

Behavior of Arsenic in hydro-geochemical environment: A short review

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Abstract

Recently, the awareness on the arsenic contamination in the environment including in water and some agricultural crop has become a one of most important issues among researchers, intellectuals and even among the general public of Sri Lanka. Although, the route cause for the arsenic contamination in this context is still not clear, it is an important to take precautionary actions to mitigate the effect of this environmental problem. However, even it is so important the geohydrochemical behavior of arsenic specially, how arsenic comes to water system and under which conditions it happens, what is the behavior of arsenic and which chemical forms of arsenic is toxic are still not well understood by many of Sri Lankans. Therefore the goal of common questions to which answers are this brief article is to provide a description of basic processes that affect arsenic occurrence and transport by providing some basic scientific information on arsenic geohydrochemical processes.

Possible sources of arsenic

The average concentration of Arsenic in the Earth's crust is 1.8mg g^{-1} and in shales and alluvium, arsenic is commonly present at five times of this level (Mason, 1966). Occasionally, elemental arsenic is found

in hydrothermal veins, but more commonly it is found either in primary arsenic bearing minerals or adsorbed onto various mineral phases such as iron and aluminium oxides, clays and iron sulphides, which can be considered as the nature's most important stores of arsenic. The most common primary arsenic minerals are Arsenic (As), Orpiment (As_2S_3), Realgar (AsS), Arsenopyrite (FeAsS) and Scorodite ($\text{FeAsO}_4 \times 2\text{H}_2\text{O}$) (Mason and Berry, 1978). Other arsenic-bearing minerals include Enargite (Cu_3AsS_4), Cobaltite (CoAsS), Niccolite (NiAs), Arsenolite (As_2O_3) and Claudetite (As_2O_3). However, these different chemical forms of arsenic are mostly occurring as accessory minerals in ore deposits (Mason and Berry, 1978), and are not known to be responsible for any cases of arsenic pollution. The most important minerals that incorporate arsenic are iron oxides and the common sulphide, pyrite (FeS_2). A wide variety of iron oxides and hydroxides commonly referred as iron oxyhydroxide are occurring in the nature, some with indistinct structures or overlapping chemical compositions. However the sediments of natural aquatic systems are containing various iron oxyhydroxide and some of common ones are amorphous iron oxides (ferrihydrite), goethite ($\alpha\text{-FeOOH}$), hematite ($\alpha\text{-Fe}_2\text{O}_3$) and magnetite (Fe_3O_4). With the exception of magnetite, which contains both Fe(II) and Fe(III), these minerals contain Fe(III) and hence they are most stable under more oxidizing conditions. In general, amorphous iron oxides is the dominant mineral type in recent sediments, and with passing time amorphous ferrihydrite may be replaced by more crystalline forms such as goethite and hematite, which are more stable, have smaller surface areas, and therefore lower adsorption capacities comparing with its original form of ferrihydrite. Amorphous iron oxides also have solubility up to five orders of magnitude greater than more

crystalline forms (Whittemore and Langmuir, 1975). Thus, the amorphous forms can be expected to represent the behavior of iron oxides in Holocene aquifers containing reducing water, while goethite and hematite better represent the behavior of older and oxic aquifers. Manganese and aluminium oxides behave in a similar way to iron oxides, but differ in their abundance and the strength of their attraction for arsenic. Manganese oxides are more easily reduced than iron oxides, and hence their sorbed load may be released and re-adsorbed by iron oxides. In this manner, iron oxides commonly have a controlling influence on arsenic mobility.

Arsenic speciation in groundwater and sediments

The speciation of arsenic is very important in its both toxicity and mobility in groundwater, and its removal in water treatment. In water, arsenic occurs in one of two main forms: a reduced form, arsenite, with a valence of +3; and an oxidized form, arsenate, with a valence of +5. These are often referred to simply by their oxidation states as As(III) and As(V). As(III) is more toxic to many biological systems than As(V). Arsenic also exists in the As^0 and As^{-3} states, but these are of little importance in natural waters (Cullen and Reimer, 1989). Arsenic can also exist in many organic forms, of which the most common are monomethylated acids (MMA) and dimethylated acids (DMA), both of which exist as As(III) and As(V) forms. However, the organic form of arsenic occurs at trace levels in natural waters, but they are important in plant and animal metabolism (Akter et al., 2005). Under oxidizing conditions, arsenic usually exists as one of a series of pentavalent (arsenate) forms such as $H_3AsO_4^0$, $H_2AsO_4^-$, $HAsO_4^{2-}$, AsO_4^{3-} ,

depending on the Eh and pH conditions (Ferguson and Gavis, 1972). The charge on the arsenate ion controls how it behaves in groundwater and water treatment systems, because negatively charged ions are readily adsorbed onto the surfaces of metal oxides, with the strength of sorption depending greatly on the pH. The variation of the proportion of these ions is shown in Figure -1, which allows the stable species in groundwater to be predicted. The uncharged H_3AsO_4^0 ion is only important in very acid waters, which are rare naturally, but are encountered in acid mine drainage. However, in the range of near neutral pH conditions (pH 6.5–8.5), both H_2AsO_4^- and HAsO_4^{2-} are likely to be present.

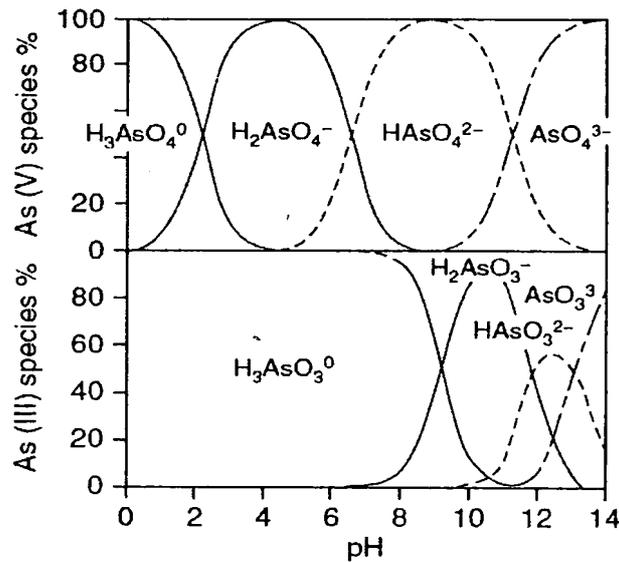


Figure 1: Distribution of inorganic arsenic species As (V) and As(III) as a function of pH at ionic strength of 0.04m (Meng et al., 2000)

pH -pe diagrams for arsenic

In order to understand the speciation of arsenic under the surface condition and subsurface condition where various pH and redox conditions are available, the pE-pH diagrams play a vital role. At

underground condition most of aquifers and sediment anoxic conditions are presence and therefore arsenic species are present in reduced form. However not only the redox condition but also the pH value is important to decide which species of arsenic is available. Thermodynamic data can be used to develop the diagrams for arsenic, shown in Figures 2 and Figure 3 that summarize the predominance fields for aqueous species and the mineral stability fields, respectively.

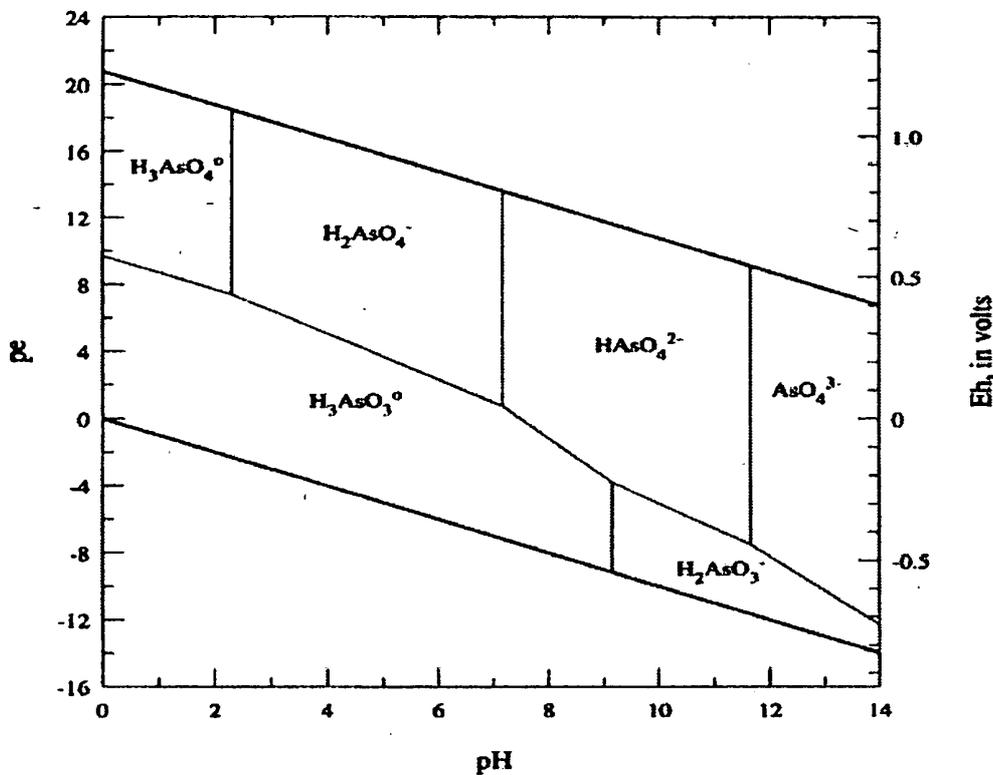


Figure 2: pE – pH diagram for predominant aqueous species of arsenic at equilibrium and 298.15 K and 1 atmosphere pressure (adapted from Nordstrom & Archer, 2003)

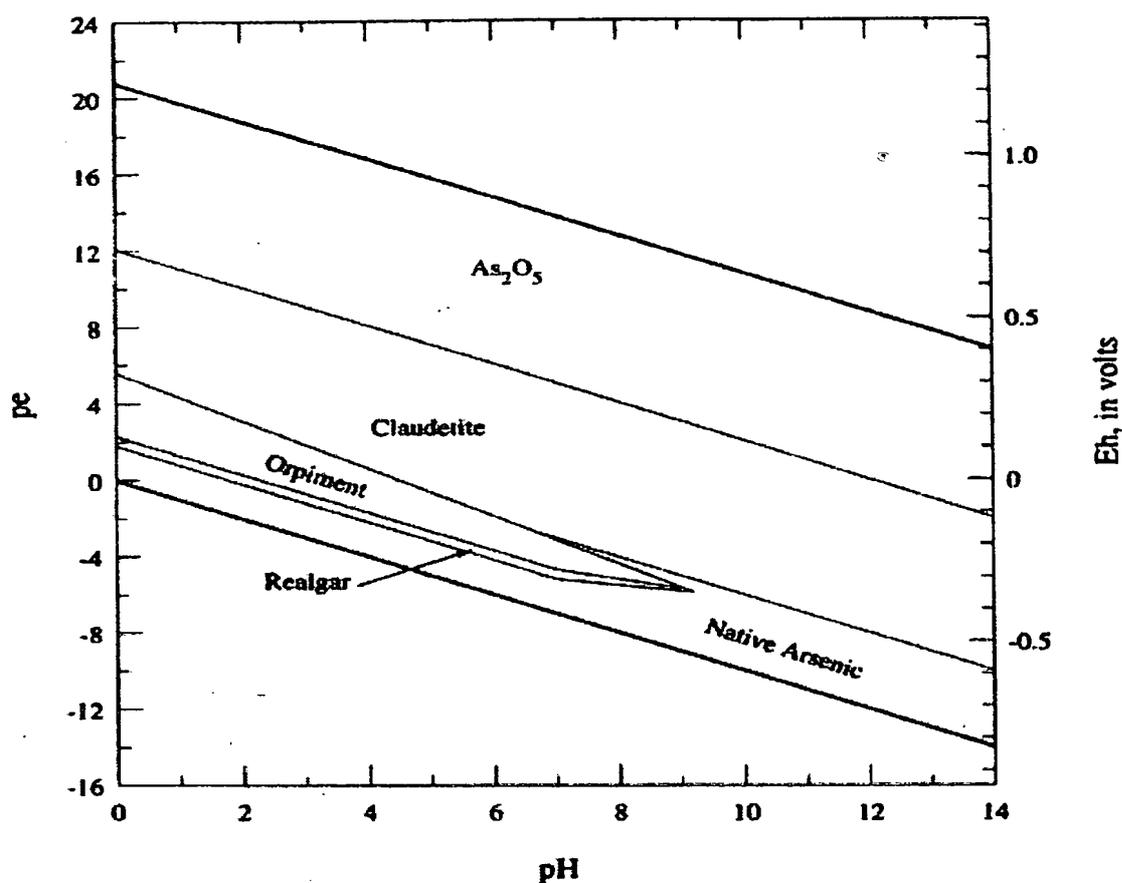


Figure 3: Pe-pH diagram for equilibrium mineral stabilities in the As-OS-H₂O system at 298.15K and 1.00 atm pressure. Total dissolved sulfur- 10^{-4} M (adapted from Nordstrom & Archer, 2003)

These diagrams also help to focus the discussion on environmentally relevant geochemical processes. The predominance area diagram of Figure 2 shows that, under oxidizing conditions, arsenate hydrolyzes to four possible species for the range of pH encountered in surface and ground waters, although the fully dissociated arsenate ion would be rare because very few waters reach a pH greater than 11.5. Under reducing conditions, the fully protonated arsenite species is predominant over a wide range of pH and because it is not ionized and adsorbs less strongly than arsenate species, dissolved arsenite tends to be much more soluble than arsenate. Hence, reducing conditions

usually lead to increased concentrations of arsenic in ground waters provided that arsenic is available in the aquifer or the sediments.

In reducing water, arsenic is present as the trivalent (arsenite) form which undergoes a similar series of dissociation reactions from H_3AsO_3^0 to H_2AsO_3^- and HAsO_3^{2-} . The important difference between arsenite and arsenate is that the uncharged ion (H_3AsO_3^0) dominates when the pH is less than 9.2, and limits the extent to which arsenite is adsorbed. While Eh–pH relationships as shown in Figure 3, help in understanding the qualitative relationships between arsenic species, quantitative use is generally not recommended because of the difficulty of making accurate and representative measurements of Eh (e.g. Langmuir, 1997), and because the phase boundaries depend on the concentrations of other components in the water.

Arsine (III) is estimated to be at the same and pH conditions as the formation of hydrogen, i.e. the lower limits for water. Hence, it does not show on this diagram. Figure 3 shows the sequence of stable minerals from fully oxidized arsenic pentoxide to fully reduced native arsenic in the presence of total dissolved sulfide. Native arsenic has a narrow stability field only under the strongest reducing conditions, consistent with field observations except that in the field it seems to form at higher temperatures than 25°C. No mineral corresponds with As(V) oxide because it is extremely soluble (about 40% of solution (Nordstrom & Archer, 2003) and the addition of the type of divalent cations commonly found in surface and ground waters would promote the precipitation of metal arsenates that are less soluble than the

pentoxide. e.g. calcium arsenate precipitation (Nishimura and Robins, 1998).

There are four major types of water sources that may mostly with dissolved Arsenic species. These types are such as

1. **Near-neutral, strongly reducing (NNR)** water, rich in bicarbonate, iron and/or manganese, and low in oxidized species such as nitrate and sulphate. Near-neutral reducing waters are dominated by As(III). These waters are associated with the **reductive-dissolution (RD)** mobilization mechanism.
2. **Alkali-oxic (AO)** waters, with $\text{pH} \geq 8.0$, containing dissolved oxygen and/or nitrate and sulphate, and low in iron and manganese. Alkali-oxic waters are dominated by As(V). These waters are associated with the **alkali-desorption (AD)** mobilization mechanism.
3. **Acid-sulphate (AS)** waters, with slightly to strongly acid ($\text{pH} < 1-6$), high sulphate concentrations, and often, high iron concentrations. Acid-sulphate waters are also dominated by As(V). These waters are associated with the **sulphide-oxidation (SO)** mobilization mechanism.
4. **Geothermal (GT)** waters, distinguished primarily by a temperature well above the background, and usually also correlation of arsenic with chloride.

However arsenic in water which was originated by any of above source may present in soluble form can be absorbed to precipitated solids or on the surface of solid minerals or clay particles. Similarly depending upon the conditions available the sorbed arsenic may desorb to aqueous medium and this process is leading for the arsenic

availability in ground water. In addition to the dissolution which transports sorbed species to liquid phase, reductive dissolution can transfer structural arsenic to the liquid phase after reduction of structural As(V) in arsenic containing minerals. Sorption can be divided into three processes: *adsorption* where a chemical adheres to the solid surface; *absorption* where the chemical is drawn into the solid; and *ion exchange* where the chemical replaces another already on the solid surface (Appelo and Postma, 1996). Because adsorption is related to edge and surface properties, the surface area, surface charge crystallinity of mineral are very important factors. (Langmuir, 1997). The surface charge of mineral or clay accounts for their pH dependency, because at low pH the surfaces are positively charged, but become negatively charged at high pH. Thus negatively charged arsenite or arsenate ions can be adsorbed only when the mineral surface is positively charged, as described by the zero point of charge (ZPC), the pH at the point of transition from positive to negative surface charge. The capacity for adsorption can then be expressed in terms of the number of surface sites that can hold charged ions. Iron (Hydro)oxides have been identified to be a most available and most important earth materials that can absorb arsenic at both As(III) and As(V) form. Goethite (αFeOOH) and ferrihydroxide ($\text{Fe}(\text{OH})_3$) are ubiquitous in most of sediments and these minerals have attraction to adsorbed both valence state of Arsenic.

Adsorption of arsenite and arsenate, as single anion solutions, on ferrihydrite and goethite as a function of increasing pH has been thoroughly studied by Dixit and Hering (2003) some of findings are summarized in Figure 4. Adsorption of arsenite (As^{3+}) on both

ferrihydrate and goethite is virtually constant between pH 5.0 and 9.0, and at all initial concentrations. By contrast, adsorption of arsenate (As^{5+}) onto minerals varies with both pH and initial concentration. At high initial concentrations of arsenate, adsorption on both ferrihydrate and goethite declines continuously from pH 4 to pH 10. However, at lower initial concentrations, adsorption of arsenate tends to be uniform on ferrihydrate up to pH 8.0, and on goethite up to pH 9.0.

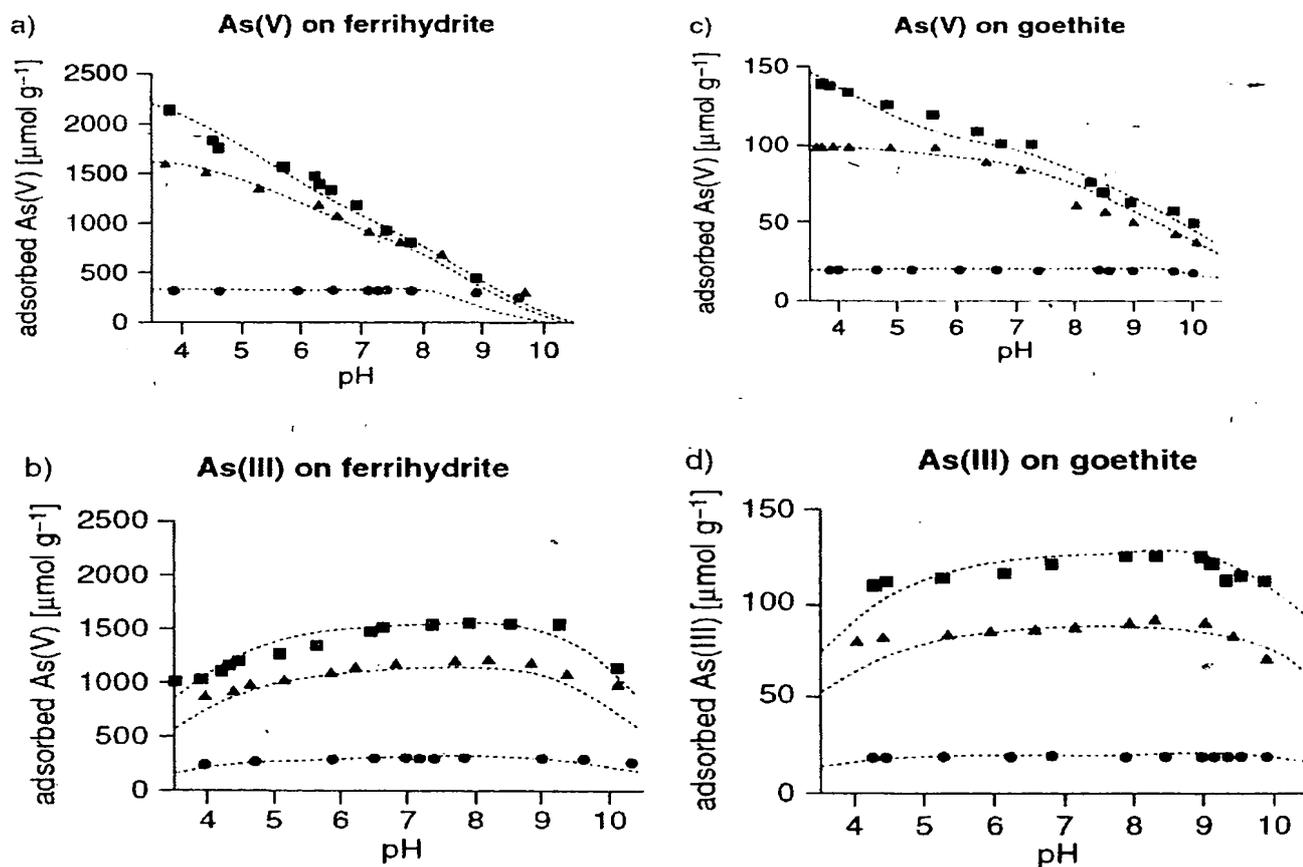


Figure 4 Adsorption of arsenic onto ferrihydrate and goethite (a) As(v) on ferrihydrate; (b) As(III)on ferrihydrate; (c) As(V) on goethite (d). As(III) on goethite. Experiments have been conducted with 0.03gL⁻¹of ferrihydrate and 0.5gL⁻¹of goethite. Symbols represent arsenic concentrations:(■) 100 μM (750 μg L⁻¹); (▲)50 μM (375 μg L⁻¹); and (●)10 μM (75 μg L⁻¹). The solutions contained 0.01M NaClO₄. The lines are best-fit surface complexation models to experimental data.

Contrary to common misconceptions, Dixit and Hering (2003) demonstrated that As(III) is strongly adsorbed and more mobile in neutral and weakly alkaline conditions. Since As(III) and As(V) are sorbed to similar extents between pH 6 and pH 9 on ferrihydrite and goethite, it follows that microbial reduction of As(V) to As(III) will not increase its mobility. Although ferrihydrite has a much larger surface area than goethite, and therefore a greater sorption capacity per unit weight, Dixit and Hering (2003) further noted that transformation of ferrihydrite to goethite does not decrease the adsorption affinity for As(V) and, if anything, appears to increase it. The sorption of arsenic species has been extensively studied for other major iron (hydro)oxides such as hematite, magnetite. Different iron minerals have various pH values at which the maximum sorption capacity was indicated (Giménez et al., 2007). However, not like in the laboratory level experiments, at subsurface conditions there are several types of dissolved ions and those can simultaneously be absorbed or competitively be absorbed on mineral surfaces.

Competitive absorption & desorption

Negatively charged ions such as phosphate, sulphate, silica and carbonate potentially compete with arsenic for adsorption sites. Most attention has been given to phosphate, which certainly affects the behavior of arsenic. Despite their opposed toxic and life-supporting natures, the chemistries of arsenate and phosphate have much in common. Jain and Loeppert (2000) found that phosphate reduces As(III) adsorption onto ferrihydrite at low pH, but that the effect become insignificant at pH 9.0. (Figure 5) At pH 7.0–8.0, conditions typical of

waters in which arsenite is dominant, the sorbed load could be reduced by 20%. The effect of phosphate on As(V) adsorption follows the opposite trend, where adsorption decreases rapidly above about pH 6.0, and by 60% at pH 9.0. However, these experiments were conducted at much higher concentrations than are normal in nature, and so the effect will be small in most practical situations. insignificant at pH 9.0 (Figure 5).

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silica will have the greatest effect on As(V) mobilisation in sodic groundwater, but may also be relevant to mobilising As(III). Despite some suggestions that carbonate promotes desorption of arsenic, there is currently little field evidence to support this idea.

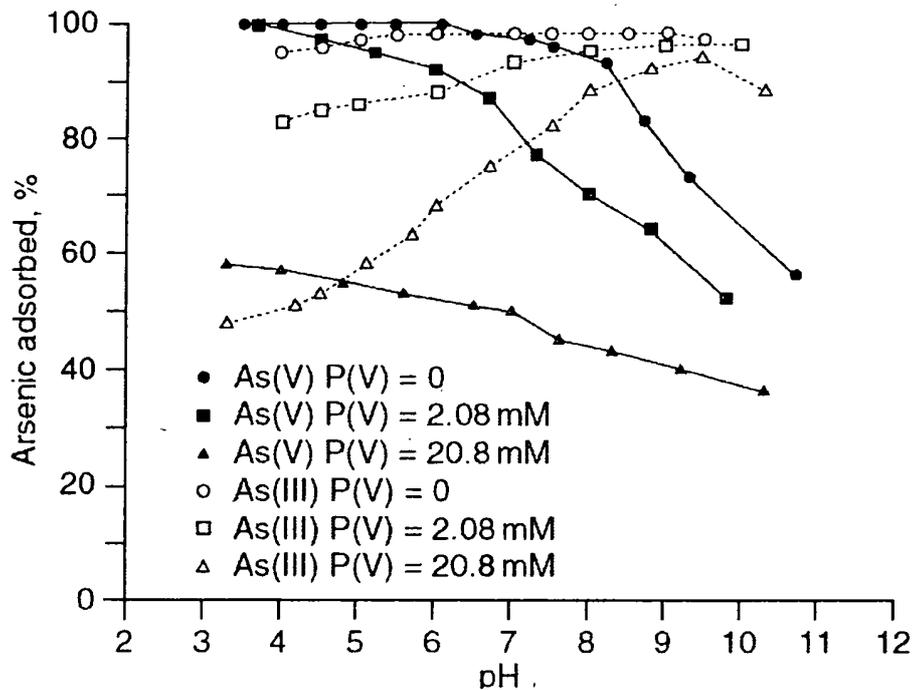


Figure 5: Influence of phosphate on adsorption of arsenic onto ferrihydrite. Experiments conducted in solutions containing 2.08 mM (156 mg L^{-1}) of As(III) or As(V) and with an ionic strength of 0.1 M and 2 g L^{-1} of ferrihydrite. Phosphate concentrations were 0, 2.08mM (198 mg L^{-1}) or 20.8 mM (1980 mg L^{-1})(source: Stollenwerk, K.G. (2003))

Effect of Natural Organic matter on Arsenic

Natural organic matter are ubiquitous in the natural environments and those are the product of long term biological activities and furthermore non-biodegradable. The effect of NOM on arsenic adsorption depends on the oxidation state of arsenic, the composition of the NOM, and the type of iron mineral present. Natural organic matter (NOM) acts in three ways to influence the behavior of arsenic in the presence of iron and

manganese oxides. First, organic matter is a potential sorbent; second dissolved organic carbon (DOC) competes for sorption sites; and third high DOC can cause the oxide minerals to which arsenic is adsorbed to dissolve. Since high concentrations of DOC are more common in reducing groundwaters, where As(III) is dominant, the interaction of DOC with As(V) tends to be less important. The effect of NOM on arsenic adsorption depends on the oxidation state of arsenic, the composition of the NOM, and the type of iron mineral present. Grafe et al. (2001, 2002) simulated the effects of DOC on As sorption on goethite and ferrihydrite using solutions of humic acid (HA), fulvic acid (FA) and citric acid (CA), as shown in Figure-6. The influence of dissolved organic carbon DOC is greater, but also more complex, on goethite than ferrihydrite, and the effects depend strongly on the specific iron phase, the form of arsenic and nature of the DOC. When ferrihydrite is the sorbent, the trend of As(III) adsorption with increasing pH shown is reduced by citric and fulvic acids across the pH ranges 3–7 and 8–11, but not at all by humic acid. However, As(V) adsorption on ferrihydrite is not affected by humic or fulvic acids at any pH, but is reduced by citric acid below pH 6.0 (Grafe et al., 2002). When goethite is the sorbent, As(V) adsorption is reduced by a small to negligible degree at all pH values. As(III) adsorption on goethite is reduced by all three acids in the order of $CA > HA > FA$.

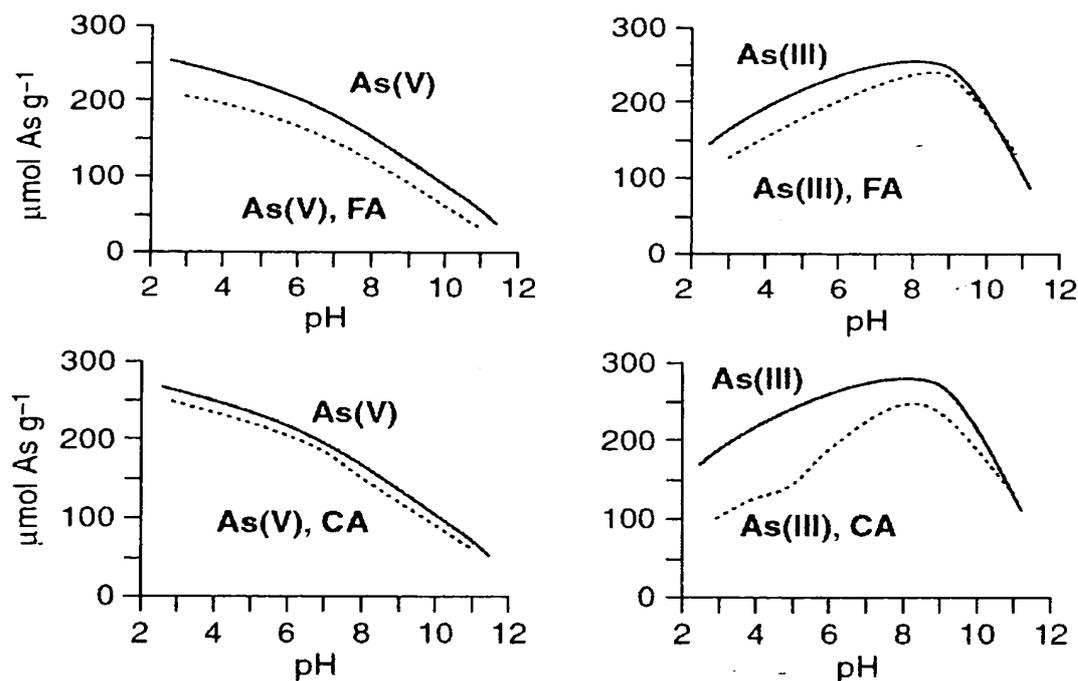


Figure 6: Influence of dissolved organic carbon (DOC) on adsorption of arsenic onto (a) ferrihydrite and (b) goethite. The dashed lines illustrate the effects of different forms of dissolved organic matter (HA, humic acid; FA, fulvic acid; CA, citric acid) on the adsorption of As(III) and As(V) onto both ferrihydrite and goethite; the solid line represents the base case of no DOC added. Points represent experimental measurements. All solutions contained 1.0 mM of DOC and 1.0 mM (75 mg L⁻¹) of As(III) or As(V).

The reductions are pH- dependent: the effect of citric acid becomes negligible at pH 8, for fulvic acid at pH 9, and for humic acid only at pH 10. Humic acid significantly reduces As(III) adsorption on goethite across the full range of pH encountered in normal groundwater. The effect of organic matter on other oxides may differ, and hence correlations with DOC measurements should be treated with caution. Stollenwerk (2003), citing earlier studies, reported that fulvic acid reduces adsorption of As(V) on Al oxides at pH values <7.

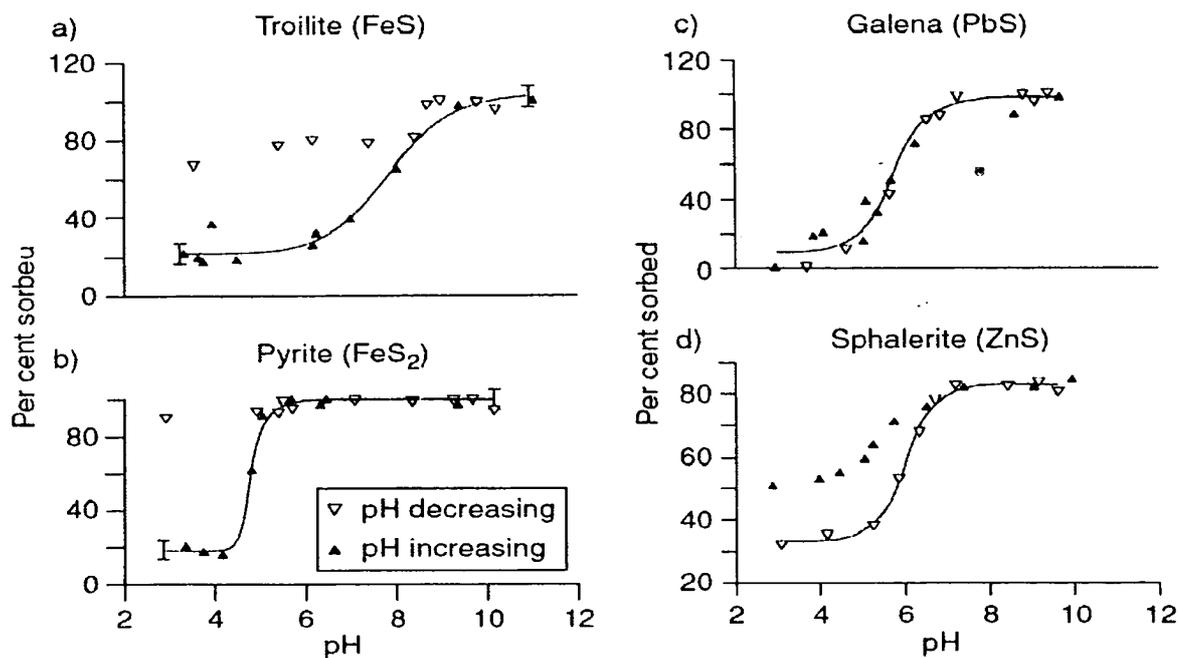


Figure 7: Adsorption of arsenic on sulphide minerals: (a) Troilite; (b) Pyrite; (c) Galena; (d) Sphalerite. All experiments were conducted with 50 μM ($3750 \mu\text{g L}^{-1}$) As, 1 g L^{-1} of sulphide and a background electrolyte of 0.01 mM NaNO_3 . The lines are sigmoidal fits to experimental data. *Source:* Bostick and Fendorf (2003) and Bostick et al. (2003)

In addition to iron oxihydroxides, sulphur compounds also have attraction to arsenic compounds and hence arsenic may be adsorbed on the iron sulphide minerals pyrite (FeS_2), troilite (FeS) and mackinawite (FeS) and, although they are less abundant, other sulphide minerals such as sphalerite (ZnS) and galena (PbS). Adsorption of arsenite onto pyrite and troilite has been studied thoroughly (Bostick and Fendorf, 2003). As shown in Figure 7, where adsorption was minimal at low pH and strongest at $\text{pH} > 5-6$, involving the formation of an “ FeAsS ” like precipitate. Because both Fe and S are incorporated into the precipitate, the process changes the nature of the mineral surface, and hence its ability to retain arsenic. Similar experiments on galena and sphalerite found that arsenite is adsorbed at $\text{pH} > 5$ and $\text{pH} > 4.5$

respectively (Bostick et al., 2003). In all cases, increasing sulphide concentrations significantly reduced adsorption of arsenite. Adsorption of arsenate was not considered because it is not normally stable in groundwater in which sulphides are stable and capable of adsorbing solutes. Wolthers et al. (2005) found that adsorption of As(III) on disordered mackinawite (tetragonal FeS), which they consider to be more representative of the Fe(II) monosulphides in natural environments, was not strongly pH-dependent in the pH range 5.5–8.5, but had a maximum of 23% at pH 7.2. However, they found that adsorption of As(V) on mackinawite was strongly pH dependent, rising rapidly to a maximum at pH 7.4 and then falling even more rapidly to a negligible level at pH 8.5. Kirk et al. (2004), McArthur et al. (2004) and O'Day et al. (2004) all recognized that the mobilization and immobilization of arsenic in reducing ground waters are determined by the balance between the quantities of Fe, S and organic carbon. Initially, an excess of organic carbon is required to reduce Fe(III) oxides completely and release the sorbed As to solution, whereafter the availability of sulphur controls the sequestration of arsenic by sulphide minerals.

Effect of microbial activity on arsenic

Iron oxides can adsorb both As(III) and As(V). Alluvial sediments probably acquire most arsenic by adsorbing As(V) in oxic environments, where As(III) is not stable. The conventional view of arsenic mobilized by reductive dissolution is that (solid) Fe(III) is reduced to release aqueous Fe(II) and As(V) into solution. Organisms such as *Shewanella alga* can increase the rate of Fe(III) reduction, accelerating the release of As(V) into solution, where other organisms could

undertake its reduction to As(III). Attention has focused on whether the transformation of As(V) in the solid phase to dissolved As(III) is a coupled process, and whether microbes can decouple reduction of the iron and arsenic. Zobrist et al. (2000) found that *Sulfurospirillum barnesii* can reduce arsenate to arsenite, both in solution and when adsorbed on ferrihydrite. However, because of the variety of organisms that can perform both the iron-reducing task and the aqueous arsenic-reducing task, Inskeep et al. (2002) considered that prior reduction of Fe(III) oxides will be the most common pathway. Nonetheless, Oremland and Stolz (2003) argued that bacteria that reduce sorbed arsenate on the solid phase may be important in the Bengal Basin. However, as Dixit and Hering (2003) pointed out, arsenite is strongly adsorbed by Fe(III) oxides in near-neutral waters, and so As reduction is probably not the critical step. Oremland and Stolz (2005) proposed three mechanisms (Figure 8) by which bacteria might mobilize arsenic from Fe(III) oxides through the action of arsenate-resistant microbes (ARM) termed dissimilatory arsenate respiring prokaryotes (DARP). The ARMs may not actually gain energy through the release of arsenic, but metabolising arsenic allows them to cope with an As-rich environment. In the first mechanism, iron-reducing bacteria such as *Geobacter* reduce Fe(III) and release As(V) directly to solution where it is converted to As(III) by biotic or abiotic means. In the second mechanism, the DARP transforms As(V) to As(III) at the solid surface prior to its release. In the third mechanism, iron-reducing DARPs, such as *Sulfurospirillum barnesii*, directly release both Fe(II) and As(III). As Oremland and Stolz (2005) note, in nature, all three mechanisms may operate simultaneously. Ferric oxides and hydroxides are ubiquitous adsorbers of arsenic and other trace elements, but will

release this arsenic when they are reduced to the ferrous state and dissolve. Hence, the mobility of arsenic depends in large part on the stability of iron oxides. Actually this mechanism is distinct from those involving desorption of arsenic from solid mineral surfaces and the redox reactions controlling iron in natural waters have been studied in great detail and the process of iron reduction by organic matter may be represented by the following equation (Hem, 1977; Langmuir, 1997)



This reaction requires the operation of a strong redox driver, usually sedimentary organic matter, which consumes all available sources of oxygen. McArthur et al. (2001) proposed that the dominant redox driver in alluvial aquifers is the microbial mineralization of buried vegetation that accumulated as peat or organic-rich mud in abandoned channels and overbank environments.

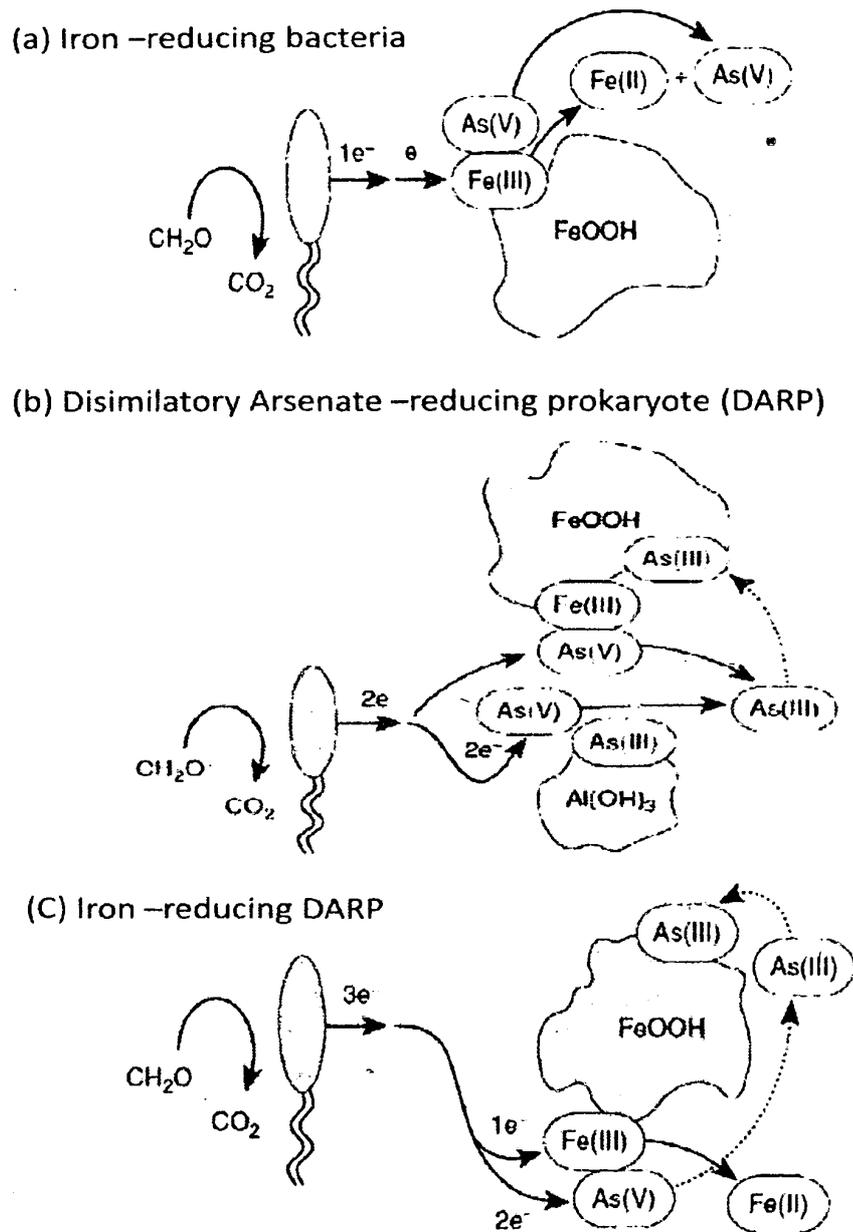


Figure 8: Three possible mechanisms of microbially mediated arsenic mobilization in anoxic environments. All the reactions are driven by oxidation of organic matter, where microbes use either Fe(III) or As(V) as the terminal electron acceptor. Adapted from Oremland and Stolz (2005)

Although the above basic phenomena plays a major role for the arsenic concentrations in ground water, the arsenic concentration in surface water and agricultural lands in the soil solution may vary from day to day as water in fields stagnates or is aerated by wind or

rain-drops, is evaporated, absorbed by soil and plants, and replenished by irrigation or rainfall. These fluctuations between aerobic and anaerobic conditions and variations in pH may be accompanied by transformations in the As species which also influence plant uptake. Similar fluctuations may occur in response to diurnal variations in respiration rate of algae living in the water and on the soil surface. Studies are further needed to quantify these fluctuations, which should also be considered in soil sampling and assessing phytotoxicity.

Conclusions

It can be noted that the availability of arsenic in the local environment depend on the severity of their expose or release from sources, the quantities of arsenic surface or subsurface soil , sediment or water may vary according to chemical speciation and the environmental factors such as pH, redox condition, type of mineral solids available and the factors that change the mineral water interfacial conditions. Similarly, other components dissolved in water and microbial activities are also significantly affect the solubility and sorption of arsenic species onto natural minerals. However the discussed factors have been thoroughly studied and scientifically proved using laboratory and field level evidences. However laboratory experimental results might be effective in somewhat differently in the real situations due to the combining effect of many of factors and therefore use of relevant models are necessary to predict the situations in the real conditions.

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