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Geogenic Arsenic and Associated Toxicity Problems in the Groundwater–Soil–Plant–Animal–Human Continuum

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Introduction

Arsenic (As), a group (VI) element, is ubiquitous in the earth's crust, and therefore all living entities could be exposed. Significant adverse impacts of geogenic As on environmental and human health have been recorded in Bangladesh (Chowdhury et al. 1999), West Bengal, India (Chakraborty and Saha 1997), and China (Zheng et al. 1996). Although reported as early as the 1930s from the ingestion of As-contaminated water, it was not until severe human poisoning was recorded in the Indian subcontinent that the need for intensive research was recognized. This chapter explores several pathways of inadvertent exposure including ingestion of food, dust, soil, and dermal absorption, especially in the Asian region where wet land farming is a major activity among the farming community. We examine the source, release, and transfer of As from the local rocks and minerals to plants and humans via water and soil. Particular references are made to the incidences of health effects recorded in the Indian subcontinent as well as to some examples from other parts of the world.

Geochemistry and Biochemistry of Arsenic

Arsenic, the 20th most abundant element in the earth's crust, has two primary oxidation states under earth surface conditions: $As^{3+}(As^{III})$ and $As^{5+}(As^{V})$. The average abundance in the earth's crust is 1–2 mg kg^{-1} (NAS 1977). In sandstones, the As content has been reported to vary between 0.6 and 120 mg kg^{-1}, while in shales and clay formations the concentrations might be as high as 490 mg kg^{-1} (NAS 1977). Arsenic is also associated with new secondary minerals in sediments as a result of weathering. The element occurs naturally, forming arsenide minerals with the metals copper, lead, silver, and gold, and commonly in combination with, or in solid solution in, the common sulfides such as pyrite (FeS_2) or as arsenopyrite (FeAsS) (Yan Chu 1994, Gaines et al. 1997). Arsenic also occurs in reduced form as orpiment As_2S_3 and realgar AsS, and oxidized as the mineral arsenolite (As_2O_3), or its polymorph, claudite (also As_2O_3). The precise mineral species formed depends on the physio–chemical conditions at the time of mineralization. When sulfide mineral deposits, or coal that contains sulfides are mined and smelted (Zheng et al. 1996), As can be an inadvertent and unwanted part of waste material, tailings, and waste water. In many cases this unwanted element in soils and sediments is a result of human activities that accelerated its release.

Arsenite (H_3AsO_3) is the predominant species of As^{III} in solution, and adsorbs strongly on clays, iron oxides, and other soil components at neutral pH. Con-

versely, arsenate (H_3AsO_4) is the common form of As^V, and shows strong adsorption at the lower pH values 4 to 7 (Smith et al. 1998). Poorly ordered aluminosilicate minerals, such as allophane and imogolite, commonly found in soils derived from volcanic ash and spodosols, have strong affinity for As due to their high surface area and high anion exchange capacity (Bhattacharya et al. 2001). Under acid pH conditions both As^{III} and As^V containing ions bind specifically with iron and manganese oxyhydroxide minerals. At pH <4, these minerals dissolve, releasing the As. Further, because the stability of iron and manganese oxyhydroxide minerals is dependent on redox potential, under reducing conditions there may also be enhanced release of As. Aqueous As concentrations are strongly linked to the formation of soluble complexes under reducing conditions (Bhattacharya et al. 1997). In addition, As^V can be readily desorbed on the increase in pH, or in the presence of competing anions like PO_4, MoO_4, SO_4, and dissolved organic acids (Smith et al. 1998).

In groundwater, inorganic As may exist both as As^V and As^{III}. Through the action of bacteria, biomethylation, organic matter is degraded and As^V becomes the more soluble As species. Anoxic conditions in aquifers may also enhance the formation of methylated As based on the local conditions and bacterial species present. Any methylated As species produced may also sorb onto Fe-oxides with an affinity in the order As^V > dimethylarsinic acid (DMAA) > As^{III} > methylarsnic acid (MMAA) (Smith et al. 1998), and affect the distribution and mobilization of As. In aqueous environments, prokaryotes and eukaryotes bind inorganic As through production of DMAA and MMAA (Kramer and Allen 1988).

Toxicity of Arsenic

The toxicity of As varies with the nature of chemical species. As^{III} is considerably more toxic than As^V (Donohue and Abernathy 1999), and organo-As is the least toxic species found in the environment. Styblo et al. (1999) comment in an article describing work with cell cultures that the classification of As as a carcinogen has been exclusively based on epidemiological studies on residents of Taiwan, or elsewhere, where people were exposed to inorganic forms of As. Some soluble forms of As are readily absorbed by the body, whereas the less soluble forms are poorly absorbed and largely excreted in the feces. Organic forms that may be formed *in vivo* are virtually completely absorbed following digestion. The organo–arsine compound arseno-betaine [$(CH_3)_3AsCH_2COOH$] (Burrow 1987) is the major source of dietary As for people consuming large amounts of seafood. This form of As is nontoxic and is excreted unchanged in urine (Crecelius 1977). This suggests that people in the Indian subcontinent, whose major dietary intake of protein is from fish and other aquatic food, but have safe water supplies, may not be at risk from As poisoning — i.e., that there is a lower threshold below which No–Adverse–Effect of As is observed. In comparison, continued ingestion of water with As at 500 μg l^{-1} can cause chronic As disease (Abernathy et al. 1996) as the poisoning in Bangladesh and West Bengal, India, attest.

Although the mode of action of As varies with the nature of As species, the most common effect is through the inactivation of enzyme systems with As^V first reduced to As^{III} *in vivo* before exerting its toxic effect (Ginsburgh and Lotspeich 1963). These investigators also claim that As^V can compete with phosphate in the phosphorylation process, producing an arsenate ester of ADP. Irrespective of the nature of the toxicity mechanisms, evidence from reported incidences of arsenicosis throughout the world indicates that As in general (As^{III}, As^V, or organo-As) can prove deleterious to animal and human health.

Chronic As poisoning has been intermittently reported in the literature (Lu 1990), with the most common incidence induced by groundwater ingestion in six districts of West Bengal, India, and in Bangladesh. The most commonly observed symptoms of As poisoning are conjunctivitis, melanosis, and hyperkeratosis (Das et al. 1996; Finkelman et al.). Studies by Chakraborty and Saha (1987) documented elevated concentrations of As in hair, urine, and skin tissue of people living in West Bengal where groundwater is the main source of potable water. More than 30,000,000 Indians are drinking water containing As with concentrations greater than the Indian drinking water guidance value of 0.05 mg l^{-1} (Chowdhury et al. 1997; total As range: 0.05–3.7 mg l^{-1}). Das et al. (1996) report that at least 175,000 people have skin lesions caused by As poisoning in this region. However, Badal

(1998) says the number is over 400,000 with clinical symptoms of As toxicity, and millions of Bangladeshis have been recorded with skin lesions (Chowdhury et al. 1999). Exposure of local people to As contaminated groundwater has also been reported in Argentina, Chile, China, Ghana, Hungary, India, Mexico, Taiwan, Thailand, the United Kingdom, and the United States (BGS/MMI 1999). In the developed countries, alternative sources of water are tapped to avoid the As toxicity problems recorded in Bangladesh and West Bengal.

Sources of Geogenic Arsenic

The occurrence, origin, and mobility of As in groundwater is primarily influenced by local geology, hydrogeology, and geochemistry of the sediments. As in groundwater has been commonly related to the dissolution of sulfide minerals (Chowdhury et al. 2001), and the dissolution or desorption from iron oxyhydroxides (Bhattacharya et al. 1997 , Nickson et al. 1998) or upflow of geothermal water (Welch et al. 1999).

Weathering of Primary Minerals

Arsenic is released in the soil environment following weathering of the common minerals arsenopyrite (FeAsS), and pyrite (FeS_2) containing As, or any other primary sulfide minerals. When pyrite is exposed to oxygen and water, the mineral weathers to form As^v,

Fe^{III} and SO_4. The overall reaction describing the oxidation of pyrite and arsenopyrite can be written as Equations 1 and 2 (Table 5.1).

The half redox reactions are written as Equations 3–6 (Table 5.1) in which S, Fe, and As are oxidized using O_2 as the electron acceptor. The weathering reactions are influenced by the: (1) presence of moisture, (2) pH, (3) composition of pore water, (4) temperature, (5) carbon dioxide equilibria, (6) solubility, and (7) redox values of the surrounding media. In summary, the oxidation of the most common mineral, As-rich pyrites, is the major source of As in groundwater in the vast tract of alluvial aquifers within the Bengal Delta Plain in Bangladesh and West Bengal (Bhattacharya et al. 2001). In addition to these reactions, biotic activity may contribute to pyrite dissolution. Following release of As from the As-containing minerals, the element can be transported by a range of physical, as well as chemical, processes (Garrels and Lerman 1977).

During the oxidation of pyrite, the released reduced Fe may be oxidized via both biotic and abiotic pathways. Abiotic Fe^{2+} oxidation is slow, but Fe^{2+} oxidation by microorganims is common in natural waters and sediments. Once oxidized to Fe^{3+} [Fe^{III}], the insoluble ferric hydroxides precipitate. The precipitation of ferric hydroxide can be expressed by the reaction in

Table 5.1: Weathering reactions

1. $4FeAsS_{(s)} + 14O_2 + 16H_2O \Leftrightarrow 4SO_4^{2-}{}_{(aq)} + 4AsO_4^{3-}{}_{(aq)} + 4Fe(OH)_3 + 20H^+{}_{(aq)}$

2. $2FeS_{2(s)} + 7H_2O + 7.5O_2 \Rightarrow 2Fe(OH)_{3(s)} + 8H^+ + 4SO_4^{2-}{}_{(aq)}$

3. $O_2 + 4H^+{}_{(aq)} + 4e^- \Rightarrow 2H_2O$ $E° = 1.23V$

4. $S^{2-}{}_{(aq)} + 4H_2O - 8e^- \Rightarrow SO_4^{2-}{}_{(aq)} + 8H^+{}_{(aq)}$ $-E° = -0.76V$

5. $AsO_2^-{}_{(aq)} + 2H_2O - 2e^- \Rightarrow AsO_4^{3-}{}_{(aq)} + 4H^+{}_{(aq)}$ $-E° = -0.56V$

6. $Fe^{2+}{}_{(aq)} - e \Rightarrow Fe^{3+}{}_{(aq)}$ $E° = -0.77 V$

7. $Fe^{3+}{}_{(aq)} + 3H_2O_{(l)} \Leftrightarrow Fe(OH)_{3(s)} + 3H^+{}_{(aq)}$

Equation 7 (Table 5.1) which has critical importance for retention and mobilization of As in soils as well as in aqueous media. These exceedingly fine-grained gel-like ferric oxyhydroxides solids are an important phase in sorption of any released As.

Both As^V and As^{III} are adsorbed on $Fe(OH)_3$, with the affinity higher for As^V as compared to As^{III}, and much lower for the organo-As species. Similar to many other oxyanions, the amount of total As sorbed by ferric hydroxide varies significantly with pH. Maximum adsorption for As^{III} is at pH 7.0, while the As^V maximum is at pH 4.0 (Smith et al. 1998). When the pH < 4 the acidophilic pyrite oxidizing bacteria *Thiobacilus ferrooxidans* can increase the rate of pyrite oxidation by several orders of magnitude. The biogenic effect may be mediated by other species as well.

Although the precise nature of mechanisms contributing to As in groundwater in the Indian subcontinent and specifically in the sedimentary aquifers of the Bengal Delta Plain are still not clear, two hypotheses have been proposed. The release of As takes place (a) during the oxidation of As-rich pyrite (FeS_2) or arsenopyrite (FeAsS) due to lowering of the water table during groundwater pumping (Saha and Chakraborty 1995) or through (b) desorption from or reductive dissolution of Feoxyhydroxides in a reducing aquifer environment (Bhattacharya and Jacks 2000, Bhattacharya et al. 1997, Nickson et al. 1998, Nickson et al. 2000, USAID 1997). According to Chowdhury et al. (2001), the As in West Bengal is natural (geogenic) and associated with pyrites in the alluvial sediments alongside the river Ganges. Groundwater withdrawal for agricultural irrigation leads to the oxygenation of the aquifer, decomposes the pyrite (FeS_2) rich in As, and the acid formed aids the release of As in a soluble form to the groundwater (Table 5.1: Equations 1 and 2). This is consistent with the suggestions of Welch et al (1988) that "mobilization of As in sedimentary aquifers may be in part a result of changes in the geochemical environment due to withdrawal of water for agricultural irrigation."

Dissolution of Oxides

Secondary minerals or salts that have adsorbed or incorporated other ions can increase the concentration of As in soils and groundwater. Work in Bangladesh and West Bengal suggests that iron oxyhydroxides, secondary minerals, are the major phase associated with As (Bhattacharya et al. 1997, Nickson et al. 2000). If the aquifers formed under aerobic conditions and sorbed As as arsenate onto iron and aluminum oxyhydroxides, but later became anaerobic, the reducing conditions would lead to dissolution of the oxyhydroxides and any associated As would be released into the groundwater. Such a scenario is common in many parts of the world (Bhattacharya et al. 1997). In the subsurface environment, the mobility of As is especially enhanced under anoxic conditions, making the risk for contamination higher in groundwater as compared to the surface water sources such as rivers, lakes, and reservoirs. The methylation of inorganic As to MMAA and DMAA, and changes in the biogeochemical microenviroment within the aquifers, are also possible. However, there is limited evidence of the presence of such species in groundwater samples in the Indian subcontinent.

Irrigation as a Source of Geogenic As in Surface Soils

It is likely that the use of groundwater for irrigation has led to or will lead to extensive contamination of soils throughout West Bengal and Bangladesh, although there is very little information on this. Similar contamination occurs in Mongolia and China where groundwater drawdown has occurred with agricultural demand. Limited studies by CSIRO Land and Water in Australia show that concentrations of As in surface soil in areas of long term irrigation in Bangladesh can exceed the guidance value of 100 mg kg^{-1} for residential soils. We can calculate the As load associated with irrigation by groundwater. Preliminary studies from two villages and a limited set of tubewell samples suggests annual deposition rates exceeding 4 tons of As per hectare.

Pathways of Human Exposure to Geogenic As

The major pathway for geogenic As exposure via the use of groundwater for domestic (drinking, cooking) purposes has been reported from several areas of the world (Bhattacharya et al. 1997, Nriagu 1994). Ingestion of crops or animals raised on either contaminated soils or with contaminated groundwater, as well as dermal absorption of As during wetland rice farming, may also lead to significant exposure to As. Only very few data have been gathered to assess these pathways.

Based on studies in Denmark, U.K., and Germany, Weigert et al. (1984) have shown that in countries where geogenic As is not present at high levels, the average intake of As via food of plant origin is 10–20 μg As day^{-1}, which is equivalent to only 10–12% of the estimated total dietary intake of As in these 3 countries. This range is similar to the recent survey by Schoof et al. (1999), which found that, for most adults, dietary inorganic As intake is of the order of 1–20 μg day^{-1} However, such investigations do not present a realistic picture of As intake in countries like Bangladesh and West Bengal, where vegetables are produced on soils subjected to over 20 years of irrigation with As-contaminated groundwater. Further, in other areas not employing As-containing irrigation water, the soils used for cropping elsewhere may have been transported from the As-rich sites. Cycling of As from parent material to soils to waters for irrigation, or surficial transport of soils containing As, eg. via erosion or deliberate shifting to augment local productivity by the farmers, could significantly elevate the total As in these regions (Naidu and Skinner 1999). The significance of geogenic As ingested through the food route is not known. In addition, incidental ingestion and inhalation of dust or indoor air derived from combustion of As contaminated materials could also be a significant exposure pathway (**Finkelman**).

Options for Minimizing Ingestion of Geogenic As

The recent incidences of As poisoning in many Asian countries has led to increased research on technologies for remediation of groundwater or for alternate options for potable water. While many treatment techniques (e.g., ion exchange, reverse osmosis, coagulation) for removing As were developed prior to the poisoning reported in these countries, their poor economy and indequate infrastructure have limited their applications. Most of the treatment technologies are based on As^V reacting with either an oxidic mineral or ion exchange surface in which the initial step in the process transforms As^{III} to As^V, which is either adsorbed on reactive surfaces or precipitated (Montgomery 1985). Oxidants such as chlorine (Cl), permanganate, solar radiation, and oxygen (O) have been commonly used (see Table 5.2).

In contrast to treatment of As-contaminated water, little effort has been directed towards remediating As-contaminated soils. Current studies for managing As-contaminated soils include soil washing (Naidu et al. 1999), chemical fixation (van der Hoek and Comans 1996), bioremediation (Frankenberger and Losi 1995), and electro-kinetic remediation (Lageman 1993).

At present no technique is available for minimizing uptake of As by crops, and it will require a comprehensive approach to address all the various pathways delineated above. An important tool for minimizing the effect of geogenic As would be to develop a map that delineates the distribution (and therefore the potential risk) posed by geogenic As in groundwater, soils, and crops at the landscape level. In this way appropriate strategies for minimising exposure could be tailored to specific areas. One could imagine the provision of water treatment or alternative water sources where water is contaminated, or the crops selectively distributed to avoid high As environments by relocating, covering, or diluting the surface soil, or by using more advanced methods such as phytoremediation. Continual upgrading of such maps could track changes in bioavailability and concentration of As over time, since ageing can decrease the bioavailability of contaminants, and any soil disturbance such tilling will gradually reduce localized surficial contamination.

Conclusions

Exposure of people to geogenic As in Bangladesh represents one example of a major hazard related to human manipulation of the natural environment. The present focus is on controlling exposure to As by either treating the groundwater before human use, which is technically possible, or providing alternative clean sources of water. Strategies for treatment that are affordable, cost-effective, and socially acceptable to all of the affected people, need more research. Importantly, there has been little consideration of alternative exposure pathways (the food and soil contamination), which can be relatively easily assessed with present analytical techniques. The challenge for the future will be to quantify these exposure routes and to devise and provide appropriate management strategies.

Table 5.2: Some treatment technologies for removal of As from water

Treatment Technology	Mechanism	Reference	Remarks
Coagulation	As^{III} +oxidant $\Rightarrow As^V$ As^V +coagulant (ferric sulfate, alum, lime) $\Rightarrow$ immobilization of As	Montgomery(1985), Paige et al. (1996)	Commonly used to remove As from drinking water in many countries
Activated alumina	As^{III} + oxidant $\Rightarrow As^V$ As^V + activated alumina $\Rightarrow$ adsorption	Gupta and Chen (1978)	Technology available with potential for regeneration of the surface
Ion exchange	Strong-base anion exchange resin	Montgomery (1985)	Resin can be recycled — technology commonly used
Reverse osmosis	Membrane technology; uses external pressure to reverse natural osmotic flow; polyvalent oxy-anions such as As are excluded in this process	Montgomery (1985)	Can be an expensive process
Fe-oxides	Based on the adsorptive capacity of these minerals; uses Al_2O_3 and/or TiO_2 quoted with newly precipitated $Fe(OH)_3$	Hlavay and Polyák (1997)	Used by many water treatment plants
Biotic-abiotic treatment	Involves oxidation of As^{III} to As^V followed by treatment with Fe-salt	Ghosh and Yuan (1987); Korte and Fernando (1991)	Emerging technology
Aquifer oxygenation	Air or O_2 injection into the aquifer to oxidize As^{III} to As^V to enhance precipitation in the aquifer	Frisbie (1996)	Attractive process but could be expensive
Passive reactive barriers	Reactive barrier system made up of natural clay/oxidic system	Naidu et al. (2000)	Expensive to install but cheap in the long term
Oxidic soils			
Three pitcher system	Oxidation of Fe^{2+} to Fe^{3+} and subsequent precipitation of Fe–OOH and removal of As via adsorption on to the oxide surface	Chowdhury et al. (2001)	Cheap option

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