

**ASSESSMENT OF ARSENATE BIOAVAILABILITY IN IRON-RICH ENVIRONMENTS:  
DEVELOPMENT OF A HIGH-PRESSURE LIQUID CHROMATOGRAPHY METHOD OF  
QUANTIFICATION FOR ARSENATE SORBED BY Fe<sup>3+</sup>-SUBSTITUTED CHELATING RESINS  
IN ARSENIC-BEARING FERRIHYDRITE SUSPENSIONS**

A Thesis

by

MELISSA DELANE ROBERTS

Submitted to the Office of Graduate Studies of  
Texas A&M University  
in partial fulfillment of the requirements for the degree of

MASTER OF SCIENCE

May 2005

Major Subject: Geology

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**ABSTRACT**

Assessment of Arsenate Bioavailability in Iron-Rich Environments: Development of a High-Pressure Liquid Chromatography Method of Quantification for Arsenate Sorbed by Fe<sup>3+</sup>-Substituted Chelating Resins in Arsenic-Bearing Ferrihydrite Suspensions. (May 2005)

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Given that the mobility, bioavailability, and toxicity of arsenate in natural systems is often controlled by the strong binding capacity of iron oxyhydroxides, the objective of this study was to document the interactions of Dowex M4195 Fe<sup>3+</sup>-substituted chelating resins (a potential field-based tool for the quantification of potential arsenate bioavailability) and arsenic-bearing ferrihydrite (AFH) as a function of suspension pH, suspension concentration, and background electrolyte concentration. In 0.5 g AFH/L (0.001 M NaNO<sub>3</sub>) suspensions, arsenate sorption to the resins was proportional to the degree of acidification of the AFH suspensions by the resins. H<sup>+</sup>-enhanced dissolution of ferrihydrite artificially increased the arsenate in solution, causing a consistent overestimation of potential arsenate bioavailability. Resin-induced acidification was decreased with increasing suspension concentration. Arsenate sorption to the resins in 0.5 g/L suspensions at pH 8 decreased with increasing NaNO<sub>3</sub> concentrations, reflecting the decreasing activity of arsenate under these conditions. The results of this study indicate that the high buffer capacity of natural soils would prevent acidification as a result of resin introduction. Thus, Dowex M4195 Fe<sup>3+</sup>-substituted chelating resins should provide a reasonable assessment of potential arsenate bioavailability from poorly-crystalline iron oxide minerals. Possibly more importantly, Dowex M4195 Fe<sup>3+</sup>-substituted chelating resins appear to be a new choice of passive equilibrium sampling device that should work well for the determination of bioavailable arsenate concentrations in the field.

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## INTRODUCTION: ESTIMATING ARSENIC BIOAVAILABILITY IN COMPLEX BIOGEOCHEMICAL SYSTEMS

Arsenic is a common contaminant in soils, sediments, surface waters, vadose zone water, and ground waters. Increased scientific interest in arsenic studies coincides with increased awareness in the lay community as a result of the well-publicized debates over lowering the arsenic drinking water standard from 50 ppb to 10 ppb. Water consumers are naturally concerned about the arsenic concentrations in their drinking water supplies, especially when considering that chronic micromolar exposure to arsenic in drinking water can cause hyperpigmentation, peripheral vascular disease, skin and bladder cancer, and gangrene<sup>1,2</sup>.

According to Rodriguez et al.<sup>3</sup>, the bioavailable fraction of a given chemical is the fraction of the administered dose of the chemical that enters systemic circulation. In soils, sediments, and water systems, the most potentially bioavailable forms generally are the dissolved species<sup>4</sup>. Thus, the total concentration of arsenic in an environment cannot necessarily be used to estimate bioavailability. A complex suite of physicochemical mechanisms controls the speciation (and solubility) of arsenic in near-surface environments. Hence, arsenic is bioavailable in environments where adsorbed, coprecipitated, or otherwise insoluble arsenic forms are made soluble.

There is not a standardized field method for determining arsenic bioavailability in the environment. Recent work on arsenic bioavailability has made use of dissolved arsenic concentrations in surface waters<sup>5-7</sup>; selective dissolution and sequential extractions of local sediments<sup>3,8-11</sup>; biological monitoring and digestion of impacted organisms<sup>12,13</sup>; and speciation and adsorption modeling using much-simplified study parameters<sup>13-15</sup>. Resins, specifically iron-substituted chelating resins, are a promising means of obtaining time-averaged estimations of bioavailable arsenic that incorporate the inputs of all the transfer mechanisms.

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This thesis follows the style of *Environmental Science & Technology*.

## **Biogeochemical Cycling**

Natural geogenic sources of arsenic include volcanic emissions; oxidation of sulfide minerals; dissolution of iron, aluminum, and manganese oxides; and weathering of volcanic ash layers<sup>16</sup>. Anthropogenic sources of arsenic include pesticides, cotton defoliant, lumber preservation processes, mine tailings, ore processing, pharmaceuticals, livestock feed additives, glass/electronics production, and many others<sup>16-23</sup>. Sinks for arsenic include the formation and burial of sulfide minerals (arsenopyrite), formation and burial of iron, aluminum, and manganese oxides<sup>24</sup>, incorporation into organic compounds<sup>25,26</sup>, as well as anthropogenically-driven removal mechanisms<sup>27</sup>.

Complex geochemical and biological mechanisms (Figure 1) control the distribution of arsenic within repositories in the biosphere, hydrosphere, and lithosphere. Redox conditions, pH, and the presence of iron and manganese oxyhydroxides are generally assumed to control the speciation and distribution of arsenic in freshwater systems<sup>19,28-30</sup>. However, there is growing consensus that the metabolic activities of microorganisms and higher life forms can transform environmental arsenic species into a number of different compounds, both organic<sup>31-38</sup> (Figure 2) and inorganic<sup>25</sup>, as well as manipulate the local redox environment, driving abiotic changes in arsenic mobility and bioavailability<sup>39-41</sup>.

## **Transfer Mechanisms**

While the sources and sinks of arsenic are fairly well known, the mechanisms by which arsenic is mobilized from the lithosphere to bioavailable forms in the hydrosphere are less well known and therefore more closely scrutinized by the scientific community. Arsenic can be mobilized (or immobilized) by oxidation/reduction reactions, adsorption/desorption reactions, incorporation/coprecipitation reactions, direct precipitation/dissolution reactions, and assimilation/biotransformation reactions by organisms.

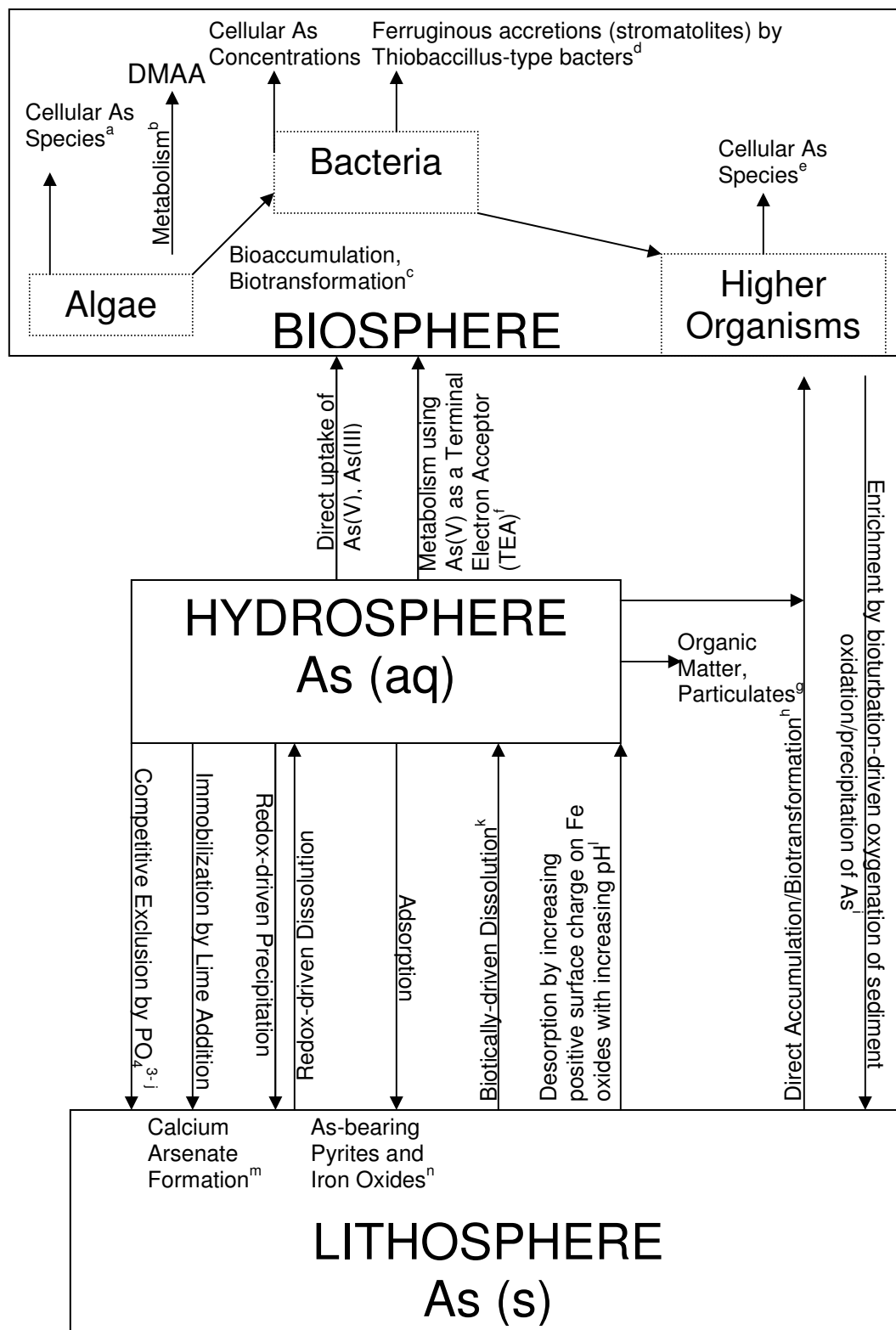


Figure 1. Arsenic transfer mechanisms among the biosphere, hydrosphere, and lithosphere. References: a<sup>31</sup>, b<sup>32</sup>, c<sup>31,42</sup>, d<sup>43</sup>, e<sup>31,33-36,43-47</sup>, f<sup>48</sup>, g<sup>17</sup>, h<sup>49</sup>, i<sup>50</sup>, j<sup>51</sup>, k<sup>39,52</sup>, l<sup>28,53,54</sup>, m<sup>27</sup>, n<sup>55-57</sup>.

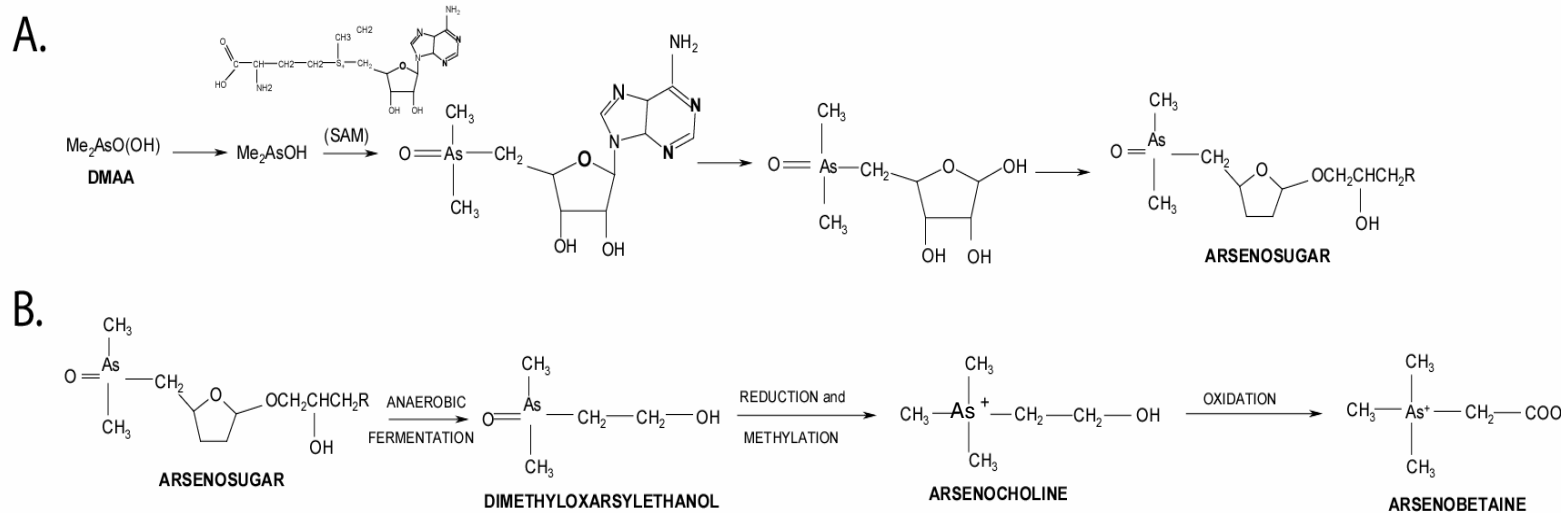


Figure 2. Possible biochemical pathways in which arsenate is substituted for phosphate. Arsenate has biochemical properties in common with phosphate, allowing its use in biochemical pathways. (A) Pathway from a methylarsenical to an arsenosugar. (B) A proposed pathway from arsenosugars to the other organoarsenicals commonly encountered in higher organisms. Structures after Maeda<sup>58</sup>.

When not in the dissolved phase, arsenic can exist in: 1) crystalline structures—arsenopyrite ( $\text{FeAsS}$ ), enargite ( $\text{Cu}_3\text{AsS}_4$ ), orpiment ( $\text{As}_2\text{S}_3$ ), and realgar ( $\text{As}_4\text{S}_4$ ); 2) ion exchange sites on positively charged oxide minerals and organic matter; 3) adsorbed (by inner-sphere or outer-sphere bonds) to surface sites on Fe, Al, and Mn oxides as well as sulfides; and 4) complexes with positively charged functional groups ( $\text{R-NH}_3^+$  and  $\text{R-SH}^+$ ) in organic compounds. Since arsenopyrite ( $\text{FeAsS}$ ), enargite ( $\text{Cu}_3\text{AsS}_4$ ), orpiment ( $\text{As}_2\text{S}_3$ ), and realgar ( $\text{As}_4\text{S}_4$ ) are redox-sensitive minerals, oxidative dissolution of these minerals can result in the release of aqueous-phase arsenic into the environment<sup>16,24,59</sup>. Since the ion exchange sites on oxide minerals and organic matter are pH dependent, an increase in soil solution pH causes the surfaces of these particles to become more negatively-charged, resulting in desorption of arsenate (arsenite actually adsorbs more strongly at basic pH)<sup>28</sup>. Desorption of arsenate from oxide and sulfide surfaces may be facilitated by ligand exchange or the introduction of competing ligands such as  $\text{PO}_4^{3-}$ <sup>60</sup>. Thus, solid-phase arsenate can transfer to the dissolved phase through redox-driven dissolution (oxidative dissolution of sulfides, reductive dissolution of metal oxides) and desorption by ion exchange or ligand exchange.

### **Role of Microbes in Biogeochemical Cycling**

Extensive research has been devoted to quantifying the role of microbes and higher organisms in the biogeochemical cycling of arsenic in the environment. Popular topics of research include arsenic uptake<sup>61</sup>; biotransformation to inorganic and organic species<sup>31,33,34,36,37,43-47,62-64</sup>; distribution and bioaccumulation in the food web<sup>49,65</sup>; and tolerance and resistance in soil microbes<sup>66</sup>. As a result of this research, microbes have been identified as driving forces in transformations of arsenic in the environment. Microbes participate in five primary reactions with environmental arsenic—mineralization, immobilization, redox, solubilization, and methylation reactions<sup>4</sup> (Figure 3).

A microbial cell may interact with environmental arsenic by both direct and indirect means. Direct interactions with environmental arsenic correspond to any actions that cause

arsenic to enter or leave the cell interior or systemic circulation. Arsenic may enter a microbial cell through two primary mechanisms, passive uptake and immobilization. In passive uptake, as the name implies, the cell does not expend any energy to bring in arsenic. Rather, arsenic enters the cell by diffusion through the cell wall or in association with cations being transported across the membrane. Immobilization refers to the transformation of inorganic arsenic species to organic arsenic species such as arsenocholine, arsenobetaine, and arsenosugars that may become part of organism biomass or be excluded from the cell. Arsenic may leave the microbial cell through excretion or mineralization. Mineralization refers to the transformation of organic arsenic species to inorganic arsenic species during the metabolic reactions that break down organic arsenic molecules into more simple, inorganic compounds while at the same time providing the organism with energy<sup>4</sup>.

The indirect interactions of environmental arsenic with microbial cells refers to superficial reactions in which arsenic is neither used as part of a biomass-building molecule nor used for energy generation. Inorganic transformations include redox, solubilization, and methylation reactions. For instance, iron-reducing bacteria or sulfur-oxidizing bacteria can increase the dissolved load of arsenic in a system by causing the dissolution of their respective source phases (iron oxides and sulfide minerals, respectively), which then releases any associated arsenic to the overlying water column. These reactions are important to the study of arsenic bioavailability because these reactions possibly play a significant role in the flux of arsenic around the globe<sup>4</sup>.

To diminish arsenic toxicity, organisms can biotransform arsenic into less toxic organic arsenic species, and couple arsenic species conversion with export from the cell/organism<sup>67</sup>. Research on bacteria, yeast, and Archaea identified similar *ars* genome systems produced by convergent evolution; this genome is responsible for maintaining intracellular arsenic concentrations by pumping As(III) out of the cell<sup>68</sup>. The vast array of possible biochemical processes through which environmental arsenic may pass has emphasized the need for a field-based means of quantifying potentially bioavailable arsenic.

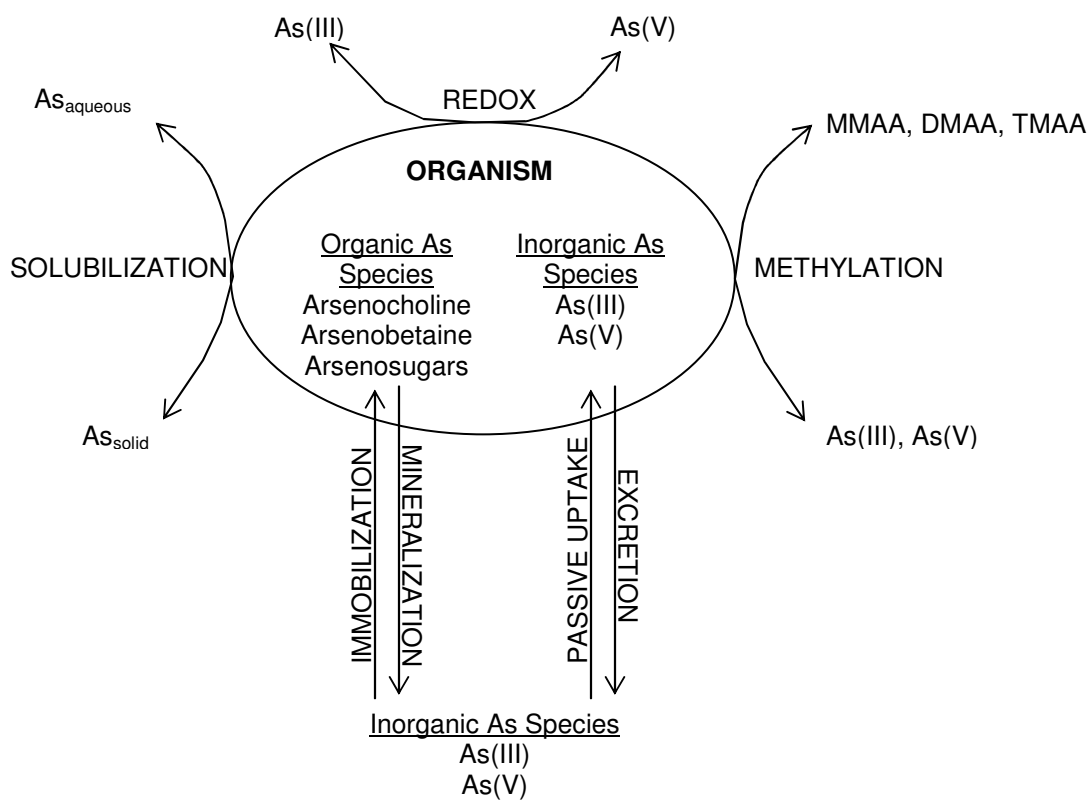


Figure 3. Conceptual diagram of the reactions involving arsenic driven by microbes and higher organisms in near surface environments.

### Quantification of Bioavailability

While there is no standardized method of measuring potential arsenate bioavailability in either laboratory or field settings, both biological and chemical methods are commonly reported in scholarly journals. Biological methods try to assess bioavailability using the concentration of arsenic taken up by an organism during growth, measured either by loss from the solution phase or growth medium. Biological studies have also used the increase in concentration within the cell, organ, or total organism to assess arsenic bioavailability. In more passive studies, bioavailability is assessed by comparing the arsenic contents of organisms from areas of high



arsenic concentration to organisms supposed to represent non-polluted, background concentrations. For instance, Farag et al.<sup>12</sup> assessed arsenic bioavailability by associating total recoverable arsenic and total dissolved arsenic concentrations with survival of fish populations, total fish biomass and biomass density, as well as tissue concentrations and individual fish's concentrations of metal-binding proteins. Similarly, identification and measurement of inorganic and organic arsenic species in terrestrial organisms such as earthworms<sup>61</sup>, vascular plants<sup>47</sup>, ants<sup>33</sup>, and radishes<sup>62</sup> have also been used in bioavailability assays. Measurement of arsenic metabolites in the environment may also be used<sup>37</sup>. However, an empirical method of measuring truly bioavailable arsenic in the environment cannot be achieved without using organisms. However, even using organisms, such as green algae, cannot provide blanket statements of availability because each species, and possibly each individual organism, has unique or characteristic uptake and exclusion mechanisms and tolerances to arsenic.

While biological methods are commonly used, there are many extraneous variables confounding the universal application of specific bioavailability indices using organisms (as previously mentioned). Operationally defined (chemical) methods of estimating chemical availability, as a proxy of bioavailability, have also been devised. Chemical methods of estimating potential arsenate bioavailability employ digestions, simple extractions, sequential extractions of sediments, and chemical leaching of particulates. Extractions target a specific bonding mechanism. Arsenic can exist in: 1) crystalline structures—arsenopyrite (FeAsS), enargite (Cu<sub>3</sub>AsS<sub>4</sub>), orpiment (As<sub>2</sub>S<sub>3</sub>), and realgar (As<sub>4</sub>S<sub>4</sub>); 2) ion exchange sites on positively charged oxide minerals and organic matter; 3) adsorbed (specifically or nonspecifically) to surface sites on Fe, Al, and Mn oxides as well as sulfides; and 4) complexes with positively charged functional groups (R-NH<sub>3</sub><sup>+</sup> and R-SH<sup>+</sup>) in organic compounds<sup>69</sup>. Thus, arsenic bound in crystalline structures is targeted using mineral dissolution techniques (reductive vs. oxidative dissolution, acid vs. base-enhanced dissolution, or ligand-enhanced dissolution). Arsenic bound to pH-dependent charged sites is targeted using ion-exchange techniques (commonly CaCl<sub>2</sub> for “plant available” arsenic). Surface adsorbed arsenic is targeted using techniques such as ligand

exchange, ligand-enhanced desorption, and chelation. Arsenic complexes with organic matter typically are destroyed using hydrogen peroxide or perchloric acid. These steps can be performed sequentially (hence, sequential extraction) to give a “complete” characterization of a soil<sup>11,69-72</sup>. However, the choice of extractant and the conditions of use are key; the target phase is frequently not the only phase to be extracted. For instance, HCl dissolves all iron oxides through kinetically controlled reactions (first dissolving the most poorly-crystalline oxides). At the same time, HCl destroys any sulfide phases present. Iron oxides and sulfides are considered the dominant controlling phases in arsenic cycling. Given that iron oxides and sulfides respond differently to changes in Eh and pH (in general, iron oxides precipitate in oxidizing conditions whereas sulfides dissolve), an extraction step that includes both elucidates little about the concentration of bioavailable arsenic that could be released with a shift in Eh/pH. Thus, sequential extractions of sediments can be of limited value in predicting bioavailable arsenic concentrations. As a result of the ambiguities inherent in using chemical extraction techniques, resins are becoming a popular means of assessing bioavailability because the mechanisms by which the arsenic binding mechanism can be determined and should cross-cut environmental boundaries without the ambiguities and uncertainties associated with the aforementioned biological and chemical methods.

## **Resins**

There is a well-developed history of use of resins and other artificial particles for removal of arsenic during metal refining and cleanup of acid mine drainage and other contaminated water bodies. Resins have also been used in bioavailability studies. For instance, Guerro et al.<sup>73</sup> tested anion and cation exchange chromatography resin as a model for the role of sediments in controlling pentachlorophenol bioavailability (both uptake and accumulation) to a freshwater clam species. However, resins are a relatively new technique in pure environmental studies of arsenic. As a result, adaptations of industrial techniques may be a good starting point in method development for the use of resins in environmental studies, specifically bioavailability studies.

As part of this method development, the following unknowns must be clarified: 1) the impact of the resins on redox/pH conditions and mineral solubility, 2) the influence of environmental pH, redox, ionic strength, mineralogy on the ability of the resins to assess bioavailable arsenic concentrations, and 3) correlations between organism uptake and resin uptake.

A number of different types of resins have been used as adsorbents of arsenic. Dambies et al.<sup>74</sup> used chitosan gel beads functionalized with molybdate to remove bulk concentrations of arsenic from low-pH (2-3) industrial effluents. Cation exchange resins using hydrous ferric and zirconium oxides as functional groups effectively removed arsenate plus phosphate and silicate from concentrated solutions of molybdate and tungstate<sup>75</sup>. Chanda et al.<sup>76</sup> studied the arsenic sorption characteristics of Dowex M4195 anion-exchange resins using two different functional groups, H<sup>+</sup> and Fe<sup>3+</sup>.

There are both advantages and disadvantages to the use of resins in field studies of potential arsenic bioavailability. Resins provide an estimate of time-integrated arsenic concentration rather than instantaneous concentrations given by water grab samples. Also, resins support the development of standardized methods because of their limited variability compared to biological organisms. For instance, when using algae as bioindicators, fluctuations in incoming light could cause cell density or mortality changes unrelated to fluctuations in arsenic. Finally, resins can be quickly and inexpensively regenerated for repeated use.

However, there are also significant disadvantages to the use of resins to estimate potential arsenic bioavailability. Resin loss, either by disintegration of the bagging or by loss during isolation of the resins from the matrix (particularly in soils), is a significant problem that will underestimate arsenic bioavailability. Also, extraction of the arsenic from the resins requires extensive post-field processing which increases the likelihood of analyte loss and/or contamination. In addition, it is possible that the introduction of the resins themselves can disrupt the local environment, causing changes that may change or intensify local transferal mechanisms such as mineral dissolution driven by redox or pH changes. Also, resins may lack specificity in adsorbing arsenic; possible competition with other anions for binding sites on the

resin surface may underestimate potential arsenic bioavailability. Finally, there are many other unknowns specific to the resin being used that have yet to be defined for many resins commonly used in metallurgical and acid mine drainage studies. The influences of ionic strength, the distribution coefficient of the resin, and the resin's effects on the mineralogy of surrounding sediments should be defined in any environmental application.

### **Research Objectives**

Dowex M4195 Fe<sup>3+</sup>-substituted chelating resin is a promising tool in field-based studies on potential arsenic bioavailability. The goal of this research is to define some of the background behavior of these resins in iron-rich environments. Thus, the objectives of this research are as follows:

1. Develop a method for the analysis of arsenate in sodium hydroxide solutions using high-pressure ion chromatography.
2. Determine the sorption efficiency of Fe<sup>3+</sup>-substituted DOWEX M4195 resins at pH 5, 6.5, and 8 and in ionic strengths of 0.001 M, 0.01 M, and 0.1 M NaNO<sub>3</sub>.
3. Determine if the adsorption of arsenic by Fe<sup>3+</sup>-substituted Dowex M4195 resins is sufficient to enhance mineral dissolution/weathering of arsenic-bearing ferrihydrite.
4. Determine if the pH of the arsenate-bearing ferrihydrite suspension influences the dissolution/weathering rate of arsenic-bearing ferrihydrite in the presence of Fe<sup>3+</sup>-substituted Dowex M4195 resins.
5. Verify that the dissolved/resin-sorbed arsenic concentrations are proportional to the arsenic-bearing ferrihydrite concentration.
6. Determine if the solution ionic strength influences the dissolution/weathering rate of arsenic-bearing ferrihydrite and subsequent adsorption of aqueous arsenate by Fe<sup>3+</sup>-substituted Dowex M4195 resins.

### **Project Implications**

Dowex M4195 Fe<sup>3+</sup>-substituted anion exchange resins have been used in the South Texas Uranium Mining District in an attempt to quantify potential arsenic bioavailability in different geologic environments<sup>77</sup>. These environments contain different concentrations of ferric oxyhydroxides. After the experiments were concluded, questions were raised about the behavior of iron oxyhydroxides in conjunction with the resins and the source from which the resin-bound arsenic was being obtained. The experiments reported in this paper will define the interactions between arsenic-bearing ferrihydrite and Dowex M4195 Fe<sup>3+</sup>-substituted chelating resins. As a result, more definitive statements may be made concerning the potential bioavailability of arsenic coprecipitated with ferric oxyhydroxides as estimated by Dowex M4195 Fe<sup>3+</sup>-substituted chelating resins in field experiments.

## DEVELOPMENT OF A HIGH-PRESSURE LIQUID CHROMATOGRAPHY METHOD FOR THE ANALYSIS OF ARSENATE IN SODIUM HYDROXIDE SOLUTIONS

### Introduction

Chanda et al.<sup>76</sup> demonstrated that nearly 100% of adsorbed arsenate is stripped from Dowex M4195 iron-substituted chelating resins using 1.0 M NaOH. As stated previously, sodium interference (presenting as flames and smoke within the tube) prevents the use of even 0.1 M sodium hydroxide eluent for resin stripping when using graphite furnace atomic absorption spectroscopy.  $\text{NH}_4\text{OH}$  as stripping eluent circumvents chemical interference in the graphite tube but has low (~40% found by Chanda et al.<sup>76</sup>, ~25% found by Lake<sup>77</sup>) stripping efficiency. Improved stripping efficiency is required in order to increase the accuracy of mass balance calculations used to assess the precision and accuracy of the chosen method. Ion chromatography is a common technique for the separation of arsenic species, frequently used in tandem with an element-specific detector such as HG-AAS or ICP-MS to achieve part per trillion (ppt) detection limits<sup>64,78-80</sup>. Therefore, the goal of this study is the development of a method for analysis of total arsenate using high-pressure liquid chromatography with minimized interferences from the designated stripping eluent (NaOH).

Our studies on the potential bioavailability of arsenic in fresh surface waters required a method of analysis that was sensitive to low part per billion levels. Existing methods in our laboratory suffered from several inadequacies. Anodic stripping voltammetry 1) required the handling and disposal of mercury, 2) used long sample analysis times, 3) was insufficiently sensitive, 4) required manual sample change-out, and 5) was incapable of multi-element detection. Graphite furnace atomic absorption spectroscopy (GF-AAS) was determined to be a better method for the analysis of arsenic in aqueous solutions. Advantages included relatively short sample analysis time (<2 minutes per analysis), small sample volumes (2 mL), and allowed multi-element determination. Disadvantages included: 1) required expensive ultrapure  $\text{HNO}_3$  as carrier solution, 2) sodium interference produced flames and smoke within the tube, causing

accelerated degradation of the graphite tube (effectively shortening the life of the graphite tube), and 3) required expensive modifiers such as nickel or palladium to minimize interferences with other elements in solution. Hydride generation atomic absorption spectroscopy (HG-AAS) was not available in our analytical laboratory.

Dowex M4195 iron-substituted chelating resin is a promising tool in field-based studies on potential arsenic bioavailability. Since 1.0 M NaOH is the most efficient stripping solution for this resin, the Dionex DX-600 high-pressure liquid chromatography system with anion exchange separation columns potentially provides a new method for the quantification of arsenic in sodium hydroxide matrixes. Thus, the objective of this research was to develop a method for the analysis of arsenate in sodium hydroxide as well as sodium nitrate solutions using high-pressure ion chromatography.

## **Materials and Methodology**

### ***Reagents***

All reagents were analytical grade or better. A 9.91 M NaOH stock solution was prepared using double-distilled water. Fresh ppb-level arsenate standards were prepared daily from 50 ppm arsenate stock solutions made using  $\text{Na}_2\text{HAsO}_4 \cdot 7\text{H}_2\text{O}$  and appropriately-diluted NaOH solutions.

### ***Instrumentation/Equipment***

The high-pressure liquid chromatography system consisted of a DX600 Ion Chromatograph with a CD25 Conductivity Detector and a GP50 Gradient Pump (Dionex, Sunnyvale, CA, USA; Appendix I). Background electrolyte conductivity was suppressed via an Anion Atlas Electrolytic Suppressor (AAES). An IonPac® AS14 4x250 mm analytical column and an IonPac® AG14 4x50 mm guard column were used for sample separations. High purity helium (Botco, Bryan, TX) provided backpressure. Sample volumes of 1000  $\mu\text{L}$  were introduced automatically using a Dionex AS40 Automatic Sampler. The sample loop volume used was 200

$\mu\text{L}$  to ensure maximum peak detection. Standards and samples were analyzed in triplicate. *Peaknet* chromatography software (Dionex) was used for data manipulation.

### ***Preliminary Choice of Conditions***

The purpose of using the following preliminary conditions was 1) identify non-optimum occurrences such as overlapping of signal peaks with other anions or the occurrence of overly-wide peaks; and 2) to evaluate the need for modifying the initial parameters. Initial analyses used an eluent composed of 3.5 mM  $\text{Na}_2\text{CO}_3$  and 1.0 mM  $\text{NaHCO}_3$  and a flow rate of 1.2 mL/min as used in the Dionex Consumables Quality Assurance testing reported with the AS/AG 14 chromatography columns. The conductivity suppressor was set at 33 mA as suggested by the *Peaknet* software based on eluent component concentrations. A 200  $\mu\text{L}$  sample loop volume with 0.8 mL injection volume (4x sample loop volume) was used to provide maximum sample volume introduction in order to increase response.

## **Results and Discussion**

### ***Chromatogram of 1.0 M NaOH***

Figure 4 shows a typical chromatogram of a 1.0 M NaOH solution using 3.5 mM  $\text{CO}_3^{2-}$ /1.0 mM  $\text{HCO}_3^-$  eluent, 200  $\mu\text{L}$  sample loop, 1.0 mL sample volume, and background conductivity suppression of 33 mA. Notice that the peak plateaus at approximately 2700  $\mu\text{S}$ . Passage of 1.0 M NaOH through the column produces a wide (4 minutes duration), chair-shaped peak. After passage of the peak, the baseline is depressed as the suppressor overcompensates for the background conductivity.

The background suppressor was not designed to handle greater than 150 milliequivalents of charge. In order to use the recommended NaOH concentration, a number of modifications to the stripping eluent and IC method were suggested: 1) separation without suppression (turn off the background conductivity suppressor); 2) decrease the sample volume;



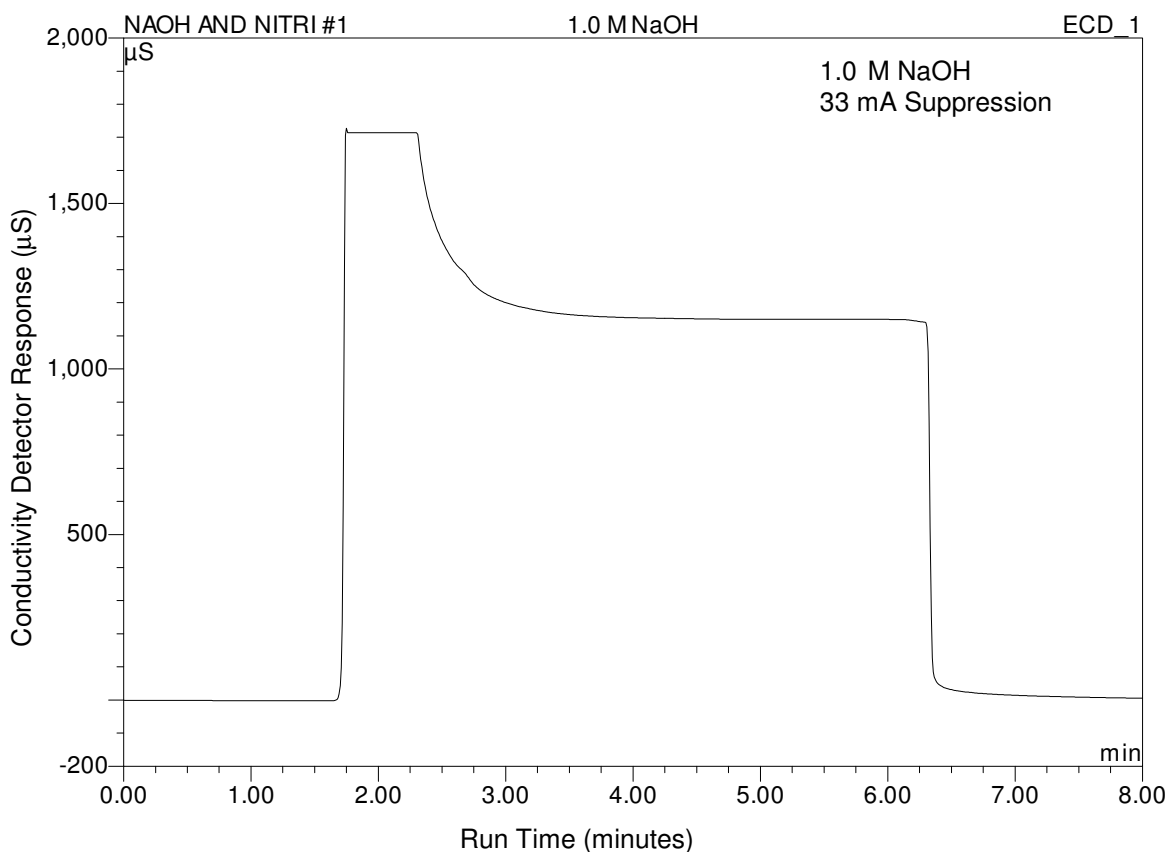


Figure 4. Chromatogram of 1.0 M NaOH in 3.5 mM  $\text{CO}_3^{2-}$ /1.0 mM  $\text{HCO}_3^-$  with background conductivity suppression of 33 mA.

3) neutralize  $\text{OH}^-$  with ultrapure  $\text{HNO}_3$ ; 4) neutralize  $\text{OH}^-$  using  $\text{H}^+$ -saturated cation-exchange resins.

### ***Separation without Suppression***

Because the background conductivity suppressor was not designed to handle more than 150 milliequivalents of charge (1.0 M NaOH = 1000 meq charge), separation and analysis was attempted without background noise suppression. As the 1.0 M NaOH solution passed through the column, the baseline was first depressed then rapidly increased (Fig. 5). Return to flat, horizontal baseline did not occur in the allotted twenty-minute run time. Under this condition, the arsenate peak was not distinguished from background noise. Because of the low detection limits

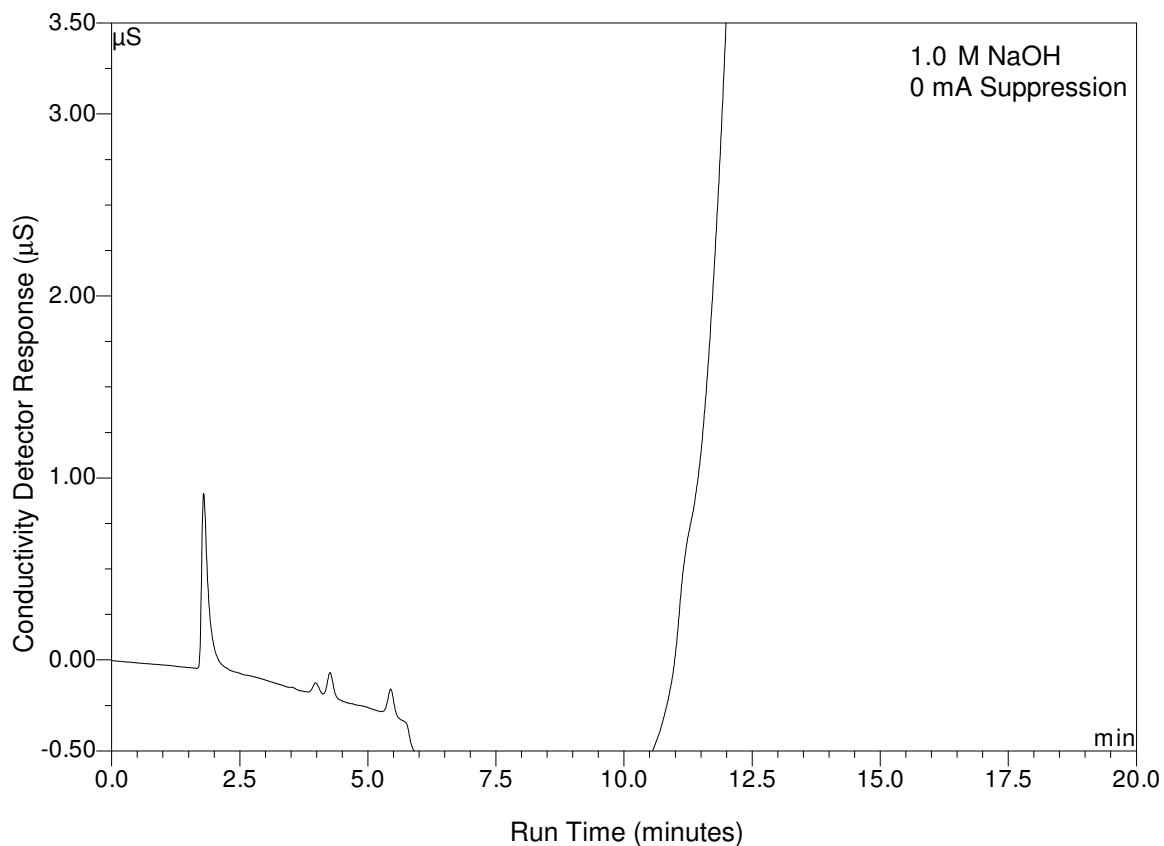


Figure 5. Chromatogram of 1.0 M NaOH in 3.5 mM  $\text{CO}_3^{2-}$ /1.0 mM  $\text{HCO}_3^-$  without background conductivity suppression.

required (ppb range) for arsenate, the use of unsuppressed ion-chromatography was rejected as a suitable method for arsenate analysis in sodium hydroxide solutions.

### ***Decreased Sample Volume***

The sample loop length controls the volume of sample entering the column; although approximately four-times the sample loop volume is injected into the system, only the volume in the sample loop is actually injected into the column. Thus, the sample loop volume was decreased in order to decrease the effective concentration of sodium hydroxide entering the column. The chromatograms produced by decreasing the sample loop volume are shown in

Figures 6 and 7. As expected, the peaks decreased in magnitude with decreasing sample loop volume. Although the peaks associated with the sodium hydroxide were diminished, the arsenate peak was also diminished. Thus, decreasing the sample loop volume increased the limits of detection. Again, the low detection limits required for surface water analyses prevented using decreased sample loop volume as a viable option for analysis of arsenate in sodium hydroxide matrices.

### ***Neutralization of Sample Conductivity***

Because the background conductivity suppressor was not designed to handle more than 150 milliequivalents of charge (1.0 M NaOH = 1000 meq charge), neutralization of sample conductivity was attempted as a pretreatment step prior to analysis by HPLC. To lower the overall negative charge of the sample, ultrapure HNO<sub>3</sub> was added to the sample prior to introduction. The following calculation was used to determine the volume of ultrapure 15.9 M HNO<sub>3</sub> required to neutralize 10 mL of 1.0 M NaOH:

$$10 \text{ mL sample} * \frac{1.0 \text{ mol NaOH}}{1000 \text{ mL}} * \frac{1.0 \text{ mol OH}^-}{1.0 \text{ mol NaOH}} = \chi \text{ mL HNO}_3 * \frac{15.9 \text{ mol HNO}_3}{1000 \text{ mL}} * \frac{1.0 \text{ mol H}^+}{1.0 \text{ mol HNO}_3}$$

$$10 \text{ mol OH}^- = \chi \text{ mL HNO}_3 * 15.9 \text{ mol H}^+$$

$$\frac{10 \text{ mol OH}^-}{15.9 \text{ mol H}^+} = \chi \text{ mL HNO}_3$$

$$\chi = 0.63 \text{ mL HNO}_3$$

Figure 8 shows the chromatogram for a theoretical neutralization of 10 mL 1.0 M NaOH with 0.63 mL 15.9 M HNO<sub>3</sub> (ultrapure). Although the second plateau was significantly lowered, the

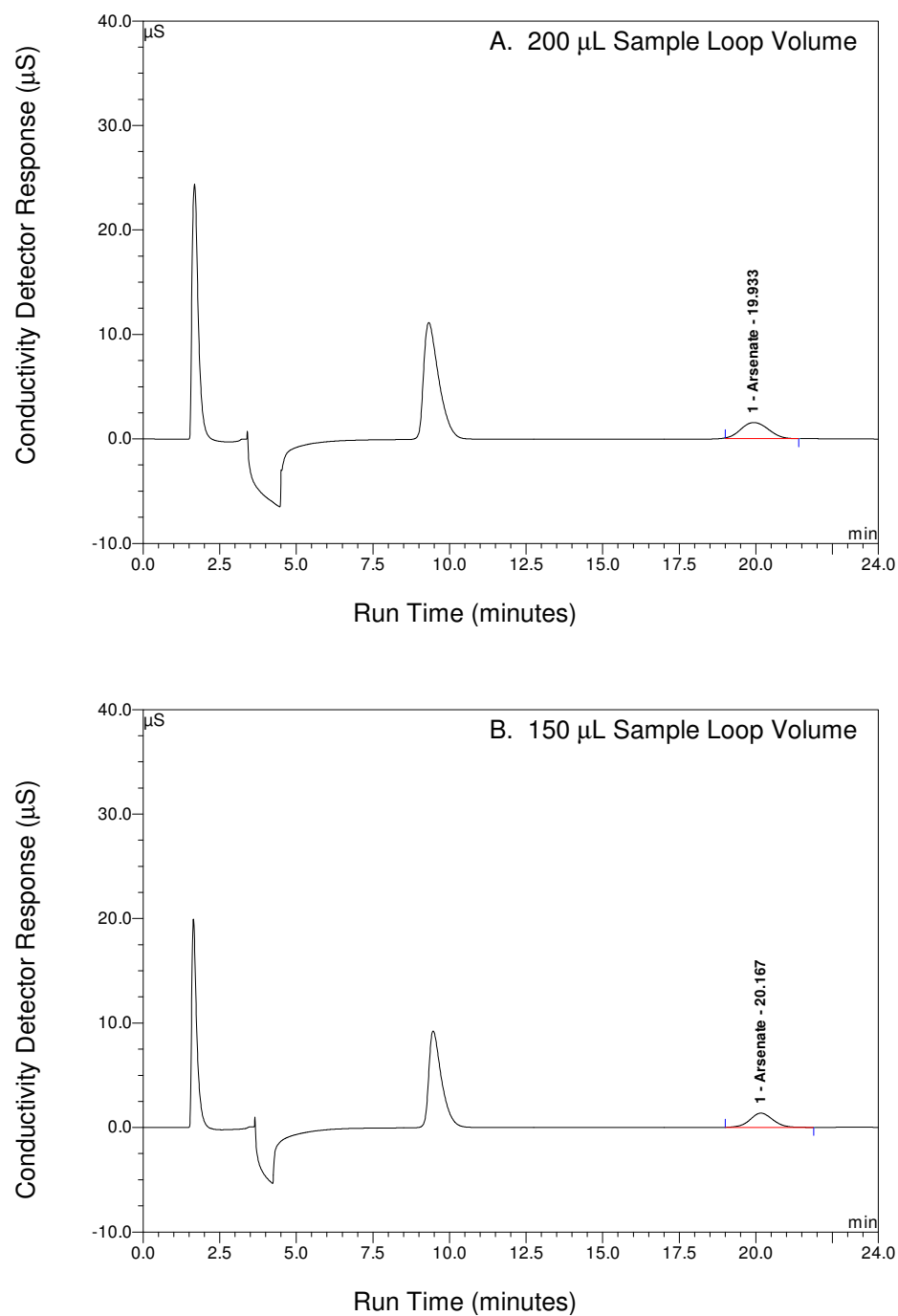


Figure 6. Chromatogram of 0.1 M NaOH in 3.5 mM  $\text{CO}_3^{2-}$ /1.0 mM  $\text{HCO}_3^-$  with background conductivity suppression showing the change in arsenate peak area caused by using a 200 µL sample loop volume (A) and 150 µL sample loop volume (B).

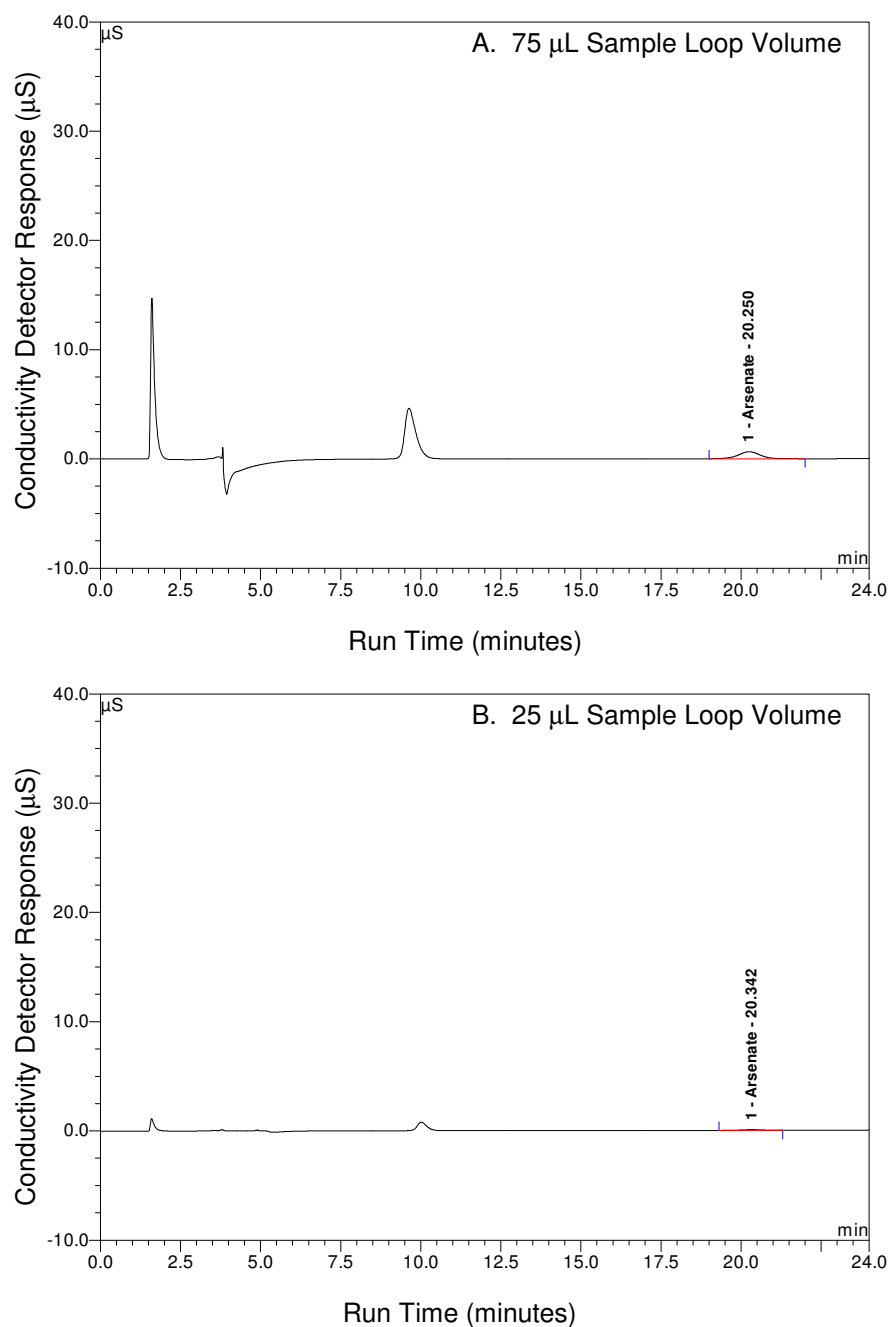


Figure 7. Chromatogram of 0.1 M NaOH in 3.5 mM  $\text{CO}_3^{2-}$ /1.0 mM  $\text{HCO}_3^-$  with background conductivity suppression showing the change in arsenate peak area caused by using a 75  $\mu\text{L}$  sample loop volume (A) and 25  $\mu\text{L}$  sample loop volume (B).

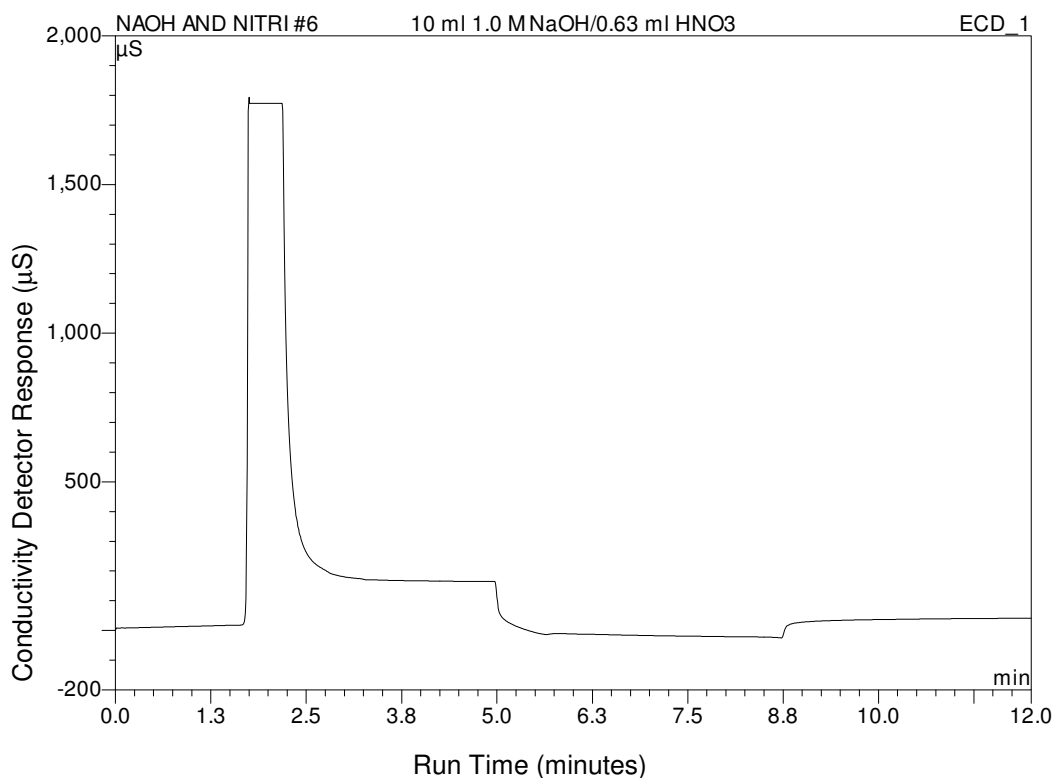


Figure 8. Chromatogram of 10 mL 1.0 M NaOH neutralized with 0.63 mL ultrapure  $\text{HNO}_3$ , showing continued baseline disruption.

main peak was not diminished. The persistent baseline disruption prevented the use of 0.63 mL  $\text{HNO}_3$  as a viable option for analysis of arsenate in sodium hydroxide matrices.

Cation-exchange resins were also tried as a means of reducing overall sample conductivity. It was theorized that  $\text{Na}^+$  in the NaOH solutions would be replaced by  $\text{H}^+$  from the cation-exchange resins; the  $\text{H}^+$  would then combine with  $\text{OH}^-$  to form  $\text{H}_2\text{O}$ . Figure 9 shows both an untreated 0.1 M NaOH solution (Figure 9A) and a 0.1 M NaOH sample passed through a cation-exchange column prior to introduction to the chromatograph (Figure 9B). None of the peaks corresponded exactly. The large peak at 11 minutes may correspond to the arsenate peak (based upon proximity of retention time and peak magnitude). However, the broad peak at 23 minutes is more characteristic of arsenic and more closely matches the retention time

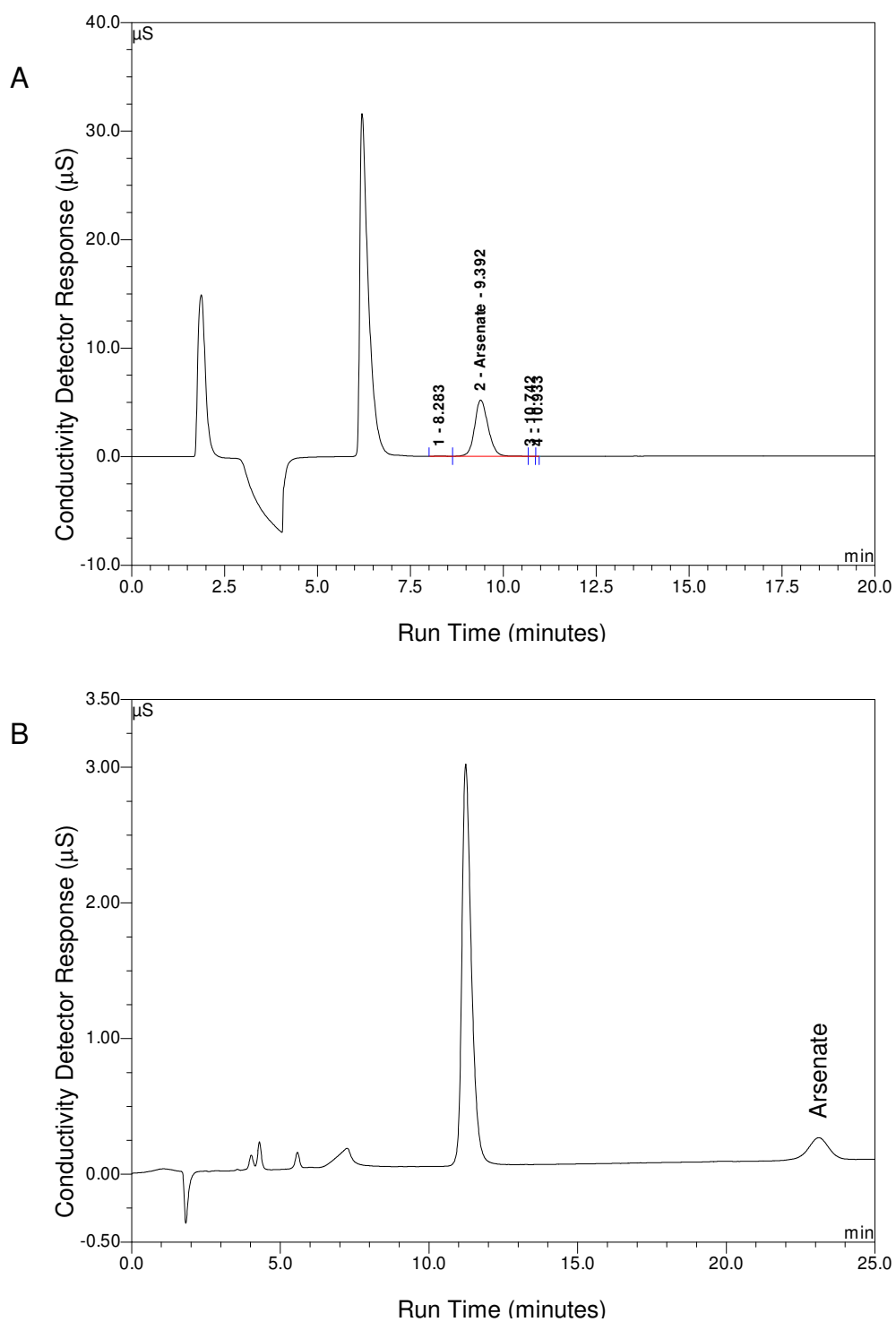


Figure 9. Comparison of chromatograms produced with and without the use of cation-exchange resins for lowering overall sample conductivity. A. Chromatogram of 0.1 M NaOH containing 25 ppm  $\text{AsO}_4^{3-}$ . B. Chromatogram of 0.1 M NaOH containing 25 ppm  $\text{AsO}_4^{3-}$  passed through an SCX cation-exchange column prior to sample introduction.

predicted by column simulation software. Since both peaks consistently occur in both blank and arsenic-spiked samples, a calibration curve would have to be produced. The peak producing the best fit would be defined as the arsenate peak. This calibration with cation-exchange treatment was not attempted for a number of reasons. First, dilution from the hydration and flushing water used in the SCX columns caused dilution and peak diminution. Second, there were concerns that optimal exchange required the use of new SCX columns for each sample (i.e., the SCX column had to be recharged after each sample). The large number of samples (>450) would have made this an extremely time-consuming task. It was determined that the potential benefits from using the SCX columns (possible minimization of baseline disruption and background noise) did not outweigh the disadvantages of this new method alteration and was rejected as a viable option for analysis of arsenate in sodium hydroxide matrices.

### **Summary and Conclusions**

Sodium hydroxide is the most effective eluent used to strip arsenate from Fe<sup>3+</sup>-substituted Dowex M4195 chelating resins. Nearly 100% stripping efficiency was achieved by Chanda et al.<sup>75</sup> using 1.0 M NaOH. Thus, method development was attempted for analysis of arsenate using anion-exchange high pressure ion chromatography. However, introduction of 1.0 M NaOH into the system caused a chair-shaped baseline disruption of more than 4 minutes duration. The background conductivity suppressor was not designed to suppress more than 150 milliequivalents of charge. A number of potential fixes to this problem were tested, including 1) separation and analysis without background conductivity suppression, 2) decreased sample volume through a shorter sample loop, and 3) neutralization of sample conductivity using ultrapure nitric acid and cation exchange cleanup columns. Attempts at arsenate analysis without using background conductivity suppression were unsuccessful. Passage of 1.0 M NaOH through the column caused significant baseline disruption. An arsenate peak was not distinguished in these unsuppressed chromatograms. Return to “normal” baseline (a flat, horizontal line at 0 meq specific conductance) was not achieved within a 30-minute run time.



Thus, analysis of arsenate without background conductivity suppression was not considered a viable solution.

The second method adjustment involved decreasing the sample loop volume, which controls the actual volume of sample injected into the separatory column. Decreasing the sample loop volume (tested at 200, 150, 75, and 25 mL) decreased the peak responses. However, because arsenate is not highly electronegative, arsenate produced small peaks initially, which were further diminished by decreasing the sample loop volume. The current research required low-ppb detection limits, which could not be achieved with shortened sample loops.

The third method adjustment involved attempting to decrease the overall sample conductivity by either neutralizing  $\text{OH}^-$  with  $\text{H}^+$  or replacing  $\text{Na}^+$  with  $\text{H}^+$  (which would also neutralize  $\text{OH}^-$ ). Neutralization of  $\text{OH}^-$  with  $\text{H}^+$  in the form of  $\text{HNO}_3$  (required volume based on a mole per mole basis) diminished, but did not remove, the chair-shaped peak and caused significant baseline displacement. The arsenate peak still could not be distinguished. Cation-exchange resins were also used as a means of lowering the overall sample conductivity. It was thought that the SCX resins would exchange  $\text{Na}^+$  for  $\text{H}^+$ , which would then neutralize  $\text{OH}^-$ . While the large-magnitude NaOH peaks were removed, the presence of new peaks with different retention times made interpretations ambiguous.

The goal of this research was development of a method of analyzing arsenate in sodium hydroxide solutions using anion-exchange HPLC. Attempts to modify sample treatment and analysis failed to overcome equipment disruptions caused by using concentrated sodium hydroxide (1.0 M). Therefore, it was decided that 0.1 M NaOH solutions would be used in future experiments as the resin extractant. This ten-fold decrease in sodium hydroxide concentration diminished system disruptions enough to obtain reliable analyses while also achieving sufficiently low ppb detection limits.

**POTENTIAL ARSENATE BIOAVAILABILITY FROM ARSENIC-BEARING FERRIHYDRITE AS  
ESTIMATED BY DOWEX M4195 Fe<sup>3+</sup>-SUBSTITUTED CHELATING RESINS**

**Introduction**

Arsenic is a common natural and anthropogenic contaminant in sediments, surface waters, and ground waters. Recent changes in water quality standards concomitant with greater understanding of arsenic toxicity have increased the necessity for methods of determining potentially bioavailable arsenic in field environments.

Bioavailability refers to the concentration of a target chemical that actually enters the systemic circulation of an organism from an administered dose<sup>81</sup> (commonly considered the total concentration of the chemical present in the organism's habitat or environment). It is generally assumed that dissolved phases are most bioavailable. Resins provide an estimation of the concentration of bioavailable arsenic by adsorbing solution-phase arsenic. Because resins generally remain in the field for extended periods of time, they provide a time-integrated, average available arsenic concentration. Dowex M4195 Fe<sup>3+</sup>-substituted chelating resin has been used successfully to measure dissolved arsenate in field experiments<sup>77</sup>. However, because the technique was adapted from acid mine drainage studies that were purely interested in maximum arsenic removal from solution, the influence of a number of geochemical master variables were unknown.

Given that resins can be left in the field for an extended period of time, it rapidly becomes unclear which phases in the environment are being sampled. Certainly, dissolved concentrations are being accounted for with total resin arsenate concentration. However, it is possible that arsenic adsorbed to or precipitated with poorly-crystalline or soluble minerals could also be contributing to the total arsenic bound to the resins. It is possible that the resins can strip arsenic from mineral surfaces or cause dissolution of acid-sensitive minerals. Given that

iron oxides generally control arsenic speciation in near-surface environments, the interactions between arsenic, iron, and Fe<sup>3+</sup>-substituted M4195 resins are very important.

It is commonly reported that iron, when present in the environment, controls the mobility, fate, and bioavailability of aqueous arsenic by converting bioavailable arsenite and arsenate species to immobilized forms adsorbed or coprecipitated in iron oxides. Iron oxides are commonly found as colloidal precipitates in surface and ground waters as well as coatings/films on pre-existing surfaces. Naturally occurring arsenic-bearing iron oxides include scorodite (FeAsO<sub>4</sub>·2H<sub>2</sub>O), pitticite (Fe<sup>III</sup>-SO<sub>4</sub>-As<sub>2</sub>O<sub>5</sub>-H<sub>2</sub>O), and amorphous Fe<sup>III</sup> arsenate (FeAsO<sub>4</sub>·xH<sub>2</sub>O). Arsenic is also commonly found coprecipitated with and/or sorbed to the surfaces of ferrihydrite, goethite, and schwertmannite. During coprecipitation, arsenic disrupts the crystalline structure of iron oxide minerals and causes mineral degradation<sup>82</sup>.

Arsenic interacts with ferric oxyhydroxide minerals through a number of different mechanisms, including inner-sphere bonds, outer sphere bonds, ligand-exchange reactions, and coprecipitation/inclusion reactions. Arsenate forms bidentate inner sphere bonds with 4 oxygens on the oxide surface<sup>83</sup>. Fendorf and others<sup>84</sup> demonstrated that, as the percent surface coverage increases, the predominant bonding mechanism changes from monodentate to bidentate. After arsenic binds to the ferric oxyhydroxide surface, a new layer of ferric oxyhydroxide can precipitate around the particle, thus blurring the boundary between coprecipitation *sensu strictu* and adsorption. However, laboratory experiments cannot exactly model arsenic interactions with natural ferric oxyhydroxides, given that natural hydrous ferric oxides are intercomplexed with natural organic matter, common cations, and trace metals and may have different mobilities and sorbent properties from lab-made iron oxyhydroxides<sup>85</sup>.

Iron oxides can release arsenic as well as demobilize arsenic. Processes which can release arsenic into the environment include competition with other inner-sphere-bond-forming oxyanions (predominantly PO<sub>4</sub><sup>3-</sup>)<sup>86</sup>, changes in crystallinity and mineral stability which can exclude arsenic from the crystal lattice, and reductive dissolution by pure redox changes or microbial metabolism<sup>39,52</sup>. Desorption by increasing positive surface charge on iron oxides with

increasing pH also releases free arsenic to the environment<sup>28,53,54</sup>. These processes contribute to the total concentration of potentially bioavailable arsenic in the environment.

Dowex M4195 iron-substituted chelating resin is a promising tool in field-based studies on potential arsenic bioavailability, especially in iron-rich environments. The goal of this research is to provide some of the background behavior of these resins in iron-rich environments. Thus, the objectives of this research are as follows:

1. Determine the sorption efficiency of Fe<sup>3+</sup>-substituted DOWEX M4195 chelating resins at pH 5, 6.5, and 8 and in ionic strengths of 0.001 M, 0.01 M, and 0.1 M NaNO<sub>3</sub>.
2. Determine if the adsorption of arsenic by Fe<sup>3+</sup>-substituted Dowex M4195 chelating resins is sufficient to enhance mineral dissolution/weathering of arsenic-bearing ferrihydrite.
3. Determine if the pH of the arsenate-bearing two-line ferrihydrite suspension influences the dissolution/weathering rate of arsenic-bearing ferrihydrite in the presence of Fe<sup>3+</sup>-substituted Dowex M4195 chelating resins.
4. Verify that the dissolved/resin-sorbed arsenic concentrations are proportional to the arsenic-bearing ferrihydrite concentration.
5. Determine if the solution background electrolyte concentration influences the dissolution/weathering rate of arsenic-bearing ferrihydrite and subsequent adsorption of aqueous arsenate by Fe<sup>3+</sup>-substituted Dowex M4195 chelating resins.

This paper describes a lab-based experiment in assessing the potential bioavailability of arsenic from arsenic-bearing ferrihydrite as measured by Dowex M4195 Fe<sup>3+</sup>-substituted chelating resins. The primary variables manipulated were ferrihydrite suspension pH, ferrihydrite suspension concentration, and background ionic strength.

## **Materials and Methodology**

### ***Reagents***

Ultrapure water of conductivity <18.2 mΩ/cm was obtained from a Nanopure deionization system. Sodium arsenate, sodium nitrate, and sodium hydroxide solutions were

analytical grade or better. Chromatography eluents were prepared by dilution of stock solutions of 0.5 M carbonate anion eluent concentrate (P/N 037161, Dionex) and 0.5 M bicarbonate anion eluent concentrate (P/N 037163, Dionex) with Nanopure water. Eluents were degassed for 30 minutes by sonication.

### ***Instrumentation/Equipment***

The high-pressure ion chromatography system consisted of a DX600 Ion Chromatograph with a CD25 Conductivity Detector and a GP50 Gradient Pump (Dionex, Sunnyvale, CA, USA). Background electrolyte conductivity suppression was obtained using an Anion Atlas Electrolytic Suppressor (AAES). An IonPac® AS14 4x250 mm analytical column and an IonPac® AG14 4x50 mm guard column were used in all sample separations. High purity helium (Botco, Bryan, TX) provided backpressure. Sample volumes of 1000  $\mu\text{L}$  were introduced automatically using a Dionex AS40 Automatic Sampler. The sample loop volume used was 200  $\mu\text{L}$  to ensure maximum peak detection. All standards and samples were analyzed in triplicate. *Peaknet* chromatography software (Dionex) was used for data manipulation.

Samples were divided into 4 subgroups according to sample matrix (0.001 M  $\text{NaNO}_3$ , 0.01 M  $\text{NaNO}_3$ , 0.1 M  $\text{NaNO}_3$ , and 0.1 M  $\text{NaOH}$ ). Eluent carbonate and bicarbonate

**Table 1.** Optimized parameters for the measurement of arsenate using DX-600 anion-exchange chromatography system.

Matrix	Carbonate (mM)	Bicarbonate (mM)	Suppressor Conductivity (mA)	Flow Rate (mL/min)	Run Time (min)
0.001 M $\text{NaNO}_3$	2.8	0.78	26	1.2	17.5
0.01 M $\text{NaNO}_3$	2.4	0.1	23	1.75	18
0.1 M $\text{NaNO}_3$	2.4	0.1	23	1.75	18
0.1 M $\text{NaOH}$	3.5	1	47	1.75	10

concentrations were adjusted to provide good separation of the large-magnitude nitrate and phosphate peaks from the arsenate peak. See Table 1 for optimized run conditions.

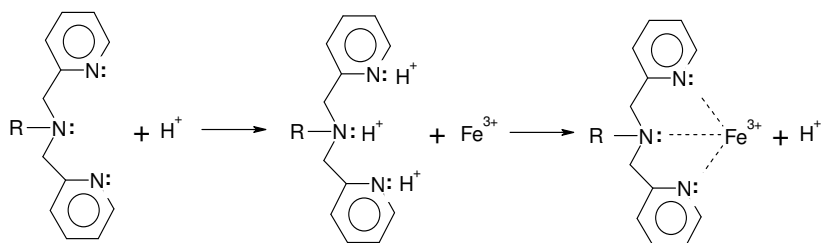
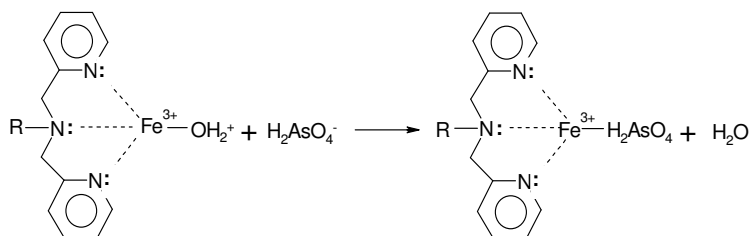
### ***Preparation of M4195 Resin Sorbent***

Dowex M4195 Fe<sup>3+</sup>-substituted chelating resin was selected as the sorbent used for potential bioavailability estimates in this study. Resin properties included a styrene-divinylbenzene macroporous matrix with bis-picolamine functional groups. Dowex M4195 was iron-saturated using a modified method after Chanda<sup>76</sup> and Lake<sup>77</sup>. A large mass of M4195 resin was initially conditioned by rinsing twice with an excess of double distilled water then was converted to its acidic form by treatment with 2 M HCl for 10 min at 100 rpm to activate the resin. Then, the resin was rinsed with double distilled water until the residual water was near reached pH 2. M4195 was loaded with Fe<sup>3+</sup> by washing with an excess of 0.09 M FeCl<sub>3</sub>·6H<sub>2</sub>O (pH 2), once for 10 minutes and again for 20 hours, at 110 rpm to chelate Fe(III) which became the new functional group (Figure 10A). The Fe<sup>3+</sup>-loaded resins were then rinsed twice with pH 2 double distilled water and three times with pH 8 double distilled water to remove excess iron and slowly raise the residual pH of the resins to minimize iron oxide precipitation. Because the pH of the residual water continued to be approximately pH 2 after these washes, the resins were doubly-enclosed in fine-mesh polypropylene bags and continually washed with ambient pH distilled water. Final pH adjustments to the resins were attempted by washing repeatedly for 10 minutes (110 rpm) in double-distilled water of the desired pH. Final solution pH of the resins was 4.11.

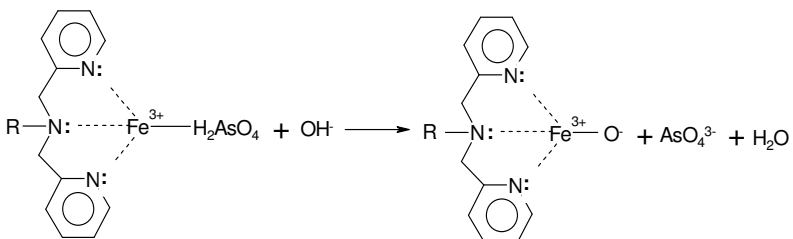
### ***Sorption and Extraction Efficiency***

Sorption efficiency of Fe<sup>3+</sup>-substituted M4195 chelating resin was determined for As(V) as a function of pH and sodium nitrate concentration to ascertain possible interferences. All experiments were carried out in batch at room temperature. According to Chanda et al.<sup>76</sup>, arsenate sorbs to the Fe<sup>3+</sup>-substituted M4195 resin through ion exchange with hydroxyl groups (counterion to Fe<sup>3+</sup>) followed by complexation of arsenate anion to the metal cation (Figure 10B).

## A. DOWEX M4195 IRON SPECIFICATION

B. DOWEX M4195: ANION EXCHANGE WITH  $\text{H}_2\text{AsO}_4^-$ 

## C. DOWEX M4195 STRIPPING



## D. DOWEX M4195 REGENERATION

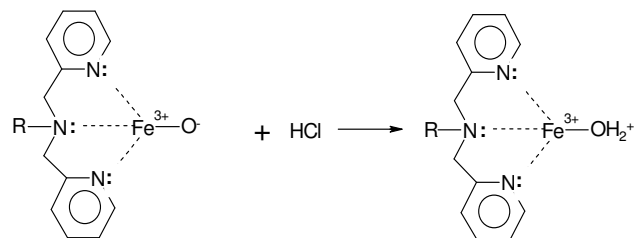


Figure 10. Reactions occurring during the use of Dowex M4195  $\text{Fe}^{3+}$ -substituted chelating resins. (A) Iron specification (chelation) of the resins, which changes the functional group from  $\text{H}^+$  to  $\text{Fe}^{3+}$ . (B) Anion-exchange reaction during sorption of arsenate. Arsenate replaces the  $\text{OH}^-$  functional group. (C) Stripping reaction by which arsenate is removed from the surface of the resin. A 0.1 M NaOH eluent has been used in these experiments. (D) Regeneration of the resin for repeated use. The hydroxide groups are protonated by washing with 2 M HCl.

Given that  $\text{FeOH}_2^+ \leftrightarrow \text{H}^+ + \text{FeOH}$  ( $\text{pK}_{a1} = 5.3$ ) and  $\text{FeOH} \leftrightarrow \text{H}^+ + \text{FeO}^-$  ( $\text{pK}_{a2} = 8.8$ ), a change in solution pH changes the functional groups on the resins, also changing the specificity for different arsenic species (arsenate at  $\text{pH} < 5.3$ , arsenite at  $\text{pH} > 5.3$ )<sup>87</sup>. In the resin sorption study, a 1:100 wet resin mass to solution volume ratio was used. To a conical bottom centrifuge tube was added 25 mL of the arsenate and nitrate standard at the desired pH. Approximately 0.25 g wet resin was added and the tube was put on the shaker at 110 rpm. An aliquot of the pre-sorption solution was saved for chromatographic analysis. After 24 hours equilibration time, the tubes were removed from the shaker. A sample of the supernatant solution was retained for chromatographic analysis. Then, the pH of the solution was measured, the resins were isolated, and the stripping procedure was started. The stripping procedure utilized a ligand-exchange reaction with hydroxide to force arsenate off the function groups of the resin beads, thus sending the bound arsenate into solution (Figure 10C). All experiments were performed in triplicate.

#### ***Preparation of Arsenic-Bearing Ferrihydrite***

Arsenic-bearing ferrihydrite calculated to contain 0.07 M As: 1 M Fe (as suggested by Ford<sup>2</sup>) was produced using an hydrolysis and precipitation method for ferrihydrite production modified from Raven et al.<sup>88</sup> To 500 mL double-distilled water was added 40 g  $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$  and 2.1618 g  $\text{Na}_2\text{HAsO}_4 \cdot 7\text{H}_2\text{O}$ . While vigorously stirring this solution in a plastic container, 310 mL 1.0 M KOH was added through a burette at a rate of approximately 100 mL/min. The suspension pH was then adjusted to pH 7.5 using 1.0 M KOH. The suspension was centrifuged at 2000 rpm for 30 minutes. The centrifugation sediment was resuspended and washed with 0.1 M NaCl three times. The centrifugation sediment was then resuspended and washed with 1.0 M  $\text{MgCl}_2$  (pH 7.5, 25 °C) for two hours to remove arsenic possibly ionically-bound to the ferrihydrite surfaces. After a double distilled water wash, the centrifugation sediment was resuspended and washed in 1.0 M  $\text{KH}_2\text{PO}_4$  (pH 7.5, 25 °C) once for 16 hours then once for 24 hours to remove any specifically-sorbed arsenate from the ferrihydrite surfaces. Following two 30-minute double distilled water washes, the precipitate was spread in an aluminum pan and dried at 60 °C for 24



hours. The dried sediment then was pulverized using a ceramic mortar and pestle to pass a 100-mesh screen (150  $\mu\text{m}$  aperture). Following this procedure, Ford characterized the sediment as arsenic coprecipitated with hydrous ferric oxide and implied no specific bonding mechanism<sup>89</sup>. Thus, the sediment produced in this experiment is referred to as arsenic-bearing ferrihydrite (AFH).

In order to determine the exact concentration of arsenate and iron in the ferrihydrite sediment, approximately 0.25 g sediment was dissolved in 10 mL 2.0 M ultrapure  $\text{HNO}_3$  by shaking for one hour at 110 rpm. Arsenate and iron analyses were performed using a Varian Instruments graphite furnace atomic absorption spectrophotometer (programs courtesy Christopher Markley, TAMU; Tables 2, 3; Appendix II).

#### ***Preparation of Reaction Chambers***

In each treatment, the arsenic-bearing ferrihydrite (AFH) sediment was resuspended by rapid stirring prior to and during transfer from the stock suspension to the centrifuge tubes. A 25 mL aliquot of the respective AFH suspension was pipetted into acid-washed conical bottom centrifuge tubes for all time periods of the treatment and control sequences. All treatments and control samples were prepared in triplicate, placed on the shaker at 110 rpm and allowed to equilibrate for 0, 1, 3, 6, 10, or 15 days. A 1:100 ratio of sorbent solid (g) to suspension or solution volume (mL) was used in all experiments. A wet mass of approximately 0.25 g resin was added to the treatment tubes.

#### ***Collection and Analysis Methodology***

After the specified reaction time, the tubes were removed from the shaker and the pH of the suspension was measured. Control suspensions (containing no resin) were filtered using 0.2  $\mu\text{m}$  polycarbonate membranes (Poretics Corporation Polycarbonate Membranes, Cat. No. 11013) and then directly analyzed in triplicate by ion chromatography. The contents of the resin-

Table 2. GF-AAS temperature program for analysis of arsenate in ferrihydrite digest.

Step	Temp (C)	Time (s)	Flow (L/min)	Gas Type	Read	Signal Storage
1	95	5.0	3.0	Normal	No	No
2	100	60.0	3.0	Normal	No	No
3	12	10.0	3.0	Normal	No	No
4	1200	5.0	3.0	Normal	No	No
5	1200	10.0	3.0	Normal	No	No
6	1200	2.0	0.0	Normal	No	Yes
7	2600	0.7	0.0	Normal	Yes	Yes
8	2600	2.0	0.0	Normal	Yes	Yes
9	2600	2.0	3.0	Normal	No	Yes
10	100	30.0	3.0	Normal	No	No

Table 3. GF-AAS temperature program for analysis of iron in ferrihydrite digest.

Step	Temp (C)	Time (s)	Flow (L/min)	Gas Type	Read	Signal Storage
1	85	5.0	3.0	Normal	No	No
2	95	40.0	3.0	Normal	No	No
3	120	10.0	3.0	Normal	No	No
4	700	5.0	3.0	Normal	No	No
5	700	1.0	3.0	Normal	No	No
6	700	2.0	3.0	Normal	No	Yes
7	2300	1.1	0.0	Normal	Yes	Yes
8	2300	2.0	0.0	Normal	Yes	Yes
9	2300	2.0	3.0	Normal	No	Yes
10	100	16.2	3.0	Normal	No	No

bearing tubes were poured through a fine-mesh nylon screen to isolate the resins from the AFH suspension. The resins were immediately rinsed twice with 50 ml Nanopure water for 10 minutes at 110 rpm. Following these rinses, the resins were extracted twice using 10 mL 0.1 M NaOH (resin eluent) for 24 hours at 100 rpm. The resin eluent was directly analyzed in triplicate by ion chromatography. Estimated dissolved arsenate in solution as estimated by the concentration of resin-bound arsenate was calculated using the following equation:

$$\text{mmol AsO}_4^{3-} / \text{L} = \frac{E_V * T_S}{S_V * FW_{As} * EF_{Ave} * 10^6}$$

where  $E_V$  = resin eluent volume (mL),  $T_S$  = total resin eluent  $\text{AsO}_4^{3-}$  concentration (ppb),  $S_V$  = suspension volume (L),  $\text{FW}_{\text{As}}$  = formula weight of  $\text{AsO}_4^{3-}$  (138.92 g), and  $\text{EF}_{\text{Ave}}$  = decimal value of average extraction efficiency (0.50).

### ***Treatment and Control Conditions***

Batch equilibration experiments were used to determine the concentration of arsenate released from arsenic-bearing ferrihydrite as a function of suspension pH, suspension concentration, and background electrolyte concentration.

Experiment 1 was designed to examine the influence of suspension pH on total arsenate sorption by 0.25 g wet  $\text{Fe}^{3+}$ -substituted M4195 resin. Three one-liter arsenic-bearing ferrihydrite suspensions of 0.5 g/L in 0.001 M  $\text{NaNO}_3$  were equilibrated at pH 5, pH 6.5, and pH 8, respectively, using 1% ultrapure  $\text{HNO}_3$  and 0.25 M  $\text{NaOH}$ . The suspension pH was assumed equilibrated when the pH stabilized to the desired pH after two successive shakings for 30 minutes at 110 rpm.

Experiment 2 was designed to examine the influence of ferrihydrite suspension concentration on total arsenate sorption by 0.25 g wet  $\text{Fe}^{3+}$ -substituted M4195 chelating resin. Arsenic-bearing ferrihydrite suspensions of 0.05, 0.5, and 5 g/L were equilibrated to pH 8 in 0.001 M  $\text{NaNO}_3$  background electrolyte solution.

Experiment 3 was designed to examine the influence of background electrolyte concentrations on total arsenate sorption by 0.25 g wet  $\text{Fe}^{3+}$ -substituted M4195 chelating resin. A mass of approximately 0.5 g ferrihydrite was suspended in 1 L of 0.001 M, 0.01 M, or 0.1 M  $\text{NaNO}_3$ . The pH of the suspensions were adjusted to pH 8 and assumed equilibrated after maintaining the desired pH after two successive shakings for 30 minutes at 110 rpm.

All treatment samples contained approximately 0.25 g M4195 resin. Control samples were prepared in the same way as the treatments except no resins were added.

## Results and Discussion

Analytical data tables for the following experiments may be found in Appendix III.

### *Sorption and Extraction Efficiency*

Sorption efficiency was determined for Fe<sup>3+</sup>-substituted M4195 chelating resin at pH values of 5, 6.5, and 8 and electrolyte concentrations of 0.001 M, 0.01 M, and 0.1 M NaNO<sub>3</sub>. Arsenate standard concentrations used were 250 ppb, 500 ppb, and 750 ppb. Sorption efficiency (defined as the difference between initial and final AsO<sub>4</sub><sup>3-</sup> concentration in solution, divided by the initial AsO<sub>4</sub><sup>3-</sup> concentration in solution) was 100% in this concentration range and was unaffected by solution pH or electrolyte concentration. According to Chanda et al.<sup>76</sup>, the saturation constant for M4195 resins prepared using the aforementioned procedure was 0.609 mmol As/g wet resin.

Extraction efficiency was defined as the total AsO<sub>4</sub><sup>3-</sup> stripped from the resin, divided by the initial AsO<sub>4</sub><sup>3-</sup> concentration in solution and was calculated for solutions of 0.001 M NaNO<sub>3</sub> at pH 5, 6.5, and 8 using 0.1 M NaOH as stripping eluent. Approximately 43 ± 15% (pH 5), 46 ± 7% (pH 6.5), and 61 ± 7% (pH 8) bound arsenate was stripped from the resins using 0.1 M NaOH and 24 hour stripping time. These extraction efficiencies are lower than that reported by Chanda et al. (approximately 85%) using 0.1 M NaOH and a 30 minute stripping time<sup>76</sup>.

### *Arsenic-bearing Ferrihydrite Characteristics*

The ferrihydrite precipitation procedure produced a very fine grained, dark red-brown precipitate. Drying the precipitate produced approximately 18 grams dry sediment, which was then ground to produce particles less than 150 μm in diameter. Figure 11 shows four, stacked short-range diffractograms, confirming the poorly-crystalline nature of the precipitate and lack of significant contamination by silicates. The broad, shallow peaks produced by the AFH differ markedly from the distinct peaks seen in pure ferrihydrite, reflecting disruption of the crystal lattice by coprecipitated arsenic noted by Ford<sup>89</sup>.

The concentration of As and Fe in the AFH precipitate was calculated using the following equation:

$$\text{Measured As Concentration (mol As/g AFH)} = \frac{V_{\text{AFH}} * [\text{As}]_{\text{GFAAS}} * \text{DF}}{M_{\text{AFH}}}$$

where  $V_{\text{AFH}}$  = volume of AFH suspension digested (10 mL),  $[\text{As}]_{\text{GFAAS}}$  = As concentration reported by GFAAS ( $\mu\text{g/L}$ ), DF = dilution factor (1000), and  $M_{\text{AFH}}$  = mass of AFH digested (approximately 0.025 g). The precipitate contained  $6.29 \times 10^{-5}$  mol As and  $6.43 \times 10^{-3}$  mol Fe per gram dry precipitate (Table 4), resulting in an As/Fe ratio of approximately 9.8 mmol As: 1 mol Fe. These masses are consistent with the arsenic-bearing hydrous ferric oxides produced by Ford (5 to 70 mmol As/ mol Fe)<sup>89</sup>.

### ***Sources of Dissolved Arsenate in AFH Suspensions***

Because the dissolved arsenate fraction is likely the most bioavailable arsenate fraction, it is important to define the physical and chemical processes by which arsenate moves from the solid phase to the aqueous phase. Desorption may be favored by a number of factors, including: 1) recrystallization (resulting in fewer surface sites available for adsorption); 2) pH (which also favors dissolution, another process by which arsenate moves from the solid phase to the aqueous phase); and 3) competing anions (particularly inner-sphere bond forming anions). Thus, the possible processes supplying dissolved arsenate in these experiments include:

1. Desorption of arsenate adsorbed to AFH surfaces that were not stripped off by the phosphate solutions (Fig. 12).
2. Desorption of arsenate adsorbed to surfaces physically blocked from the anion washes.
3. Arsenate incorporated as solid solution or occluded in crystal vacancies/defects and released by mineral dissolution.
4. Desorption of arsenate adsorbed to AFH surfaces as a result of recrystallization of the poorly-crystalline AFH to a more crystalline form, resulting in fewer sites available for adsorption.

Table 4. Arsenic and iron concentration in ferrihydrite sediment.

Sample	Ferrihydrite Mass	Measured As Concentration	Measured Fe Concentration	As/Fe Ratio
	g	mol/g	mol/g	mmol/mol
A	0.0252	6.62E-05	7.07E-03	9.37
B	0.0259	6.54E-05	6.18E-03	10.58
C	0.0256	5.71E-05	6.04E-03	9.45
Average	0.0256	6.29E-05	6.43E-03	9.80

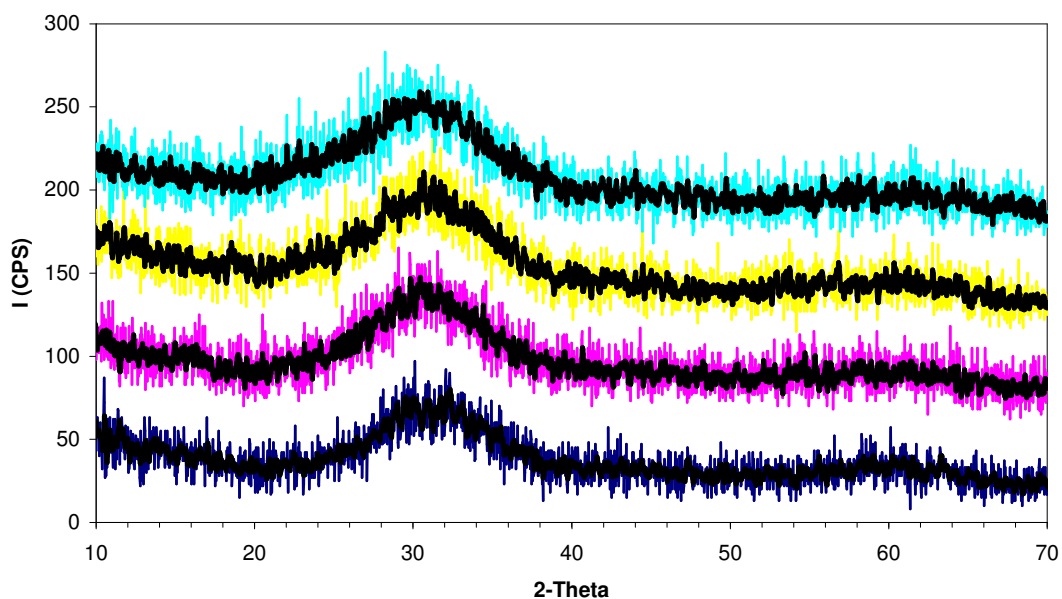
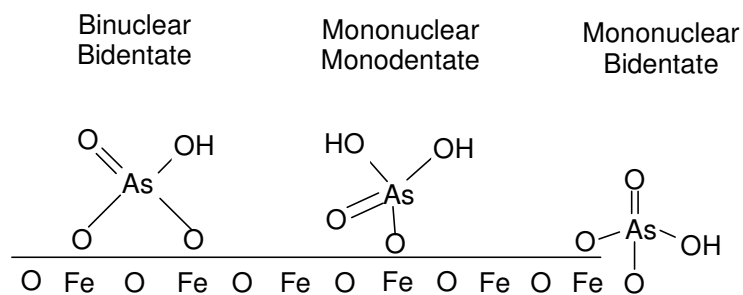
Figure 11. Stacked X-ray diffractograms of poorly-crystalline arsenic-bearing two-line ferrihydrite prepared according to modifications of Ford<sup>2</sup> and Raven et al.<sup>4</sup>

Figure 12. Potential inner-sphere bonding sites for arsenate on the surface of two-line ferrihydrite and other iron oxide minerals.

### ***Effect of Suspension pH on Sorption Capacity***

Three AFH suspensions were made by adding 0.5 g arsenic-bearing ferrihydrite to one liter 0.001 M NaNO<sub>3</sub> (as background electrolyte). These batches were equilibrated at pH 5, 6.5, and 8.0. After the initial equilibration prior to the start of the experiments, the pHs of the suspensions were not adjusted.

#### *Experimental Control*

The effect of time on the AFH suspension pH (Fig. 13A) and dissolved arsenate mass (Fig. 13B) is presented in order to define the influence of initial suspension pH in control solutions. Initial equilibrations were assumed stabilized after maintaining the desired pH for 1 hour. However, the AFH suspensions were clearly not in equilibrium. After one day, control series 8.0 approached a stable pH of  $7.32 \pm 0.11$ , while the pH 5.0 suspension approached  $5.76 \pm 0.12$  and the pH 6.5 suspension approached  $6.68 \pm 0.16$ .

After the first 24 hours, the dissolved arsenate concentration for each series is scattered about  $7.5 \times 10^{-5}$  mmol As in solution; there are no significant trends in dissolved arsenate as a function of initial suspension pH over time. The dissolved mass of arsenate in the control suspensions is slightly more than one order of magnitude lower than the total arsenate in the suspension.

#### *Experimental Treatment*

The effect of time on the AFH suspension pH (Fig. 14A) and estimated dissolved arsenate mass (Fig. 14B) is presented in order to define the influence of initial suspension pH in treatment solutions. In the presence of 0.25 g wet Fe<sup>3+</sup>-substituted M4195 chelating resin, the suspension pHs decreased as much as 0.6 pH units from control sample pH. The dissolved arsenate concentration as estimated by Fe<sup>3+</sup>-substituted M4195 resins also showed less scatter than the control samples. These treatment concentrations decrease according to pH 8 > pH 5 >

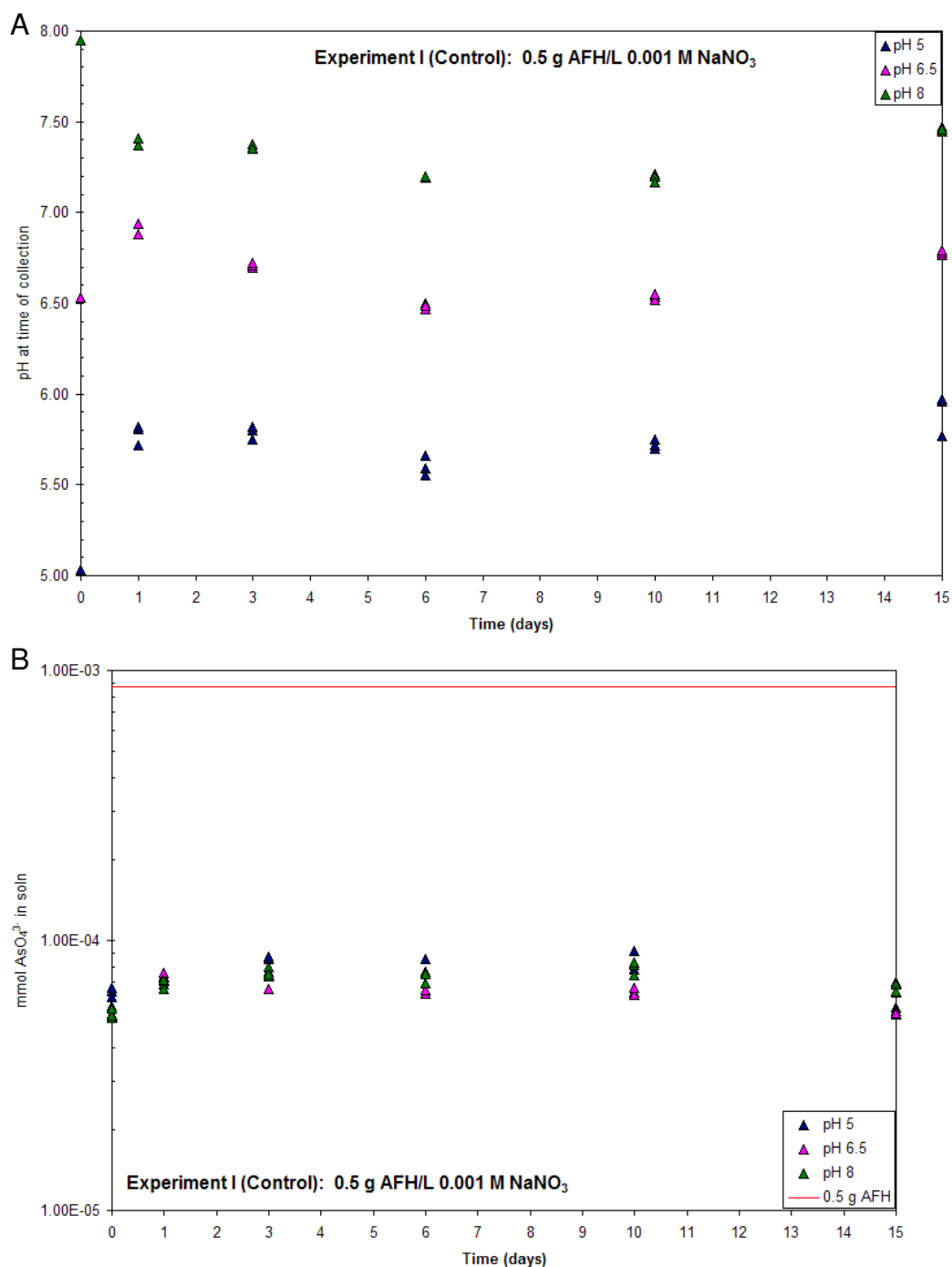


Figure 13. The effect of time on the AFH suspension pH (A) and dissolved arsenate mass (B) to quantify the effect of initial suspension pH in control solutions. The suspensions contained 25 mL 0.5 g AFH/L in 0.001 M NaNO<sub>3</sub> background electrolyte solution, initially equilibrated at pH 5, 6.5, and 8. The total mol ( $8.7 \times 10^{-4}$  mol) of AsO<sub>4</sub><sup>3-</sup> in the solid phase is represented by the red line.



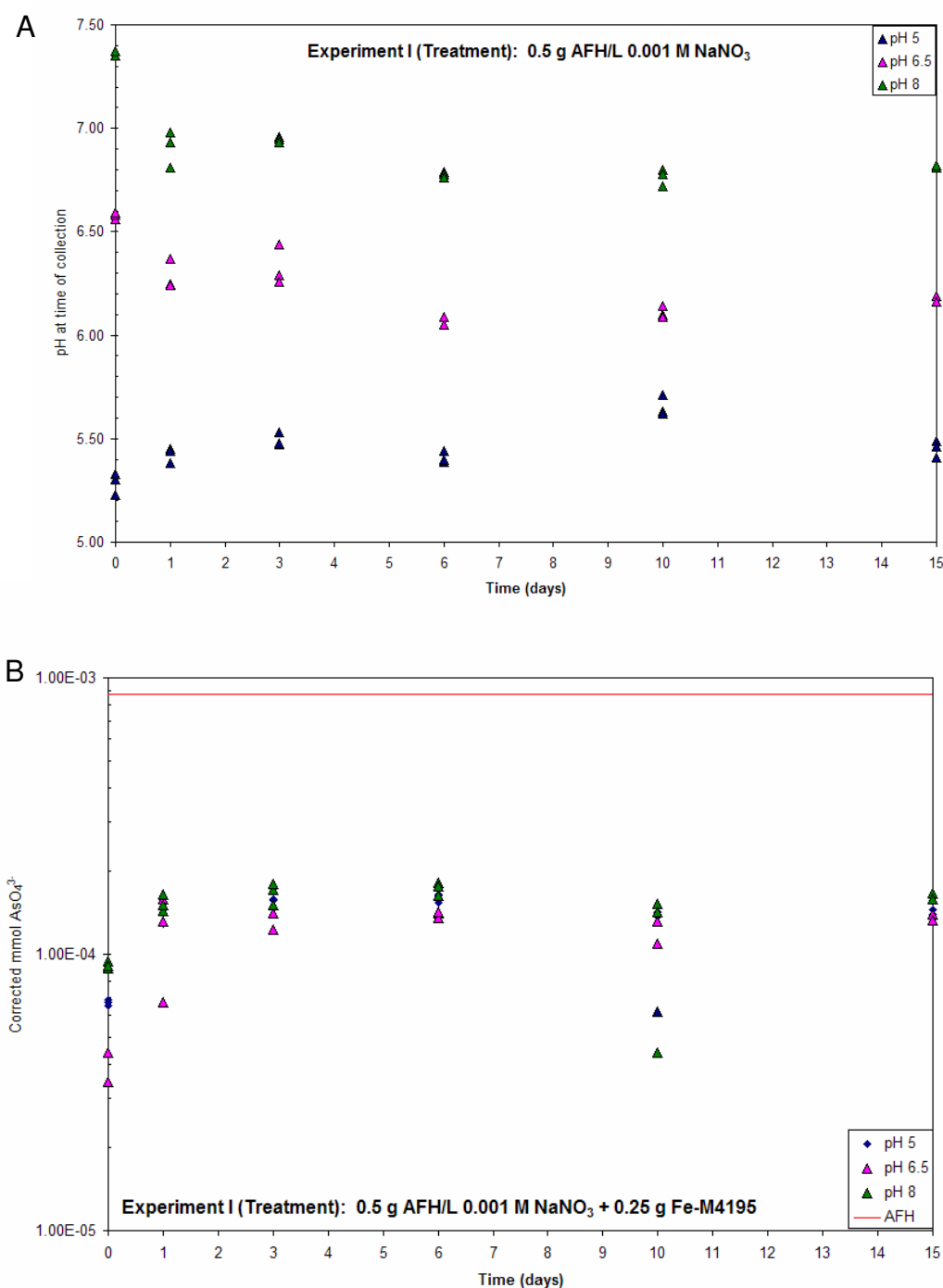


Figure 14. The effect of time on the AFH suspension pH (A) and estimated dissolved arsenate mass (B) in treatment solutions to quantify the effect of initial suspension pH and presence of 0.25 g Fe<sup>3+</sup>-substituted M4195 resin. The suspensions contained 25 mL 0.5 g AFH/L in 0.001 M NaNO<sub>3</sub> background electrolyte solution, initially equilibrated at pH 5, 6.5, and 8. The estimated mass of arsenate in the treatment solutions was corrected to account for extraction efficiency. The total mol ( $8.7 \times 10^{-4}$  mol) of AsO<sub>4</sub><sup>3-</sup> in the solid phase is represented by the red line.

pH 6.5. This trend is consistent with the results of arsenate sorption studies using iron oxides, which show that maximum As(V) sorption occurs at  $\text{pH} < 7^{9,82,84,88-94}$ .

### *Discussion*

The degree and pattern of fluctuations in pH documented in this experiment were somewhat unexpected. The decrease in pH noted for the pH 8 control series is likely caused by adsorption of  $\text{OH}^-$  in solution to surface sites on the  $\text{FeOOH}$  particles. The decreases in pH noted in the treatment samples also are likely exacerbated by residual  $\text{H}^+$  in the pores of the resin beads. It has been suggested that the pH changes and drift documented in this, and the following, experiments may be partially attributable to the drying step used in the production of the arsenic-bearing ferrihydrite. Drying the sediment caused the clay-sized particles to compact. Time-dependent hydration (uptake of  $\text{OH}^-$  in solution) of once-occluded sites during the breakup of large AFH flocs and resuspension of these clay-sized particles might account in part for the decrease in pH documented in this, and the following, experiments. The increase in pH noted for the pH 5 and 6.5 control series may be attributable to mineral recrystallization, resulting in fewer available surface bonding sites for  $\text{OH}^-$  and release of extra  $\text{OH}^-$  to the solution phase. However, this process is unlikely given the short time frame of this experiment. Thus, the causes of these documented fluctuations in pH in the pH series is unknown at this time.

The effect of time on the ratio of estimated treatment arsenate to control solution arsenate mass is presented in order to define the influence of initial suspension pH (Fig. 15). Active pH-driven dissolution and/or desorption from the surfaces of the AFH solid phase by the resins would be indicated by ratios greater than one. The initial increase from day 0 to day 1 likely is insignificant because it reflects the kinetic lag for arsenate sorption to the resins. After 1 day of equilibration, the values show significant scatter between 1.5 and 2.5 with no significant distinctions apparent among the pH series. The saturation constant is 0.609 mmol As/g wet resin; these samples used  $<0.1\%$  of the available sorption capacity. Thus, while these values do indicate enhanced desorption and/or dissolution of As-bearing AFH, this behavior results from

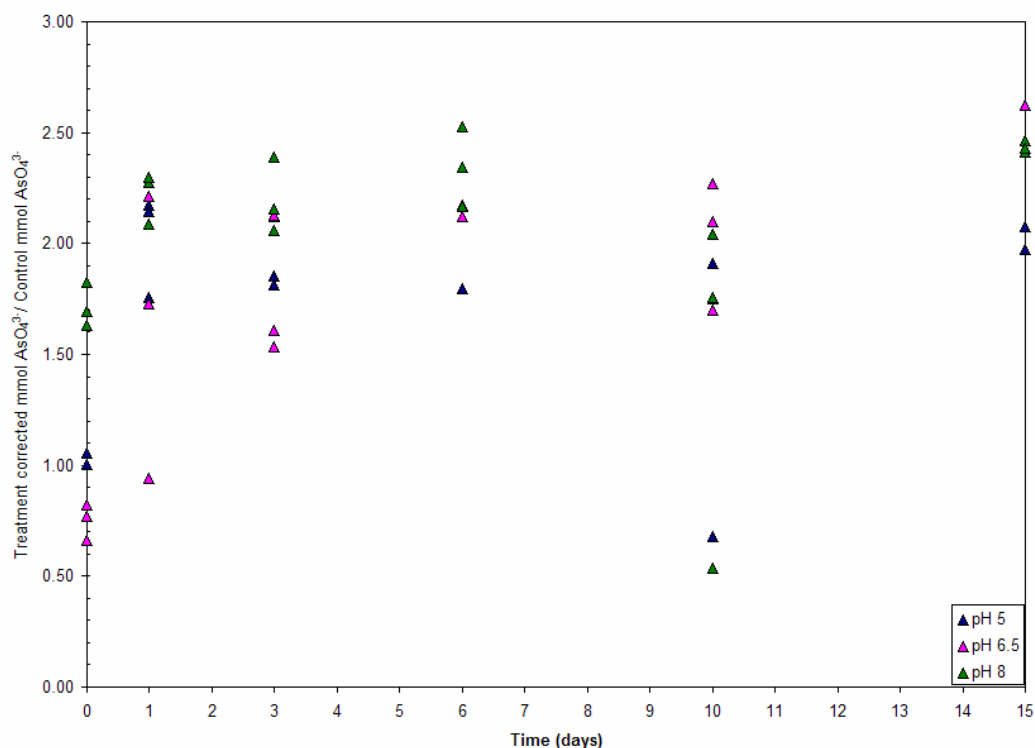


Figure 15. The effect of time on the ratio of estimated treatment arsenate to control solution arsenate mass to quantify the effect of initial suspension pH. A ratio of 1.0 represents the ideal situation where the resins accurately represent the dissolved (and bioavailable) fraction of arsenate in the system. The estimated mass of arsenate in the treatment solutions was corrected to account for extraction efficiency.

resin-driven solution acidification rather than any kind of solution pH-driven influence on arsenate sorption to the resin. Further research of sorption efficiency and soil solution pH using buffered solutions would be useful in assessing the application of  $\text{Fe}^{3+}$ -substituted M4195 chelating resins in acidic, circumneutral, and calcareous soils. Also, further experiments should consider the removal of the drying step during AFH production to eliminate the issue of hydration and pH change during resuspension. The objective of this subexperiment was to determine if the adsorption of arsenic by  $\text{Fe}^{3+}$ -substituted resin is sufficient to enhance mineral dissolution/weathering of AFH. Because of the uncontrolled fluctuations in pH of both the control and treatment solutions, san given the sensitivities of ferrihydrite and desorption reactions to

fluctuations in pH, a definitive determination of the role of pH (not caused by introduction of resin) could not be made.

### ***Effect of Suspension Concentration of Sorption Capacity***

Three AFH suspensions were made by adding 0.05 g, 0.50 g, or 5.0 g AFH to 1 L 0.001 M NaNO<sub>3</sub> as background electrolyte. These batches were equilibrated at pH 8.0. After the initial equilibration prior to the start of the experiments, the pHs of the suspensions were not adjusted.

### ***Experimental Control***

The effect of time on the AFH suspension pH (Fig. 16A) and dissolved arsenate mass (Fig. 16B) is presented in order to define the influence of initial suspension concentration in control solutions. pH equilibrium was not achieved by the preliminary pH adjustments. The AFH particles buffered the pH in proportion to the mass in solution. Thus, the greatest pH decrease in the control suspensions was seen in the 0.05 g/L suspension while the least change was seen in the 5.0 g/L suspension.

The distribution of dissolved arsenate in the control samples reflects the orders of magnitude difference in total arsenate present in the system (a function of the mass of arsenic-bearing ferrihydrite added: 5.0 g/L > 0.5 g/L > 0.05 g/L). By day 3, the dissolved arsenate concentration for the 0.5 g and 5.0 g AFH suspensions stabilized at  $6.1 \times 10^{-5}$  and  $3.8 \times 10^{-4}$  mmol AsO<sub>4</sub><sup>3-</sup>, respectively. In each control series, the dissolved arsenate concentration is approximately one order of magnitude less than the total arsenate mass available for dissolution. Given that  $As_{\text{sorbed}} \leftrightarrow As_{\text{aq}}$  (assuming that the adsorption-desorption reaction is reversible at least to some degree), increasing the mass of sorbed arsenate by increasing the AFH suspension concentration should increase the concentrations of dissolved arsenate according to Le Chatelier's Principle.

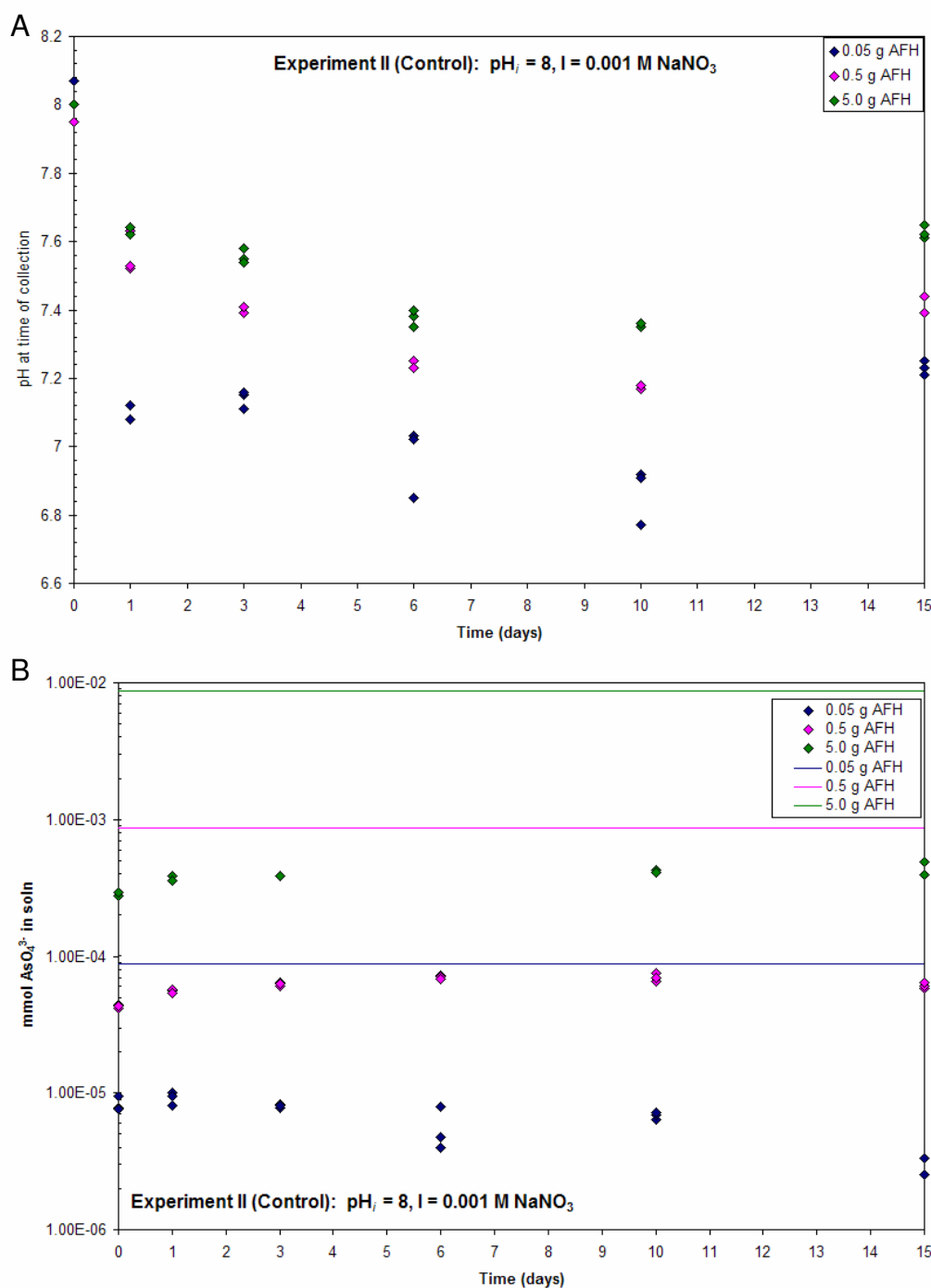


Figure 16. The effect of time on the AFH suspension pH (A) and dissolved arsenate mass (B) to quantify the effect of initial suspension concentration in control solutions. The suspensions contained 0.05, 0.5, or 5.0 g AFH/L in 0.001 M  $\text{NaNO}_3$  background electrolyte solution initially equilibrated to pH 8. The total mol  $\text{AsO}_4^{3-}$  in each suspension is represented by the colored lines.

### *Experimental Treatment*

The effect of time on the AFH suspension pH (Fig. 17A) and estimated dissolved arsenate mass (Fig. 17B) is presented in order to define the influence of initial suspension concentration in treatment solutions. In the presence of 0.25 g Fe<sup>3+</sup>-substituted M4195 chelating resin, the pH of the treatment samples became more acidic in inverse proportion to the mass of AFH in the suspension. Thus, the pH of the 5.0 g/L suspensions only decreased by 0.2 pH units while the pH of the 0.05 g/L suspensions decreased by 1.3 pH units.

### *Discussion*

The effect of time on the ratio of estimated treatment arsenate to control solution arsenate mass is presented to define the effect of initial AFH suspension concentration. The 0.5 g/L and 5.0 g/L AFH suspensions have insignificant slopes. There is a clear correlation between the degree of acidification of the treatment suspensions and the concentrations of resin-bound arsenate. The large positive slope of the 0.05 g/L suspension indicates active dissolution of the ferrihydrite solids. However, this active dissolution is driven by H<sup>+</sup> introduced to the solution by the resins (H<sup>+</sup>-enhanced dissolution) and not caused by either concentration gradients between the solid phase and solution phase or a larger resin-surface K<sub>d</sub> than ferrihydrite surface K<sub>d</sub>. The suspensions do not show orders of magnitude difference in AsO<sub>4</sub><sup>3-</sup> after 1 day of equilibration in the presence of the resins, the effective concentration for all series stabilizes to slightly more than 1.0 \* 10<sup>-4</sup> mmol AsO<sub>4</sub><sup>3-</sup> in solution.

The results of this experiment suggest that suspension concentration should be considered carefully in both closed laboratory-scale experiments and field experiments using Fe<sup>3+</sup>-substituted M4195 resin. At low suspension concentrations, potential arsenate bioavailability could be overestimated by more than an order of magnitude. While the 5.0 g AFH suspensions used <0.1% of the sorption capacity, it is possible that the higher solution pH

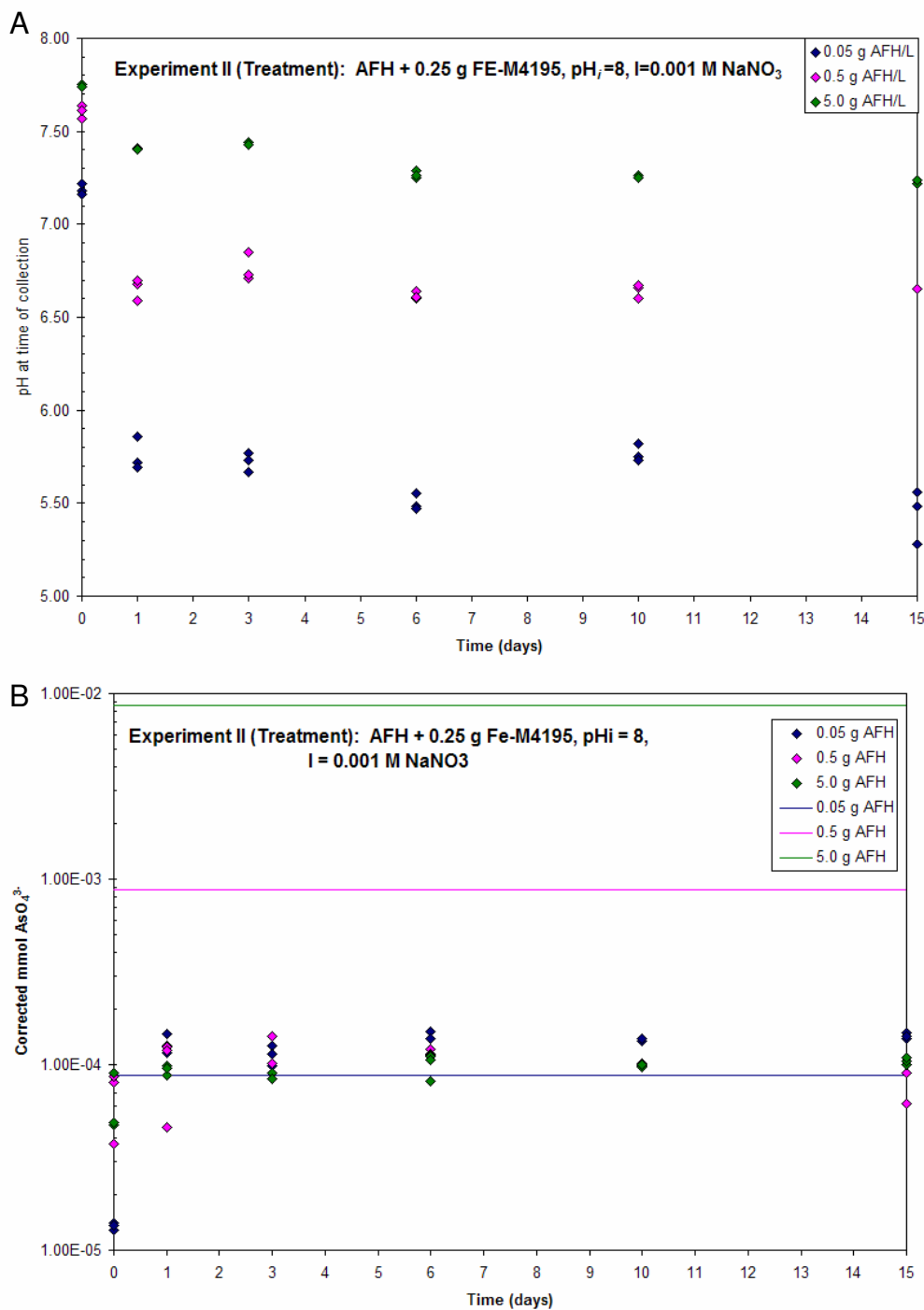


Figure 17. The effect of time on the AFH suspension pH (A) and dissolved arsenate mass (B) to quantify the effect of initial suspension concentration in treatment solutions. The suspensions contained 0.05, 0.5, or 5.0 g AFH/L in 0.001 M NaNO<sub>3</sub> background electrolyte solution initially equilibrated to pH 8. The estimated mass of arsenate in the treatment solutions was corrected to account for extraction efficiency. The total mol AsO<sub>4</sub><sup>3-</sup> in each suspension is represented by the colored lines.

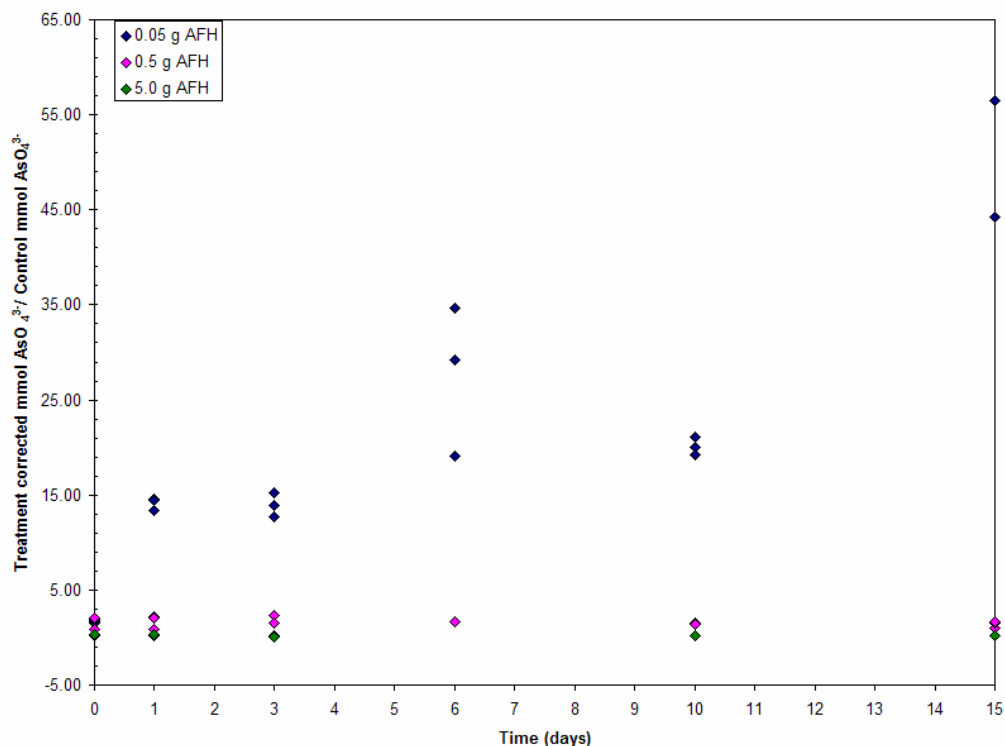


Figure 18. The effect of time on the ratio of estimated treatment arsenate to control solution arsenate mass to quantify the effect of initial suspension concentration. A ratio of 1.0 represents the ideal situation where the resins accurately represent the dissolved (and bioavailable) fraction of arsenate in the system. The estimated mass of arsenate in the treatment solutions was corrected to account for extraction efficiency.

changed the major functional group to prefer arsenite to arsenate, resulting in lower apparent concentrations.

### ***Effect of Electrolyte Concentration on Sorption Capacity***

Three AFH suspensions were made by adding 0.5 g arsenic-bearing two-line ferrihydrite to 0.001, 0.01, or 0.1 M  $\text{NaNO}_3$  background electrolyte solution. The batches were equilibrated at pH 8.0. After the initial equilibrations prior to the start of the experiment, the pH of the suspensions were not adjusted.



### *Experimental Control*

The effect of time on the AFH suspension pH (Fig. 19A) and dissolved arsenate mass (Fig. 19B) is presented in order to define the influence of background electrolyte strength in control solutions. pH equilibrium was not achieved by the preliminary pH adjustments. The pH of the three electrolyte suspensions matched closely. pH values decreased to a minimum of  $7.3 \pm 0.15$  at day 6, then increased to a final pH of  $7.5 \pm 0.15$ . However, the control dissolved arsenate concentrations in all series appear to fluctuate independently of solution pH between  $1.7$  and  $8.5 \times 10^{-5}$  mmol  $\text{AsO}_4^{3-}$ .

### *Experimental Treatment*

The effect of time on the AFH suspension pH (Fig. 20A) and estimated dissolved arsenate mass (Fig. 20B) is presented in order to define the influence of background electrolyte strength in treatment solutions. The pH of the treatment suspensions became more acidic inversely proportional to suspension electrolyte concentration ( $\text{pH } 0.1 \text{ M} > 0.01 \text{ M} > 0.001 \text{ M}$ ) in the presence of  $0.25 \text{ g Fe}^{3+}$ -substituted M4195 chelating resin.

### *Discussion*

The effect of time on the ratio of estimated treatment arsenate to control solution arsenate mass is presented in order to define the effect of initial background electrolyte concentration in control solutions (Fig. 21). The sharp decreasing trends observed for all series between 0 and 3 days reflects the slow kinetics of desorption documented in the control samples. Estimated dissolved arsenate concentrations in the treatment samples decrease over the time range of the experiment for the  $0.01 \text{ M}$  and  $0.001 \text{ M}$  series. In the  $0.001 \text{ M}$  and  $0.01 \text{ M}$  series, a 1:1 correlation is most closely achieved after 15 days. However, the  $0.1 \text{ M}$  series least overestimated dissolved arsenate concentrations between 0 and 6 days and then sharply overestimates arsenate bioavailability over 10 days. This behavior is not understood. However, it is apparent that the estimated dissolved arsenate concentration using arsenate mass bound to

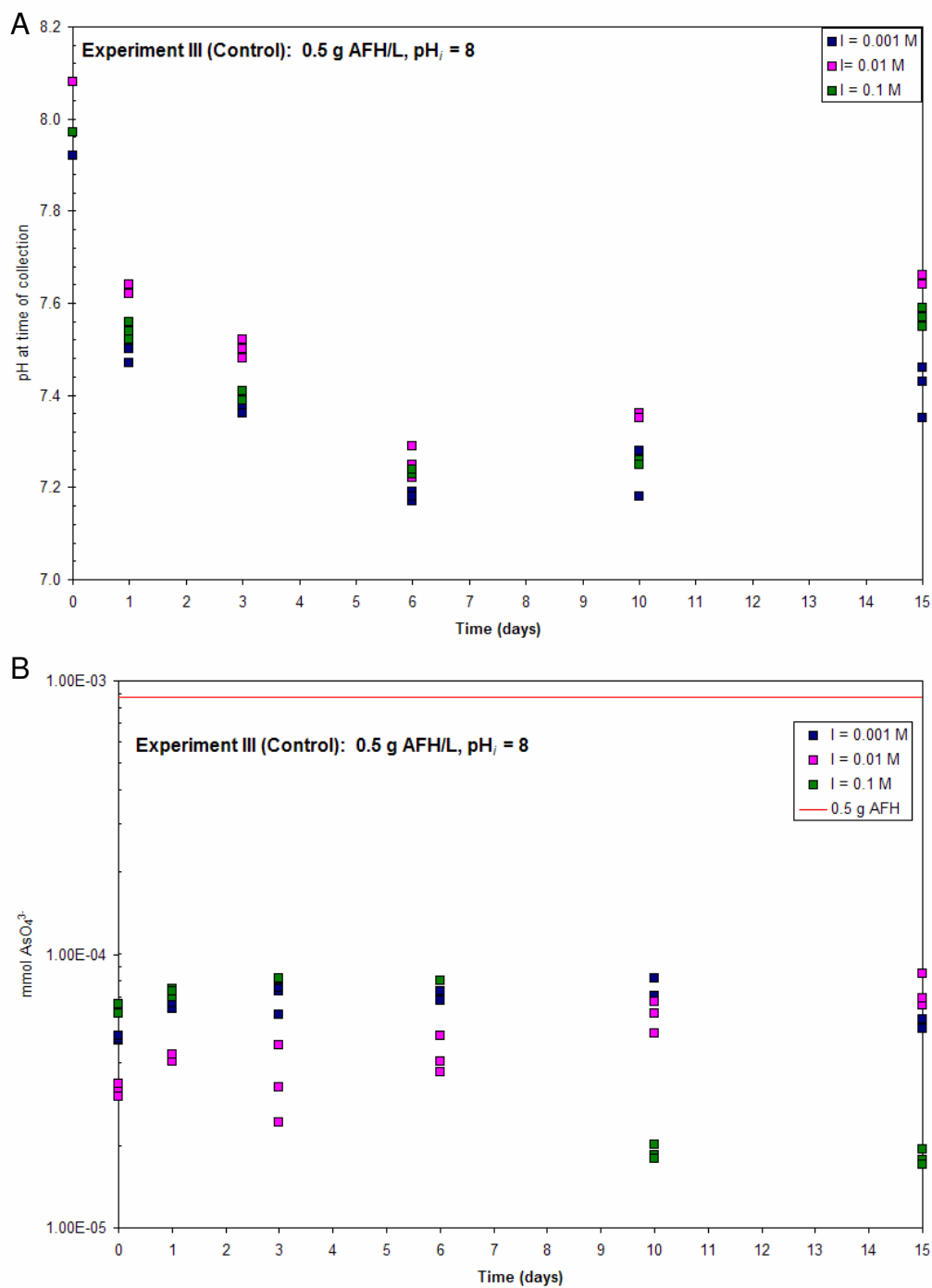


Figure 19. The effect of time on the AFH suspension pH (A) and dissolved arsenate mass (B) to quantify the effect of background electrolyte strength in control solutions. The suspensions were made using 0.001, 0.01, or 0.1 M  $NaNO_3$  background electrolyte solutions. The suspensions contained 25 mL 0.5 g AFH/L initially equilibrated to pH 8. The total mol ( $8.7 \times 10^{-4}$  mol) of  $AsO_4^{3-}$  in the solid phase is represented by the red line.

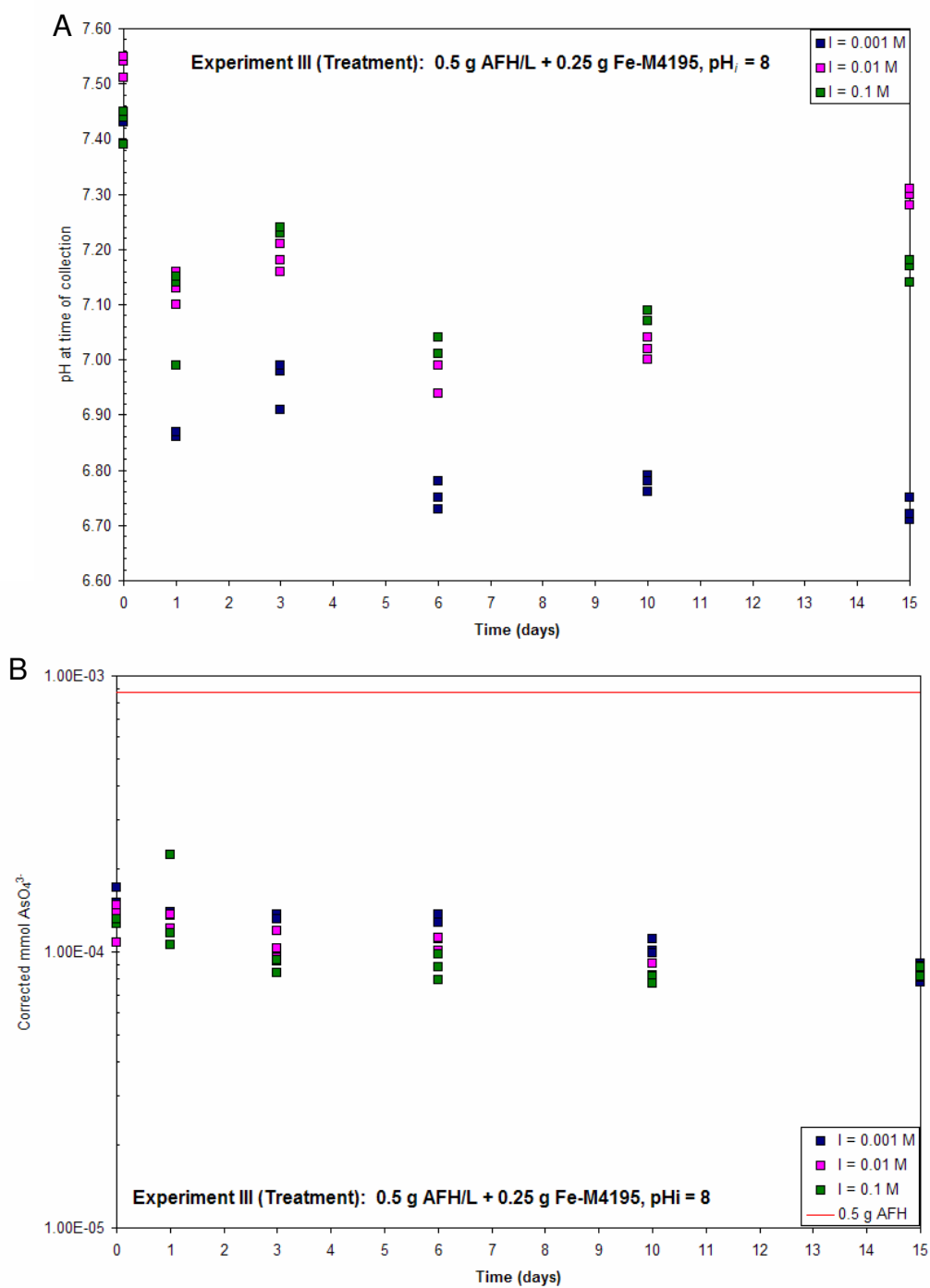


Figure 20. The effect of time on the AFH suspension pH (A) and dissolved arsenate mass (B) to quantify the effect of initial background electrolyte strength in treatment solutions. The suspensions contained 0.001, 0.01, or 0.1 M NaNO<sub>3</sub>. The estimated mass of arsenate in the treatment solutions was corrected to account for extraction efficiency. The total mol AsO<sub>4</sub><sup>3-</sup> in suspension is represented by the red line.

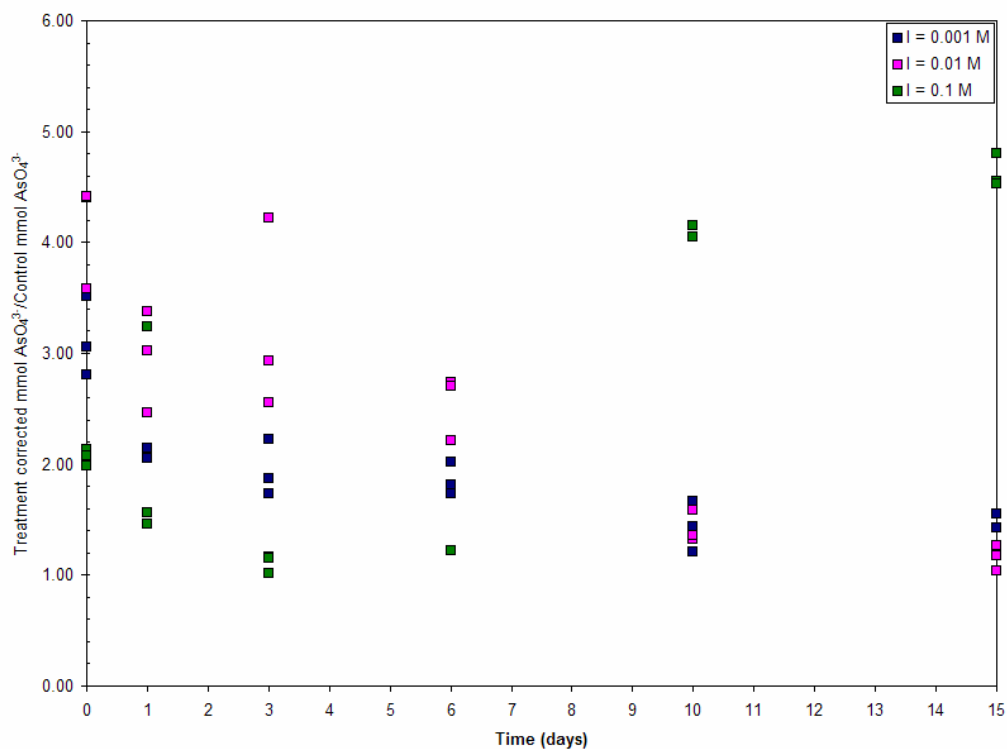


Figure 21. The effect of time on the ratio of estimated treatment arsenate to control solution arsenate mass to quantify the effect of initial background electrolyte concentration.

$\text{Fe}^{3+}$ -substituted M4195 chelating resin was influenced by background electrolyte concentration as a function of time.

### Implications

Arsenate, a toxic oxyanion, is a common natural and anthropogenically-derived contaminant. Recent changes in water quality standards have made studies of the source, distribution, and bioavailability of arsenate a popular topic for scientific research. Iron(III)-substituted chelating resins have been used successfully in a previous study<sup>76</sup> to estimate potential arsenic bioavailability in the field. However, because these resins had never before been used in environmental studies, there were major unknowns about how these resins interacted with common soil minerals. The studies of arsenate sorption on  $\text{Fe}^{3+}$ -substituted

Dowex M4195 chelating resin extend previous work by examining sorption at increasing arsenic-bearing ferrihydrite suspension pH, increasing arsenic-bearing ferrihydrite suspension concentration, and increasing background electrolyte concentration. In general, the results of this study are consistent with the adsorption and dissolution characteristics of two-line ferrihydrite. The resins are acidic in nature and can acidify suspensions as a function of the initial pH and the mass of solids available to buffer  $H^+$  ion activity. Acidification of the suspensions facilitates  $H^+$ -enhanced dissolution of the arsenic-bearing ferrihydrite, causing an overestimation of potentially bioavailable arsenate in the environment. In experiments testing background electrolyte concentration, the resins adsorb only arsenate molecules free from other ion interactions and thus provide an estimation of the arsenate activity in solution. This activity measurement should provide a better estimate of potentially bioavailable arsenic than total arsenate concentrations in waters or sequential extractions of sediments. Thus, future laboratory-scale studies should include consideration of the possible effects of resin-driven acidification that could possibly cause dissolution of the solid phase of interest and possible underestimation of solution-phase arsenic as a result of common anions in the soil solution. Given that these resins respond to the activity of arsenate rather than the total concentration of arsenate in solution, care should be taken to present the results as activity-based concentrations. Otherwise, the resin-bound arsenate concentration should be calibrated to total freely dissolved arsenate concentration to account for ionic strength effects.

The distribution of poorly crystalline ferric oxide minerals is highly heterogeneous. Soil solution pH and ionic strength also vary according to local soil mineralogy (also spatially heterogeneous). Although the pH buffer capacity of real soil samples is much greater than the ferrihydrite buffer capacity used in these experiments and would not be acidified upon addition of these resins, these experiments provide pertinent information for bench-scale laboratory studies in which concentrations and sample size are frequently scaled down. Also, these experiments in simple systems may be used to validate trends seen in more complex systems. The purpose of these experiments was to establish whether the resins adsorb the arsenic sequestered by iron

oxyhydroxides in addition to arsenate in solution. Except in extreme conditions such as extremely high soil ionic strength, the results of these experiments suggest that the resins do not adsorb arsenic sequestered by iron oxyhydroxides. Therefore, Dowex M4195 Fe<sup>3+</sup>-substituted chelating resins are likely to be usefully in bioavailability estimates of arsenate in field-based research.

## SUMMARY AND CONCLUSIONS

Arsenic is a common contaminant in soils, sediments, surface waters, vadose zone waters, and ground waters. There is not a standardized field method for determining what fraction of this environmental arsenic is available for uptake by organisms. Neither is there a regulated method of arsenate analysis in the laboratory. As is the case in research projects, each analytical method is adapted to meet the demands of the research objectives. The objectives of this research were multifold. First, a high-pressure liquid chromatography method for the quantification of arsenate in the greatest sodium hydroxide concentration possible was desired to facilitate greater stripping efficiency of the resins with minimal instrumental interference, particularly damage to instrumentation. This instrumentation/analytical method was used in the following objectives involving Fe<sup>3+</sup>-substituted chelating resins.

Dowex M4195 Fe<sup>3+</sup>-substituted chelating resin is a promising tool in field-based studies on potential arsenic bioavailability. The objectives of this research included 1) the determination of the sorption efficiency of Fe<sup>3+</sup>-substituted Dowex M4195 chelating resins at circumneutral pHs and a range of background ionic strengths; 2) definition of the acidification properties of these resins; 3) determination of the correlation between the dissolved and resin-bound arsenate concentration in bench studies; and 4) determination of the influence of the background ionic strength on the sorption capacity of the resins in bench studies.

This study is important because it provides necessary background information required for the use of Dowex M4195 Fe<sup>3+</sup>-substituted chelating resins in field studies of potential arsenate bioavailability. This research demonstrates that poorly-crystalline iron oxides should not dissolve when this form of resin is introduced in natural soil environments because soils' ability to buffer pH is much greater than the resins' ability to acidify their surroundings. This research also demonstrates that while field-scale studies need not be concerned about resin-induced acidification, small-scale laboratory studies may require external buffering to prevent H<sup>+</sup>-

enhanced dissolution of acid sensitive minerals. Such enhanced dissolution in bench-scale studies would cause overestimations of solution-phase arsenic.

The results of a treatment using a constant arsenic-bearing ferrihydrite particle concentration in increasingly concentrated  $\text{NaNO}_3$  background electrolyte solutions indicated that the arsenate concentration stripped from the resin reflected the arsenate activity ( $a_{\text{As}}$ ), and not the truly-dissolved arsenate concentration ( $m_{\text{As}}$ ). Events that result in introduction of large volumes of fresh water, i.e. the 500-year flood the South Texas coastal plain experienced in 2002, could increase the “apparent” concentration of potentially bioavailable arsenic by decreasing the solution ionic strength bathing the resins. Given the pH-controlled environment caveats, there is a good correlation between solution-phase arsenate and resin-bound arsenate. Further experiments would be required to see if ionic strength influences total and time-dependent desorption of arsenate from Dowex M4195  $\text{Fe}^{3+}$ -substituted chelating resins.

Lake<sup>77</sup> assessed arsenic bioavailability in soil microcosms as a function of time and geology using soil slurries made from oven-dried soils wetted to saturation with double-distilled water. Since the ionic strength of any given sediment microcosm was not controlled or measured (for comparison among geologic environments), comparisons of resin-bound arsenic among geochemically diverse sediments could be misinterpreted. Such conditions (specifically, introduction of distilled water to dried sediment) allow changes in ionic strength over time, which will dictate the corresponding resin-bound arsenic masses. Such conditions are not representative of field conditions, where migration of ion-bearing water through the sediment likely maintains a relatively constant soil solution ionic strength. Assuming that the trends seen in the arsenic-bearing ferrihydrite experiments described in this research hold true for real sediments, these sediment microcosms would show a larger mass of potentially bioavailable arsenic than actually present. However, the relative magnitudes of the trends among the samples would likely stay the same. Thus, the absolute values of arsenic bound to the resin may not reflect the true concentration of potentially bioavailable arsenic in Lake’s sediment



microcosm experiments but could still adequately identify hotspots of arsenic bioavailability based on sediment properties.

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**APPENDIX I**



Example of DX-600 Chromatograph program.

```
Pressure.LowerLimit = 0
Pressure.UpperLimit = 4000
%A.Equate = "%A"
%B.Equate = "%B"
%C.Equate = "%C"
%D.Equate = "%D"
Data_Collection_Rate = 2.0
Temperature_Compensation = 1.7
DS3_Temperature = 35
Suppressor_Type = AAES
; Carbonate = 3.5
; Bicarbonate = 1.0
; Hydroxide = 0.0
; Recommended Current = 47
Suppressor_Current = 47
Flow = 1.75
%B = 25.0
%C = 25.0
%D = 25.0
Curve = 5
-2.300 PUMP_TTL_1.0V      Duration=10.00

0.000 ECD.Autozero
      InjectPosition      Duration=60.00
      ECD_1.AcqOn

10.000 ECD_1.AcqOff

      End
```

**APPENDIX II**

## Analytical parameters for the analysis of arsenate and iron using GF-AAS.

## Analytical parameters for the analysis of arsenate using GF-AAS.

## Arsenate Analysis

## Arsenate-bearing Ferrihydrite Digest

Date:	5/14/2003 20:39	Reslope Rate:	100
Worksheet:	BG11-As-SC mdr 01	Reslope Standard No.:	2
Method:	As-wtr_Ni_mod	Reslope Lower Limit:	75.00%
Instrument type:	Furnace	Reslope Upper Limit:	125.00%
Concentration Units:	$\mu\text{g/L}$	Recalibration Rate:	100
Sampling Mode:	AutoMix	Calibration Algorithm:	Rational
Calibration Mode:	Concentration	Cal. Lower Limit:	20.00%
Measurement Mode:	Peak Height	Cal. Upper Limit:	150.00%
Replicates:	3		
		Workhead Height:	0.0 mm
Expansion Factor:	1	Total Volume:	24 $\mu\text{L}$
Minimum Reading:	Disabled	Sample Volume:	16 $\mu\text{L}$
Smoothing:	10 point	Volume Reduction Factor:	2
Wavelength:	193.7 nm	Bulk Concentration:	160.000 $\mu\text{g/L}$
Slit Width:	0.5 nm	Hot Inject:	On
EHT:	288 Volts	Hot Inject Temp:	95 deg C
Lamp Current:	10.0 mA	Hot Inject Rate:	4
Background Correction:	On	Modifier 1 Mode:	Co Inject
		Modifier 1 Volume:	3 $\mu\text{L}$

## Analytical parameters for the analysis of iron using GF-AAS.

## Iron Analysis

## Arsenate-bearing Ferrihydrite Digest

Date:	5/14/2003 20:39	Reslope Rate:	100
Worksheet:	BG11-As-SC mdr 01	Reslope Standard No.:	2
Method:	As-wtr_Ni_mod	Reslope Lower Limit:	75.00%
Instrument type:	Furnace	Reslope Upper Limit:	125.00%
Concentration Units:	$\mu\text{g/L}$	Recalibration Rate:	100
Sampling Mode:	AutoMix	Calibration Algorithm:	Rational
Calibration Mode:	Concentration	Cal. Lower Limit:	20.00%
Measurement Mode:	Peak Height	Cal. Upper Limit:	150.00%
Replicates:	3		
		Workhead Height:	0.0 mm
Expansion Factor:	1	Total Volume:	24 $\mu\text{L}$
Minimum Reading:	Disabled	Sample Volume:	16 $\mu\text{L}$
Smoothing:	10 point	Volume Reduction Factor:	2
Wavelength:	193.7 nm	Bulk Concentration:	160.000 $\mu\text{g/L}$
Slit Width:	0.5 nm	Hot Inject:	On
EHT:	288 Volts	Hot Inject Temp:	95 deg C
Lamp Current:	10.0 mA	Hot Inject Rate:	4
Background Correction:	On	Modifier 1 Mode:	Co Inject
		Modifier 1 Volume:	3 $\mu\text{L}$

**APPENDIX III**

TREATMENT 1, pH 5 DATA

Sample ID	Initial Equilibrated Suspension pH	Mass Wet Resin g	Initial pH	pH at time of collection	Ionic Strength M NaNO3	Ferrihydrate Suspension Concentration g/L	mmol As in initial suspension	Time (days)	ppb	
									Strip 1 Arsenate Concentration	Strip 2 Arsenate Concentration
T1-PH5-0A	5.03	0.2547	5.30	5.30	0.001	0.5007	8.70E-04	0	406.6	67.9
T1-PH5-0B	5.03	0.2540	5.23	5.23	0.001	0.5007	8.70E-04	0	377.4	88.8
T1-PH5-0C	5.03	0.2578	5.33	5.33	0.001	0.5007	8.70E-04	0	357.5	95.9
T1-PH5-1A	5.03	0.2517	5.31	5.38	0.001	0.5007	8.70E-04	1	909.3	161.6
T1-PH5-1B	5.03	0.2576	5.34	5.45	0.001	0.5007	8.70E-04	1	939.8	156.8
T1-PH5-1C	5.03	0.2538	5.35	5.44	0.001	0.5007	8.70E-04	1	755.7	135.6
T1-PH5-3A	5.03	0.2563	5.34	5.53	0.001	0.5007	8.70E-04	3	917.5	180.8
T1-PH5-3B	5.03	0.2593	5.36	5.47	0.001	0.5007	8.70E-04	3	938.4	157.6
T1-PH5-3C	5.03	0.2564	5.40	5.48	0.001	0.5007	8.70E-04	3	932.9	160.5
T1-PH5-6A	5.03	0.2528	5.35	5.44	0.001	0.5007	8.70E-04	6	930.7	199.0
T1-PH5-6B	5.03	0.2548	5.37	5.39	0.001	0.5007	8.70E-04	6	948.9	193.3
T1-PH5-6C	5.03	0.2575	5.38	5.40	0.001	0.5007	8.70E-04	6	890.9	174.3
T1-PH5-10A	5.03	0.2542	5.36	5.63	0.001	0.5007	8.70E-04	10	797.1	191.9
T1-PH5-10B	5.03	0.2536	5.36	5.62	0.001	0.5007	8.70E-04	10	776.4	172.2
T1-PH5-10C	5.03	0.2537	5.39	5.71	0.001	0.5007	8.70E-04	10	343.8	88.2
T1-PH5-15A	5.03	0.2590	5.34	5.49	0.001	0.5007	8.70E-04	15	764.7	182.7
T1-PH5-15B	5.03	0.2570	5.37	5.41	0.001	0.5007	8.70E-04	15	847.5	154.7
T1-PH5-15C	5.03	0.2535	5.41	5.46	0.001	0.5007	8.70E-04	15	789.4	174.3

TREATMENT 1, pH 5 DATA (Continued)

Sample ID	ppb		mmol AsO <sub>4</sub> <sup>3-</sup> /g wet resin		mmol AsO <sub>4</sub> <sup>3-</sup> stripped/ mmol AsO <sub>4</sub> <sup>3-</sup> in Ferrihydrate		mmol AsO <sub>4</sub> <sup>3-</sup> stripped/ mmol AsO <sub>4</sub> <sup>3-</sup> in Ferrihydrate		
	Uncorrected Strip Concentration	Uncorrected Total	Uncorrected	Uncorrected	Uncorrected	Corrected	Corrected	Corrected	
T1-PH5-0A	474.5		1.34E-04	3.42E-05	3.93E-02	2.68E-04	9.49E+02	6.83E-05	7.85E-02
T1-PH5-0B	466.2		1.32E-04	3.36E-05	3.86E-02	2.64E-04	9.32E+02	6.71E-05	7.72E-02
T1-PH5-0C	453.4		1.27E-04	3.26E-05	3.75E-02	2.53E-04	9.07E+02	6.53E-05	7.50E-02
T1-PH5-1A	1071.0		3.06E-04	7.71E-05	8.86E-02	6.13E-04	2.14E+03	1.54E-04	1.77E-01
T1-PH5-1B	1096.7		3.06E-04	7.89E-05	9.07E-02	6.13E-04	2.19E+03	1.58E-04	1.81E-01
T1-PH5-1C	891.3		2.53E-04	6.42E-05	7.37E-02	5.06E-04	1.78E+03	1.28E-04	1.47E-01
T1-PH5-3A	1098.3		3.08E-04	7.91E-05	9.09E-02	6.17E-04	2.20E+03	1.58E-04	1.82E-01
T1-PH5-3B	1096.0		3.04E-04	7.89E-05	9.07E-02	6.09E-04	2.19E+03	1.58E-04	1.81E-01
T1-PH5-3C	1093.4		3.07E-04	7.87E-05	9.05E-02	6.14E-04	2.19E+03	1.57E-04	1.81E-01
T1-PH5-6A	1129.7		3.22E-04	8.13E-05	9.35E-02	6.43E-04	2.26E+03	1.63E-04	1.87E-01
T1-PH5-6B	1142.2		3.23E-04	8.22E-05	9.45E-02	6.45E-04	2.28E+03	1.64E-04	1.89E-01
T1-PH5-6C	1065.2		2.98E-04	7.67E-05	8.81E-02	5.96E-04	2.13E+03	1.53E-04	1.76E-01
T1-PH5-10A	989.0		2.80E-04	7.12E-05	8.18E-02	5.60E-04	1.98E+03	1.42E-04	1.64E-01
T1-PH5-10B	948.7		2.69E-04	6.83E-05	7.85E-02	5.39E-04	1.90E+03	1.37E-04	1.57E-01
T1-PH5-10C	432.0		1.23E-04	3.11E-05	3.57E-02	2.45E-04	8.64E+02	6.22E-05	7.15E-02
T1-PH5-15A	947.4		2.63E-04	6.82E-05	7.84E-02	5.27E-04	1.89E+03	1.36E-04	1.57E-01
T1-PH5-15B	1002.2		2.81E-04	7.21E-05	8.29E-02	5.61E-04	2.00E+03	1.44E-04	1.66E-01
T1-PH5-15C	963.7		2.74E-04	6.94E-05	7.97E-02	5.47E-04	1.93E+03	1.39E-04	1.59E-01

## TREATMENT 1, pH 6.5 DATA

Sample ID	Initial Equilibrated Suspension pH	Mass Wet Resin	Initial pH	pH at time of collection	Ionic Strength	Ferrihydrate Suspension Concentration	mmol As in initial suspension	Time (days)	Strip 1 Arsenate		Strip 2 Arsenate	
									Concentration	ppb	Concentration	ppb
M NaNO <sub>3</sub>												
g/L												
g												
T1-PH6.5-0A	6.53	0.2578	6.56	6.56	0.001	0.5008	8.70E-04	0	205.1	34.2	0.5008	8.70E-04
T1-PH6.5-0B	6.53	0.2553	6.58	6.58	0.001	0.5008	8.70E-04	0	188.0	118.9	0.5008	8.70E-04
T1-PH6.5-0C	6.53	0.2526	6.59	6.59	0.001	0.5008	8.70E-04	0	189.8	115.6	0.5008	8.70E-04
T1-PH6.5-1A	6.53	0.2561	6.58	6.25	0.001	0.5008	8.70E-04	1	319.9	146.4	0.5008	8.70E-04
T1-PH6.5-1B	6.53	0.2537	6.59	6.24	0.001	0.5008	8.70E-04	1	940.5	160.0	0.5008	8.70E-04
T1-PH6.5-1C	6.53	0.2519	6.59	6.37	0.001	0.5008	8.70E-04	1	752.3	162.2	0.5008	8.70E-04
T1-PH6.5-3A	6.53	0.2555	6.58	6.29	0.001	0.5008	8.70E-04	3	809.3	165.1	0.5008	8.70E-04
T1-PH6.5-3B	6.53	0.2566	6.58	6.44	0.001	0.5008	8.70E-04	3	687.1	162.6	0.5008	8.70E-04
T1-PH6.5-3C	6.53	0.2552	6.58	6.26	0.001	0.5008	8.70E-04	3	702.9	151.7	0.5008	8.70E-04
T1-PH6.5-6A	6.53	0.2594	6.58	6.05	0.001	0.5008	8.70E-04	6	780.6	192.3	0.5008	8.70E-04
T1-PH6.5-6B	6.53	0.2551	6.58	6.09	0.001	0.5008	8.70E-04	6	747.6	189.3	0.5008	8.70E-04
T1-PH6.5-6C	6.53	0.2591	6.57	6.09	0.001	0.5008	8.70E-04	6	808.8	177.3	0.5008	8.70E-04
T1-PH6.5-10A	6.53	0.2547	6.57	6.10	0.001	0.5008	8.70E-04	10	603.7	158.1	0.5008	8.70E-04
T1-PH6.5-10B	6.53	0.2522	6.57	6.14	0.001	0.5008	8.70E-04	10	726.5	186.2	0.5008	8.70E-04
T1-PH6.5-10C	6.53	0.2580	6.57	6.09	0.001	0.5008	8.70E-04	10	862.5	191.7	0.5008	8.70E-04
T1-PH6.5-15A	6.53	0.2560	6.56	6.19	0.001	0.5008	8.70E-04	15	802.3	165.4	0.5008	8.70E-04
T1-PH6.5-15B	6.53	0.2551	6.57	6.19	0.001	0.5008	8.70E-04	15	754.9	167.4	0.5008	8.70E-04
T1-PH6.5-15C	6.53	0.2591	6.57	6.16	0.001	0.5008	8.70E-04	15	733.9	167.4	0.5008	8.70E-04





## TREATMENT 1, pH 8 DATA

Sample ID	Initial Equilibrated Suspension pH	Mass Wet Resin	Initial pH	pH at time of collection	Ionic Strength	Ferrihydrate Suspension Concentration	mmol As in initial suspension	Time (days)	ppb			
									Strip 1 Arsenate Concentration	Strip 2 Arsenate Concentration		
									g	M NaNO3	g/L	ppb
T1-PH8-0A	7.95	0.2578	7.35	7.35	0.001	0.5015	8.71E-04	0	462.8	194.7		
T1-PH8-0B	7.95	0.2527	7.37	7.37	0.001	0.5015	8.71E-04	0	425.3	193.9		
T1-PH8-0C	7.95	0.2582	7.37	7.37	0.001	0.5015	8.71E-04	0	434.1	197.1		
T1-PH8-1A	7.95	0.2526	7.39	6.93	0.001	0.5015	8.71E-04	1	737.1	263.8		
T1-PH8-1B	7.95	0.2583	7.39	6.81	0.001	0.5015	8.71E-04	1	783.8	262.5		
T1-PH8-1C	7.95	0.2568	7.38	6.98	0.001	0.5015	8.71E-04	1	868.1	271.2		
T1-PH8-3A	7.95	0.2562	7.40	6.96	0.001	0.5015	8.71E-04	3	887.8	303.7		
T1-PH8-3B	7.95	0.2574	7.38	6.95	0.001	0.5015	8.71E-04	3	766.7	282.9		
T1-PH8-3C	7.95	0.2563	7.39	6.93	0.001	0.5015	8.71E-04	3	927.6	317.6		
T1-PH8-6A	7.95	0.2525	7.39	6.79	0.001	0.5015	8.71E-04	6	925.5	328.6		
T1-PH8-6B	7.95	0.2582	7.40	6.78	0.001	0.5015	8.71E-04	6	812.5	321.3		
T1-PH8-6C	7.95	0.2559	7.40	6.76	0.001	0.5015	8.71E-04	6	870.0	353.2		
T1-PH8-10A	7.95	0.2574	7.41	6.80	0.001	0.5015	8.71E-04	10	744.3	314.0		
T1-PH8-10B	7.95	0.2517	7.40	6.78	0.001	0.5015	8.71E-04	10	695.0	293.4		
T1-PH8-10C	7.95	0.2574	7.40	6.72	0.001	0.5015	8.71E-04	10	0.0	307.5		
T1-PH8-15A	7.95	0.2555	7.41	6.81	0.001	0.5015	8.71E-04	15	830.3	267.4		
T1-PH8-15B	7.95	0.2581	7.42	6.81	0.001	0.5015	8.71E-04	15	847.3	306.5		
T1-PH8-15C	7.95	0.2586	7.41	6.82	0.001	0.5015	8.71E-04	15	808.5	285.3		

## TREATMENT 1, pH 8 DATA (Continued)

Sample ID	ppb		mmol AsO <sub>4</sub> <sup>3-</sup> /g wet resin		mmol AsO <sub>4</sub> <sup>3-</sup> stripped/ mmol AsO <sub>4</sub> <sup>3-</sup> in Ferrihydrate		mmol AsO <sub>4</sub> <sup>3-</sup> stripped/ mmol AsO <sub>4</sub> <sup>3-</sup> in Ferrihydrate	
	Uncorrected Strip Concentration	Uncorrected Total	Uncorrected	Uncorrected	Uncorrected	Uncorrected	Corrected Strip Concentration	Corrected
T1-PH8-0A	657.5	1.84E-04	4.73E-05	5.43E-02	1.31E+03	3.67E-04	9.47E-05	1.09E-01
T1-PH8-0B	619.2	1.76E-04	4.46E-05	5.11E-02	1.24E+03	3.53E-04	8.91E-05	1.02E-01
T1-PH8-0C	631.2	1.76E-04	4.54E-05	5.21E-02	1.26E+03	3.52E-04	9.09E-05	1.04E-01
T1-PH8-1A	1000.9	2.85E-04	7.21E-05	8.27E-02	2.00E+03	5.70E-04	1.44E-04	1.65E-01
T1-PH8-1B	1046.3	2.92E-04	7.53E-05	8.64E-02	2.09E+03	5.83E-04	1.51E-04	1.73E-01
T1-PH8-1C	1139.2	3.19E-04	8.20E-05	9.41E-02	2.28E+03	6.39E-04	1.64E-04	1.88E-01
T1-PH8-3A	1191.5	3.35E-04	8.58E-05	9.84E-02	2.38E+03	6.70E-04	1.72E-04	1.97E-01
T1-PH8-3B	1049.5	2.94E-04	7.55E-05	8.67E-02	2.10E+03	5.87E-04	1.51E-04	1.73E-01
T1-PH8-3C	1245.2	3.50E-04	8.96E-05	1.03E-01	2.49E+03	6.99E-04	1.79E-04	2.06E-01
T1-PH8-6A	1254.1	3.58E-04	9.03E-05	1.04E-01	2.51E+03	7.15E-04	1.81E-04	2.07E-01
T1-PH8-6B	1133.8	3.16E-04	8.16E-05	9.37E-02	2.27E+03	6.32E-04	1.63E-04	1.87E-01
T1-PH8-6C	1223.2	3.44E-04	8.81E-05	1.01E-01	2.45E+03	6.88E-04	1.76E-04	2.02E-01
T1-PH8-10A	1058.4	2.96E-04	7.62E-05	8.74E-02	2.12E+03	5.92E-04	1.52E-04	1.75E-01
T1-PH8-10B	988.4	2.83E-04	7.11E-05	8.17E-02	1.98E+03	5.65E-04	1.42E-04	1.63E-01
T1-PH8-10C	307.5	8.60E-05	2.21E-05	2.54E-02	6.15E+02	1.72E-04	4.43E-05	5.08E-02
T1-PH8-15A	1097.6	3.09E-04	7.90E-05	9.07E-02	2.20E+03	6.18E-04	1.58E-04	1.81E-01
T1-PH8-15B	1153.7	3.22E-04	8.30E-05	9.53E-02	2.31E+03	6.44E-04	1.66E-04	1.91E-01
T1-PH8-15C	1093.8	3.04E-04	7.87E-05	9.04E-02	2.19E+03	6.09E-04	1.57E-04	1.81E-01

## TREATMENT 2, 0.05 g/L DATA

Sample ID	Initial Equilibrated Suspension pH	Mass Wet Resin	Initial pH	pH at time of collection	Ionic Strength	Ferrihydrate Suspension Concentration	mmol As in initial suspension	Time (days)	ppb	
									Strip 1 Arsenate Concentration	Strip 2 Arsenate Concentration
					M NaNO <sub>3</sub>		g/L			
					g					ppb
T2-50-0A	8.07	0.2574	7.18	7.18	0.001	0.0502	8.72225E-05	0	0.0	89.0
T2-50-0B	8.07	0.2594	7.16	7.16	0.001	0.0502	8.72225E-05	0	0.0	97.8
T2-50-0C	8.07	0.2567	7.22	7.22	0.001	0.0502	8.72225E-05	0	0.0	93.9
T2-50-1A	8.07	0.2587	7.34	5.86	0.001	0.0502	8.72225E-05	1	933.1	82.3
T2-50-1B	8.07	0.2552	7.35	5.72	0.001	0.0502	8.72225E-05	1	679.2	128.6
T2-50-1C	8.07	0.2587	7.35	5.69	0.001	0.0502	8.72225E-05	1	746.4	126.7
T2-50-3A	8.07	0.2582	7.36	5.77	0.001	0.0502	8.72225E-05	3	585.5	96.0
T2-50-3B	8.07	0.2591	7.36	5.73	0.001	0.0502	8.72225E-05	3	761.4	117.2
T2-50-3C	8.07	0.2580	7.34	5.67	0.001	0.0502	8.72225E-05	3	677.2	114.8
T2-50-6A	8.07	0.2582	7.35	5.48	0.001	0.0502	8.72225E-05	6	886.1	159.6
T2-50-6B	8.07	0.2561	7.38	5.55	0.001	0.0502	8.72225E-05	6	828.8	135.6
T2-50-6C	8.07	0.2546	7.38	5.47	0.001	0.0502	8.72225E-05	6	813.2	146.3
T2-50-10A	8.07	0.2521	7.44	5.82	0.001	0.0502	8.72225E-05	10	787.7	143.7
T2-50-10B	8.07	0.2584	7.44	5.75	0.001	0.0502	8.72225E-05	10	812.8	150.1
T2-50-10C	8.07	0.2543	7.43	5.73	0.001	0.0502	8.72225E-05	10	806.1	157.5
T2-50-15A	8.07	0.2532	7.33	5.56	0.001	0.0502	8.72225E-05	15	885.8	143.7
T2-50-15B	8.07	0.2540	7.44	5.48	0.001	0.0502	8.72225E-05	15	836.4	116.1
T2-50-15C	8.07	0.2545	7.08	5.28	0.001	0.0502	8.72225E-05	15	843.7	142.1

## TREATMENT 2, 0.05 g/L DATA (Continued)

Sample ID	Uncorrected Total		Uncorrected		Uncorrected		Corrected Total		Corrected		Corrected	
	Strip Concentration	mmol AsO <sub>4</sub> <sup>3-</sup> /g wet resin	mmol AsO <sub>4</sub> <sup>3-</sup> mmol AsO <sub>4</sub> <sup>3-</sup>	mmol AsO <sub>4</sub> <sup>3-</sup> stripped/ mmol AsO <sub>4</sub> <sup>3-</sup> in Ferrihydrate	Strip Concentration	mmol AsO <sub>4</sub> <sup>3-</sup> mmol AsO <sub>4</sub> <sup>3-</sup> /g wet resin	mmol AsO <sub>4</sub> <sup>3-</sup> stripped/ mmol AsO <sub>4</sub> <sup>3-</sup> in Ferrihydrate	mmol AsO <sub>4</sub> <sup>3-</sup> mmol AsO <sub>4</sub> <sup>3-</sup> /g wet resin	mmol AsO <sub>4</sub> <sup>3-</sup> mmol AsO <sub>4</sub> <sup>3-</sup>	mmol AsO <sub>4</sub> <sup>3-</sup> mmol AsO <sub>4</sub> <sup>3-</sup>	mmol AsO <sub>4</sub> <sup>3-</sup> stripped/ mmol AsO <sub>4</sub> <sup>3-</sup> in Ferrihydrate	mmol AsO <sub>4</sub> <sup>3-</sup> mmol AsO <sub>4</sub> <sup>3-</sup>
T2-50-0A	89.0	2.49E-05	6.41E-06	7.35E-02	1.78E+02	4.98E-05	1.28E-05	1.47E-01				
T2-50-0B	97.8	2.71E-05	7.04E-06	8.07E-02	1.96E+02	5.43E-05	1.41E-05	1.61E-01				
T2-50-0C	93.9	2.63E-05	6.76E-06	7.75E-02	1.88E+02	5.26E-05	1.35E-05	1.55E-01				
T2-50-1A	1015.4	2.83E-04	7.31E-05	8.38E-01	2.03E+03	5.65E-04	1.46E-04	1.68E+00				
T2-50-1B	807.8	2.28E-04	5.82E-05	6.67E-01	1.62E+03	4.56E-04	1.16E-04	1.33E+00				
T2-50-1C	873.1	2.43E-04	6.28E-05	7.21E-01	1.75E+03	4.86E-04	1.26E-04	1.44E+00				
T2-50-3A	681.4	1.90E-04	4.91E-05	5.62E-01	1.36E+03	3.80E-04	9.81E-05	1.12E+00				
T2-50-3B	878.6		6.32E-05	7.25E-01	1.76E+03	4.88E-04	1.26E-04	1.45E+00				
T2-50-3C	792.0	2.21E-04	5.70E-05	6.54E-01	1.58E+03	4.42E-04	1.14E-04	1.31E+00				
T2-50-6A	1045.7	2.92E-04	7.53E-05	8.63E-01	2.09E+03	5.83E-04	1.51E-04	1.73E+00				
T2-50-6B	964.4	2.71E-04	6.94E-05	7.96E-01	1.93E+03	5.42E-04	1.39E-04	1.59E+00				
T2-50-6C	959.6	2.71E-04	6.91E-05	7.92E-01	1.92E+03	5.43E-04	1.38E-04	1.58E+00				
T2-50-10A	931.3	2.66E-04	6.70E-05	7.69E-01	1.86E+03	5.32E-04	1.34E-04	1.54E+00				
T2-50-10B	962.8	2.68E-04	6.93E-05	7.95E-01	1.93E+03	5.36E-04	1.39E-04	1.59E+00				
T2-50-10C	963.5	2.73E-04	6.94E-05	7.95E-01	1.93E+03	5.45E-04	1.39E-04	1.59E+00				
T2-50-15A	1029.5	2.93E-04	7.41E-05	8.50E-01	2.06E+03	5.85E-04	1.48E-04	1.70E+00				
T2-50-15B	952.5	2.70E-04	6.86E-05	7.86E-01	1.91E+03	5.40E-04	1.37E-04	1.57E+00				
T2-50-15C	985.8	2.79E-04	7.10E-05	8.14E-01	1.97E+03	5.58E-04	1.42E-04	1.63E+00				

ppb

## TREATMENT 2, 0.5 g/L DATA

Sample ID	Initial Equilibrated Suspension pH	Mass Wet Resin	Initial pH	pH at time of collection	Ionic Strength	Ferrihydrate Suspension Concentration	mmol As in initial suspension	Time (days)	ppb	
									Strip 1 Arsenate Concentration	Strip 2 Arsenate Concentration
									g/L	
									M NaNO <sub>3</sub>	
									g	
T2-500-0A	7.95	0.2560	7.64	7.64	0.001	0.5015	8.71E-04	0	160.8	100.4
T2-500-0B	7.95	0.2543	7.57	7.57	0.001	0.5015	8.71E-04	0	456.8	103.8
T2-500-0C	7.95	0.2520	7.61	7.61	0.001	0.5015	8.71E-04	0	500.4	102.9
T2-500-1A	7.95	0.2548	7.61	6.68	0.001	0.5015	8.71E-04	1	696.3	164.0
T2-500-1B	7.95	0.2599	7.65	6.59	0.001	0.5015	8.71E-04	1	681.3	150.1
T2-500-1C	7.95	0.2570	7.62	6.70	0.001	0.5015	8.71E-04	1	235.6	83.9
T2-500-3A	7.95	0.2587	7.62	6.71	0.001	0.5015	8.71E-04	3	820.9	171.2
T2-500-3B	7.95	0.2571	7.57	6.73	0.001	0.5015	8.71E-04	3	564.3	137.5
T2-500-3C	7.95	0.2505	7.64	6.85	0.001	0.5015	8.71E-04	3	160.3	160.3
T2-500-6A	7.95	0.2593	7.62	6.60	0.001	0.5015	8.71E-04	6	653.9	182.7
T2-500-6B	7.95	0.2532	7.67	6.64	0.001	0.5015	8.71E-04	6	614.9	177.0
T2-500-6C	7.95	0.2585	7.67	6.61	0.001	0.5015	8.71E-04	6	597.7	179.8
T2-500-10A	7.95	0.2578	7.64	6.66	0.001	0.5015	8.71E-04	10	523.4	185.0
T2-500-10B	7.95	0.2551	7.63	6.67	0.001	0.5015	8.71E-04	10	498.4	190.9
T2-500-10C	7.95	0.2574	7.65	6.60	0.001	0.5015	8.71E-04	10	476.9	194.3
T2-500-15A	7.95	0.2555	7.66	6.65	0.001	0.5015	8.71E-04	15	316.0	112.2
T2-500-15B	7.95	0.2556	7.66	6.65	0.001	0.5015	8.71E-04	15	483.6	140.3
T2-500-15C	7.95	0.2550	7.66	6.65	0.001	0.5015	8.71E-04	15	592.1	170.7

TREATMENT 2, 0.5 g/L DATA (Continued)

Sample ID	ppb		mmol AsO <sub>4</sub> <sup>3-</sup> /g wet resin		mmol AsO <sub>4</sub> <sup>3-</sup> stripped/ mmol AsO <sub>4</sub> <sup>3-</sup> in Ferrihydrate		mmol AsO <sub>4</sub> <sup>3-</sup> stripped/ mmol AsO <sub>4</sub> <sup>3-</sup> in Ferrihydrate	
	Uncorrected Strip Concentration	Uncorrected Total	Uncorrected	Uncorrected	Uncorrected	Uncorrected	Corrected Strip Concentration	Corrected
T2-500-0A	261.2	7.34E-05	1.88E-05	2.16E-02	5.22E+02	1.47E-04	3.76E-05	4.32E-02
T2-500-0B	560.6	1.59E-04	4.04E-05	4.68E-02	1.12E+03	3.17E-04	8.07E-05	9.26E-02
T2-500-0C	603.3	1.72E-04	4.34E-05	4.98E-02	1.21E+03	3.45E-04	8.69E-05	9.97E-02
T2-500-1A	860.3	2.43E-04	6.19E-05	7.11E-02	1.72E+03	4.86E-04	1.24E-04	1.42E-01
T2-500-1B	831.4	2.30E-04	5.98E-05	6.87E-02	1.66E+03	4.61E-04	1.20E-04	1.37E-01
T2-500-1C	319.5	8.95E-05	2.30E-05	2.64E-02	6.39E+02	1.79E-04	4.60E-05	5.28E-02
T2-500-3A	992.1	2.76E-04	7.14E-05	8.20E-02	1.98E+03	5.52E-04	1.43E-04	1.64E-01
T2-500-3B	701.9	1.97E-04	5.05E-05	5.80E-02	1.40E+03	3.93E-04	1.01E-04	1.16E-01
T2-500-3C								
T2-500-6A	836.5	2.32E-04	6.02E-05	6.91E-02	1.67E+03	4.64E-04	1.20E-04	1.38E-01
T2-500-6B	791.9	2.25E-04	5.70E-05	6.54E-02	1.58E+03	4.50E-04	1.14E-04	1.31E-01
T2-500-6C	777.6	2.17E-04	5.60E-05	6.42E-02	1.56E+03	4.33E-04	1.12E-04	1.28E-01
T2-500-10A	708.4	1.98E-04	5.10E-05	5.85E-02	1.42E+03	3.96E-04	1.02E-04	1.17E-01
T2-500-10B	689.4	1.95E-04	4.96E-05	5.69E-02	1.38E+03	3.89E-04	9.92E-05	1.14E-01
T2-500-10C	671.2	1.88E-04	4.83E-05	5.54E-02	1.34E+03	3.75E-04	9.66E-05	1.11E-01
T2-500-15A	428.2	1.21E-04	3.08E-05	3.54E-02	8.56E+02	2.41E-04	6.16E-05	7.07E-02
T2-500-15B	623.9	1.76E-04	4.49E-05	5.15E-02	1.25E+03	3.51E-04	8.98E-05	1.03E-01
T2-500-15C	762.8	2.15E-04	5.49E-05	6.30E-02	1.53E+03	4.31E-04	1.10E-04	1.26E-01

## TREATMENT 2, 5.0 g/L DATA

Sample ID	Initial Equilibrated Suspension pH	Mass Wet Resin	initial pH	pH at time of collection	Ionic Strength	Ferrihydrate Suspension Concentration	mmol As in initial suspension	Time (days)	ppb		
									Strip 1 Arsenate Concentration	Strip 2 Arsenate Concentration	
									M NaNO <sub>3</sub>	g/L	ppb
T2-5000-0A	8	0.2575	7.74	7.74	0.001	5.003	8.69E-03	0	208.8	121.0	
T2-5000-0B	8	0.2522	7.75	7.75	0.001	5.003	8.69E-03	0	228.6	108.8	
T2-5000-0C	8	0.2594	7.74	7.74	0.001	5.003	8.69E-03	0	462.4	164.7	
T2-5000-1A	8	0.256	7.73	7.41	0.001	5.003	8.69E-03	1	451.2	157.1	
T2-5000-1B	8	0.2575	7.73	7.4	0.001	5.003	8.69E-03	1	505.8	176.4	
T2-5000-1C	8	0.2559	7.75	7.4	0.001	5.003	8.69E-03	1	482.5	182.0	
T2-5000-3A	8	0.253	7.73	7.44	0.001	5.003	8.69E-03	3	484.6	139.8	
T2-5000-3B	8	0.2572	7.74	7.43	0.001	5.003	8.69E-03	3	446.2	139.2	
T2-5000-3C	8	0.2544	7.73	7.43	0.001	5.003	8.69E-03	3	570.6		
T2-5000-6A	8	0.2569	7.73	7.25	0.001	5.003	8.69E-03	6	567.6	196.7	
T2-5000-6B	8	0.2515	7.74	7.29	0.001	5.003	8.69E-03	6	553.2	185.1	
T2-5000-6C	8	0.2513	7.74	7.26	0.001	5.003	8.69E-03	6	422.2	143.0	
T2-5000-10A	8	0.2552	7.73	7.26	0.001	5.003	8.69E-03	10	483.9	196.4	
T2-5000-10B	8	0.2591	7.75	7.25	0.001	5.003	8.69E-03	10	494.9	175.6	
T2-5000-10C	8	0.2541	7.74	7.25	0.001	5.003	8.69E-03	10	511.6	187.8	
T2-5000-15A	8	0.2545	7.73	7.22	0.001	5.003	8.69E-03	15	539.0	152.2	
T2-5000-15B	8	0.2528	7.74	7.22	0.001	5.003	8.69E-03	15	534.1	192.7	
T2-5000-15C	8	0.2578	7.75	7.24	0.001	5.003	8.69E-03	15	599.6	158.4	

## TREATMENT 2, 5.0 g/L DATA (Continued)

Sample ID	ppb		mmol AsO <sub>4</sub> <sup>3-</sup> /g wet resin		mmol AsO <sub>4</sub> <sup>3-</sup> stripped/ mmol AsO <sub>4</sub> <sup>3-</sup> in Ferrihydrate		mmol AsO <sub>4</sub> <sup>3-</sup> stripped/ mmol AsO <sub>4</sub> <sup>3-</sup> in Ferrihydrate			
	Uncorrected Strip Concentration	Uncorrected Total	Uncorrected	Uncorrected	Uncorrected	Uncorrected	Corrected Strip Concentration	Corrected Total	Corrected	Corrected
T2-5000-0A	329.9	9.22E-05	2.37E-05	2.79E-03	6.60E+02	1.84E-04	4.75E-05	5.46E-03		
T2-5000-0B	337.4	9.63E-05	2.43E-05	2.79E-03	6.75E+02	1.93E-04	4.86E-05	5.59E-03		
T2-5000-0C	627.1	1.74E-04	4.51E-05	5.19E-03	1.25E+03	3.48E-04	9.03E-05	1.04E-02		
T2-5000-1A	608.3	1.71E-04	4.38E-05	5.04E-03	1.22E+03	3.42E-04	8.76E-05	1.01E-02		
T2-5000-1B	682.2	1.91E-04	4.91E-05	5.65E-03	1.36E+03	3.81E-04	9.82E-05	1.13E-02		
T2-5000-1C	664.5	1.87E-04	4.78E-05	5.50E-03	1.33E+03	3.74E-04	9.57E-05	1.10E-02		
T2-5000-3A	624.4	1.87E-04	4.49E-05	5.17E-03	1.25E+03	3.55E-04	8.99E-05	1.03E-02		
T2-5000-3B	585.5	1.64E-04	4.21E-05	4.85E-03	1.17E+03	3.28E-04	8.43E-05	9.70E-03		
T2-5000-3C										
T2-5000-6A	764.3	2.14E-04	5.50E-05	6.33E-03	1.53E+03	4.28E-04	1.10E-04	1.27E-02		
T2-5000-6B	738.3	2.11E-04	5.31E-05	6.11E-03	1.48E+03	4.23E-04	1.06E-04	1.22E-02		
T2-5000-6C	565.2	1.62E-04	4.07E-05	4.68E-03	1.13E+03	3.24E-04	8.14E-05	9.36E-03		
T2-5000-10A	680.3	1.92E-04	4.90E-05	5.63E-03	1.36E+03	3.84E-04	9.79E-05	1.13E-02		
T2-5000-10B	670.5	1.92E-04	4.83E-05	5.55E-03	1.34E+03	3.73E-04	9.65E-05	1.11E-02		
T2-5000-10C	699.3	1.98E-04	5.03E-05	5.79E-03	1.40E+03	3.96E-04	1.01E-04	1.16E-02		
T2-5000-15A	691.1	1.95E-04	4.98E-05	5.72E-03	1.38E+03	3.91E-04	9.95E-05	1.14E-02		
T2-5000-15B	726.8	2.07E-04	5.23E-05	6.02E-03	1.45E+03	4.14E-04	1.05E-04	1.20E-02		
T2-5000-15C	758.0	2.12E-04	5.46E-05	6.28E-03	1.52E+03	4.23E-04	1.09E-04	1.26E-02		



## TREATMENT 3, 0.001 M DATA

Sample ID	Initial Equilibrated Suspension pH	Mass Wet Resin	Initial pH	pH at time of collection	Ionic Strength	Ferrihydrate Suspension Concentration	mmol As in initial suspension	Time (days)	ppb	
									Strip 1 Arsenate Concentration	Strip 2 Arsenate Concentration
									g/L	
									M NaNO <sub>3</sub>	
									g	
T3-0.001-0A	7.92	0.2583	7.43	7.43	0.001	0.5007	8.70E-04	0	912.2	271.5
T3-0.001-0B	7.92	0.2555	7.43	7.43	0.001	0.5007	8.70E-04	0	793.0	248.5
T3-0.001-0C	7.92	0.2532	7.45	7.45	0.001	0.5007	8.70E-04	0	788.0	197.3
T3-0.001-1A	7.92	0.2556	7.47	6.86	0.001	0.5007	8.70E-04	1	826.8	142.5
T3-0.001-1B	7.92	0.2563	7.48	6.86	0.001	0.5007	8.70E-04	1	787.4	153.1
T3-0.001-1C	7.92	0.2537	7.50	6.87	0.001	0.5007	8.70E-04	1	787.0	157.8
T3-0.001-3A	7.92	0.2579	7.53	6.98	0.001	0.5007	8.70E-04	3	806.8	123.0
T3-0.001-3B	7.92	0.2513	7.51	6.91	0.001	0.5007	8.70E-04	3	798.0	155.5
T3-0.001-3C	7.92	0.2564	7.54	6.99	0.001	0.5007	8.70E-04	3	761.9	148.3
T3-0.001-6A	7.92	0.2523	7.55	6.75	0.001	0.5007	8.70E-04	6	749.5	142.6
T3-0.001-6B	7.92	0.2545	7.54	6.73	0.001	0.5007	8.70E-04	6	789.7	158.7
T3-0.001-6C	7.92	0.2540	7.56	6.78	0.001	0.5007	8.70E-04	6	724.3	159.3
T3-0.001-10A	7.92	0.2551	7.57	6.76	0.001	0.5007	8.70E-04	10	639.7	134.1
T3-0.001-10B	7.92	0.2558	7.56	6.79	0.001	0.5007	8.70E-04	10	563.4	139.1
T3-0.001-10C	7.92	0.2533	7.56	6.78	0.001	0.5007	8.70E-04	10	567.0	117.6
T3-0.001-15A	7.92	0.2570	7.57	6.71	0.001	0.5007	8.70E-04	15	411.1	126.5
T3-0.001-15B	7.92	0.2532	7.57	6.75	0.001	0.5007	8.70E-04	15	447.2	131.7
T3-0.001-15C	7.92	0.2571	7.57	6.72	0.001	0.5007	8.70E-04	15	500.5	127.9

TREATMENT 3, 0.001 M DATA (Continued)

Sample ID	ppb		mmol AsO <sub>4</sub> <sup>3-</sup> /g wet resin		mmol AsO <sub>4</sub> <sup>3-</sup> stripped/ mmol AsO <sub>4</sub> <sup>3-</sup> in Ferrihydrate		mmol AsO <sub>4</sub> <sup>3-</sup> stripped/ mmol AsO <sub>4</sub> <sup>3-</sup> in Ferrihydrate	
	Uncorrected Strip Concentration	Uncorrected Total	Uncorrected mmol AsO <sub>4</sub> <sup>3-</sup> /g wet resin	Uncorrected mmol AsO <sub>4</sub> <sup>3-</sup>	Uncorrected mmol AsO <sub>4</sub> <sup>3-</sup> stripped/ mmol AsO <sub>4</sub> <sup>3-</sup> in Ferrihydrate	Corrected Strip Concentration	Corrected mmol AsO <sub>4</sub> <sup>3-</sup> /g wet resin	Corrected mmol AsO <sub>4</sub> <sup>3-</sup> stripped/ mmol AsO <sub>4</sub> <sup>3-</sup> in Ferrihydrate
T3-0.001-0A	1183.7		3.30E-04	8.52E-05	9.79E-02	2.37E+03	6.60E-04	1.70E-04
T3-0.001-0B	1041.5		2.93E-04	7.50E-05	8.62E-02	2.08E+03	5.87E-04	1.50E-04
T3-0.001-0C	985.3		2.80E-04	7.09E-05	8.15E-02	1.97E+03	5.60E-04	1.42E-04
T3-0.001-1A	969.2		2.73E-04	6.98E-05	8.02E-02	1.94E+03	5.46E-04	1.40E-04
T3-0.001-1B	940.5		2.64E-04	6.77E-05	7.78E-02	1.88E+03	5.28E-04	1.35E-04
T3-0.001-1C	944.7		2.68E-04	6.80E-05	7.82E-02	1.89E+03	5.36E-04	1.36E-04
T3-0.001-3A	929.8		2.60E-04	6.69E-05	7.69E-02	1.86E+03	5.19E-04	1.34E-04
T3-0.001-3B	953.5		2.73E-04	6.86E-05	7.89E-02	1.91E+03	5.46E-04	1.37E-04
T3-0.001-3C	910.2		2.56E-04	6.55E-05	7.53E-02	1.82E+03	5.11E-04	1.31E-04
T3-0.001-6A	892.2		2.55E-04	6.42E-05	7.38E-02	1.78E+03	5.09E-04	1.28E-04
T3-0.001-6B	948.3		2.68E-04	6.83E-05	7.85E-02	1.90E+03	5.36E-04	1.37E-04
T3-0.001-6C	883.6		2.50E-04	6.36E-05	7.31E-02	1.77E+03	5.01E-04	1.27E-04
T3-0.001-10A	773.7		2.18E-04	5.57E-05	6.40E-02	1.55E+03	4.37E-04	1.11E-04
T3-0.001-10B	702.5		1.98E-04	5.06E-05	5.81E-02	1.41E+03	3.95E-04	1.01E-04
T3-0.001-10C	684.6		1.95E-04	4.93E-05	5.66E-02	1.37E+03	3.89E-04	9.86E-05
T3-0.001-15A	537.7		1.51E-04	3.87E-05	4.45E-02	1.08E+03	3.01E-04	7.74E-05
T3-0.001-15B	578.9		1.65E-04	4.17E-05	4.79E-02	1.16E+03	3.29E-04	8.33E-05
T3-0.001-15C	628.4		1.76E-04	4.52E-05	5.20E-02	1.26E+03	3.52E-04	9.05E-05

TREATMENT 3, 0.01 M DATA

Sample ID	Initial Equilibrated Suspension pH	Mass Wet Resin	Initial pH	pH at time of collection	Ionic Strength	Ferrihydrate Suspension Concentration	mmol As in initial suspension	Time (days)	ppb				
									Strip 1 Arsenate Concentration	Strip 2 Arsenate Concentration			
									g	M NaNO3	g/L	ppb	ppb
T3-0.01-0A	8.08	0.2524	7.51	7.51	0.01	0.5004	8.69E-04	0	749.0	220.8			
T3-0.01-0B	8.08	0.2560	7.54	7.54	0.01	0.5004	8.69E-04	0	781.5	245.2			
T3-0.01-0C	8.08	0.2533	7.55	7.55	0.01	0.5004	8.69E-04	0	465.4	283.5			
T3-0.01-1A	8.08	0.2553	7.58	7.10	0.01	0.5004	8.69E-04	1	780.8	170.2			
T3-0.01-1B	8.08	0.2570	7.59	7.16	0.01	0.5004	8.69E-04	1	696.9	150.6			
T3-0.01-1C	8.08	0.2532	7.58	7.13	0.01	0.5004	8.69E-04	1	589.5	147.7			
T3-0.01-3A	8.08	0.2579	7.62	7.21	0.01	0.5004	8.69E-04	3	584.9	129.9			
T3-0.01-3B	8.08	0.2521	7.62	7.18	0.01	0.5004	8.69E-04	3	516.6	144.2			
T3-0.01-3C	8.08	0.2570	7.62	7.16	0.01	0.5004	8.69E-04	3	706.2	122.3			
T3-0.01-6A	8.08	0.2557	7.65	6.94	0.01	0.5004	8.69E-04	6	613.8	158.3			
T3-0.01-6B	8.08	0.2547	7.64	6.99	0.01	0.5004	8.69E-04	6	642.3	134.9			
T3-0.01-6C	8.08	0.2530	7.64	6.99	0.01	0.5004	8.69E-04	6	556.1	143.1			
T3-0.01-10A	8.08	0.2519	7.67	7.02	0.01	0.5004	8.69E-04	10	425.4	133.7			
T3-0.01-10B	8.08	0.2511	7.65	7.04	0.01	0.5004	8.69E-04	10	423.0	145.8			
T3-0.01-10C	8.08	0.2561	7.66	7.00	0.01	0.5004	8.69E-04	10	487.1	143.8			
T3-0.01-15A	8.08	0.2560	7.67	7.28	0.01	0.5004	8.69E-04	15	458.8	113.8			
T3-0.01-15B	8.08	0.2594	7.67	7.30	0.01	0.5004	8.69E-04	15	444.7	119.0			
T3-0.01-15C	8.08	0.2530	7.68	7.31	0.01	0.5004	8.69E-04	15	495.6	119.6			

TREATMENT 3, 0.01 M DATA (Continued)

Sample ID	ppb		mmol AsO <sub>4</sub> <sup>3-</sup> /g wet resin		mmol AsO <sub>4</sub> <sup>3-</sup> stripped/ mmol AsO <sub>4</sub> <sup>3-</sup> in Ferrihydrate		mmol AsO <sub>4</sub> <sup>3-</sup> stripped/ mmol AsO <sub>4</sub> <sup>3-</sup> in Ferrihydrate	
	Uncorrected Strip Concentration	Uncorrected Total	Uncorrected mmol AsO <sub>4</sub> <sup>3-</sup> /g wet resin	Uncorrected mmol AsO <sub>4</sub> <sup>3-</sup>	Uncorrected mmol AsO <sub>4</sub> <sup>3-</sup> stripped/ mmol AsO <sub>4</sub> <sup>3-</sup> in Ferrihydrate	Corrected Strip Concentration	Corrected mmol AsO <sub>4</sub> <sup>3-</sup> /g wet resin	Corrected mmol AsO <sub>4</sub> <sup>3-</sup> stripped/ mmol AsO <sub>4</sub> <sup>3-</sup> in Ferrihydrate
T3-0.01-0A	969.9		2.77E-04	6.98E-05	8.03E-02	1.94E+03	5.53E-04	1.40E-04
T3-0.01-0B	1026.7		2.89E-04	7.39E-05	8.50E-02	2.05E+03	5.77E-04	1.48E-04
T3-0.01-0C	749.0		2.13E-04	5.39E-05	6.20E-02	1.50E+03	4.26E-04	1.08E-04
T3-0.01-1A	951.0		2.68E-04	6.85E-05	7.87E-02	1.90E+03	5.36E-04	1.37E-04
T3-0.01-1B	847.5		2.37E-04	6.10E-05	7.02E-02	1.70E+03	4.75E-04	1.22E-04
T3-0.01-1C	737.2		2.10E-04	5.31E-05	6.10E-02	1.47E+03	4.19E-04	1.06E-04
T3-0.01-3A	714.7		1.99E-04	5.14E-05	5.92E-02	1.43E+03	3.99E-04	1.03E-04
T3-0.01-3B	660.8		1.89E-04	4.76E-05	5.47E-02	1.32E+03	3.77E-04	9.51E-05
T3-0.01-3C	828.5		2.32E-04	5.96E-05	6.86E-02	1.66E+03	4.64E-04	1.19E-04
T3-0.01-6A	772.1		2.17E-04	5.56E-05	6.39E-02	1.54E+03	4.35E-04	1.11E-04
T3-0.01-6B	777.2		2.20E-04	5.59E-05	6.43E-02	1.55E+03	4.39E-04	1.12E-04
T3-0.01-6C	699.3		1.99E-04	5.03E-05	5.79E-02	1.40E+03	3.98E-04	1.01E-04
T3-0.01-10A	559.1		1.60E-04	4.02E-05	4.63E-02	1.12E+03	3.20E-04	8.05E-05
T3-0.01-10B	568.7		1.63E-04	4.09E-05	4.71E-02	1.14E+03	3.26E-04	8.19E-05
T3-0.01-10C	630.9		1.77E-04	4.54E-05	5.22E-02	1.26E+03	3.55E-04	9.08E-05
T3-0.01-15A	572.6		1.61E-04	4.12E-05	4.74E-02	1.15E+03	3.22E-04	8.24E-05
T3-0.01-15B	563.6		1.56E-04	4.06E-05	4.67E-02	1.13E+03	3.13E-04	8.11E-05
T3-0.01-15C	615.2		1.75E-04	4.43E-05	5.09E-02	1.23E+03	3.50E-04	8.86E-05

## TREATMENT 3, 0.1 M DATA

Sample ID	Initial Equilibrated Suspension pH	Mass Wet Resin	Initial pH	pH at time of collection	Ionic Strength	Ferrihydrate Suspension Concentration	mmol As in initial suspension	Time (days)	ppb	
									Strip 1 Arsenate Concentration	Strip 2 Arsenate Concentration
									g/L	
									M NaNO3	
									g	ppb
T3-0.1-0A	7.97	0.2578	7.39	7.39	0.1	0.5007	8.70E-04	0	0.0	897.5
T3-0.1-0B	7.97	0.2593	7.44	7.44	0.1	0.5007	8.70E-04	0	722.0	153.6
T3-0.1-0C	7.97	0.2552	7.45	7.45	0.1	0.5007	8.70E-04	0	721.4	188.3
T3-0.1-1A	7.97	0.5089	7.47	6.99	0.1	0.5007	8.70E-04	1	1277.2	289.3
T3-0.1-1B	7.97	0.2587	7.51	7.14	0.1	0.5007	8.70E-04	1	632.5	179.6
T3-0.1-1C	7.97	0.2581	7.51	7.15	0.1	0.5007	8.70E-04	1	598.2	141.3
T3-0.1-3A	7.97	0.2556	7.54	7.23	0.1	0.5007	8.70E-04	3	505.6	140.0
T3-0.1-3B	7.97	0.2549	7.55	7.24	0.1	0.5007	8.70E-04	3	513.9	133.1
T3-0.1-3C	7.97	0.2540	7.53	7.24	0.1	0.5007	8.70E-04	3	454.5	126.6
T3-0.1-6A	7.97	0.2581	7.57	7.01	0.1	0.5007	8.70E-04	6	557.6	122.9
T3-0.1-6B	7.97	0.2562	7.57	7.04	0.1	0.5007	8.70E-04	6	470.3	143.2
T3-0.1-6C	7.97	0.2565	7.57	7.04	0.1	0.5007	8.70E-04	6	445.0	106.9
T3-0.1-10A	7.97	0.2579	7.59	7.07	0.1	0.5007	8.70E-04	10	427.2	141.1
T3-0.1-10B	7.97	0.2549	7.59	7.09	0.1	0.5007	8.70E-04	10	400.9	131.4
T3-0.1-10C	7.97	0.2594	7.59	7.09	0.1	0.5007	8.70E-04	10	434.6	124.0
T3-0.1-15A	7.97	0.2560	7.59	7.17	0.1	0.5007	8.70E-04	15	438.2	128.9
T3-0.1-15B	7.97	0.2582	7.60	7.18	0.1	0.5007	8.70E-04	15	476.0	135.2
T3-0.1-15C	7.97	0.2579	7.60	7.14	0.1	0.5007	8.70E-04	15	476.0	135.2

TREATMENT 3, 0.1 M DATA (Continued)

Sample ID	ppb		mmol AsO <sub>4</sub> <sup>3-</sup> /g wet resin		mmol AsO <sub>4</sub> <sup>3-</sup> stripped/ mmol AsO <sub>4</sub> <sup>3-</sup> in Ferrihydrate		mmol AsO <sub>4</sub> <sup>3-</sup> stripped/ mmol AsO <sub>4</sub> <sup>3-</sup> in Ferrihydrate	
	Uncorrected Strip Concentration	Uncorrected Total	Uncorrected mmol AsO <sub>4</sub> <sup>3-</sup> /g wet resin	Uncorrected mmol AsO <sub>4</sub> <sup>3-</sup>	Uncorrected mmol AsO <sub>4</sub> <sup>3-</sup> stripped/ mmol AsO <sub>4</sub> <sup>3-</sup> in Ferrihydrate	Corrected Strip Concentration	Corrected mmol AsO <sub>4</sub> <sup>3-</sup> /g wet resin	Corrected mmol AsO <sub>4</sub> <sup>3-</sup> stripped/ mmol AsO <sub>4</sub> <sup>3-</sup> in Ferrihydrate
T3-0.1-0A	897.5		2.51E-04	6.46E-05	7.43E-02	1.79E+03	5.01E-04	1.29E-04
T3-0.1-0B	875.6		2.43E-04	6.30E-05	7.25E-02	1.75E+03	4.86E-04	1.26E-04
T3-0.1-0C	909.7		2.57E-04	6.55E-05	7.53E-02	1.82E+03	5.13E-04	1.31E-04
T3-0.1-1A	1566.5		2.22E-04	1.13E-04	1.30E-01	3.13E+03	4.43E-04	2.26E-04
T3-0.1-1B	812.1		2.26E-04	5.85E-05	6.72E-02	1.62E+03	4.52E-04	1.17E-04
T3-0.1-1C	739.5		2.06E-04	5.32E-05	6.12E-02	1.48E+03	4.12E-04	1.06E-04
T3-0.1-3A	645.6		1.82E-04	4.65E-05	5.34E-02	1.29E+03	3.64E-04	9.29E-05
T3-0.1-3B	647.0		1.83E-04	4.66E-05	5.35E-02	1.29E+03	3.65E-04	9.32E-05
T3-0.1-3C	581.1		1.65E-04	4.18E-05	4.81E-02	1.16E+03	3.29E-04	8.37E-05
T3-0.1-6A	680.5		1.90E-04	4.90E-05	5.63E-02	1.36E+03	3.80E-04	9.80E-05
T3-0.1-6B	613.5		1.72E-04	4.42E-05	5.08E-02	1.23E+03	3.45E-04	8.83E-05
T3-0.1-6C	551.9		1.55E-04	3.97E-05	4.57E-02	1.10E+03	3.10E-04	7.95E-05
T3-0.1-10A	568.3		1.59E-04	4.09E-05	4.70E-02	1.14E+03	3.17E-04	8.18E-05
T3-0.1-10B	532.3		1.50E-04	3.83E-05	4.40E-02	1.06E+03	3.01E-04	7.66E-05
T3-0.1-10C								
T3-0.1-15A	558.6		1.57E-04	4.02E-05	4.62E-02	1.12E+03	3.14E-04	8.04E-05
T3-0.1-15B	567.1		1.58E-04	4.08E-05	4.69E-02	1.13E+03	3.16E-04	8.16E-05
T3-0.1-15C	611.1		1.71E-04	4.40E-05	5.06E-02	1.22E+03	3.41E-04	8.80E-05

CONTROL 1, pH 5 DATA

Sample ID	pH at time of collection	Ionic Strength	Ferrihydrite Suspension Concentration	Time	Average Measured Arsenate	mmol AsO <sub>4</sub> <sup>3-</sup> in soln	mmol As in initial suspension	M NaNO <sub>3</sub>	
								g/L	ppb
C1-PH5-0A	5.03	0.001	0.5007	0	360.3	6.48E-05	8.70E-04		
C1-PH5-0B	5.03	0.001	0.5007	0	371.1	6.68E-05	8.70E-04		
C1-PH5-0C	5.03	0.001	0.5007	0	343.4	6.18E-05	8.70E-04		
C1-PH5-1A	5.72	0.001	0.5007	1	394.7	7.10E-05	8.70E-04		
C1-PH5-1B	5.81	0.001	0.5007	1	409.4	7.37E-05	8.70E-04		
C1-PH5-1C	5.82	0.001	0.5007	1	406.1	7.31E-05	8.70E-04		
C1-PH5-3A	5.75	0.001	0.5007	3	414.2	7.45E-05	8.70E-04		
C1-PH5-3B	5.80	0.001	0.5007	3	473.0	8.51E-05	8.70E-04		
C1-PH5-3C	5.82	0.001	0.5007	3	482.0	8.67E-05	8.70E-04		
C1-PH5-6A	5.59	0.001	0.5007	6			8.70E-04		
C1-PH5-6B	5.55	0.001	0.5007	6			8.70E-04		
C1-PH5-6C	5.66	0.001	0.5007	6	474.1	8.53E-05	8.70E-04		
C1-PH5-10A	5.70	0.001	0.5007	10	414.2	7.45E-05	8.70E-04		
C1-PH5-10B	5.72	0.001	0.5007	10	433.4	7.80E-05	8.70E-04		
C1-PH5-10C	5.75	0.001	0.5007	10	508.3	9.15E-05	8.70E-04		
C1-PH5-15A	5.77	0.001	0.5007	15	313.8	5.65E-05	8.70E-04		
C1-PH5-15B	5.96	0.001	0.5007	15	386.0	6.95E-05	8.70E-04		
C1-PH5-15C	5.97	0.001	0.5007	15	390.9	7.03E-05	8.70E-04		

## CONTROL 1, pH 6.5 DATA

Sample ID	pH at time of collection	Ionic Strength	Ferrihydrite Suspension Concentration	Time days	Average Measured Arsenate ppb	mmol AsO <sub>4</sub> <sup>3-</sup> in soln	mmol As in initial suspension	M NaNO <sub>3</sub>	
								g/L	ppb
C1-PH6.5-0A	6.53	0.001	0.5008	0	290.0	5.22E-05	8.70E-04		
C1-PH6.5-0B	6.53	0.001	0.5008	0	318.2	5.73E-05	8.70E-04		
C1-PH6.5-0C	6.53	0.001	0.5008	0	296.7	5.34E-05	8.70E-04		
C1-PH6.5-1A	6.94	0.001	0.5008	1	395.8	7.12E-05	8.70E-04		
C1-PH6.5-1B	6.88	0.001	0.5008	1	398.1	7.16E-05	8.70E-04		
C1-PH6.5-1C	6.88	0.001	0.5008	1	423.5	7.62E-05	8.70E-04		
C1-PH6.5-3A	6.70	0.001	0.5008	3	366.0	6.59E-05	8.70E-04		
C1-PH6.5-3B	6.71	0.001	0.5008	3	442.6	7.97E-05	8.70E-04		
C1-PH6.5-3C	6.72	0.001	0.5008	3	425.1	7.65E-05	8.70E-04		
C1-PH6.5-6A	6.47	0.001	0.5008	6			8.70E-04		
C1-PH6.5-6B	6.50	0.001	0.5008	6	352.9	6.35E-05	8.70E-04		
C1-PH6.5-6C	6.49	0.001	0.5008	6	363.3	6.54E-05	8.70E-04		
C1-PH6.5-10A	6.54	0.001	0.5008	10	358.1	6.44E-05	8.70E-04		
C1-PH6.5-10B	6.52	0.001	0.5008	10	348.2	6.27E-05	8.70E-04		
C1-PH6.5-10C	6.55	0.001	0.5008	10	371.5	6.69E-05	8.70E-04		
C1-PH6.5-15A	6.77	0.001	0.5008	15	295.0	5.31E-05	8.70E-04		
C1-PH6.5-15B	6.78	0.001	0.5008	15	303.9	5.47E-05	8.70E-04		
C1-PH6.5-15C	6.79	0.001	0.5008	15	298.2	5.37E-05	8.70E-04		



CONTROL 1, pH 8 DATA

Sample ID	pH at time of collection	Ionic Strength	Ferrihydrite Suspension Concentration	Time	Average Measured Arsenate	mmol AsO <sub>4</sub> <sup>3-</sup> in soln	mmol As in initial suspension	M NaNO <sub>3</sub>	
								g/L	ppb
C1-PH8-0A	7.95	0.001	0.5015	0	288.3	5.19E-05	8.71E-04		
C1-PH8-0B	7.95	0.001	0.5015	0	292.6	5.27E-05	8.71E-04		
C1-PH8-0C	7.95	0.001	0.5015	0	310.1	5.58E-05	8.71E-04		
C1-PH8-1A	7.37	0.001	0.5015	1	383.9	6.91E-05	8.71E-04		
C1-PH8-1B	7.41	0.001	0.5015	1	367.4	6.61E-05	8.71E-04		
C1-PH8-1C	7.41	0.001	0.5015	1	396.8	7.14E-05	8.71E-04		
C1-PH8-3A	7.36	0.001	0.5015	3	441.9	7.95E-05	8.71E-04		
C1-PH8-3B	7.38	0.001	0.5015	3	407.8	7.34E-05	8.71E-04		
C1-PH8-3C	7.35	0.001	0.5015	3	417.0	7.51E-05	8.71E-04		
C1-PH8-6A	7.20	0.001	0.5015	6	428.0	7.70E-05	8.71E-04		
C1-PH8-6B	7.19	0.001	0.5015	6	418.6	7.53E-05	8.71E-04		
C1-PH8-6C	7.20	0.001	0.5015	6	386.9	6.96E-05	8.71E-04		
C1-PH8-10A	7.21	0.001	0.5015	10	415.0	7.47E-05	8.71E-04		
C1-PH8-10B	7.20	0.001	0.5015	10	449.8	8.09E-05	8.71E-04		
C1-PH8-10C	7.17	0.001	0.5015	10	459.1	8.26E-05	8.71E-04		
C1-PH8-15A	7.45	0.001	0.5015	15	356.4	6.41E-05	8.71E-04		
C1-PH8-15B	7.47	0.001	0.5015	15	382.8	6.89E-05	8.71E-04		
C1-PH8-15C	7.46	0.001	0.5015	15	360.0	6.48E-05	8.71E-04		

CONTROL 2, 0.05 g/L DATA

Sample ID	pH at time of collection	Ionic Strength	Ferrihydrite Suspension Concentration	Time	Average Measured Arsenate	mmol AsO <sub>4</sub> <sup>3-</sup> in soln	mmol As in initial suspension	M NaNO <sub>3</sub>	
								g/L	ppb
C2-50-0A	8.07	0.001	0.0502	0	42.9	7.73E-06	8.7223E-05		
C2-50-0B	8.07	0.001	0.0502	0	52.8	9.50E-06	8.7223E-05		
C2-50-0C	8.07	0.001	0.0502	0	42.4	7.62E-06	8.7223E-05		
C2-50-1A	7.12	0.001	0.0502	1	55.7	1.00E-05	8.7223E-05		
C2-50-1B	7.12	0.001	0.0502	1	44.7	8.04E-06	8.7223E-05		
C2-50-1C	7.08	0.001	0.0502	1	52.2	9.39E-06	8.7223E-05		
C2-50-3A	7.15	0.001	0.0502	3	43.0	7.75E-06	8.7223E-05		
C2-50-3B	7.11	0.001	0.0502	3	46.0	8.27E-06	8.7223E-05		
C2-50-3C	7.16	0.001	0.0502	3	45.4	8.17E-06	8.7223E-05		
C2-50-6A	7.03	0.001	0.0502	6	43.8	7.89E-06	8.7223E-05		
C2-50-6B	6.85	0.001	0.0502	6	22.3	4.01E-06	8.7223E-05		
C2-50-6C	7.02	0.001	0.0502	6	26.3	4.73E-06	8.7223E-05		
C2-50-10A	6.77	0.001	0.0502	10	35.3	6.36E-06	8.7223E-05		
C2-50-10B	6.92	0.001	0.0502	10	38.4	6.90E-06	8.7223E-05		
C2-50-10C	6.91	0.001	0.0502	10	40.2	7.24E-06	8.7223E-05		
C2-50-15A	7.25	0.001	0.0502	15	18.6	3.35E-06	8.7223E-05		
C2-50-15B	7.23	0.001	0.0502	15					
C2-50-15C	7.21	0.001	0.0502	15	13.9	2.51E-06	8.7223E-05		

## CONTROL 2, 0.5 g/L DATA

Sample ID	pH at time of collection	Ionic Strength	Ferrihydrite Suspension Concentration	Time days	Average Measured Arsenate	mmol AsO <sub>4</sub> <sup>3-</sup> in soln	mmol As in initial suspension	M NaNO <sub>3</sub>	
								g/L	ppb
C2-500-0A	7.95	0.001	0.5015	0	245.2	4.41E-05	8.71E-04		
C2-500-0B	7.95	0.001	0.5015	0	231.6	4.17E-05	8.71E-04		
C2-500-0C	7.95	0.001	0.5015	0	241.5	4.35E-05	8.71E-04		
C2-500-1A	7.52	0.001	0.5015	1	307.7	5.54E-05	8.71E-04		
C2-500-1B	7.63	0.001	0.5015	1	315.6	5.68E-05	8.71E-04		
C2-500-1C	7.53	0.001	0.5015	1	297.9	5.36E-05	8.71E-04		
C2-500-3A	7.41	0.001	0.5015	3	337.1	6.07E-05	8.71E-04		
C2-500-3B	7.39	0.001	0.5015	3	357.3	6.43E-05	8.71E-04		
C2-500-3C	7.41	0.001	0.5015	3	352.2	6.34E-05	8.71E-04		
C2-500-6A	7.25	0.001	0.5015	6	403.7	7.26E-05	8.71E-04		
C2-500-6B	7.38	0.001	0.5015	6	395.8	7.12E-05	8.71E-04		
C2-500-6C	7.23	0.001	0.5015	6	375.7	6.76E-05	8.71E-04		
C2-500-10A	7.17	0.001	0.5015	10	363.6	6.54E-05	8.71E-04		
C2-500-10B	7.17	0.001	0.5015	10	417.2	7.51E-05	8.71E-04		
C2-500-10C	7.18	0.001	0.5015	10	384.3	6.92E-05	8.71E-04		
C2-500-15A	7.39	0.001	0.5015	15	325.9	5.87E-05	8.71E-04		
C2-500-15B	7.39	0.001	0.5015	15	339.4	6.11E-05	8.71E-04		
C2-500-15C	7.44	0.001	0.5015	15	355.8	6.40E-05	8.71E-04		

## CONTROL 2, 5.0 g/L DATA

Sample ID	pH at time of collection	Ionic Strength	Ferrihydrite Suspension Concentration	Time days	Average Measured Arsenate	mmol AsO <sub>4</sub> <sup>3-</sup> in soln	mmol As in initial suspension	M NaNO <sub>3</sub>	
								g/L	ppb
C2-5000-0A	8.00	0.001	5.003	0	1548.5	2.79E-04	8.69E-03		
C2-5000-0B	8.00	0.001	5.003	0	1536.5	2.77E-04	8.69E-03		
C2-5000-0C	8.00	0.001	5.003	0	1612.7	2.90E-04	8.69E-03		
C2-5000-1A	7.62	0.001	5.003	1	1975.8	3.56E-04	8.69E-03		
C2-5000-1B	7.62	0.001	5.003	1	2132.7	3.84E-04	8.69E-03		
C2-5000-1C	7.64	0.001	5.003	1	1971.9	3.55E-04	8.69E-03		
C2-5000-3A	7.55	0.001	5.003	3	2165.2	3.90E-04	8.69E-03		
C2-5000-3B	7.58	0.001	5.003	3			8.69E-03		
C2-5000-3C	7.54	0.001	5.003	3	2157.4	3.88E-04	8.69E-03		
C2-5000-6A	7.38	0.001	5.003	6			8.69E-03		
C2-5000-6B	7.35	0.001	5.003	6			8.69E-03		
C2-5000-6C	7.40	0.001	5.003	6			8.69E-03		
C2-5000-10A	7.35	0.001	5.003	10	2368.6	4.26E-04	8.69E-03		
C2-5000-10B	7.35	0.001	5.003	10	2276.4	4.10E-04	8.69E-03		
C2-5000-10C	7.36	0.001	5.003	10	2289.8	4.12E-04	8.69E-03		
C2-5000-15A	7.61	0.001	5.003	15	2195.9	3.95E-04	8.69E-03		
C2-5000-15B	7.62	0.001	5.003	15	2712.3	4.88E-04	8.69E-03		
C2-5000-15C	7.65	0.001	5.003	15	2694.2	4.85E-04	8.69E-03		

## CONTROL 3, 0.001 M DATA

Sample ID	pH at time of collection	Ionic Strength	Ferrihydrite Suspension Concentration	Time days	Average Measured Arsenate	mmol AsO <sub>4</sub> <sup>3-</sup> in soln	mmol As in initial suspension	M NaNO <sub>3</sub>	
								g/L	ppb
C3-0.001-0A	7.9	0.001	0.5007	0	269.8	4.85E-05	8.70E-04		
C3-0.001-0B	7.9	0.001	0.5007	0	272.7	4.91E-05	8.70E-04		
C3-0.001-0C	7.9	0.001	0.5007	0	280.8	5.05E-05	8.70E-04		
C3-0.001-1A	7.5	0.001	0.5007	1	375.9	6.76E-05	8.70E-04		
C3-0.001-1B	7.5	0.001	0.5007	1	351.1	6.32E-05	8.70E-04		
C3-0.001-1C	7.5	0.001	0.5007	1	367.3	6.61E-05	8.70E-04		
C3-0.001-3A	7.4	0.001	0.5007	3	335.2	6.03E-05	8.70E-04		
C3-0.001-3B	7.4	0.001	0.5007	3	407.4	7.33E-05	8.70E-04		
C3-0.001-3C	7.4	0.001	0.5007	3	421.3	7.58E-05	8.70E-04		
C3-0.001-6A	7.2	0.001	0.5007	6	393.2	7.08E-05	8.70E-04		
C3-0.001-6B	7.2	0.001	0.5007	6	376.7	6.78E-05	8.70E-04		
C3-0.001-6C	7.2	0.001	0.5007	6	407.1	7.33E-05	8.70E-04		
C3-0.001-10A	7.3	0.001	0.5007	10	372.7	6.71E-05	8.70E-04		
C3-0.001-10B	7.2	0.001	0.5007	10	391.4	7.04E-05	8.70E-04		
C3-0.001-10C	7.2	0.001	0.5007	10	452.6	8.14E-05	8.70E-04		
C3-0.001-15A	7.4	0.001	0.5007	15	302.6	5.45E-05	8.70E-04		
C3-0.001-15B	7.4	0.001	0.5007	15	298.0	5.36E-05	8.70E-04		
C3-0.001-15C	7.5	0.001	0.5007	15	322.9	5.81E-05	8.70E-04		

## CONTROL 3, 0.01 M DATA

Sample ID	pH at time of collection	Ionic Strength	Ferrihydrite Suspension Concentration	Time days	Average Measured Arsenate	mmol AsO <sub>4</sub> <sup>3-</sup> in soln	mmol As in initial suspension	M NaNO <sub>3</sub>	
								g/L	ppb
C3-0.01-0A	8.1	0.01	0.5004	0	176.3	3.17E-05	8.69E-04		
C3-0.01-0B	8.1	0.01	0.5004	0	186.1	3.35E-05	8.69E-04		
C3-0.01-0C	8.1	0.01	0.5004	0	167.2	3.01E-05	8.69E-04		
C3-0.01-1A	7.6	0.01	0.5004	1	225.6	4.06E-05	8.69E-04		
C3-0.01-1B	7.6	0.01	0.5004	1	224.5	4.04E-05	8.69E-04		
C3-0.01-1C	7.6	0.01	0.5004	1	239.0	4.30E-05	8.69E-04		
C3-0.01-3A	7.5	0.01	0.5004	3	135.6	2.44E-05	8.69E-04		
C3-0.01-3B	7.5	0.01	0.5004	3	180.6	3.25E-05	8.69E-04		
C3-0.01-3C	7.5	0.01	0.5004	3	259.1	4.66E-05	8.69E-04		
C3-0.01-6A	7.2	0.01	0.5004	6	225.6	4.06E-05	8.69E-04		
C3-0.01-6B	7.3	0.01	0.5004	6	281.0	5.06E-05	8.69E-04		
C3-0.01-6C	7.3	0.01	0.5004	6	207.2	3.73E-05	8.69E-04		
C3-0.01-10A	7.4	0.01	0.5004	10	337.9	6.08E-05	8.69E-04		
C3-0.01-10B	7.4	0.01	0.5004	10	286.5	5.16E-05	8.69E-04		
C3-0.01-10C	7.4	0.01	0.5004	10	372.2	6.70E-05	8.69E-04		
C3-0.01-15A	7.7	0.01	0.5004	15	362.3	6.52E-05	8.69E-04		
C3-0.01-15B	7.7	0.01	0.5004	15	382.4	6.88E-05	8.69E-04		
C3-0.01-15C	7.6	0.01	0.5004	15	472.8	8.51E-05	8.69E-04		

CONTROL 3, 0.1 M DATA

Sample ID	pH at time of collection	Ionic Strength	Ferrihydrite Suspension Concentration	Time	Average Measured Arsenate	mmol AsO <sub>4</sub> <sup>3-</sup> in soln	mmol As in initial suspension	M NaNO <sub>3</sub>	
								g/L	ppb
C3-0.1-0A	7.97	0.1	0.5007	0	336.8	6.06E-05	8.70E-04		
C3-0.1-0B	7.97	0.1	0.5007	0	337.0	6.06E-05	8.70E-04		
C3-0.1-0C	7.97	0.1	0.5007	0	366.8	6.60E-05	8.70E-04		
C3-0.1-1A	7.56	0.1	0.5007	1	386.5	6.96E-05	8.70E-04		
C3-0.1-1B	7.54	0.1	0.5007	1	415.6	7.48E-05	8.70E-04		
C3-0.1-1C	7.52	0.1	0.5007	1	406.1	7.31E-05	8.70E-04		
C3-0.1-3A	7.41	0.1	0.5007	3	443.7	7.99E-05	8.70E-04		
C3-0.1-3B	7.41	0.1	0.5007	3	450.9	8.11E-05	8.70E-04		
C3-0.1-3C	7.39	0.1	0.5007	3	455.4	8.19E-05	8.70E-04		
C3-0.1-6A	7.23	0.1	0.5007	6	445.8	8.02E-05	8.70E-04		
C3-0.1-6B	7.23	0.1	0.5007	6			8.70E-04		
C3-0.1-6C	7.24	0.1	0.5007	6			8.70E-04		
C3-0.1-10A	7.25	0.1	0.5007	10	112.2	2.02E-05	8.70E-04		
C3-0.1-10B	7.26	0.1	0.5007	10	102.6	1.85E-05	8.70E-04		
C3-0.1-10C	7.25	0.1	0.5007	10	99.6	1.79E-05	8.70E-04		
C3-0.1-15A	7.57	0.1	0.5007	15	98.1	1.76E-05	8.70E-04		
C3-0.1-15B	7.59	0.1	0.5007	15	94.4	1.70E-05	8.70E-04		
C3-0.1-15C	7.55	0.1	0.5007	15	108.0	1.94E-05	8.70E-04		

## VITA

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Geological Society of America

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### **Poster Presentations at National or Regional Meetings:**

- |      |                                                                                                                                                                                                                                                    |
|------|----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
| 1999 | Roberts, M. D., Andersen, C. B., Sargent, K., and Wheeler, S. K., Natural attenuation of trace metals in a contaminated stream, Enoree River Basin, Greenville, SC, Geol. Soc. Am., Abstracts Prog.                                                |
| 2000 | Roberts, M. D., Weinstein, K., Andersen, C. B., Davies, B., Sargent, K., Transport and attenuation of Zn, Mn, and Al in the Upper Enoree River, SC, Southeastern Geol. Soc. Am., Abstracts Prog.;                                                  |
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