

CHAPTER 7

MEDICAL GEOLOGY OF ARSENIC

INTRODUCTION

One of the worlds biggest environmental disasters, the arsenic poisoning of millions of people in Bangladesh and West Bengal, had its origins in the arsenic-bearing clay or peat layers at shallow depths within the Quaternary deltaic sediments of the Ganges-Brahmaputra delta. As Berger (1999) pointed out, the irony was that the problem arose only recently as people started using water from tube wells drilled through international assistance programmes to provide cleaner water than available on the surface.

The magnitude of the problem of arsenic poisoning was so great that WHO having recognized the enormous health implications lowered the provisional guideline value for arsenic in drinking water from 50 $\mu\text{g/L}$ to 10 $\mu\text{g/L}$. Among the countries which have well documented case studies of arsenic poisoning are Bangladesh, India (West Bengal), Vietnam, Taiwan, China, Mexico, Chile and many parts of the USA and Argentina (Figure 7.1). Recently, countries such as Nepal, Myanmar and Cambodia have also been added to the list of countries which have concentrations of As indicating water exceeding 50 $\mu\text{g/L}$ in some sources. Table 7.1 summarizes the documented cases of naturally occurring As-poisoning in world groundwaters. A technical report of the British Geological Survey (2001) highlights the magnitude of the issue of arsenic poisoning in Bangladesh as follows.

“A survey of well waters ($n = 3534$) from throughout Bangladesh, excluding the Chittagong Hill Tracts has shown that water from 27% of the shallow tube wells, that is wells less than 150 m deep, exceeded the Bangladesh standard for arsenic in drinking water (50 $\mu\text{g/L}$), 46% percent exceeded the WHO guideline value of 10 $\mu\text{g/L}$. Figures for ‘deep wells’ (greater than 150 m deep) were 1% and 5%, respectively. Since it is

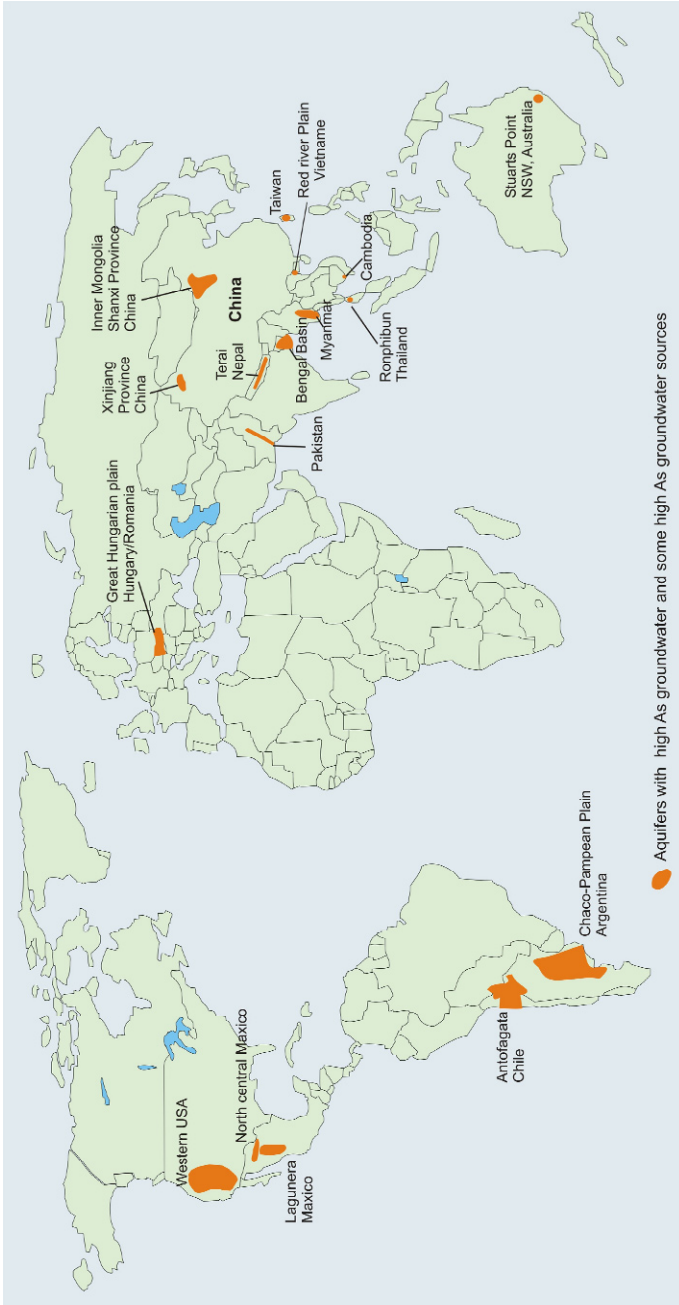


Fig. 7.1. Arsenic contaminated aquifers in the world (sources: Smedley and Kinniburgh, 2002)

believed that there are a total of some 6-11 million tube wells in Bangladesh mostly exploiting the depth range 10-50 m, some 1.5-2.5 million wells are estimated to be contaminated with arsenic according to the Bangladesh standard. Thirty five million people are believed to be exposed to an arsenic concentration in drinking water exceeding 50 $\mu\text{g/L}$ and 57 million people exposed to a concentration exceeding 10 $\mu\text{g/L}$ ”.

The above description clearly illustrates the enormity of the disaster and the importance of the understanding of the medical geochemistry of trace elements known to have an impact on the health of populations.

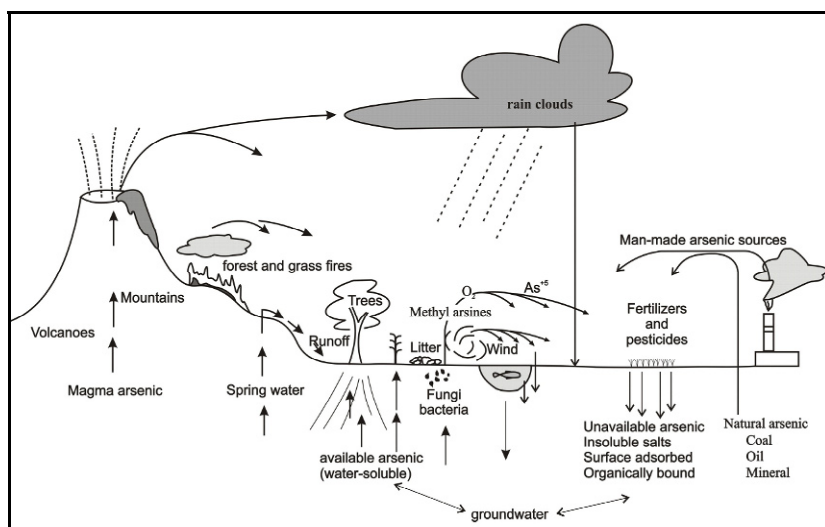


Fig. 7.2. Environmental transfer of arsenic (National Academy of Science, 1977)

The element arsenic (valence configurations $3d^{10} 4s^2 4p^3$) is a pollutant known to exist in four major oxidation states +5, +3, 0 and -3. It is found as a commonly distributed element in the atmosphere, rocks, minerals, soil, water and in the biosphere. Figure 7.2 is a diagrammatic representation of the arsenic cycle in nature. Arsenic mobilization in the environment occurs mostly under geogenic conditions though anthropogenic influences also affect the arsenic cycle to a significant degree. From among these, mining activity, combustion of fossil fuels, use of arsenic in agrochemicals is of particular importance. The medical geochemistry of arsenic is predominantly the aqueous chemistry of arsenic in the geological environment and its bioavailability. As shown in Figure 7.2, arsenic may be derived from a variety of sources and may enter the food chain through the aqueous medium. Groundwater interacting closely with arsenic-rich sediments

is a notable source of natural arsenic pollution. Table 7.2 shows the environmental forms of arsenic and Figure 7.3 illustrates the environmental chemistry of arsenic.

Table 7.1. Global arsenic contamination in ground water (Nordstrom, 2002)

Country/Region	Potential Exposed Population	Concentration ($\mu\text{g/L}$)	Environmental Conditions
Bangladesh	30,000,000	<1 to 2500	Natural; alluvial/deltaic sediments with high phosphate, organics
West Bengal, India	6,000,000	<10 to 3200	Similar to Bangladesh
Vietnam	>1,000,000	1 to 3050	Natural; alluvial sediments
Thailand	15,000	1 to >5000	Anthropogenic, mining, dredged alluvium
Taiwan†	100,000 to 200,000	10 to 1820	Natural; coastal zones, black shales
Inner Mongolia	100,000 to 600,000	<1 to 2400	Natural; alluvial and lake sediments; high alkalinity
Xinjiang, Shanxi	>500	40 to 750	Natural; alluvial sediments
Argentina	2,000,000	>1 to 9900	Natural; loess and volcanic rocks, thermal springs; high alkalinity
Chile	400,000	100 to 1000	Natural and anthropogenic volcanic sediments; closed basin; lakes, thermal springs, mining
Bolivia	50,000	-	Natural; similar to Chile and parts of Argentina
Brazil	-	0.4 to 350	Gold mining
Mexico	400,000	8 to 620	Natural and anthropogenic; volcanic sediments, mining
Germany	-	<10 to 150	Natural; mineralized sandstone
Hungary, Romania	400,000	<2 to 176	Natural; alluvial sediments, organics
Spain	>50,000	<1 to 100	Natural; alluvial sediments
Greece	150,000	-	Natural and anthropogenic; thermal springs and mining
United Kingdom	-	<1 to 80	Mining; southwest England
Ghana	<100,000	<1 to 175	Anthropogenic & natural; gold mining
USA and Canada	-	<1 to >100000	Natural and anthropogenic; mining, pesticides, As_2O_3 stockpiles, thermal springs, alluvial, closed basin lakes, various rocks

Arsenic in Rocks and Minerals

From among the rocks, igneous rocks have relatively small concentrations of arsenic (Table 7.3). Volcanic glasses show the highest arsenic content and as shown in Figure 7.2, volcanoes are important sources of As in the environment. The other igneous rocks however, do not show any marked variations. Metamorphic rocks contain about 5 mg/kg with pelitic rocks exemplified by phyllites and shales having arsenic as much as 18 mg/kg.

Sedimentary rocks are by far the more important sources of arsenic pollution and these are known to contain arsenic in the range 5-10 mg/kg. The argillaceous sedimentary rocks have higher arsenic contents as compared to the more arenaceous types such as sandstones, the values being 13 mg/kg for the former and 4 mg/kg for the latter. As shown in Table 7.3, shales of marine origin are heavily enriched in arsenic possibly due to the presence of significant amounts of sulphur and pyrite. Organic rich-sediments also contain high levels of arsenic with some coals having arsenic up to 35,000 mg/kg.

Arsenic has great affinity for sulphur and this results in arsenic being present in significantly higher concentrations in sulphides such as pyrites. Arsenian pyrite for example is a common mineral in some ore bodies and the ability of arsenic to substitute for sulphur gives rise to high As concentrations. As shown in Table 7.4, sulphides dominate the mineralogy of arsenic. Considering the rock-forming minerals (Table 7.4) arsenic, in view of its ability to substitute for Si^{4+} , Al^{3+} , Fe^{3+} and Ti^{4+} , tends to be present in many mineral structures.

It is known that authigenic pyrite is present in significant abundance in sediments of rivers, lakes and oceans as well as in aquifers. These minerals had been formed under reducing environmental conditions and they form an important link in the geochemical cycle of arsenic.

Arsenic in Soils

As shown in Table 7.3, the concentrations of arsenic in soils range from 5 to 10 mg/kg. Due to the presence of sulphide minerals, organic-rich soils tend to have higher concentrations of arsenic. Peats and bogs, for example have an average As concentration of 13 mg/kg. In Vietnam, some acid sulphate soils contain as much as 41 mg/kg. These acid sulphate soils are formed by the oxidation of pyrite in sulphide-rich terrains. It is also worthy

of note that anthropogenic influences particularly from the fertilizers, also provide an input into the arsenic budget in soils.

Table 7.2. Environmental forms of arsenic (Braman, 1975)

Compound	Source
Water	
As(III), arsenite ion and As(V), arsenate ion	Sea water
CH ₃ AsO(OH) ₂	Fresh water ponds, rivers, lakes
	Sea water, fresh water ponds, rivers, lakes
	Sea water, fresh water
(CH ₃) ₃ As (or other oxides)	Fresh water
Air	
As(III) and As(V)	Particulate
CH ₃ AsH ₂	Over As-treated soil
(CH ₃) ₂ AsH	Over treated soil
(CH ₃) ₃ As	Over treated soil
Biological samples	
Types	Forms
Sea weed and epiphytes	As(III), As(V), CH ₃ AsO(OH) ₂ , (CH ₃) ₂ AsO(OH), (CH ₃) ₃ As
Urine	As(III), As(V), CH ₃ AsO(OH) ₂ , (CH ₃) ₂ AsO(OH)
Methanobacterium cultures	(CH ₃) ₂ AsH
Aerobic cultures (Fungi and mixed)	(CH ₃) ₃ As, CH ₃ AsO(OH) ₂ , (CH ₃) ₂ AsO(OH),

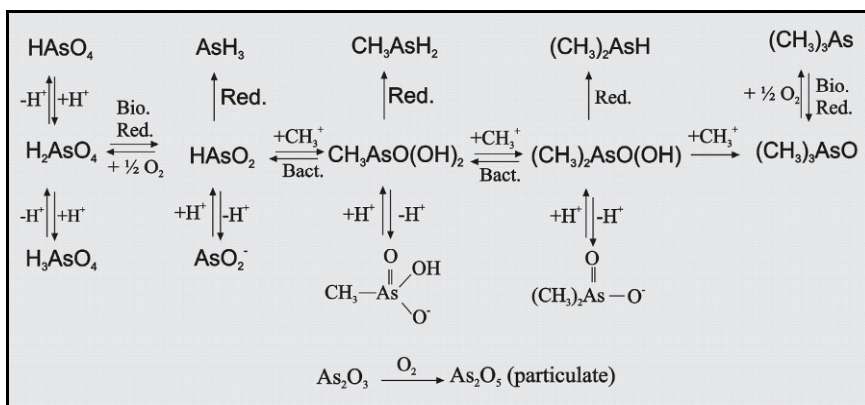


Fig. 7.3. Environmental chemistry of arsenic (Braman, 1975)

Table 7.3. Typical arsenic concentrations in rocks, sediments, soils and other surficial deposits (Smedley and Kinniburgh, 2002)

Rock / Sediment Type	Avg. Conc. (Range) (mg/Kg)
Igneous rocks	
Ultrabasic rocks (peridotite, dunite, kimberlite etc.)	1.5 (0.03-15.8)
Basic rocks (basalt)	2.3 (0.18-113)
Basic rocks (gabbro, dolerite)	1.5 (0.06-28)
Intermediate (andesite, trachyte, latite)	2.7 (0.5-5.8)
Intermediate (diorite, granodiorite, syenite)	1.0 (0.09-13.4)
Acidic rocks (rhyolite)	4.3 (3.2-5.4)
Acidic rocks (granite, aplite)	1.3 (0.2-15)
Acidic rocks (pitchstone)	1.7 (0.5-3.3)
Volcanic glasses	5.9 (2.2-12.2)
Metamorphic rocks	
Quartzite	5.5 (2.2-7.6)
Hornfels	5.5 (0.7-11)
Phyllite / slate	18 (0.5-143)
Schist / gneiss	1.1 (<0.1-18.5)
Amphibolite and greenstone	6.3 (0.4-45)
Sedimentary rocks	
Marine shale / mudstone	3-490
Shale (Mid-Atlantic Ridge)	174 (48-361)
Non-marine shale/mudstone	3.0-12
Sandstone	4.1 (0.6-120)
Limestone / dolomite	2.6 (0.1-20.1)
Phosphorite	21 (0.4-188)
Iron formations and Fe-rich sediment	1-2900
Evaporites (gypsum / anhydrite)	3.5 (0.1-10)
Coals	0.3-35,000
Bituminous shale (Kupferschiefer, Germany)	100-900
Unconsolidated sediments	
Various	3 (0.6-50)
Alluvial sand (Bangladesh)	2.9 (1.0-6.2)
Alluvial mud / clay (Bangladesh)	6.5 (2.7-14.7)
River bed sediments (Bangladesh)	1.2-5.9
Lake sediments, Lake Superior	2.0 (0.5-8.0)
Lake sediments, British Columbia	5.5 (0.9-44)
Glacial till, British Columbia	9.2 (1.9-170)
World average river sediments	5
Stream and lake silt (Canada)	6 (<1-72)
Loess silts, Argentina	3-18
Continental margin sediments	2.3-8.2

Soils	
Various	7.2 (0.1-55)
Peaty and bog soils	13 (2-36)
Acid sulphate soils (Vietnam)	6-41
Acid sulphate soils (Canada)	1.5-45
Soils near sulphide deposits	126 (2-8000)
Contaminated surficial deposits	
Mining-contaminated lake sediment	342 (80-1104)
Mining-contaminated reservoir sediment, Montana	100-800
Mine tailings, British Columbia	903 (396-2000)
Soils and tailings-contaminated soil, UK	120-52,600
Tailings-contaminated soil, Montana	up to 1100
Industrially polluted inter-tidal sediments, USA	0.38-1260
Soils below chemicals factory, USA	1.3-4770
Sewage sludge	9.8 (2.4-39.6)

Arsenic in natural waters

Smedley and Kinniburgh (2002), Matschullat (2000) and Furguson and Gavis (1972) have written extensive reviews on the geochemistry of arsenic in water and the reader is referred to these articles for further detailed information. In the natural aquatic systems, As(V) and As(III) are the dominant arsenic species. The As(V) is an oxidant, which exists as H_2AsO_4^- , HAsO_4^{2-} and AsO_4^{3-} and under mildly reducing conditions (e.g. Eh $< +100$ mV), the As(III) state is stable and occurs as H_3AsO_3 , H_2AsO_3^- , and HAsO_3^- (Appelo and Postma, 1994).

The solubility of arsenic is particularly known for its strong dependence on pH and is mobilized at pH values normally found in groundwaters (pH 6.5-8.5) and under both oxidizing and reducing conditions. Figure 7.4 illustrates the Eh-pH diagram for aqueous arsenic species in the system at 25 °C and at 1 bar total pressure and Figure 7.5 shows the arsenic speciation as a function of pH. Since arsenic is a strongly redox sensitive element, its mobility in natural systems is strongly influenced by the oxidation state in which it occurs. Some of the salient features of the arsenic aqueous chemistry as discussed by Smedley and Kinniburgh (2002) are as follows:

Table 7.4. Typical arsenic concentrations in common rock-forming minerals (Smedley and Kinniburgh, 2002)

Mineral	As conc. range (mg/kg)
Sulphide minerals	
Pyrite	100-77000
Pyrrhotite	5-100
Marcasite	20-600
Galena	5-10000
Sphalerite	5-17000
Chalcopyrite	10-5000
Oxide minerals	
Hematite	up to 160
Fe oxide (undifferentiated)	up to 2000
Fe(III) oxyhydroxide	up to 76000
Magnetite	2.7-41
Ilmenite	<1
Silicate minerals	
Quartz	0.4-1.3
Feldspar	<0.1-2.1
Biotite	1.4
Amphibole	1.1-2.3
Olivine	0.08-0.17
Pyroxene	0.05-0.8
Carbonate minerals	
Calcite	1-8
Dolomite	<3
Siderite	<3
Sulphate minerals	
Gypsum/anhydrite	<1-6
Barite	<1-12
Jarosite	34-1000
Other minerals	
Apatite	<1-1000
Halite	<3
Fluorite	<2

- (a) Most oxyanions including arsenate tend to become strongly sorbed as the pH increases. This is in contrast to most trace-metal cations which show low solubility due to precipitation or co-precipitation with an oxide, hydroxide, carbonate or phosphate mineral or due to strong adsorption to metal oxides, clay or organic matter. Arsenic is thus an important trace contaminant in groundwaters.

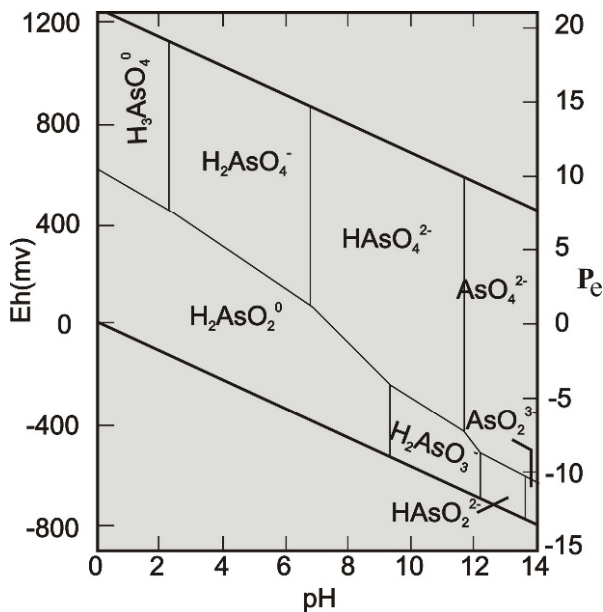


Fig. 7.4. Eh-pH diagram for aqueous As species in the system As-O₂-H₂O at 25°C and 1 bar total pressure (Smedley and Kinniburgh, 2002)

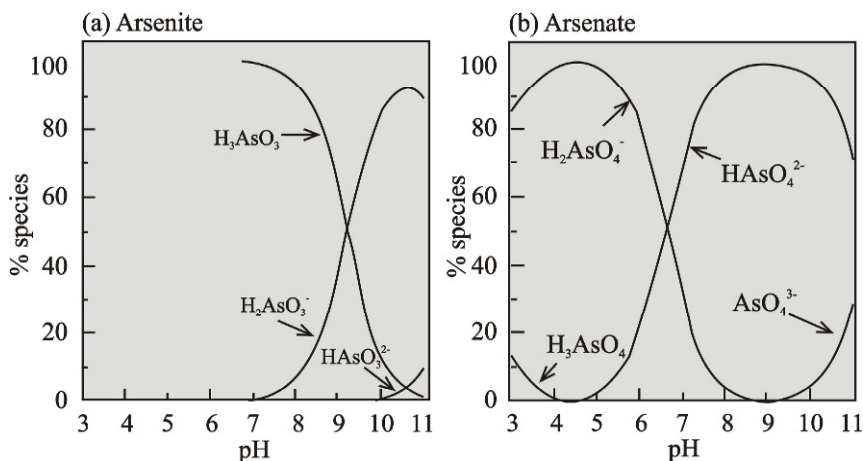


Fig. 7.5. (a) Arsenite and (b) arsenate speciation as a function of pH (ionic strength of about 0.01 M) (Smedley and Kinniburgh, 2002)

- (b) Arsenic shows marked mobility under reduced conditions. It can be found at concentrations in the mg/L range when all other oxyanion-forming elements are present in the $\mu\text{g/L}$ range.

-
- (c) When strongly reducing acidic conditions prevail, precipitation of sulphides such as orpiment (As_2S_3) and realgar (AsS) occur resulting in low-arsenic waters.
 - (d) The concentrations of arsenic in groundwaters vary markedly depending on the source and amount of arsenic as well as the geochemical environment. When the water-rock interactions exert a strong influence, As concentrations reach high levels, in the aqueous phase due to increased mobilization and accumulation.
 - (e) In atmospheric precipitation, arsenic is mainly in the form of $\text{As(III)}_2\text{O}_3$ dust particles. As shown by Nriagu and Pacyna (1988), anthropogenic sources of atmospheric arsenic amounts to 70% of the global atmospheric As flux.
 - (f) The arsenic concentrations of river water vary depending on the recharge composition, base flow contribution and bedrock lithology. In areas where there are high geothermal inputs, high arsenic concentrations can be expected. In some arid areas where surface water is dominated by river base flow, high arsenic levels may be observed and these often correlate with salinity.
 - (g) The oxidation and adsorption of As species onto river sediments and the dilution by surface recharge and run off tends to lower the arsenic concentration in the river water even if the bed rock may show high amounts of As.
 - (h) River waters can also be affected by high arsenic inputs from anthropogenic sources, bearing in mind that As is a well known industrial contaminant.
 - (i) In lake water arsenic concentrations tend to show evidence of stratification as a result of varying redox conditions. The As(III) to As(V) ratio may increase with depth. Higher arsenic concentrations are also observed at deeper lake waters when O_2 is depleted due to influence of microbial activity.
 - (j) In groundwater, there is a large range of arsenic concentrations reported in the literature. Most high-As groundwater provinces are the result of natural occurrence of As.

A review of the geochemical processes that control arsenic mobility indicates that the main processes of arsenic mobility in aquifers is (a) adsorption and desorption reactions (b) solid-phase precipitation and dissolution reactions. Arsenic adsorption and desorption reactions are influenced by pH changes, redox reactions, presence of competing anions and solid-phase structural changes at the atomic level.

Arsenic Adsorption and Desorption: Role of Fe, and Mn Oxides and Clays

Arsenate and arsenite adsorb onto surfaces of materials in the aqueous medium, and most notably onto iron oxides, aluminium oxides and clay minerals. As observed by Dzombak and Morel (1990) adsorption and desorption reactions between arsenate and iron oxide surfaces are of great importance as controlling reactions. Iron oxides are ubiquitous in the aqueous environment as coatings on solids (Figure 7.6). Arsenate adsorbs very strongly to these iron oxide surfaces in acidic and near-neutral pH water and desorbs as pH increases.

Iron oxide surfaces are also known to adsorb arsenite, and both arsenate and arsenite adsorb onto aluminium oxides and clay mineral surfaces. Under the typical environmental pH conditions these adsorption-desorption reactions however, appear to be less active than those between arsenate and iron-oxides surfaces.

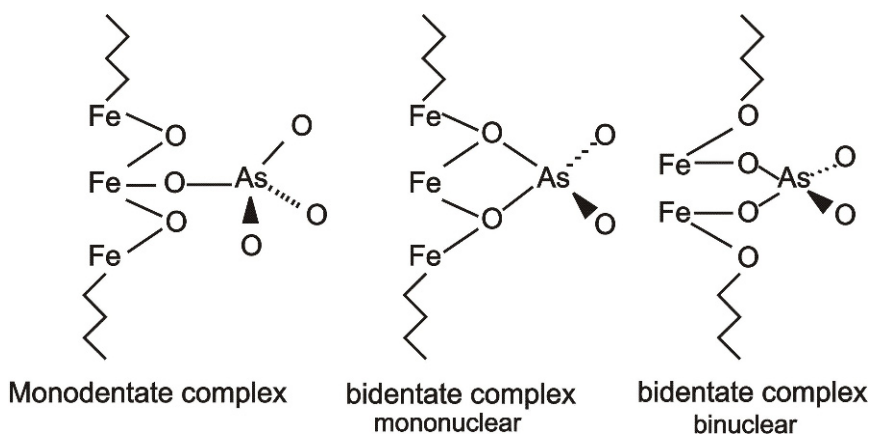


Fig. 7.6. Schematic illustration of the proposed adsorption mechanisms of arsenate onto goethite (O'Reilly et al., 2001)

Recent work (Goldberg and Johnston, 2001), using spectroscopic, sorption and electrophoretic mobility measurements show that arsenate forms inner sphere surface complexes (Figure 7.7) on both amorphous Al and Fe oxides while arsenite forms both inner and outer sphere surface complexes on amorphous Fe oxides and outer sphere surface complexes on amorphous Al oxide. Arsenic adsorption on amorphous Al and Fe-oxides and the clay minerals, kaolinite, montmorillonite and illite was investigated by Goldberg (2002) as a function of solution pH and As redox state, i.e., As(III) and As(V) (Figure 7.8). The results indicated that arsenate adsorption on oxides and clays was maximal at low pH and decreased with increasing pH above pH 9 for Al oxides, pH 7 for Fe oxide and pH 5 for clays. Arsenite adsorption exhibited parabolic behaviour with an adsorption maximum around pH 8.5 for all materials. There was no competitive effect of the presence of equimolar arsenite on arsenate adsorption.

Microorganisms and their impact on arsenic speciation and mobility

It is well known that microorganisms are ubiquitous in the geochemical environment and that they influence the biogeochemical cycles of many elements. Arsenic is such an element that inter-converts species which show markedly contrasting behaviour. The role of microorganisms is now of special importance in view of the extremely large scale of arsenic poisoning in West Bengal and Bangladesh. Many theories have been proposed to explain the subsurface mobilization of arsenic. Among these are:

- (a) Oxidation of arsenic containing pyrites.
- (b) Release of As(V) from reduction of iron oxides by autochthonous organic matter such as peat.
- (c) Reduction of iron oxides by allochthonous organic matter (from dissolved organics in recharging waters)
- (d) Exchange of adsorbed As(V) with fertilizer phosphates.

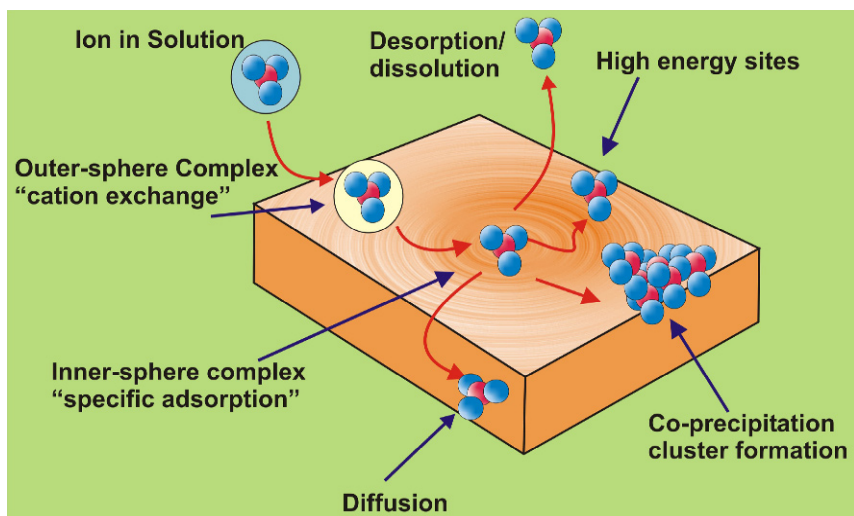


Fig. 7.7. Sorption mechanism at the mineral/water interface (Goldberg and Johnston, 2001)

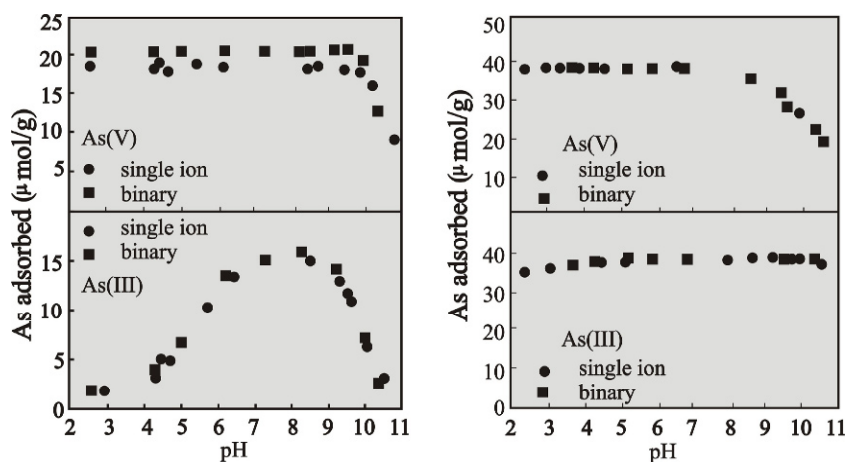


Fig. 7.8. Arsenic adsorption on kaolinite and montmorillonite as a function of pH and As redox state. Single ion layer systems: $\text{As(V)}^- - 20\mu\text{M}$, Binary system $\text{As(III)}^+ - \text{As(V)}^- - 20\mu\text{M}$. Suspension density 40 g/L (Goldberg and Johnston, 2001)

Oremland and Stolz (2003) have suggested that the above processes are not mutually exclusive, but that over time, microorganisms probably play an essential role in both the direct reduction and oxidation of the arsenic species, as well as the iron minerals contained in the aquifers. Microorgan-

isms catalyze chemical reactions in order to obtain energy for metabolic growth. They obtain this much needed energy from the environment and as a result of the chemical reactions catalyzed by the microorganisms, extremely important biochemical transformation may occur. The greatest energy-generating reactions of the biosphere are redox reactions and these cause marked alterations in the behaviour of their substrates (Stumm and Morgan, 1996). The great need for microbes to catalyze the energy-generating reactions causes rapid chemical transformation in contrast to the somewhat sluggish rates of abiotic reactions. The microorganisms catalyze the redox reactions by means of aerobic and anaerobic respiration and these processes influence the arsenic biogeochemistry.

The discovery that in spite of its toxicity, As(V) is actually used as a respiratory oxidant had opened up further avenues for microbial biogeochemical research. Two types of related bacteria, namely *Sulfurospirillum arsenophilum* and *Sulfurospirillum barresii* were the first microbes reported that carried out this process (Ahman et al., 1994; Oremland and Stolz, 2003). Such microbes are termed dissimilatory arsenate-reducing prokaryotes (DARPs) and have been isolated from fresh water sediments, estuaries, soda lakes, hot springs and even gold mines (Oremland et al., 2002). Figure 7.9 illustrates the diversity of the arsenic-metabolizing prokaryotes. It is of interest to note that some of these microbes have been isolated from the aquifer materials of Bangladesh and gastrointestinal tract of animals. There are also the extremophiles adapted to high temperature, pH and/or salinity (Oremland and Stolz, 2003). These authors formulated a conceptual model for the geochemical scenario of Bangladesh arsenic-rich aquifer systems (Figure 7.10).

The sequence of the mechanism proposed is as follows:

- i) Oxidation of the original As(III) containing minerals. (eg. Arsenopyrite) during transport and sedimentation by pioneering chemolithoautotrophic arsenite oxidizers (CAOs) and heterotrophic arsenate oxidizers (HAOs) taking place over recent geological time periods.
- ii) Accumulation of As(V) onto surfaces of oxidized minerals such as ferrihydrite.
- iii) Later anthropogenic activities such as irrigated agriculture, digging of wells, lowering of groundwater table by water extraction etc.

- would provide oxidants (e.g. oxygen, nitrates) which would stimulate As(III) oxidation.
- iv) This would cause a build up of microbial mass and hence organic matter thereby creating anoxic conditions.
- v) These and other organic matter such as peat would promote the dissimilatory reduction of absorbed As (V) by DARPs and the subsequent dissolution of absorbent minerals such as ferrihydrite.

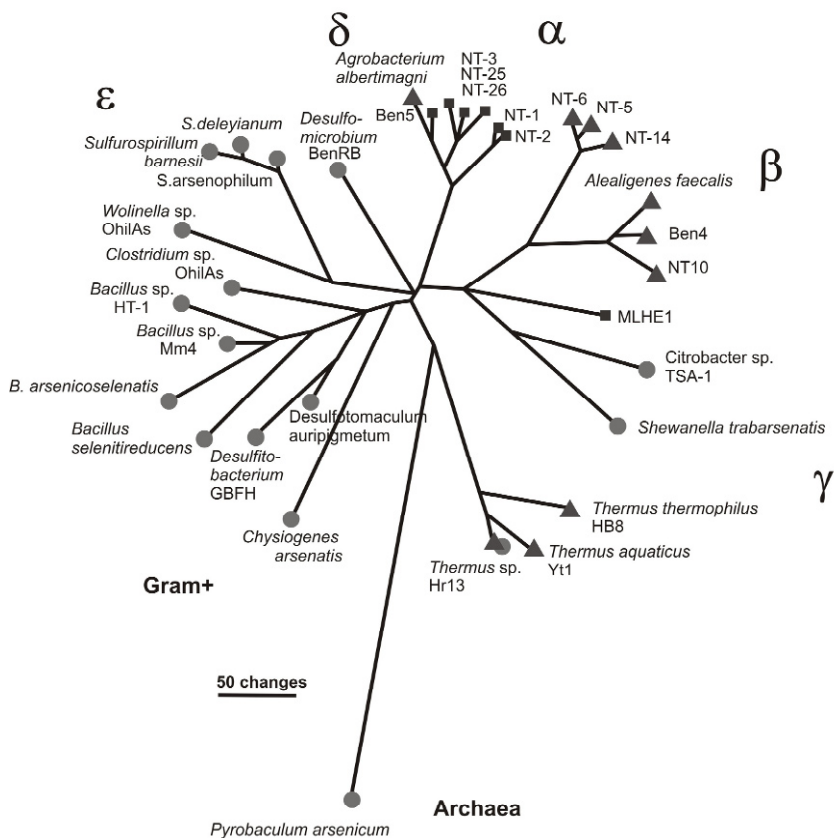


Fig. 7.9. Phylogenetic diversity of representative arsenic-metabolizing prokaryotes. Dissimilatory arsenate-respiring prokaryotes (DARPs) are indicated by yellow circles, heterotrophic arsenite oxidizers (HOAs) are indicated by green triangles, and chemoautotrophic arsenite oxidizers (CAOs) are indicated by red squares. In some cases (e.g. *Thermus* sp. strain HR13), the microbe has been found able to both respire As(V) and oxidize As(III) (Oremland and Stolz, 2003; reprinted with kind permission from AAAS)

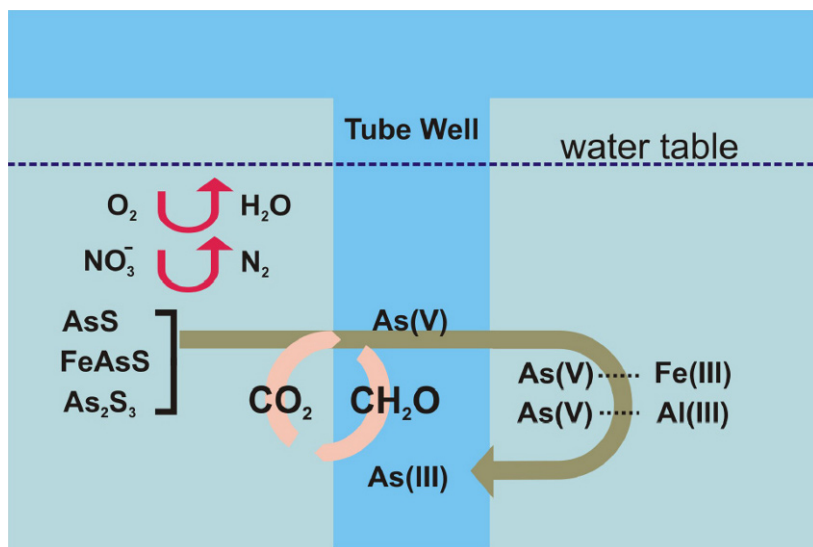


Fig. 7.10. A conceptual model of how arsenic-metabolizing prokaryotes may contribute to the mobilization of arsenic from the solid phase into the aqueous phase in a subsurface drinking water aquifer. Arsenic is originally present primarily in the form of chemically reduced minerals, like realgar (AsS), orpiment (As_2S_3), and arsenopyrite ($FeAsS$). These minerals are attacked by CAOs, which results in the oxidation of $As(III)$, as well as iron and sulfide, with the concurrent fixation of CO_2 into organic matter. Construction of wells by human activity accelerates this process by providing the necessary oxidants like molecular oxygen or, in the case of agricultural regions, nitrate. The $As(V)$ can subsequently be adsorbed onto oxidized mineral surfaces like ferrihydrite or alumina. The influx of substrate organic materials derived either from buried peat deposits, recharge of surface waters, or the microbial mats themselves promotes microbial respiration and the onset of anoxia. DARPs then respire adsorbed $As(V)$, resulting in the release of $As(III)$ into the aqueous phase (Oremland and Stolz, 2003; reprinted with permission from AAAS)

The research studies of Saikat et al. (2001) also show evidence of microbial activity which mediate in arsenic transformations in the Bangladesh aquifer sediments.

The bacterial dissimilatory reduction of arsenate and sulphate has been studied in detail by Oremland et al. (2000) in Mono Lake California. The stratified (meromictic) water column of alkaline and hypersaline Mono Lake contains high concentrations of dissolved inorganic arsenic ($\sim 200 \mu\text{mol/L}$). Arsenic speciation changed from $As(V)$ to $As(III)$ with the transition from oxic surface waters (mixolimnion) to anoxic bottom waters (monolimnion). A radio assay devised to measure the reduction of $^{73}As(V)$

to $^{73}\text{As(III)}$ and tested using cell suspensions of the As(V)-respiring *Bacillus selenitireducens* showed complete reduction of $^{73}\text{As(V)}$.

Anoxic environments host a variety of microorganisms and these generate energy by coupling the oxidation of H_2 or organic carbon to the reduction of inorganic As(V) to As(III). Because arsenate reduction is an energy-generating process for the microorganisms involved, and because arsenite is both toxic and more mobile than arsenate, this process is expected to greatly influence the geochemistry of arsenic in anoxic systems, particularly with respect to arsenic mobilization (Ahman et al., 1997; Cummings et al., 1999).

As discussed earlier, sorption onto oxides of Fe and Mn and precipitation on sulphide solids in anoxic environments are the two main processes that influence arsenic mobility in aqueous, soil and sedimentary environments. Microbial impacts on Fe and Mn oxides therefore influence arsenic geochemistry. Since the reduced forms of Fe and Mn are highly soluble, these oxides dissolve readily upon microbial reduction, simultaneously releasing sorbed substances such as arsenic (Ahman et al., 1997). Further, microbial sulphate reduction can yield sufficient sulphide to precipitate arsenic in solids such as amorphous arsenic sulphide, realgar or orpiment. While the geochemical significance of the reductive processes for arsenic cycling is well-established, the significance of the oxidative pathways is much less understood.

Apart from energy generation, microorganisms need to protect themselves from toxic substances. The mechanism of arsenic toxicity is for arsenate to enter the microbial cell through phosphate uptake proteins facilitated by the structural similarity of arsenate to phosphate. The phosphate in the Adenosine Triphosphate (ATP) is displaced by the arsenate thereby reducing its energy. It should however be noted that there are many cells which are highly phosphate-specific and which exclude arsenate (Torriani, 1990). Arsenite on the other hand enters the cytoplasm possibly by diffusion across the membrane and then cross-links sulphhydryl groups on enzyme. These cause the inactivity of the enzyme.

The mechanisms adopted by the microorganisms to remove the effects of arsenic poisoning are of special interest. The microbial reduction of arsenate to arsenite is by means of the As system an enzymatic process. Other mechanisms involve detoxification by reduction to arsine, As(III) in inorganic and methylated forms (Cullen and Reimer, 1989). Extensive studies

are now being done on these microbial arsenic detoxification mechanisms in order to utilize them in cleaning up polluted environments.

MEDICAL GEOLOGY OF ARSENIC- THE WEST BENGAL, BANGLADESH EXAMPLE

The arsenic poisoning in Bangladesh caused by high As concentration in aquifers is the largest mass poisoning in history. With up to 125 million of Bangladesh's population at risk, the case of arsenic poisoning in Bangladesh, and West Bengal is a classic example of the importance of the understanding of medical geology.

Bangladesh Basin-Geography and Geology

The geological, geographical, sedimentological and hydrological feature of the Bangladesh Basin, particularly with reference to the arsenic problem has been discussed exhaustively in the British Geological Survey Report of 2001 and the reader is referred to this valuable source of information for details. Only a brief outline is presented here.

The Bengal Basin comprising of a 15 km thick sequence of Cretaceous to Recent sediments and occupying about 100,000 km² of lowland flood plain and delta is one of the largest in the world. The combined deltas of the Ganges, Brahmaputra and Meghna (GMB) river systems, all of which lie within Bangladesh produce the greatest sediment load of any river system in the world (Figure 7.11). The sediment loads are known to vary by two orders of magnitude seasonally and these are mostly derived from the glacial and periglacial activity of the high Himalayas. Among the rocks that had undergone erosion are the ultrabasics of the northern high Himalayas and the granitic and high-grade metamorphic rocks from the central and southern parts. The extensive delta system has developed as a result of a series of glacio-eustatic sea level cycles and long-term tectonic activity. The very large number of aquifer systems underlying Bangladesh is a result of the deposition of Pleistocene to Recent fluvial and estuarine sediments. As shown in Figure 7.12, the surficial materials comprise mainly of alluvium, clay, muds, gravels, sand and peat.

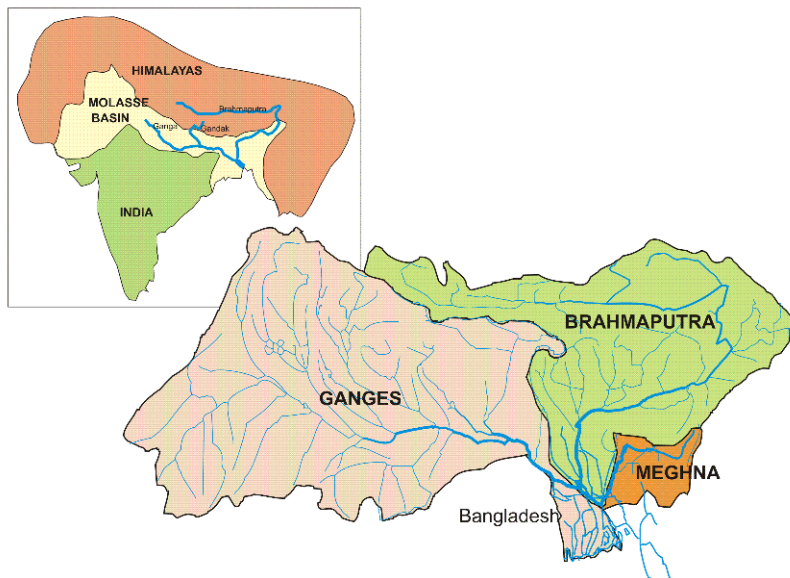


Fig. 7.11. Ganga-Brahmaputra-Meghna (GMB) river systems

Sediment characteristics

The British Geological Survey (2001) using limited borehole data constructed a hydrogeological cross section from north to south across Bangladesh and series of cycles of sedimentation has been observed. In the zone of subsidence at the northern end is a wedge of coarse sediments deposited as conglomerates. In the zone of uplift at Rangpur saddle the sediments thin out. The coarse-grained sediments thin and pinch out south of Hinge Zone and pass laterally into sandy deltas within the subsiding Faridpur Trough. Towards the south in the coastal zone, a series of aquifers is seen with alternations of sandstones and silts. The aquifers located away from the saline intrusions have been united to form a single body of fresh water.

Hydrochemical and mineralogical studies had revealed that the sediments containing groundwaters with the highest concentration of arsenic are the shallow fine-grained highstand deposits which had radiocarbon dates generally less than 10 ka. These are found to be localized in the tidal zones of the present Ganges, old Ganges, lower Meghna and lower Brahmaputra delta areas.

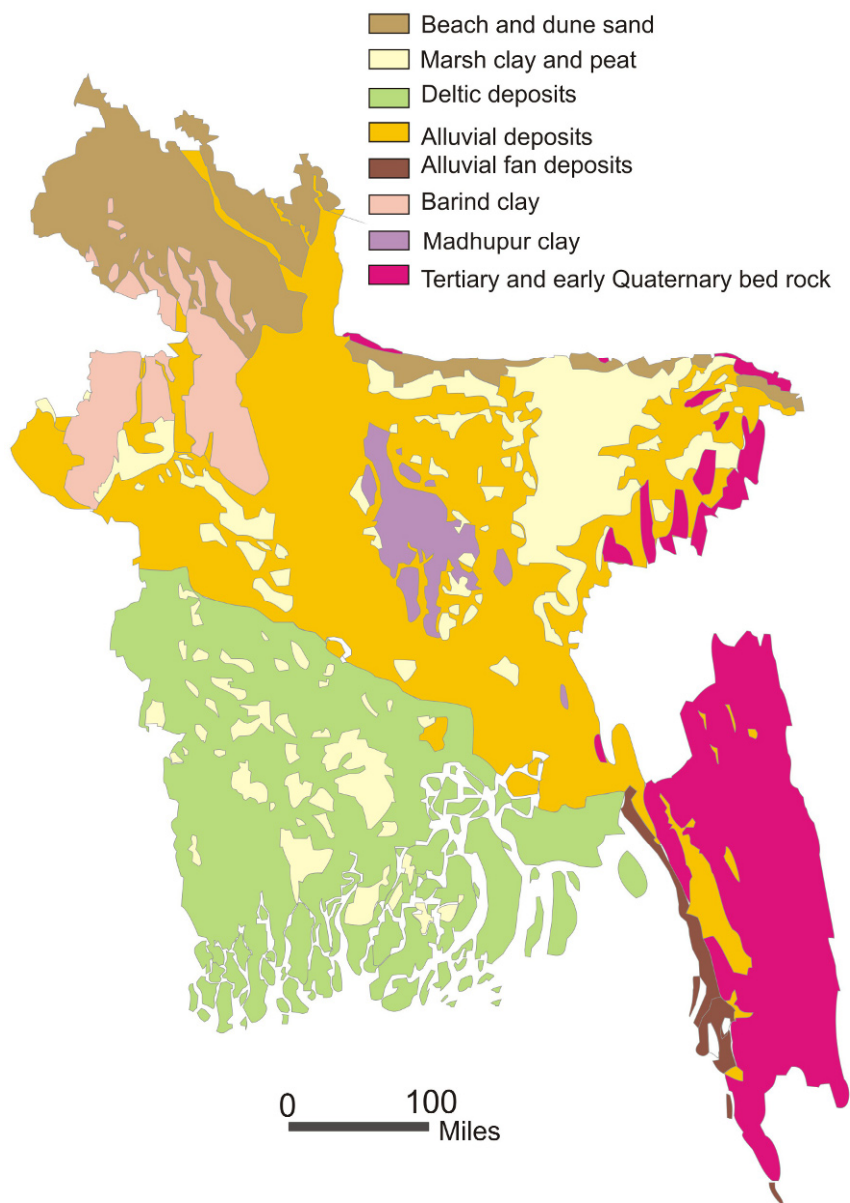


Fig. 7.12. Simplified geological map of Bangladesh (Alam et al., 1990)

Mineralogy and geochemistry of sediments

The mineralogy of the aquifer sediments have been studied by a large number of investigators, in different parts of the Bengal basin. Pal et al. (2002) studied the mineralogical constituents in two bore holes in the Chakdah area, West Bengal, and observed that clay and peat layers are richest in arsenic while the silty sand layers contain lesser amounts of arsenic. Figure 7.13 illustrates the distribution of Fe and As in two sediment cores beneath Deulhi Village (D3) and Smata Village (D4) near Jessore, south western Bangladesh. Peat has been observed (Ravenscroft et al., 2001).

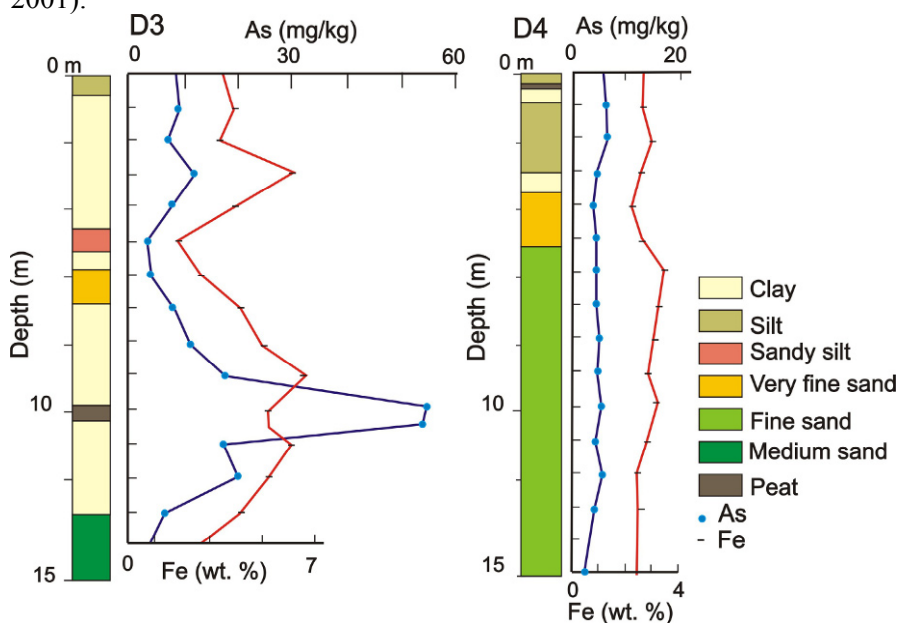


Fig. 7.13. Distribution of Fe and As in two sediment cores beneath Deulhi Village (D3) and Samta Village (D4) near Jessore, SW Bangladesh showing the occurrence of peat (Ravenscroft et al., 2001)

Pal et al. (2002) studied arsenious zone and ‘safe water zone’ of the West Bengal sections, and noted that the sandy aquifer material underlying the clay, peat and silty layers in both arsenic-rich and arsenic-poor zones had silt to sand-sized grains (96-99%) and interstitial clay (1-4%). The coarser components consisted of (a) a non-magnetic fraction such as stain-free quartz, feldspar, carbonate and lithic fragments and (b) minerals with variable magnetic intensity constituting 12-36% and which included (i) strongly magnetic phases such as iron oxide/hydroxide with residual magnetite and ilmenite (ii) feebly magnetic phases such as illite, biotite, iron

oxyhydroxide-coated sand grains, siderite concretion, muscovite, garnet, hornblende, tourmaline, rutile, kyanite, sillimanite, epidote, apatite, staurolite, zircon. The finer interstitial clay fraction contained e.g. quartz, feldspar, kaolinite, illite, montmorillonite and chlorite.

An important feature worthy of special note, is the total absence of arsenic-bearing clastic phases such as arsenopyrite and arsenious pyrite. The British Geological Survey (2001) also noted that arsenopyrite was never seen and that in general, sediments are sulphur-poor. They confirmed the general observation that the highest concentrations of most elements, including arsenic, are found in the fine-grained, especially clay, sediments. The hypothesis that iron oxides are a primary source of As in Bangladesh groundwaters was supported by the BGS data. Areas which had high concentrations of iron oxides with their adsorbed and co-precipitated As had the most arsenic-rich ground waters.

Organic matter

The presence of organic matter, notably peat, in some of the aquifer sediments of the aquifer sediments of the Bengal Basin has influenced some workers to hypothesize on the role of organic matter in the arsenic geochemistry. Ahmed et al. (1998); Brammer (1996), Safiullah (1998), DPHE (1999), Ishiga et al. (2000) noted the presence of peat beds in deferent parts of the Bengal Basin. Further locations of peat are given in Ravenscroft et al. (2001), who report that biogenic methane is common in groundwater over large areas, in places in amounts sufficient to provide domestic fuel. This was taken as a clear indicator of a substantial amount of organic matter undergoing microbial degradation. Human organic wastes from latrines, some of which are located very close to wells are also considered as contributors to pollution. Ravenscroft et al. (2001) considered peat degradation as a major redox driver of arsenic pollution (Figure 7.14).

The scale of the problem

Termed as the biggest mass poisoning in history, the arsenic problem in the Bengal Basin, in view of the sheer numbers of people involved (estimated to be over 130 million) is by far the biggest arsenic groundwater problem in the world. Up to half of Bangladesh's tube wells (Figure 7.15), about 10 million in number, are thought to be contaminated and the expected deaths resulting from arsenic poisoning is expected to run into thousands. It is estimated that 95% of the population of Bangladesh use

groundwater as drinking water. It is the shallow aquifer system (10-70 m below ground level) that is known to be the main cause of the arsenic problem. The deep aquifer system (150-200 m) is known to have relatively less arsenic.

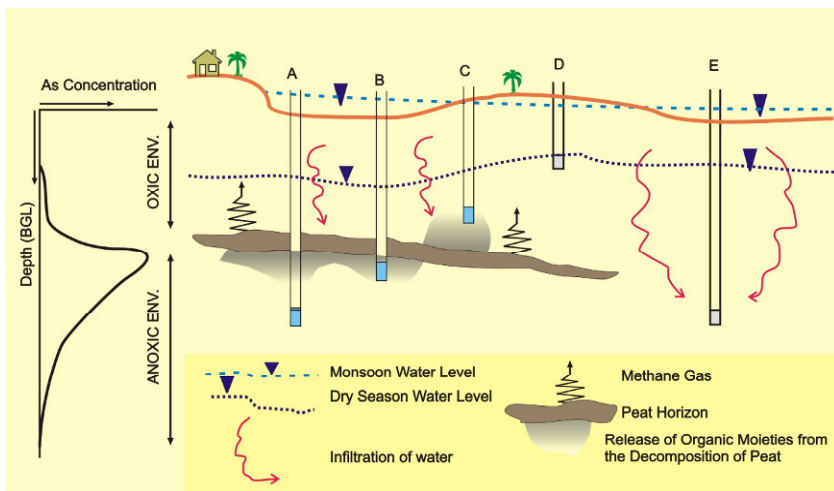


Fig. 7.14. Model of how arsenic pollution occurs in Bengal Basin and in any sedimentary sequence hosting buried swampland and marsh. In shallow Bangladesh sequences, hydraulic gradients cause downward movement of water during the wet season. In other sequences hydraulic gradients may cause upward flow of water through peat (Ravenscroft et al., 2001)

Well A- Low concentrations of organic moieties from distant peat cause some FeOOH reduction, the release of small amounts of arsenic and so low arsenic concentrations.

Well B- High amount of organic moieties from near by peat cause much FeOOH reduction, the release of large amount of arsenic and high arsenic concentrations.

Well C- Arsenic pollution above a peat layer caused by migration of arsenic in response to strong pumping and also migration of organic moieties upwards to cause local FeOOH reduction and additional arsenic release.

Well D- Uncontaminated, oxic, hand dug well. Seasonally dry and is safe from arsenic pollution.

Well E- A well that is currently uncontaminated. The likelihood of contamination depends on the distance organic moieties travelling laterally before being consumed by redox reactions and on the rate of movement of dissolved arsenic.



Fig. 7.15. There are millions of tube wells in Bangladesh, providing 95% of the drinking water in this country

The geochemical mechanisms of arsenic mobility in the Bengal basin

Distribution of Arsenic in the Aquifer System

The extensive work carried out by the British Geological Survey in 41 of the 64 districts in 1998 showed that from among 2022 samples analyzed

- i) 51% of the samples were above 10 $\mu\text{g/L}$ (WHO guideline value)
- ii) 35% were above 50 $\mu\text{g/L}$
- iii) 25% were above 100 $\mu\text{g/L}$
- iv) 8.4% were above 300 $\mu\text{g/L}$
- v) 0.1% were above 1000 $\mu\text{g/L}$

Only about 20% were considered to be essentially ‘arsenic-free’.

The survey also showed that the groundwaters are characteristic of reduced waters as indicated by high dissolved Fe, Mn and low sulphate. Unusually high phosphate concentrations were also observed (median 0.6 mg/L). Figure 7.16 illustrates the map showing the distribution of arsenic in groundwater in Bangladesh. The occurrences of arsenic correlates strongly

with surface geology and geomorphology, the most affected aquifers being those alluvial deposits lying beneath the Recent flood plains. From among the flood plains, the Brahmaputra and Tista rivers had the lowest levels while those of the Meghna flood plains southeast Bangladesh had much higher concentrations.

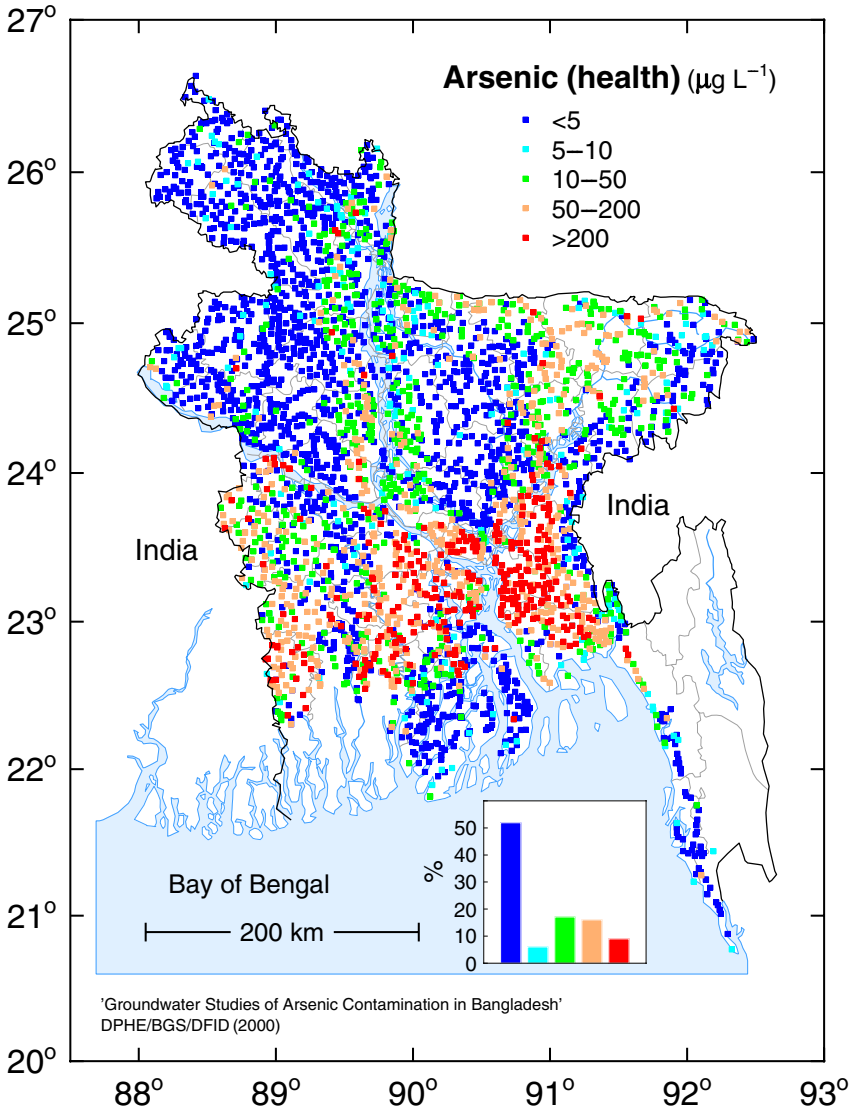


Fig. 7.16. Distribution of arsenic in groundwater in Bangladesh (reprinted with kind permission from the British Geological Survey, 2001)

Geochemical Mechanism of Arsenic Mobility

There are at present three main mechanisms attributed by different workers to the mechanism of enrichment of arsenic waters in the Bengal Basin. These could be summarized as:

i) **Mechanisms of As-bearing pyrite oxidation**

In this hypothesis (Mallick and Rajagopal, 1996; Das et al., 1996; Mandal et al., 1998), arsenic is released by the oxidation of arsenic-bearing pyrite in the sediments when groundwater irrigation lowers the water table to allow atmospheric oxygen into the aquifer sediments.

ii) **Competitive (anion) exchange mechanism**

The arsenite/arsenate anions sorbed to aquifer minerals are displaced into solution by competitive exchange with other oxy-anions, such as phosphate silicate or bicarbonate. In the Bengal Basin (Achryya et al., 2000) the source of phosphate was considered to be the super-phosphate fertilizer that was applied in excess and which allowed the leaching of arsenic into the groundwaters.

iii). **FeOOH reduction mechanism**

Naturally occurring arsenic sorbed onto iron oxyhydroxides (FeOOH) is released when these are reduced at anoxic conditions developed during sediment burial (Bhattacharya et al. 1997; Nickson et al., 1998; 2000; McArthur et al., 2001), possibly driven by microbial actions.

The mechanism of arsenic-bearing pyrite oxidation has not found much favour among the large number of researchers investigating into the mechanism of arsenic mobilization. Arsenopyrite has not been identified among the common minerals in Bangladesh sediments (Pal et al., 2002). The lack of high sulphate concentrations in arsenic-rich groundwater is used as a key evidence against the pyrite oxidation hypothesis.

The second mechanism concerning the competitive anion exchange with phosphates and others stemmed from the increased use of phosphatic fertilizers in Bangladesh. The sorbed arsenic on FeOOH was thought to be classified as a result of phosphate leached from soils on account of an excessive use of phosphatic fertilizer. However, this idea has been rejected (Ravenscroft et al., 2001) in view of the fact that there are certain areas where the groundwater is essentially free of both arsenic and phosphorus

but where irrigation and application of fertilizer is highest. Some experimental work carried out by Manning and Goldberg (1997) showed that P/As mole partition ratios for desorption of arsenic by phosphate were around 5000. Thus, no more than 2 µg/L of arsenic was expected to be desorbed by a phosphorous (as P) concentration in groundwater of 5 mg/L. Further, uranium which normally accompanies phosphorus in fertilizers was found to be very low in the Bangladesh groundwaters. Even when uranium was high, phosphorus was very low. Thus most accepted hypothesis for arsenic enrichment of Bangladesh aquifer is the iron oxide reduction hypothesis.

Arsenic is known to show slow release from recently buried sediments in rivers, lakes and ocean (Smedley and Kinniburgh, 2002). The iron oxide/hydroxide phases adsorb arsenic on their surfaces, bearing in mind that many minerals have the surface-coated iron oxide/hydroxide and which therefore becomes arsenic-rich. The reduction of FeOOH is driven by a microbial metabolism of organic matter and is accompanied by microbial reduction of arsenate to arsenite (Zobrist et al., 2000).

The desorption of the above arsenic by some process will undoubtedly enrich the groundwaters in arsenic. The oxidation of fresh organic matter during burial of sediments results in anaerobic conditions, thus aiding the release of arsenic. Arsenic release is probably due to the following processes (BGS, 2001):

- (a) Reductive desorption of arsenic due to transformation of As(V) to As(III).
- (b) Iron oxide reduction: reductive dissolution of iron oxides, and a change in surface structure and specific surface area of the iron oxides during diagenesis.
- (c) Competition from other anions such as phosphates that may be strongly bound.

The very large volume of the sediments in the Bengal Delta causes a massive total accumulation of arsenic, even though the actual mean arsenic concentration may not be excessively high. The geochemical processes occurring in the delta causes the enrichment of arsenic-rich groundwaters.

The studies of Ravenscroft et al. (2001) and Harvey et al. (2002) indicate a distinct role played by organic matter. In their model of arsenic mobilization in the Bangladesh aquifer sediments, Ravenscroft et al. (2001) hypothesise that small organic species such as short-chain carboxylic acids

and methylated amines drained from biodegradation of peat drives the FeOOH reduction and ammonium production. The strong dependence of arsenic distribution on depth was taken to suggest that these small organic molecules have not migrated far and lie close to the peat source. Their model (Figure 7.14) emphasizes the importance of the biodegradation of buried peat deposits in the extreme reduction of FeOOH and high arsenic groundwaters. Harvey et al. (2002) are also of the view that arsenic mobilization is associated with the recent inflow of carbon. High concentrations of radio-carbon methane indicated that young carbon has driven the recent biogeochemical processes.

Arsenic in Rice and Other Crops

The arsenic-enriched water in Bangladesh is used commonly to irrigate paddy (rice) fields and vegetable plots. Arsenic therefore gets into the food chain quite easily. Paddy rice (*Oryza sativa* L.) is the staple food of the millions of Bangladeshis and the nature of the uptake of arsenic by the rice plant is of special importance, bearing in mind that tens of kilograms of rice per year per person is consumed.

Meharg and Rahman (2003) carried out a survey of paddy soils and rice grains throughout Bangladesh. The survey of the paddy soils showed that where arsenic groundwater is used for irrigation, the arsenic contents were elevated. Arsenic levels in the rice grains from an area of Bangladesh with low levels of arsenic in groundwaters and in paddy soils showed that the levels were typical of other regions of the world. The rice grains grown on regions where soil arsenic was high, had markedly high arsenic contents, with three rice grain samples having as much as 1.7 $\mu\text{g/g}$ As. A study by Huq et al. (2006) showed that from among the crops, Arum (*colocassia antiquorum*) and Boro rice had the highest arsenic build up (Figure 7.17).

The uptake kinetics of arsenic species in rice plants has been studied by Abedin et al. (2002). They showed that As species found in soil solution from a greenhouse experiment where rice was irrigated with arsenate contaminated water were, arsenite, arsenate, dimethylarsinic acid and monomethylarsonic acid. Competitive inhibition of uptake with phosphate showed that arsenite and arsenate were taken up by different uptake systems because arsenate uptake was strongly suppressed in the presence of phosphate, whereas arsenite transport was not affected by phosphate. Abedin et al. (2002) also showed that there was a hyperbolic uptake of monomethylarsonic acid and limited uptake of dimethyl arsenic acid, at a slow rate.

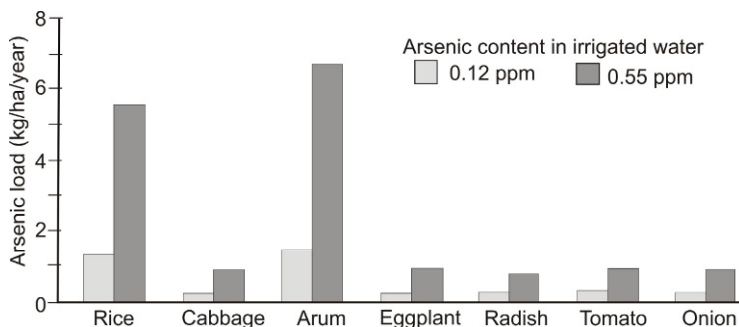
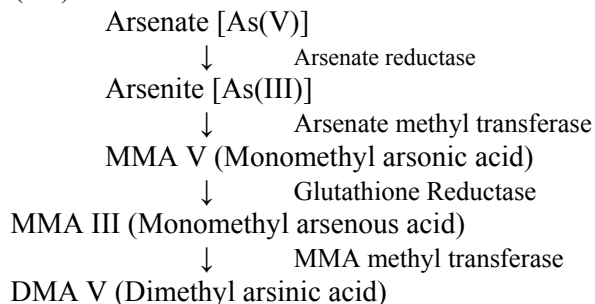


Fig. 7.17. Arsenic load from irrigation water for some crops compared to that of rice (Huq et al., 2006)

HEALTH EFFECTS OF ARSENIC

Arsenic found in the natural environment can enter the human body through food, water, soil and air. Skin contact with arsenic-rich soil and water could also be a source of irrigation. The particular arsenic species in the environment is not normally determined in routine procedures and hence the level and nature of arsenic exposure may not be known.

Arsenic is known as a protoplasmic poison due to its effect on the thiol group (-SH) of protein molecules in cells affecting normal enzymatic action, cell respiration and mitosis (Gordon and Quastel, 1948). In the bio-transformation of arsenic (Scheme shown below), monomethyl arsenous acid (MMA III) is reported to be the most toxic to the cells (Aposhian et al., 2000) and a powerful inhibitor of glutathione reductase and thioredoxin reductase (TR).



Arsenic is classified as a hazardous material suspected to be a carcinogen affecting the lungs and skin. It is also a teratogen which means that it can

cross the placental membrane into the metabolic system of unborn children. It is also known as a cumulative substance passing out of the body through urine, hair, finger, toe nails and skin. Most of the arsenic poisoning symptoms have been identified in Bangladesh. Among these are patients with melanosis (93.5%), leuco-melanosis (39.1%), keratosis (68.3%), hyperkertosis (37.6%), dorsum, non-petting oedema, gangrene and skin cancers (Karim, 2000). Tables 7.5 and 7.6 show the concentrations of arsenic in urine, hair and nails in some areas of the world, and the magnitude of the arsenic problem in Bangladesh, respectively. Figure 7.18 shows the impact of arsenic poisoning on the health of people living in affected areas. Saha (2003) in a review of arsenicosis in West Bengal discussed the severity of the arsenic problem in West Bengal. Arsenicosis is classified into 4 stages (i) preclinical (ii) clinical (iii) complication and (iv) malignancy (Saha et al., 1999) (Tables 7.7 and 7.8).

Table 7.5. Concentration of arsenic in urine, hair and nails of the affected people in different arsenic contaminated water ingestion episodes (Karim, 2000)

Location	Concentration in urine (mg/L)	Concentration in hair (mg/kg)	Concentration in nails (mg/kg)
Fairbank (USA)	0.18	1.0	4.0
Millard Country (USA)	0.025-0.66	010-4.7	-
Antofagasta Chile	0.025-0.77	4.00-83.4	-
Lassen Country (USA)	0.04-0.26	0.01-2.00	-
Taiwan	0.03-2.0	-	-
West Bengal, India	0.03-2.0	1.81-31.05	1.47-52.03
Bangladesh	0.05-9.42	1.1-19.84	1.3-33.98

Table 7.6. Arsenic in different body tissues collected from Bera, Ishurdi and Kushiata areas-Bangladesh (the urine arsenic content were estimated on the assumption that a total discharge of urine at one day is 1.5L) (Karim, 2000)

Sample	Total Samples	Normal Category		Safety range	Higher than normal		Arsenic conc.
		No.	%		No.	%	
Finger-nails	74	4	5	0.43-1.08 mg/kg	70	95	1.3-33.98 mg/kg
Hair	74	3	4	0.08-0.25 mg/kg	71	96	1.1-19.84 mg/kg
Skin	65	0	0	na	65	100	0.28-23.5 mg/L
Urine	63	4	6	0.005-0.04 mg/dl	59	94	0.075-14.13 mg/dl
Water	41	14	34	0.01-0.05 mg/L	27	66	0.01-9.0 mg/L

Table 7.7. Stage-wise gradation of arsenicosis (Saha et al., 1999)

Stages	Grades	Inference
I. Preclinical	0	Preclinical
	0-a	Labile-Blood phase
	0-b	Stable-Tissue phase
II. Clinical	1	Melanosis
	1-a	Diffuse melanosis in palm
	1-b	Spotted melanosis in trunk
	1-c	Generalized melanosis
	2	Spotted keratosis in palms and soles
	2-a	Mild (1- 6 nodules)
	2-b	severe (>6 nodules)
	2-c	large nodules
	3	Diffuse keratosis in palms and soles
	3-a	Partial- in palms or soles
	3-b	Partial- in palms and soles
	3-c	Complete
	4	Dorsal keratosis
4-a	In hands or legs	
4-b	In hands and legs	
4-c	Generalized	
III. Complications	5	Hepatic disorder
	5-a	Palpable liver
	5-b	Jaundice
	5-c	Ascitis
IV. Malignancy	6	Malignancy
	6-a	Single lesion
	6-b	Two lesions
	6-c	More than two lesions

Table 7.8. Increasing incidences of arsenicosis in West Bengal (1983-1998) (* estimated figure) (Saha et al., 1999)

Year	Affected districts	Affected blocks	Affected villages	Arsenical Dermatitis patients
1983	4	5	5	127
1984	5	12	15	241
1985	6	17	24	485
1986	6	30	40	1068
1987	6	40	61	1214
1988	6	42	78	2026
1989	6	43	79	2185
1990	6	44	123	24000*
1993	6	47	415	83000*
1994	6	47	428	85600*
1995	6	54	544	108800*
1996	7	60	638	200000*
1997	9	74	966	>200000*
1998	9	76	1206	>225000*



Fig. 7.18. Impact of arsenic poisoning on the health of people living in affected areas of West Bengal (photos sent by Prof. Surendra Kumar)