

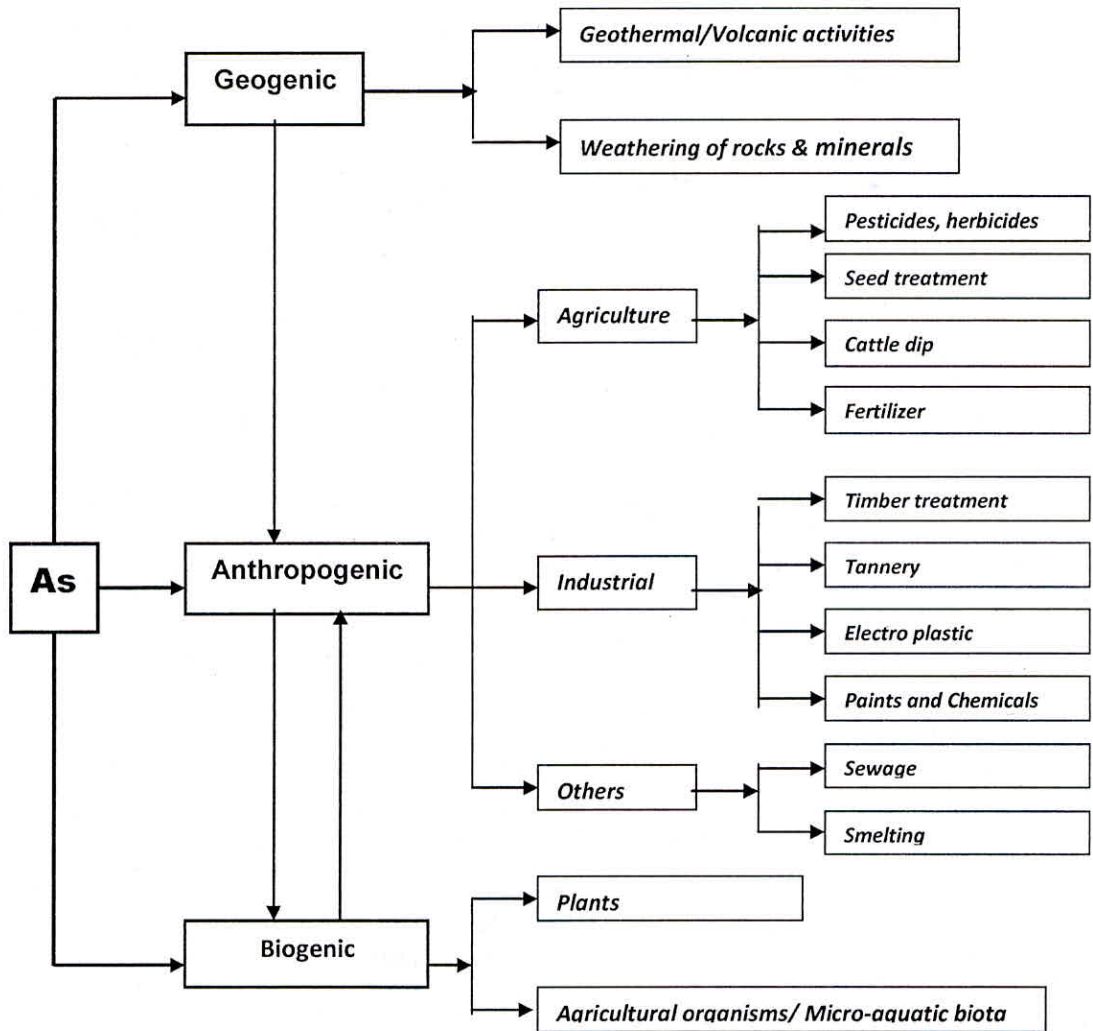
## Chapter -1

# **Arsenic: Source, Occurrence and Geochemistry**

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Arsenic that has the symbol 'As', and atomic number 33, atomic weight 74.92 is often referred to as a metal but, it is classified chemically as a nonmetal or metalloid belonging to Group-15 of the periodic table. The most common oxidation states for arsenic are : -3 (arsenides: usually alloy-like intermetallic compounds), +3 (arsenites (As(III)), and most organoarsenic compounds), and +5 (arsenates(As(V)): the most stable inorganic arsenic oxycompounds). Arsenic is always present as compounds with oxygen, chlorine, sulphur, carbon and hydrogen on one hand, and with lead, gold and iron on the other. It can exist in inorganic or organic form; inorganic arsenic is generally more toxic than organic arsenic. Inorganic arsenic occurs naturally in many kinds of rocks and it is most commonly found with sulfide ores as arsenopyrite. Inorganic arsenic compounds are known to be human carcinogens. Arsenic combined with carbon and hydrogen is classified as organic arsenic. Both inorganic and organic compounds are typically white to colorless powders. Arsenic in element form is insoluble in water. It is soluble in oxidized form.

Arsenic is found in the natural environment in abundance in the Earth's crust and in small quantities in rock, soil, water and air. The average concentration of arsenic in the continental crust is 1-2 mg/kg. The mean concentration of arsenic in igneous rocks ranges from 1.5 to 3.0 mg/kg, whereas in sedimentary rocks it ranges from 1.7 to 400 mg/kg. About one third of the arsenic in the atmosphere comes from natural sources. Volcanic action is the most important natural source of arsenic. The next most important natural source is the arsenic-containing vapor that is generated from solid or liquid forms of arsenic salts at low temperatures. The rest two third comes from man-made sources. Mining, metal smelting, burning of fossil fuels and coal-fired powder plants are the major industrial processes that contribute arsenic contamination to air, water and soil. Elemental arsenic is produced commercially from arsenic trioxide. Arsenic trioxide is a by-product of metal smelting operations. Environmental contamination also occurs from pesticides used in agriculture and from chemicals used for timber preservation. About 70% of the world production of arsenic is used in timber treatment, 22% in agricultural chemicals, and the remainder in glass, pharmaceuticals and metallic alloys. Thus, the sources of arsenic can be categorized as: (i) geological (geogenic), (ii) anthropogenic (human activities), and (iii) biological (biogenic). Figure-1.1 depicts a schematic diagram of major sources and routes of arsenic in soil and aquatic ecosystem. Important arsenic bearing minerals are given in Table-1.1, in which, the most common is Arsenopyrite (**FeAsS**).



**Figure 1.1:** Major sources and routes of Arsenic in soils and aquatic ecosystem  
( Source : Donald L. Sparks, 2005)

**Table 1.1:** Important Arsenic Bearing Minerals

| Mineral                         | Arsenic content (%) |
|---------------------------------|---------------------|
| Arsenopyrite ( $\text{FeAsS}$ ) | 46                  |
| Lollingite ( $\text{FeAs}_2$ )  | 73                  |
| Orpiment                        | 61                  |
| Realger                         | 70                  |
| Native Arsenic                  | 90 – 100            |

The transport and distribution of arsenic in the environment is complex due to the many chemical forms in which it may be present and because there is continuous cycling of different forms of arsenic through air, soil and water. Arsenic dissolved in water can be present in several different forms. In well-oxygenated water and sediments, nearly all arsenic is present in the stable form of arsenate (V). Some arsenite (III) and arsenate (V) forms are less stable and are interchangeable, depending on the chemical and biological conditions. Some chemical forms of arsenic adhere strongly to clay and organic matter, which can affect their behavior in the environment. Weathered rock and soil, containing arsenic, may be transported by wind or water erosion. Arsenic releases into the atmosphere by industrial processes or volcanic activity and attaches to particles that are dispersed by the wind and fall back to the ground.

Long term exposure to arsenic in drinking water has variety of health concerns including several types of cancers, cardiovascular diseases, diabetes, and neurological effects. Many countries, including Bangladesh, India, Taiwan, Mongolia, Vietnam, Argentina, Chile, Mexico, Ghana and the United States, exposed to arsenic have problems because the sources of arsenic are primarily natural rather than anthropogenic or geothermal. Inorganic arsenic of geological origin has been recognized as the main form of arsenic in groundwater.

Different Countries have set different standards of arsenic content for drinking-water quality. WHO's norms for drinking-water quality go back to 1958; in that year, the international Standard for drinking-water was established at 200 µg/L as an allowable concentration for As. In 1963 the standard was re-evaluated and reduced to 50 µg/L. The WHO guidelines have been revised during the recent past and the permissible limits have been reduced from 50 µg/L to 10 µg/L (10 ppb) in year 1993 due to adverse health reports arising from different parts of the world where arsenic is causing severe health problems. India has set its maximum permissible limit for arsenic to 50 µg/L. The standards set by different countries for As for drinking-water quality are given in Table-1.2.

**Table 1.2:** Standards of Arsenic in potable water set by different Countries.

| <b>Country/Institution</b> | <b>Allowable level of Arsenic in drinking water</b> |
|----------------------------|---|
| US-EPA, USA                | 10 µg/L or 10 ppb                                   |
| Australia                  | 7µg/L or 7 ppb                                      |
| Canada                     | 25 µg/L or 25 ppb                                   |
| BIS, India                 | 50 µg/L or 50 ppb                                   |
| Latest, WHO's norm (1993)  | 10 µg/L or 10 ppb                                   |

## **1.1 Occurrences in Groundwater**

Arsenic is introduced into soil and groundwater during weathering of rocks and minerals followed by subsequent leaching and runoff. It can also be introduced into soil and groundwater from anthropogenic sources. These sources are localized and therefore, important in some geologic settings; biogenic sources can be predominant in marine ecosystem, whereas natural sources are primarily from the parent (or rock) material from which they are derived and therefore, are main causes of concern. There is another mode of occurrence of arsenic, namely Organoarsenic, which is mostly less toxic than both As(III) and As(V) and therefore, less harmful than other two forms. In groundwater, inorganic arsenic commonly exists as arsenate [As(V)] and arsenite [As(III)]. Inter-conversion of As(V) and As(III) takes place by oxidation of As(III) to As(V) and reduction of As(V) to As(III). High concentrations of arsenic tend to occur in sulphide minerals and metal oxides, especially iron oxides. Many factors control arsenic concentration and transport in groundwater. An understanding of factors controlling the distribution of arsenic in groundwater requires knowledge of arsenic sources and of processes controlling arsenic mobility. This knowledgebase would help in guiding monitoring and remediation efforts.

## **1.2 Geochemistry of Arsenic**

Geochemistry of arsenic is controlled by many factors, that include:

- Red-ox potential
- Adsorption/ desorption
- Precipitation/dissolution
- Arsenic speciation
- pH
- Biological transformation

In general, most naturally occurring arsenic compounds are insoluble in water.

### **1.2.1 Red-ox potential**

Redox potential, symbolically termed as Eh is also known as reduction potential, means the tendency of a chemical species to acquire electrons and thereby to reach to a reduced state. Arsenic is a redox-sensitive element. This means that arsenic may gain or lose electrons in redox reactions. As a result, it may be present in a variety of redox states. Arsenate generally predominates under oxidizing conditions, while arsenite predominates when conditions become sufficiently reducing. Under the pH conditions of most groundwater, arsenate is present as the negatively charged oxyanions  $\text{H}_2\text{AsO}_4^-$  or  $\text{HAsO}_4^{2-}$ , whereas arsenite is present as the uncharged species  $\text{H}_3\text{AsO}_3$ . Natural geochemical and biological processes play critical role in controlling the fate and transformation of arsenic in the subsurface. Arsenite is thermodynamically unstable in aerobic environments and oxidizes to As(V). Presence of other oxides such as FeO,  $\text{Fe}_2\text{O}_3$ ,  $\text{MnO}_2$  and even clay minerals is capable of oxidizing As(III).

### **1.2.2 Adsorption/ Desorption**

Two categories of processes largely control arsenic mobility in aquifers: (i) adsorption and desorption reactions, and (ii) solid-phase precipitation and dissolution reactions. Attachment of arsenic to an iron oxide surface is an example of an adsorption reaction. The reverse of this reaction i.e., detachment of arsenic from such a surface, is an example of desorption. Arsenic adsorption and desorption reactions are influenced by changes in pH, occurrence of redox (reduction/oxidation) reactions, presence of competing anions, and solid-phase structural changes at the atomic level.

Arsenate and arsenite adsorb to surfaces of a variety of aquifer materials, including iron oxides, aluminum oxides, and clay minerals. Adsorption and desorption reactions between arsenate and iron-oxide surfaces are important controlling reactions because arsenate adsorbs strongly to iron-oxide surfaces in acidic and near-neutral-pH water. However, desorption of arsenate from iron-oxide surfaces becomes favored as pH values become alkaline. As a result of the pH dependence of arsenic adsorption, changes in groundwater pH can promote adsorption or desorption of arsenic. Similarly, redox reactions can control aqueous arsenic concentrations by their effects on arsenic speciation and hence, arsenic adsorption and desorption. Arsenic adsorption can also be affected by the presence of competing ions. Structural changes in solid phases at the atomic level also affect arsenic adsorption and desorption.

### **1.2.3 Precipitation and Dissolution**

The various solid phases (minerals, amorphous oxides, volcanic glass, and organic carbon) of aquifer material can exist in a variety of thermodynamic states. Solid-phase precipitation is the formation of a solid phase from components present in aqueous solution. Precipitation of the mineral calcite, from calcium and carbonate present in groundwater, is an example of solid-phase precipitation. Dissolution of volcanic glass within an aquifer is an example of solid-phase dissolution. At any given time, some aquifer solid phases undergo dissolution, whereas others precipitate from solution. Arsenic contained within solid phases, either as a primary structural component or an impurity in any of a variety of solid phases, is released to groundwater when those solid phases dissolve. Similarly, arsenic is removed from groundwater when solid phases containing arsenic precipitate from aqueous solution. As an example, arsenic often co-precipitates with iron oxide; iron oxide, in such case, may act as an arsenic source (case of dissolution) or a sink (case of precipitation) for groundwater. Solid-phase dissolution contributes not only arsenic contained within that phase, but also any arsenic adsorbed to the solid-phase surface. The process of release of adsorbed arsenic, as a result of solid-phase dissolution, is distinct from the process of desorption from stable solid phases. Solid-phase precipitation and dissolution reactions are controlled by solution chemistry, including pH, redox state, and chemical composition.

#### **1.2.4 Arsenic Speciation**

Speciation of an element in water sample means determination of the concentration of different physico-chemical forms of the element which together make up its total concentration in the sample. The speciation of arsenic in environmental material is of interest because of the different levels of toxicity exhibited by various species. Species illustrate the various oxidation states that arsenic commonly exhibits (-3, 0, +3, +5) and the resulting complexities of its chemistry in the environment. Nearly two dozen arsenic species are present in the environmental and biological systems. Arsenic in groundwater is present in various species like,  $\text{H}_3\text{AsO}_3$ ,  $\text{H}_2\text{AsO}_3$ ,  $\text{HAsO}_3$ ,  $\text{H}_3\text{AsO}_4$ ,  $\text{H}_2\text{AsO}_4$ , and  $\text{HAsO}_4$ . Arsenic species are generally present as arsenate [As(V)] or arsenite [As(III)] for Eh conditions prevalent in most groundwater. Both As(V) and As(III) form protonates oxyanions in aqueous solutions and the degree of protonation depends on pH. Differences in their toxicity, biochemical and environmental behaviors require the determination of these individual arsenic species.

#### **1.2.5 Influence of pH**

Alteration in the state of arsenic oxidation is usually influenced by Eh and pH. The most suitable pH for arsenic dissolution is low acidic (pH < 2), but it can be dissolved in other pH ranges from 2 to 11 under suitable chemical and physical conditions. Arsenious acids, usually formed at low pH under mildly reduced conditions, are easily replaced by  $\text{H}_2\text{O}_3$  when pH increases.  $\text{HAsO}_3$  is usually formed at very high alkaline pH > 12.

#### **1.2.6 Influence of competing ions**

Other intrinsic factors of a system which can also exert marked influence on the concentration and speciation of arsenic include: solution composition, competing ions especially, the ratio of Phosphorous to As, and Selenium to As, nature and composition of solid phases present, reaction kinetics and flow regime.

#### **1.2.7 Biological transformation**

Arsenic undergoes a series of biological transformations in the aquatic environment, yielding a large number of compounds, especially organo-arsenicals. Certain reactions, such as oxidation of As(III) to As(V), may occur both in the presence and absence of microorganisms, whereas other reactions such as methylation, are not thermodynamically favorable in water and can occur only in the presence of organisms, which indicates that many aquatic organisms are capable of accumulating arsenic and may catalyse the oxidation of As(III) to As(V). Biological transformation is significantly important in marine ecology.

*The adsorption and desorption reactions, arsenic species, Eh, pH and solid-phase dissolutions and precipitations may vary from aquifer to aquifer that depend upon the geological settings, geo-chemistry and geo-environmental conditions of the aquifer. Therefore, rigorous geochemical investigation for adequate understanding of arsenic geochemistry under different hydrogeological and geo-environmental conditions of aquifers is essentially required for evolving sustainable solutions.*

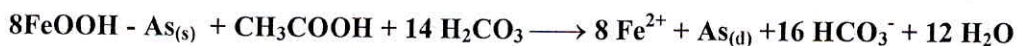
### 1.3 Hypotheses on Mechanism of Arsenic Mobilization

Widely accepted mechanisms of arsenic mobilization in groundwater are still to be established. However, based on arsenic geochemistry, three hypotheses describing probable mechanisms of As mobilization in groundwater specially, with reference to Holocene aquifers like in West Bengal and Bangladesh, have been suggested ( Bose and Sharma, 2002). These are:

- (i) Mobilization of arsenic due to the oxidation of As-bearing pyrite minerals: Insoluble As-bearing minerals, such as Arsenopyrite (FeAsS), are rapidly oxidized when exposed to atmosphere, realizing soluble As(III), sulfate ( $\text{SO}_4^{2-}$ ), and ferrous iron ( $\text{Fe}^{2+}$ ). The dissolution of these As-containing minerals is highly dependent on the availability of oxygen and the rate of oxidation of sulfide. The released As(III) is partially oxidized to As(V) by microbially mediated reactions. The chemical reaction is given by:



- (ii) Dissolution of As-rich iron oxyhydroxides (FeOOH) due to onset of reducing conditions in the subsurface: Under oxidizing conditions, and in the presence of Fe, inorganic species of As are predominantly retained in the solid phase through interaction with FeOOH coatings on soil particles. The onset of reducing conditions in such environments can lead to the dissolution of FeOOH coatings. Fermentation of peat in the subsurface releases organic molecules (e.g., acetate) to drive reducing dissolution of FeOOH, resulting in release of  $\text{Fe}^{2+}$ ,  $\text{As}^{3+}$ , and  $\text{As}^{5+}$  present on such coatings. The chemical reaction is given by:



where As(s) is sorbed As, and As(d) is dissolved As.

- (iii) Release of As sorbed to aquifer minerals by competitive exchange with phosphate ( $\text{H}_2\text{PO}_4^-$ ) ions that migrate into aquifers from the application of fertilizers to subsurface soil.

The second mechanism involving dissolution of FeOOH under reducing conditions is considered to be the most probable reason for excessive accumulation of As in groundwater.

## 1.4 Summary

Arsenic (**As**) in soil and aquatic ecosystem can occur from: (i) geological (geogenic), (ii) anthropogenic (human activities), and (iii) biological (biogenic) sources. In soil and groundwater, it can be introduced during weathering of rocks and minerals followed by subsequent leaching and runoff or from anthropogenic sources. Biogenic sources are predominant in marine ecosystem. The most common Arsenic bearing mineral is Arsenopyrite ( $\text{FeAsS}$ ). In sediments and waters, **As** can be present in the form of arsenite ( $\text{As(III)}$ ) and arsenate ( $\text{As(V)}$ ).  $\text{As(III)}$  is normally 60 times more toxic than  $\text{As(V)}$ . In groundwater, arsenic species can be present in various forms of arsenic acids, such as;  $\text{H}_3\text{AsO}_3$ ,  $\text{H}_2\text{AsO}_3$ ,  $\text{HAsO}_3$ ,  $\text{H}_3\text{AsO}_4$ ,  $\text{H}_2\text{AsO}_4$ , and  $\text{HAsO}_4$ . The standards of arsenic for drinking-water quality set by WHO and BIS are:  $10 \mu\text{g/L}$  and  $50 \mu\text{g/L}$ , respectively. Many factors control arsenic concentration, distribution and transport in groundwater. The factors, which govern the geochemistry of arsenic, are: red-ox potential, adsorption/desorption, precipitation/dissolution, arsenic speciation, pH, presence and concentration of competing ions, and biological transformation. These factors vary from aquifer to aquifer that depend upon the geological settings, geo-chemistry and eco-environmental conditions.

Out of three hypotheses describing (i) oxidation of **As**-bearing pyrite minerals and subsequent release of  $\text{As(III)}$ , (ii) dissolution of **As**-rich iron oxyhydroxides ( $\text{FeOOH}$ ) and resulting release of  $\text{Fe(II)}$ ,  $\text{As(III)}$ , and  $\text{As(V)}$ , and (iii) release of **As** sorbed to aquifer minerals by competitive exchange with phosphate ( $\text{H}_2\text{PO}_4^-$ ) ions as probable mechanisms of **As** mobilization in groundwater specially with reference to Holocene aquifers, the second hypothesis is believed to be the probable reason for excessive accumulation of **As** in groundwater. The oxidation model is the one in which  $\text{As(III)}$  is oxidized to  $\text{As(V)}$  while in the reduction model  $\text{As(V)}$  is reduced to  $\text{As(III)}$ .

### *Questions thus to be answered are:*

- (i) Whether the available literatures are adequate to resolve the issues of arsenic contamination in groundwater in India or, there is further need for investigation and study to strengthen understanding of geochemical processes for different hydro-geological conditions?
- (ii) Whether suggested hypotheses of **As**-mobilization in groundwater hold well for all hydro-geological and geochemical settings or for a select few?
- (iii) Whether occurrences of **As** in groundwater and their chemical composition contain similar proposition?
- (iv) What are the controlling factors for **As** in different geochemical environments?