Organic Controls on Aqueous Arsenic in Freshwater
Arsenic

• toxic trace element

• natural component of earth’s crust that is widely distributed in environment

• occurs in inorganic and organic compounds and also less commonly in the elemental form
Oxidation States and Species

- –3, 0, +3, and +5 oxidation states

- In aqueous environments, inorganic arsenic species arsenite (As +3) and arsenate (As +5) are most abundant.

- Aqueous arsenic occurs primarily as oxyacids of these species, commonly as arsenous acid (As +3) and arsenic acid (As +5), or their salts.
Eh-pH diagram for arsenic in an aqueous environment

- In oxidizing environments, arsenate oxyanions \( \text{H}_n\text{AsO}_4^{n-3} \) predominates.
- In most reducing conditions, arsenite \( \text{H}_n\text{AsO}_3^{n-3} \) predominates.
- Elemental arsenic and arsine are formed under strongly reducing conditions.
Oxidation States and Species

• Inorganic As compounds can be methylated (hydroxyl groups replaced by methyl groups) by microorganisms to organic arsenic compounds
  – monomethylarsonic acid (MMA)
  – dimethylarsinic acid (DMA)

• In anaerobic conditions, methylated As can be further transformed by microorganisms to volatile forms
  – arsine $\text{AsH}_3$
  – Mono, di & trimethylarsine $\text{H}_2\text{AsCH}_3$ ; $\text{HAs(CH}_3)_2$ ; $\text{As(CH}_3)_3$

• In aerobic conditions, oxidation of methylated As to inorganic species can occur.
Table 1. Dissociation constants for arsenic species

<table>
<thead>
<tr>
<th></th>
<th>pK₁</th>
<th>pK₂</th>
<th>pK₃</th>
</tr>
</thead>
<tbody>
<tr>
<td>H₃AsO₃</td>
<td>9.2</td>
<td>12.1</td>
<td>13.4</td>
</tr>
<tr>
<td>H₃AsO₄</td>
<td>2.2</td>
<td>7.0</td>
<td>11.5</td>
</tr>
<tr>
<td>MMA</td>
<td>3.6</td>
<td>8.2</td>
<td>–</td>
</tr>
<tr>
<td>DMA</td>
<td>6.3</td>
<td>–</td>
<td>–</td>
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</tbody>
</table>

- The aqueous solubility of arsenical salts varies depending on the pH and the ionic environment.
Sources and Occurrence

• Arsenic is widely distributed in the earth’s crust and usually occurs in trace quantities in rock, soil, water and air.

• It ranks 20\textsuperscript{th} in the abundance of elements in the earth’s crust
  – total amount in the upper crust estimated to average 6mg/kg
Sources and Occurrence

• Arsenic concentrations in natural waters
  – less than 0.5 µg/L to more than 5000 µg/L

• typical concentrations in freshwater
  – less than 10 µg/L and often less than 1 µg/L
Sources and Occurrence

• Rarely, much higher concentrations occur, particularly in groundwater.

• Ground water in US typically contains 1 µg/L or less, but about 10% exceed 10 µg/L.

• Well-known high-arsenic groundwater areas are located in Argentina, Chile, Mexico, China, Hungary, West Bengal (India), Bangladesh, and Vietnam.
Sources and Occurrence

• Areas with large-scale natural high As concentrations in groundwater mainly tend to be found in either
  – inland or closed basins in arid to semi-arid areas
  – strongly reducing aquifers

• Geologically young sediments often occur in these environments and the groundwater flow is sluggish due to the areas being flat and low-lying.

• Any arsenic released from the sediments following burial in these poorly flushed aquifers has been able to accumulate in the groundwater.
Sources and Occurrence

• Groundwater high in arsenic is also found in geothermal areas.

• On a smaller-scale, high arsenic concentrations are found in
  – areas with mining activity
  – where oxidation of sulfide minerals has occurred
Sources and Occurrence

• Arsenic is the main constituent of more than 200 mineral species and occurs in more than 245 minerals.
Sources and Occurrence

- As is found associated with many types of mineral deposits, especially sulfide minerals.
- The most common arsenic mineral
  - Arsenopyrite (FeAsS)
- Other important arsenic-bearing minerals
  - Orpiment ($\text{As}_2\text{S}_3$)
  - Realgar (AsS)
  - Loellingite (FeAs$_2$)
  - Niccolite (NiAs)
  - Cobaltite (CoAsS)
  - Tennantite ($\text{Cu}_{12}\text{As}_4\text{S}_{13}$)
  - Enargite ($\text{Cu}_3\text{AsS}_4$)
Sources and Occurrence

- Naturally occurring As commonly is found
  - in volcanic glass
  - volcanic rocks of rhyolitic to intermediate composition
  - adsorbed to and coprecipitated with metal oxides
  - adsorbed to clay-mineral surfaces
  - associated with sulfide minerals and organic carbon
Sources and Occurrence

• High arsenic concentrations generally result from natural processes, although human activities locally increase arsenic.

• The most prevalent causes in groundwater are release from iron oxide and sulfide minerals.

• Volcanic action is another source of arsenic.
Sources and Occurrence

• Anthropogenic sources of As contamination of water
  – disposal of industrial waste
  – mining and smelting of arsenic bearing minerals
  – burning of fossil fuels
  – application of arsenic compounds in products such as fertilizers and pesticides
  – phosphate detergents made with arsenic bearing rock phosphate
  – Civil War-era embalming fluid
Concerns

• The greatest concern about aqueous arsenic is its impact on human health through contamination of drinking water.

• Arsenic is considered one of the prominent environmental causes of cancer mortality in the world.

• Generally, inorganic arsenic is more toxic than organic arsenic, and arsenite is more toxic than arsenate.
The area affected worst in terms of human health is the Bengal Basin where more than 40 million people drink water containing a high arsenic concentration.
Overview of Arsenic Mobility

• Inorganic arsenic mobility in freshwater is the most important issue in terms of impact on health
• Their mobility influenced by
  – pH
  – redox potential
  – presence of adsorbents such as oxides and hydroxides of Fe(+3), Al(+3), Mn(+3/+5), humic substances, and clay minerals
Overview of Arsenic Mobility

- Processes that largely control arsenic mobility
  - Adsorption reactions
    - attachment of arsenic to a surface such as iron oxide
  - desorption reactions
    - arsenic becoming detached from a surface
  - solid-phase precipitation
    - formation of a solid phase from components present in aqueous solution
  - solid-phase dissolution reactions.
    - opposite of precipitation
Overview of Arsenic Mobility

• The most prevalent causes high concentrations are release from iron oxide surfaces (a desorption reaction) and sulfide mineral oxidation (a dissolution reaction).

• Adsorption and desorption reactions between arsenate and iron-oxide surfaces are particularly important because iron oxides are widespread in the hydrogeologic environment as coatings on other solids, and because arsenate adsorbs strongly to iron-oxide surfaces in acidic to near-neutral-pH water.
## Principal Reactions Affecting Inorganic As Concentrations in Ground Water

<table>
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<tr>
<th>Redox Condition</th>
<th>Important Phases</th>
<th>Important Reactions</th>
<th>Conditions That Affect Arsenic Mobility</th>
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<tr>
<td>Oxidizing</td>
<td>Fe-oxides</td>
<td>Adsorption/ desorption</td>
<td>pH; presence of competing adsorbent; oxygen and Fe$^{3+}$</td>
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<td>Precipitation</td>
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<td></td>
<td>Sulfide minerals</td>
<td>Sulfide oxidation</td>
<td>pH and microbial activity; oxygen and NO$_3$</td>
</tr>
<tr>
<td>Reducing</td>
<td>Fe-oxides</td>
<td>Adsorption/ desorption and precipitation</td>
<td>Oxidation state of As</td>
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<td>pH</td>
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<tr>
<td></td>
<td></td>
<td>Dissolution</td>
<td>Presence of organic carbon</td>
</tr>
<tr>
<td>Reducing &amp; Sulfidic</td>
<td>Sulfide minerals</td>
<td>Precipitation</td>
<td>Sulfide, iron, and As concentrations</td>
</tr>
</tbody>
</table>
Overview of Arsenic Mobility

- Methylation and demethylation reactions are also important transformations controlling the mobilization and distribution of arsenic.
Overview of Arsenic Mobility

- Redox reactions can control aqueous arsenic concentrations by their effects on arsenic speciation.

- Arsenic adsorption also can be affected by the presence of competing ions.
  - Phosphate in particular is significant because phosphate and arsenate have similar geochemical behavior, and as such, both compete for sorption sites.

- Solid phase structural changes at the atomic level may cause changes such as decrease in density of adsorption sites which can result in desorption of adsorbed arsenic.
Organic Controls on Arsenic Concentrations

- Organic controls play a significant role in arsenic concentrations.
  
  - organic molecules from natural and anthropological sources can affect As concentration directly and indirectly
  
  - microbes may be involved in the transformations and concentration of arsenic
Influence of Microorganisms on Arsenic Concentrations
Sulfide Mineral Oxidation

- Some bacteria (Thiobacillus ferrooxidans, Thiobacillus thiooxidans, and Leptospirillum ferrooxidans) can increase reaction rates for sulfide mineral oxidation by about five orders of magnitude compared with abiotic reaction rates.
Sulfide Mineral Oxidation

• Pyrite is the most common sulfide mineral of concern in relation to arsenic.
• Pyrite oxidation is a complex chemical process summarized by

\[
\text{FeS}_2 + \frac{15}{4} \text{O}_2 + \frac{7}{2} \text{H}_2\text{O} \rightarrow \text{Fe(OH)}_3 + 2 \text{H}_2\text{SO}_4
\]

• This reaction can release a considerable amount of arsenic to the aqueous phase because arsenic concentrations in pyrite generally range from about 0.02% to 0.5%, and may be as large as 6.5%.
Sulfide Mineral Oxidation

- T. ferrooxidans and L. ferrooxidans increase the oxidation rate indirectly by catalyzing the reaction between dissolved oxygen and Fe(+2) to form Fe(+3).

- The Fe (+3) can then oxidize pyrite, which is a much faster reaction than the reaction of pyrite directly by dissolved oxygen.
Sulfide Mineral Oxidation

• Bacterial oxidation of pyrite involving oxygen appears to occur only in water with a pH less than 4, except in water with high nitrate concentrations.

• Aqueous nitrate in the presence of oxygen can oxidize pyrite at pH values greater than 5. This reaction is summarized by

$$10 \text{FeS}_2 + 30 \text{NO}_3^- + 20 \text{H}_2\text{O} \rightarrow 10 \text{Fe(OH)}_3 + 15 \text{N}_2 + 15 \text{SO}_4^{2-} + 5 \text{H}_2\text{SO}_4$$
Sulfide Mineral Oxidation

• Bacterial oxidation of Fe(+2) by Gallionella ferruginea and sulfur in pyrite by T. denitrificans promotes this reaction.

• Pyrite oxidation involving nitrate has produced arsenic concentrations well above 50 µg/L.
Sulfide Mineral Oxidation

• Arsenopyrite oxidation by Fe(+3) is about 10 times faster than the reaction with pyrite and is more rapid in the presence of *T. ferrooxidans*.

• *T. ferrooxidans* increases the reaction rate by oxidizing Fe(II) to Fe(III). This reaction is summarized by

\[
\text{FeAsS} + \frac{7}{2} \text{O}_2 + 4 \text{H}_2\text{O} \rightarrow \text{Fe(OH)}_3 + \text{H}_3\text{AsO}_4 + \text{H}_2\text{SO}_4
\]
Reduction of arsenate to arsenite

• Some microorganisms in anaerobic environments are able to generate energy by coupling the oxidation of $\text{H}_2$ or organic carbon to the reduction of inorganic As(+5), arsenate, forming inorganic As(+3), arsenite.

• Arsenite is both more toxic and more mobile than arsenate.

• Arsenite is more mobile because sorption onto clay minerals and metal oxides appears to be less rapid and/or less stable in aqueous systems.
Reduction of metal-oxides

- Anaerobic respirations couple the oxidation of an electron donor to the reduction of an alternative electron acceptor such as nitrate, Fe(+3), or sulfate, generating.

- Iron and manganese reduction that occur in this way are commonly the dominant redox processes in anoxic environments.

- The microbial reduction iron and manganese oxides simultaneously releases any sorbed arsenic.
Reduction of metal-oxides

- A specific biologically mediated reaction, called dissimilatory iron reduction, can release arsenic from iron oxide and involves organic carbon.
Detoxification Processes

• Certain bacteria and fungi appear to detoxify arsenicals by reducing them to arsine in both inorganic and methylated forms.

• A variety of other microorganisms have been shown to oxidize arsenite to arsenate by non-energy-generating mechanisms.

• Also, certain bacteria and algae, as well as many higher organisms, may incorporate arsenic into organic compounds such as arsenocholine, arsenobetaine, and other arsenosugars.
Influence of Organic Molecules on Arsenic Concentration

• Natural organic matter (NOM) may significantly influence arsenic geochemistry.

• Humic and fulvic acids may interfere strongly with arsenic adsorption under some circumstances.

• NOM molecules possess unique combinations of functional groups, including carboxylic, esteric, phenolic, quinone, amino, nitroso, sulfhydryl, hydroxyl, and other moieties, the majority of which are negatively charged at neutral pH.
Influence of Organic Molecules on Arsenic Concentration

• In general, it appears that NOM readily forms both aqueous and surface inner-sphere complexes with cationic metals and metal oxides.

• These aqueous NOM-metal complexes may associate strongly with other dissolved anion diminishing the tendencies of such anions to form surface complexes.
Influence of Organic Molecules on Arsenic Concentration

• Redman et al. (2002) found that in a sample containing hematite and NOM, the presence of NOM dramatically prevented and delayed the attainment of sorption equilibrium of As.

• Furthermore, the amount of adsorbed arsenate and arsenite decreased significantly in the presence of NOM.
Summary

• Many factors influence the concentration of arsenic in freshwaters including the pH, the redox potential, and the presence of adsorbents such as metal oxides and hydroxides, natural organic matter substances, clay minerals, anthropogenic influences, and sulfide minerals.
Summary

• Organic controls play a significant role in arsenic concentrations.
  • Microorganisms can reduce iron and manganese oxides though anaerobic respiration, which simultaneously releases any arsenic adsorbed to these metal oxides.
  • Microorganisms can also significantly increase the rates of reactions responsible for the oxidation of arsenic bearing sulfide minerals, thereby increasing aqueous arsenic concentrations.
  • Organic molecules may increase aqueous arsenic concentrations by complexing arsenic. These complexes may associate strongly with other dissolved arsenic diminishing arsenic adsorption to surfaces.