Arsonic In The Soil Environment: A Soil Chemistry Review

Michael Aide and Donn Beighley* and David Dunn**

Southeast Missouri State University
E-mail: mtaide@semo.edu
Fisher Delta Research Center
University Missouri

Abstract

Arsenic in the soil environment has gained renewed interest because of the emerging acknowledgement that arsenic accumulation in rice is a global concern. This review reflects the current state of research being provided to the understanding of arsenic in the soil environment with an emphasis on arsenic uptake in rice. Arsenic speciation and the chemical reactions associated with arsenite, arsenate and methylated-arsenic species is of prime importance. The chemistry of soil arsenic is both abiotic and biotic and its chemistry is complicated by (i) oxidation-reduction processes, (ii) acid-base reactions, (iii) adsorption-precipitation reactions, and (iv) plant uptake and accumulation. Ultimately plant genetics and emerging irrigation regimes, predicated on our collective understanding of the role soil chemistry, provide the opportunity to alter agriculture production to safeguard the global food supply.

Keywords: arsenate, arsenite, methylarsenic acid, rice, water quality

Arsenic In Rice Production Soils: A Soil Chemistry Review:

Introduction

Arsenic (As), has atomic number 33 in Group V of the Periodic Table and it is a metalloid elementhaving an [Ar] 3d^{10}4s^{2}p^{3} electronic configuration. Electron removal readily produces two stable valence states: (i) As(III) or arsenite having an electronic configuration [Ar] 3d^{10}4s^{2}and (ii) As(V) or arsenatehaving an electronic configuration [Ar] 3d^{10}. Arsenic and phosphorus are both Group V elements and share similarities in their soil chemistry. As an example, the covalent atomic radius of phosphorus is 106 picometers and arsenic is 119 picometers (Greenwood and Earnshaw, 1984).
The World Health Organization has established a provisional maximum tolerable daily intake of inorganic arsenic at 2 µg As/kg body weight (Tuli et al., 2010). Inorganic arsenic intake may lead to gastrointestinal, cardiovascular and central nervous symptoms, bone marrow depression, haemolysis, hepatomegaly, melanosis, polyneuropathy, and encephalopathy. Inorganic As is a non-threshold class 1 carcinogen (Tuli et al., 2010). The key sources of dietary arsenic intake include drinking water and selected plant materials derived from their cultivation in soils having enhanced arsenic uptake. World Health Organization (WHO) and the United States Environmental Protection Agency (USEPA) drinking water limits for arsenic are identical at 10 µg As/liter.

**Arsenic in the Pristine Environment**

Naturally occurring soil arsenic concentrations may be attributed to mineral weathering of As-bearing minerals and the subsequent migration of arsenic-bearing geologic and pedogenic pathways. Soils are considered open thermodynamic systems and are available to exchange mass and energy with their surroundings. Thus, earth and soil processes involving atmospheric deposition, the hydrologic cycle, plant and soil organism biocycling, and soil chemical processes all function to disperse and also intensify arsenic concentrations. Most streams and lakes in non-impacted regions of the USA have arsenic concentrations less than 1 µg dissolved As/liter. Similarly, precipitation in non-impacted areas is commonly less than 1 µg dissolved As/liter, thus precipitation in non-impacted areas in not a major arsenic source.

Commonly occurring As-bearing minerals include: arsenopyrite (FeAsS), cobalite ((Co,Fe)AsS), enargite (Cu₃AsS₄), erythrite(Co₃(AsO₄)₅ ⋅8H₂O), orpiment (As₂S₃), proustite (Ag₃AsS₃), realgar (AsS), and tennantite (Cu₁₂As₄S₁₃). Minor arsenate minerals include: annabergite (Ni₃(AsO₄)₂⋅8H₂O), ausbite (CaZn(AsO₄)(OH), clinoclase (Cu₃(AsO₄)(OH)₃, conichalcite (Cu₃(AsO₄)(OH), cornubite (Cu₅AsO₄)₂(OH)₄, and mimetite (Pb₆(AsO₄)₃Cl). Arsenide minerals include: loellingite (FeAs₂), safflorite (CoAs), niccolite (NiAs), and rammelsbergite (NiAs₂). Mineral weathering is a complex set of geologic and pedogenic processes influenced by precipitation, temperature, soil drainage class, and biotic processes involving microbial and plant populations.

Arsenopyrite is commonly accepted as the most abundant arsenic mineral. Pyrite (FeS₂), galena (PbS), sphalerite (Zn,FeS), marcasite (FeS₂) and chalcopyrite (Cu,FeS₂) are commonly known to contain arsenic as an impurity. Pyrite oxidation has received significant research attention because of its occurrence in mine tailings and subsequent creation of acid mine drainage. The overall stoichiometric oxidation of pyrite overall may be written as:

$$\text{FeS}_2 + 3.75 \text{O}_2 + 4 \text{H}_2\text{O} = \text{Fe(OH)}_3 + \text{H}_3\text{AsO}_4 + \text{H}_2\text{SO}_4.$$  

Pyrite oxidation may be an entirely abiotic process; however the reaction rates are substantially greater if mediated by *Thiobacillus ferrooxidans*, *Thiobacillus thiooxidans*, and *Leptosprillum ferrooxidans* (Dorofeev et al., 1990; Harrington et al., 1998; Zeman et al., 1995).
The oxidation of pyrite may also be accelerated by nitrates and associated prokaryotic organisms (Appelo and Postma, 1993):

$$10\text{FeS}_2 + 30\text{NO}_3^- + 20\text{H}_2\text{O} = \text{Fe(OH)}_3 + \text{H}_3\text{AsO}_4 + \text{H}_2\text{SO}_4.$$

The stoichiometric oxidation of arsenopyrite may be expressed as:

$$\text{FeAsS} + 3.5\text{O}_2 + 4\text{H}_2\text{O} = \text{Fe(OH)}_3 + \text{H}_3\text{AsO}_4 + \text{H}_2\text{AsO}_4.$$

It is also important that arsenic sulfite ($\text{As}_2\text{O}_3$) may abiotically form in non-thermal waters.

Argillaceous sediments generally have greater arsenic concentrations (trace to 13 mg As/kg) than other sediment types (Kabata-Pendias, 2001). Arsenic surface soil horizon concentrations vary from 0.1 to 67 mg As / kg, with a geometric mean of 5.8 mg As/kg, with much of the variation attributed to soil order or parent material inheritance (Heitkemper et al., 2009; Kabata-Pendias, 2011). Pettry and Switzer (2001) surveyed parent materials and more than 200 soils in the State of Mississippi, observing parent material arsenic concentrations spanning from 1.8 mg As/kg in the Wilcox Formation to 33.8 mg As/kg in the Winona Formation. Soil arsenic levels ranged from 0.26 to 24.4 mg As/kg. Chen et al. (2001) investigated 448 Florida soils for baseline assessment of arsenic. They observed for undisturbed soils a baseline of 6.2 mg As/kg and a baseline of 7.3 mg As/kg for disturbed soils. Chen et al. (2008) observed arsenic placement in California soils as a result of micronutrient fertilizer placement. They documented that arsenic was correlated with P and Zn fertilization in one subregion and correlation of arsenic with Zn in another subregion. In Missouri, Aide et al. (2013) discussed soil arsenic concentrations in 22 soil profiles having no history of arsenic contamination and reported that the surface horizons exhibited arsenic concentrations ranging from 2 to 12 mg As/kg. Subsurface horizons, particularly argillic horizons, possess substantially greater arsenic concentrations, ranging from 10 to 30 mg As/kg. Most of the examined soils exhibited significant As-Fe concentration correlations. As an example, the Alred series (Loamy-skeletal over clayey, siliceous, semiactive, mesicTypicPaleudalfs: very deep, well-drained soil formed in cherty hillslope sediments and the underlying clayey residuum) shows approximately 1 mg As / kg in the A horizon and appreciably greater arsenic abundances in the deeper argillic horizon. In an earlier study, Aide et al. (2005) demonstrated that arsenic was strongly associated with pedogenic Fe and Mn-bearing nodules in poorly-drained Missouri Alfisols developed on silty terraces.

**Anthropogenic Activities and Arsenic as a Contaminant**

Staed et al. (2009) surveyed soil lead (Pb) and arsenic concentrations in the Arkansas Ozark Highlands having a history of Pb-arsenate applications to control agricultural pests. These authors observed significant soil Pb-As concentration correlations with arsenic concentrations ranging from trace to approximately 20 mg As/kg. Menjoulet et al. (2009) investigated the arsenic runoff potential from Arkansas soils impacted by As-bearing poultry litter. During some rainfall events, flow weighted mean arsenic concentrations of the runoff waters exceeded maximum contaminant levels for drinking water. Lead arsenate (PbHASO_4) usage in Washington orchards substantially impacted soil arsenic concentrations, with appreciable arsenic migration below the near-surface soil horizons (Peryea, 1991). Phosphorus fertilization of these
Washington soils promoted arsenic availability (Davenport and Peryea, 1991). Cullen and Reimer (1989) noted the biotransformations of arsenic in sediments, documenting the production of organic arsenic and its potential threat to ground water. Anthropogenic arsenic activities that impact soil include: (i) deposition of coal-fired power plants particulates and aerosols, (ii) mining and smelting operations, (iii) application of As-bearing agricultural pesticides, (iv) poultry feed additives, and (v) irrigation with As-bearing water (Belefant-Miller and Beaty, 2007; Biswas et al., 2014; Chen, 2008b; Roussel et al., 2000; Staed et al., 2009; Tuli et al., 2010; Vicky-Singh 2010., Yan et al., 2008; Welch et al., 2000; Garcia-Manyes et al., 2002). Arsenite is considered to be 25 to 60 times more toxic than arsenate (Miretzky and Cirelli, 2010). In the Mid-South region of the United States, soil arsenic concentrations because of As-bearing herbicides previously applied to cotton (Gossypium hirsutum L.) is a concern. Huang and Kretzchmar (2010) developed a sequential selective extraction protocol for arsenic species in soil. Toor and Haggard (2009) observed that arsenic in poultry litter and granulates did not enhance arsenic availability when litter application rates were based on phosphorus soil test recommendations. Fox and Doner (2003) observed arsenic, molybdenum and vanadium in constructed wetlands. Unique to this study is that the surface of the constructed wetland was anoxic; whereas the deeper layers were suboxic to oxic. Total arsenic concentrations decreased with sediment depth in the constructed wetland, a feature more attributed to arsenic loss at the deeper depths than arsenic surface accumulation. In the deeper layers moderate reducing conditions favored Fe-oxyhydroxide dissolution, whereas in the more intensely reducing surface layers As-sulfides may be more stable. Radu et al. (2005) investigated water flow in Fe-oxide coated sand, noting that arsenite was more mobile at pH 4.5 than pH 9. These authors also observed that increasing pore water velocities resulted in greater arsenite mobility’s. Zhang and Selim (2007) investigated the likelihood that colloidal dispersion and the subsequent transport of arsenic adsorbed to a colloidal fraction in leachate waters was a substantial factor influencing arsenic mobility in soils. Mobilization of colloidal material and facilitated As(III)- colloidal Fe-oxide material was indicated. Roussel et al. (2000) investigated drainage waters from As-bearing mine tailings in France. Arsenic transport was 220 times greater as suspended particulate material (SPM) than dissolved arsenic. Selective sequential extractions revealed that approximately 78% of the arsenic in the SPM was associated with hydrous oxides, notably lepidocrocite. The authors cautioned that oxidation-reduction and pH changes during water transport from the mine tailings to surface water has the potential to strongly influence arsenic speciation. Ackermann et al. (2010) studied the bioavailability of German floodplain soils impacted by long term mining activities. Incubated sediments from the Mulde River were subjected to selective arsenic extractions, demonstrating that arsenic was primarily bound to ammonium oxalate Fe-oxyhydroxides (poorly crystalline Fe-oxyhydroxides) and that these Fe-oxyhydroxides were subject to change during cycling oxidation and reduction regimes. In point-of-fact, the frequency of the cyclic oxidation-reduction regimes was important in influencing arsenic and Fe equilibrium attainment. The authors did
confirm that frequent episodes promoted increased soluble arsenite concentrations. Variations in the arsenite and arsenate concentration ratios implied little equilibrium attainment because of both biotic and abiotic processes. Devesa-Ray et al. (2008) fractionated soils from Spain demonstrating that arsenic was strongly associated with Al-Fe oxides and the residual fractions. In the Freiberg/Saxony region, Schug et al. (1999) selected 159 soils for aqua-regia digestion and reported a mean recovery of 23.6 mg As/kg and having a range of 0.74 to 6690 mg As/kg. Jones et al. (1999) irrigation influences on soils in the Madison River Basin, Montana. Arsenic in the Madison River averaged 0.24 µM; however, the headwaters, near Yellowstone National Park, possessed 5 µM arsenic. Ground water near Yellowstone National Park averaged 0.67 µM arsenic. Soil receiving irrigation water; however, did not demonstrate enhanced arsenic solubility and selective sequential extractions did not demonstrate any differences in their arsenic fractionation. In the Indo-Gangetic Plains of northwestern India, Vicky-Singh et al. (2010) documented surface horizons of selected soils and surface and ground water for arsenic. They observed that tube-well water ranged from 5.33 to 17.27 µg/liter and soils ranges from 1.09 to 2.48 mg As/kg. Statistical analysis revealed that tube well water was correlated with soil arsenic concentrations, suggesting that irrigation impacted these soils.

**Soil Chemistry of Arsenic**

In the natural environment arsenic exists as two distinct chemically species: (i) arsenite as a hydroxyl species($H_3AsO_3$ –$H_2AsO_3^{1-}$) and (ii) arsenate as an oxyanian ($H_2AsO_4^{1-}$ or $HAsO_4^{2-}$). In soils, arsenite and arsenate (i) form complexes with soil organic matter, (ii) become adsorbed onto Al- and Fe-oxyhydroxides, (iii) become adsorbed onto phyllosilicates, (iv) leach or percolate to deeper soil horizons, and (v) undergo plant uptake (Bowell, 1994; Chen et al., 2008a; Fendorf et al., 2004; Fox and Doner, 2003; Roussel et al., 2000; Xu et al., 2009; Liu et al., 2005).

**Arsenate and Arsenate as Acids**

Given the high pKa1 for arsenite, the dominant species will be $H_3AsO_3$ (Goldberg, 2002):

\[
\begin{align*}
(1) \quad H_3AsO_3 & = H_2AsO_3^{1-} + H^+ \quad \text{pKa1 = 9.2} \\
\text{and} \quad H_2AsO_3^{1-} & = HAsO_3^{2-} + H^+ \quad \text{pKa2 = 12.7}.
\end{align*}
\]

Simulation of arsenite speciation with a total arsenic concentration of 0.01 mole/liter is displayed in Figure 1. Clearly, in acidic and neutral soil pH environments $H_3AsO_3$ will be the dominant species, with $H_2AsO_3^{1-}$ only a major species in strongly alkaline soil environments.
Figure 1. Simulation of species distribution involving arsonite [As(III)] across pH at an initial arsenic concentration of 0.01 mole/liter.

Arsenate will more readily behave as an acid, with approximately equal molar concentrations of $\text{H}_2\text{AsO}_4^-$ and $\text{HAsO}_4^{2-}$ near a pH of 7. The acid-base behavior of arsenate may be represented as:

(3) $\text{H}_3\text{AsO}_4 = \text{H}_2\text{AsO}_4^1^- + \text{H}^+$ \quad pK_a1 = 2.3
(4) $\text{H}_2\text{AsO}_4^- = \text{HAsO}_4^{2-} + \text{H}^+$ \quad pK_a2 = 6.8
(5) $\text{HAsO}_4^{2-} = \text{AsO}_4^{3-} + \text{H}^+$ \quad pK_a3 = 11.6.

Simulation of arsenate speciation with a total arsenic concentration of 0.01 mole/liter is displayed in Figure 2.

Figure 2. Simulation of species distribution involving arsenate [As(V)] across pH at an initial arsenic concentration of 0.01 mole/liter.
Dissociation constants for methylated species (referenced in Jackson and Miller, 2000) include monomethylarsonic acid (MMA or CH₃AsO(OH)₂ with pK₁ = 3.6 and pK₂ = 8.2) and dimethylarsenic acid (DMA or (CH₃)₂AsO(OH) with pK₁ = 6.2). The simulated pH-dependent speciation for MMA and DMA are displayed in Figure 3 and Figure 4, respectively.

**Figure 3.** Simulation of species distribution involving monomethylarsonic acid or MMA across pH at an initial arsenic concentration of 0.01 mole/liter.

**Figure 4.** Simulation of species distribution involving dimethylarsinic acid or DMA across pH at an initial arsenic concentration of 0.01 mole/liter.

**Arsenite and Arsenate as Oxidation and Reduction Species**

Half-cell equations are readily obtained from the standard free energies of formation (Wagman et al., 1982). For arsenate to arsenite reduction the following reactions are valid:
A predominance diagram (Figure 5) illustrates the relative stability regions for the various protonated arsenite and arsenate species. Oxic, suboxic and anoxic partitioning in the predominance diagram was patterned after Essington (2004).

The likelihood for arsenite formation in anoxic soil environments is more readily favored in increasingly acidic soil environments. The protonation-deprotonation pH transition for arsenate is near pH 7, showing that oxic soils support the arsenate species. Using Minteqa2/Prodefa2, a geochemical assessment model for environmental systems simulation (Allison et al., 1991), Aide (unpublished material) employed drainage water concentrations (unpublished data) for background concentrations of Ca\(^{2+}\), Mg\(^{2+}\), K\(^+\), Na\(^+\), NH\(_4\)\(^+\), NO\(_3\)\(^-\), SO\(_4\)\(^{2-}\), H\(_2\)PO\(_4\)\(^-\), with the CO\(_2\) partial pressure set at atmospheric concentrations. The pH was set at pH 5.0 to simulate arsenic speciation at pe levels of (i) 0 (Eh = 0.0 mv) for anoxic conditions, (ii) 7 (Eh = 414 mv) for suboxic conditions, and (iii) 12 (Eh = 710 mv) for oxic conditions. Ionic strength and activity coefficients were determined using the Davis Equation, and the As(III)-As(V) oxidation-reduction couple was employed. For simulated oxic conditions, H\(_3\)AsO\(_3\) (3.87 x 10\(^{-23}\) mole/l) and H\(_2\)AsO\(_4\)\(^{2-}\) (2.95 x 10\(^{-5}\)) were the dominant species, with arsenate the predominant species. On transition from oxic to suboxic and then to anoxic conditions, the arsenite species become increasingly more dominant, culminating with the anoxic system having H\(_2\)AsO\(_3\)\(^{1-}\) at 1.61 x 10\(^{-9}\) mole/l and H\(_3\)AsO\(_3\) at 2.997 x 10\(^{-5}\) mole/l, with H\(_2\)AsO\(_4\)\(^{1-}\) at 2.29 x 10\(^{-11}\) mole/l.

Hundal et al. (2013) documented arsenic in alluvial soils in Punjab (India) and observed that soils amended with arsenic and incubated for selected time periods under anaerobic conditions demonstrated arsenate reduction to arsenite. Arsenite was

\[
\begin{align*}
0.5 H_2AsO_4^- + e^- +1.5 H^+ &= 0.5 As(OH)_3^- + 0.5 H_2O \quad pK = -10.84 \\
0.5 HAsO_4^{2-} + e^- +2 H^+ &= 0.5 As(OH)_3^- + H_2O \quad pK = -14.22 \\
0.5 H_2AsO_4^- + e^- + H^+ &= 0.5 As(OH)_3^- + 0.5 H_2O \quad pK = -9.72 \\
0.5 H_2AsO_4^{2-} + e^- +1.5 H^+ &= 0.5 As(OH)_3^- + H_2O \quad pK = -9.29
\end{align*}
\]

**Figure 5.** Predominance diagram showing zone of species predominance given pe and pH as master variables.
observed to be a more mobile species than arsenate. Orpiment (As$_2$S$_3$) was proposed as a potential arsenic precipitation product as was ferrous sulfite (FeS$_2$) and vivianite (Fe$_3$(PO$_4$)$_2$ 8H$_2$O). The reductive dissolution of Fe-oxyhydroxides did not result in increased arsenic solubility, a feature attributed to arsenic adsorption on remaining Fe-oxyhydroxides.

Hu et al. (2013) performed rice field trials having aerobic, intermittent, conventional and flood irrigation regimes. Acid extractable soil arsenic was shown to transition to increasing concentrations from the more oxic aerobic irrigation regime (aerobic) to the more anoxic irrigation regime (Flood), whereas cadmium demonstrated an opposite trend. Rice cultivars did show differences in the arsenic and cadmium concentrations, with hybrids typically have a greater arsenic accumulation.

Mn-oxyhydroxides exist in the soil environment and have been implicated in the oxidation of arsenate to arsenate (He and Hering, 2009; Ackermann et al., 2010; Bravin et al., 2008; Radu et al., 2007). Mn-oxyhydroxides are frequently present in smaller abundances than Fe-oxyhydroxides; however, they are thermodynamically favored to oxidize arsenate to arsenate. Birnessite (δ-MnO$_2$), cryptomelane (α-MnO$_2$), and pyrolusite (β-MnO$_2$) are three Mn-oxide polymorph forms. Pyrolusite typically has a better ordered crystalline structure and a higher point of zero charge (pH=6.4), thus is a better candidate for interaction with arsenic oxyanions. Arsenate oxidation may be assumed to follow a stoichiometry given by Nesbitt et al. (1998):

\[
\text{MnO}_2 + \text{H}_3\text{AsO}_3 + 2\text{H}^+ = \text{Mn}^{2+} + \text{H}_3\text{AsO}_4 + \text{H}_2\text{O}.
\]

Ying et al. (2012) observed arsenic adsorption onto Fe and Mn oxides. Subsequently Ying et al. (2013) performed a flow through reactor experiment involving arsenic presorbed on sand grains coated with ferrihydrite and birnessite. These authors noted that As, Mn and Fe migrated from the reduced aggregate interiors to the more aerated exterior, where Mn-oxide formation was coupled with As(III) oxidation.

Radu et al. (2008) proposed that the first step in arsenite oxidation with MnO$_2$ involves As(III) inner sphere surface complex formation with the displacement of OH$^-$ and H$_2$O as ligand substitution. Transfer of two electrons from As(III) results in the release of Mn$^{2+}$ and arsenate. The presence of small quantities of Mn$^{3+}$ in the original MnO$_2$ usually results in a molar ratio release of Mn/As equal to or exceeding unity.

Arsenite oxidation to arsenate by birnessite was investigated to assess whether Fe$^{2+}$ could assist in arsenate sequestration (He and Hering, 2009). These authors observed that the absence of Fe$^{2+}$ the arsenate production resulted in an arsenate concentration increase in the aqueous phase; however, in the presence of Fe$^{2+}$ the arsenate was almost completely sequestered. Arsenite addition to soils has been shown to result in the rapid oxidation of arsenite to arsenate, wherein both species may be adsorbed (Manning and Suarez, 2000).

Arsenic oxidation and reduction may be strongly mediated by microbial populations (Saltikov and Olson, 2002). Dissimilatory arsenate-reducing bacteria are able to effectively reduce arsenate to arsenite by using arsenate as a terminal electron acceptor in anoxic soils or sediments. A gram-negative dissimilatory arsenic-reducing bacterium (Citrobacter sp. NC-1) was recently isolated from As-bearing soil that was shown to rapidly and completely reduce arsenate solutions (Chang et al., 2012).
Focardi et al. (2010) documented anaerobic bacterial strains capable of using arsenate and sulfate as electron acceptors, yielding arsenic sulfide precipitates. Recent research suggests that aquatic macrophyte roots harbor active populations of Fe reducers that substantially influence carbon flow and the many aspects of biogeochemical cycling (King and Garey, 1999). Yoshida et al. (2008) examined cylindrical soil nodules composed of Fe-oxyhydroxides. They isolated microbial 16s rDNA associated with Fe-oxidizing bacteria, suggesting that the pedogenic nodules were created along roots whose rhizosphere harbored these Fe-oxidizing bacteria.

**Gleization and Arsenic Availability**

In the United States rice production relies on either (i) drill-seeded, delayed flood regimes or (ii) permanent flood regimes. Permanent flood regimes use airplane seeding of pre-germinated seed into standing water. Recently, center-pivot irrigation systems and furrow irrigated systems are being evaluated for commercial rice production. Both drill-seeded and delayed flood and permanent flood regimes result in soils having a suboxic layer, typically one to several centimeters in soil later thickness, superimposed on a deeper anoxic soil layer. With the onset of oxygen depletion and with an energy source (CH$_2$O), nitrate reduction proceeds via the denitrification process:

\[ 5\text{CH}_2\text{O} + 4\text{NO}_3^- = 5\text{HCO}_3^- + 2\text{N}_2 + 2\text{H}_2\text{O} + \text{H}^+ \]

As soils become increasingly anoxic, manganese oxide dissolution may proceed, followed sequentially by Fe-oxyhydroxide dissolution:

\[ \text{CH}_2\text{O} + 4\text{Fe(OH)}_3 + 7\text{H}^+ = \text{HCO}_3^- + 4\text{Fe}^{2+} + 10\text{H}_2\text{O} \]

Arsenic may be co-precipitated with Fe-oxyhydroxides and the reductive dissolution of these Fe-oxyhydroxides may promote the release of arsenate:

\[ \text{CH}_2\text{O} + 4\text{Fe(OH)}_3(\text{H}_2\text{AsO}_4^-) + 7\text{H}^+ = \text{HCO}_3^- + 4\text{Fe}^{2+} + 4\text{H}_2\text{AsO}_4^- + 10\text{H}_2\text{O} \]

The arsenate may be subsequently reduced to arsenite:

\[ \text{CH}_2\text{O} + 2\text{H}_2\text{AsO}_4^- + \text{H}^+ = \text{HCO}_3^- + 2\text{H}_3\text{AsO}_3. \]

Thus, the natural soil process of gleization and its acceleration in suboxic to anoxic rice culture acts to convert arsenic from a relatively low state of bioavailability to an easily plant assimilated species. Herbal and Fendorf (2006) formed Fe-oxyhydroxides via microbial reduction and documented that released arsenic may be re-sequestered by these newly synthesis reduction products. Similarly Pedersen et al. (2006) documented that As(V) was strongly sorbed onto Fe(II) catalyzed formation of ferrihydrite and lepidocrocite formation and that arsenic was rendered non-labile on transition of these reduction products to crystalline Fe(III) oxides.

**Microbially Assisted Arsenic Oxidation and Reduction Processes**

The microbial populations in soil and water resources likely account for the majority of life forms on planet earth. Prokaryotic organisms in the soil environment project a profound influence on the type of soil processes that are viable, both in terms of which processes may readily proceed and their reaction kinetics (Cullen and Reimer, 1989; Meng et al., 2003; Campbell et al., 2006; Blodau et al., 2008; Tufano et al., 2008; Fendorf et al., 2010).
Microbial Inter- and Extracellular Bonding (Sequestration)

Arsenic does not have a necessary metabolic or nutrient role in microorganisms (Huang (2014), thus no specific arsenic uptake pathway has been identified. Arsenic uptake appears to occur using existing transporting systems evolved primarily for other chemical species, most likely phosphate. Prokaryotic organisms have evolved metabolic strategies to either exclude arsenic or bind arsenic within the cell.

The extracellular polymeric substance surrounding many prokaryotic species is composed of anionic functional groups (uronic acids and proteins) and cationic functional groups (amino sugars) that chemically function as molecular sieves. Huang (2014) identified recent research suggesting a complex chemistry involving the bacterial matrix and cell wall constituents with arsenic species which reduces the intercellular arsenic uptake potential (Illustration 1). Arsenate uptake by the prokaryotic cell may simply be followed by arsenate efflux from the cell or arsenate is rapidly reduced to arsenite (detoxification reduction). Arsenite concentrations in the prokaryotic cell may be protein bound to reduce their metabolic influence (intercellular sequestration) or oxidized to arsenate and ejected from the cell (respiratory oxidation). Arsenic species may be methylated \((\text{CH}_3)_x\text{AsH}_{(3-x)}\) and ejected from the cell as either gaseous or solubilized species (Huang, 2014).

An emerging area of research involves prokaryotic organism genetic isolation or genetic engineering to support arsenic methylation. Chen et al. (2013) documented the potential of *Pseudomonas putida* to support arsenic methylation. Methyl arsenic species formed by bacteria having an arsM gene may result in the transfer of gaseous methyl arsenic species or the diffusion of these methyl arsenic species into an aqueous phase (Jia et al., 2013). Engineered bacterial cells having an ArsR metalloregulatory protein are selective towards As(III) and accumulate arsenic. Arsenic dissolution may proceed in the presence of Geobacter sp OR-1 bacteria possessing a respiratory As(V) reductase gene (Ohtsuka et al., 2013). Huang and Metzner (2007) observed that dimethylarsenic acid shows an order of magnitude greater membrane permittivity than monomethylarsonic acid, thus potentially explaining the greater presence of dimethylarsenic acid in natural catchment waters. Srivastava et al. (2011) demonstrated that the soil fungi *Rhizopus* sp, *Trichoderma* sp, and *Neocosmospora* support arsenic bio-volatilization.

Illustration 1. The overview of microbial arsenic interactions.
Microbial Arsenic Oxidation, Reduction and Methylation Reactions

Major arsenic microbial soil transformations include oxidation reduction and methylation-demethylation reactions. Ajith et al. (2013) proposed that microbial Mn oxidation and reduction reactions support arsenic mobilization involving pathways similar to those proposed for Fe-oxyhydroxides. Iron(II) activated goethite inhibited arsenate reduction and arsenite oxidation to arsenate was augmented by the presence of ferrous ions. Lafferty and Loeppert (2005) proposed that arsenic mobility is species dependent and the proposed mobility order was methyl-As(III) >> methyl-As(V) > As(III) > As(V). Dixit and Hering (2003) noted that arsenic mobility was limited by arsenite to arsenate oxidation.

Kocar et al. (2006) investigated the dissimilatory reduction of Fe(III) and As(V) and reported that Fe(III) inhibited As sulfide sequestration. Similarly Saalfield and Bostick (2009) showed that iron reduction in the presence of sulfide promoted magnetite, elemental sulfur and trace amounts of Fe- and As-sulfides that limited arsenic mobility. Sun et al. (2009) reported on an arsenic remediation strategy involving nitrate, wherein Fe(II) and As(III) in anoxic soil conditions yielded As(V) adsorbed onto synthesized Fe(III)-oxyhydroxides.

Arsenite and Arsenate Precipitation

In the soil environment Fe-As precipitates include: scorodite (FeAsO$_4$●2H$_2$O), phenmacosiderite (Fe$_4$(AsO$_4$)$_3$(OH)$_3$●6H$_2$O) and parasymplesite (Fe$_3$(AsO$_4$)$_2$●8H$_2$O). Calcium arsenate precipitation reactions yielding raventhalite (Ca$_3$(PO$_4$)$_2$●10H$_2$O) are similar to precipitation reactions involving calcium and phosphate to form calcium hydroxyapatite or octacalcium phosphate (Dungkaew et al., 2012). Gemeinhardt et al. (2006) focused on enhancing arsenic retention in contaminated soils using FeSO$_4$ amendments. Sequential extractions indicated that arsenic was immobilized into the Fe-oxyhydroxide (non-crystalline and crystalline forms) and residual fractions. The authors speculated that arsenic immobilization was attributed to the (i) precipitation of FeAs (scorodite), (ii) inner sphere adsorption onto Fe-oxyhydroxides, or (iii) coprecipitation and occlusion with newly synthesized Fe-oxyhydroxides.

Parisio et al. (2006) in New York documented that reduced Fe leachates having arsenic originating from solid waste landfills frequently showed a “severe effects level” towards aquatic life. Upon entering oxygenated environments the formation of iron precipitates (Fe-floc) were shown to be enriched in arsenic.

The Surface Adsorption Process

Surface adsorption is a chemical process involving the accumulation of dissolved substrate (adsorbate) at the interface of a solid (adsorbent). In the purest context, the adsorbate is distinguished by its discrete positioning with respect to specific sites on the adsorbent and its dimension normal to the interface is that of the dimensions of the adsorbate. Conversely, precipitation is the three-dimensional growth of a structure. Frequently, investigators may not be able to distinguish adsorption from precipitation and the characteristic term “sorption” is applied to the process.
Charge creation on the adsorbent may be permanent charge or pH-dependent charge. Permanent charge typically arises from isomorphic substitution and therefore is a characteristic of the adsorbent. Phyllosilicates typically are the more abundant examples in the soil environment, especially 2:1 layer silicates; such as, montmorillonite, illite, vermiculite, beidellite, and nontronite. Adsorbents having pH-dependent charge (variable charge surfaces) typically possess surface hydroxyl groups [=SOH, where S is a metal] that may experience protonation or deprotonation reactions. Examples of soil solids having pH-dependent charge capabilities include: edge regions of phyllosilicates, crystalline and noncrystalline (amorphous) metal oxides, metal hydroxides and metal oxyhydroxides. The reactivity of the surface hydroxyl groups is primarily a function of the structural metal atoms bound to the surface hydroxyl groups, the valence and coordination number of the structural metal atoms.

As an example, surface hydroxyl groups in goethite are characterized as Type A, Type B, and Type C: where,

Type A:  \( \equiv \text{FeOH}^{0.5} \) (terminal, where hydroxyl is directly coordinated to Fe),
Type B:  \( \equiv \text{Fe}_3\text{OH}^{0.5} \), (surface hydroxyl is shared with three Fe)
Type C:  \( \equiv \text{Fe}_2\text{OH}^0 \) (surface hydroxyl is shared with two Fe).

Note that the charge density of the two and three Fe atoms in Type B and Type C surfaces would not permit protonation of the surface hydroxyl groups. Stoichiometry of the surface groups may be expressed in two ways, depending on the theoretical approach of the investigator. The more classical method, with goethite as an example, involves:

\[ \equiv \text{FeOH}^0 + H^+ = \equiv \text{FeOH}_2^+ \quad K_1 = 10^{+6.2} \]
\[ \equiv \text{FeOH}^0 = \equiv \text{FeO}^- + H^+ \quad K_2 = 10^{-11.8} \]

Simulated protonated and deprotonated Fe-site distributions are illustrated in Figure 7. The second approach uses the electrostatic valence principle, which involves the bond strength (s) as determined by the cation charge (+3) divided by the coordination number (+6): s=0.5. Given that the Fe atom has +0.5 units of charge directed along 6 coordination directions, the surface charge is determined as:

\( \equiv \text{FeOH}_2^{+0.5} = \equiv \text{FeOH}^{0.5} + H^+ \), where \( K = 10^{8.5} \).

This formalization permits the surface site acidity to be a function of metal coordination and valency (M-O bond strength), the bond strength to bond length ratio, and the metal’s electronegativity. Simulated protonated and deprotonated Fe-site distributions for the electrostatic valence principle are illustrated in Figure 6.

**Figure 6.** Simulated protonation-deprotonate Fe-sites on goethite using a classical approach.
Ligand exchange adsorption mechanisms involve direct coordination of the adsorbate, with expulsion of either OH$^-$ or H$_2$O from the adsorbent. The process may be expressed as:

\[ \equiv \text{Metal-OH}_2^{+0.5} + \text{H}_2\text{PO}_4^{1-} = \equiv \text{Metal-OPO}_3^{+0.5} + \text{H}_2\text{O}. \]

### Adsorption of Arsenite and Arsenate Species

The arsenite and arsenate species experience pH-dependent adsorption and coprecipitation on/with Fe-oxyhydroxides, most notably ferrihydrate (β-FeOOH), lepidocrocite (γ-FeOOH), goethite (α-FeOOH), and hematite (Fe$_2$O$_3$) (Miretzky and Cirelli, 2010). Surface protonation of goethite may be represented as (Luxton et al., 2006):

\[ \equiv \text{Fe(OH)}^{0.5} + \text{H}^+ \leftrightarrow \equiv \text{Fe(OH)}^{+0.5} \quad \text{pK} = -9.59. \]

Surface protonation allows the interface to acquire sufficient positive surface charge densities to promote arsenite adsorption. Arsenite adsorption may be either monodentate or bidentate:

**Monodentate:**

\[ \equiv \text{Fe(OH)}^{0.5} + \text{As(OH)}_3 \leftrightarrow \equiv \text{FeOAsO}_2^{-2.5} + \text{H}_2\text{O} + 2\text{H}^+ \quad \text{pK} = +11.35 \]

\[ \equiv \text{Fe(OH)}^{0.5} + \text{As(OH)}_3 \leftrightarrow \equiv \text{FeOAs(OH)}^{1.5} + \text{H}_2\text{O} + \text{H}^+ \quad \text{pK} = +0.85 \]

\[ \equiv \text{Fe(OH)}^{0.5} + \text{As(OH)}_3 \leftrightarrow \equiv \text{FeOAs(OH)}^{2.5} + \text{H}_2\text{O} \quad \text{pK} = -5.24 \]

**Bidentate**

\[ 2\equiv \text{Fe(OH)}^{0.5} + \text{As(OH)}_3 \leftrightarrow \equiv \text{(FeO)}_2\text{As(OH)}^{0.5} + \text{H}_2\text{O} \quad \text{pK} = -15.47 \]

Arsenate adsorption on Fe-oxyhydroxides may be represented as:

\[ \equiv \text{Fe(OH)}^{0.5} + \text{H}_2\text{AsO}_4 \leftrightarrow \equiv \text{FeHAsO}_4^{0.5} + \text{H}_2\text{O} \]
The optimal pH for the adsorption of arsenite on Al- and Fe-oxyhydroxides ranges from pH 7 to 10, depending on experimental protocols and the presence of phosphate, silicic acid, naturally occurring organic acids, and other competing anions (Goldberg, 2002; Luxton et al., 2006; Grafe et al., 2001 and 2002; Pigna et al., 2006; Zhang and Selim, 2008), whereas the optimal pH for the adsorption of arsenate on Al- and Fe-oxyhydroxides varies across the pH range of 4 to 7 (Bowell, 1994; Jain and Loeppert, 2000; Vetterlein et al., 2007; Saeki, 2008; Xu et al., 2008; Toor and Haggard, 2009; Jackson and Miller, 2008; Smith et al., 2002 and 2009). In general, arsenate adsorption increases in acidic media, reaches maximal adsorption at pH in the range of 3 to 7; whereas arsenite adsorption reaches maximal levels in the pH range of 7 to 8 (Jain and Loeppert, 2000; Goldberg, 2002). Arsenate typically exhibits greater adsorption than arsenite in acidic to neutral pH levels; whereas arsenite may exhibit greater adsorption in alkaline environments. Conversely, Oscarson et al. (1983) observed that arsenite is adsorbed to a greater extent than arsenate on noncrystalline Fe-oxyhydroxides. Jain and Loeppert (2000) showed arsenate adsorption on ferrihydrate was greatest in acidic media and arsenite adsorption was maximized at higher pH levels. Quaghebeur et al. (2005) performed both batch and flow-through desorption on columns packed with kaolinite to compare their ability to desorb arsenate. Not surprisingly, the batch protocol underestimated arsenate desorption. Goldberg (2002) noted that arsenate and arsenite adsorption on reference phyllosilicates (kaolinite, illite and montmorillonite) was pH-dependent with arsenate adsorption less evident on transition to alkaline media, whereas arsenite adsorption exhibited less pH dependency with moderate adsorption increases on transition from acidic to alkaline media. Goldberg (2002) also showed that arsenate adsorption on amorphous aluminum oxides and amorphous iron oxides was relatively constant from acidic environments to near pH levels exceeding pH 9; after which, arsenate adsorption declined. Arsenite adsorption showed a maximum adsorption near pH 8 for amorphous aluminum oxides and exhibited little pH dependence on amorphous Fe-oxides.

The conversion of arsenite to arsenate in the presence of Fe-oxyhydroxides is easily shown to be thermodynamically favorable from the application of free energies of formation. Jackson and Miller (2000) investigated arsenate adsorption on noncrystalline Fe-oxyhydroxides with and without the presence of goethite. Using oxalate and hydroxylamine as selective digestive agents for the noncrystalline Fe-oxyhydroxides, they observed that in the absence of goethite arsenate concentration were greater after Fe-oxyhydroxide dissolution, whereas in the presence of goethite the arsenate appeared to be re-adsorbed onto the goethite and the arsenate concentrations did not appreciably increase. They also reported that phosphate addition inhibited the adsorption of arsenate onto goethite. Cornu et al. (2003) observed the adsorption of arsenate onto kaolinite and also kaolinite pretreated with humic acids. Their observations also involved contrasting calcium and sodium nitrate ionic strength electrolytes. In this study the sodium adjusted media exhibited an arsenate pH dependency with both kaolinite and humic acid coated kaolinite, with kaolinite having greater arsenate adsorption, especially in acidic media. Conversely,
in calcium adjusted media, kaolinite did not exhibit any arsenate pH-dependent adsorption, whereas humic acid coated arsenate showed only an incident pH-dependency. Jackson and Miller (2000) evaluated various concentrations of phosphate (pH 3 and 7) to extract arsenite, arsenate, dimethylarsinic acid, monoethylarsonic acid, arsanilic acid and roxarsonesorbed onto goethite and amorphous Fe-oxides. Phosphate was demonstrated to displace arsenite and arsenate. In the presence of goethite, a portion of the arsenite was oxidized to arsenate. Khaodhia et al. (2000) prepared iron oxide coated sand (Fe$_2$O$_3$) and used completely mixed batch reactors to establish isotherm adsorption curves involving arsenate and arsenate-chromate systems. Arsenate was established to form inner-sphere complexes with the Fe-oxides, noting that the concentration of the NaNO$_3$ electrolyte had little influence on arsenate adsorption. Arsenate adsorption was strongly adsorbed at acidic to slightly acidic pH values and adsorption decreased with increasing pH. The equilibrium sorption constants for arsenate on the iron oxide coated sand were:

$$\text{SOH} + \text{AsO}_4^{3-} + 3 \text{H}^+ = \text{SH}_2\text{AsO}_4^+ + \text{H}_2\text{O} \quad pK = -26.26$$

$$\text{SOH} + \text{AsO}_4^{3-} + 2 \text{H}^+ = \text{SHAsO}_4^{3-} + \text{H}_2\text{O} \quad pK = -20.22$$

$$\text{SOH} + \text{AsO}_4^{3-} = \text{SOHAsO}_4^{3-} + \text{H}_2\text{O} \quad pK = -7.48$$

Grafe et al. (2001) investigated arsenite and arsenate adsorption on goethite spanning pH range of 3 to 11. These authors showed that arsenate adsorption was greatest at pH 3 and that arsenate adsorption decreased gradually and continuously from pH 3 to pH 11. Arsenite adsorption was shown to have a maximum adsorption at pH 9. The influence of either fulvic acid or humic acid addition resulted in a reduction in adsorption for both arsenite and arsenate. Sun and Doner, (1996, 1998) reported that arsenite adsorption is inner sphere based on Fourier transform infrared spectroscopy.

**Arsenic and the Rhizosphere in Anaerobic Soils**

Aquatic plants, including rice, produce aerenchyma in the root cortex that facilitates oxygen diffusion towards the root tips (Wu et al., 2011). Oxygen diffusion in rice aerenchyma supports a partial oxidation of a thin soil layer (rhizosphere) adjacent to the root surface, permitting radial oxygen diffusion towards the bulk soil. Wang et al. (2013) observed Fe-oxyhydroxide synthesis within and extending from the root epidermis into the rhizosphere. The synthesis of Fe-oxyhydroxides (Fe-plaque) has the potential to sequester metal(loids) via adsorption and/or precipitation reactions. Wang et al (2013) documented that the concentrations of iron, cadmium and arsenic associated with Fe-plaque increased with greater radial oxygen loss activities. Chen et al. (2005) observed that Fe-plaque was selective for the preferential adsorption of arsenite relative to arsenate. Wu et al. (2013) employed a greenhouse experimental design with rice cultivars and induced arsenic stress attributed to soil additions of arsenate. Arsenic stress produced a slight increase in Fe-plaque formation; however, the radial oxygen loss rates declined. With increasing arsenic stress seed DMA concentrations increased as a percentage of total arsenic whereas relative and absolute inorganic arsenic concentrations increase in stem and root tissues. Wu et al. (2011)
cultured 20 rice genotypes with arsenic bearing irrigation water, documenting differences in aerenchyma, arsenic accumulation and speciation. As expected, genotypes differed in aerenchyma, which was correlated with radial oxygen loss. Radial oxygen loss was inversely related to total and inorganic arsenic accumulation, suggesting that varietal selection may be important in reducing arsenic accumulation.

Adsorption of Arsenite and Arsenate Species in the Presence of Competing Anions

Competing anions may either: (i) previously or preferentially attach to a potential binding site and negate access for arsenic bonding, or (ii) displace arsenic by competitive competition for the binding site. The most widely investigated counter anions include: phosphate, sulfate, carbonate, silicic acid, dissolved organic materials (DOM). Sulfate, carbonate and DOM have been shown to be relatively less effective in displacing arsenic (Jain and Loeppert, 2000). Weng et al. (2009) reported that adsorbed soil organic matter facilitated arsenic sorption. Using goethite as the bonding surface, Luxton et al. (2005) showed that silicic acid (H₄SiO₄) was able to effectively displace arsenite by forming an inner sphere complex involving silicic acid and goethite by ligand exchange with hydroxyl functional groups. Swedlund and Webster (1999) and also Meng et al. (2000) demonstrated that H₄SiO₄ may displace arsenite from ferrihydrate.

In Australia, Smith et al. (1999) surveyed ten well-drained soils, observing that after arsenic amendments, arsenate adsorption was greater than arsenite. They further observed that phosphate inhibited arsenate adsorption. In a subsequent study, Smith et al. (2002) studied the influence of phosphate, calcium and sodium on arsenate adsorption in Alfisols, Vertisols and Oxisols. They reported that phosphate inhibited arsenate adsorption in soils testing low in Fe-oxyhydroxides, whereas phosphate did not influence arsenate adsorption in soils having higher Fe-oxyhydroxide abundances. They attributed the phosphate inhibition on arsenate adsorption in soils having smaller Fe-oxyhydroxide abundances as being due to competition for reactive sites. Smith and Naidu (2009) using flow through reactors demonstrated that arsenate adsorption was initially rapid, having 58 to 91 percent of the arsenate adsorbed within 15 minutes. Subsequent adsorption continued as a slower rate of adsorption. These authors also suggested that arsenate adsorption was inhibited by phosphate. In Australia, Smith et al. (1999) surveyed ten well-drained soils, observing that after arsenic amendments, arsenate adsorption was greater than arsenite. They further observed that phosphate inhibited arsenate adsorption.

Liu et al. (2014) investigated silicic acid (H₄SiO₄) additions to soils in greenhouse conditions and cultured to two rice cultivars. Silicic acid additions increased dimethylarsinic acid (DMA) solubility, whereas inorganic arsenic solubility was only marginally increased. Silicic acid was proposed to inhibit DMA adsorption or support DMA desorption. Silicic acid additions promoted DMA concentrations in rice stem, leaf and seed, reinforcing a concept that DMA concentrations in rice plant components are entirely attributed to soil chemistry influences and plant physiology is not involved in arsenic methylation. Swedlund and Webster (1999) demonstrated that
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silicic acid inhibits arsenate/arsenite adsorption on ferrihydrate. Luxton et al. (2006) observed that silicic acid inhibits arsenite adsorption on goethite.

**Spectroscopic Investigations Involving Arsenite and Arsenate Bonding Mechanisms**

Arsenite and arsenate adsorption may result in both monodentate and bidentate bonding structures (Fendorf et al., 2004). Fendorf et al. (1997) and Waychunas et al. (1993) employed extended x-ray absorption fine structure spectroscopy to document that arsenate adsorption on goethite and synthetic Fe-oxhydroxides is inner sphere. Mononuclear and binuclear bridging has been also proposed for arsenate adsorption reactions (Miretzky and Cirelli, 2010; Jackson and Miller, 2000; Fendorf et al., 2004; Goldberg, 2002).

**Rice Irrigation and Arsenic Availability**

Traditionally, United States rice production relies on either (i) drill-seeded, delayed flood irrigation or (ii) permanent flood irrigation. Permanent flood regimes use airplane seeding of pre-germinated seed into standing water. Recently, center-pivot irrigation systems and furrow irrigated systems are being evaluated for commercial rice production. Both delayed flood and permanent flood irrigation result having a suboxic soil layer, typically having a thickness of several centimeters, superimposed on a deeper anoxic soil layer. Thus the suboxic soil layer may have a less negative redox potential that may permit nitrification. With the onset of oxygen depletion and with an energy source, subsequent nitrate reduction could proceed via the denitrification process.

In China Hu et al. (2013) optimized water management to lower rice uptake of both cadmium and arsenic without appreciable yield loss. Using flooded, conventional, intermittent and aerobic irrigation strategies, these authors observed that the conventional and flood irrigations increased arsenic and decreased cadmium uptake compared to the intermittent and aerobic irrigation strategies. These authors further suggested that maintaining flood until full tillering stage, then switching to intermittent irrigation was the best compromise for maintaining yield and reducing both arsenic and cadmium uptake. The mean arsenic concentrations were 0.20 to 0.28 mg As / kg-dry weight for the aerobic and intermittent irrigation strategies, whereas the conventional irrigation (0.27 to 0.3 mg As / kg-dry weight) and flood irrigation (0.3 to 0.48 mg As / kg-dry weight) demonstrated greater arsenic uptake.

Lombi et al. (2009) estimated total and speciated arsenic concentrations in husk, bran and endosperm from rice cultured in contaminated Chinese soil. Total arsenic was 0.54 mg – As/ kg (husk), 6.24 mg As / kg (bran) and 12.42 mg As / kg (endosperm). Inorganic arsenic constituted 74% of the arsenic in the husk, 75% of the arsenic in the bran and 54% of the arsenic in the endosperm. Liang et al. (2010) also investigated total and speciated arsenic concentrations in Chinese rice. Using numerous rice samples the total arsenic concentrations ranges from 65.3 to 274.2 µg As / kg, with a mean of 114.4 µg As / kg.

In Taiwan, Syu et al. (2014) investigated arsenic uptake among rice genotypes cultivated in arsenic contaminated soils. Iron plaque associated with the rice roots
sequestered arsenic; however, no correlation between the quantity of arsenic associated with the iron plaque and rice tissue arsenic concentrations were observed. Liu et al. (2005) using hydroponics observed that iron plaque showed an adsorption affinity for arsenate relative to arsenite. Using a microcosm approach, Chen et al. (2008a) observed that nitrate reduced the concentrations of ferrous iron, whereas ammonium enhanced ferric iron reduction. These authors concluded that nitrate decreased iron plaque formation, resulting in increased arsenic uptake by rice. Hossain et al. (2009) observed that ferrous iron reduced arsenic concentrations in rice grain and increased rice yields. Addition of phosphate increased arsenic uptake. In China, Liu et al. (2004) established iron plaque on rice seedling roots in a solution culture experiment, observing that 75 to 89 percent of the total arsenic was sequestered by the iron plaque. Arsenic root concentrations were equivalent among the rice genotypes; however, rice shoots showed significant arsenic concentration variation. Huang et al. (2012) employed a microcosm experiment and documented the rate of iron plaque degradation post-harvest, noting at 76 percent of the arsenic sequestered by the iron plaque was released to the soil solution in 27 days.

**Areas for Productive Future Research**

- Alternative irrigation strategies to reduced arsenic accumulation in rice
- Rice breeding programs to select cultivars that limit arsenic accumulation
- Soil biology investigations to quantify the microbial roles involved in arsenic speciation
- Global initiatives to quantify arsenic concentrations in drinking and irrigation waters
- Quantitative modelling of the arsenic pathways in soil
- Understanding the formation and effectiveness of Fe-plaque on arsenic uptake by aquatic plants
- Routine soil tests to predict arsenic plant availability.

**REFERENCES**


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