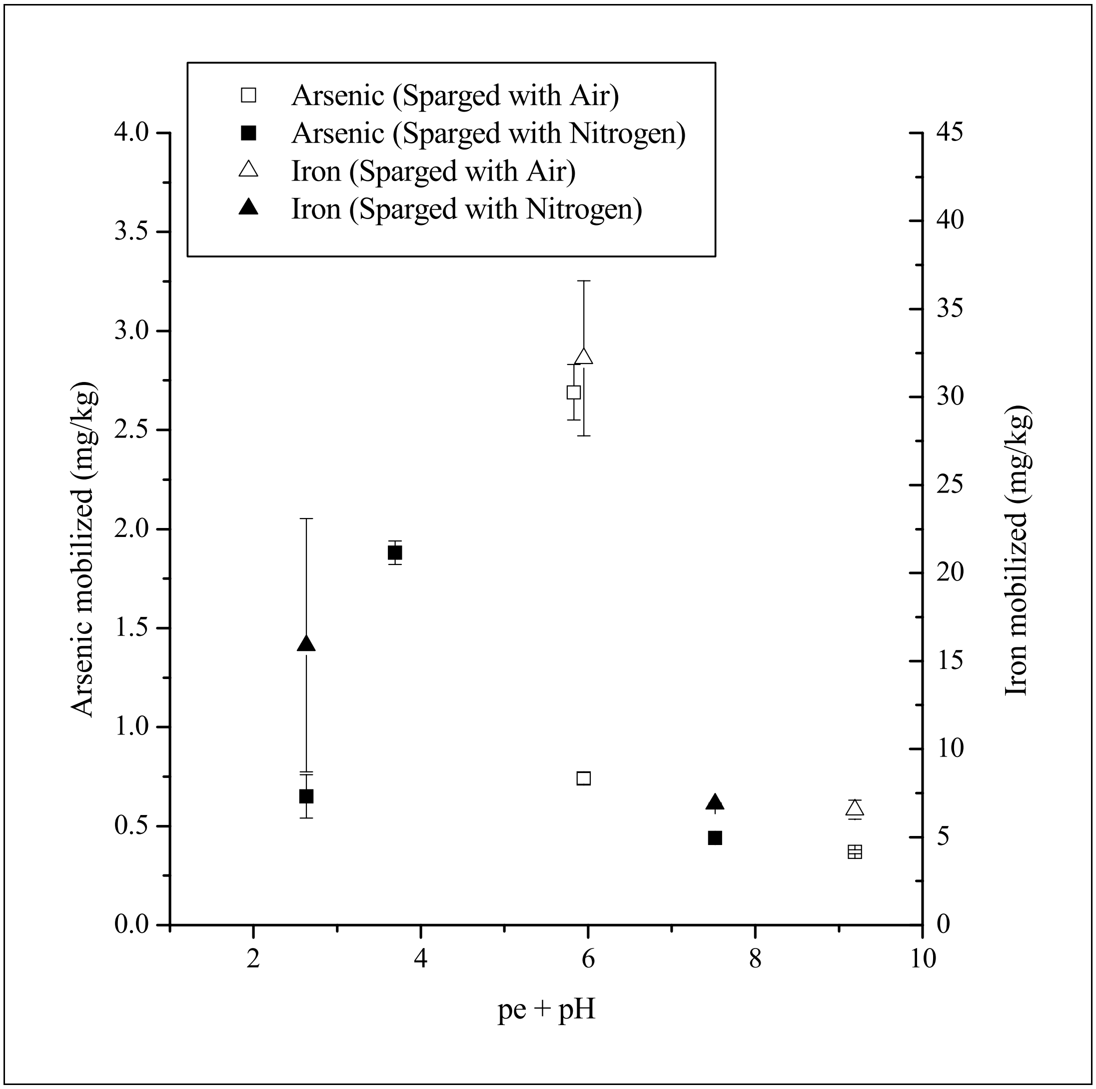

FIGURE 31. Arsenic mobilization from AUES3 with respect to measured pe + pH levels. The pH levels were controlled by using buffers and changes in pe were induced by sparging with air or nitrogen. The symbols represent average of duplicates and error bars represent one standard deviation.

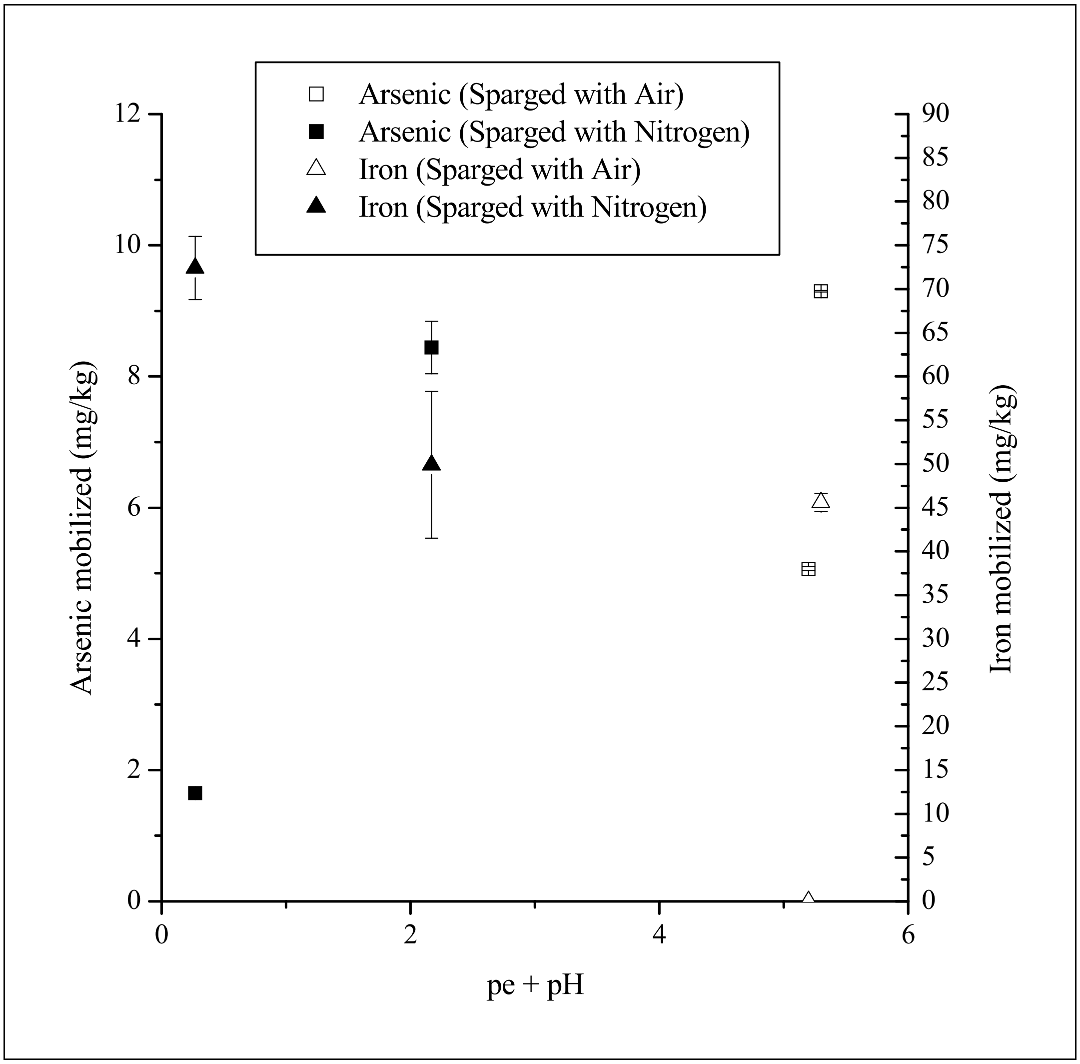

FIGURE 32. Arsenic mobilization from PL with respect to measured pe + pH levels. The pH levels were controlled by using buffers and changes in pe were induced by sparging with air or nitrogen. The symbols represent average of duplicates and error bars represent one standard deviation.

TABLE 10. Peak concentrations of arsenic in mobilization experiments for individual samples.

Sample	Peak arsenic concentration (mg/kg)	Conditions at peak	Cumulative arsenic concentration for highly mobile fractions group (mg/kg)	Average simulated human oral bioavailable arsenic concentration (mg/kg)	Average total arsenic concentration by microwave digestion (mg/kg)
WF	30.9 ± 3.98	final pe + pH 9.54 ± 0.156 (air with pH 5.5 buffer)	118 ± 6.1	111 ± 0.24	156 ± 21.1
AUES3	2.69 ± 0.14	final pe + pH 5.83 ± 0.156 (air with pH 10 buffer)	23 ± 0.4	n/a	165 ± 22.4
PL	9.30 ± 0.086	final pe + pH 5.30 ± 0.23 (air with pH 10 buffer)	10.4 ± 0.24	n/a	27.2 ± 2.31

The peak arsenic concentration mobilized in the experiment for the PL sample, however, was similar to the highly mobile fractions group of the sequential extraction method for the sample and approximately half of the cumulative arsenic concentration in the sequential extraction method and approximately one third of the arsenic concentration by microwave digestion for the same sample.

4.4.4 Analysis of arsenic mobilization trends.

Iron levels did not diminish with decreasing pe as strikingly for these samples as with the mine tailings and associated samples. In addition, some of the situations where Trizma-HCl was used as the buffer, dissolved iron was observed for the WF, AUES3 and PL samples, unlike the mine tailing samples.

The WF sample results showed a trend of three phases as pe + pH decreased: a decrease in dissolved arsenic as dissolved iron concentrations increased; followed by a drop in dissolved arsenic concentrations; followed by increased dissolved arsenic concentrations. In the first two phases, this progression may suggest gradual reductive dissolution of iron and formation of sulfides coupled with precipitation of arsenic in sulfidic minerals. If the rate of dissolution of iron oxyhydroxides increased with decreasing pe + pH, less arsenic may be expected to be incorporated in sulfidic minerals as pyrite may become the dominant precipitate (see discussion in Chapter 3). The increased dissolved arsenic concentration at the lowest pe + pH point is similar to some of the mine tailing samples, including M27, which was also a sample of sediment.

CHAPTER 5. CONCLUSIONS AND RECOMMENDED FURTHER STUDIES

5.1 CONCLUSIONS

Total iron and arsenic concentrations were moderately correlated in many of the mine tailing and associated samples, but other mineral associations seem to have arsenic associations in some other samples. Arsenic sulfides such as realgar or orpiment may be expected to precipitate under certain conditions with high arsenic and sulfur concentrations. A sequential extraction method showed that in most of the mine tailings and associated samples, the highest arsenic extraction occurred in the step targeting easily reducible oxides. A low percentage of iron relative to total iron concentrations (by microwave digestion) was extracted and was highly correlated in the mine tailings samples with extracted arsenic in the same step. Subsequent reducing steps typically resulted in a higher percentage of iron extraction, but low or insignificant extraction of arsenic. This suggests that if arsenic that is extracted by the easily reducible oxides step is associated with iron minerals, it could be as the following:

- non-exchangeable adsorbed arsenic on iron oxyhydroxide structures on particle surfaces,
- non-exchangeable adsorbed arsenic on less crystalline and more easily reducible iron oxyhydroxide minerals,
- or arsenic-iron minerals that are easily reducible

The simulated human oral bioavailable extraction method yielded significantly lower concentrations of arsenic mobilization compared to total arsenic concentrations. This or a similar method may be useful to characterize arsenic contamination at sites where a pathway for oral exposure to the arsenic-contaminated materials may exist. In particular, the simulated human oral bioavailable extraction method might be useful for the remediation prioritization of locations within a site. Negligible concentrations of iron were extracted in the simulated human oral bioavailable extraction method, suggesting that the arsenic mobilized in the method is not associated with dissolution of iron minerals. The highly mobile fractions of arsenic in the sequential extraction method were highly correlated with the simulated human oral bioavailable extraction method. This correlation suggests that the soluble arsenic, anion-exchangeable adsorbed arsenic, and arsenic associated with carbonates may be expected to be mobilized under the simulated human digestive system conditions.

The sequential extraction method provides a useful means of determining the fractionation and reticence of arsenic in different materials. The sequential extraction method is a fairly simple method, which may lend to extensive use. Coupling the determination of total arsenic concentrations in samples by microwave digestion or other robust extraction procedures with the sequential extraction procedure analyzed in this study provides some useful redundancy. In certain samples evaluated, the microwave digestion method employed underestimated total arsenic concentrations as determined by the sequential extraction method. In the majority of samples, however, some of the arsenic observed by the microwave digestion extraction was not extracted by the sequential extraction method. This method also shows promise in possibly simplifying measurement of simulated human oral bioavailable arsenic concentrations, as shown with a correlation of certain steps of the sequential extraction method to the simulated human oral bioavailable extraction method.

5.2 RECOMMENDED FURTHER STUDIES

The methods evaluated in this study were promising, but collection and evaluation of a wider variety of samples would be necessary to confirm or prove coincidental the observed correlation between steps of the sequential extraction method and the simulated human oral bioavailable extraction.

Other researchers attempted to identify fingerprints using sequential extraction methods evaluated spiked samples with known arsenical minerals or arsenic laden minerals. This approach may also be useful for the particular sequential extraction method considered in this study.

Further understanding of the usefulness of the sequential extraction method and other methods may be obtained by additional experiments on the mobilization of arsenic by varying pH and redox conditions. Some of the uncertainty in the results of the experiments in this study might be reduced in future experiments by analyzing the reactor solutions for sulfate and sulfide, as well as distinguishing the speciation and oxidation state of iron and arsenic. Different buffers for controlling pH may be useful due to the potential conflicts that the buffers used in this study may have presented. Additional characterization of the samples with x-ray diffraction techniques to determine mineral and particle associations of arsenic prior to and following the experiment may also be useful in understanding the processes that are occurring. Evaluating samples using a similar experiment with different time periods will likely provide different results. The length of time used in the experiments in this study was fixed.

The involvement of microorganisms on mobilization of arsenic was not thoroughly considered in this study, but is an active research area. Microorganisms that utilize arsenic or associated chemicals may cause changes in the sequential extraction method fractionation, also influencing the mobility of arsenic. Microorganisms can also affect the kinetics of important arsenic reactions affecting speciation and mobility.

Studies involving the treatment by fixation of arsenic at contaminated locations have utilized sequential extraction methods to characterize the treatment effectiveness. Materials employed for removing arsenic from contaminated water, such as activated alumina, iron, or ion exchange resins, might be characterized by the sequential extraction method for consideration of effectiveness or even optimization.

Evaluation of precipitation of different sulfidic minerals will also be very useful for understanding potential mobilization implications for arsenic, iron, and sulfur. Varying pH, redox conditions, and constituent concentrations could confirm thermodynamic predictions. The impacts of other constituents, potentially found in the environment such as phosphates and carbonates, on the precipitation and possible adsorption mechanisms should also be studied.

APPENDIX A. CONTROL OF PH WITH “GOOD” BUFFERS

"Good" buffers MES, Trizma-HCl, and CAPS were used in the investigation of pH effects on the mobility of arsenic. The primary rationale for utilizing these buffers is that the chemicals are considered biologically not reactive, and do not influence enzyme activity. Our findings indicate that for the Trizma-HCl buffer, there are some effects on mobilization of arsenic independently of pH (see following experiment). However, other buffers, such as phosphate buffer systems, are generally believed to influence mobilization of arsenic independently of pH. Additionally, phosphate can potentially influence enzyme activity. Some metal chelation may occur with the "Good" buffers, but future studies may involve investigation of microbial activity and the influence on mobilization of arsenic, so the "Good" buffers were used in this study.

An experiment with Trizma-HCl and blank with two soils was used to check variation of mobilization at a given pH. Trizma-HCl was evaluated as a buffer for two different samples with respect to blank electrolyte solutions. Trizma-HCl was selected for evaluation due to the fact that its buffer range (pH 7 to pH 9.5) lies within the soil pH range of the samples evaluated in this study.

The buffered solutions contained 0.01 N Trizma-HCl and 0.15 N $NaClO_4$. The blank electrolyte solution contained 0.15 N $NaClO_4$. The buffered solution for sample M2 was adjusted to pH 8.5 and the buffered solution for sample WF was adjusted to pH 6.95 using trace metal grade HCl and NaOH solutions. Each sample was evaluated in triplicate for both the buffer solution and for the blank electrolyte solution. In each replicate, approximately 1 g of sample was measured into a polystyrene centrifuge tube (actual mass recorded), was combined with 20 mL of solution, and then mixed via end-over-end shaking for approximately 14 hours. Following the mixing, the pH of each sample was measured and recorded. Then the samples were centrifuged for 10 m at 4000 rpm, the supernatant was filtered, and finally measured for total arsenic concentrations.

The experimental data is summarized in TABLE 11. In the case of sample M2, a significantly higher amount of arsenic was mobilized by the Trizma-HCl buffered solution than by the electrolyte blank solution. However in the case of sample WF, the Trizma-HCl buffered solution mobilized slightly less arsenic than the electrolyte blank solution. The difference between the amount of arsenic mobilized between the two samples indicates that the arsenic chelation interactions of Trizma-HCl may not be easily predicted. However, since the mass of arsenic mobilized was very low compared to the total concentrations of arsenic in the samples, we chose to use Trizma-HCl as a buffer in arsenic mobility experiments. Other researchers have referenced low chelation effects from MES. The CAPS buffer was not evaluated due to the buffer range being outside of the soil pH levels for the available samples. No information about other studies on chelation effects of CAPS was identified.

TABLE 11. Average Arsenic and Iron mobilization (with standard deviation) from two soils by buffered solution (0.01N Trizma-HCl, 0.15N NaClO4) and by electrolyte blank solution (0.15N NaClO4).

Soil	Buffer Mobilized arsenic (mg/kg)	pH_{final}	Blank Mobilized arsenic (mg/kg)	pH_{final}
M2	3.41 ± 0.05	8.53 ± 0	1.57 ± 0.07	8.42 ± 0.05
WF	10.34 ± 0.27	6.35 ± 0.01	12.37 ± 0.7	5.77 ± 0.01

APPENDIX B. CONSTRUCTION OF PE-PH DIAGRAM

The construction of the pe-pH predominance diagram in FIGURE 25 is based on the formulae in TABLE 12. Total concentrations of arsenic and sulfur species for the pe-pH predominance diagram were both 1 mM.

TABLE 12 Arsenic and sulfur species formulae important at experimentally observed pe and pH levels.

No.	Equilibrium equation	Log K	Source
(1)	$HAsO_2^0 + 2 H_2O \leftrightarrow HAsO_4^{2-} + 4 H^+ + 2 e^-$	-28.60	*(12)*
(2)	$AsO_2^- + H^+ \leftrightarrow HAsO^0$	-9.29	*(12)*
(3)	$H_2AsO_4^- \leftrightarrow HAsO_4^{2-} + H^+$	-6.94	*(12)*
(4)	$HAsO_2^0 + 2 H_2O \leftrightarrow H_2AsO_4^- + 2 H^+ + 2e^-$	-22.6	*(64)*
(5)	$AsO_2^- + 2 H_2O \leftrightarrow HAsO_4^{2-} + 3 H^+ + 2 e^-$	-19.31	*(12)*
(6)	$As_2S_2 + 4 H_20 \leftrightarrow 2 HAsO_2^0 + 2 SO_4^- + 22 H^+ + 18 e^-$	-123.48	*(12, 64)*
(7)	$As_2S_2 + 12 H_20 \leftrightarrow 2 AsO_2^{2-} + 2 SO_4^- + 24 H^+ + 18 e^-$	-141.95	*(12, 64)*
(S1)	$SO_4^{2-} + 10 H^+ + 8 e^- \leftrightarrow H_2S_{(aq)} + 4 H_2O$	41.0	*(64)*
(S2)	$H_2S_{(aq)} \leftrightarrow H^+ + HS^-$	-7.0	*(64)*
(S3)	$SO_4^{2-} + 9 H^+ + 8 e^- \leftrightarrow HS^- + 4 H_2O$	34.0	*(64)*

REFERENCES

(1) Welch, A. H.; Westjohn, D. B.; Helsel, D. R.; Wanty, R. B. *Ground Water.* **2000**, *38*, 589-604.

(2) Hering, J. G.; Chiu, V. Q. *Journal of Environmental Engineering.* **2000,** *126,* 471-474.

(3) Berg, M.; Tran, H. C.; Nguyen, T. C.; Pham, H. V.; Schertenleib, R.; Giger, W. *Environmental Science and Technology.* **2001**, *35*, 2621-2626.

(4) US ATSDR. *Toxicological Profile for Arsenic.* **2000.**

(5) Corwin, D. L.; David, A., and Goldberg, S. *Journal of Contaminant Hydrology.* **1999,** *39,* 35-58.

(6) Akhter, H.; Cartledge, F. K.; Miller, J.; McLearn, M. *Journal of Environmental Engineering.* **2000**, *126*, 999-1003.

(7) Dyken, J. J.; Crellin, J. R. *Practice Periodical of Hazardous, Toxic, and Radioactive Waste Management.* **2004**, *8*, 155-160.

(8) USACE, Baltimore District. *Engineering Evaluation/Cost Estimate for Arsenic in Soil, Spring Valley Operable Units 4 and 5.* **2003**

(9) Davis, A.; Sherwin, D.; Ditmars, R.; Hoenke, K. A. *Environmental Science and Technology.* **2001**. *35*, 2401-2406.

(10) Dudka, S.; Miller, W. P. *Water, Air, and Soil Pollution.* **1999**, *113*, 127-132.

(11) EPA. http://cfpub.epa.gov/iris/quickview.cfm?substance_nmbr=0278, 11 2004, (may 30/ 2005).

(12) Sadiq, M. *Water, Air, and Soil Pollution.* **1997,** *93*, 117-136.

(13) O'Neill, P. In *Heavy Metals in Soils*; Alloway, B. J., Ed. Wiley: New York, 1990; pp 83-99.

(14) Frost, R. R.; Griffin, R. A. *Soil Science Society of America Journal.* **1977,** *41,* 53-57.

(15) Xu, H.; Allard, B.; Grimvall, A. *Water, Air, and Soil Pollution.* **1991**, *57-58*, 269-278.

(16) Smith, E.; Naidu, R.; Alston, A. M. *Journal of Environmental Quality.* **1999**, *28*, 1719-1726.

(17) Manning, B. A.; Goldberg, S. *Soil Science*. **1997**, *162*, 886-895.

(18) Ullah, S. S.; Islam, Z.; Sarker, A. K.; Haider, S. Z.; Choudhury, M. H. *Bangledesh. Journal of Bangledesh Academy of Sciences.* **1998**, *22,* 143-147.

(19) Masscheleyn, P. H.; Delaune, R. D.; Patrick, Jr. W. H. *Journal of Environmental Quality.* **1991,** *20,* 522-527.

(20) Goldberg, S. *Soil Science Society of America Journal.* **1986**, *50*, 1154-1157.

(21) Reynolds, J. G.; Naylor, D. V.; Fendorf, S. E. *Soil Science Society of America Journal.* **1999**, *63*, 1149-1156.

(22) Hongshao, Z.; Stanforth, R. *Environmental Science and Technology.* **2001**, 35, 4753-4757.

(23) Davenport, J. R.; Peryea, R. J. *Water, Air, and Soil Pollution.* **1991**, *57-58,* 101-110.

(24) Peryea, F. J.; Kammereck, R. *Water, Air, and Soil Pollution.* **1997**, *93,* 243-254.

(25) Jones, C. A.; Inskeep, W. P.; Neuman, D. R. *Journal of Environmental Quality.* **1997**, *26*, 433-439.

(26) Pantsar-Kallio, M.; Manninen, P. K. G. *The Science of the Total Environment.* **1997**, *204*, 193-200.

(27) Robins, R. G. *Metallurgical Transactions.* **1981**, *12B*, 103-109.

(28) Kim, M.; Nriagu, J.; Haack, S. *Environmental Science and Technology.* **2000,** *34*, 3094-3100.

(29) Appelo, C. A. J.; Van Der Weiden, M. J. J.; Tournassat, C.; Charlet, L. *Environmental Science and Technology.* **2002,** *36*, 3096-3103.

(30) Grundl, T. *Chemosphere.* **1994**, *28*, 613-626.

(31) Mok, W. M.; Wai, C. M. *Water Research.* **1989**, *23*, 7-13.

(32) Amrhein, C.; Mosher, P. A.; Brown, A. D. *Soil Science.* **1993**, *155*, 249-255.

(33) McGeehan, S. L. *Journal of Environmental Science Health.* **1996,** *A31*, 2319-2336.

(34) McGeehan, S. L.; Fendorf, S. E.; Naylor, D. V. *Soil Science Society of America Journal.* **1998**, *62*, 828-833.

(35) Gulens, J.; Champ, D. R.; Jackson, R. E. Influence of redox environments on the mobility of arsenic in ground water. *Chemical modeling in aqueous systems. American Chemical Society*; **1979**.

(36) McCreadie, H.; Blowes, D. W.; Ptacek, C. J.; Jambor, J. L. *Environmental Science and Technology.* **2000**, *34*, 3159-3166.

(37) Carbonell-Barrachina, A. A.; Jugsujinda, A.; Burlo, F.; Delaune, R. D.; Patrick Jr., W. H. *Water Resources.* **2000**, *34*, 216-224.

(38) Meng, X.; Korfiatis, G. P.; Jing, C.; Christodoulatos, C. *Environmental Science and Technology*. **2001**, *35*, 3476-3481.

(39) O'Day, P. A.; Vlassopoulos, D.; Root, R.; Rivera, N. *Proceedings of the National Academy of Science*. **2004**. *38*, 13703-13708.

(40) Ahmann, D.; Krumholz, L. R.; Hemond, H. F.; Lovley, D. R.; Morel, F. M. M. *Environmental Science and Technology.* **1997**, *31*, 2923-2930.

(41) Stolz, J. F.; Oremland, R. S. *FEMS Microbiology Reviews.* **1999**, *23*, 615-627.

(42) Langner, H. W.; Inskeep, W. P. *Environmental Science and Technology.* **2000**, *34*, 3131-3136.

(43) Miller, J.; Akhter, H, Cartledge, F. K.; McLearn, M. *Journal of Environmental Engineering.* **2000**, *126*, 1004-1012.

(44) Wellman, D. E.; Reid, D. A.; Ulery, A. L. *Journal of Soil Contamination.* **1999**, *8*, 329-341.

(45) Ghosh, A.; Mukiibi, M.; Ela, W. *Environmental Science and Technology.* **2004**, *38*, 4677-4682.

(46) Keon, N. E.; Swartz, C. H.; Brabander, D. J.; Harvey, C.; Hemond, H. F.; *Environmental Science and Technology.* **2001,** *35*, 2778-2784.

(47) McLaren, R. G.; Naidu, R.; Smith, J.; Tiller, K. G. *Journal of Environmental Quality.* **1998**, *27*, 348-354.

(48) Kim, J. Y.; Davis, A. P.; Kim, K. W. *Environmental Science and Technology.* **2003**, *37*, 189-195.

(49) Tokunaga, T. K.; Lipton, D. S.; Benson, S. M.; Yee, A. W.; Oldfather, J. M.; Duckart, E. C.; Johannis, P. W.; Halvorsen, K. E. *Water, Air, and Soil Pollution.* **1991**, *57-58,* 31-41.

(50) Lipton, D. S. Ph.D. Dissertation, University of California at Berkeley, California, 1991.

(51) Rodriguez, R. R.; Basta, N. T.; Casteel, S. W.; Pace, L. W. *Environmental Science and Technology.* **1999**, *33*, 642-649.

(52) Ruby, M V.; Schoof, R.; Brattin, W.; Goldade, M.; Post, G.; Harnois, M.; Mosby, D. E; Casteel, S. W.; Berti, W.; Carpenter, M.; Edwards, D.; Cragin, D.; Chappell, W. *Environmental Science and Technology.* **1999**, *21*, 3697-3705.

(53) Gutiérez-Ruiz, M. E.; Fernández-Lomelin, P.; Sommer-Cervantes, I.; Busch, J.; Martínez, J. L.; Torrents, A. Speciation and Dispersion of Arsenic in a Tailings Dam and Surrounding Soils. In Proc., Pan-Asia-Pacific Conference on Fluoride and Arsenic Research, 15-20 Aug 1999, Shenyang City, Liaoning Province, China.

(54) Albright, R. D.; Campbell, D. G. *Final Report on the World War I Poison Gas Production at the American University Experiment Station.* Government of the District of Columbia Department of Consumer and Regulatory Affairs Environmental Regulation Administration: 1996.

(55) USACE Baltimore District. http://www.nab.usace.army.mil/projects/WashingtonDC/springvalley.htm, 6 2005 (june 20/ 2005).

(56) Rutherford, D. W.; Bednar, A. J.; Garbarino, J. R.; Needham, R.; Staver, K. W.; Wershaw, R. L. *Environmental Science and Technology*. **2003**, *37*, 1515-1520.

(57) Light, T. S. *Analytical Chemistry*. **1972**, *44*, 1038-1039.

(58) Sheppard, B. S.; Heitkemper, D. T., Gaston, C. M. *Analyst.* **1994**, *119*, 1683-1686.

(59) Deaker, M.; Maher, W. *Journal of Analytical Atomic Spectrometry.* **1999**, *14,* 1193-1207.

(60) Nieuwenhuize, J.; Poley-Vos, C. H.; van den Akker, A. H.; van Delft, W. *Analyst.* **1991**, *116*, 347-351.

(61) Air Liquide S.A., *Arsine Material Safety Data Sheet.* **2002.**

(62) Bartlett, R. J.; James, B. R. *Advances in Agronomy.* **1993,** *50,* 151-208.

(63) Arai, Y.; Lanzirotti, A.; Sutton, S.; Davis, J. A.; Sparks, D. L. *Environmental Science and Technology*. **2003**, *37*, 4083-4090.

(64) Stumm, W.; Morgan, J. J. *Aquatic Chemistry*. Wiley, New York: 1981.

(65) American Chemical Society. *Journal Physical Chemistry Reference Data, Volume 11, Supplement 2.* **1982.**