Oxidation of arsenite by dissolved oxygen, manganese and iron oxyhydroxides in aqueous solutions

By

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To my Mother and Father

ABSTRACT

Oxidation of dissolved arsenite was studied in 0.05M and 0.7M NaCl aqueous solutions. The experimental conditions included a range of pH (3 to 9), presence and absence of ambient light, presence and absence of oxygen, and presence and absence of amorphous and crystalline Mn and Fe oxyhydroxides at (Mn – Ox and Fe-Ox) constant solid: solution ratios of 0.0002. All experiments were conducted at a temperature of 23 ± 4°C and initial arsenite concentration of approximately 100 ppb. Arsenic speciation was determined both in the aqueous phase and in the combined solid and aqueous phases.

Aqueous arsenite oxidation by oxygen alone is slow; only 20% of the initial As(III) was oxidized after 4 months. Light, pH, and ionic strength had no effect on the oxidation rate of arsenite by dissolved oxygen. In the presence of manganese- and iron oxyhydroxides (Mn-Ox and Fe-Ox), the oxidation of arsenite is rapid: within 15 minutes, more than 80% of the initial As(III) was oxidized to As(V) by crystalline and amorphous Fe-Ox, and by amorphous Mn-Ox. In the presence of crystalline Mn-Ox, more than 20% of the initial As(III) was oxidized within the first 5 minutes of the experiment. Dissolved oxygen was not essential for the arsenite oxidation by the metal oxides.

Where metal oxides are abundant in nature, rapid oxidation of arsenite can be expected. If metal oxides are rare, such as in the water column of a lake or ocean, oxidation of As(III) will be slow. The speciation of arsenic in environmental samples can be preserved for several months as long as a solid metal oxide phase is not present (i.e. in acidified samples). The amount of dissolved arsenic in heterogeneous media such as porewaters and groundwaters is related to the type of carrier phase: As(V) desorbs to a greater extent from amorphous Mn-Ox than

from Fe-Ox. Arsenate will preferentially adsorb to Fe-Ox. Arsenite oxidation can occur in oxygen-depleted environments, such as the suboxic zone of sediments provided metal oxides are present. As(V) forms different types of complexes on metal oxides in the presence and in the absence of O_2.

RÉSUMÉ

L'oxydation de l'arsénite dissous a été étudiée en solutions aqueuses de 0,05 et 0,7M NaCl. Les conditions expérimentales incluaient un pH variable de 3 à 9, la présence et l'absence de lumière, la présence et l'absence d'oxygène, et la présence et l'absence d'oxyhydroxydes de manganèse et de fer amorphes et cristallins à un ratio solide:solution constant de 0,0002. Toutes les expériences ont été menées à température ambiante (T = 23 ± 4 °C) et la concentration initiale d'arsénite était de 100 ppb.

L'oxydation de l'ion arsénite par l'oxygène est lente : seulement 20% de l'arsénite, As(III), initial était oxydée après 4 mois. La lumière, la pH et la force ionique n'ont aucun effet sur la vitesse d'oxydation de l'arsénite en présence d'oxygène dissous. En présence d'oxyhydroxydes de manganèse et de fer (Mn-Ox et Fe-Ox), l'oxydation de l'arsénite est rapide : en moins de 15 minutes, plus de 80% de l'As(III) initial était oxydé en As(V) par Fe-Ox cristallin et amorphe, ainsi que par Mn-Ox amorphe. En présence de Mn-Ox cristallin, 5 minutes suffisaient pour oxyder plus de 20% de l'As(III) initial. La présence d'oxygène dissous n'était pas essentielle pour l'oxydation de l'arsénite par les oxydes métalliques.

Dans les sytèmes naturels où les oxydes métalliques sont abondants, l'ion arsénite sera vraisemblablement oxydé rapidement. A l'inverse, dans un environnement pauvre en oxydes métalliques tel que la colonne d'eau, l'oxydation d'As(III) sera lente. La spéciation de l'arsenic dissous peut être maintenue dans un échantillon pour des périodes allant jusqu'à plusieurs mois tant que des oxydes métalliques solides ne sont pas présents (i.e. échantillons acidifiés). Le relargage d'arsenic dans les eaux porales et souterraines est lié au type de phase sur laquelle il est adsorbé : Mn-Ox relargue davantage d'As(V).

Les ions arsénates seront préférentiellement adsorbés sur les Fe-Ox. L'oxydation de l'arsénite peut cependant avoir lieu dans des environnements sans oxygène comme la zone suboxique des sédiments. Selon la présence ou l'absence d'oxygène, l'As(V) formera différents complexes sur les oxydes métalliques.

PREFACE

This thesis is composed of five chapters. The first chapter gives background information on arsenic diagenesis, including a review of previous work conducted in the field and in the laboratory, and a summary of the research objectives of this thesis. The second chapter provides detailed descriptions of the experimental protocols of this study, with accounts of method development and analysis. The third chapter is a presentation of the experimental results of this study with evidence of the efficiency with which manganese and iron oxides oxidize arsenite under a variety of conditions. The fourth chapter provides a treatment and interpretation of the results, with reference and comparison to other studies, and is followed by the conclusions of this thesis in Chapter 5.

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1. INTRODUCTION

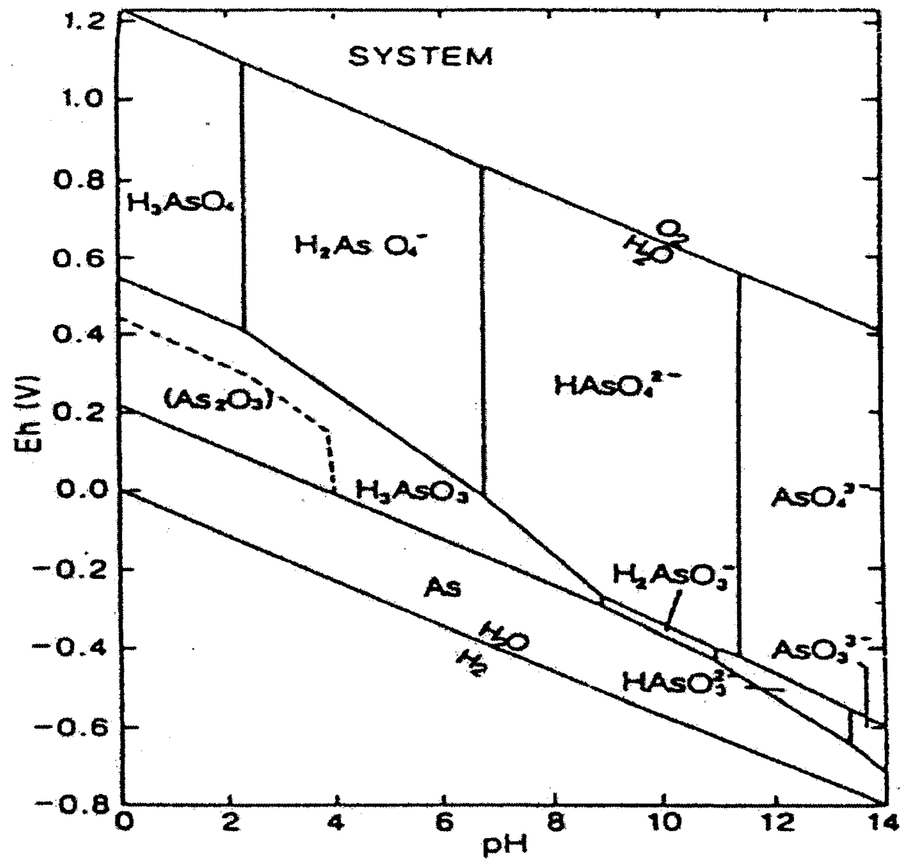
Arsenic occurs in the environment in several different oxidation states (i.e. –3, 0, +3, +5). The most abundant dissolved species of this element in natural waters are the inorganic oxyanions arsenite (As(III)) and arsenate (As(V)). The protonated forms of these trivalent and pentavalent compounds are H_3AsO_3 ($pK_1 = 9.2$, $pK_2 = 12.1$, and $pK_3 = 13.4$) and H_3AsO_4 ($pK_1 = 2.2$, $pK_2 = 6.9$, and $pK_3 = 11.5$), respectively. Arsenic can also exist as organic species after methylation by bacteria (i.e. monomethylarsonate and dimethylarsonate) but these make up only a minor component of total soluble As compounds in aquatic environments (Cullen and Reimer, 1989; Sadiq, 1997; Smedley and Kinniburgh, 2002).

Arsenic speciation is controlled by a variety of factors, the most important of which are pH and redox potential. An Eh-pH diagram of As is presented in Figure 1. At circumneutral pH (i.e. pH 6 to 8) and under oxic conditions, arsenate is the dominant As species in the forms of $H_2AsO_4^-$ and $HAsO_4^{2-}$. Under reducing conditions in the same pH range arsenite, H_3AsO_3, is the most abundant form. This species can also predominate under oxidizing conditions, but only at low pH. The pH of most interstitial waters is between 3 and 10 (Sadiq, 1997). Arsenite is more mobile in the environment than arsenate, and is the more toxic of the two species (Cullen and Reimer, 1989; Bowell, 1994; Sadiq, 1997; Smedley and Kinniburgh, 2002).

Arsenic in the environment is mobilized through a variety of natural and

Figure 1: Eh – pH diagram of As species in the aqueous phase

Figure. 1. Eh-pH diagram of As species in the aqueous phase (Figure adapted from Bowell (1994) , Smedley and Kinniburgh (2002)).



anthropogenic processes. Natural activities include weathering and volcanic emissions, as well as biological processes. Mining and the burning of fossil fuels are two important sources of As to the environment (Cullen and Reimer, 1989; Smedley and Kinniburgh, 2002). The release of arsenic to water, particularly groundwater and drinking water sources, is increasingly becoming a danger to human health worldwide. One of the largest cases of groundwater contamination by As is in the region of West Bengal and Bangladesh.

The need to understand the geochemistry of arsenic became urgent when the world community recognized groundwater contamination by arsenic in Bangladesh in 1993 (DPHE, 1999). Most areas of Bangladesh had switched to using groundwater rather than surface river water as a source of drinking water in the past 20-30 years, using tubewells as a means of extraction (Caldwell, 2003). Concentrations as high as 1.0 mg/L have been detected in these wells in Bangladesh (Nickson et al., 1998). This is two orders of magnitude higher than the World Health Organization drinking water standard, which is 0.01mg/L (DPHE, 1999). The standard in Bangladesh is 0.05 mg/l (Nickson et al., 1998). A recent study by Chakraborti et al. (2002) found that over 25 million people in Bangladesh are using water that contains more than 0.050mg/L of arsenic. Symptoms of arsenic poisoning include severe skin lesions, such as melanosis and keratosis, cancer, and gangrene (Chakraborti et al., 2002).

Initially, two main theories arose to explain the contamination of groundwater by arsenic in Bangladesh (McArthur et al, 2001; Acharyya et al., 2000; Nickson et al., 1998). The first theory stated that, as water was extracted from the aquifers and the water table lowered, arsenic adsorbed on or co-precipitated with sulfides was released to the groundwater with the oxidation of sulfide and pyrite phases upon contact with oxygen (Nickson et al., 1998; McArthur et al., 2001). This mechanism applies to areas such as Greece or Thailand (Smedley and Kinniburgh, 2002). The second theory stated that arsenic adsorbed onto Fe-oxyhydroxides was released into anoxic water following the microbially mediated reductive dissolution of those Fe-oxyhydroxides (McArthur et al, 2001; Acharyya et al., 1999; Nickson et al., 1998). The latter theory applies to Bangladesh.

Arsenic can be released to groundwater under oxidizing or reducing conditions depending on the solid phases with which it is associated. The pH of porewaters also affects the mobility of As, as is the case with mine tailings which are acidic. Understanding the mechanism by which arsenic is released to groundwater is essential for developing remediation technologies for contaminated aquifers.

1.1. Conceptual Model of Early Arsenic Sediment Diagenesis

In sediments, organic matter is remineralized (oxidized) through a series of microbially mediated reactions. The energy released in these reactions is used by microorganisms. It has been shown that, faced with several different electron acceptors, microorganisms will use preferentially the one that yields the most free energy. In sediments, O_2 will by consumed (depleted) first, followed by metal oxides and sulfate (Froelich, 1979). The result is a vertical zonation of redox environments. The top or oxic, layer, where oxygen is still present, is oxidizing. After O_2 is used up, the anoxic layer is reducing. Deeper in the anoxic layer, a zone of sulfate reduction occurs and sulfides are produced.

Based on several studies of arsenic in water column, sediments and porewaters (Aggett and O'Brien, 1985; Edenborn et al., 1986; Belzile, 1988; Belzile and Tessier, 1990; Wilderlund and Ingri 1995; Sullivan and Aller, 1996; Mucci et al., 2000) a conceptual model of arsenic diagenesis has emerged (Figure 2). Arsenic is adsorbed on solid particulate matter (i.e. metal oxides, organic matter) settling through the water column and is delivered to sediments. Upon burial, metal oxide carrier phases are reduced and dissolve in the anoxic layer. The dissolution of the carrier phases drives the release of arsenic to porewaters (see Figures 2 and 3). Some of this arsenic can migrate along established concentration gradients to sulfate reducing zones in sediments and be immobilized as sulfides. Some arsenic can also migrate back to the oxic layer, where metal oxide phases are precipitated. Arsenic, upon encountering these solids, can re-adsorb to these phases. Arsenic that is not trapped by metal oxides can escape to the overlying water column. Many researchers have proposed that metal oxides, specifically Fe- and Mn-oxyhydroxides, are the primary controls of early arsenic diagenesis (e.g. Edenborn et al., 1986; Belzile, 1988; Belzile and Tessier, 1990; Bowell, 1994; Sullivan and Aller, 1996).

Most arsenic sorbed on particulate matter in the oxygenated water column is in the form of arsenate (Edenborn et al., 1986; Belzile, 1988; Mucci et al., 2000). Once delivered to sediments, arsenic associated with organic matter can be released to porewaters when the organic component of the solid particulate matter is degraded during respiration (Mucci et al., 2000). Upon burial of the particulate matter into the reducing sediment layer, arsenate can be released to porewaters following the reductive dissolution of manganese and iron oxyhydroxides (Mn-Ox and Fe-Ox) and be subsequently reduced to arsenite (Aggett and O'Brien, 1985; Edenborn et al., 1986; Peterson and Carpenter, 1986; Belzile and Tessier, 1990; Wilderlund and Ingri, 1995; Mucci et al., 2000). Arsenate can also be reduced to arsenite and be released to interstitial waters prior to the dissolution of the metal oxide, Me-Ox, phases (Masscheleyn et al., 1991; Mucci et al., 2000). Arsenite is the predominant form of arsenic under reducing conditions (i.e. Figure 1, Edenborn et al., 1986; Masscheleyn et al., 1991). The dissolution of Mn-Ox and Fe-Ox accounts for the dissolved arsenic porewater maximum observed in sediment porewater profiles (Figure 3).

Dissolved As(III) in the suboxic/anoxic zone can either migrate back to the oxic layer or move further down in the anoxic sediments along the established concentration gradient. Figure 3 is a schematic representation of a typical steady-state porewater profile of arsenic. Some of the dissolved As(III) that diffuses further down in the anoxic layer, driven by the established concentration gradient, can adsorb to sulfides encountered in the sulfate reduction zone. Thus, iron sulfides in sediments can serve as a sink for arsenic (Aggett and O'Brien, 1985; Peterson and Carpenter, 1986; Belzile, 1988; Sullivan and Aller, 1996). Mucci et al. (2000) found as much as 1000ppm As associated with grains of authigenic pyrite. Belzile (1988) suggested that As can be trapped and incorporated into the lattice structure of pyrite. As(III) can also precipitate to form arsenic sulfides (Aggett and O'Brien, 1985; Moore et al.; 1988; Rochette et al.; 2000). In their study, Moore et al. (1988) found, where sulfate was abundant in pore water, the precipitation of As – sulfide phases in presumably anoxic sediments. Arsenite can coprecipitate with iron sulfides when dissolved sulfides are present (Edenborn et al. (1986); Mucci et al. (2000)). In laboratory studies, Rochette et al. (2000) observed that at high S:As ratios (e.g. 20:1) the precipitation of As_2S_3 occurred.

Some dissolved As(III) can migrate up to the oxic layer along the established concentration gradient. Upon entering the oxic layer, arsenite will adsorb to and be oxidized by Mn-Ox and Fe-Ox (Kuhn and Sigg, 1993; Peterson and Carpenter, 1986; Sullivan and Aller, 1996). After oxidation, As(V) will preferentially adsorb to or co-precipitate with Fe-oxides (Belzile and Tessier, 1990; Wilderlund and Ingri, 1995; Sullivan and Aller, 1996; Mucci et al., 2000). If the oxic layer is thin,

Figure 2: Conceptual model of early arsenic diagenesis.

Figure 2: Conceptual Model of Early Arsenic Diagenesis. Arrows indicate fluxes and transport of arsenic (Figure adapted from Edenborn et al. (1986) , Belzile (1988), Wilderlund and Ingri (1995), Sullivan and Aller (1996) Mucci et al (2000)).

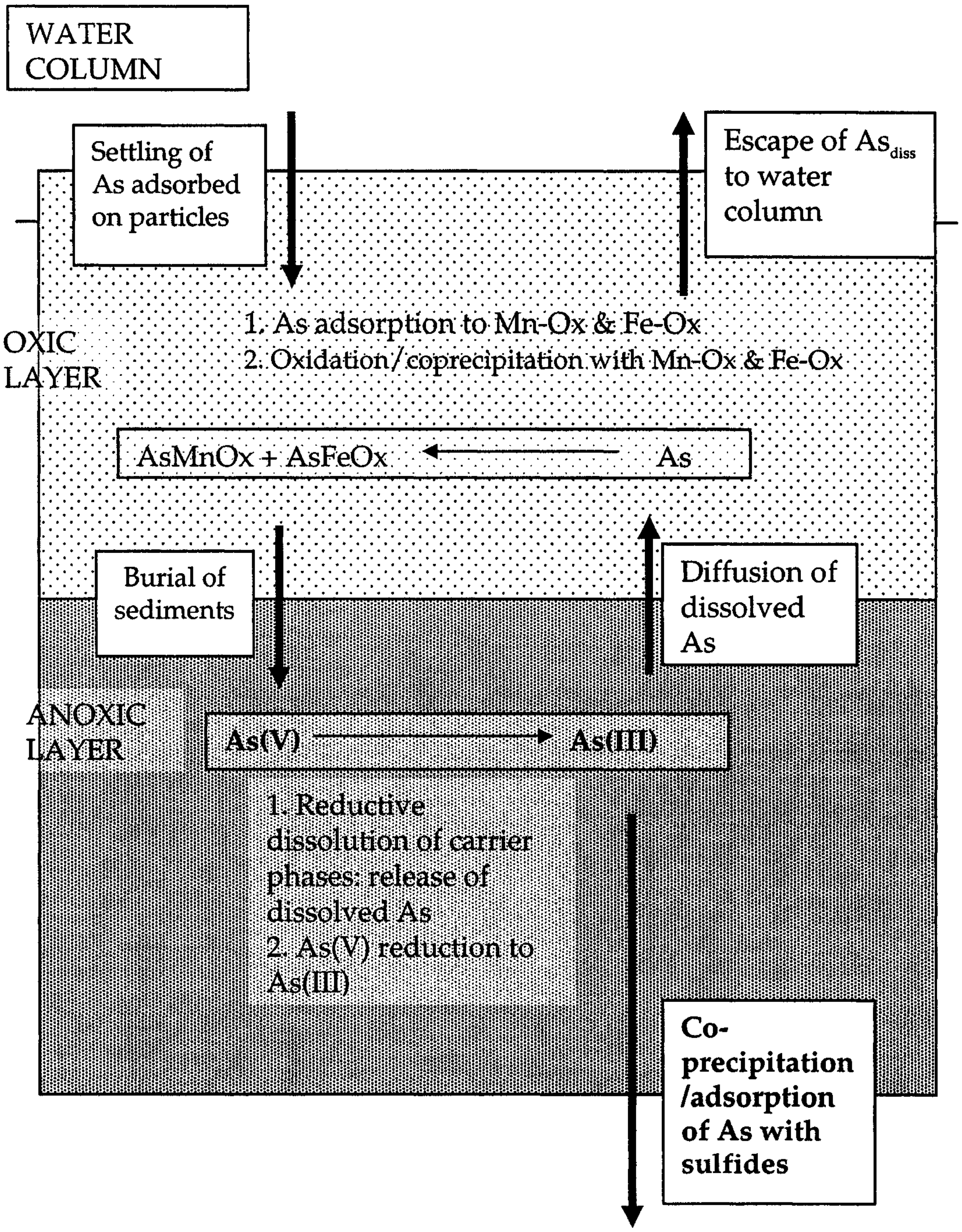
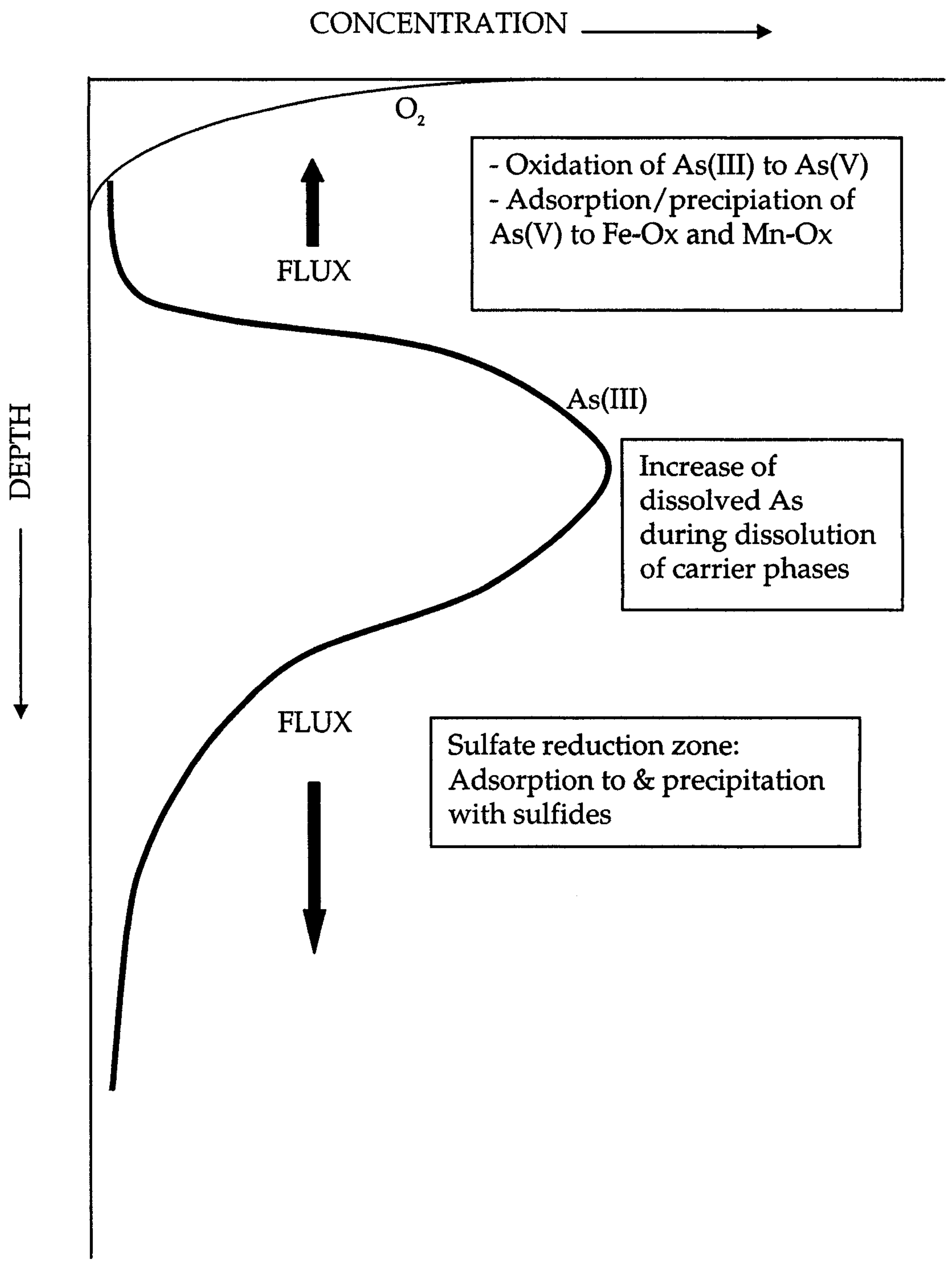


Figure 3: Typical steady state porewater profile of dissolved oxygen and arsenic in marine sediments.

Figure 3: Typical steady state porewater profile of dissolved oxygen and arsenic (Figure adapted from Edenborn et al. (1986), Mucci et al. (2000)).



some arsenic not captured by adsorption to metal oxides can be lost to overlying waters.

Because, amorphous manganese and iron oxides can sorb arsenic and act as carrier phases for arsenic transport, and oxidize arsenite, Mn-Ox and Fe-Ox play a major role in the early diagenesis of As in the water column and sediments. Through oxidation and sorption, arsenite and arsenate also affect the surface chemistry of Mn-Ox and Fe-Ox. Many researchers have examined these specific processes and the results of these studies are discussed in the following sections.

1.2. Adsorption and Oxidation of Arsenic by Manganese Oxides

A study of aqueous As(III) oxidation by MnO_2 was conducted by Oscarson et al. (1981),. Increasing concentrations of arsenite, from 0.1mg/mL (100 ppm) to 1 mg/mL (1000 ppm), were added to fixed concentrations (1.43 mg/mL) of birnessite, $\delta - MnO_2$, such that the As:solid ratios were 0.070 to 0.7 (0.07 to 0.7 g As/g $\delta - MnO_2$). The ionic strengths of these solutions were low (< 0.1M) and the pH neutral. As(V) and As(III) were measured in solution at the end of 72h. The results indicate that arsenite was converted to arsenate by these oxides, though with increasing initial As(III) concentrations, higher than 300ug/mL, aqueous concentrations of As(V) at the end of 72h did not increase significantly. In the absence of solid Mn-oxide, oxidation of As(III) was not observed during the 72h of the experiment. The influence of the crystallinity of the solid Mn-oxide on adsorption and oxidation of arsenite was also studied by Oscarson et al. (1983). The combined rate of adsorption of As(III) to the solid and oxidation to As(V) was found to be first order with respect to arsenite for all three Mn-oxides (birnessite, cryptomelane, and pyrolusite) used. The As:solid ratios in these experiments were 0.07, but only the solution was analyzed for As. Less As(III) was removed from solution by the more crystalline of the Mn-oxides, pyrolusite, than by the more amorphous oxides (Oscarson et al., 1983).

Scott and Morgan (1995) studied the effects of dissolved oxygen concentration, temperature, pH and increasing As:Mn ratios on adsorption and oxidation of arsenite by birnessite. Their experiments were also conducted in low ionic strength solutions (< 0.1M) and only the solution was analyzed for arsenic speciation and dissolved manganese. Adsorption and oxidation of arsenite onto the solid surface was found to occur rapidly; in the first half hour, more than half of the arsenite was removed from solution. With increasing initial arsenite concentrations, depletion took longer. The release of As(V) to solution, resulting from oxidation of arsenite and desorption from the solid, was also rapid, occurring within a few minutes after the addition of arsenite. Again, with increasing initial As(III) concentrations the release of As(V) took longer. The effect of changing pH, temperature, and introduction of dissolved oxygen to the reactional system had little influence on the behaviors of arsenite and arsenate in solution. Results from a later study conducted by Chiu and Herring (2000) differ from those obtained by Scott and Morgan (1995). They reported that the pH had a sizable effect on the depletion rate of As(III): the arsenite concentration, both total and dissolved, decreased faster at the lower pH (pH 4) than at the higher pH (pH 6.3).

The research conducted by Chiu and Herring (2000) differs from other studies in that they determined the total arsenic speciation in both the solid and the aqueous phases, along with arsenic speciation in the aqueous phase. The manganese oxide used in this study was manganite, γ-MnOOH, at As:Mn ratios of 0.0064 to 0.023 at pH 4 or 6.3. Ionic strengths were low (~0.01M) and experiments were conducted at room temperature. The results of Chiu and Herring (2000) indicated that a significant portion of the arsenite that was oxidized to arsenate was not released to solution, but remained adsorbed to the oxide surface.

Manning et al. (2002) studied the adsorption and oxidation of arsenite on K-birnessite using batch reactions and X-ray spectroscopy. Stirred batch reactions were conducted in 0.1M NaCl at 22°C with a As:solid ratio of 0.075 and 0.03 (g As/g solid). at a pH of 6.5. The aqueous phase was analyzed for arsenite and arsenate, and As(III) and As(V) surface complexes on the solid Mn-oxide were characterized by EXAFS, X-ray adsorption fine structure spectroscopy. The results indicated that the arsenate formed from As(III) oxidation on the surface of K-birnessite remains sorbed to the solid surface and yields complexes very similar to those that result from the interaction of As(V) alone with the solid surface (Manning et al., 2002). Surface coverage of the solid by arsenic initially in the form of As(V) was one order of magnitude lower than surface coverage of the solid by As initially in the form of As(III). This was interpreted to mean that the solid changed due to the reductive dissolution of the surface by As(III) so that the number of adsorption sites for As(V) increased.

Adsorption studies using the same solid surface as Manning et al. (2002) were conducted by Foster et al. (2003) at low ionic strengths (0.01M and 0.1M) and at room temperature over a pH range from 5 to 8. The As:Mn ratios ranged from 0.00053 to 0.009. Sorption complexes of As(V) onto synthetic hydrous manganese oxides were studied by X-ray adsorption fine structure spectroscopy. Three types of surface sorption complexes of arsenate, as represented in Figure 4, were proposed to form onto the solid Mn-oxides: bidentate binuclear, bidentate mononuclear, and monodentate mononuclear. The most likely surface complex of arsenite onto these manganese oxides was a binuclear bidentate bridging complex. Another surface complex, less common than the bidentate binuclear complex, is a bidentate mononuclear complex. Using bond valence analysis, Foster et al. (2003) predicted that As(III) would form stable complexes with a greater variety of sorption sites on these manganese oxides than As(V), thus providing an explanation for the lower affinity of arsenate for hydrous manganese oxide surfaces. Other studies (i.e. Oscarson et al., 1981; Oscarson et al., 1983) have explained these different affinities based purely on electrostatic interactions of the oxyanions with the solid surface (pKa's and pH_{zpc}s).

A reaction mechanism for the oxidation of arsenite by synthetic birnessite, followed by birnessite dissolution, was proposed by Nesbitt et al.(1998).
After the precipitation of birnessite films onto Al discs, the discs were allowed to react with arsenite at room temperature in a low ionic strength solution (< 0.1M) at an initial pH of 5.5. The redox reaction was halted after various amounts of time up to 10 hours by removing the discs and rinsing them with deionized water. The disc surface was analyzed using X-ray spectroscopy. These researchers found that oxidation of arsenite and dissolution of birnessite occurs by two consecutive one-electron transfer reactions. The manganese, Mn(IV), in birnessite is first reduced to Mn(III):

$$2MnO_2 + H_3AsO_3 + H_2O \rightarrow 2MnOOH^* + H_3AsO_4 \qquad (1)$$

The MnOOH* is an intermediate species in the overall reaction that is reduced further by arsenite:

$$2MnOOH^* + H_3AsO_3 + 4H^+ \rightarrow 2Mn^{2+} + H_3AsO_4 + 3H_2O \qquad (2)$$

Nesbitt et al. (1998) also proposed the formation of bidentate binuclear and monodentate mononuclear complexes between arsenite and the manganese oxide surface during the oxidation/reduction reaction.

Figure 4: Various types of inner – sphere complex formation of arsenite onto manganese and iron oxides.

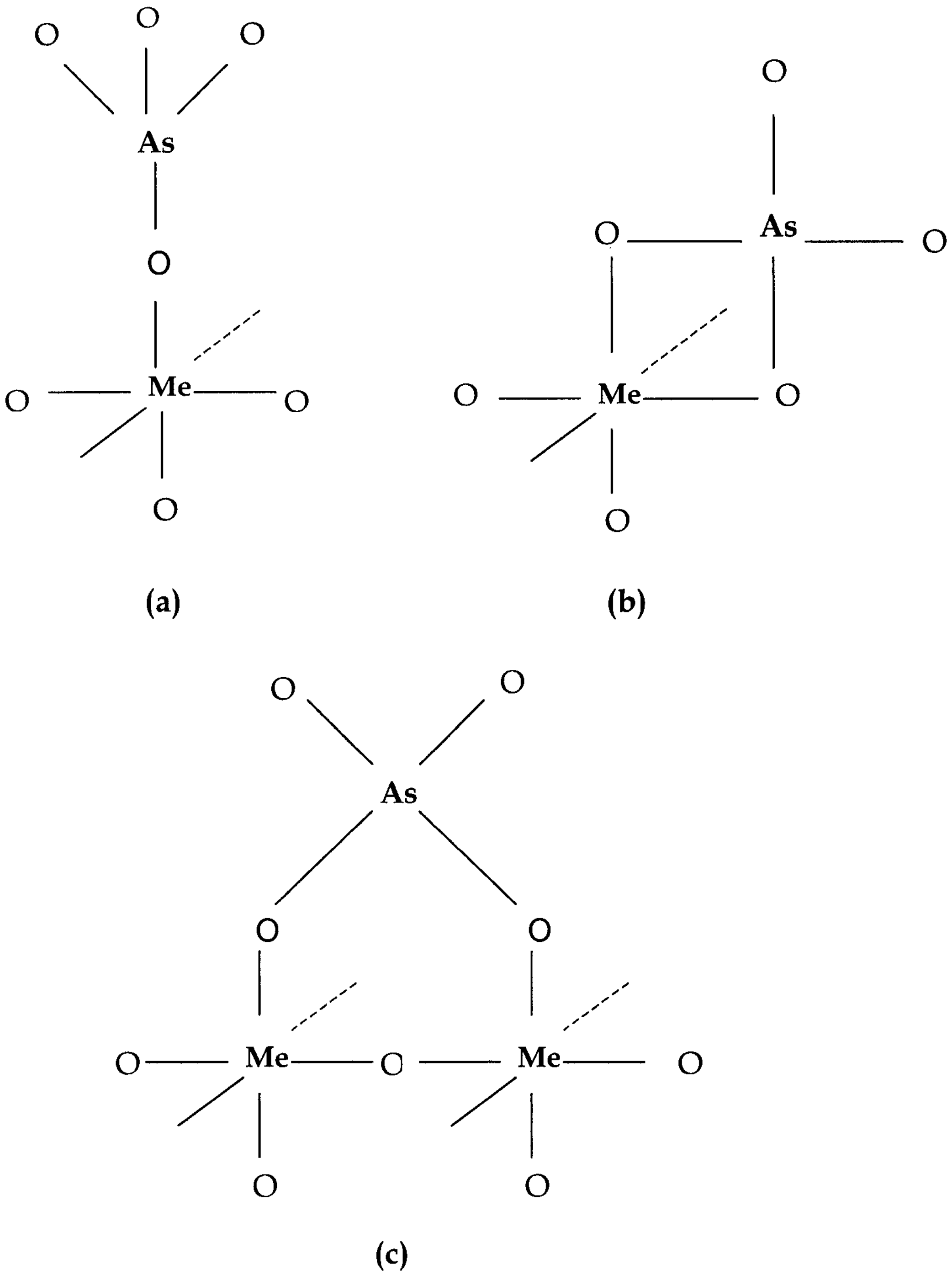


Fig 4: Various types of inner-sphere complex formation of arsenate onto manganese and iron oxides: (a) Monodentate mononuclear; (b) bidentate mononuclear; (c) bidentate binuclear. [Me = metal center, Fe or Mn]. Adapted from Fendorf et al. (1997), Manning et al. (1998), and Foster et al. (2003).

1.3. Adsorption and Oxidation of Arsenic by Iron Oxides

The oxidation of As(III) by iron oxides was studied by Oscarson et al. (1981) at a As:solid ratio of 0.07 (g As/g solid) in a low ionic strength (<0.1M) solution at pH 7.5 for 72 hours. Only the supernatant was analyzed for arsenate and arsenite. Seventy-two hours after the addition of arsenite to the suspension, no arsenate was detected in the aqueous phase and less than 5% of the initial arsenite remained in solution. In a similar experiment, As(V) was added to the iron oxide suspension at the same As:Fe ratio. After 72h, approximately 50% of the As(V) had adsorbed to the solid, indicating that it has a lesser affinity than As(III) for the solid. Following the exposure and adsorption of both As(III) and As(V), the surface of the solid was examined using X-ray spectroscopy. The researchers proposed that the two species had adsorbed without a change in their original oxidation state.

Pierce and Moore (1980) studied arsenite adsorption onto amorphous iron hydroxides. Only the supernatant was analyzed for arsenic speciation. The As:Fe ratios used in these experiments were 0.011 to 0.11. The experiments were conducted at a low ionic strength, 0.01M, over a range of pH, 4 to 10. They found that arsenite adsorbed rapidly onto the solid: more than 90% of adsorption occurred within two hours. Pierce and Moore (1980) postulated that the process was not only due to electrostatic interactions. Over the range of arsenite concentrations and pH studied, maximum adsorption occurred at pH 7. Figure 5 is a simplified representation of the results of Pierce and Moore (1980). Arsenate was also seen to adsorb quickly onto the amorphous iron hydroxides; almost 100% of adsorption was completed within 4 hours. Arsenate adsorption was

Figure 5: Simplified representation of arsenite and arsenate adsorption onto iron oxides at a fixed concentration over a range of pH.

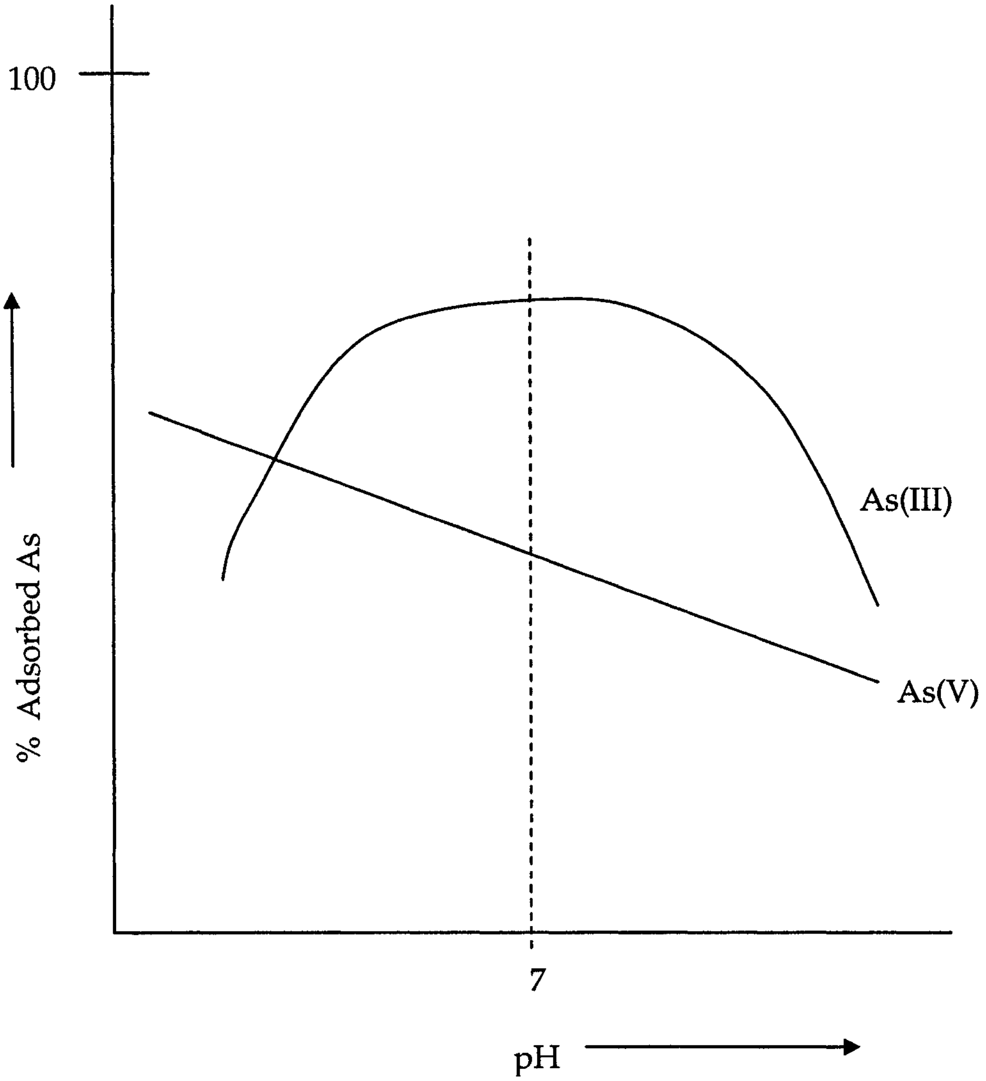


Figure 5: Simplified representation of arsenite and arsenate adsorption onto iron oxides at a fixed concentration over a range of pH (from Pierce and Moore(1980)).

more pH dependent, decreasing with increasing pH. This trend was confirmed by Raven et al. (1998). Their experimental system was purged with N_2 gas, but like previous studies the ionic strength of the solutions was low (0.1M) and only the supernatant was analyzed for As speciation. Arsenic to iron oxide, As:solid, ratios were 0.02 and 1 (g/g). The adsorption of arsenate was also found to decrease with increasing pH from pH 4 to 9. Adsorption equilibrium was achieved rapidly in this system (within hours) as in experiments carried out by Pierce and Moore (1980). One major difference in the results of these two studies is the adsorption of arsenite at different pH: Raven et al. observed that As(III) adsorption increased with increasing pH whereas Pierce and Moore observed an adsorption maximum at pH 7 (see Figure 5).

Manning et al. (1998) investigated the adsorption of arsenic on α-FeOOH, over a range of pH (3 - 11) at low ionic strength (< 0.1M). The As:solid Fe-oxide ratios were 4 to 8, and only the supernatant was analyzed for As speciation. Arsenate adsorption was seen to decrease with increasing pH, which was also observed by Pierce and Moore (1980). However, the adsorption of arsenite onto goethite was less dependent on pH than arsenate and reached a maximum at pH 7. At the higher As:Fe ratio, the pH dependence increased and the adsorption maximum at pH 7 became more pronounced, in agreement with results of the study conducted by Pierce and Moore (1980). The EXAFS analysis in Manning et al. (1998) indicated that the As(III) adsorbed to the surface of the FeOOH had remained in the +3 oxidation state and, thus, was not oxidized to As(V).

The nature of the arsenate complexes that form on the surface of synthetic goethite was determined using EXAFS (Fendorf et al., 1997). Arsenate was added to a suspension of the solid at a As:solid ratio of 0.0075 (1mM As(V) with 10g/L goethite) over a range of pH, 4 to 9, at an ionic strength of 0.1M. The EXAFS analysis showed that there are three distinct As-Fe interatomic distances, indicating three different types of arsenate surface complexes forming on goethite: bidentate binuclear, bidentate mononuclear, and monodentate mononuclear (see Figure 4). Other researchers have also observed these complexes (Waychunas et al., 1993; Manceau, 1995; Waychunas et al., 1995; Sun and Doner, 1996). Sun and Doner (1996) suggested that trinuclear complex formation was possible between arsenate and iron oxide surface. Manning et al. (1998) also proposed that the most likely structure of the arsenite – goethite surface complex was a bidentate binuclear inner-sphere complex. At low surface coverage, the most likely coordination of the arsenate surface complex was monodentate mononuclear, accounting for 30% of all As associated with the solid (Waychunas et al., 1993). The contribution (relative percentage) of the bidentate binuclear complexes increased at higher As:Fe ratios (Waychunas et al.,1993,Fendorf et al., 1997).

The mechanism by which arsenate sorbs onto iron oxides (e.g. goethite) was studied by Grossl et al. (1997) using a pressure-jump relaxation technique. They were able to distinguish two separate steps, with two distinct relaxation times, in the adsorption process. First, a hydroxyl group on the goethite surface was exchanged for an aqueous arsenate oxyanion (fast relaxation time). The researchers postulated that in this step an inner sphere monodentate complex was formed. In the next step, another hydroxyl group is exchanged with the already complexed arsenate, so that a bidentate surface complex forms (slow relaxation time).

Most investigations, so far, of arsenite oxidation by manganese – oxides and iron – oxides have been conducted at low ionic strengths. Many studies have also determined the degree of oxidation based solely on aqueous phase speciation, instead of total As speciation. Furthermore, very few experiments have been conducted to investigate As(III) oxidation by iron – oxides. The research objectives of this study were designed to address a few of these concerns.

1.4. Research Objectives

There are several objectives to this research project. The first objective was to determine the rate of As(III) oxidation by oxygen in solution over a range of pH, in both the presence and absence of light, and at high and low ionic strengths. These experiments were conducted in 0.05M NaCl and 0.7M NaCl to simulate freshwater and marine conditions. It has been postulated that the oxidation of arsenite to arsenate by oxygen in the absence of a solid phase is slow (Andrae, 1979), however this reaction has not been studied explicitly at higher ionic strengths. The effect of light on this system was also studied explicitly to determine whether, as was suggested by Andrae (1979), that the oxidation of arsenite is catalyzed by light

The second objective of this research was to determine the ability of manganese oxyhydroxides to oxidize dissolved arsenite at circumneutral pHs. To meet this objective, we used both amorphous and crystalline Mn-oxyhydroxides, in solutions of ionic strengths of 0.05 and 0.7M NaCl, and analyzed both the solid and aqueous phases. Most previous oxidation studies have been limited to low ionic strength solutions and were based on the determination of solely aqueous phase As(III)/As(V) content.

Experiments were also carried out in 0.05M NaCl at circum-neutral pH using both amorphous and crystalline iron oxyhydroxides to compare the relative efficiency of the two metal oxides (i.e., Mn and Fe) to oxidize As(III) to As(V). Again, similar previous studies focused only on the concentration and speciation of arsenic remaining in solution.

The last objective of this research was to determine the role of oxygen and manganese oxides in the oxidation of arsenite within the context of early diagenesis. Fe and Mn-oxides have been postulated to serve as electron acceptors in the electron-transfer reaction between As(III) and the solid (Oscarson et al, 1981) but nearly all previous experimental investigations involving these metal oxides were carried out in oxygenated solutions. Thus, in order to determine whether the metal oxyhydroxides themselves oxidize arsenic or if they only serve as an electron transfer medium through which oxygen oxidizes arsenic, several experiments were conducted in the absence of oxygen, using amorphous manganese oxides in low and high ionic strength solutions. The pH of these solutions were between 7 and 8 to simulate natural conditions.

2. MATERIALS AND METHODS

2.1. Solution Preparation

All sample collection tubes, syringes, and plastic bottles used for these experiments were acid-washed in a 10% HCl for a minimum of 24h, after which they were rinsed several times with doubly deionized water, Nanopure™ water, and air dried. The rubber stoppers on the plungers of the Nalgene™ syringes were wrapped in Teflon tape (P.T.F.E.) before the plungers were introduced to the acid bath. Glassware was acid-washed in a 15% nitric acid bath for at least 24h before it was rinsed several times with Nanopure™ water, after which it was dried, except volumetric flasks, which were left capped after rinsing.

All solutions used in the synthesis of the metal oxyhydroxides were prepared in distilled water. The $MnCl_2$ (Fisher Scientific) and $KMnO_4$ (AnalaR, BDH) solids were certified ACS grade. Sodium hydroxide (99.7% pure) and reagent grade $Fe_2(SO4)_3$ were obtained from Aldrich and A&C Chemicals respectively.
Initial stock solutions of 100ppm arsenite were prepared from arsenic trioxide, As_2O_3 (99.99% pure, Aldrich), by dissolving the solid (0.132g) in concentrated trace metal-free hydrochloric acid. These stock solutions were then diluted to the desired arsenite concentrations for each experiment. Arsenate solutions were made by dissolving $Na_2HAsO_4 \cdot 7H_2O$ (98.5% pure, BDH AnalaR) in Nanopure™ water and subsequently diluted. The sodium chloride (certified A.C.S. grade) used as the background electrolyte was obtained from Fisher Scientific. Reagents used for the generation of the arsenic hydride for analysis by atomic absorption

spectroscopy were prepared in Nanopure™ water. Ascorbic acid (99.7% pure) and KI (99.5% pure) were both purchased from AnalaR BDH, whereas sodium borohydride, $NaBH_4$ (99% pure) was obtained from Sigma Aldrich. Buffer solutions of TRIS in 0.7 molal NaCl were prepared using reagent grade tris-(hydroxymethyl)aminomethane from Fisher Scientific. All other chemicals and solutions used were certified A.C.S. grade.

2.2 *Solid Synthesis*

2.2.1 Manganese Oxyhydroxides

Suspensions of approximately 0.01M amorphous δ - MnO_2, were prepared following a protocol described by Laha and Luthy (1990). Briefly, 80mL of a 0.1M NaOH (0.008 mol) solution were added to 40mL of 0.1M $KMnO_4$ (0.004 mol) in a clean Erlenmeyer flask under constant stirring by a magnetic stir bar. The volume was then adjusted to 500mL using distilled water, after which 60mL of a 0.1M $MnCl_2$ (0.006mol) solution were added. This induced the rapid precipitation of a dark brown solid. The solution was stirred for another 30 minutes to allow the reaction to go to completion before the solid was separated by vacuum filtration on a Millipore™ 0.45μm HA Membrane filter. The solid was washed several times with Nanopure™ water and resuspended in 1L of Nanopure™ water yielding a slurry of ~0.01M δ -MnO_2. The crystalline solid was prepared from the amorphous δ -MnO_2 by drying on a watchglass in an oven at 110° C overnight. The dried solid was ground into fine particles with a mortar and pestle before use. All solids were used within 48 hours of their synthesis.

X-Ray diffraction analyses of both the wet and dried manganese oxyhydroxides were carried out. The XRD pattern of the dried solid matched that presented in Foster et al. (2003) of the manganese oxide vernadite, which they synthesized using a procedure almost identical to the one described in the previous paragraph. Two major peaks were evident, the first between 37° and 38° 2-theta, and the second between 66° and 67° 2Θ. The XRD pattern of the wet slurry showed a very broad peak between 26° and 32° 2Θ overlapping another broad peak between 36° and 40° 2Θ. The surface area of the solid synthesized by Laha and Luthy (1990) was reported to be 263 ± 5 m^2/g, whereas that reported by Foster et al. (2003) was 295 ± 30 m^2/g. Foster et al. (2003) reported that the pH of zero net proton charge of their synthetic vernadite was 1.5 and the average bulk oxidation state of manganese in the solid was 3.1.

2.2.2. Iron Oxyhydroxides

The amorphous iron oxyhydroxides were prepared as described by Pierce and Moore (1980). Briefly, 1.665g of $Fe_2(SO4)_3$ were dissolved in 200mL of distilled water. To this solution, 25mL of a 1M NaOH solution were added and the resulting solid was allowed to precipitate for 30-40 minutes. The suspension was vacuum filtered and washed several times with Nanopure™ water. The collected solid was resuspended in 200 mL of distilled water to a concentration of ~4.5g/l (~0.05 mol/ liter). The crystalline iron-oxyhydroxide was prepared by drying the amorphous solid in a clean watchglass overnight at 110° C. The resulting crystals were then ground to a powder in a mortar and pestle.

XRD analysis was conducted only on the dried, crystalline iron oxyhydroxide. The resulting pattern could not be matched to any single solid phase. The closest similarity appeared to be to goethite: the pattern showed three distinguishable peaks near 21°, 33°, and 36° 2-theta. It was assumed that the structure of the wet iron oxyhydroxide was less crystalline than the dried product.

2.3. *Analytical Methods*

2.3.1. Method Development: Ion Exchange Resins

In order to separate arsenite and arsenate, a set of ion-exchange resin containing tubes, called SPE were obtained from Supelco. The resin carries a quaternary amine functional group and can quantitatively retain specific anions once activated by methanol. Anions can later be eluted with a weak acid solution. Whereas arsenate is complexed by the resin, arsenite is not. Five hundred milligrams of this resin came packed between 2 polyethylene frits in a 2 mL tube with a male and female luer-lok at either end. Le et al. (2000) had previously tested this resin for arsenate retention in doubly deionized water and found that 500 μg of As(V) were retained by 500 mg of resin. These SPE tubes make the separation of arsenite and arsenate quick and simple, thereby avoiding many sample speciation and preservation problems. The tubes were tested for arsenite and arsenate retention from 0.05M NaCl and 0.7M NaCl solutions.

Three SPE tubes were attached in series and preconditioned with 8mL of CH_3OH, followed by an 8 mL wash of Nanopure™ water. The combined pore volume of the three tubes was 3.8 to 4 mL. A 5.00 mL aliquot of a 100 ppb arsenate in 0.7M NaCl solution was then passed through the three SPE tubes at a flow rate no greater than 3 mL/min. The solution was recovered in pre-weighed collection tubes. The SPE tubes were then washed with 5 mL of Nanopure™ water. The wash was also collected in the sample tube, bringing the total volume of sample plus wash to approximately 10mL. The As(V) bound in the SPE tubes was eluted with 2 x 2.5 mL aliquots of a 1N HCl solution. The acid was in contact with the resin for at least one and a half minutes. The resin was finally washed with 5 mL of Nanopure™ water. The HCl eluant and wash were combined in a separate sample collection tube. All collection tubes were weighed after the sample, eluant, and wash solutions were recovered so that the dilution factor could be calculated. This entire procedure was replicated 4 to 6 times. The samples were analyzed for total arsenic.

Another experiment was conducted to determine the retention capacity of the SPE tubes for arsenate. One tube was preconditioned with methanol and washed with Nanopure™ water. A total of 30mL of a 100ppb arsenate solution in 0.7M NaCl was passed through the tubes in 5.00mL aliquots before the As(V) retained by the resin was finally eluted. After each aliquot addition, the tube was washed with 5 mL of Nanopure™ water, and both solutions were gathered in a sample collection tube. The total arsenic content of the effluent was monitored. The same protocol was used to determine the retention capacity of the SPE tubes for As(V) at the lower ionic strength, although only a total of 20mL of 100ppb arsenate solution in 0.05M NaCl was passed through the tubes.

The retention capacity of the SPE tubes for arsenite was also determined. One SPE tube was preconditioned with methanol and washed with Nanopure™ water. A 10 mL aliquot of a 100 ppb As(III) solution in 0.7M NaCl was passed through the tube and collected. This was repeated 5 times and the arsenic content in the collected samples was determined. At the end of the 5 repetitions, the arsenic retained by the resin was eluted with a 1N HCl solution as described above.

The relative error from the replicate elution experiments was 6%. Approximately 32 ppb of the 100 ppb arsenate in the 0.7M NaCl solution was retained per SPE tube corresponding to a retention capacity of 0.160 μg As(V) per 500 mg of resin. In the 0.05M NaCl solution, approximately 1.25 μg of arsenate was retained by 500 mg of the resin. The relative error in these measurements was 6% and the reproducibility of the method (coupled with the error from the atomic absorption spectrometer) was 5%. The resin did not quantitatively retain any arsenite.

2.3.3. Atomic Absorption Spectroscopy

All arsenite and arsenate concentrations were measured using a Perkin Elmer 5100 Atomic Absorption Spectrometer. The spectrometer was used in conjunction with an AS 90 autosampler and a FIAS 200 flow injection apparatus. The total arsenic content in the samples was measured by first reducing all of the As in solution to arsenite. Samples were reduced using a 5% (w/v) ascorbic acid, 5% (w/v) KI solution in concentrated hydrochloric acid. Sample to ascorbic acid to HCl volume ratios were 10:3:1. A 10% v/v HCl solution was used as the carrier phase for this system to deliver the sample to the liquid-gas separator where the hydride, arsine, was generated. The hydride was generated by reacting the arsenite in the samples with a 0.2% (w/v) sodium borohydride in 0.05% (w/v) NaOH solution. The arsenic was delivered by argon carrier gas to the sample cell, which was heated to 900°C, in the hydride form and subsequently dissociated into its constituent parts. An EDL, electrodeless discharge lamp, was used to measure the absorbance of As in the light path.

The detection limit of arsenic using atomic absorption was calculated for matrices of samples taken from the 0.05M and 0.7M NaCl solutions, using the noise from blank measurements and the slope of the calibration curves. The arsenic detection limit was ~0.14ppb and ~0.40ppb in the lower and higher ionic strength media, respectively. Measurements below these values are reported as not detectable (ND). For further calculation and error propagation purposes, these readings were assigned a value of zero, with an error corresponding to the limit of detection.

2.4. *Experimental Protocols*

A series of experiments was conducted to determine the oxidation kinetics of arsenite in the presence of oxygen under different reaction conditions, of pH, light, and ionic strength. The experimental procedures for these control experiments are described in the following sections. The experiments that included arsenite in the presence of a solid phase (Mn-Ox or Fe-Ox) are described in detail in 2.4.2.

2.4.1. Batch Reactions of Dissolved Arsenite in Aqueous Systems Open to the Atmosphere

The pH of several 500mL solutions of 100ppb arsenite in 0.05M NaCl (initial pH ~3) was adjusted to 3, 5, 7, and 9 using dilute HCl and NaOH solutions. Half of the volume of these solutions was poured into opaque polypropylene Nalgene bottles, while the other half was kept in glass Erlenmeyer flasks. The Erlenmeyer flasks were left exposed to fluorescent light 24hours a day and to natural light during the daytime. This protocol was applied to compare the rate of arsenite oxidation by oxygen in the dark and in the presence of light. Approximately 30 minutes elapsed between the addition of the arsenite to the sodium chloride solutions and the final pH adjustment. This same experimental setup was used with 0.7M NaCl solutions. All experiments were carried out at room temperature (23°C ± 5°C).

The solutions were sampled at set time intervals (0, 0.0833, 0.25, 0.5, 1, 2, 4, 8, 24, 48h) over a period of approximately 5-6 months to monitor arsenite and arsenate concentrations. Arsenic speciation was determined using the anion-exchange resin protocol described in Section 2.3.1. A clean acid-washed 10mL Nalgene syringe, with the plunger removed, was attached to the inlet of the SPE tubes. At each sampling time, 1.00 to 4.00 mL of the reaction solution was transferred into the syringe. The syringe plunger was reinserted and the solution aliquot pushed through the SPE tubes at a flow rate no greater than 3mL/min. The tubes were washed with 6 to 9 mL of Nanopure™ water and the wash was added to the sample aliquot. The final volume of the collected sample plus wash was ~10mL. Two SPE tubes in series were used with the 0.05M NaCl solutions while three SPE tubes were used with 0.7M NaCl solutions.

The total arsenic concentration was determined at the start of the experiment and monitored throughout the duration of the study by collecting and analyzing 1.00mL sample aliquots. Arsenate concentrations were calculated by difference between the total arsenic and arsenite content. At each sampling time, the pH of the reacting solution was also determined using a Metrohm 713 pH meter. NIST-traceable pH buffers obtained from Hanna Instruments were used to calibrate the Metrohm combination glass pH electrode . A TRIS buffer solution was prepared in 0.7m NaCl according to the procedure described by Millero et al. (1987). The concentration of TRIS was 0.01 molal. All calibrations were conducted at either 20°C or 25°C.

2.4.2. Batch Reactions of Arsenite in the presence of Manganese and Iron Oxyhydroxides

The conditions under which the oxidation reactions in the presence of manganese and iron oxyhydroxides were conducted are summarized in Table 1. In this section, the experimental procedures used in experiments open to the atmosphere (i.e. in the presence of dissolved oxygen) are described first followed by descriptions of the procedures used in closed reactors purged with nitrogen in order to exclude dissolved oxygen.

Batch Reactions in Open Systems

Arsenite was added to 500 mL solutions of either 0.05M NaCl or 0.7M NaCl at a final concentration of 100 ppb. The pH was adjusted to between 7 and 8 using dilute solutions of HCl and NaOH, and a sample of this solution was stored for total As and As speciation analyses using the SPE tube protocol described in Section 2.3.1. The solutions were left open to the atmosphere to admit oxygen. Then, 25-30mL of the amorphous •-MnO_2 slurry was added to obtain an approximate solid to solution ratio of 0.1g/500mL. The solutions were stirred with an overhead stirring rod to prevent grinding the solid.

Two – mL aliquots of the reacting solution were taken at set time intervals (0.0833, 0.25, 0.5, 1, 2, 4, 8h) with 10mL Nalgene syringes in order to determine the concentration of arsenic species in the aqueous phase. The aliquots were filtered through 0.45 μm microfilters, obtained from Gelman Sciences, with supported acrylic copolymer membranes attached to the inlet of the SPE tubes, and the filtrate passed through the tubes at a flow rate no greater than 3mL/min. After the 0.45 μm filter was removed, an 8.00mL wash of Nanopure™

Table 1: Summary of experimental conditions under which arsenite oxidation was carried out in the presence of manganese and iron oxyhydroxides. The initial pH of all systems was between 7 and 8.

	0.05M NaCl		0.7M NaCl	
	w/ O_2	w/o O_2	w/ O_2	w/o O_2
Amorphous Mn-Ox	X	X	X	X
Crystalline Mn-Ox	X		X	
Amorphous Fe-Ox	X			
Crystalline Fe-Ox	X			

water was then passed through the tubes and added to the sample. Two-mL aliquots of the reaction solution was sampled and filtered to determine total arsenic in solution.

In order to measure the total arsenic concentrations in the combined solid and aqueous phase, a 1mL aliquot of stirred unfiltered sample was added to 4.00mL of 6N HCl. The solid dissolved in 6N HCl within 15-20 minutes. This sample was later subsampled to determine total As and total As(III). Arsenate was obtained by difference. To test the preservation of the original arsenic speciation present after dissolution of the solids in concentrated HCl, a 100mL stock solution of 1000ppm arsenite was prepared in 12N HCl acid as described in section 2.1. After 2-3 weeks, this solution was diluted to a concentration of 8ppb arsenic and analyzed for arsenite content. The result was 7.8 ± 0.9 ppb. It was assumed that the arsenic speciation was also preserved in 6N HCl.

Sampling protocols and all other experimental conditions, such as initial arsenite concentrations, pH, and temperature, were the same as described above for all subsequent experiments using crystalline Mn-Ox, and amorphous and crystalline Fe-Ox. The solid:solution ratios in all heterogeneous reaction systems (i.e. in the presence of metal oxyhydroxides) was 0.1g/500mL. Slurries of Fe-Ox were stirred with a floating magnetic stir bar. The pH of the mixed (i.e. experimental slurry) solution was not monitored for the duration of the experiments.

Batch Reactions in Closed Systems in the Absence of Oxygen

One set of experiments was carried out to establish whether the metal oxyhydroxides oxidize arsenite themselves or if they only serve as an electron transfer medium (i.e. catalyst) for oxidation by oxygen. Only amorphous manganese-oxide was used in these reactions, which were conducted in a glove-box in an inert nitrogen atmosphere.

Before starting the experiment, solutions of 0.05M NaCl and 0.7M NaCl containing 100ppb As(III) were purged with nitrogen for at least 30 minutes. A slurry of ~0.01M amorphous manganese oxyhydroxide was also purged with nitrogen for the same length of time before adding it to the arsenite solutions. The solid to solution ratio was 0.1g/500mL. Experimental conditions such as pH and temperature were the same as described in the previous section. Before adding the solid, the aqueous phase of each solution was sampled for arsenite and total arsenic. The aqueous phase and the combined aqueous and solid phases were then sampled for arsenite and total arsenic at set time intervals (0.08, 5.5, 22, 30, 47, and 54.5h). Dissolved and total arsenate concentrations were determined by difference.

3. RESULTS

The results the experiments described above are presented in graphical form in the following sections. The raw numerical data, including sampling intervals, pH measurements, and relative arsenic species concentrations are presented in Appendices 1 – 6. All errors were calculated at the 95% Confidence Level. Due to instrumental or manipulation errors, the arsenic content of some samples were only measured once so that no standard deviation and no error limits could be reported. Average instrumental relative errors were between 5 and 10%. The control experiments are presented first, followed by the experiments with solid metal oxyhydroxides and oxygen present. The experiments where dissolved oxygen was excluded are discussed in the last section.

3.1. Oxidation of Arsenite in Systems Open to the Atmosphere

The kinetics of arsenite oxidation was first evaluated in aqueous solutions with oxygen as the only oxidant present. These control experiments were conducted at two different ionic strengths and over a pH range of 3 to 9. The influence of light on the conversion of arsenite to arsenate was also evaluated. These experiments were conducted over a period of 3 to 4 months.

The first series of kinetic experiments was conducted in 0.05M NaCl at pH 3, 5, 7,

Figure 6: Percentage of total arsenic in the form of dissolved arsenite as a function of time in a system open to the atmosphere in 0.05M NaCl in the presence of light at various pH.

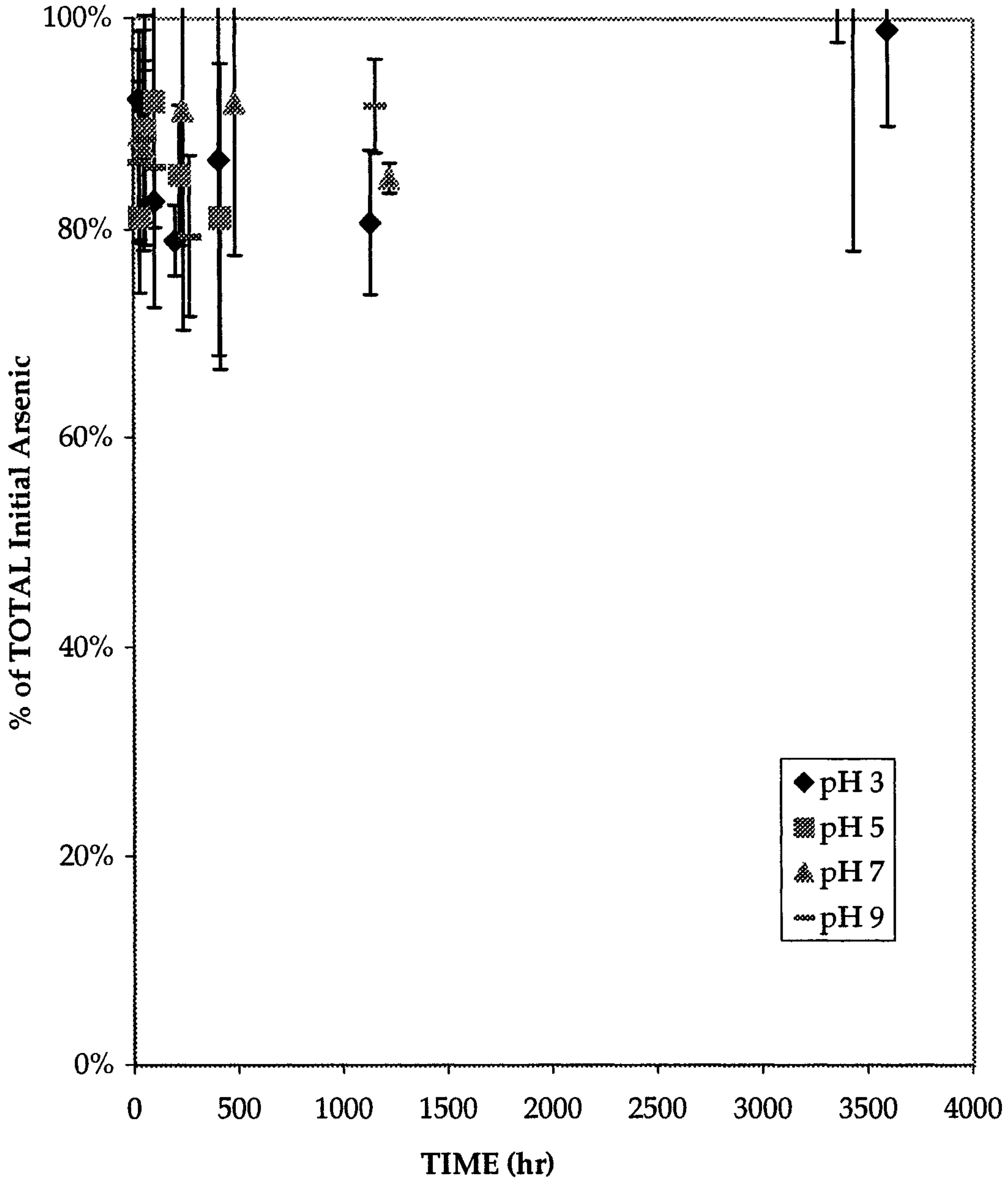


Fig 6: Percent of total arsenic in the form of dissolved arsenite as a function of time in a system open to the atmosphere in 0.05M NaCl in the presence of light at various pH.

Figure 7: Percentage of total arsenic in the form of dissolved arsenite as a function of time in a system open to the atmosphere in 0.05M NaCl in the absence of light at various pH.

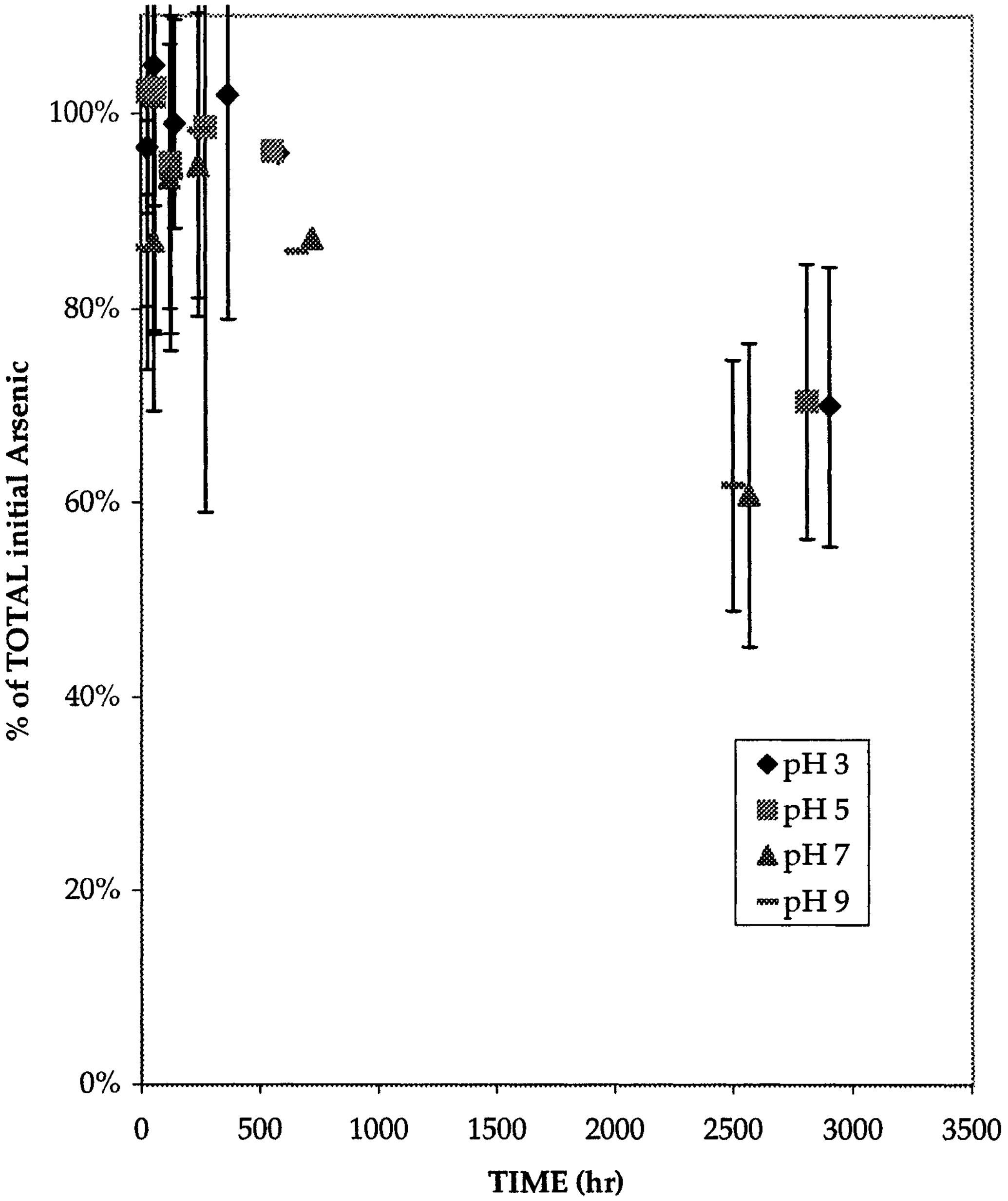


Fig 7: Percent of total arsenic in the form of dissolved arsenite as a function of time in a system open to the atmosphere in 0.05M NaCl in the absence of light at various pH.

and 9, in the light and in the dark, over a period of four months. The concentrations of arsenite and arsenate are reported as a percentage of the initial total arsenic (in the form of arsenite) concentration (i.e., ~100ppb). Figure 6 shows the results of the experiments conducted under light conditions and Figure 7 shows the results obtained from the experiments conducted in the dark. In both cases, there appears to be little oxidation of the arsenite over the 4 month duration of the experiments. By the end of the experiment, the difference in the arsenite concentrations over the pH range studied was not significant. Within the experimental errors, the light and dark experiments gave similar results.

Some oxidation did occur over the duration of these experiments. The results were similar over the pH range studied: the arsenate concentration at the end of the experiment was about 10-20% of total arsenic. Arsenate concentrations appear to have stabilized at the level in the dark, but in the presence of light, As(III) ~ 100% As_{int}.

The second series of control experiments was conducted at a higher salt concentration: 0.7M NaCl. Other parameters were kept the same with the oxidation reactions conducted at pH 3, 5, 7, and 9, in the light and in the dark. The results from these experiments are illustrated in Figures 8 and 9. The amounts of arsenite and arsenate measured at each sampling time, presented as percentages of the total initial arsenic concentration (i.e. 100ppb) can be found in Appendix 2.

The presence of light in the 0.7M NaCl solutions in the pH range studied, appears to have little effect on the reaction. Within the experimental errors, the light and dark experiments gave similar results. The difference in relative arsenate concentrations at the various pHs was also not significant. It appears

Figure 8: Percentage of total arsenic in the form of dissolved arsenite as a function of time in a system open to the atmosphere in 0.7M NaCl in the presence of light at various pH.

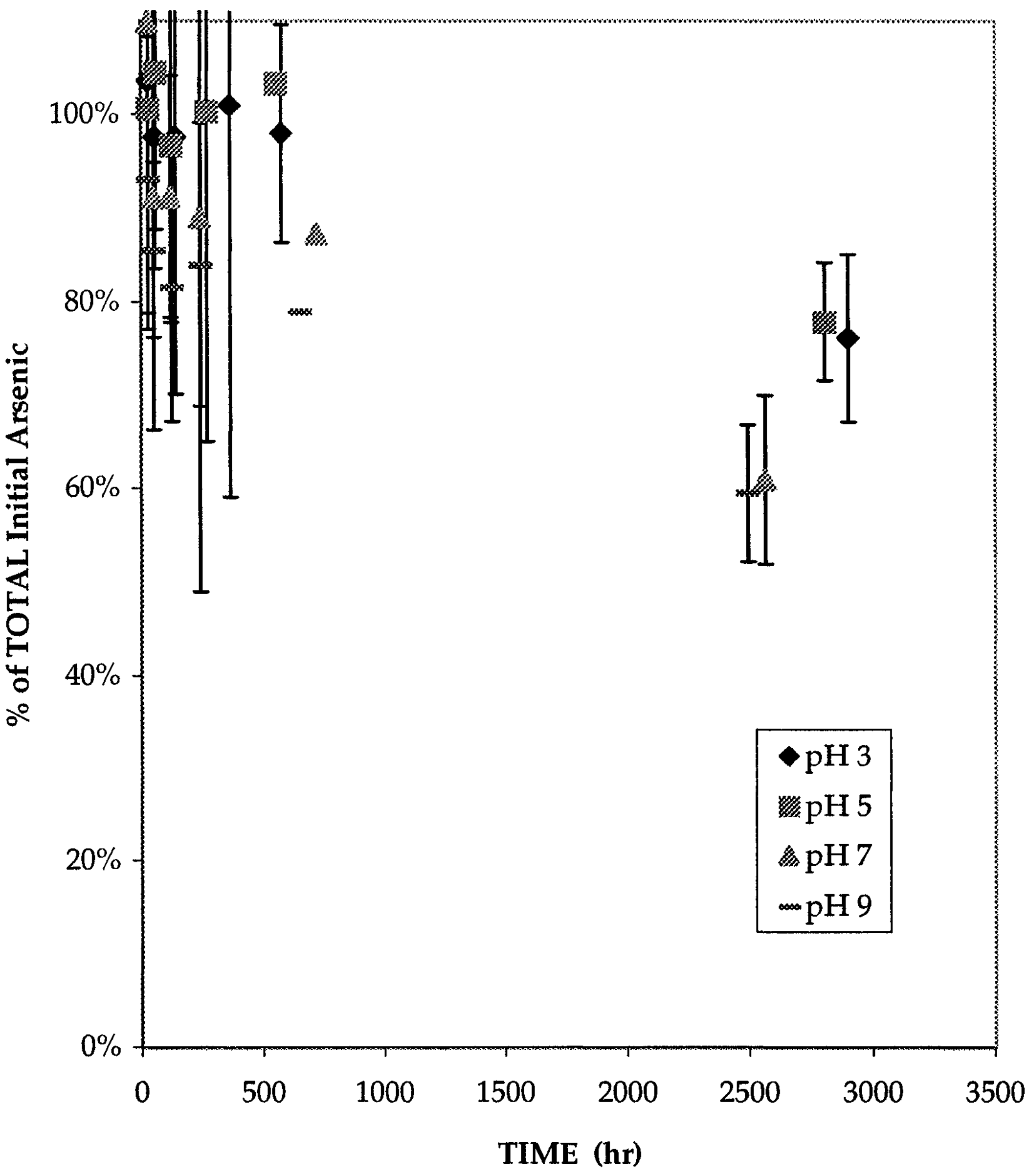


Fig 8: Percent of total arsenic in the form of dissolved arsenite as a function of time in a system open to the atmosphere in 0.7M NaCl in the presence of light at various pH.

Figure 9: Percentage of total arsenic in the form of dissolved arsenite as a function of time in a system open to the atmosphere in 0.7M NaCl in the absence of light at various pH.

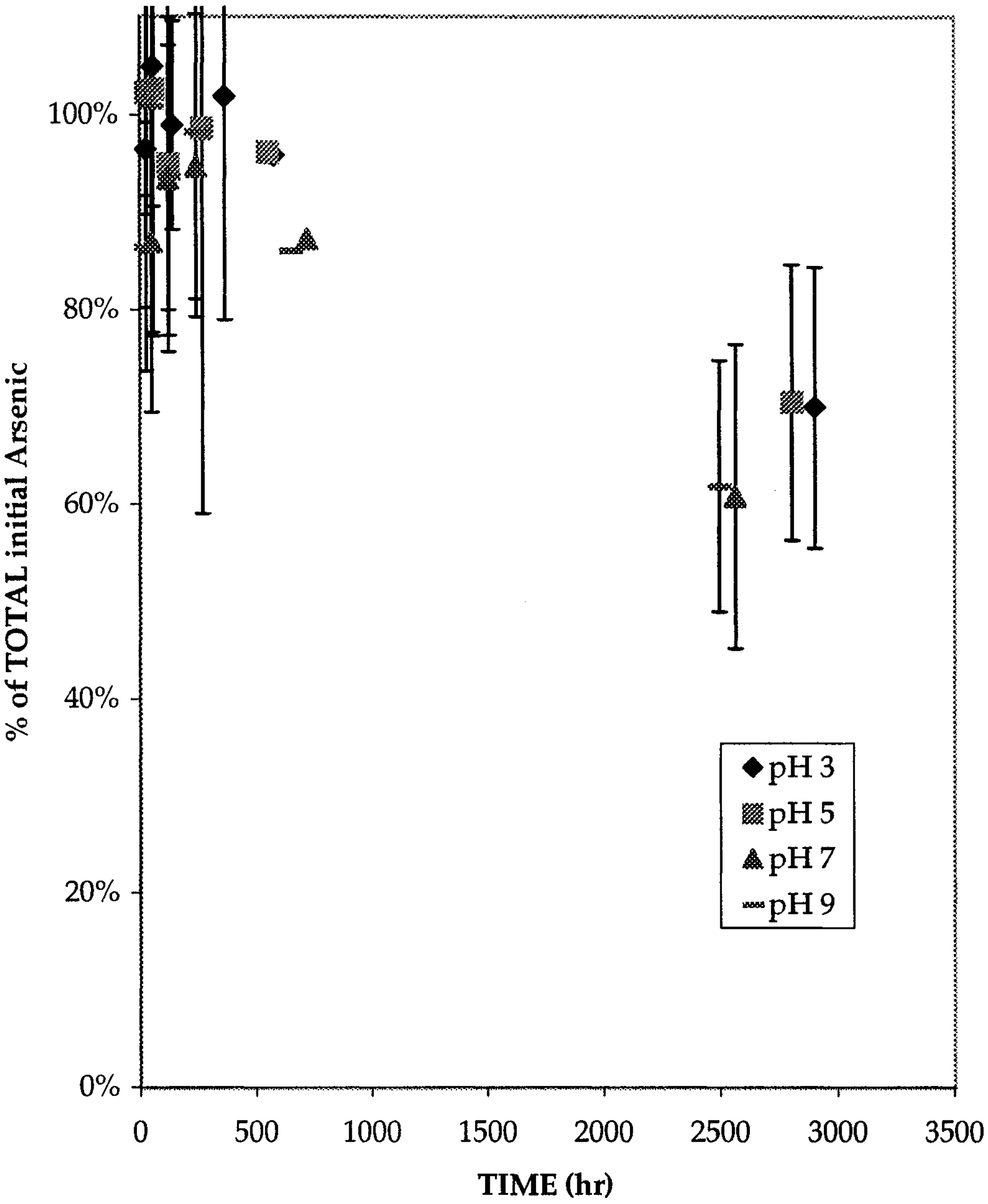


Fig 9: Percent of total arsenic in the form of dissolved arsenite as a function of time in a system open to the atmosphere in 0.7M NaCl in the absence of light at various pH.

that a greater degree of arsenite oxidation occurs at the higher ionic strength than at the lower ionic strength in the presence of light.

3.2. Oxidation of Arsenite in Systems Open to the Atmosphere in the Presence of Iron and Manganese Oxyhydroxides

The results of the oxidation experiments with solid manganese and iron oxyhydroxides, both crystalline and amorphous, are presented in the following section. The experiments were carried out in both 0.05M NaCl and 0.7M NaCl at circum-neutral pH in order to simulate both fresh-water and marine conditions. The concentrations of dissolved and total As species along with their respective errors can be found in Appendices 3 – 5.

3.2.1. Oxidation of Arsenite in the Presence of Amorphous Manganese Oxyhydroxides

The oxidation of arsenite in the presence of amorphous manganese oxyhydroxides was studied in 0.05M and 0.7M NaCl solutions. The relative percentages of arsenite and arsenate in the aqueous phase from the experiment conducted in 0.05M NaCl are shown in Figures 10 . The results from the experiment conducted in 0.7M NaCl are shown in Figures 12 . The initial pH of each experiment was between 7 and 8.

The percentages of arsenite and arsenate in the aqueous phase of both the lower and higher ionic strength solutions exhibited similar trends. Within the first 10 minutes after the addition of the solid, the arsenite in the aqueous phase became

Figure 10: Percent of total initial arsenic in the form of dissolved arsenite [●] and arsenate [■] as a function of time in a system open to the atmosphere and in the presence of amorphous manganese oxyhydroxides in 0.05M NaCl. Initial pH was between 7 and 8. Total [As] = 103 ± 10 ppb.

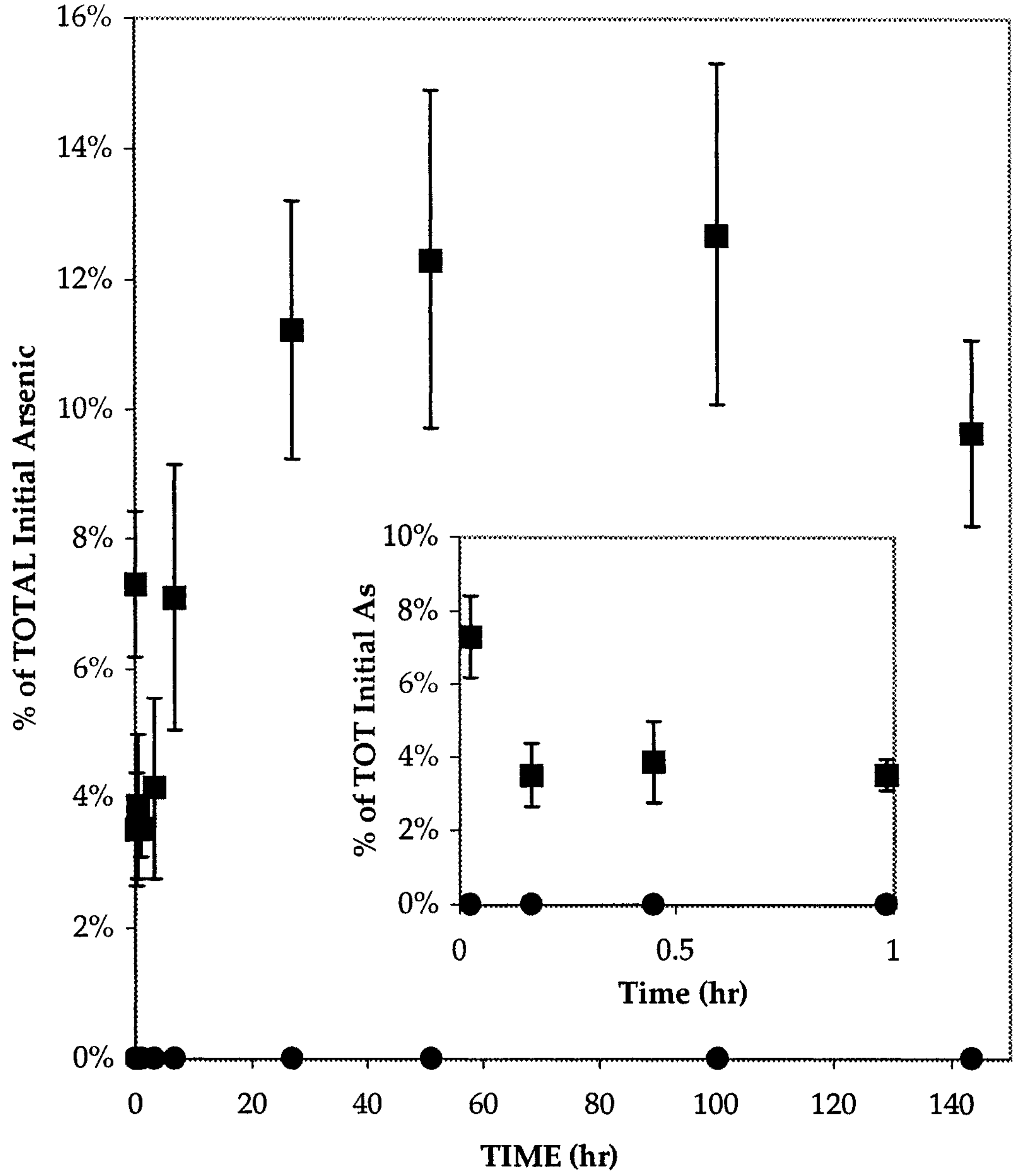


Fig 10: Percent of total initial arsenic in the form of dissolved arsenite [•] and arsenate [■] as a function of time in a system open to the atmosphere and in the presence of amorphous manganese oxyhydroxides in 0.05M NaCl. Initial pH was between 7 and 8. Total [As]=103 ± 10ppb. Inset shows results from first hour (0 < t ≤ 1hr).

Figure 11: Percent of total initial arsenic in the form of arsenite [●] and arsenate [■] in the combined aqueous and solid phases with time in a system open to the atmosphere in the presence of amorphous manganese oxyhydroxides in 0.05M NaCl. Initial pH was between 7 and 8. Total [As] = 103 ± 10 ppb.

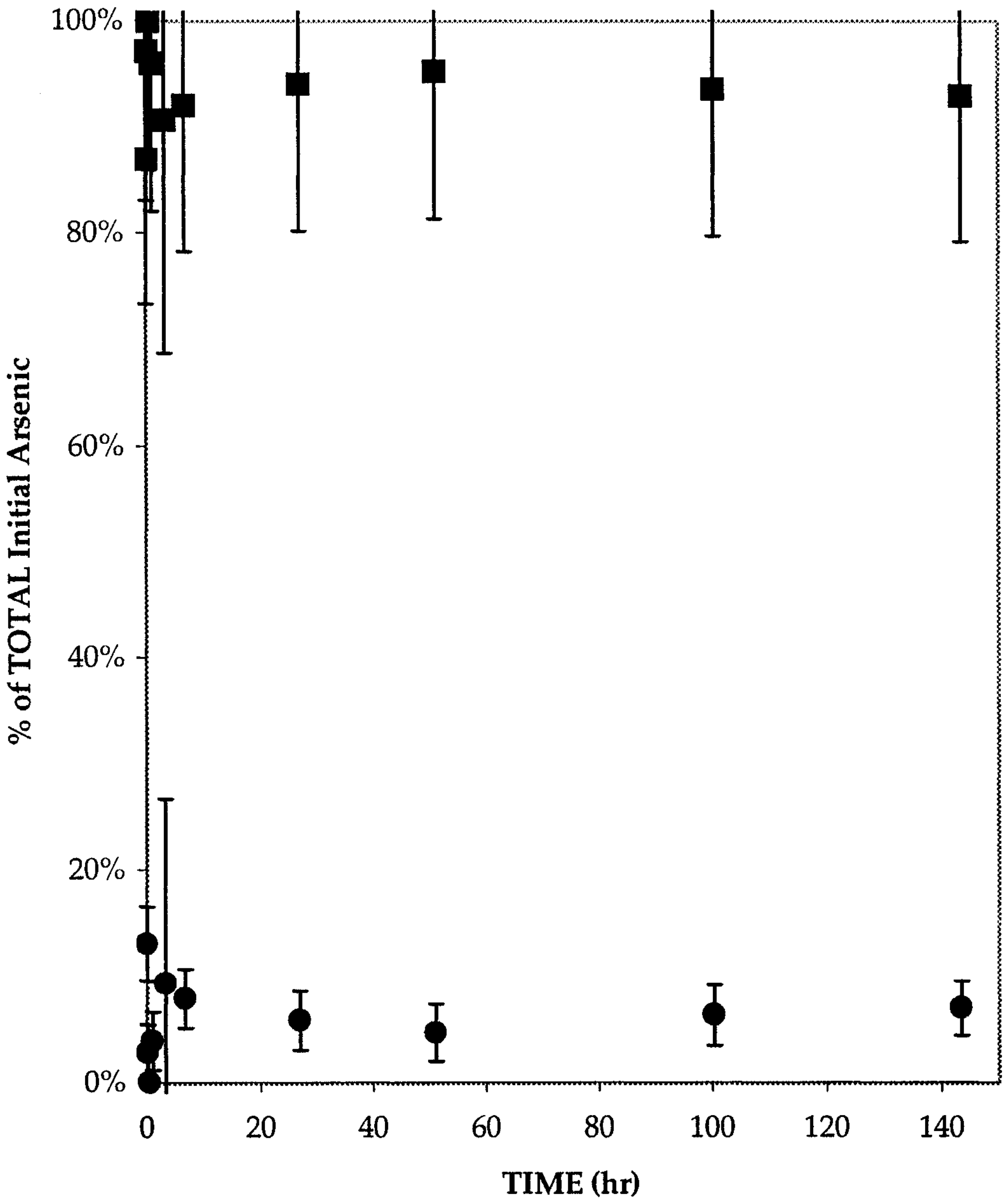


Fig 11: Percent of total initial arsenic in the form of arsenite[•] and arsenate[■] in the combined aqueous and solid phases with time in a system open to the atmosphere in the presence of amorphous manganese oxyhydroxides in 0.05M NaCl.

Initial pH was between 7 and 8. Total [As] = 103 ± 10 ppb.

Figure 12: Percent of total initial arsenic in the form of dissolved arsenite [•] and arsenate [■] as a function of time in a system open to the atmosphere and in the presence of amorphous manganese oxyhydroxides in 0.7M NaCl. Initial pH was between 7 and 8. Total [As] = 99 ± 5 ppb.

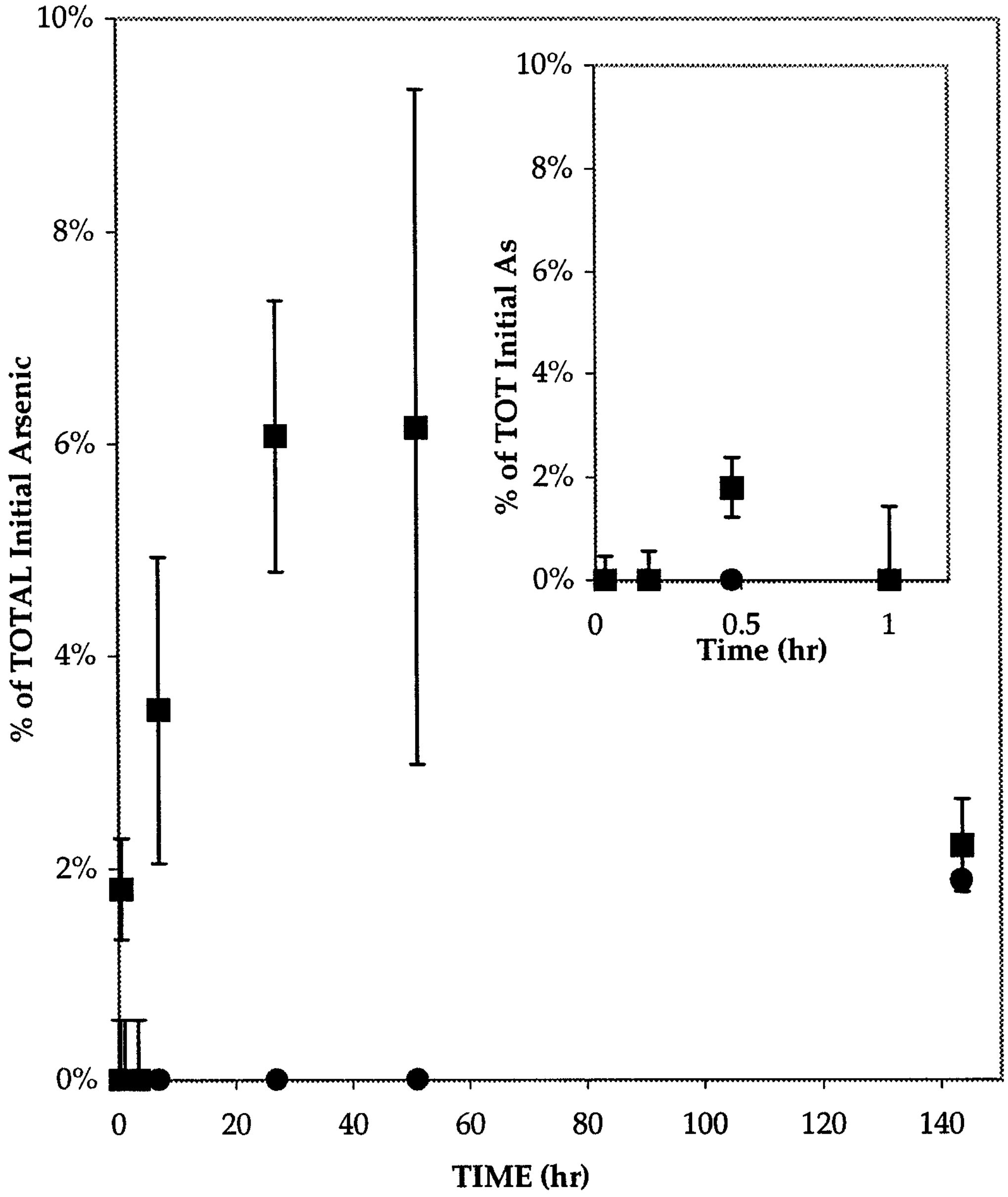


Fig 12: Percent of total initial arsenic in the form of dissolved arsenite [•] and arsenate [■] as a function of time in a system open to the atmosphere and in the presence of amorphous manganese oxyhydroxides in 0.7M NaCl. Initial pH was between 7 and 8. Total [As] = 99 ± 5 ppb. Inset shows results from first hour (0 < t ≤ 1hr).

Figure 13: Percent of total initial arsenic in the form of arsenite [●] and arsenate [■] in the combined aqueous and solid phases with time in a system open to the atmosphere in the presence of amorphous manganese oxyhydroxides in 0.7M NaCl. Initial pH was between 7 and 8. Total [As] = 99 ± 5 ppb.

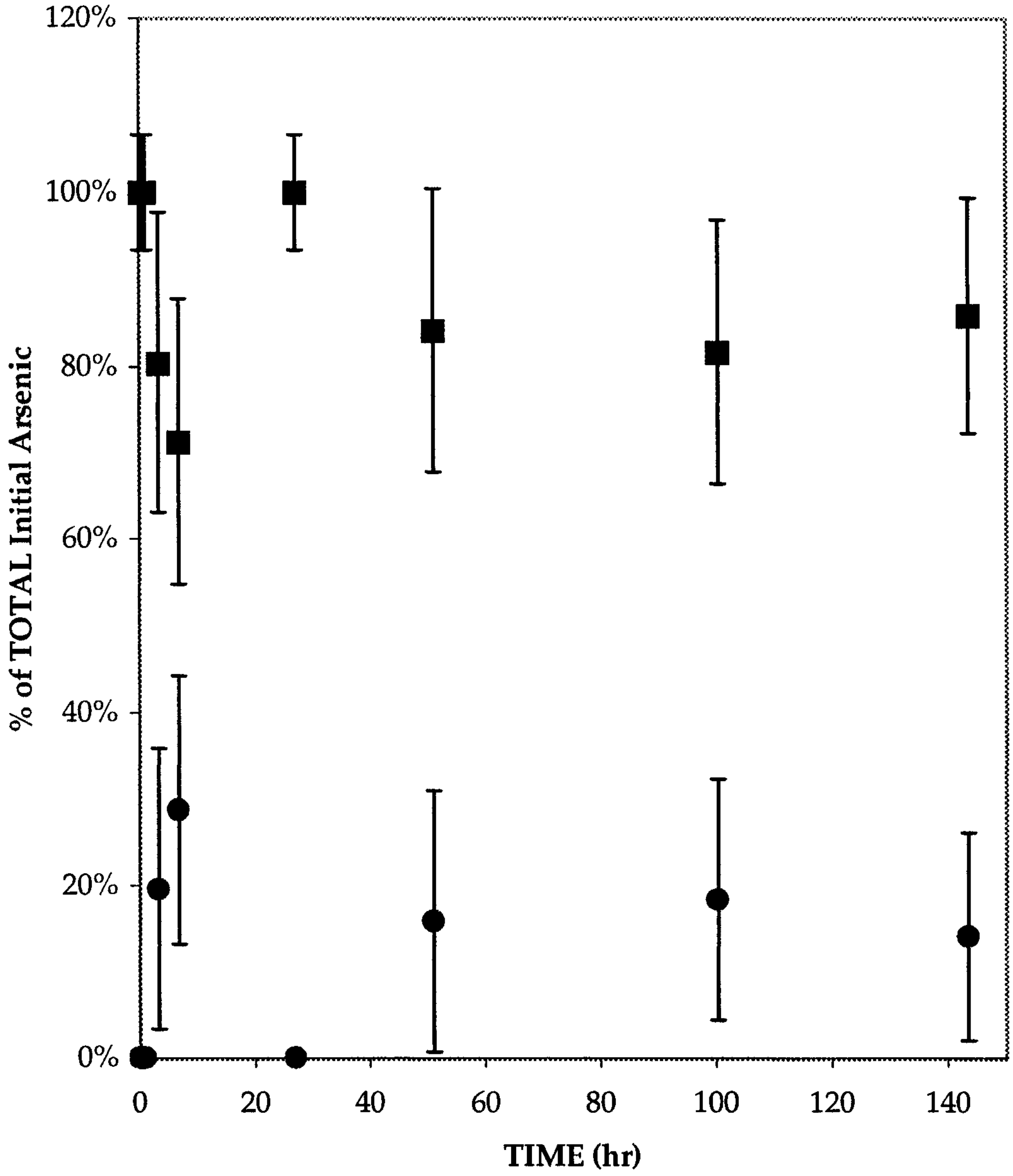


Fig 13: Percent of total initial arsenic in the form of arsenite[●] and arsenate[■] in the combined aqueous and solid phases with time in a system open to the atmosphere in the presence of amorphous manganese oxyhydroxides in 0.7M NaCl.
Initial pH was between 7 and 8. Total [As] = 99 ± 5 ppb.

undetectable (i.e. < 0.14ppb for the lower ionic strength solution, and <0.5ppb for the higher ionic strength solution). Arsenate in the aqueous phase increased slowly over the first 60 hours of the experiment, then remained nearly constant over the next 5 to 6 days before decreasing. The concentration of dissolved arsenate, about 12% of total initial As, in the lower ionic strength solution was greater than in the higher ionic strength solution, which was ~6% or less of total initial As.

Total arsenite and arsenate in the combined solid and aqueous phases from the experiment conducted in the 0.05M NaCl and 0.7M NaCl solutions are presented in Figures 11 and Figure 13 respectively. All of the arsenite was converted to arsenate within the first 15 minutes at both ionic strengths. The rate of oxidation was so rapid that kinetic parameters (i.e. reaction order and rate constants) could not be calculated from the acquired data.

3.2.2. Oxidation of As(III) in Systems Open to the Atmosphere in the Presence of Crystalline Manganese Oxyhydroxides

The oxidation of arsenite to arsenate in the presence of crystalline manganese oxides in 0.05M NaCl and 0.7M NaCl solutions are presented in Figures 14, 15, 16, and 17. The initial pH was between 7 and 8 for each experiment.

The temporal variations of the relative proportions of arsenite and arsenate in the aqueous phase were similar at both ionic strengths as revealed in Figures 14 and 16. The relative concentration (% of initial) of As(III) in solution decreased rapidly. Within the first 60 minutes of the experiment, less than 2% of the initial As(III) remained in solution. During the remainder of the experiment, arsenite was undetectable in the aqueous phase. The relative concentration of As(V) in

Figure 14: Percent of total initial arsenic in the form of dissolved arsenite [•] and arsenate [■] as a function of time in a system open to the atmosphere and in the presence of crystalline manganese oxyhydroxides in 0.05M NaCl. Initial pH was between 7 and 8. Total [As] = 97 ± 25 ppb.

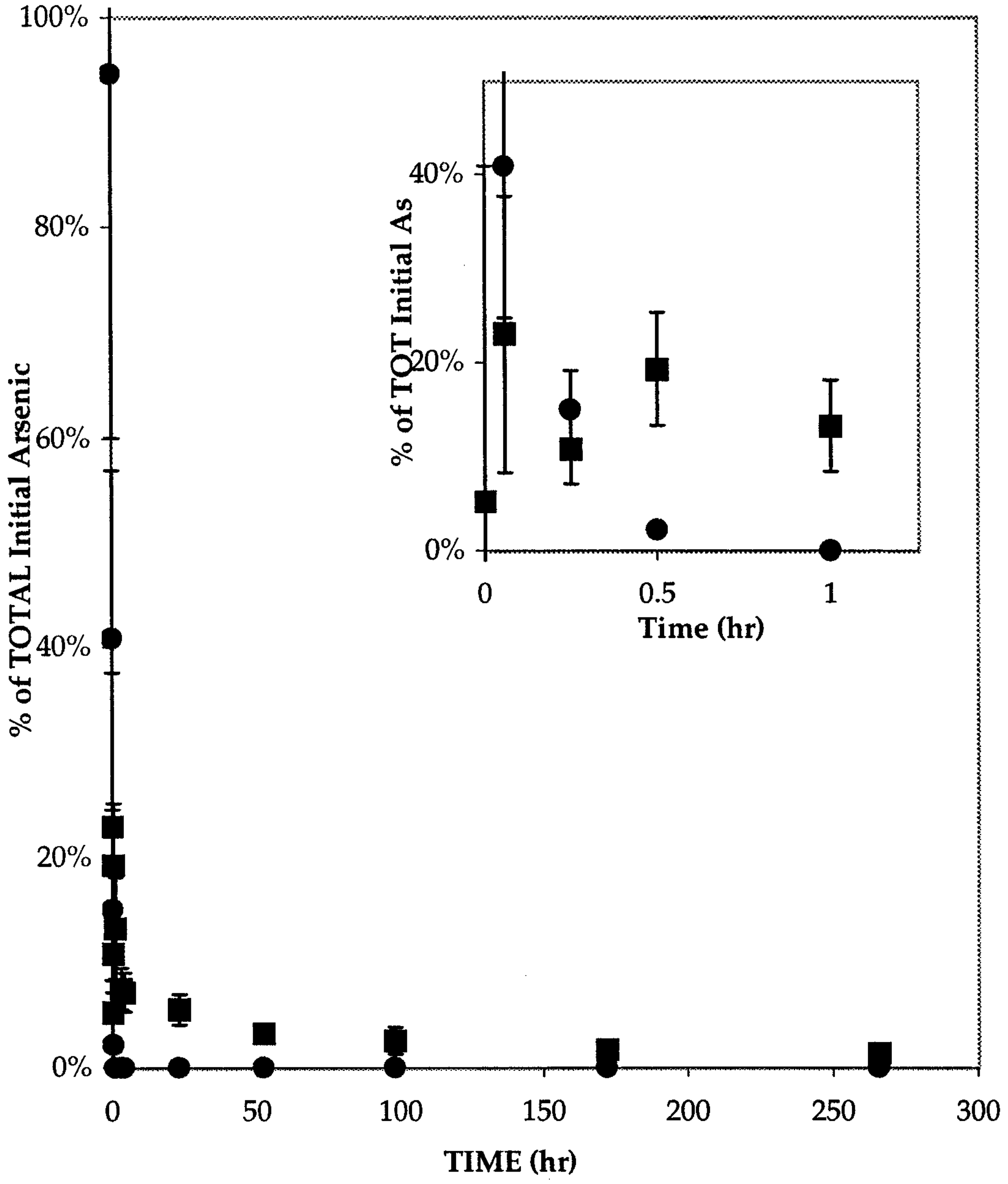


Fig 14: Percent of total initial arsenic in the form of dissolved arsenite[●] and arsenate [■] as a function of time in a system open to the atmosphere and in the presence of crystalline manganese oxyhydroxides in 0.05M NaCl. Initial pH was between 7 and 8. Total [As]=97 ± 25 ppb. Inset shows results from first hour ($0 < t \leq 1$hr).

Figure 15: Percent of total initial arsenic in the form of arsenite [●] and arsenate [■] in the combined aqueous and solid phases with time in a system open to the atmosphere in the presence of crystalline manganese oxyhydroxides in 0.05M NaCl. Initial pH was between 7 and 8. Total [As] = 97 ± 25 ppb.

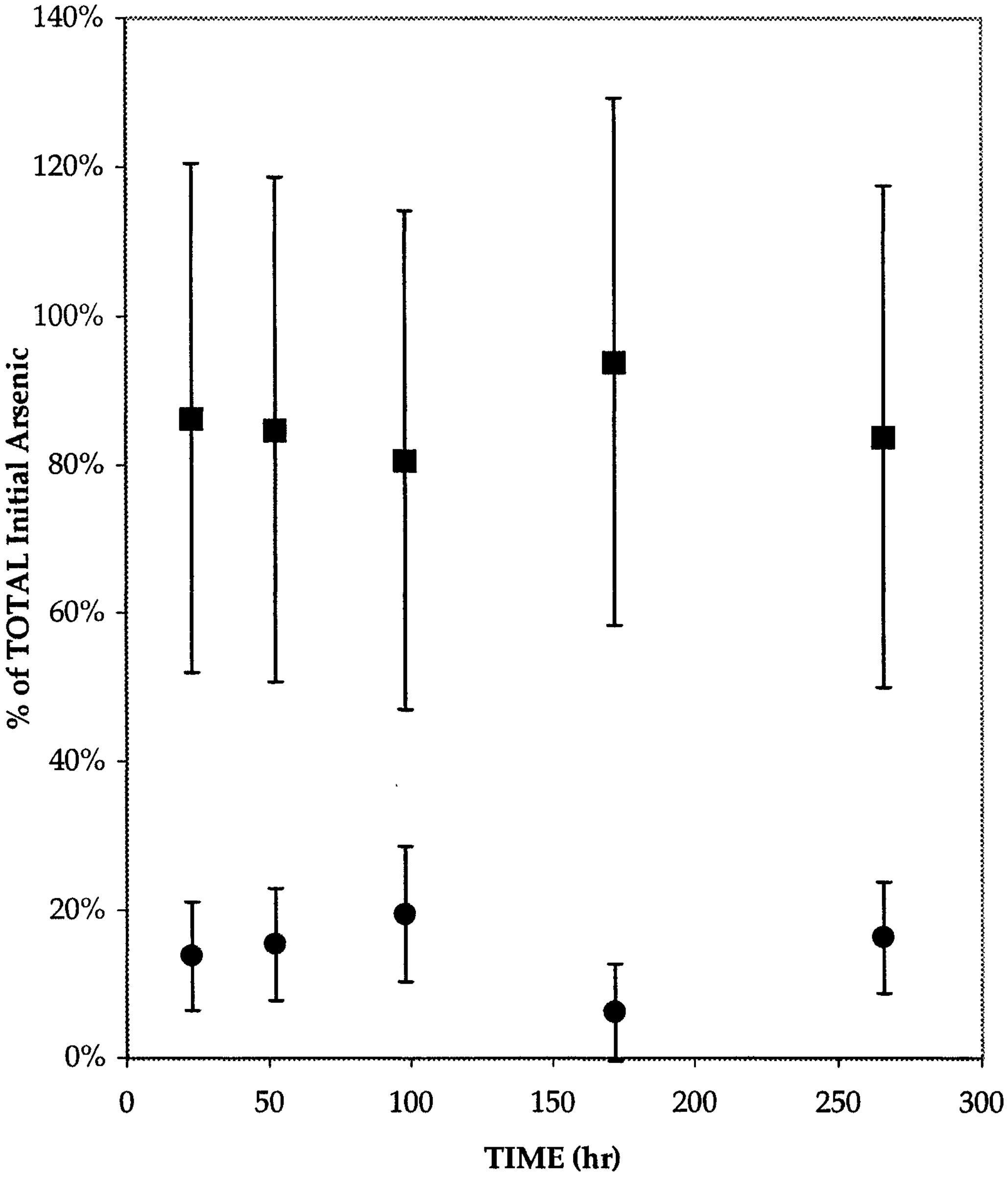


Fig 15: Percent of total initial arsenic in the form of arsenite[●] and arsenate[■] in the combined aqueous and solid phases with time in a system open to the atmosphere in the presence of crystalline manganese oxyhydroxides in 0.05M NaCl.
Initial pH was between 7 and 8. TOTAL [As] = 97 ± 25 ppb.

Figure 16: Percent of total initial arsenic in the form of dissolved arsenite [●] and arsenate [■] as a function of time in a system open to the atmosphere and in the presence of crystalline manganese oxyhydroxides in 0.7M NaCl. Initial pH was between 7 and 8. Total [As] = 103 ± 22 ppb.

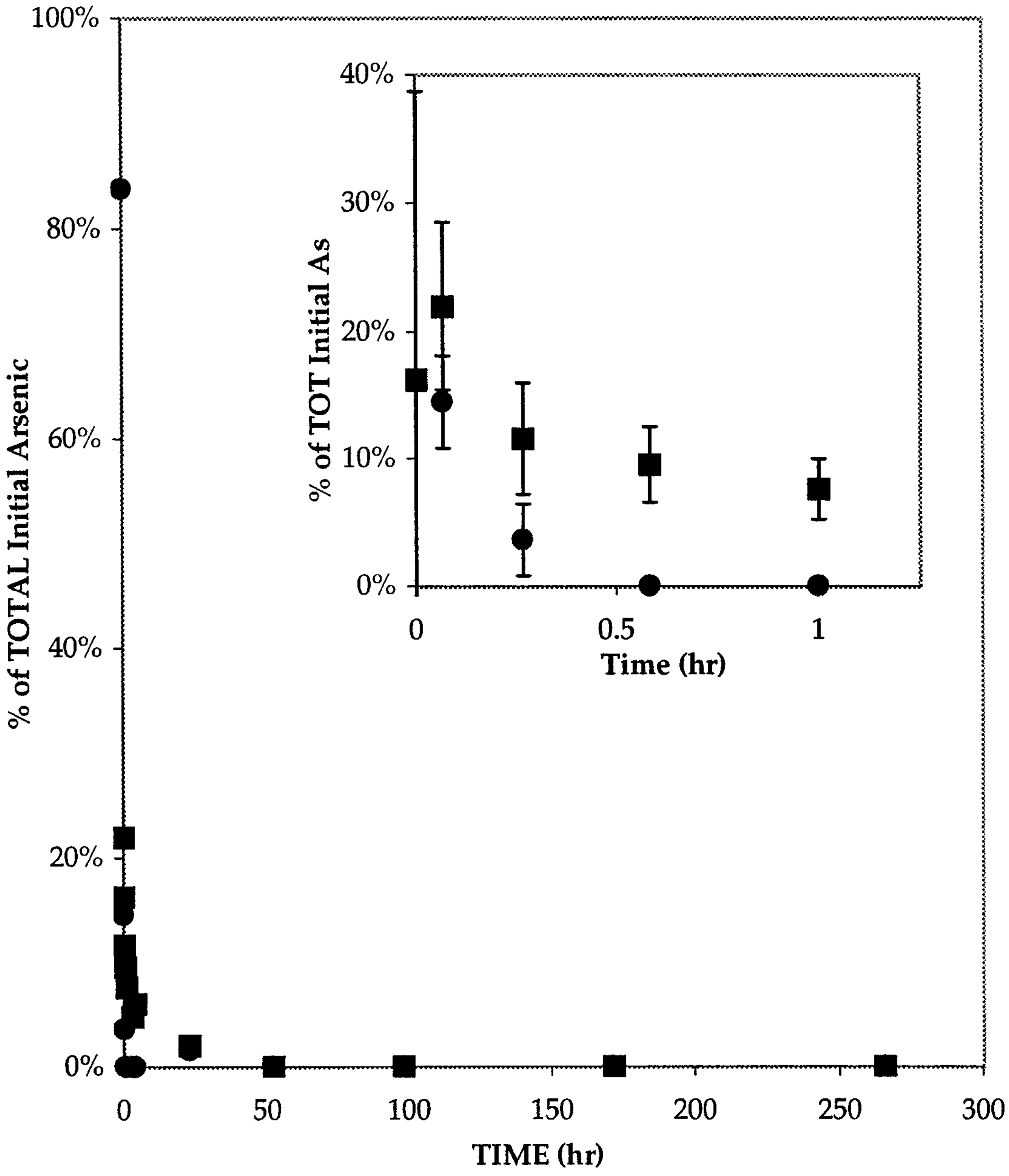


Fig 16:Percent of total initial arsenic in the form of dissolved arsenite [●] and arsenate [■] as a function of time in a system open to the atmosphere and in the presence of crystalline manganese oxyhydroxides in 0.7M NaCl. Initial pH was between 7 and 8. Total [As]=103 ± 22 ppb. Inset shows results from first hour ($0 < t \leq 1$hr).

Figure 17: Percent of total initial arsenic in the form of arsenite [•] and arsenate [▪] in the combined aqueous and solid phases with time in a system open to the atmosphere in the presence of crystalline manganese oxyhydroxides in 0.7M NaCl. Initial pH was between 7 and 8. Total [As] = 103 ± 22 ppb.

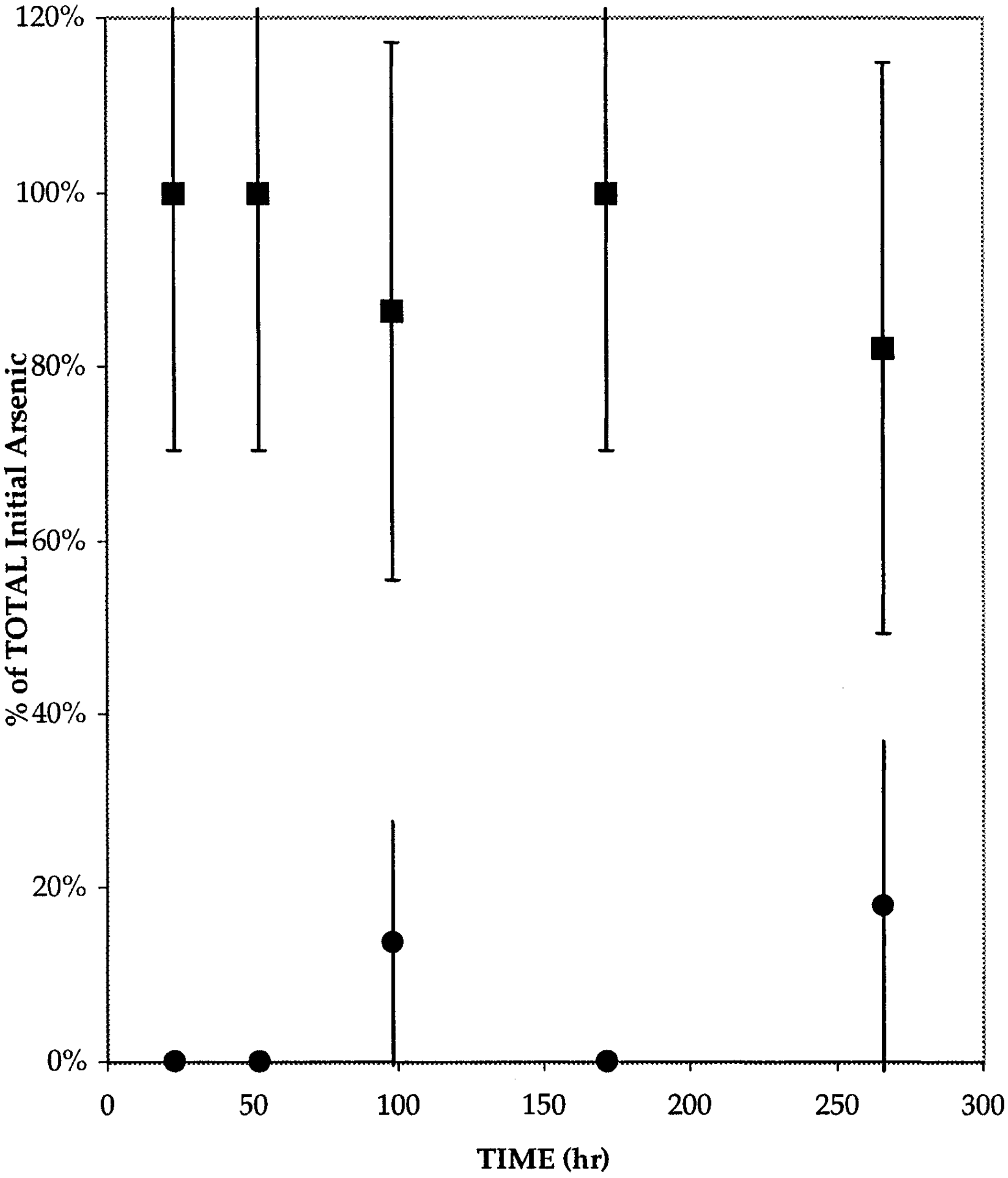


Fig 17: Percent of total initial arsenic in the form of arsenite[•] and arsenate[■] in the combined aqueous and solid phases with time in a system open to the atmosphere in the presence of crystalline manganese oxyhydroxides in 0.7M NaCl.

Initial pH was between 7 and 8. Total [As] = 103 ± 22 ppb.

solution increased during the first 15 minutes to ~20%; then it also decreased. After the first three to four hours, 7% or less of the total As remained in the aqueous phase in the form of As(V).

The relative proportion of total arsenate and total arsenite in the combined solid and aqueous phases is presented in Figures 15 and 17. Since the speciation of total arsenic in the combined solid and aqueous phases was not determined in the first 24 hours of the experiment, the rate of oxidation of arsenite could not be quantitatively determined. Within the first 24 hours most of the arsenic (80 - 90% of the total) was in the pentavalent form at both ionic strengths indicating that the oxidation reaction had nearly gone to completion.

3.2.3. Oxidation of As(III) in Systems Open to the Atmosphere in the Presence of Iron Oxyhydroxides

Two oxidation experiments were conducted in order to compare the relative performance of iron and manganese oxyhydroxides as oxidants of arsenite. The reactions were carried out with crystalline and amorphous iron oxides, in 0.05M NaCl. The concentrations of the species of interest (i.e., As(III), As(V), total As) can be found in Appendix 5. All other experimental conditions for these experiments (e.g. temperature, initial pH, As:solid ratios) were the same as for experiments carried out with Mn-Ox.

The aqueous phase was sampled for arsenite, arsenate, and total arsenic as in the experiments with the manganese oxides. The behaviors of these species were similar in both iron oxide experiments. The results from the experiment conducted with the crystalline Fe-Ox are presented in Figures 20 and 21. The results with amorphous Fe-Ox are given in Figures 18 and 19. Dissolved arsenite

Figure 18: Percent of total initial arsenic in the form of dissolved arsenite [•] and arsenate [■] as a function of time in a system open to the atmosphere and in the presence of amorphous iron oxyhydroxides in 0.05M NaCl. Initial pH was between 7 and 8. Total [As] = 95 ± 15 ppb.

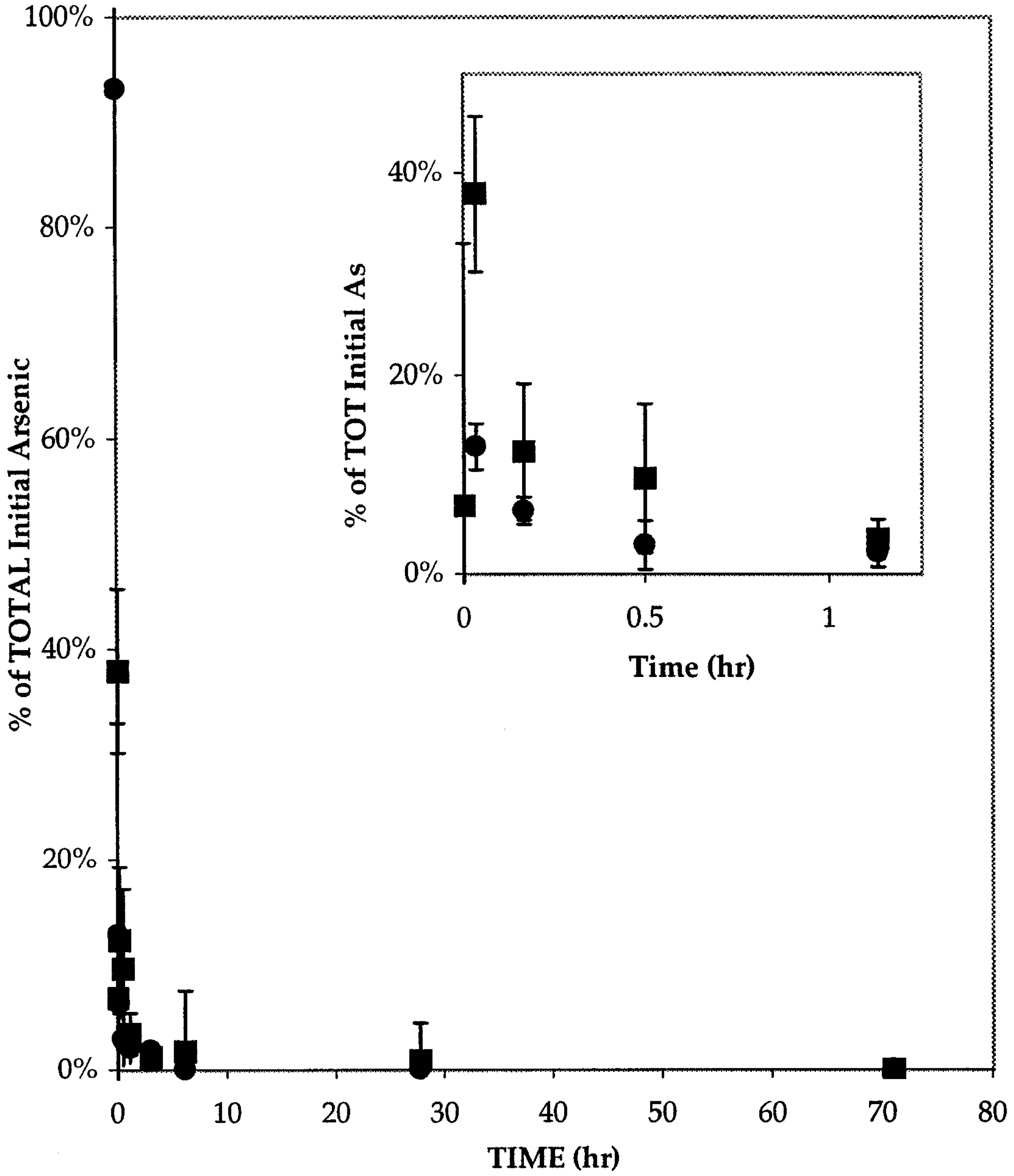


Fig 18: Percent of total initial arsenic in the form of dissolved arsenite[●] and arsenate [■] as a function of time in a system open to the atmosphere and in the presence of amorphous iron oxyhydroxides in 0.05M NaCl. Initial pH was between 7 and 8. TOTAL [As] = 95 ± 15 ppb. Inset shows results from first hour ($0 < t \leq 1$hr).

Figure 19: Percent of total initial arsenic in the form of arsenite [•] and arsenate [■] in the combined aqueous and solid phases with time in a system open to the atmosphere in the presence of amorphous iron oxyhydroxides in 0.05M NaCl. Initial pH was between 7 and 8. Total [As] = 95 ± 15 ppb.

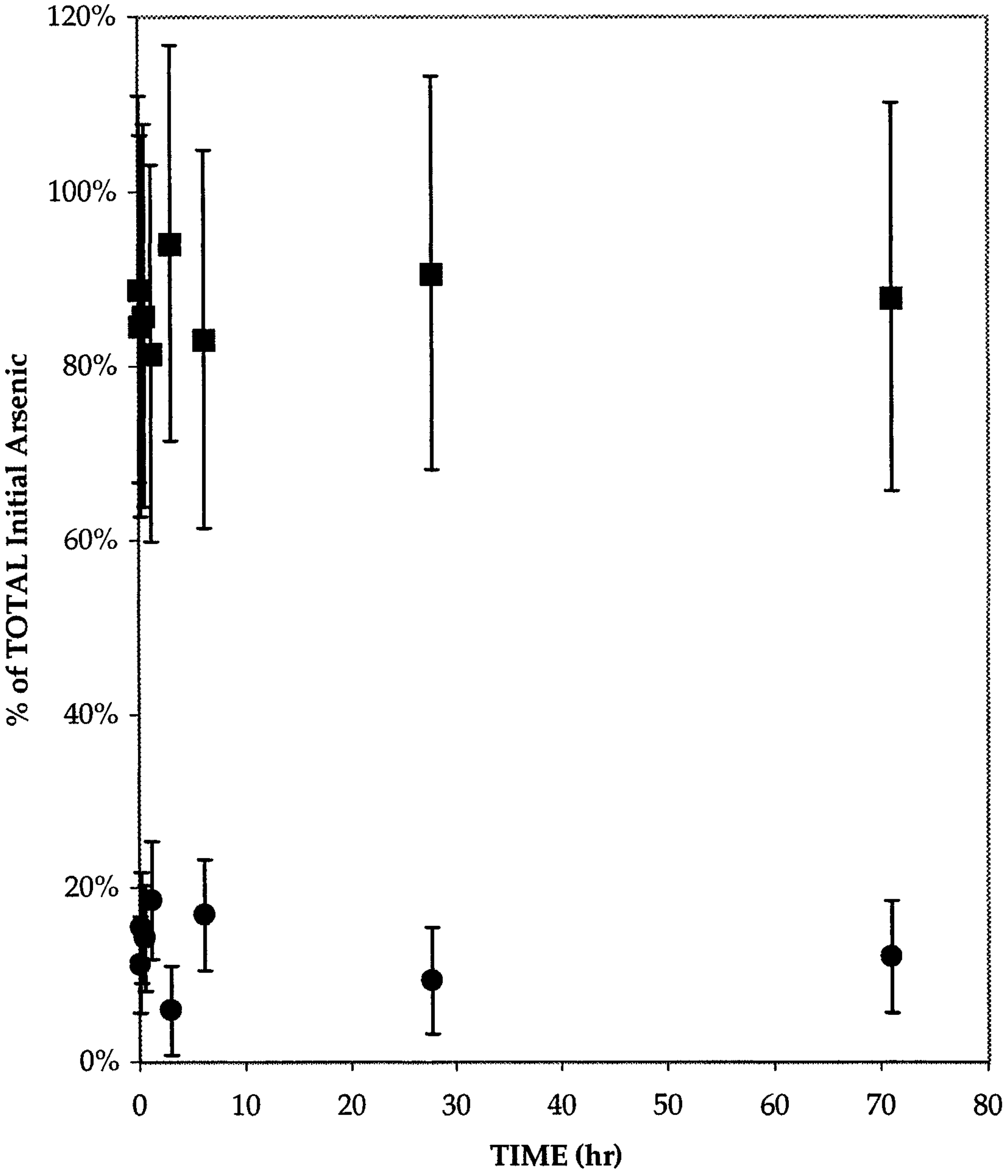


Fig 19: Percent of total initial arsenic in the form of arsenite[•] and arsenate[▪] in the combined aqueous and solid phases with time in a system open to the atmosphere in the presence of amorphous iron oxyhydroxides in 0.05M NaCl.

Initial pH was between 7 and 8. TOTAL [As] = 95 ± 15 ppb.

Figure 20: Percent of total initial arsenic in the form of dissolved arsenite [●] and arsenate [■] as a function of time in a system open to the atmosphere and in the presence of crystalline iron oxyhydroxides in 0.05M NaCl. Initial pH was between 7 and 8. Total [As] = 96 ± 5 ppb.

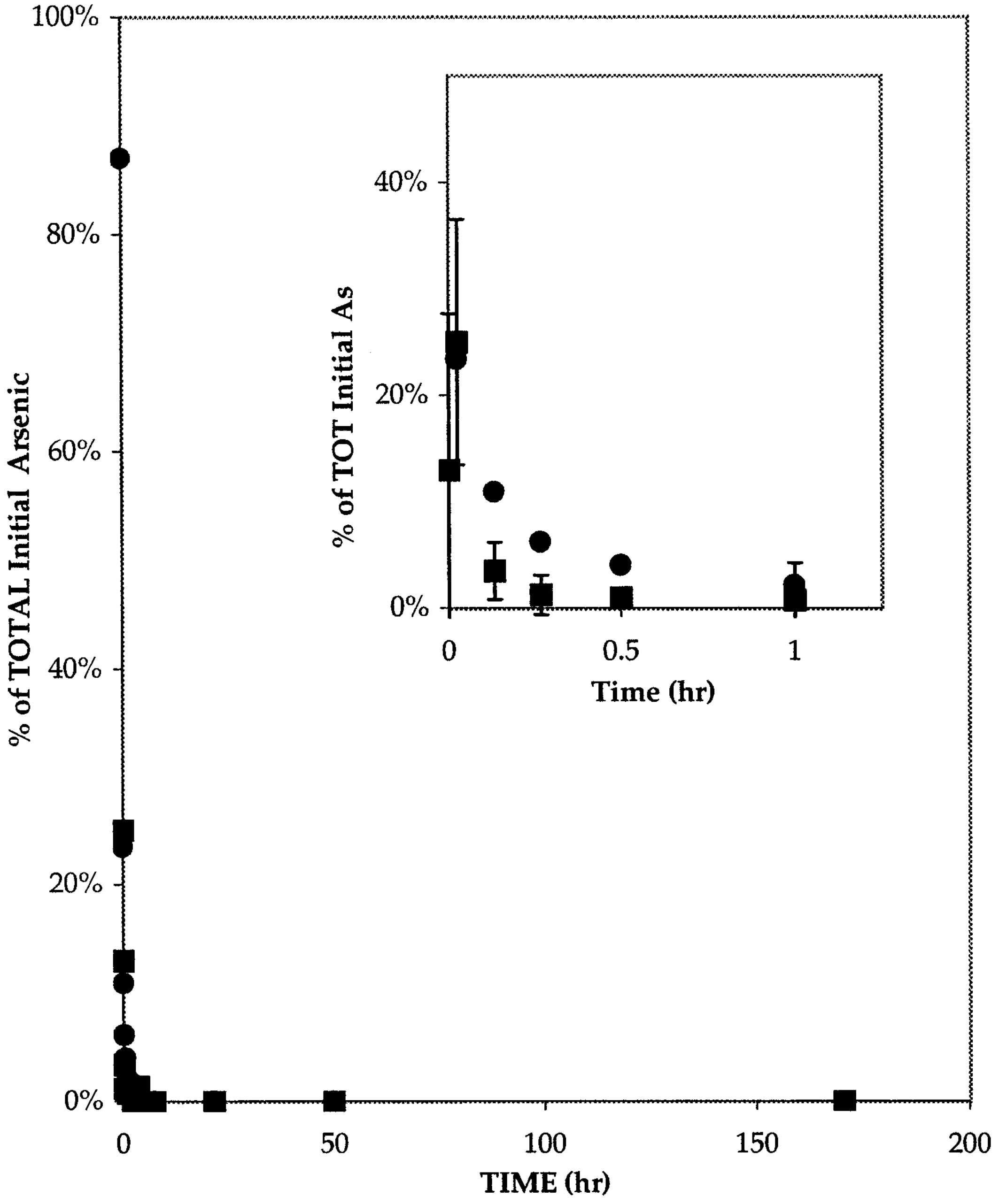


Fig 20: Percent of total initial arsenic in the form of dissolved arsenite [•] and arsenate [■] as a function of time in a system open to the atmosphere and in the presence of crystalline iron oxyhydroxides in 0.05M NaCl. Initial pH was between 7 and 8. TOTAL [As] = 96 ± 5 ppb. Inset shows results from first hour ($0 < t \leq 1$hr).

Figure 21: Percent of total initial arsenic in the form of arsenite [•] and arsenate [■] in the combined aqueous and solid phases with time in a system open to the atmosphere in the presence of crystalline iron oxyhydroxides in 0.05M NaCl. Initial pH was between 7 and 8. Total [As] = 96 ± 5 ppb.

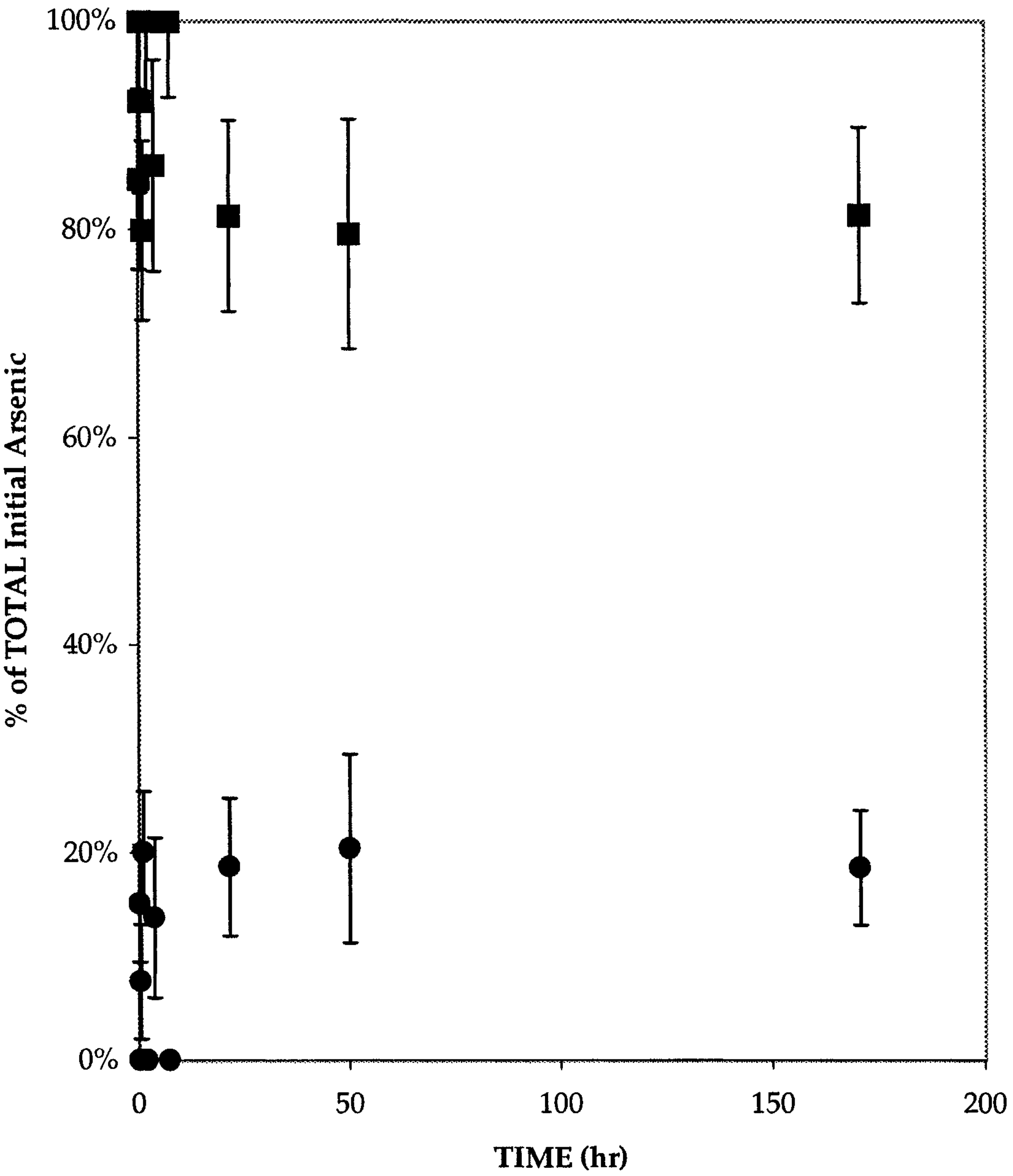


Fig 21: Percent of total initial arsenic in the form of arsenite [●] and arsenate [■] in the combined aqueous and solid phases with time in a system open to the atmosphere in the presence of crystalline iron oxyhydroxides in 0.05M NaCl.

Initial pH was between 7 and 8. TOTAL [As] = 96 ± 5 ppb.

concentrations decreased rapidly and within one hour became nearly undetectable. Dissolved arsenate reached a maximum within the first 10 minutes, then decreased. After 6 hours, arsenate in solution was below the detection limit. The maximum %As(V) was higher in the amorphous Fe-Ox reaction system (~40%) than in crystalline Fe-Ox system (~25%).

The total arsenite and arsenate concentrations in the combined solid and aqueous phases are represented in Figures 19 (amorphous Fe-Ox) and 21 (crystalline Fe-Ox). The oxidation of arsenite occurred rapidly in the presence of these iron oxides. Within the first 15 minutes ~80-85% had been converted to arsenate, indicating that the oxidation of arsenite to arsenate was nearly complete. This is similar to the results with manganese oxyhydroxides. Iron-oxyhydroxide is thus as effective an oxidant as Mn-Ox.

3.3. Oxidation Kinetics of Arsenite in the Presence of Amorphous Manganese Oxyhydroxides Purged of Oxygen Systems

Two experiments were conducted to determine whether the metal oxides act only as an electron transfer medium that catalyzes the oxidation of As(III) by dissolved oxygen or whether, the oxides themselves can oxidize As(III).

Figures 22 and 24 presents the results from the experiment conducted in 0.05M NaCl and 0.7M NaCl, respectively. The influence of ionic strength is seen most strongly in the behavior of aqueous phase As(V) while the As(III) in solution is unaffected. At both ionic strengths, the arsenite in the aqueous phase behaved similarly. Its concentration decreased rapidly within the first hour, and after 5 minutes less than 10% of the arsenic was in the form of As(III). At the lower

Figure 22: Percent of total initial arsenic in the form of dissolved arsenite [●] and arsenate [■] as a function of time in a closed system purged with nitrogen and in the presence of amorphous manganese oxyhydroxides in 0.05M NaCl. Initial pH was between 7 and 8. Total [As] = 100 ± 10 ppb.

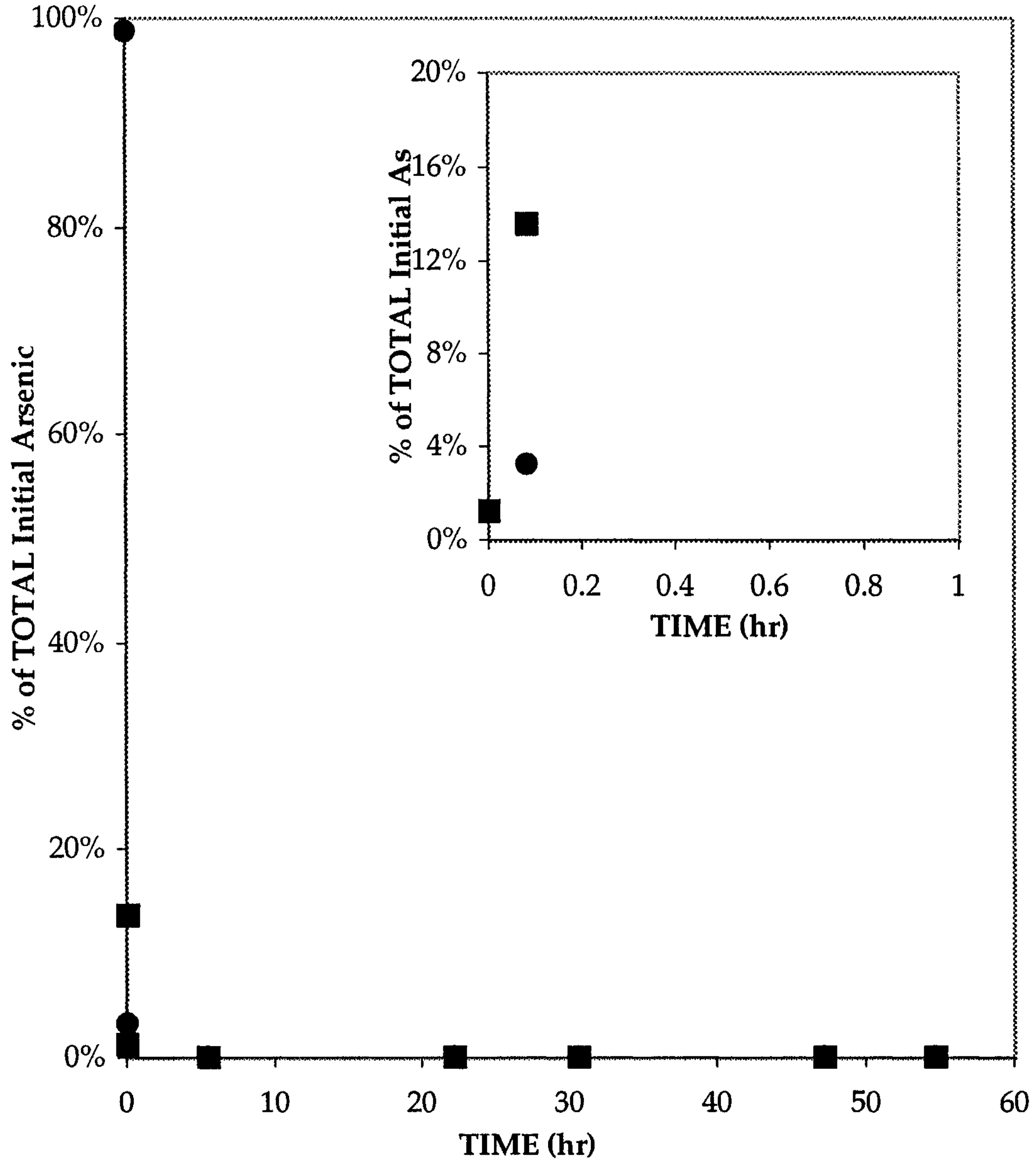


Fig 22: Percent of total initial arsenic in the form of dissolved arsenite [•] and arsenate [■] as a function of time in a closed system purged with nitrogen and in the presence of amorphous manganese oxyhydroxides in 0.05M NaCl. Initial pH was between 7 and 8. Total [As]=100 ± 10ppb. Inset shows results from first hour ($0 < t \leq 1$)

Figure 23: Percentage of total initial arsenic in the form of arsenite [●] and arsenate [■] in the combined aqueous and solid phases with time in a closed system purged with nitrogen and in the presence of amorphous manganese oxyhydroxides in 0.05M NaCl. Initial pH was between 7 and 8. Total [As] = 100 ± 10ppb

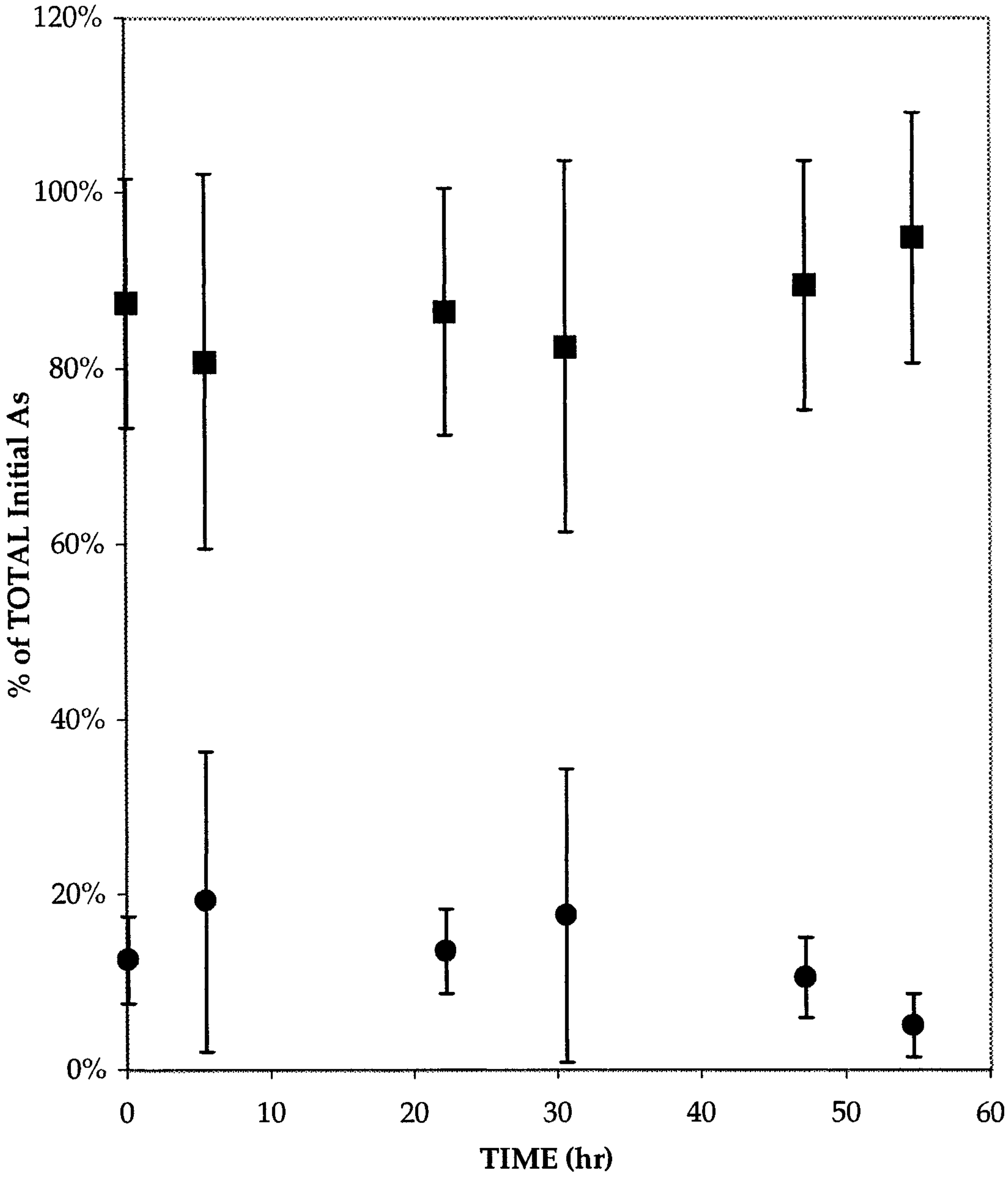


Fig 23: Percent of total initial arsenic in the form of arsenite[●] and arsenate[■] in the combined aqueous and solid phases with time in a closed system purged with nitrogen and in the presence of amorphous manganese oxyhydroxides in 0.05M NaCl.

Initial pH was between 7 and 8. Total [As] = 100 ± 10ppb.

Figure 24: Percent of total initial arsenic in the form of dissolved arsenite [•] and arsenate [■] as a function of time in a closed system purged with nitrogen and in the presence of amorphous manganese oxyhydroxides in 0.7M NaCl. Initial pH was between 7 and 8. Total [As] = 100 ± 10 ppb.

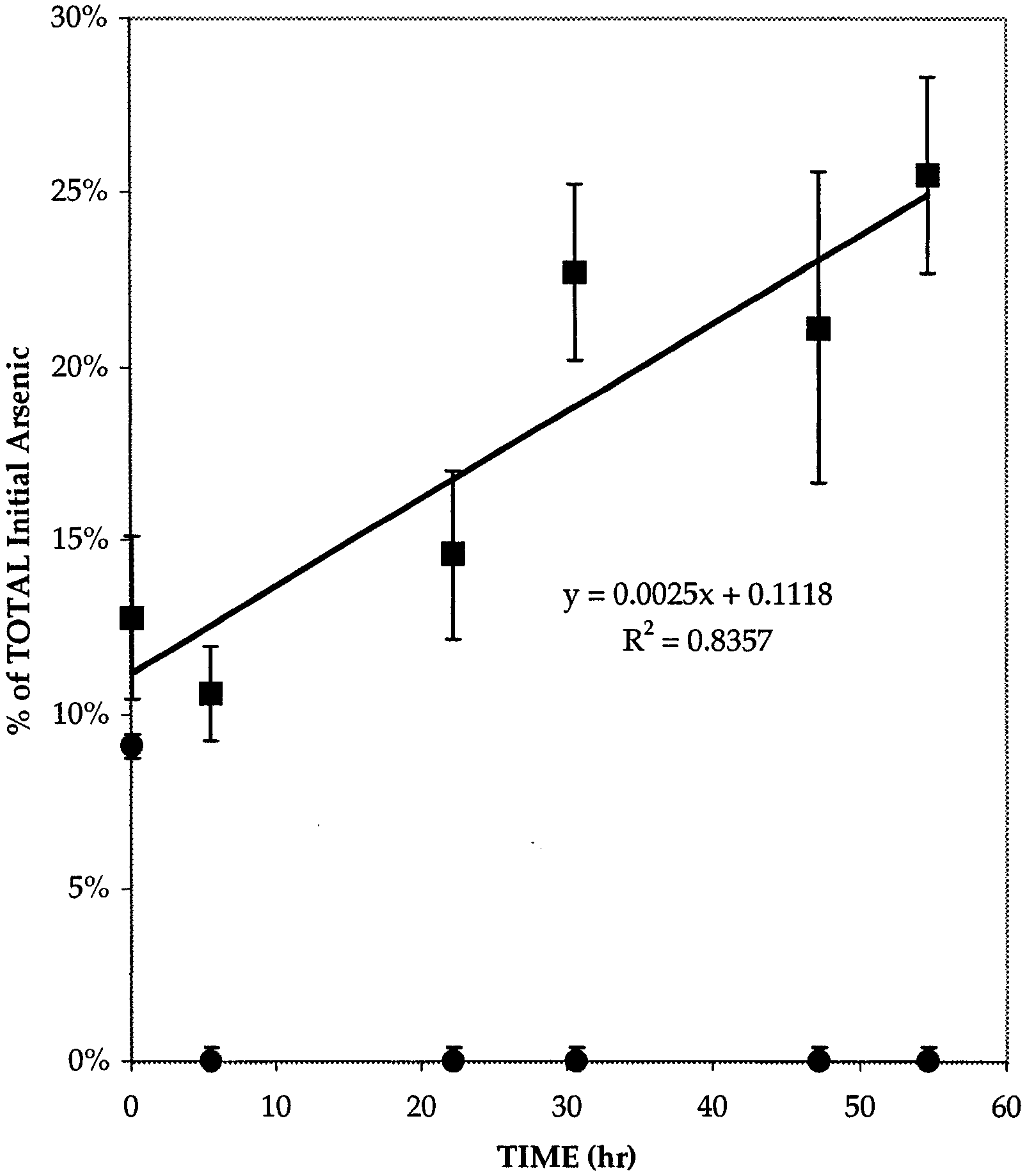


Fig 24: Percent of total initial arsenic in the form of dissolved arsenite [●] and arsenate [■] as a function of time in a closed system purged with nitrogen and in the presence of amorphous manganese oxyhydroxides in 0.7M NaCl.
Initial pH was between 7 and 8. Total [As] = 100 ± 10 ppb.

Figure 25: Percentage of total initial arsenic in the form of arsenite [•] and arsenate [■] in the combined aqueous and solid phases with time in a closed system purged with nitrogen and in the presence of amorphous manganese oxyhydroxides in 0.7M NaCl. Initial pH was between 7 and 8. Total [As] = 100 ± 10 ppb.

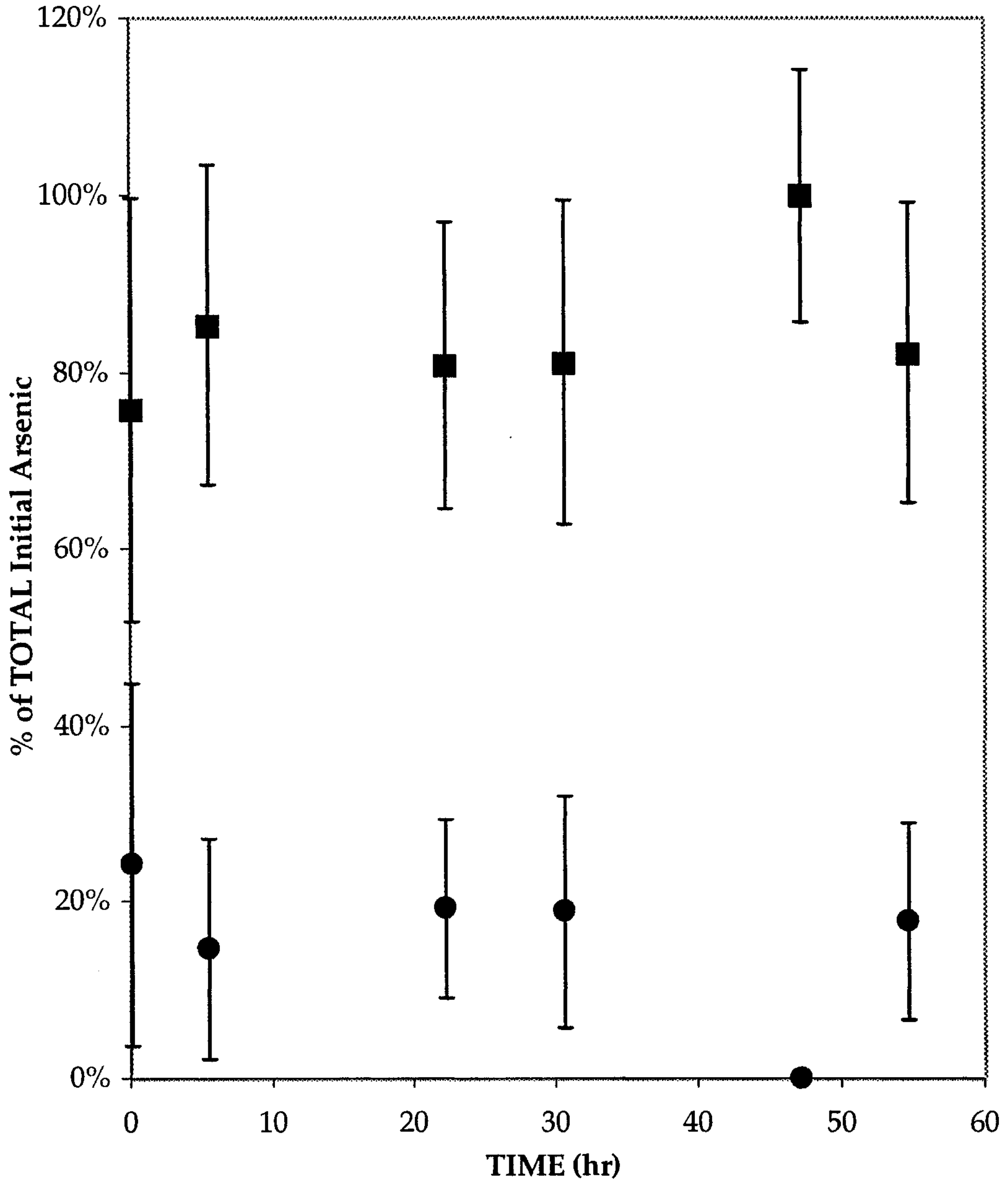


Fig 25: Percent of total initial arsenic in the form of arsenite[•] and arsenate [■] in the combined aqueous and solid phases with time in a closed system purged with nitrogen and in the presence of amorphous manganese oxyhydroxides in 0.7M NaCl.

Initial pH was between 7 and 8. Total [As] = 100 ± 10 ppb.

ionic strength, arsenate appeared briefly in the early part of the experiment but decreased progressively until, after 5 hours, it became undetectable. In contrast, in 0.7M NaCl the arsenate concentration in the aqueous phase increased almost linearly with time. At the end of the experiment (55h) ~25% of the arsenic in the system was in the form of dissolved arsenate.

To confirm that the arsenite was indeed oxidized, total arsenite and arsenate concentrations were also determined. Results from the 0.05M NaCl and 0.7M NaCl systems (Figure 23 and 25 respectively) reveal that, within 10 minutes, nearly all As is present as As(V). This indicates that amorphous manganese oxides can oxidize arsenite themselves. Oxygen is not required.

4. DISCUSSION

Oxidation of arsenite by oxygen at room temperature in 0.05M and 0.7M NaCl is slow (Fig. 6 to 9). Over the pH range studied, 3 to 9, the rate of oxidation was not affected significantly by light which contrasts with the results of Andrae (1979). However, that study had been conducted in seawater, so one of the constituents of seawater may have influenced the reaction.

A greater percentage of the initial As(III) was converted to As(V) at the higher ionic strength: by the end of the ~4 month experiment, as much as 40% had been oxidized, compared to 20% at the lower ionic strength (Fig. 6 to 9). However, the greatest effect on the oxidation rate was upon the addition of iron or manganese oxyhydroxide, Fe-Ox or Mn-Ox, to the reaction system. This led to the rapid oxidation of arsenite to arsenate. Irrespective of the crystallinity of the solid metal oxyhydroxides (Me-Ox), more than 80% of the initial As(III) was oxidized within 5-10 minutes.

The evolution of total and dissolved arsenic species in the presence of Fe-Ox and Mn-Ox can be represented by three general reactions: the adsorption of arsenite to the solid metal oxyhydroxide surface, the oxidation of As(III) to As(V), and, finally, the desorption of As(V) from the solid surface. These reactions are described in greater detail in the following sections.

4.1. Reactions of Arsenite and Arsenate with Solid Iron and Manganese Oxyhydroxides

The manganese and iron oxyhydroxide experimental systems were more complex than the control experiments. The reason for this is that the behavior of arsenic species in the reaction system in the presence of the solid metal oxyhydroxides (Me-Ox) can be described by three competing reactions. The first is the adsorption of arsenite to the surface of the oxyhydroxides; in a simplified form it can be represented by the following reaction:

$$\equiv\text{SOH} + \text{As(III)} \leftrightarrow \equiv\text{SOAs(III)} + \text{H}^+ \qquad (3)$$

where $\equiv$SOH represents an adsorption site on the solid and $\equiv$SOAs(III) represents the sorbed species. In the case of metal oxyhydroxides:

$$\equiv\text{Fe(III)OH} + \text{As(III)} \leftrightarrow \equiv\text{Fe(III)OAs(III)} + \text{H}^+ \qquad (4)$$

$$\equiv\text{Mn(IV)OH} + \text{As(III)} \leftrightarrow \equiv\text{Mn(III)OAs(III)} + \text{H}^+ \qquad (5)$$

Depending on solution pH and mineral acidity constants, adsorption sites on solid iron and manganese oxyhydroxides can be deprotonated (Eq. 6) or protonated (Eq. 7):

$$\equiv\text{SOH} \leftrightarrow \equiv\text{SO}^- + \text{H}^+ \qquad (6)$$

$$\equiv\text{SOH} + \text{H}^+ \leftrightarrow \equiv\text{SOH}_2^+. \qquad (7)$$

The point of zero charge of manganese and iron oxyhydroxides lies, on average, between pH 2 to 3 and 8 to 9, respectively (Sadiq, 1997). At circum-neutral pH, the Mn-Ox surface should carry a net negative charge (i.e. most sorption sites are deprotonated), whereas the Fe-Ox surface should carry a small net positive charge (i.e. sorption sites are protonated or remain neutral). For the purposes of this discussion, the simplified reaction (Eq. 1) representing the adsorption of arsenite to the solid surface will be used to describe our reaction system.

The second competing reaction is the oxidation of arsenite to arsenate via the metal oxyhydroxides. It can be represented in simplified form:

$$\equiv \mathrm{S1As(III)} \rightarrow \equiv \mathrm{S2As(V)} + \mathrm{S1} \tag{8}$$

where S1 and S2 represent two different oxidation states of the same metal. The third reaction (in the sequence that leads to the oxidation of arsenite and release of arsenate) is the reversible adsorption/desorption of arsenate from the solid surface:

$$\equiv \mathrm{SOAs(V)} + \mathrm{H^+} \leftrightarrow \ \equiv \mathrm{SOH} + \mathrm{As(V)} \tag{9}$$

where $\equiv$SOAs(V) represents the sorbed species. Other reactions can be used to describe the metal oxide experimental systems more accurately. The soluble reduced manganese and iron that are produced according to Eq. 8 can readsorb to the solid and compete with arsenic species to occupy adsorption sites on the solid oxyhydroxide (Nesbitt et al., 1998). Once sorbed to these sites, Mn(II) and Fe(II) can be re-oxidized. This reaction should not significantly affect the kinetics of As(III) oxidation at the relatively low As:solid ratios used in our investigation. Thus, the results of this study were interpreted using the three main reactions described above.

4.1.2. Arsenite Oxidation in Open Systems by Mn-Oxyhydroxides

Adsorption of Arsenite

The crystallinity of the manganese oxyhydroxides does not significantly affect the rate of adsorption and oxidation of arsenite at the As:solid ratios used in this study, although the rate of As(III) depletion from solution, through adsorption and oxidation to As(V), was slightly faster with the amorphous Mn-Ox. Oscarson et al. (1983) investigated the effect of crystallinity of various manganese oxides on the rates of arsenite adsorption onto the solid, and they found that the rate at which As(III) was depleted from solution decreased as the crystallinity of the oxides increased. They proposed that fewer sites are available for arsenite adsorption as the oxide structure becomes more ordered and the surface area decreases. Amorphous manganese oxyhydroxides are more porous than crystalline oxyhydroxides, and arsenite oxyanions should therefore be able to enter the pores and migrate to the interior of the solid (Oscarson et al., 1983).

At the pH of this investigation, H_3AsO_4 ($pK_1 = 9.1$, see Figure 1) is a neutral species whereas the surface of Mn - Ox is negatively charged (Sadiq, 1997; Foster et al., 2003). If the adsorption process of arsenic oxyanions on solid surfaces was purely electrostatic, the reaction should be fast (Pierce and Moore, 1980; Sadiq, 1997). Although the adsorption of As(III) on amorphous Mn-Ox was very fast in this study, it does not necessarily imply that only electrostatic interactions are occurring. Other factors, such as the large surface area of the amorphous Mn-Ox used and the low As:solid ratios, may also have contributed to the fast As(III) depletion rate.

Although the rate of As(III) depletion in our study was faster (Fig. 10, 12, 14, and 16), our results are nevertheless consistent with those reported by Oscarson et al. (1983) and Manning et al. (2002). They found that more than 50% of the initial

As(III) was depleted from solution in less than one hour when birnessite was present. The XRD pattern of birnessite solid in Manning et al. (2002) is comparable to the XRD pattern of the more crystalline manganese oxide used in this study. Both used similar As:solid ratios (i.e. between 0.07 and 0.08). In our study, less than 50% of the initial As(III) remained 5 minutes after it was added to the manganese oxyhydroxide suspensions. The two orders of magnitude lower As:solid ratios in our study may account for the faster depletion rate.

Oxidation of Arsenite

The kinetics of arsenite oxidation in the presence of amorphous and crystalline manganese oxyhydroxides was not quantified in our study. The rate of oxidation in the presence of amorphous Mn-Ox was so rapid at room temperature that kinetic parameters (i.e. reaction order and rate constants) could not be calculated from the acquired data. In the presence of crystalline manganese oxyhydroxides, the total speciation of arsenic in the combined solid and aqueous phases was not determined in the first 24 hours. However, other researchers have been able to propose reaction pathways of arsenite oxidation and their interpretations are presented in the following section.

The oxidation of arsenite to arsenate can be represented in several ways. Nesbitt et al. (1998) detailed the oxidation of arsenite by birnessite according to the following reactions:

$$2\mathrm{Mn(IV)O_2} + \mathrm{H_3AsO_3} + \mathrm{H_2O} \leftrightarrow 2\mathrm{MnOOH^*} + \mathrm{H_3AsO_4} \qquad (10)$$

$$2\mathrm{MnOOH^*} + \mathrm{H_3AsO_3} + 4\mathrm{H^+} \leftrightarrow 2\mathrm{Mn^{2+}} + \mathrm{H_3AsO_4} + 3\mathrm{H_2O}. \qquad (11)$$

In the above reactions, MnOOH* represents an intermediate reaction product, and soluble manganese(II) is finally released to solution. If the solid manganese oxide is in the form of Mn(III)OOH, the oxidation of As(III) to As(V) would proceed as follows:

$$2MnOOH + H_3AsO_3 + 4H^+ \leftrightarrow 2Mn^{2+} + H_3AsO_4 + 3H_2O \qquad (12)$$

Both electron transfer and substitution reaction mechanisms were proposed as possible pathways for the oxidation of arsenite (Nesbitt et al., 2003). The substitution reaction mechanism proposed by Nesbitt et al. (2003) was similar to that proposed by Scott and Morgan (1995).

The first reaction pathway, an electron transfer reaction mechanism, involves the formation of an inner-sphere bidentate binuclear complex of arsenite onto the synthetic birnessite (Nesbitt et al., 2003). Other studies also support this scenario. Results from EXAFS and XANES analysis of birnessite reacted with arsenite indicated that binuclear bidentate inner-sphere complexes were formed by arsenate on the solid once As(III) was oxidized to As(V). Results from X-Ray adsorption fine structure analyses reported in Foster et al. (2003) also showed that arsenate forms bidentate binuclear complexes on synthetic birnessite and vernadite.

Arsenate Desorption

The influence of the crystallinity of the solids is mostly reflected in the adsorption of arsenate. When amorphous manganese oxyhydroxides are used, arsenate appears progressively in solution over a period of several days, before it begins to adsorb on the oxyhydroxide. This behavior is similar in both low and high ionic strength solutions.

From the determination of total arsenic speciation (Figures 11 and 13), greater than 85% of the initial arsenic was in the form of As(V) within the first 15 minutes in the presence of amorphous Mn-Ox. Therefore, since most of the arsenite was oxidized, desorption is the most likely mechanism for the appearance of arsenate in solution. The point of zero charge of these solids lies between pH 2 and 3 (Laha and Luthy, 1990; Sadiq, 1997; Foster et al., 2003), and below 4 for most manganese oxides (Sadiq, 1997). In the pH range our reaction system, 7 to 8, the surface of the Mn-Ox carries a net negative charge and the most abundant form of arsenite (Fig. 1) is the uncharged species H_3AsO_3 (pK_1 = 9.2). The charge distributions on the two species should not impede As(III) adsorption onto the Mn-Ox surface. In contrast, the most abundant arsenate species between pH 7 and 8, $HAsO_4^{2-}$ and $H_2AsO_4^-$, are negatively charged (Fig. 1), and therefore more energy is required to overcome the repulsion of charges between As(V) and the solid in order for As(V) to adsorb to the surface. Because it is already in contact with the solid, arsenate that forms on the surface of the Mn-Ox after the oxidation of sorbed As(III) would not have to overcome this energy barrier (Oscarson et al., 1983).

Arsenate, produced by oxidizing arsenite, may be released to solution due to greater charge repulsion between As(V) and the solid surface, or As(V) could also be forming ion-pairs with sodium in solution (Gao and Mucci, 2001; Gao and Mucci, 2003). The formation of ion-pairs could stabilize As(V) in the aqueous phase and would be more significant in 0.7M NaCl. However, we found a larger percentage of arsenate in solution at the lower ionic strength (see Figures 10 and 12).

Arsenate and arsenite complexes on the surface of metal oxides may be different. As(V) could also be forming outer-sphere complexes on the oxide surface in which case the concentration of arsenate in solution would increase with increasing ionic strength. Our results (see Figures 10, 12, 14, and 16) do not support this hypothesis, since the ionic strength of the solution appears to have little effect on the sorption of As(III) and As(V). Bond valence analysis of the surface functional groups on hydrous manganese oxides predicts that a greater number of surface sites will form stable complexes with arsenite than with arsenate, which could explain desorption of arsenate from the solid (Foster et al., 2003).

In the presence of amorphous Mn-oxyhydroxides, dissolved arsenate persists for several days (Fig. 10 and 12). In the presence of crystalline Mn-Ox, dissolved As(V) concentrations peak in the first hour and then steadily decrease (Fig. 14 and 16). Oscarson et al. (1983), when studying the adsorption of As(V) on manganese oxides observed that the more crystalline Mn-oxide, pyrolusite, despite its low surface area, sorbed more As(V) per unit surface area than the other oxides. Arsenate may form more stable complexes on crystalline Mn-Ox than on amorphous Mn – Ox. Oscarson et al. (1983) also determined that the point of zero charge of manganese oxides increased with increasing crystallinity. Analogously, in our study, the point of zero charge, PZC, of the crystalline Mn-Ox may also be higher than the PZC of the amorphous Mn-Ox, and carry less negative charge at circum-neutral pH. Therefore arsenate, which also carries a negative charge at circum-neutral pH, would have a greater affinity for the crystalline Mn – Ox surface than the amorphous Mn – Ox due to lower electrostatic repulsion.

4.2.2. Arsenite Oxidation by Fe-Oxyhydroxides

The rate of depletion of As(III) and the subsequent desorption/adsorption of As(V) in the presence of crystalline and amorphous forms of Fe-Ox were nearly identical (Figures 18 – 21). Arsenite was depleted rapidly from solution and became undetectable within 2 hours (see Figures 18 and 20). The dissolved arsenate concentration went through a maximum within the first ten minutes, after which it was progressively depleted. It became undetectable after a few hours. This was most likely due to slow adsorption of arsenate on the solid surface, since most of the arsenic (i.e. > 80%) in the system was already in the pentavalent form after as little as 7 minutes. The ratio of total As(V) to total As(III) in the system (i.e. dissolved plus adsorbed) remained the same throughout the duration of the experiment (Figure 19 and 21). The oxidation of arsenite was rapid in the presence of Fe-Ox, whether amorphous or crystalline.

Our results agree well with those of Pierce and Moore (1980 and 1982). They found that the rate of arsenite adsorption on amorphous iron hydroxides was rapid, and that more than 90% of the initial As(III) had sorbed to the solid after 15 minutes. This is consistent with our observations for both crystalline and amorphous Fe-Ox. Pierce and Moore (1982) also observed that amorphous iron hydroxides have a high sorption capacity for arsenic. They described the solid as having a loose, porous structure, with more than one type of adsorption sites. Arsenite and arsenate oxyanions can move through these pores and not be restricted to the exterior surface of the solid.

Goldberg and Johnston (2001) using Raman and FTIR spectroscopy and solution chemistry, found that As(V) forms inner-sphere complexes on amorphous iron oxides whereas As(III) can form both inner- and outer-sphere complexes, depending on suspension densities and pH. Sun and Doner (1996) observed that arsenite mainly formed bidentate binuclear bridging complexes onto goethite. They found that both arsenite and arsenate were bonded strongly to the solid, since only a fairly strong extraction procedure (e.g. 1.0M NaOH at 70°C) recovered more than 70% of the total As(III) and As(V). These findings may explain the similar depletion rate of both dissolved arsenite and arsenate in the presence of Fe-Ox, as both species will bind strongly to the solid.

The purpose of reacting arsenite with Fe-Ox was to determine whether Fe-Ox could oxidize As(III). Iron oxyhydroxides can in effect oxidize arsenite and, within the experimental conditions of this study, are just as effective oxidants of As(III) as manganese oxyhydroxides. Our findings are consistent with those reported by De Vitre et al. (1991), who determined that Fe-oxyhydroxides oxidized at least half of the initial As(III) within 2 days. They used both natural and synthetic iron oxyhydroxides in batch experiments with solution ionic strengths of 0.01M over a range of pH (4.7 – 10.2) at Fe:As molar ratios of 3.4×10^{-3} and initial As(III) concentrations of 1.2μM. Although we used similar As:solid ratios, ~0.0005 compared to ~0.0003, we observed a much faster oxidation rate: more than 75% of initial As(III) (100 μg/L) was oxidized to As(V) within 15 minutes, irrespective of the crystallinity of the solid. The faster rate of oxidation may be due to differences in the synthesis procedure of our respective iron oxyhydroxides. De Vitre et al. (1991) prepared their solids by oxidation of a Fe(II) solution over two days at pH 6.5. Our results conflict with those of Oscarson et al. (1981), who stated that amorphous iron oxides did not oxidize arsenite within 72 hours. Their As:solid ratios (initial As(III) concentrations of 100 mg/L) were two orders of magnitude greater than ours and this difference in initial As(III) concentrations may explain our contradictory results.

4.2.3. Arsenite Oxidation in Systems Purged with Nitrogen

Our experiments show that the metal oxides do not act simply as an electron transfer medium catalyzing the oxidation of arsenite by oxygen. These oxides oxidize arsenite themselves. When oxygen was excluded, Mn-Ox oxidized more than 70% of the As(III) in the system within 5-6 minutes (Figures 23 and 25) in both the low and high ionic strength solutions.

Scott and Morgan (1995) observed that the presence or absence of oxygen did not affect the rate of release of arsenate from the solid phase, synthetic birnessite ($\delta-MnO_2$), to the aqueous phase. In our reaction systems the absence of dissolved O_2 does have a significant effect on the desorption of As(V) from the solid Mn-Ox. Their As:solid ratios, with initial As(III) concentrations ranging from 100 μM to 400 μM, were 100 times larger than ours, and the pH of their system was 4, instead of 7. These variations as well as a different method of solid synthesis may explain the discrepancies between our results.

Although dissolved oxygen concentrations did not affect total arsenite and arsenate concentrations in the combined solid plus aqueous phases, it did affect the desorption of As(V) from the solid Mn-Ox (Figures 10, 12, 22, and 24). Gao and Mucci (2001) suggested that carbonate and bicarbonate ions could compete for adsorption sites on goethite, for example as a result of atmospheric CO_2 dissolving in solution forming CO_3^{2-} and HCO_3^-. By analogy, these ions could compete with As(V) for adsorption on manganese oxyhydroxides as well. In experimental systems purged with nitrogen containing MnOx, the uptake of atmospheric carbon dioxide should not be significant. This may explain why As(V) appears in the aqueous phase at low ionic strengths in systems open to the atmosphere and not in the N_2-purged systems (see Figures 22 and 24).

The different desorption rates of dissolved arsenate in the presence and absence of O_2 may also be due to different types of complex formation or different sorption sites. Ionic strength does affect the desorption of As(V) from manganese oxyhydroxides in the nitrogen purged systems (Figures 22 and 24). The formation of outer-sphere complexes could explain the release of arsenate to solution at the higher ionic strength and not at the lower. Spectroscopic studies would need to be conducted to confirm the types of complexes formed. Scott and Morgan (1995), using low ionic strength solutions (i.e. 0.1M $NaClO_4$) in the absence of dissolved oxygen, still observed the desorption of As(V) from synthetic birnessite to the aqueous phase. Their differing As:solid ratios, which were 100 times greater than ours, and pH of their systems (pH 4 vs. pH7) may explain the variation between our results.

4.3. Formation of Solid Iron- and Manganese-As(V) Phases

The decreasing arsenate concentrations that followed the initial increase in the presence of iron and manganese oxyhydroxides (Figures 10, 12, 14, 16, 18, 20, and 22) can be explained if As(V) is re-adsorbed on the metal oxyhydroxides (Me-Ox) or coprecipitates with iron and manganese.

Arsenate and iron can coprecipitate to form a solid phase. Waychunas et al. (1993) coprecipitated arsenate with ferrihydrite at various As/Fe ratios. By adding As(V) and Fe(III) concurrently to a 0.1N $NaNO_3$ solution, they found that arsenate, even at low concentrations, retarded Fe-O-Fe polymerization and the formation of ferrihydrite. With aging, however, polymerization increased as crystallization of ferrihydrite continued. As a result, arsenate was expelled from the solid to the solution over time. Masscheleyn et al. (1991 suggested that an arsenate-iron solid would most likely dissolve, according to the following reaction:

$$FeAsO_4{\cdot}2H_2O + H_2O \rightarrow H_2AsO_4^- + Fe(OH)_3 + H^+. \qquad (13)$$

Accordingly arsenate would be released back to the solution. In the latter part of our experiments, a As – Fe coprecipitate may have formed, accounting for the decreasing concentrations of dissolved As(V), but this solid would most likely re-dissolve releasing As(V) back into solution.

Oscarson et al. (1981), Masscheleyn et al. (1991), and Tournassat et al. (2002) have proposed that the formation of an arsenate-manganese phase is likely. Masscheleyn et al. (1991) proposed a possible reaction pathway for the formation of this precipitate:

$$3Mn^{2+} + 2HAsO_4^{2-} \leftrightarrow Mn_3(AsO_4)_2 + 2H^+. \tag{14}$$

They observed that As(V) persists in porewaters under reducing conditions even after dissolution of iron oxyhydroxides. The persistence of arsenate in the presence of dissolved Mn(II) could favor the precipitation of $Mn_3(AsO_4)_2$ (Masscheleyn et al., 1991). In the latter part of our experiments dissolved Mn(II), resulting from the reductive dissolution of manganese oxyhydroxide by arsenite (Eq. 12), can coprecipitate with dissolved As(V) to form an arsenate – manganese phase.

Tournassat et al. (2002) proposed the formation of another arsenate-manganese precipitate, krautite. The formation of this precipitate can be represented by the following reaction:

$$Mn^{2+} + H_2AsO_4^- + H_2O \leftrightarrow MnHAsO_4{\cdot}H_2O + H^+. \tag{15}$$

Arsenite was added to a suspension of H-birnessite at low ionic strength (i.e. <0.1M) under an argon atmosphere. They observed that dissolved As(V) and Mn(II) concentrations in solution increased to a maximum and then decreased. The gradual decrease was attributed to the formation of a manganese(II)-arsenate precipitate, instead of solely the uptake of As(V) and Mn(II) by solid birnessite. Computer modeling along with SEM-EDS and AFM analysis of the solid at several points during the reaction of birnessite with As(III), supported the hypothesis of precipitation of krautite. XRD patterns of delta – MnO_2 reacted with As(V) by Foster et al. (2003) exhibited a broad peak that was attributed to the formation of a new phase, or the transformation of Mn-Ox phases.

5. CONCLUSIONS

1. By itself, oxygen is not an efficient oxidant of arsenite. During a 4 – month experiment, less than 20% of the initial As(III) was oxidized in 0.05M NaCl and 0.7M NaCl over a range of pH (3-9) whether in the presence or absence of ambient light. If metal oxides are rare, such as in the water column, oxidation of As(III) will be slow. Arsenic speciation in environmental samples can be preserved for several months when a solid metal oxide phase is not present (i.e. acidified samples).

2. Manganese and iron oxyhydroxides are effective and efficient oxidants of As(III). More than 80% of initial As(III) was oxidized to As(V) within 15 minutes, irrespective of the crystallinity of the metal oxyhydroxides or the ionic strength of the solution. These results indicate that even a thin oxic layer in sediments will effectively trap upwardly diffusing arsenic species in pore water.

3. Arsenate desorbs to a greater extent from amorphous Mn – Ox than from Fe-Ox. Arsenate will preferentially adsorb to Fe – Ox.

4. Solid metal oxyhydroxides alone can oxidize As(III) . Oxygen is not necessary for the oxidation to proceed. Arsenite oxidation can occur in oxygen – depleted environments, such as the suboxic zone of sediments, when metal oxides are present.

5. As(V) will form different types of sorption complexes on Mn-Ox depending on the presence and absence of oxygen. The ionic strength of solutions affects the adsorption of arsenate onto amorphous Mn – Ox.

Future Work

Results from experiments investigating the oxidation of arsenite by iron – oxyhydroxides in N_2 purged systems at low and high ionic strength solutions would be very interesting. These results would provide more information as to the types of complex formation (i.e. inner – sphere vs. outer – sphere) of As(III) and As(V) onto the solid surface of the metal oxides in anoxic environments. Conducting experiments at a lower temperature (i.e. T = 4°C) may retard the rate of As(III) oxidation enough so that kinetic parameters can be determined. Lower temperatures are also more representative of most natural aquatic environments. There are also other oxidants available in sediments, such as nitrate. Studying As(III) oxidation by these oxidants would provide a more comprehensive model of As diagenesis. Varying the concentration of dissolved oxygen in reactional systems containing As(III) in the presence of Mn – Ox or Fe –Ox would simulate the transition between the oxic and anoxic zones of sediments and would provide more details of the diagenetic behavior of arsenic.

The predictions of arsenic interactions with Mn-Ox and Fe-Ox, and possibly nitrate, from experiments can be tested by reproducing freshwater and marine sediment environments in the laboratory. Redox zones can be established by the addition of microbes and organic matter. Dissolved Mn, Fe, and As (arsenite and arsenate) concentrations can be monitored *in situ* using voltammetric techniques (i.e. Jagner et al., 1981; Florence, 1986; Taillefert et al., 2000) and microelectrodes, which allow have sub-millimeter depth resolution. Dissolved Mn, Fe, and As can also be monitored in the field to further test predictions resulting from the experiments.

REFERENCES

Acharyya S. K., Chakraborti P., Lahiri S., Raymahashay B. C., Guha S., and Bhowmik A. (1999) Arsenic poisoning in the Ganges delta. *Nature* **401**, 545.

Acharyya S. K., Lahiri S., Raymahashay B. C., and Bhowmil A. (2000) Arsenic toxicity of groundwater in parts of the Bengal basin in India and Bangladesh: the role of Quaternary stratigraphy and Holocene sea-level fluctuation. *Environ. Geol.* **39**, 1127 - 1137.

Aggett J. and O'Brien G. (1985) Detailed model for the mobility of arsenic in lacustrine sediments based on measurements in Lake Ohakuri. *Environ. Sci. Technol.* **19**, 231-238.

Andreae M. O. (1979) Arsenic speciation in seawater and interstitial waters: The influence of biological-chemical interactions on the chemistry of a trace element. *Limnol. Oceanogr.* **24**, 440-452.

Belzile N. (1988) The fate of arsenic in sediments of the Laurentian Trough. Geochim. Cosmochim. Acta **52**, 2293-2302.

Belzile N. and Tessier A. (1990) Interactions between arsenic and iron oxyhydroxides in lacustrine sediments. *Geochim. Cosmochim. Acta* **54**, 103-109.

Bowell R. J. (1994) Sorption of arsenic by iron oxides and oxyhydroxides in soils. *App. Geochem.* **9**, 279 – 286.

Caldwell B. K., Caldwell J. C., Mitra S. N., and Smith W. (2003) Searching for an optimum solution to the Bangladesh arsenic crisis. *Soc. Sci. Medicine.* **56**, 2089 – 2096.

Chakraborti D., Rahman M. M., Paul K., Chowdhury U. K., Sengupta M. K., Lodh D., Chanda C. R., Saha K. C., and Mukherjee S. C. (2002) Arsenic calamity in the Indian subcontinent. What lessons have been learned? *Talanta* **58**, 2 – 33.

Chiu V. Q. and Hering J. G. (2000) Arsenic adsorption and oxidation at manganite surfaces. 1. Method for simultaneous determination of adsorbed and dissolved arsenic species. *Environ. Sci. Technol.* **34**, 2029-2034.

Cullen W. R. and Reimer K. J. (1989) Arsenic speciation in the environment. *Chem. Rev.* **89**, 713-764.

De Vitre R., Belzile N., and Tessier A. (1991) Speciation and adsorption of arsenic on diagenetic iron oxyhydroxides. *Limnol. Oceanogr.* **36**, 1480-1485.

DPHE/BGS/MML (1999) Groundwater studies for arsenic contamination in Bangladesh. Phase I: Rapid investigation phase. (BGS/MML Technical Report to Department for International Development, UK), 6 volumes.

Edenborn H.M., Belzile N., Mucci A., Lebel J., and Silverberg N. (1986) Observation on the diagenetic behavior of arsenic in a deep coastal sediment. *Biogeochem.* **2**, 359-376.

Fendorf S., Eick M. J., Grossl P., and Sparks D. L. (1997) Arsenate and chromate retention mechanisms on goethite. 1. Surface structure. *Environ. Sci. Technol.* **31**, 315-320.

Florence T.M. (1986) Electrochemical approaches to trace element speciation in waters a review. *Analyst* **111**, 489 - 505.

Foster A. L., Brown G. E. Jr., and Parks, G. E. (2003) X-Ray adsorption of fine structure study of As(V) and Se(IV) sorption complexes on hydrous Mn oxides. *Geochim. Cosmochim. Acta* **67**, 1937-1953.

Froelich P. N., Klinkhammer G. P., Bender M. L., Luedtke N. A., Heath G. R., Cullen D., and Dauphin P. (1979) Early oxidation of organic matter in pelagic sediments of the eastern equatorial Atlantic: suboxic diagenesis. *Geochim. Cosmochim. Acta* **43**, 1075-1090.

Gao Y. and Mucci A. (2001) Acid base reactions, phosphate and arsenate complexation, and their competitive adsorption at the surface of goethite in 0.7M NaCl solution. *Geochim. Cosmochim. Acta* **65**, 2361-2378.

Gao Y. and Mucci A. (2003) Individual and competite adsorption of phosphate and arsenate on goethite in artificial seawater. *Chem. Geo.* **199**, 91-109.

Goldberg S. and Johnston C. T. (2001) Mechanisms of arsenic adsorption on amorphous oxides evaluated using macroscopic measurements, vibrational spectroscopy, and surface complexation modeling. *J. Colloid Interface Sci.* **234**, 204-216.

Grossl P. R., Eick M., Sparks D. L., Goldberg S., and Ainsworth C. C. (1997) Arsenate and chromate retention mechanisms on goethite. 2. Kinetic evaluation using a pressure-jump relaxation technique. *Environ. Sci. Technol.* **31**, 321-326.

Jagner D., Josefson M., and Westerlund S. (1981) Determination of Arsenic(III) by computerized potentiometric stripping analysis. *Anal Chem.* **53**, 2144 - 2146.

Kuhn A. and Sigg L. (1993) Arsenic cycling in eutrophic Lake Greifen, Switzerland: Influence of seasonal redox processes. *Limnol. Oceanogr.* **38**, 1052 – 1059.

Laha S. and Luthy R. G. (1990) Oxidation of aniline and other primary aromatic amines by manganese dioxide. *Environ. Sci. Technol.* **24**, 363-373.

Le X. C., Yalcin S., and Ma M. (2000) Speciation of submicrogram per liter levels of arsenic in water: On-site species separation integrated with sample collection. *Environ. Sci. Technol.* **34**, 2342-2347.

Manceau A. (1995) The mechanism of anion adsorption on iron oxides: Evidence for the bonding of arsenate tetrahedra on free Fe(O, OH)$_6$ edges. *Geochim. Cosmochim. Acta* **59**, 3647-3653.

Manning B. A., Fendorf S. E., Bostick B., and Suarez D. L. (2002) Arsenic(III) oxidation and arsenic(V) adsorption reactions on synthetic birnessite. *Environ. Sci. Technol.* **36**, 976-981.

Manning B. A., Fendorf S. E., and Goldberg S. (1998) Surface structures and stability of arsenic(III) on goethite: Spectroscopic evidence for inner-sphere complexes. *Environ. Sci. Technol.* **32**, 2383-2388.

Masscheleyn P. H., Delaune R. D., and Patrick W. H. Jr. (1991) Effect of redox potential and pH on arsenic speciation and solubility in a contaminated soil. *Environ. Sci. Technol.* **25**, 1414-1419.

McArthur J.M., Ravenscroft P., Safiulla S., and Thirwall M.F. (2001) Arsenic in groundwater: Testing pollution mechanisms for sedimentary aquifers in Bangladesh. *Water Resources* **37**, 109 – 117.

Millero F. J., Hershey, J. P., and Fernandez M. (1987) The pK* of TRISH$^+$ in Na-K-Mg-Ca-Cl-SO$_4$ brines — pH scales. *Geochim. Cosmochim. Acta* **51**, 707-711.

Moore J. N., Ficklin W. H., Johns C. (1988) Partitioning of arsenic and metals in reducing sulfidic sediments. *Environ. Sci. Technol.* **22**, 432 – 437.

Mucci A., Richard L., Lucotte M., and Guignard C. (2000) The differential geochemical behavior of arsenic and phosphorus in the water column and sediments of the Saguenay Fjord, Canada. *Aquatic Geochem.* **00**, 1 – 32.

Nesbitt H. W., Canning G. W., and Bancroft G. M. (1998) XPS study of reductive dissolution of 7A-birnessite by H_3AsO_3, with constraints on reaction mechanism. *Geochim. Cosmochim. Acta* **62**, 2097-2110.

Nickson R., McArthur J.M., Burgess W., Ahmed M., Ravenscroft P. and Rahman M. (1998) Arsenic poisoning of Bangladesh groundwater. *Nature* **395**, 338.

Oscarson D. W., Huang P. M., Defosse C., and Herbillon A. (1981) Oxidative power of Mn(IV) and Fe(III) oxides with respect to As(III) in terrestrial and aquatic environments. *Nature* **291**, 50-51.

Oscarson D. W., Huang P. M., Liaw W. K., and Hammer U. T. (1983) Kinetics of oxidation of arsenite by various manganese dioxides. *Soil Sci. Soc. Am. J.* **47**, 644-648.

Peterson M. L. and Carpenter R. (1986) Arsenic distributions in porewaters and sediments of Puget Sound, Lake Washington, the Washington coast and Saanich Inlet, B.C. *Geochim. Cosmochim. Acta* **50**, 353-369.

Pierce M. L. and Moore C. B. (1980) Adsorption of arsenite on amorphous iron hydroxide from dilute aqueous solution. *Environ. Sci. Technol.* **14**, 214-216.

Pierce M. L. and Moore C. B. (1982) Adsorption of arsenite and arsenate on amorphous iron hydroxide. *Water Res.* **16**, 1247-1253.

Raven K. P., Jain A., and Loeppert R. H. (1998) Arsenite and arsenate adsorption on ferrihydrite: Kinetics, equilibrium, and adsorption envelopes. *Environ. Sci. Technol.* **32**, 344-349.

Rochette E. A., Bostick B. C., Li G., and Fendorf S. (2000) Kinetics of arsenate reduction by dissolved sulfide. *Environ. Sci. Technol.* **34**, 4714 – 4720.

Sadiq M. (1997) Arsenic chemistry in soils: An overview of thermodynamic predictions and field observations. *Water, Air, and Soil Pollut.* **93**, 117-136.

Scott M. J. and Morgan J. J. (1995) Reactions at oxide surfaces. 1. Oxidation of As(III) by synthetic birnessite. *Environ. Sci. Technol.* **29**, 1898-1905.

Smedley P. L. and Kinniburgh D. G. (2002) A review of the source, behaviour and distribution of arsenic in natural waters. *App. Geochem.* **17**, 517-568.

Sullivan K.A. and Aller R.C. (1996) Diagenetic cycling of arsenic in Amazon shelf sediments. *Geochim. Cosmochim. Acta* **60**, 1465-1477.

Sun X. and Doner H. E. (1996) An investigation of arsenate and arsenite bonding structures on goethite by FTIR. *Soil Sci.* **161**, 865-872.

Sun X. and Doner H. E. (1998) Adsorption and oxidation of arsenite on goethite. *Soil Sci.* **163**, 278-287.

Taillefert M., Luther G.W. III, and Nuzzio D.B. (2000) The application of electrochemical tools for in situ measurements in aquatic systems. *Electroanalysis* **12**, 401 - 412.

Tournassat C., Charlet L., Bosbach D., and Manceau A. (2002) Arsenic(III) oxidation by birnessite and precipitation of manganese(II) arsenate. *Environ. Sci. Technol.* **36**, 493-500.

Waychunas G. A., Davis J. A., and Fuller C. C. (1995) Geometry of sorbed arsenate on ferrihydrite and crystalline FeOOH: Re-evaluation of EXAFS results and topological factors in predicting sorbate geometry, and evidence for monodentate complexes. *Geochim. Cosmochim. Acta* **59**, 3655-3661.

Waychunas G. A., Rea B. A., Fuller C. C., and Davis J. A. (1993) Surface chemistry of ferrihydrite: Part 1: EXAFS studies of the geometry of coprecipitation and adsorbed arsenate. *Geochim. Cosmochim. Acta* **57**, 2251-2269.

Widerlund A. and Ingri J. (1995) Early diagenesis of arsenic in sediments of the Kalix River estuary, northern Sweden. *Chem. Geo.* **125**, 185-196.

APPENDIX 1: Oxidation of Dissolved As(III) in Aqueous Systems Open to the Atmosphere in 0.05M NaCl at Various pH (3, 5, 7, 9).

APPENDIX 1

Percent of Total Arsenic in the form of Dissolved Arsenite [As(III)] and Arsenate [As(V)] as a function of time in a System Open to the Atmosphere in the presence of ambient light in 0.05M NaCl at pH 3. TOTAL [As] = 104.7 ± 4.4ppb

SAMPLE	TIME (hr)	pH	%[As(III)]	%[As(V)]*
1	0.00	3.03	97 ± 20	3 ± 20
2	0.07	3.03	86 ± 7	14 ± 7
3	0.25	3.03	97 ± 9	3 ± 9
4	0.50	3.04	103 ± 7	-3 ± -7
5	0.98	3.03	94 ± 33	6 ± 33
6	2.08	3.04	90 ± 11	10 ± 12
7	4.83	3.06	3 ± 1	97 ± 6
8	10.27	3.05	89 ± 12	11 ± 12
9	27.42	3.15	92 ± 5	8 ± 5
10	52.45	3.13	91 ± 5	9 ± 5
11	100.25	3.34	83 ± 10	17 ± 10
12	198.42	3.37	79 ± 3	21 ± 4
13	406.40	3.22	87 ± 19	13 ± 19
14	1133.00	3.29	81 ± 7	19 ± 7
15	3597.50		99 ± 9	1 ± 9

* %[As(V)] = 100 - %[As(III)]

Percent of Total Arsenic in the form of Dissolved Arsenite [As(III)] and Arsenate [As(V)] as a function of time in a System Open to the Atmosphere in the dark in 0.05M NaCl at pH 3. TOTAL [As] = 129.4 ± 12.6ppb

SAMPLE	TIME (hr)	pH	%[As(III)]	%[As(V)]*
1	0.00	3.03	91 ± 32	9 ± 32
2	0.09	3.03	83 ± 10	17 ± 11
3	0.28	3.03	88 ± 14	12 ± 15
4	0.52	3.03	83 ± 10	17 ± 12
5	1.00	3.03	81 ± 8	19 ± 10
6	2.10	3.03	83 ± 11	17 ± 13
7	4.85	3.04	89 ± 18	11 ± 19
8	10.30	3.05	80 ± 9	20 ± 11
9	27.43	3.14	71 ± 11	29 ± 13
10	52.48	3.11	71 ± 7	29 ± 10
11	100.23	3.34		
12	198.33	3.37		
13	406.33	3.23	62 ± 10	38 ± 13
14	1133.00	3.31	63 ± 7	37 ± 11
15	3597.50		73 ± 16	27 ± 18

* %[As(V)] = 100 - %[As(III)]

APPENDIX 1

Percenatage of Total Arsenic in the form of Dissolved Arsenite [As(III)] & Arsenate [As(V)] as a function of time in a System Open to the Atmosphere in th presence of ambient light in 0.05M NaCl at pH 5. TOTAL [As] = 104.4 ± 8.1ppb

SAMPLE	TIME	pH	%[As(III)]	%[As(V)]*
1	0.00	5.007	92 ± 8	8 ± 8
2	0.08	5.026	90 ± 10	10 ± 11
3	0.32	5.069	89 ± 12	11 ± 13
4	0.50	5.042	92 ± 13	8 ± 13
5	1.02	5.062	90 ± 15	10 ± 15
6	2.00	5.15	89 ± 15	11 ± 16
7	4.00	5.201	90 ± 8	10 ± 8
8	9.87	5.366	88 ± 11	12 ± 12
9	28.12	5.665	81 ± 7	19 ± 9
10	56.00	5.829	89 ± 11	11 ± 11
11	99.93	5.798	92 ± 10	8 ± 10
12	218.83	5.906	85 ± 7	15 ± 8
13	410.83	5.85	81 ± 15	19 ± 15
14	1204.08	5.62		

*** %[As(V)] = 100 - %[As(III)]**

Percenatage of Total Arsenic in the form of Dissolved Arsenite [As(III)] & Arsenate [As(V)] as a function of time in a System Open to the Atmosphere in the dark in 0.05M NaCl at pH 5. TOTAL [As] = 103.5 ± 6.1ppb

SAMPLE	TIME (hr)	pH	%[As(III)]	%[As(V)]*
1	0.00	5.01	102 ± 10	-2 ± -10
2	0.08	4.94	91 ± 6	9 ± 6
3	0.32	4.95	95 ± 11	5 ± 11
4	0.50		94 ± 10	6 ± 10
5	1.02	4.97	93 ± 13	7 ± 13
6	2.00	4.97	98 ± 12	2 ± 12
7	4.00	4.97	95 ± 9	5 ± 9
8	9.87	5.07	96 ± 12	4 ± 12
9	28.12	5.38	90 ± 10	10 ± 10
10	56.00	5.50	95 ± 10	5 ± 10
11	99.93	5.55	98 ± 13	2 ± 13
12	218.83	5.61		
13	410.83	5.54	85 ± 10	15 ± 10
14	1204.08	5.42		
15	3551.83		79 ± 14	21 ± 15

*** %[As(V)] = 100 - %[As(III)]**

APPENDIX 1

Percent of Total Arsenic in the form of Dissolved Arsenite [As(III)] and Arsenate [As(V)] as a function of time in a System Open to the Atmosphere in the presence of ambient light in 0.05M NaCl at pH 7. TOTAL [As] = 101.1 ± 1.7ppb

SAMPLE	TIME (hr)	pH	%[As(III)]	%[As(V)]*
1	0.00	7.03		
2	0.10	7.06	114 ± 9	-14 ± -9
3	0.28	7.08	89 ± 10	11 ± 10
4	0.57	7.14	91 ± 8	9 ± 8
5	1.00	7.23	93 ± 13	7 ± 13
6	2.38	7.32	89 ± 8	11 ± 8
7	4.37	7.36	92 ± 6	8 ± 6
8	10.15	7.47	89 ± 6	11 ± 6
9	27.82	7.53	89 ± 10	11 ± 10
10	52.17	7.59	88 ± 7	12 ± 7
11	121.35	7.64		
12	238.00	7.60	91 ± 21	9 ± 21
13	482.75	7.62	92 ± 14	8 ± 14
14	1226.00	7.51	85 ± 1	15 ± 2
15	3431.25		103 ± 24	-3 ± -24

*** %[As(V)] = 100 - %[As(III)]**

Percent of Total Arsenic in the form of Dissolved Arsenite [As(III)] and Arsenate [As(V)] as a function of time in a System Open to the Atmosphere in the dark in 0.05M NaCl at pH 7. TOTAL [As] = 102.3 ± 4.7ppb

SAMPLE	TIME (hr)	pH	%[As(III)]	%[As(V)]*
1	0.00	7.06	93 ± 10	7 ± 10
2	0.10		90 ± 14	10 ± 14
3	0.28	7.03	90 ± 10	10 ± 10
4	0.57	7.15	94 ± 6	6 ± 7
5	1.00	7.22	81 ± 27	19 ± 27
6	2.38	7.24	88 ± 18	12 ± 19
7	4.37	7.27	86 ± 5	14 ± 6
8	10.15	7.33	86 ± 15	14 ± 15
9	27.82	7.47	87 ± 5	13 ± 6
10	52.17	7.55	87 ± 10	13 ± 10
11	121.35	7.56		
12	238.00	7.55	88 ± 9	12 ± 9
13	482.75	7.55	83 ± 8	17 ± 8
14	1226.00	7.49	81 ± 5	19 ± 5
15	3431.25		87 ± 9	13 ± 9

*** %[As(V)] = 100 - %[As(III)]**

APPENDIX 1

Percent of Total Arsenic in the form of Dissolved Arsenite [As(III)] and Arsenate [As(V)] as a function of time in a System Open to the Atmosphere in the presence of ambient light in 0.05M NaCl at pH 9. TOTAL [As] = 98.2 ± 4.7ppb

SAMPLE	TIME	pH	%[As(III)]	%[As(V)]*
1	0.00	9.01	88 ± 44	12 ± 44
2	0.08	8.99	78 ± 7	22 ± 8
3	0.27	8.96	83 ± 10	17 ± 11
4	0.52	8.94	84 ± 7	16 ± 7
5	1.00	8.90	80 ± 5	20 ± 6
6	2.50	8.83	86 ± 9	14 ± 10
7	4.87	8.73	88 ± 9	12 ± 9
8	7.77	8.62	83 ± 11	17 ± 11
9	26.50	8.40	86 ± 8	14 ± 8
10	50.97	8.30	88 ± 10	12 ± 11
11	98.25	8.31	86 ± 6	14 ± 6
12	266.00	8.36	79 ± 8	21 ± 8
13	410.42	8.32	128 ± 14	-28 ± -13
14	1154.25	8.21	92 ± 4	8 ± 5
15	3359.25		109 ± 11	-9 ± -11

*** %[As(V)] = 100 - %[As(III)]**

Percent of Total Arsenic in the form of Dissolved Arsenite [As(III)] and Arsenate [As(V)] as a function of time in a System Open to the Atmosphere in the dark in 0.05M NaCl at pH 9. TOTAL [As] = 96.6 ± 7.8ppb

SAMPLE	TIME	pH	%[As(III)]	%[As(V)]*
1	0.00	9.01	87 ± 8	13 ± 9
2	0.08	8.92	79 ± 9	21 ± 11
3	0.27	8.91	68 ± 8	32 ± 11
4	0.52	8.89	80 ± 13	20 ± 14
5	1.00	8.86	84 ± 10	16 ± 11
6	2.50	8.80	81 ± 8	19 ± 9
7	4.87	8.73	87 ± 8	13 ± 9
8	7.77	8.64	84 ± 10	16 ± 11
9	26.50	8.43	83 ± 7	17 ± 9
10	50.97	8.30	84 ± 10	16 ± 11
11	98.25	8.29	81 ± 8	19 ± 10
12	266.00	8.34	86 ± 25	14 ± 25
13	410.42	8.29		
14	1154.25	8.01	86 ± 10	14 ± 11
15	3359.25		91 ± 17	9 ± 17

*** %[As(V)] = 100 - %[As(III)]**

APPENDIX 2: Oxidation of Dissolved As(III) in Aqueous Systems Open to the Atmosphere in 0.7M NaCl at Various pH (3, 5, 7, 9).

APPENDIX 2

Percent of Total Arsenic in the form of Dissolved Arsenite [As(III)] and Arsenate [As(V)] as a function of time in a System Open to the Atmosphere in the presence of ambient light in 0.7M NaCl at pH 3. TOTAL [As] = 97.3 ± 11.5ppb

SAMPLE	TIME (hr)	pH	%[As(III)]	%[As(V)]*
1	0.00	3.00	107.1 ± 28.6	-7.1 ± -28.3
2	0.10	3.00	100.4 ± 22.1	-0.4 ± -22.1
3	0.27	3.00	91.4 ± 20.6	8.6 ± 21.2
4	0.50	3.00	106.1 ± 29.2	-6.1 ± -28.9
5	1.00	3.00	81.0 ± 15.9	19.0 ± 17.5
6	2.42	3.00	105.3 ± 23.2	-5.3 ± -22.9
7	4.02	3.00	100.2 ± 34.4	-0.2 ± -34.4
8	9.42	3.00	113.2 ± 42.9	-13.2 ± -42.5
9	27.42	2.86	103.6 ± 24.7	-3.6 ± -24.5
10	56.08	3.01	97.6 ± 14.0	2.4 ± 14.2
11	142.33	2.86	97.6 ± 27.5	2.4 ± 27.6
12	365.67	2.90	101.0 ± 41.9	-1.0 ± -41.9
13	579.50	2.98	98.0 ± 11.6	2.0 ± 0.2
14	1604.83			
15	2903.50		76.1 ± 9.0	23.9 ± 12.2

* %[As(V)] = 100 - %[As(III)]

Percent of Total Arsenic in the form of Dissolved Arsenite [As(III)] and Arsenate [As(V)] as a function of time in a System Open to the Atmosphere in the dark in 0.7M NaCl at pH 3. TOTAL [As] = 96.0 ± 8.0ppb

SAMPLE	TIME (hr)	pH	%[As(III)]	%[As(V)]*
1	0.00	3.00	124.9 ± 45.3	-24.9 ± -44.9
2	0.10	2.99	111.5 ± 15.0	-11.5 ± -14.4
3	0.27	3.00	115.6 ± 28.4	-15.6 ± -28.0
4	0.50	3.00	110.8 ± 13.3	-10.8 ± -12.7
5	1.00	2.99	117.0 ± 28.4	-17.0 ± -28.0
6	2.42	2.99	91.9 ± 33.7	8.1 ± 33.8
7	4.02	2.99	103.1 ± 26.7	-3.1 ± -26.6
8	9.42	3.00	95.9 ± 8.2	4.1 ± 8.6
9	27.42	2.86	96.5 ± 16.3	3.5 ± 16.4
10	56.08	3.00	104.8 ± 14.1	-4.8 ± -13.9
11	142.33	2.86	99.0 ± 10.6	1.0 ± 10.7
12	365.67	2.89	101.9 ± 22.9	-1.9 ± -22.8
13	579.50	2.99	96.0	4.0
14	1604.83			
15	2903.50		70.0 ± 14.5	30.0 ± 15.8

* %[As(V)] = 100 - %[As(III)]

APPENDIX 2

Percent of Total Arsenic in the form of Dissolved Arsenite [As(III)] and Arsenate[As(V)] as a function of time in a System Open to the Atmosphere in the presence of ambient light in 0.7M NaCl at pH 5. TOTAL [As] = 96.3 ± 7.3ppb

SAMPLE	TIME (hr)	pH	%[As(III)]	%[As(V)]*
1	0.00	5.05	94.7 ± 12.7	5.3 ± 12.9
2	0.10	5.06	95.5 ± 19.7	4.5 ± 19.9
3	0.27	5.06	98.7 ± 21.2	1.3 ± 21.2
4	0.53	5.07	79.9 ± 9.8	20.1 ± 10.9
5	0.98	5.09	98.9 ± 8.7	1.1 ± 8.8
6	2.17	5.12	94.0 ± 8.1	6.0 ± 8.5
7	3.97	5.16	97.4 ± 9.1	2.6 ± 9.2
8	8.17	5.25	97.1 ± 18.0	2.9 ± 18.0
9	28.75	5.56	100.6 ± 7.7	-0.6 ± -7.7
10	59.00	6.07	104.5 ± 16.7	-4.5 ± -16.5
11	123.92	6.58	96.7 ± 18.9	3.3 ± 19.0
12	269.67	6.64	100.3 ± 35.4	-0.3 ± -35.4
13	554.25	6.75	103.3 ± 7.8	-3.3 ± -7.6
14	1508.42			
15	2807.75		77.9 ± 6.4	22.1 ± 8.1

* **%[As(V)] = 100 - %[As(III)]**

Percent of Total Arsenic in the form of Dissolved Arsenite [As(III)] and Arsenate[As(V)] as a function of time in a System Open to the Atmosphere in the dark in 0.7M NaCl at pH 5. TOTAL [As] = 94.4 ± 9.2ppb

SAMPLE	TIME (hr)	pH	%[As(III)]	%[As(V)]*
1	0.00	5.09	92.3 ± 17.0	7.7 ± 17.4
2	0.10	5.09	78.3 ± 12.7	21.7 ± 14.2
3	0.27	5.14	75.8 ± 17.6	24.2 ± 18.9
4	0.53	5.18	98.2 ± 20.4	1.8 ± 20.5
5	0.98	5.23	94.2 ± 10.1	5.8 ± 10.7
6	2.17	5.30	91.6 ± 18.8	8.4 ± 19.2
7	3.97	5.35	100.6 ± 10.4	-0.6 ± -10.3
8	8.17	5.51	100.5 ± 21.9	-0.5 ± -21.9
9	28.75	5.99	102.3 ± 10.4	-2.3 ± -10.2
10	59.00	6.49	102.6 ± 25.3	-2.6 ± -25.2
11	123.92	6.67	95.0 ± 19.4	5.0 ± 19.6
12	269.67	6.62	98.7 ± 39.6	1.3 ± 39.7
13	554.25	6.76	96.3 ± 0.0	3.7 ± 0.0
14	1508.42			
15	2807.75		70.5 ± 14.2	29.5 ± 16.1

* **%[As(V)] = 100 - %[As(III)]**

APPENDIX 2

Percent of Total Arsenic in the form of Dissolved Arsenite [As(III)] and Arsenate [As(V)] as a function of time in a System Open to the Atmosphere in the presence of ambient light in 0.7M NaCl at pH 7. TOTAL [As] = 112.1 ± 5.4 ppb

SAMPLE	TIME (hr)	pH	%[As(III)]	%[As(V)]*
1	0.00	7.53	104 ± 10	-4 ± -10
2	0.08		102 ± 22	-2 ± -22
3	0.28	7.30	112 ± 22	-12 ± -22
4	0.52	7.13	114 ± 22	-14 ± -22
5	1.02	7.33	111 ± 15	-11 ± -15
6	2.17	7.19	109 ± 18	-9 ± -18
7	5.33	7.08	115 ± 20	-15 ± -20
8	9.67	6.89	114 ± 13	-14 ± -13
9	28.58	6.56	110 ± 9	-10 ± -8
10	52.00	6.48	91 ± 25	9 ± 25
11	122.00	6.45	91 ± 13	9 ± 13
12	242.50	6.42	89 ± 40	11 ± 40
13	723.50	6.44	87 ± 0	13 ± 0
14	2567.50		61 ± 9	39 ± 10

*** %[As(V)] = 100 - %[As(III)]**

Percent of Total Arsenic in the form of Dissolved Arsenite [As(III)] and Arsenate [As(V)] as a function of time in a System Open to the Atmosphere in the dark in 0.7M NaCl at pH 7. TOTAL [As] = 112.1 ± 5.4ppb

SAMPLE	TIME (hr)	pH	%[As(III)]	%[As(V)]*
1	0.00	7.00	110 ± 24.0	-10 ± -24
2	0.08		108 ± 12.1	-8 ± -12
3	0.28		106 ± 5.8	-6 ± -6
4	0.52	6.90	114 ± 14.1	-14 ± -14
5	1.02	6.76	116 ± 19.9	-16 ± -20
6	2.17	6.67	116 ± 15.5	-16 ± -15
7	5.33	6.58	108 ± 17.7	-8 ± -18
8	9.67	6.52	109 ± 32.6	-9 ± -32
9	28.58	6.43	112 ± 22.0	-12 ± -22
10	52.00	6.41	87 ± 17.7	13 ± 18
11	122.00	6.48	94 ± 13.5	6 ± 14
12	242.50	6.43	95 ± 15.5	5 ± 16
13	723.50	6.43	87 ± 0.0	13 ± 0
14	2567.50		61 ± 15.6	39 ± 16

*** %[As(V)] = 100 - %[As(III)]**

APPENDIX 2

Percent of Total Arsenic in the form of Dissolved Arsenite [As(III)] and Arsenate [As(V)] as a function of time in a System Open to the Atmosphere in the presence of ambient light in 0.7M NaCl at pH 9. TOTAL [As] = 124.9 ± 12.8ppb

SAMPLE	TIME (hr)	pH	%[As(III)]	%[As(V)]*
1	0.00	9.09	97 ± 26	3 ± 27
2	0.08	9.09	83 ± 9	17 ± 11
3	0.25	9.06	83 ± 33	17 ± 34
4	5.00	9.06	87 ± 12	13 ± 13
5	1.00	9.04	85 ± 11	15 ± 13
6	2.50	9.00	86 ± 31	14 ± 32
7	4.75	8.93	86 ± 40	14 ± 41
8	10.00	8.80	93 ± 19	7 ± 19
9	27.20	8.39	93 ± 16	7 ± 17
10	52.50	7.76	86 ± 9	14 ± 11
11	126.08	7.29	82 ± 14	18 ± 16
12	243.33	7.30	84 ± 15	16 ± 16
13	653.58	7.25	79 ± 0	21 ± 0
14	2497.75		60 ± 7	40 ± 12

* %[As(V)] = 100 - %[As(III)]

Percent of Total Arsenic in the form of Dissolved Arsenite [As(III)] and Arsenate [As(V)] as a function of time in a System Open to the Atmosphere in the dark in 0.7M NaCl at pH 9. TOTAL [As] = 109.5 ± 1.5ppb

SAMPLE	TIME (hr)	PH	%[As(III)]	%[As(V)]*
1	0.00	9.09	93 ± 9	7 ± 9
2	0.08	9.09	89 ± 11	11 ± 11
3	0.25	9.08	87 ± 7	13 ± 7
4	5.00	9.04	90 ± 16	10 ± 16
5	1.00	?	83 ± 10	17 ± 10
6	2.50	8.91	91 ± 18	9 ± 18
7	4.75	8.81	84 ± 6	16 ± 6
8	9.92	8.56	91 ± 5	9 ± 5
9	27.17	7.75	86 ± 13	14 ± 13
10	52.42	7.36	101 ± 23	-1 ± -23
11	126.08	7.28	94 ± 16	6 ± 16
12	243.33	7.34	98 ± 17	2 ± 17
13	653.58	7.14	86 ± 0	14 ± 0
14	2497.75		62 ± 13	38 ± 13

* %[As(V)] = 100 - %[As(III)]

APPENDIX 3: Oxidation of As(III) by Amorphous Mn-Ox in Systems Open to the Atmosphere in 0.05M and 0.7M NaCl.

APPENDIX 3

Percent of initial total arsenic in the form of dissolved arsenite (%[As(III)]aq), arsenate (%[As(V)]aq), and total dissolved As (%[As]aq) as a function of time in the presence of amorphous manganese oxyhydroxides. Experimental conditions: 0.05M NaCl solutions open to the atmosphere. Initial pH was between 7 and 8. TOTAL [As] = 103 ± 10 ppb

SAMPLE	TIME (hr)	% [As(III)]aq	% [As(V)]aq *	% [As]aq
1	0.03	0.0 ± 0.1	7.3 ± 1.1	7.3 ± 1.1
2	0.17	0.0 ± 0.1	3.5 ± 0.9	3.5 ± 0.9
3	0.45	0.0 ± 0.1	3.9 ± 1.1	3.9 ± 1.1
4	0.98	0.0 ± 0.1	3.5 ± 0.4	3.5 ± 0.4
5	3.25	0.0 ± 0.1	4.2 ± 1.4	4.2 ± 1.4
6	6.75	0.0 ± 0.1	7.1 ± 2.0	7.1 ± 2.0
7	27.00	0.0 ± 0.1	11.2 ± 2.0	11.2 ± 2.0
8	51.00	0.0 ± 0.1	12.3 ± 2.6	12.3 ± 2.6
9	100.25	0.0 ± 0.1	12.7 ± 2.6	12.7 ± 2.6
10	143.50	0.0 ± 0.1	9.6 ± 1.4	9.6 ± 1.4

*** %[As(V)]aq = %[As]aq - %[As(III)]aq**

Percent of initial total arsenic in the combined solid and aqueous phases in the form of arsenite (%[As(III)]tot) and arsenate (% [As(V)]tot) as a function of time in the presence of amorphous manganese oxyhydroxides. Experimental conditions: 0.05M NaCl solutions open to the atmosphere. Initial pH was between 7 and 8. TOTAL [As] = 103 ± 10 ppb

SAMPLE	TIME	% [As(III)]tot	% [As(V)]tot*
1	0.03	13.1 ± 3.5	87 ± 14
2	0.17	2.8 ± 2.7	97 ± 14
3	0.45	0.0 ± 0.1	100 ± 14
4	0.98	4.0 ± 2.8	96 ± 14
5	3.25	9.4 ± 17	91 ± 22
6	6.75	8.0 ± 2.7	92 ± 14
7	27.00	5.9 ± 2.8	94 ± 14
8	51.00	4.7 ± 2.7	95 ± 14
9	100.25	6.4 ± 2.9	94 ± 14
10	143.50	7.0 ± 2.6	93 ± 14

*** % [As(V)]tot = 100 - % [As(III)]tot**

APPENDIX 3

Percent of initial total arsenic in the form of dissolved arsenite (%[As(III)]aq), arsenate (%[As(V)]aq), and total dissolved As (%[As]aq) as a function of time in the presence of amorphous manganese oxyhydroxides. Experimental conditions: 0.7M NaCl solutions open to the atmosphere. Initial pH was between 7 and 8. TOTAL [As] = 99 ± 5 ppb

SAMPLE	TIME (hr)	% [As(III)]aq	% [As(V)]aq*	% [As]aq
1	0.03	0.0 ± 0.4	0.0 ± 0.6	0.0 ± 0.4
2	0.18	0.0 ± 0.4	0.0 ± 0.6	0.0 ± 0.4
3	0.47	0.0 ± 0.4	1.8 ± 0.5	1.8 ± 0.2
4	1.00	0.0 ± 0.4	0.0 ± 0.6	0.0 ± 0.4
5	3.25	0.0 ± 0.4	0.0 ± 0.6	0.0 ± 0.4
6	6.75	0.0 ± 0.4	3.5 ± 1.4	3.5 ± 1.4
7	27.00	0.0 ± 0.4	6.1 ± 1.3	6.1 ± 1.2
8	51.00	0.0 ± 0.4	6.2 ± 3.2	6.2 ± 3.2
9	100.25			7.0 ± 4.5
10	143.50	1.9 ± 0.4	2.2 ± 0.4	4.1 ± 0.2

*** %[As(V)]aq = %[As]aq - %[As(III)]aq**

Percent of initial total arsenic in the combined solid and aqueous phases in the form of arsenite (%[As(III)]tot) and arsenate (% [As(V)]tot) as a function of time in the presence of amorphous manganese oxyhydroxides. Experimental conditions: 0.7M NaCl solutions open to the atmosphere. Initial pH was between 7 and 8. TOTAL [As] = 99 ± 5 ppb

SAMPLE	TIME	% [As(III)]tot	% [As(V)]tot
1	0.03	0 ± 0.4	100 ± 7
2	0.18	0 ± 0.4	100 ± 7
3	0.47	0 ± 0.4	100 ± 7
4	1.00	0 ± 0.4	100 ± 7
5	3.25	20 ± 16	80 ± 17
6	6.75	29 ± 15	71 ± 16
7	27.00	0 ± 0.4	100 ± 7
8	51.00	16 ± 15	84 ± 16
9	100.25	18 ± 14	82 ± 15
10	143.50	14 ± 12	86 ± 14

*** % [As(V)]tot = 100 - % [As(III)]tot**

APPENDIX 4: Oxidation of As(III) by Crysalline Mn – Ox in Systems Open to the Atmosphere in 0.05M and 0.7M NaCl.

APPENDIX 4

Percent of initial total arsenic in the form of dissolved arsenite (%[As(III)]aq), arsenate (%[As(V)]aq), and total dissolved As (%[As]aq) as a function of time in the presence of crystalline manganese oxyhydroxides. Experimental conditions: 0.05M NaCl solutions open to the atmosphere. Initial pH was between 7 and 8. TOTAL [As] = 97 ± 25 ppb

SAMPLE	TIME (hr)	%[As(III)]aq	%[As(V)]aq *	% [As]aq
1	0.06	40.8 ± 0.0	23.0 ± 0.0	63.8 ± 0.0
2	0.25	15.0 ± 16.2	10.9 ± 14.6	26 ± 17
3	0.50	2.2 ± 4.1	19.3 ± 3.7	21.5 ± 6.9
4	1.00	0.0 ± 0.6	13.3 ± 5.9	13.3 ± 6.4
5	3.00	0.0 ± 0.1	7.5 ± 4.8	7.5 ± 4.8
6	4.08	0.0 ± 0.1	7.2 ± 2.0	7.2 ± 2.0
7	23.00	0.0 ± 0.1	5.6 ± 1.8	5.6 ± 1.8
8	52.25	0.0 ± 0.1	3.3 ± 1.4	3.3 ± 1.4
9	98.08	0.0 ± 0.1	2.6 ± 0.9	2.6 ± 0.9
10	171.83	0.0 ± 0.1	1.7 ± 1.3	1.7 ± 1.3
11	265.75	0.0 ± 0.1	1.4 ± 0.9	1.4 ± 0.9

*** %[As(V)]aq = %[As]aq - %[As(III)]aq**

Percent of initial total arsenic in the combined solid and aqueous phases in the form of arsenite (%[As(III)]tot) and arsenate (% [As(V)]tot) as a function of time in the presence of crystalline manganese oxyhydroxides. Experimental conditions: 0.05M NaCl solutions open to the atmosphere. Initial pH was between 7 and 8. TOTAL [As] = 97 ± 25 ppb

SAMPLE	TIME (hr)	% [As(III)]tot	% [As(V)]tot *
7	23.00	14 ± 7	86 ± 34
8	52.25	15 ± 8	85 ± 34
9	98.08	19 ± 9	81 ± 34
10	171.83	6 ± 7	94 ± 35
11	265.75	16 ± 8	84 ± 34

*** % [As(V)]tot = 100 - % [As(III)]tot**

APPENDIX 4

Percentage of initial total arsenic in the form of dissolved arsenite (%[As(III)]aq), arsenate (%[As(V)]aq), and total dissolved As (%[As]aq) as a function of time in the presence of crystalline manganese oxyhydroxides.
Experimental conditions: 0.7M NaCl solutions open to the atmosphere.
Initial pH was between 7 and 8. TOTAL [As] = 103 ± 22 ppb

SAMPLE	TIME (hr)	%[As(III)]aq	%[As(V)]aq *	% [As]aq
1	0.07	14.5 ± 3.7	22.0 ± 6.5	36.5 ± 8.7
2	0.27	3.6 ± 2.8	11.6 ± 4.4	15 ± 4
3	0.58	0.0 ± 0.4	9.6 ± 3.0	9.6 ± 2.9
4	1.00	0.0 ± 0.4	7.6 ± 2.4	7.6 ± 2.4
5	3.00	0.0 ± 0.4	4.8 ± 3.7	4.8 ± 3.7
6	4.08	0.0 ± 0.4	6.0 ± 1.3	6.0 ± 1.3
7	23.00	1.6 ± 0.3	2.0 ± 1.6	3.6 ± 1.7
8	52.25	0.0 ± 0.4	0.0 ± 0.5	0.0 ± 0.4
9	98.08	0.0 ± 0.4	0.0 ± 0.5	0.0 ± 0.4
10	171.83	0.0 ± 0.4	0.0 ± 0.5	0.0 ± 0.4
11	265.75	0.0 ± 0.4	0.0 ± 0.5	0.0 ± 0.4

*** %[As(V)]aq = %[As]aq - %[As(III)]aq**

Percent of initial total arsenic in the combined solid and aqueous phases in the form of arsenite (%[As(III)]tot) and arsenate (% [As(V)]tot) as a function of time in the presence of crystalline manganese oxyhydroxides.
Experimental conditions: 0.7M NaCl solutions open to the atmosphere.
Initial pH was between 7 and 8. TOTAL [As] = 103 ± 22 ppb

SAMPLE	TIME (hr)	% [As(III)]tot	% [As(V)]tot *
7	23.00	0.0 ± 0.4	100 ± 30
8	52.25	0.0 ± 0.4	100 ± 30
9	98.08	14 ± 14	86 ± 31
10	171.83	0.0 ± 0.4	100 ± 30
11	265.75	18 ± 19	82 ± 33

*** % [As(V)]tot = 100 - % [As(III)]tot**

APPENDIX 5: Oxidation of As(III) by Amorphous and Crystalline Fe – Ox in Systems Open to the Atmosphere in 0.05M NaCl.

APPENDIX 5

Percent of initial total arsenic in the form of dissolved arsenite(%[As(III)]aq), arsenate(%[As(V)]aq), and total dissolved As (%[As]aq) as a function of time in the presence of crystalline iron oxyhydroxides.
Experimental conditions: 0.05M NaCl solutions open to the atmosphere.
Initial pH was between 7 and 8. TOTAL [As] = 96 ± 5 ppb

SAMPLE	TIME (hr)	% [As(III)]aq	% [As(V)]aq*	% [As]aq
1	0.03	23.4 ± 8.5	25.0 ± 12	48.4 ± 8.1
2	0.13	10.8 ± 0.7	3.5 ± 3	14.3 ± 2.7
3	0.27	6.1 ± 0.9	1.2 ± 2	7.4 ± 1.7
4	0.50	4.0 ± 0.5	1.0 ± 0.6	5.0 ± 0.5
5	1.00	2.1 ± 1.0	0.7 ± 3	2.9 ± 3.3
6	2.08	1.6 ± 0.3	0.1 ± 1	1.7 ± 1.0
7	3.58	0.0 ± 0.1	1.5 ± 0.9	1.5 ± 0.9
8	7.33	0.0 ± 0.1	0.0 ± 0.2	0.0 ± 0.1
9	21.50	0.0 ± 0.1	0.0 ± 0.2	0.0 ± 0.1
10	49.92	0.0 ± 0.1	0.0 ± 0.2	0.0 ± 0.1
11	170.50	0.0 ± 0.1	0.0 ± 0.2	0.0 ± 0.1

*** %[As(V)]aq = %[As]aq - %[As(III)]aq**

Percent of initial total arsenic in the combined solid and aqueous phases in the form of arsenite (%[As(III)]tot) and arsenate (% [As(V)]tot) as a function of time in the presence of crystalline iron oxyhydroxides.
Experimental conditions: 0.05M NaCl solutions open to the atmosphere.
Initial pH was between 7 and 8. TOTAL [As] = 96 ± 5 ppb

SAMPLE	TIME (hr)	% [As(III)]tot	% [As(V)]tot*
2	0.13	15 ± 6	85 ± 9
3	0.27	0 ± 0.1	100 ± 7
4	0.50	8 ± 6	92 ± 9
5	1.00	20 ± 6	80 ± 9
6	2.08	0 ± 0.1	100 ± 7
7	3.58	14 ± 8	86 ± 10
8	7.33	0 ± 0	100 ± 7
9	21.50	19 ± 7	81 ± 9
10	49.92	20 ± 9	80 ± 11
11	170.50	19 ± 6	81 ± 9

*** % [As(V)]tot = 100 - % [As(III)]tot**

APPENDIX 5

Percent of initial total arsenic in the form of dissolved arsenite(%[As(III)]aq), arsenate (%[As(V)]aq), and total dissolved As (%[As]aq) as a function of time in the presence of amorphous iron oxyhydroxides.
Experimental conditions: 0.05M NaCl solutions open to the atmosphere.
Initial pH was between 7 and 8. TOTAL [As] = 95 ± 15 ppb

SAMPLE	TIME (hr)	% [As(III)]aq	% [As(V)]aq *	% [As]aq
1	0.03	13 ± 2	38 ± 8	51 ± 9
2	0.17	6 ± 1	12 ± 7	19 ± 7
3	0.50	3 ± 2	10 ± 8	12 ± 7
4	1.13	2 ± 1	3 ± 2	6 ± 2
5	3.00	1.8 ± 0.7	1 ± 1	3 ± 1
6	6.17	0.0 ± 0.1	2 ± 6	2 ± 6
7	27.75	0.0 ± 0.1	1 ± 4	1 ± 4
8	71.00	0.0 ± 0.1	0.0 ± 0.2	0.0 ± 0.1

*** %[As(V)]aq = %[As]aq - %[As(III)]aq**

Percent of initial total arsenic in the combined solid and aqueous phases in the form of arsenite (%[As(III)]tot) and arsenate (% [As(V)]tot) as a function of time in the presence of amorphous iron oxyhydroxides.
Experimental conditions: 0.05M NaCl solutions open to the atmosphere.
Initial pH was between 7 and 8. TOTAL [As] = 95 ± 15 ppb

SAMPLE	TIME (hr)	% [As(III)]tot	% [As(V)]tot*
1	0.03	11 ± 6	89 ± 22
2	0.17	15 ± 6	85 ± 22
3	0.50	14 ± 6	86 ± 22
4	1.13	19 ± 7	81 ± 22
5	3.00	6 ± 5	94 ± 23
6	6.17	17 ± 6	83 ± 22
7	27.75	9 ± 6	91 ± 23
8	71.00	12 ± 6	88 ± 22

*** % [As(V)]tot = 100 - % [As(III)]tot**

APPENDIX 6: Oxidation of As(III) by Amorphous Mn – Ox in Systems Purged with Nitrogen in 0.05M and 0.7M NaCl.

APPENDIX 6

Percent of initial total arsenic in the form of dissolved arsenite(%[As(III)]aq), arsenate (%[As(V)]aq), and total dissolved As (%[As]aq) as a function of time in the presence of amorphous manganese oxyhydroxides. Experimental conditions: 0.05M NaCl in a closed system purged with nitrogen. Initial pH was between 7 and 8. TOTAL [As] = 100 ± 10 ppb

SAMPLE	TIME (hr)	% [As(III)]aq	% [As(V)]aq *	% [As]aq
1	0.08	3.2 ± 1.5	13.6 ± 3.0	16.9 ± 3.1
2	5.50	0.0 ± 0.1	0.0 ± 0.2	0.0 ± 0.1
3	22.25	0.0 ± 0.1	0.0 ± 0.2	0.0 ± 0.1
4	30.67	0.0 ± 0.1	0.0 ± 0.2	0.0 ± 0.1
5	47.25	0.0 ± 0.1	0.0 ± 0.2	0.0 ± 0.1
6	54.67	0.0 ± 0.1	0.0 ± 0.2	0.0 ± 0.1

*** %[As(V)]aq = %[As]aq - %[As(III)]aq**

Percent of initial total arsenic in the combined solid and aqueous phases in the form of arsenite (%[As(III)]tot) and arsenate (% [As(V)]tot) as a funtion of time in the presence of amorphous manganese oxyhydroxides. Experimental conditions: 0.05M NaCl in a closed system purged with nitrogen. Initial pH was between 7 and 8. TOTAL [As] = 100 ± 10 ppb

SAMPLE	TIME (hr)	% [As(III)]tot	% [As(V)]tot *
1	0.08	13 ± 5	87 ± 14
2	5.50	19 ± 17	81 ± 21
3	22.25	14 ± 5	86 ± 14
4	30.67	18 ± 17	82 ± 21
5	47.25	11 ± 5	89 ± 14
6	54.67	5 ± 4	95 ± 14

*** % [As(V)]tot = 100 - % [As(III)]tot**

APPENDIX 6

Percent of initial total arsenic in the form of dissolved arsenite(%[As(III)]aq), arsenate (%[As(V)]aq), and total dissolved As (%[As]aq) as a function of time in the presence of amorphous manganese oxyhydroxides. Experimental conditions: 0.7M NaCl in a closed system purged with nitrogen. Initial pH was between 7 and 8. TOTAL [As] = 100 ± 10 ppb

SAMPLE	TIME (hr)	% [As(III)]aq	% [As(V)]aq *	% [As]aq
1	0.08	9.1 ± 0.4	12.8 ± 2.3	21.9 ± 2.9
2	5.50	0.0 ± 0.4	10.6 ± 1.4	10.6 ± 1.3
3	22.25	0.0 ± 0.4	14.6 ± 2.4	14.6 ± 2.4
4	30.67	0.0 ± 0.4	22.7 ± 2.5	22.7 ± 2.5
5	47.25	0.0 ± 0.4	21.1 ± 4.4	21.1 ± 4.4
6	54.67	0.0 ± 0.4	25.5 ± 2.8	25.5 ± 2.8

*** %[As(V)]aq = %[As]aq - %[As(III)]aq**

Percent of initial total arsenic in the combined solid and aqueous phases in the form of arsenite (%[As(III)]tot) and arsenate (% [As(V)]tot) as a function of time in the presence of amorphous manganese oxyhydroxides. Experimental conditions: 0.7M NaCl in a closed system purged with nitrogen. Initial pH was between 7 and 8. TOTAL [As] = 100 ± 10 ppb

SAMPLE	TIME (hr)	% [As(III)]tot	% [As(V)]tot *
1	0.08	24 ± 21	76 ± 24
2	5.50	15 ± 12	85 ± 18
3	22.25	19 ± 10	81 ± 16
4	30.67	19 ± 13	81 ± 18
5	47.25	0 ± 0	100 ± 14
6	54.67	18 ± 11	82 ± 17

*** % [As(V)]tot = 100 - % [As(III)]tot**