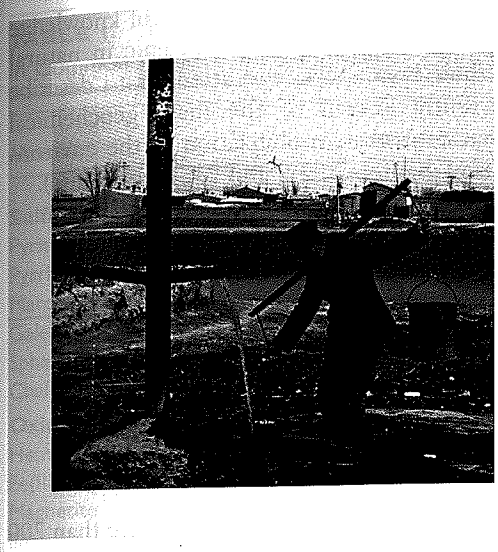

CHAPTER 11

ARSENIC IN GROUNDWATER AND THE ENVIRONMENT

PAULINE SMEDLEY AND DAVID G. KINNIBURGH
British Geological Survey

CONTENTS

I. INTRODUCTION

Arsenic is a ubiquitous element in the environment. It may be mobilized through a combination of natural processes such as weathering and erosion, biological activity, and volcanic emissions (see Volcanic Emissions and Health, this volume), as well as through the activities of man. Although most environmental arsenic problems are the result of mobilization under natural conditions, anthropogenic impacts have been significant in places due to activities such as mining; fossil fuel combustion, use of arsenical pesticides, herbicides, and crop desiccants, and arsenic-based additives in livestock feed. Although such pesticides and herbicides have been used much less over the last few decades, arsenic is still used widely in wood preservation and such sources may still pose a localized threat to the environment.

Human exposure to arsenic may be through a number of pathways, including air, food, water, and soil (Cullen & Reimer, 1989; NRC, 1999). The relative impacts of these vary depending on local circumstances, but of the potential sources of arsenic available, drinking water poses one of the greatest threats to human health and has been shown to have direct detrimental effects in many parts of the world. Drinking water may be obtained from a number of sources (surface water, rainwater, groundwater) depending on local availability. The concentrations of arsenic in these sources are highly variable and the observed ranges vary over several orders of magnitude. Excepting localized sources of anthropogenic contamination, the highest aqueous arsenic concentrations tend to be found in groundwaters because of natural water–rock interaction processes and the high solid/solution ratios found in aquifers. Groundwaters therefore pose the greatest overall threat to health. Groundwaters with arsenic concentrations sufficiently high to be detrimental to humans, or with already detectable health impacts, have

been reported in Bangladesh, India, Taiwan, Thailand, China, Hungary, Vietnam, Nepal, Myanmar, Mexico, Argentina, and Chile, and it is likely that occasional problems will be found in many other countries.

Some of the groundwater arsenic problems have been recognized for a considerable time. Probably the earliest cases of health effects from arsenic contamination of drinking water were recognized in a mining area of Poland in the 1890s. Here, contamination of water supplies by oxidation of arsenic-bearing sulfide minerals produced localized health problems (see Tseng et al., 1968). In central Argentina, arsenic-related health problems were first documented in 1917 (Círculo Médico del Rosario, 1917) and problems in Taiwan and Chile were first identified in the 1960s (Tseng et al., 1968; Smith et al., 1998). However, in each of these cases the problems were solved primarily by engineering solutions, which for the most part provided alternative supplies of surface water or of treated water. Hence, geochemical investigations into the processes controlling the arsenic mobilization in these areas have generally not been carried out until relatively recently. Even today, many of the arsenic-affected areas have received little attention and much remains unknown about the precise mechanisms involved. Hence, the problems observed in seriously impacted regions such as the Bengal Basin and Vietnam were not anticipated by water providers or the scientific community and have emerged only recently.

Both advisory guideline values and national standards for arsenic in drinking water have been reduced in recent years following mounting evidence of its chronic toxic effects. The World Health Organization (WHO) guideline value for arsenic in drinking water was provisionally reduced in 1993 from $50\,\mu g\,L^{-1}$ to $10\,\mu g\,L^{-1}$. Many other regulatory authorities in the western world have subsequently reduced their limits for arsenic in line with this recommendation. The EC maximum permissible value for arsenic in drinking water was reduced to $10\,\mu g\,L^{-1}$ in 2000. The U. S. Environmental Protection Agency (EPA) maximum contaminant level (MCL) was also reduced to $10\,\mu g\,L^{-1}$ in 2001, although the revision has been the subject of long debate over the last few years, largely because of the major cost implications to the U. S. water supply industry. While many national authorities are seeking to reduce their limits in line with the WHO guideline value, many countries and indeed all affected developing countries, still adopt the former WHO value of $50\,\mu g\,L^{-1}$, in part because of a lack of adequate testing facilities for measuring lower concentrations. Concentrations of $10\,\mu g\,L^{-1}$ and $50\,\mu g\,L^{-1}$ are therefore both often used as yardsticks for the testing and reporting of arsenic.

This chapter reports the current state of knowledge of the sources and distributions of arsenic in natural waters and their host rocks, and attempts to describe what is currently known of the main geochemical processes that control its mobilization in the environment (see also Chapters 2, 22, and 23, this volume).

II. SOURCES OF ARSENIC IN THE NATURAL ENVIRONMENT

A. Minerals

Arsenic occurs as a major constituent in more than 200 minerals including elemental arsenic, arsenides, sulfides, oxides, arsenates, and arsenites. Most are ore minerals or their alteration products. These minerals are relatively rare in the natural environment. Among the most common occurrences in ore zones are arsenian pyrite ($Fe(S,As)_2$), arsenopyrite (FeAsS), realgar (AsS), orpiment (As_2S_3), cobaltite (CoAsS), niccolite (NiAs), and scorodite ($FeAsO_4.2H_2O$). Arsenian pyrite ($Fe(S,As)_2$) is probably the most important source of arsenic in ore zones (Nordstrom, 2000). The arsenic ore minerals also often contain high concentrations of transition metals, as well as cadmium, lead, silver, gold, antimony, phosphorus, tungsten, and molybdenum.

Arsenic is often present in varying concentrations in other common rock-forming minerals. As the chemistry of arsenic follows sulfur closely, the greatest concentrations tend to occur in sulfide minerals, of which pyrite (FeS_2) is the most abundant. Arsenic concentrations in pyrite, chalcopyrite, galena, and marcasite can be highly variable, even within a given grain, but in some cases exceed 10 wt% (Table I). Pyrite is an important component of ore bodies and is also formed in low-temperature sedimentary environments under reducing conditions. Such authigenic pyrite plays a very important role in present-day geochemical cycles. It is present in the sediments of many rivers, lakes, and the oceans as well as in many aquifers. During pyrite formation, it is likely that some of the soluble arsenic will also be incorporated into the pyrite. Pyrite is not stable in aerobic systems and oxidizes to iron oxides with the release of significant amounts of sulfate, and acidity and associated trace constituents, including arsenic. The presence of pyrite in mineralized veins is responsible for the production of acid mine drainage and for the pres-

TABLE I. Typical Ranges of Arsenic Concentrations in Common Rock-Forming Minerals

Mineral	*Arsenic concentration range ($mg\,kg^{-1}$)*
Sulfide minerals	
Pyrite	100–77,000
Pyrrhotite	5–100
Marcasite	20–126,000
Galena	5–10,000
Sphalerite	5–17,000
Chalcopyrite	10–5000
Oxide minerals	
Hematite	up to 160
Fe(III) oxyhydroxide	up to 76,000
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
Sulfate minerals	
Gypsum/anhydrite	<1–6
Barite	<1–12
Jarosite	34–1000
Other minerals	
Apatite	<1–1000
Halite	<3–30
Fluorite	<2

From sources summarized in Smedley and Kinniburgh, 2002.

ence of arsenic problems around coal mines and areas of intensive coal burning.

High arsenic concentrations are also found in many oxide minerals and hydrous metal oxides, either as part of the mineral structure or as adsorbed species. Concentrations in Fe oxides can also reach several weight percent (Table I), particularly where they form as the oxidation products of primary iron sulfide minerals, which have an abundant supply of arsenic. Adsorption of arsenate to hydrous iron oxides is particularly strong and adsorbed loadings can be great even where concentrations in solution are low (e.g., Goldberg, 1986). Adsorption of arsenic is complicated because the two most common oxidation states of dissolved arsenic, As(III) and As(V), behave quite differently and because the amount of adsorption of these varies greatly with the concentration of other dissolved species. Adsorption to hydrous aluminum and manganese oxides may also be important if these oxides are present in quantity (Goldberg, 1986; Stollenwerk, 2003). Sorption to the edges of clays may also occur, although the loadings are much smaller on a weight basis than for the iron oxides (Smedley & Kinniburgh, 2002). Adsorption reactions are responsible for the relatively low concentrations of arsenic found in most natural waters.

Arsenic concentrations in phosphate minerals can also reach high values, for example, up to $1000\,mg\,kg^{-1}$ in apatite (Table I). However, phosphate minerals are much less abundant than oxide minerals and thus make a correspondingly small contribution to the arsenic concentration in most sediments. Arsenic tends to be present at much lower concentrations in the rock-forming minerals, although low concentrations are invariably present. Most common silicate minerals (including quartz, feldspar, micas, amphiboles) contain around $1\,mg\,kg^{-1}$ or less (Table I). Carbonate minerals usually contain concentrations less than $10\,mg\,kg^{-1}$.

B. Rocks, Sediments, and Soils

Arsenic occurs ubiquitously but at variable concentrations in rocks, unconsolidated sediments, and soils. Average crustal abundance is around $1.5\,mg\,kg^{-1}$. In igneous rocks concentrations are generally low. Ure and Berrow (1982) quoted an average value of $1.5\,mg\,kg^{-1}$ for undifferentiated igneous rocks. Other averages quoted are generally slightly higher than this value but usually less than $5\,mg\,kg^{-1}$. Volcanic glasses are slightly higher with an average of around $6\,mg\,kg^{-1}$ (Smedley & Kinniburgh, 2002). Overall, there is relatively little difference between the different igneous rock types (see also Chapter 2, this volume).

Arsenic concentrations in metamorphic rocks tend to reflect the concentrations in their igneous and sedimentary precursors. Most contain around $5\,mg\,kg^{-1}$ or less. Pelitic rocks (slates, phyllites) typically have the highest concentrations (Table II), with an average of around $18\,mg\,kg^{-1}$.

Concentrations in sedimentary rocks are typically in the range of $5–10\,mg\,kg^{-1}$ (Webster, 1999). Average sediments are enriched in arsenic relative to igneous and

TABLE II. Typical Ranges of Arsenic Concentrations in Rocks, Sediments, Soils, and Other Superficial Deposits

Rock/sediment type	*As concentration range (mg kg^{-1})*
Igneous rocks	
Ultrabasic rocks	0.03–15.8
Basic rocks	0.06–113
Intermediate rocks	0.09–13.4
Acidic rocks	0.2–15
Metamorphic rocks	
Quartzite	2.2–7.6
Hornfels	0.7–11
Phyllite/slate	0.5–143
Schist/gneiss	<0.1–18.5
Amphibolite and greenstone	0.4–45
Sedimentary rocks	
Marine shale/mudstone	3–15 (up to 490)
Shale (mid-Atlantic ridge)	48–361
Non-marine shale/mudstone	3.0–12
Sandstone	0.6–120
Limestone/dolomite	0.1–20.1
Phosphorite	0.4–188
Iron formations and Fe-rich sediment	1–2900
Evaporites (gypsum/anhydrite)	0.1–10
Coals	0.3–35,000
Unconsolidated sediments	
Alluvial sand (Bangladesh)	1.0–6.2
Alluvial mud/clay (Bangladesh)	2.7–14.7
River bed sediments (Bangladesh)	1.2–5.9
Lake sediments	0.5–44
Glacial till	1.9–170
World average river sediments	5
Stream and lake silt	<1–72
Loess silts, Argentina	5.4–18
Continental margin sediments	2.3–8.2
Soils	
Mixed soils	0.1–55
Peaty and bog soils	2–36
Peat	up to 9T
Acid sulfate soils	1.5–45
Soils near sulfide deposits	2–8000
Contaminated superficial deposits	
Mining-contaminated lake sediment	80–1104
Mining-contaminated reservoir sediment	100–800
Mine tailings	396–2000
Soils and tailings-contaminated soil	120–52,600
Industrially polluted intertidal sediments	0.38–1260
Soils below chemicals factory	1.3–4770

From sources summarized in Smedley and Kinniburgh, 2002.

metamorphic rocks because they contain greater quantities of minerals with high adsorbed arsenic loads. Of the sediments, sands and sandstones tend to have the lowest concentrations which reflect the low arsenic concentrations in their dominant minerals: quartz and feldspars. Average sandstone arsenic concentrations are around 4 mg kg^{-1}. Ure and Berrow (1982) gave a lower average value of 1 mg kg^{-1}.

Argillaceous deposits have a broader range of concentrations than sandstones (Table II), with a typical average of around 13 mg kg^{-1} (Ure & Berrow, 1982). The higher values reflect the larger proportion of sulfide minerals, oxides, organic matter, and clays present. Black shales have arsenic concentrations at the upper end of the range, principally because of their enhanced pyrite content. Marine clays appear to have higher concentrations than non-marine equivalents. This may also be a reflection of the grain-size distributions with potential for a higher proportion of fine material in offshore pelagic sediments. Marine shales also tend to contain more sulfur and hence are likely to contain more pyrite. High arsenic concentrations have been found in mid-ocean ridge shales (Table II).

Arsenic concentrations in coals and bituminous deposits are often high, in part because they are closely associated with sulfide minerals. Organic-rich shales from Germany have arsenic concentrations of 100–900 mg kg^{-1} (Riedel & Eikmann, 1986). Some coal samples have concentrations up to 35,000 mg kg^{-1} (Belkin et al., 2000) (Table II), although lower concentrations of 2.5–17 mg kg^{-1} are more typical (e.g., Palmer & Klizas, 1997). Some of the highest observed arsenic concentrations are found in ironstones and Fe-rich rocks. James (1966) collated data for ironstones from various parts of the world and reported arsenic concentrations up to 800 mg kg^{-1} in a chamosite-limonite oolite from the former USSR. Boyle and Jonasson (1973) reported concentrations for iron-rich rocks up to 2900 mg kg^{-1} (Table II). Phosphorites are also relatively enriched in arsenic with concentrations up to around 400 mg kg^{-1} reported. Carbonate rock types typically have low arsenic concentrations (around 3 mg kg^{-1}) as a result of the low concentrations of their constituent minerals (Tables I and II).

Unconsolidated sediments have arsenic concentrations that do not differ significantly from their indurated equivalents. As noted above, muds and clays usually have higher concentrations than sands and carbonates. Values are typically 3–10 mg kg^{-1}, depending on texture and mineralogy (Table II). High concentrations tend to reflect the amounts of pyrite or iron oxides present. There is often a significant positive correlation

between the iron and arsenic concentrations in sediments. High arsenic concentrations are also common in mineralized areas. Placer deposits in streams can have very high concentrations as a result of the abundance of sulfide minerals. Average arsenic concentrations for stream sediments in England and Wales are in the range of 5–8 mg kg^{-1} (AGRG, 1978). Similar concentrations have also been found in river sediments where groundwater arsenic concentrations are high: Datta and Subramanian (1997) found concentrations in sediments from the River Ganges averaging 2.0 mg kg^{-1}, from the Brahmaputra River averaging 2.8 mg kg^{-1}, and from the Meghna River averaging 3.5 mg kg^{-1}.

Cook et al. (1995) found concentrations in Canadian lake sediments ranging between 0.9 and 44 mg kg^{-1} (median 5.5 mg kg^{-1}) but noted that the highest concentrations were present up to a few kilometers downslope of mineralized areas. They also found concentrations in glacial till of 1.9–170 mg kg^{-1} (median 9.2 mg kg^{-1}) (Table II) and noted the highest concentrations downice of mineralized areas. Relative arsenic enrichments have been observed in reducing sediments in both nearshore and continental shelf deposits (Peterson & Carpenter, 1986; Legeleux et al., 1994). Legeleux et al. (1994) noted concentrations increasing with depth (up to 30 cm) in continental shelf sediments as a result of the generation of increasingly reducing conditions. Concentrations varied between sites, but generally increased with depth in the range 2.3–8.2 mg kg^{-1} (Table II).

Concentrations of arsenic in uncontaminated soils are generally of the order of 5–15 mg kg^{-1}. Boyle and Jonasson (1973) quoted an average in world soils of 7.2 mg kg^{-1} (Table II) and Shacklette et al. (1974) quoted an average of 7.4 mg kg^{-1} for American soils. Ure and Berrow (1982) gave an average of 11.3 mg kg^{-1}. Peats and bog soils can have higher concentrations (average 13 mg kg^{-1}, Table II), but this is principally because of an increased prevalence of sulfide mineral phases under the reduced conditions. Shotyk (1996) found a maximum of 9 mg As kg^{-1} in two Swiss peat profiles and in the profile with the lower mineral content, i.e., the purer peat, the As content was 1 mg kg^{-1} or lower.

Acid sulfate soils that are generated by the oxidation of pyrite in sulfide-rich terrains such as pyritic shales, mineral veins, and dewatered mangrove swamps can also be relatively enriched in arsenic. Acid sulfate soils from the weathering of pyrite-rich shales in Canada have arsenic concentrations up to 45 mg kg^{-1} (Dudas, 1984). Gustafsson and Tin (1994) found similarly high concentrations (up to 41 mg kg^{-1}) in acid sulfate soils from the Mekong delta of Vietnam.

Additional arsenic inputs to soils may be derived locally from industrial sources such as smelting and fossil fuel combustion products and agricultural sources such as pesticides and phosphate fertilizers. Ure and Berrow (1982) gave concentrations in the range 366–732 mg kg^{-1} in orchard soils following historical application of arsenical pesticides to fruit crops. Long-term use of phosphate fertilizers may also add significant arsenic to soil.

Concentrations of arsenic in sediments and soils contaminated by the products of mining activity, including tailings and effluent, can be orders of magnitude higher than under natural conditions. Concentrations in tailings piles and tailings-contaminated soils up to several thousands of mg kg^{-1} have been reported (Table II). The values reflect not only increased abundance of primary arsenic-rich sulfide minerals, but also secondary iron arsenates and iron oxides formed as reaction products of the original ore minerals. The primary sulfide minerals are susceptible to oxidation in the tailings pile and the secondary minerals have varying solubility under oxidizing conditions in groundwaters and surface waters. Scorodite ($FeAsO_4.2H_2O$) is a common sulfide oxidation product and its solubility is likely to control arsenic concentrations in such environments. Secondary arsenolite (As_2O_3) is also often represented in such environments. Arsenic is also often strongly bound to iron oxides (see below) and is relatively immobile, particularly under oxidizing conditions.

III. ARSENIC IN GROUNDWATER

A. Aqueous Speciation

Compared to many other toxic trace elements, arsenic is relatively mobile at the pH values typically found in natural waters (pH 6.5–8.5) and under both oxidizing and reducing conditions. Arsenic can occur in the environment in a number of oxidation states (–3, –1, 0, +3, and +5), but under natural conditions it is mostly found in inorganic form as trivalent arsenite (As(III)) or as oxyanions of pentavalent arsenate (As(V)). Organic arsenic species may be produced by biological activity, mostly in surface waters, but are rarely quantitatively important in groundwater. Exceptions potentially occur in cases of industrial pollution.

Redox potential (Eh) and pH are the most important factors controlling arsenic speciation in aqueous systems.

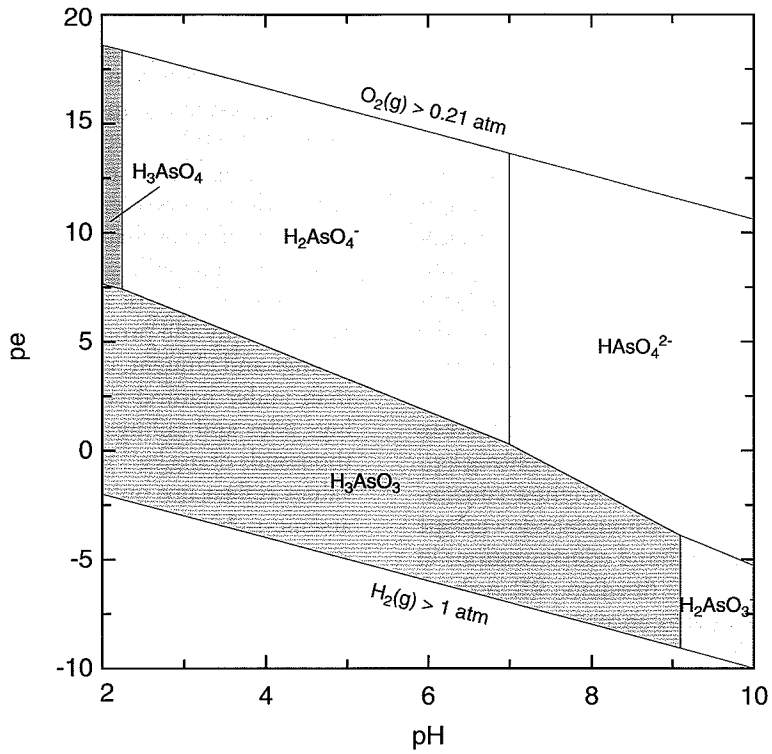

FIGURE 1 pe-pH diagram for soluble arsenic species in the system As-O_2-H_2O ($As_T = 10^{-5}$ M, NaCl = 10^{-2} M; 25°C).

Under oxidizing conditions, $H_2AsO_4^-$ is dominant at low pH (less than about pH 6.9), while at higher pH, $HAsO_4^{2-}$ it dominates (Figure 1). In extremely acidic conditions, $H_3AsO_4^0$ is important whereas AsO_4^{3-} may be present in alkaline conditions. Under reducing conditions where pH is less than about 9.2, the uncharged arsenite species $H_3AsO_3^0$ predominates. Native arsenic may be present under extremely reducing conditions.

As(III) and As(V) may form aqueous complexes with reduced sulfur (e.g., thioarsenite) and carbonate ligands, and these may be significant in some groundwaters. In the presence of extremely high concentrations of reduced dissolved sulfur at low pH, dissolved arsenic sulfide species can be formed. Reducing, acidic conditions also favor precipitation of orpiment (As_2S_3), realgar (AsS), or other sulfide minerals containing co-precipitated arsenic (Cullen & Reimer, 1989). As a result, high-arsenic waters are not expected where there is a high concentration of free sulfide (Moore et al., 1988).

The ratio of As(III) to As(V) in groundwaters varies with the redox status of the aquifer, which in turn depends upon the abundance of the redox-active solids, especially organic carbon, and the flux of potential oxidants (oxygen, nitrate, and sulfate). Microorganisms play a key role in these redox reactions, and in environments of high microbial activity can be responsible for lack of redox equilibrium between the arsenic species. In strongly reducing aquifers, typified by Fe(III) and sulfate reduction, As(III) typically dominates, as expected from the redox sequence. In oxidizing systems, As(V) is typically dominant. The extent of redox equilibrium with respect to arsenic in natural waters has been a matter of considerable debate. Although observations of the rate of oxidation of As(III) in groundwater are difficult under field conditions, the rates are generally believed to be slow. Microbial activity is also generally low in groundwaters, but this is compensated for to some extent by the long time scales usually involved in groundwater flow that are typically decades and longer.

Reducing arsenic-rich groundwaters from Bangladesh have As(III)/As_T ratios varying between 0.1 and 0.9 but are typically around 0.5 and 0.6 (Smedley et al., 2001). Ratios in reducing groundwaters from Inner Mongolia are typically 0.6–0.9 (Smedley et al., 2003).

Concentrations of organic forms are generally low or negligible in groundwaters (Del Razo et al., 1990; Chen et al., 1995).

B. Arsenic Abundance and Distribution in Groundwater

Aquifers have high solid/solution ratios, typically 3–20 kg L^{-1} and as a result, groundwaters within them are especially vulnerable to the buildup of arsenic in solution. In addition, aquifers more often have the physical and chemical conditions favorable for arsenic mobilization and transport than is the case in surface waters. Despite this, the occurrence of high arsenic concentrations in groundwaters is the exception rather than the rule. Concentrations in groundwater are in most countries less than 10 μg L^{-1} and often substantially lower. However, values quoted in the literature show a very large range from <0.5 to 5000 μg L^{-1}, i.e., more than four orders of magnitude (Smedley & Kinniburgh, 2002).

Mobilization of arsenic in solution is favored, especially under oxidizing conditions at high pH and under strongly reducing conditions. Evaporative concentration can also increase arsenic (and other element) concentrations substantially and may be important in some arid areas. Additional arsenic problems are encountered in some geothermal areas and in many areas of sulfide mineralization and mining. Cases of industrial arsenic pollution (including those from agriculture) have also been reported. Although these may be severe locally, occurrences are relatively rare and can usually be anticipated.

Investigations worldwide have revealed a number of major aquifers with significant groundwater arsenic problems (concentrations exceeding 50 μg L^{-1}). The hydrogeological and geochemical conditions in these affected aquifers vary, although some common unifying features are apparent. Aquifers at greatest risk appear to be those found in large alluvial and delta plains as well as large inland basins, the latter especially in arid and semi-arid areas. In each case, geologically young (Quaternary) aquifers are particularly prone to developing and preserving high-arsenic groundwater. Aquifers in alluvial and delta plains with recognized arsenic problems include Bangladesh, West Bengal (India), Nepal, northern China, Taiwan, Hungary, Romania, and Vietnam. Those from inland and closed basins include parts of Argentina, Chile, Mexico, and areas of the United States, particularly the southwest (Figure 2). In many of these areas, significant numbers of wells have arsenic concentrations of several hundreds of micrograms per liter, with occasional sources in the milligram per liter range. Arsenic-related health problems have been recognized in the resident populations in some areas as a result. Recent reconnaissance surveys of groundwater quality in other areas such as parts of Myanmar, Pakistan, and Cambodia have also revealed concentrations of arsenic in some wells exceeding 50 μg L^{-1}. However, documentation of the affected aquifers in these areas is thus far limited. Little is known about other large deltas, for example, that of the Nile (Egypt), Chao Phraya (Thailand), Niger (Nigeria), Huang Ho (China), and Yangste (China), although they have many geological characteristics similar to other arsenic-affected areas. The regions of the world having major aquifers with recognized arsenic problems are outlined below and categorized in terms of their environmental conditions. The distributions of arsenic in the environment related to geothermal activity as well as mining and mineralization are also described.

1. Alluvial Plains and Deltas

a. Bangladesh and India (West Bengal)

Promoted by the presence of fertile land and plentiful supplies of water, the Bengal delta of Bangladesh and West Bengal (India) is one of the most densely populated regions on Earth. Traditional sources of water for the region included rivers and ponds as well as shallow hand-dug wells. These have long been the source of significant problems from life-threatening diarrheal diseases. As a response, the last few decades have seen a proliferation in the development of groundwater by the installation of boreholes, both for domestic supply and irrigation. This has been aided by the presence of abundant groundwater at shallow depths in the unconsolidated sediments and the ease of drilling. Today, there are estimated to be up to 11 million boreholes in Bangladesh alone (BGS & DPHE, 2001), and the vast majority are private hand-pumped boreholes for domestic use. Although the discovery of arsenic problems in the aquifers of West Bengal was made by local physicians as early as the 1980s, the problem was not widely recognized until the mid-1990s and the scale of the problem has emerged only recently.

Arsenic problems in groundwater of the Bengal Basin occur within young, mainly Holocene, shallow aquifers (<150 m depth), composed of alluvial and deltaic sediments deposited by the vast river systems of the Ganges, Brahmaputra, and Meghna and their tributaries. These alluvial and deltaic sediments typically include in the

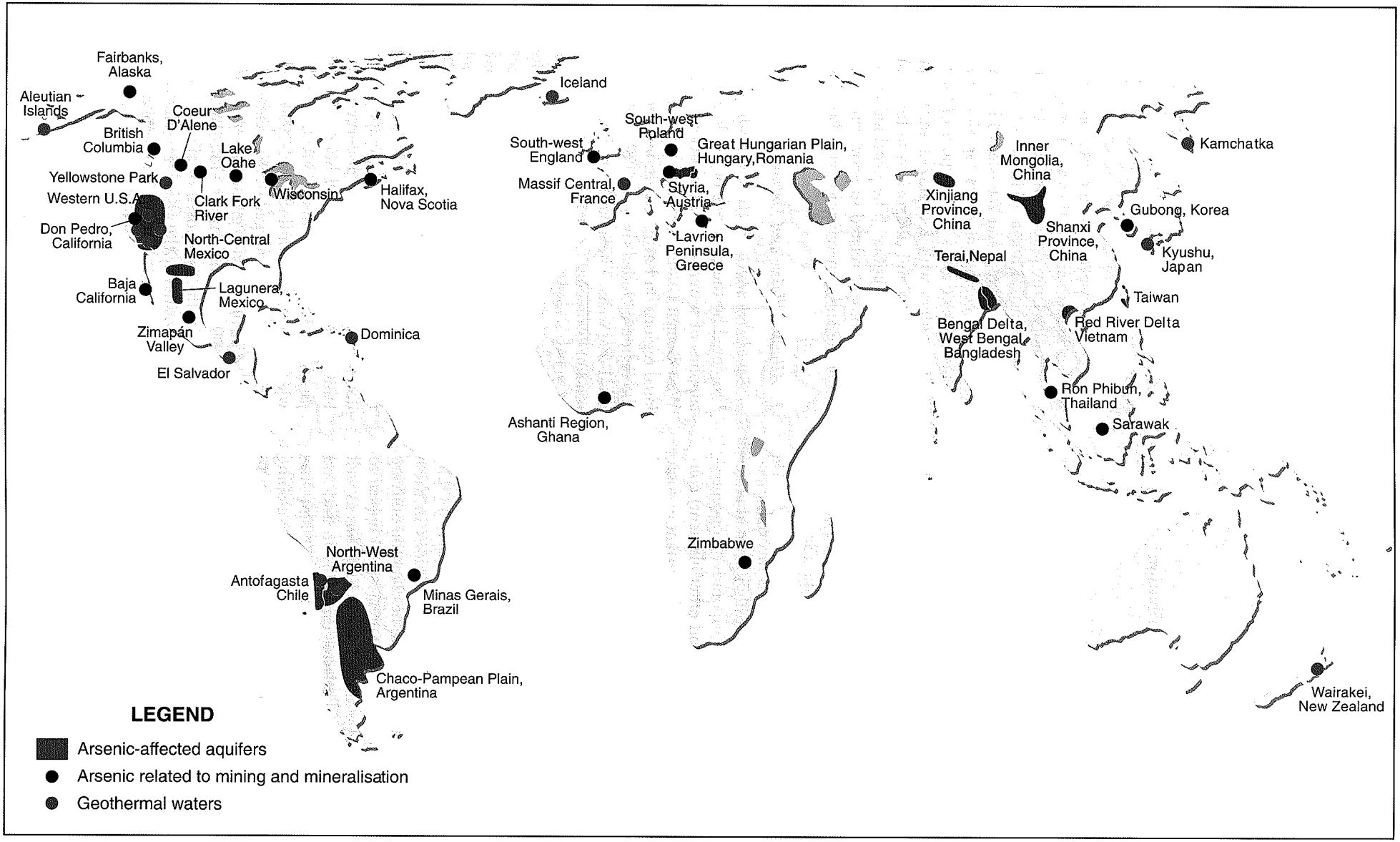

FIGURE 2 Occurrence of documented arsenic problems in groundwater (arsenic >50 $\mu g L^{-1}$) in major aquifers and (Smedley and Kinniburgh, 2002). Related to mining and geothermal sources.

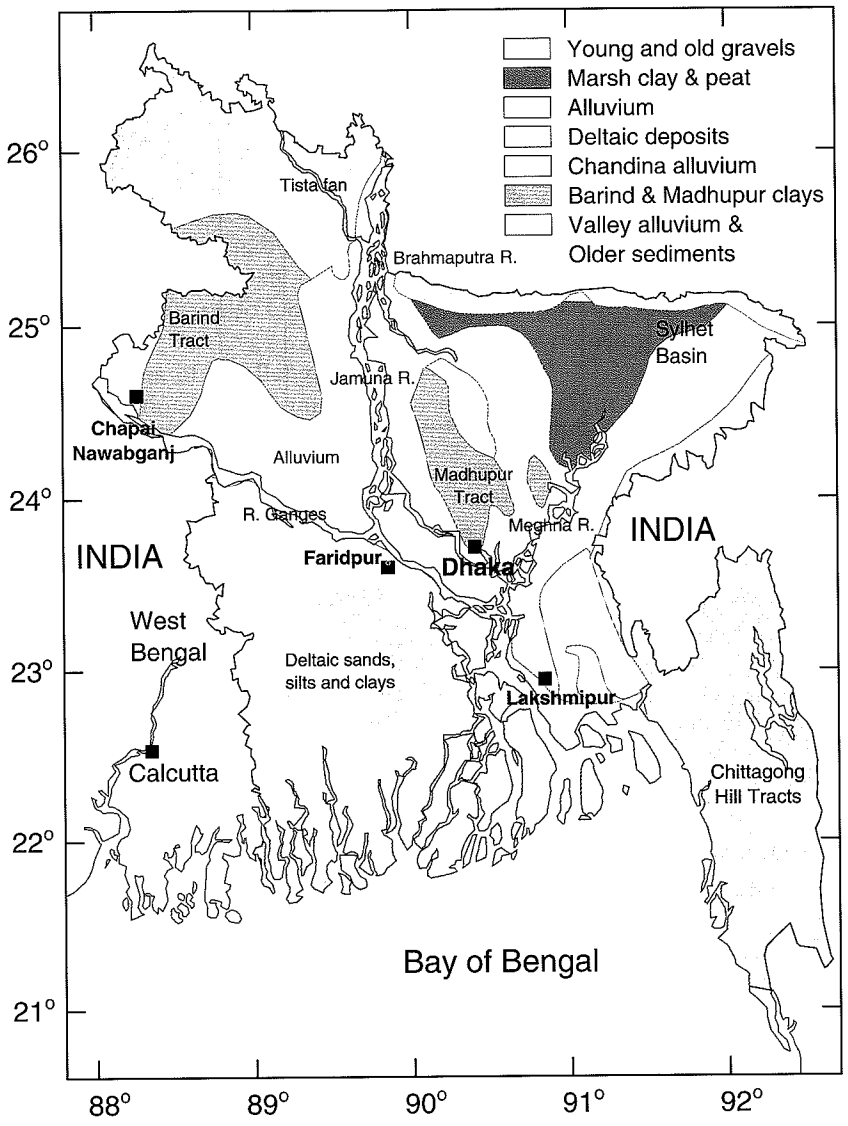

FIGURE 3 Simplified geological map of Bangladesh. (Alam et al., 1990.)

upper reaches coarse alluvial fan deposits (e.g., the Tista Fan; Figure 3) with dominant sand and gravel. In the middle parts of the basin, meander belts consist of levee, backswamp, ox-bow lake, and abandoned channel deposits. In the lower reaches of the delta, marsh and tidal flat deposits mainly consist of fine silts and clays, but with some sand horizons. Buried channel deposits in particular tend to contain sand and gravel and frequently make good aquifers. The sediments are highly heterogenous both laterally and with depth, although fining-upwards sequences are commonly observed. The sediments include some contemporaneous disseminated organic matter and occasional peat horizons. The lower parts of the basin have a surface cover of fine alluvial overbank silts and clays of variable thickness (around 10–80 m; BGS & DPHE, 2001; Chakraborti et al., 2001). These are in large part responsible for restricting the diffusion of oxygen to the underlying aquifers and, together with the presence of organic matter, have led to the widespread development of reducing conditions, particularly in the distal parts of the basin. These alluvial and deltaic sediments cover the majority of Bangladesh (Figure 3) and a large proportion of West Bengal.

In terms of the populations at risk, groundwater arsenic problems in Bangladesh and West Bengal represent the most serious occurrences identified globally. Observed concentrations have a very large range from

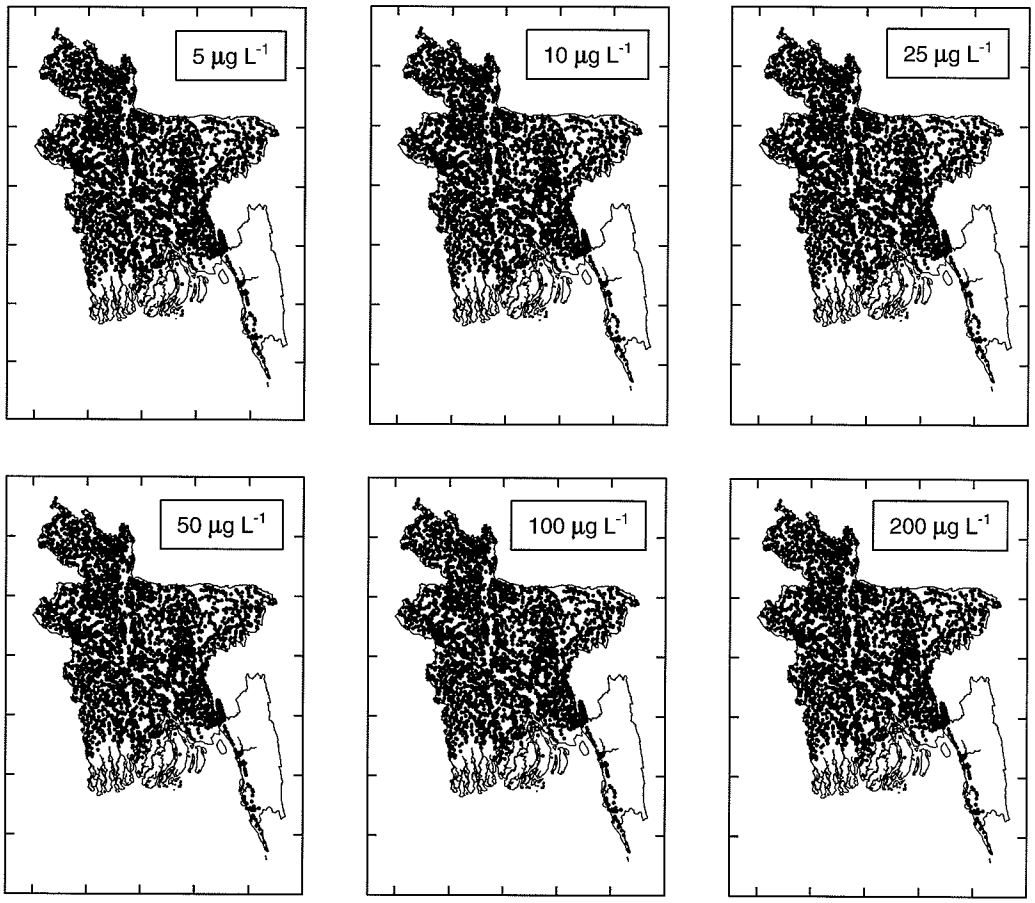

FIGURE 4 Map of Bangladesh showing the distributions of arsenic in groundwater from shallow (<150 m) tubewells at various threshold concentrations. Blue symbols denote values less than the indicated threshold; red symbols denote values above. (From BGS & DPHE, 2001.)

<0.5 µg L^{-1} to around 3200 µg L^{-1}. Chakraborti et al. (2001) reported that, of 90,000 water analyses measured by them in West Bengal, some 34% exceeded the national standard for arsenic in drinking water of 50 µg L^{-1} and 55% exceeded the WHO guideline value of 10 µg L^{-1}. These problems occur mainly to the east of the Bhagirathi River in a relatively narrow strip bordering Bangladesh. They also reported that of 27,000 analyses carried out in Bangladesh, 59% exceeded 50 µg L^{-1} while 73% exceeded 10 µg L^{-1}. These percentages differ somewhat from the survey by BGS and DPHE (2001) of around 3500 wells sampled randomly across Bangladesh, where 27% of samples from shallow wells (<150 m depth) contained arsenic concentrations exceeding 50 µg L^{-1} and 46% contained more than 10 µg L^{-1}. The differences most probably relate to differing sampling strategies and sample populations. The worst-affected area of Bangladesh is the southeast (Figure 4) where in the worst-affected district, BGS and DPHE (2001) identified more than 90% of wells having arsenic concentrations >50 µg L^{-1}. The indications are that the degree of contamination is not as severe in West Bengal as in the worst districts of Bangladesh. Certainly, the overall areal extent of contamination in West Bengal is less than in Bangladesh. Around 35 million people in Bangladesh and 6 million people in West Bengal were estimated to be at risk from arsenic in drinking water at concentrations above 50 µg L^{-1} by Smedley & Kinniburgh (2002).

Recognized health problems resulting from chronic exposure to arsenic in drinking water consist mainly of skin disorders, notably pigmentation changes (melanosis) and keratosis, although skin cancer has also been identified. Around 5000 patients have been identified with arsenic-related health problems in West Bengal (including skin pigmentation changes), although some estimates put the number of patients with arsenicosis at more than 200,000 (Smith et al., 2000). The

number with recognized problems in Bangladesh is of the order of 14,000 though many more may be unrecognised or in a preclinical stage. Thus far, data do not show a strong relationship between groundwater arsenic concentrations and health problems in Bangladesh, but epidemiological studies are ongoing. The prevalence of internal arsenic-related health problems, including cancers, is also not known, but could be appreciable given the growing evidence of the toxic effects of chronic arsenic exposure (see also Chapters 22 and 23, this volume).

The high-arsenic groundwaters of the Bengal Basin have variable chemical compositions, but a number of features are commonly observed and highlight the strongly reducing nature of the affected groundwaters. Measured redox potentials are typically less than 100 mV, dissolved oxygen is usually very low or absent ($<1\,mg\,L^{-1}$), and high concentrations of dissolved iron (often several milligrams per liter, up to $60\,mg\,L^{-1}$), manganese (often $>0.5\,mg\,L^{-1}$, up to $8\,mg\,L^{-1}$), bicarbonate (often $>500\,mg\,L^{-1}$; up to about $1100\,mg\,L^{-1}$), and ammonium-N ($>1\,mg\,L^{-1}$) are typical (Table III) (BGS & DPHE, 2001). Correlations between these parameters have been found in some studies of localized areas such as villages, but they are generally poor on a regional scale. High concentrations of phosphorus (often $>0.5\,mg\,L^{-1}$; up to $20\,mg\,L^{-1}$) are also a common feature. The dissolved iron and manganese most likely derive from reductive dissolution of iron and manganese oxides in the sediments. Bicarbonate is in part derived from reaction of carbonate minerals and partly from the oxidation of organic matter. Phosphorus is likely to be derived from both iron oxides and organic matter, although dissolution of detrital apatite may also be involved. Derivation of phosphate by leaching of fertilizers from overlying soils has been suggested by some workers (Acharyya et al., 1999), although this is considered unlikely given the widespread occurrence of phosphate in the groundwater and its presence in deep groundwaters (>150 m) as well as in shallower groundwaters. The groundwaters are generally fresh, but salinity has increased in the southern coastal region as a result of saline intrusion.

Additional indicators of reducing conditions in the arsenic-affected aquifers include low concentrations of nitrate, except for a number of shallow polluted wells, and low to very low concentrations of sulfate (typically $<1\,mg\,L^{-1}$). A general negative correlation observed between arsenic and sulfate concentrations (BGS & DPHE, 2001) suggests that arsenic mobilization occurs under the most strongly reducing conditions—alongside sulfate reduction and iron oxide dissolution. Arsenic speciation studies have revealed a large range in the relative proportions of dissolved arsenate and arsenite in the groundwaters. However, arsenite is generally dominant; the modal proportion in pumped groundwaters from Bangladesh is around 60% of the total arsenic (BGS & DPHE, 2001). The variable ratios may reflect lack of redox equilibrium in the aquifers or the presence of mixed groundwater from a strongly stratified aquifer. Some of the groundwaters of Bangladesh are sufficiently reducing for methane generation to have taken place.

The origin of the arsenic in the Bengal groundwaters has been in dispute in recent years, but it is generally accepted to be of natural origin. The widespread development of strongly reducing conditions in the affected aquifers is likely the main factor controlling the mobilization. This has probably occurred in a complex combination of redox changes brought on by rapid burial of the alluvial and deltaic sediments, which include reduction of the solid-phase arsenic to As(III), desorption of arsenic from iron oxides, reductive dissolution of the oxides themselves, and likely diagenetic changes in iron-oxide structure and surface properties following the onset of reducing conditions (BGS & DPHE, 2001; Smedley & Kinniburgh, 2002). Competition for adsorption sites between dissolved arsenic species and other constituents such as phosphate and bicarbonate may also be involved. It has recently been suggested from a study of groundwaters in the Munshiganj district, southern Bangladesh, that arsenic mobilization in the aquifers has resulted from increased drawdown of organic carbon of anthropogenic origin as a result of recent irrigation (Harvey et al., 2002). However, the evidence for this is scant and not altogether convincing, and it remains to be seen whether this process is of widespread significance.

The distribution of arsenic in the groundwaters of Bangladesh and West Bengal is known to be spatially highly variable, with large differences in arsenic concentration in wells over short lateral distances. This is likely a reflection of the considerable heterogeneity in composition, texture, and permeability of the sediments. At a practical level, the variability makes prediction of arsenic concentrations from well to well extremely difficult, although where the density of sampling is very high, distinct patterns within villages have been observed. Despite this, on a regional scale the distribution shows a clear geological control (Figure 4). Wells in older uplifted Plio-Pleistocene sediments of the Barind and Madhupur Tracts of north and central Bangladesh (including those of the city of Dhaka) have

TABLE III. Summary of Documented High-Arsenic Groundwater Provinces and Their Typical Chemical and Hydrogeological Characteristics

Groundwater environment/aquifer type	*Examples*	*Typical aquifer conditions*	*Typical chemical features of high-arsenic groundwaters*	*Likely mechanisms of arsenic mobilization*
Strongly reducing groundwater	Alluvial/deltaic aquifers of Bangladesh, West Bengal, northern China, Taiwan, Myanmar, Nepal, Hungary, Romania	Young (Quaternary) sediments, slow groundwater flow, low-lying parts of aquifers; rapidly accumulated sediments	High Fe (>1 $mg l^{-1}$), Mn (>0.5 $mg L^{-1}$), NH_4-N (>1 $mg l^{-1}$), high HCO_3 (>500 $mg L^{-1}$); low NO_3-N (<1 $mg l^{-1}$), low SO_4 (<5 $mg L^{-1}$); often high P (>0.5 $mg l^{-1}$); sometimes high concentrations of dissolved organic matter, including humic acid; arsenic dominated by As(III)	Reductive desorption of As from metal oxides, reductive dissolution of Fe, Mn oxides; possible competition between arsenic and other anionic species (including P, HCO_3)
Aerobic groundwater, high pH	Inland basins or closed basins (arid and semi-arid areas): Argentina, Mexico, parts of the western United States, parts of Chile	Young (Quaternary) sediments, slow groundwater flow, low-lying parts of aquifers	pH typically >8, high HCO_3 (>500 $mg L^{-1}$), low Fe, Mn, often correspondingly high F, U, B, V, Mo, Se; some groundwaters have high salinity due to evaporation; arsenic dominated by As(V)	Desorption of As and other oxyanion-forming elements from metal oxides, especially of Fe and Mn; evaporative concentration
Geothermally influenced groundwater	Parts of Kamchatka, Chile, Argentina, the western United States, Japan, New Zealand	Any aquifers affected by geothermal inputs, especially in rift zones	High Si, B, Li, often high salinity (Na, Cl); high pH (>7); increased groundwater temperature	Mixing of fresh groundwater with geothermal solutions
Groundwater from sulfide mineralized/ mining areas	Parts of the United States, Canada, southwest England, Thailand, South Korea, Poland, Greece, Ghana, Zimbabwe, Brazil	Groundwater in fractures in crystalline rocks or alluvial placer deposits	Oxidizing or mildly reducing conditions possible; high SO_4 concentrations (typically hundreds of $mg L^{-1}$ or higher); acidic (unless buffered by carbonate minerals); often increased concentrations of other trace metals (Ni, Pb, Zn, Cu, Cd)	Oxidation of sulfide minerals

low arsenic concentrations (less than $10\,\mu g\,L^{-1}$ and usually $<0.5\,\mu g\,L^{-1}$; Figure 4).

Arsenic concentrations also vary with depth as shown by both individual wells at a given site and by the distribution of arsenic with depth for wells from different sites. The concentration vs. depth profile typically is a bell-shaped curve with low concentrations in shallow (<10 m) and deep wells (>150–200 m) and with the largest concentrations in wells from the 10- to 70-m depth range. Typically wells are drilled to the minimum depth required for an adequate yield and acceptable quality (in terms of salinity and sometimes iron content). This often corresponds with a high-arsenic depth interval. Little is known about the exact variation of arsenic concentration at greater depths.

In the BGS and DPHE (2001) survey, practically all deep wells, tapping depths greater than 100–200 m, had low arsenic concentrations. These were mostly from the extreme south and north-east of the country. Although the stratigraphy of Bangladesh aquifers at depth is poorly understood, these are also likely to be Plio-Pleistocene aquifers of comparable facies and composition to those of the Barind and Madhupur Tracts. The source of arsenic in the few identified deep wells with increased arsenic concentrations is uncertain. However, the deep aquifer itself is not necessarily the dominant source. Downward leakage of groundwater from the shallow aquifer(s) and multilevel screening of wells are likely alternative explanations. Dug wells in Bangladesh and West Bengal are also observed to have generally low arsenic concentrations, typically $<10\,\mu g\,L^{-1}$ (BGS & DPHE, 2001; Chakraborti et al., 2001).

Several workers have suggested that the source of the arsenic in the Bengal sediments derives from discrete high-arsenic mineralized zones upstream of the affected areas (e.g., Acharyya, et al., 1999). However, the high-arsenic groundwaters occur in sediments with total arsenic concentrations typically in the range of <2–20 $mg\,kg^{-1}$, i.e., not exceptionally high concentrations (Table II). Many studies have shown that fine-grained sediments (silts and clays) tend to have greater arsenic concentrations than coarse-grained sediments. BGS and DPHE (2001) found concentrations of 1.3–10 $mg\,kg^{-1}$ in sediments from three arsenic-affected areas of Bangladesh. Chakraborti et al. (2001) also reported low concentrations in most of their samples analyzed from West Bengal. In one borehole from 24 South Parganas, 108 samples had an arsenic range of 8–12 $mg\,kg^{-1}$. The near-average concentrations observed are not surprising considering the scale of the Bengal arsenic problem, with the affected aquifer sediments derived from a very large catchment area of the Himalayas. They are therefore by definition likely to be "close to average." However, BGS and DPHE (2001) also found the concentrations of readily extractable arsenic, probably largely associated with iron oxides, to be higher in Bangladesh sediments from the badly affected aquifers than from elsewhere. The iron oxides also tend to be more concentrated in the finer-grained sediments in the lower, distal part of the delta than elsewhere. This is probably a further contributory factor in the distribution of arsenic problems across the basin. The distribution may reflect the high biotite mica content of these sediments, because the weathering of biotite provides a potential source of iron oxides.

The reasons for the distinction between groundwater arsenic concentrations in the shallow and deep aquifers of the Bengal Basin are not yet well-understood. Differences between the sediments at depth may occur in terms of absolute arsenic concentrations and in the oxidation states, structure, and binding properties of their iron oxides (BGS & DPHE, 2001; van Geen et al., 2003). It is also possible that the history of groundwater movement and aquifer flushing in the Bengal Basin has been important in generating the differences in dissolved concentrations between the shallow and deep aquifers. Older, deeper sediments have been subject to longer periods of groundwater flow, aided by greater hydraulic heads during the Pleistocene period when glacial sea levels around the Bangladesh landmass were as much as 130 m lower than today (Umitsu, 1993). Flushing of the deeper older aquifers with groundwater is therefore likely to have been much more extensive than in the shallow Holocene sediments deposited during the last 5000–10,000 years. Hence, much of the arsenic released during diagenesis of the deep sediments may have already been flushed away. Models of the hydrogeology and geochemical processes believed to be controlling the arsenic mobilization in the Bengal Basin aquifers are shown schematically in Figure 5. This model is discussed more fully by BGS and DPHE (2001).

b. Nepal

Groundwater is abundant in the Quaternary alluvial sediments of the lowland Terai region of southern Nepal and is an important resource for domestic and agricultural use. The region is estimated to have around 200,000 boreholes which supply groundwater for some 11 million people (Chitrakar & Neku, 2001). Both shallow and deep aquifers occur throughout most of the Terai region. The shallow aquifer appears to be mostly unconfined and well-developed, although it is thin or absent in some areas. The deep aquifer (precise depth uncertain) is artesian. Quaternary alluvium also infills

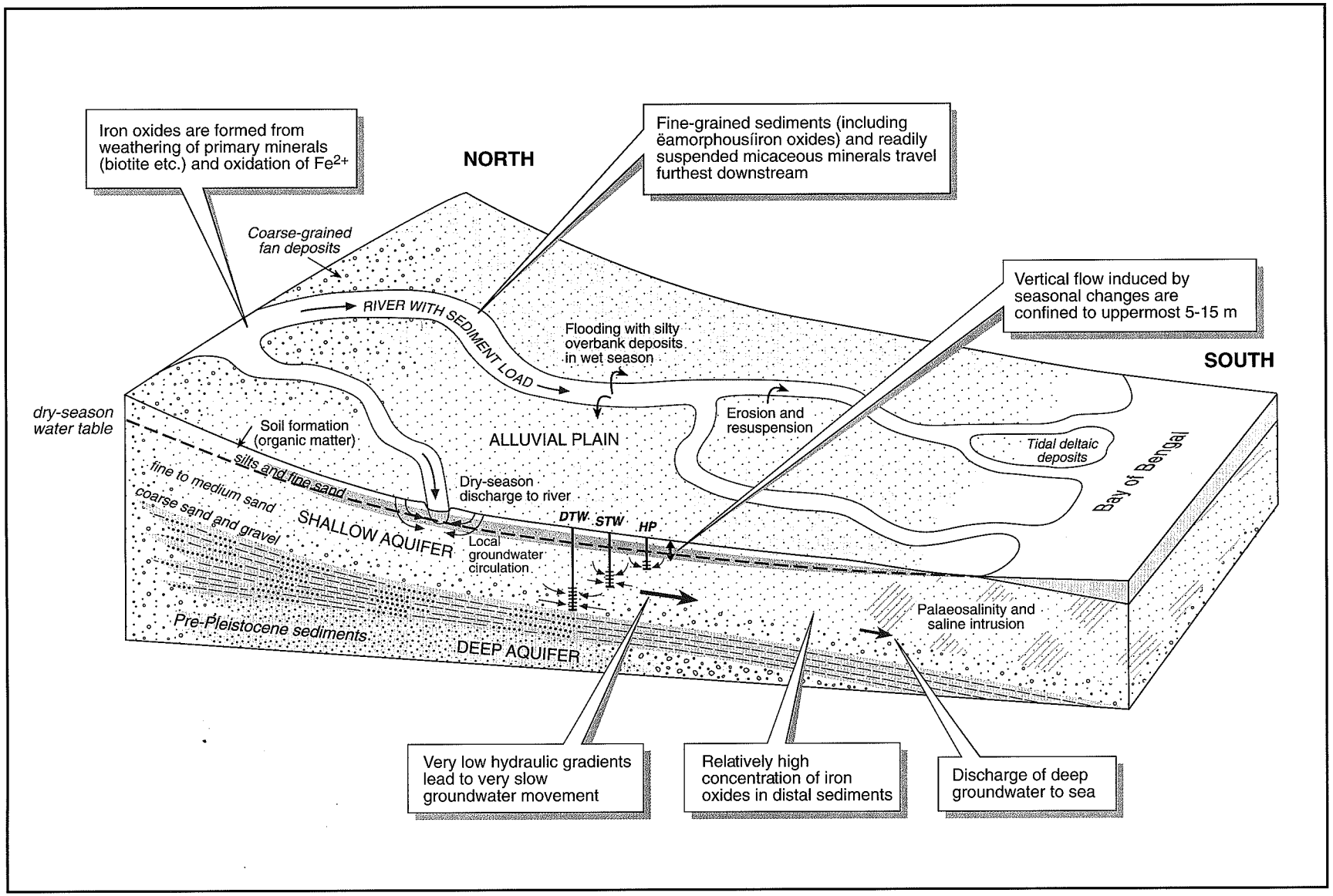

FIGURE 5(A) Block diagrams showing schematically (A) simplified geology and hydrogeology and (B) principal geochemical processes involved in the generation of high-arsenic groundwaters in Bangladesh. (From BGS & DPHE, 2001, from which further details of geochemical processes and the groundwater flow model can be found.)

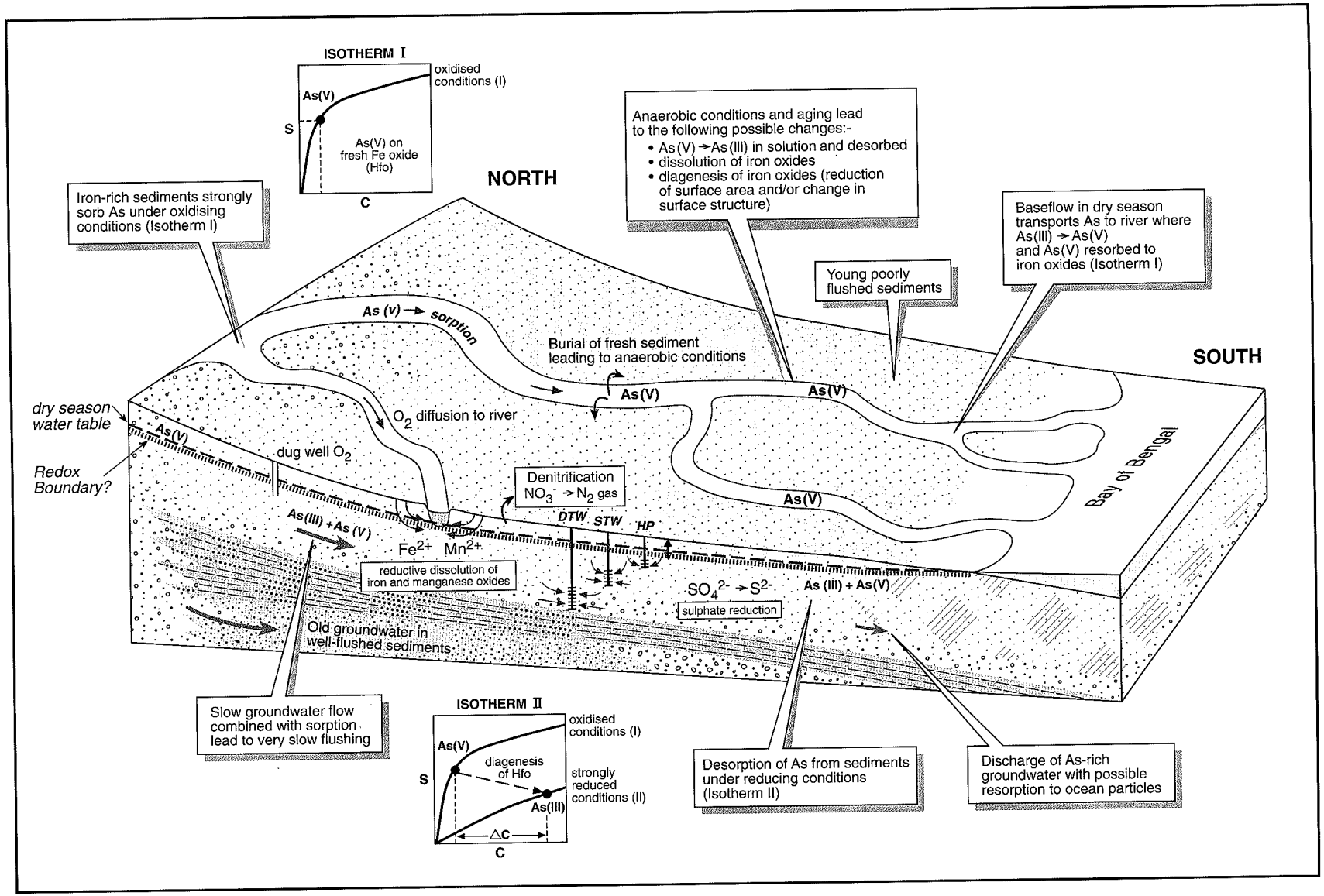

FIGURE 5(B) *Continued*

several intermontaine basins in Nepal, most notably that of the Kathmandu Valley of central Nepal (about 500 km^2) where sediment thickness reaches in excess of 300 m.

A number of surveys of groundwater quality in the Terai region have revealed the presence of arsenic at high concentrations in some samples from shallow boreholes (<50 m depth), though most analyzed samples appear to have <10 $\mu g L^{-1}$ (Smedley, 2003). The Nepal Department of Water Supply and Sewerage (DWSS) carried out a survey of some 4000 tubewells from the 20 Terai districts, which were mostly analyzed by field-test kits but with laboratory replication of some. Results from the survey indicated that 3% of the samples had arsenic concentrations of >50 $\mu g L^{-1}$ (Chitraker and Neku, 2001). The worst affected districts were found to be Rautahat, Nawalparasi, Parsa, and Bara in the central area of the Terai. The highest observed concentration was 343 $\mu g L^{-1}$ (Parsa District). From testing in 17 of the 20 Terai districts, the Nepal Red Cross Society (NRCS) also found 3% of groundwater sources sampled to have concentrations above 50 $\mu g L^{-1}$; the highest observed concentration was 205 $\mu g L^{-1}$. The spatial distribution of the worst affected areas was found to be similar to that reported by Chitrakar and Neku (2001). More recent results indicate that of 25,000 analyses carried out so far in the Terai, 8% exceed 50 $\mu g L^{-1}$ and 31% exceed 10 $\mu g L^{-1}$ (Shrestha et al., 2004).

The high arsenic concentrations occur in anaerobic groundwaters and are often associated with high concentrations of dissolved Fe. The number of samples with exceedances above 50 $\mu g L^{-1}$ are generally small, but are nonetheless cause for further testing and remedial action.

Surveys appear to indicate that deeper boreholes (>50 m depth) in the Terai usually have lower arsenic concentrations (<10 $\mu g L^{-1}$). Preliminary investigations also suggest that the Kathmandu Valley does not have an arsenic problem, although more analysis is required for verification.

c. Taiwan

Arsenic problems in groundwaters in Taiwan were first recognized during the 1960s (e.g., Tseng et al., 1968), and related chronic health problems have been well documented since then (e.g., Chen et al., 1985). Blackfoot disease (a peripheral vascular disorder similar to gangrene) is a well-publicized health problem of the region and is most likely linked to the high arsenic concentrations, although the high humic acid concentration in groundwaters of the region has also been cited as a possible causal factor. A number of other diseases, including internal cancers, have also been described. High groundwater arsenic concentrations have been recognized in both the southwest (Tseng et al., 1968) and northeast (Hsu et al., 1997) parts of the island.

Arsenic concentrations in groundwater samples from southwest Taiwan have been found in the range 10–1800 $\mu g L^{-1}$ and a significant number of samples are more than 400 $\mu g L^{-1}$ (references cited in Smedley & Kinniburgh, 2002). In northeastern Taiwan, arsenic concentrations exceed 600 $\mu g L^{-1}$ in some groundwaters and a recent survey of 377 water samples gave an average of 135 $\mu g L^{-1}$ (Hsu et al., 1997).

In the southwest, the high arsenic concentrations are found in groundwaters from deep artesian wells (mostly 100–280 m) abstracted from sediments which include fine sands, muds, and black shale (Tseng et al., 1968). Groundwaters abstracted from the northeast of Taiwan are also artesian, but of shallower depth (typically in the range 16–40 m; Hsu et al., 1997). In each area the groundwaters are likely to be strongly reducing, which is supported by the observation that the arsenic is present largely as As(III) (Chen et al., 1994). However, both the geochemistry of the groundwaters and the mineral sources in Taiwan are poorly defined. Groundwater samples taken from shallow, open dug wells are observed to have low arsenic concentrations (Guo et al., 1994).

d. Northern China

Arsenic has been found at high concentrations (in excess of the Chinese national standard of 50 $\mu g L^{-1}$) in groundwaters from a number of areas in northern China, including Xinjiang, Shanxi, Jilin, and Liaoning Provinces as well as Inner Mongolia (Figure 2) (Sun et al., 2001; Smedley et al., 2003). The earliest problems were recognized in Xinjiang Province. Wang and Huang (1994) reported concentrations of 40–750 $\mu g L^{-1}$ in deep artesian groundwater from the Dzungaria (Junggar) Basin on the north side of the Tianshan Mountains. Wells were up to 660 m deep. The basin has been a zone of subsidence since at least Mesozoic times and is composed of a 10-km thick sequence of sediments, which include a substantial upper sequence of Quaternary age. The high-arsenic zone extends from Aibi Lake in the west to Mamas River in the east (about 250 km). Wang and Huang (1994) found that arsenic concentrations increased with depth in the artesian groundwater. Shallow (non-artesian) groundwaters had arsenic concentrations between <10 $\mu g L^{-1}$ (the detection limit) and 68 $\mu g L^{-1}$.

In the Datong and Jinzhong Basins of Shanxi Province, arsenic concentrations have been found to exceed 50 $\mu g L^{-1}$ in 35% of 2373 randomly selected

groundwater samples (Sun et al., 2001). Concentrations in Shanyin county, the worst affected of the regions in Shanxi Province, reached up to 4.4 mg L^{-1}. Groundwaters from the Hetao Plain of Inner Mongolia also have high concentrations. Guo et al. (2001) found concentrations up to 1350 µg L^{-1} and observed that concentrations were generally much higher in groundwater from boreholes (depth range 15–30 m) than open dug wells (3–5 m depth). Tian et al. (2001) also reported arsenic concentrations between 50 and 1800 µg L^{-1} in groundwater from the Ba Men region of west central Inner Mongolia.

In the Huhhot Basin, part of the Tumet Plain of Inner Mongolia, arsenic problems are found in groundwaters from mainly Holocene alluvial and lacustrine aquifers. As with the Bengal Basin, these occur under highly reducing conditions and the problems are worst in the lowest lying parts of the basin (Smedley et al., 2003). The reducing high-arsenic groundwaters have characteristically moderate to high concentrations of dissolved iron, manganese, bicarbonate, and ammonium and low concentrations of nitrate and sulfate (Luo et al., 1997; Smedley et al., 2003). Arsenic concentrations reach up to 1500 µg L^{-1} in the groundwaters, with a significant proportion (>60%) of the arsenic present as As(III). The mechanisms of arsenic mobilization are believed to be very similar to those taking place in the Bengal Basin. However, unlike Bangladesh, deep aquifers in the area have relatively high arsenic concentrations (up to 300 µg L^{-1}). This may relate to differences in sediment chemistry and diagenetic history between the two regions. Alternatively, paleohydrogeological differences may have played a role because hydraulic gradients in Inner Mongolia, an inland basin remote from the sea, would have been less affected by sea-level changes during the Quaternary (Section V.C). Another distinction from Bangladesh is the observation that groundwater in many of the old hand-dug wells in the low-lying part of the Huhhot Basin also has relatively high arsenic concentrations. Concentrations up to 550 µg L^{-1} have been reported by Smedley et al. (2003). The high concentrations are believed to be due to the maintenance of relatively reducing conditions in the well waters as a result of high organic-matter content (solid and dissolved) in the shallow aquifer of the region.

The high groundwater arsenic concentrations have resulted in the development of chronic health problems in the affected areas of China, with the best documented cases in Xinjiang Province and Inner Mongolia. The problems are most notably manifested by skin lesions which include melanosis and hyperkeratosis. In the affected region of Inner Mongolia, additional health problems including lung, skin, and bladder cancer have been recognized and are documented by Luo et al. (1997).

e. Vietnam

The aquifers of the large deltas of the Mekong and Red Rivers are now widely exploited for drinking water. The total number of tubewells in Vietnam is unknown but could be of the order of one million, with perhaps 150,000 in the Red River delta region. The majority of these are private tubewells. The capital city, Hanoi, is largely dependent on groundwater for its public water supply. The aquifers exploited are of both Holocene and Pleistocene age. In parts of the Red River delta region (Figure 2), Holocene sediments form the shallow aquifer which may be only 10–15 m deep. Where Holocene sediments are absent, older Pleistocene sediments are exposed at the surface. Unlike Bangladesh, even when the Holocene sediments are present, there is not always a layer of fine silt-clay at the surface. Normally the Holocene sediments are separated from the underlying Pleistocene sediments by a clay layer several meters thick, although "windows" in this clay layer exist where there is hydraulic continuity between the Holocene and Pleistocene aquifers. The total thickness of sediments is typically 100–200 m.

The groundwaters in the delta regions are usually strongly reducing with high concentrations of iron, manganese, and ammonium. Much of the shallow aquifer in the Vietnamese part of the Mekong delta region is affected by salinity and cannot be used for drinking water. Little was known about the arsenic concentrations in groundwater in Vietnam until recently. Results from Hanoi indicate that there is a significant problem in shallow tubewells in the city, particularly in the south (Berg et al., 2001). Concentrations were found in the range of 1–3050 µg L^{-1} (average 159 µg L^{-1}). Early indications suggest that arsenic concentrations are not high in the groundwaters of the Mekong delta of Vietnam, though some groundwaters have been found with concentrations >50 µg L^{-1} further upstream in the Mekong Valley of Cambodia. Investigations are also ongoing in the same aquifer in neighboring Laos.

f. Hungary and Romania

Concentrations of arsenic above 50 µg L^{-1} have been identified in groundwaters from alluvial sediments in the southern part of the Great Hungarian Plain of Hungary and neighboring parts of Romania (Figure 2). Concentrations up to 150 µg L^{-1} (average 32 µg L^{-1}, 85 samples) have been found by Varsányi et al. (1991). The

Plain, about 110,000 km^2 in area, consists of a thick sequence of subsiding Quaternary sediments. Groundwaters vary from Ca-Mg-HCO_3 type in the recharge areas of the basin margins to Na-HCO_3 type in the low-lying discharge regions. Groundwaters in deep parts of the basin (80–560 m depth) with high arsenic concentrations are reducing with high concentrations of iron and ammonium and many have reported high concentrations of dissolved organic matter (humic acid quoted as up to 20 mg L^{-1}; Varsányi et al., 1991). The groundwaters have the largest arsenic concentrations in the lowest parts of the basin where the sediment is fine-grained. Gurzau and Gurzau (2001) reported concentrations up to 176 μg L^{-1} in the associated aquifers of neighboring Romania.

2. *Inland Basins in Arid and Semi-Arid Areas*

a. Mexico

The Comarca Lagunera of north central Mexico has a well-documented arsenic problem in groundwater with significant resulting chronic health problems. The region is arid and groundwater is an important resource for potable supply. Groundwaters are predominantly oxidizing with neutral to high pH. Del Razo et al. (1990) quoted pH values for groundwaters in the range of 6.3–8.9. They found arsenic concentrations in the range of 8–624 μg L^{-1} (average 100 μg L^{-1}, n = 128), with half the samples having concentrations greater than 50 μg L^{-1}. They also noted that most (>90%) of the groundwater samples investigated had arsenic present predominantly as As(V). The Comarca Lagunera is a closed basin and arsenic concentrations are typically highest in the low-lying parts of the basin. Del Razo et al. (1994) determined the average concentration of arsenic in drinking water from Santa Ana town as 404 μg L^{-1}. The estimated population exposed to arsenic in drinking water with >50 μg L^{-1} is around 400,000 in the Comarca Lagunera (Del Razo et al., 1990). The groundwater also has high concentrations of fluoride (up to 3.7 mg L^{-1}; Cebrián et al., 1994). High arsenic concentrations have also been identified in groundwaters from the state of Sonora in northwest Mexico, where Wyatt et al. (1998) reported concentrations in the range of 2–305 μg L^{-1} (76 samples). The arsenic concentrations were also positively correlated with fluoride, with maximum fluoride concentrations of 7.4 mg L^{-1}, which were significantly greater than the WHO guideline value for fluoride in drinking water of 1.5 mg L^{-1}.

b. Chile

Health problems related to arsenic in drinking water were first recognized in northern Chile in 1962. Typical symptoms included skin pigmentation changes, keratosis, squamous-cell carcinoma (skin cancer), cardiovascular problems, and respiratory disease. More recently, chronic arsenic ingestion has been linked to lung and bladder cancer. It has been estimated that around 7% of all deaths occurring in Antofagasta between 1989 and 1993 were due to past exposure to arsenic in drinking water at concentrations of the order of 500 μg L^{-1} (Smith et al., 1998). Since exposure was chiefly during the period from 1955 to 1970, this pointed to a long latency of cancer mortality. Other reported symptoms include impaired resistance to viral infection and lip herpes (Karcher et al., 1999).

High arsenic concentrations have been reported in surface waters and groundwaters from Administrative Region II (incorporating the cities of Antofagasta, Calama, and Tocopilla) of northern Chile (Cáceres et al., 1992). The region is arid and is part of the Atacama Desert, and water resources are limited. High As concentrations are accompanied by high salinity and high concentrations of boron and lithium. This in part relates to evaporation but is also significantly affected by geothermal inputs from the El Tatio geothermal field. Arsenic concentrations below 100 μg L^{-1} in surface waters and groundwaters are apparently quite rare, and concentrations up to 21,000 μg L^{-1} have been found. Karcher et al. (1999) quoted ranges of 100 μg L^{-1} to 1000 μg L^{-1} in untreated surface waters and groundwaters (average 440 μg L^{-1}).

The affected groundwaters of Chile are taken to be predominantly oxidizing (with dissolved oxygen present), largely because the arsenic is reported to be present in the waters as arsenate. However, the geochemistry of the aquifers of Chile is still poorly understood. The aquifers are composed of volcanic rocks and sediments, but the arsenic sources are not well-characterized. In Antofagasta, concentrations of arsenic in the sediments are about 3.2 mg kg^{-1} (Cáceres et al., 1992). Sediments from the Rio Loa and its tributaries have much higher concentrations (26–2000 mg kg^{-1}) as a result of geothermal inputs from the river system (Romero et al., 2003). Additional exposure to arsenic from the smelting of copper ore has also been noted in northern Chile (Cáceres et al., 1992).

c. Argentina

The Chaco-Pampean Plain of central Argentina constitutes perhaps one of the largest regions of high-arsenic groundwaters known, covering around 1 million km^2. High concentrations of arsenic have been found in the provinces of Córdoba, La Pampa, Santa Fe, Buenos Aires, and Tucumán in particular. Symptoms typical of

chronic arsenic poisoning, including skin lesions and some internal cancers, have been recorded in these areas. The climate is temperate with increasing aridity toward the west. The high-arsenic groundwaters are from Quaternary deposits of loess (mainly silt) with intermixed rhyolitic or dacitic volcanic ash (Nicolli et al., 1989, 2001; Smedley et al., 2002). The sediments display abundant evidence of post-depositional diagenetic changes under semi-arid conditions with common occurrences of calcrete in the form of cements, nodules, and discrete layers that are sometimes many centimeters thick.

Nicolli et al. (1989) found arsenic concentrations in groundwaters from Córdoba in the range of 6–11,500 $\mu g L^{-1}$ (median 255 $\mu g L^{-1}$). Smedley et al. (2002) found concentrations for groundwaters in La Pampa Province in the range of <4–5280 $\mu g L^{-1}$ (median 145 $\mu g L^{-1}$). Nicolli et al. (2001) found concentrations in groundwaters from Tucumán Province of 12–1660 $\mu g L^{-1}$ (median 46 $\mu g L^{-1}$). The groundwaters often have high salinity and are also predominantly oxidizing with low dissolved Fe and Mn concentrations. Arsenic is predominantly present as As(V) (Smedley et al., 2002). Under the arid conditions, silicate and carbonate weathering reactions are pronounced and the groundwaters often have high pH values. Smedley et al. (2002) found pH values typically of 7.0–8.7 and Nicolli et al. (2001) found values of 6.3–9.2. Metal oxides in the sediments (especially iron and manganese oxides) are thought to be the main source of the dissolved arsenic with the mobilization promoted by desorption under high-pH conditions (Smedley et al., 2002). Positive correlations between arsenic and pH are apparent in the groundwaters (Figure 6) and the arsenic is also generally well correlated with other anion and oxyanion elements (F, V, HCO_3, Mo, and B; Figure 6), some of these elements having very high concentrations. Dissolution of volcanic glass has been proposed as an alternative potential source of the dissolved arsenic (Nicolli et al., 1989).

d. Southwest United States

Many areas have been identified in the United States with arsenic problems in groundwater. Most of the worst affected and best documented cases occur in the southwestern states of Nevada, California, and Arizona. Within the last decade, aquifers in Maine, Michigan, Minnesota, South Dakota, Oklahoma, and Wisconsin have been found with concentrations of arsenic exceeding 10 $\mu g L^{-1}$ and smaller areas of high-arsenic groundwaters have been found in many other states. Much water analysis has been carried out in the United States, particularly in view of the recent reduction in the U. S. EPA drinking-water maximum contaminant level. Occurrences in groundwater are therefore found to be widespread, although of those reported, relatively few have significant numbers of sources with concentrations greater than 50 $\mu g L^{-1}$. A review of the analyses of some 17,000 water analyses from the United States concluded that around 40% exceeded 1 $\mu g L^{-1}$ and about 5% exceeded 20 $\mu g L^{-1}$ (Welch et al., 2000). The arsenic appears to be derived from various sources, which include natural dissolution/desorption reactions, geothermal water, and mining activity. The natural occurrences of arsenic in groundwater occur under both reducing and oxidizing conditions in different areas. Concentration by evaporation is thought to be an important process in the more arid areas.

In Nevada, Fontaine (1994) reported at least 1000 private wells with arsenic concentrations in excess of 50 $\mu g L^{-1}$. Welch and Lico (1998) also reported high concentrations that often exceeded 100 $\mu g L^{-1}$ but with extremes up to 2600 $\mu g L^{-1}$ in shallow groundwaters from the southern Carson Desert. These are largely present under reducing conditions. The groundwaters also have associated high pH (>8) and high concentrations of phosphorus (locally >4 $mg L^{-1}$) and uranium (>100 $\mu g L^{-1}$; Welch and Lico, 1998). The high arsenic and uranium concentrations were thought to be due to evaporative concentration of groundwater combined with the influence of redox and desorption processes involving metal oxides.

In California, high arsenic concentrations have been reported in the Tulare Basin of the San Joaquin Valley. A range from <1 to 2600 $\mu g L^{-1}$ was found by Fujii and Swain (1995). Redox conditions in the aquifers are variable and high arsenic concentrations are found in both oxidizing and reducing conditions. The proportion of groundwater arsenic present as As(III) increases with increasing well depth. The groundwaters from the Basin are often strongly affected by evaporation with resultant high concentrations of total dissolved solids. Many also have high concentrations of Se (up to 1000 $\mu g L^{-1}$), U (up to 5400 $\mu g L^{-1}$), B (up to 73,000 $\mu g L^{-1}$), and Mo (up to 15,000 $\mu g L^{-1}$) (Fujii & Swain, 1995).

In Arizona, Robertson (1989) also noted the occurrence of high arsenic concentrations in some groundwaters under oxidizing conditions in alluvial aquifers of the Basin and Range Province. Dissolved oxygen concentrations in the groundwaters were in the range of 3–7 mg L^{-1}. Only limited analysis of arsenic species was carried out, but results obtained suggested that the arsenic was present predominantly as As(V). The dissolved arsenic generally correlated positively with pH, Mo, and V (Figure 6) as well as Se and F. Groundwater pH values

been reported to have very high arsenic concentrations locally (up to 48,000 $\mu g L^{-1}$). Well-documented cases include the Fairbanks gold mining district of Alaska, the Coeur d'Alène Pb-Zn-Ag mining area of Idaho, Bunker Hill mine in Idaho, Leviathan Mine and Mother Lode in California, Kelly Creek Valley in Nevada, Clark Fork river area in Montana, and Lake Oahe in South Dakota.

Many other areas have above-average concentrations of arsenic in water, soils, sediments, and vegetation as a result of local mineralization exacerbated by mining activity. Documented cases include the Zimapán Valley of Mexico, Baja California (Mexico), the Lavrion region of Greece, the Iron Quadrangle of Minas Gerais (Brazil), the Styria region of Austria, the Zloty Stok area of southwest Poland, parts of southwest England, eastern Zimbabwe, South Korea, and Sarawak (Malaysia) (Figure 2) (Smedley & Kinniburgh, 2002 and references cited therein). Doubtless, arsenic problems also exist in many other undocumented mining areas.

Increased concentrations of dissolved arsenic have also been found in parts of the world with local mineralization which has not been mined. In Wisconsin in the United States, arsenic and other trace-element problems in groundwater have arisen as a result of the oxidation of sulfide minerals (pyrite and marcasite) present as a discrete secondary cement horizon in the regional Ordovician sandstone aquifer. Concentrations of arsenic up to 12,000 $\mu g L^{-1}$ have been found in the well waters (Schreiber et al., 2000). The oxidation appears to have been promoted by groundwater abstraction which has led to the lowering of the piezometric surface at a rate of around 0.6 m $year^{-1}$ since the 1950s, which resulted in a partial dewatering of the aquifer. The high arsenic concentrations were observed where the piezometric surface intersects, or lies close to, the sulfide cement horizon.

Boyle et al. (1998) recorded arsenic concentrations up to 580 $\mu g L^{-1}$ in groundwaters from an area of sulfide mineralization in Bowen Island, British Colombia. Heinrichs and Udluft (1999) found many high concentrations in groundwater from the Upper Triassic Keuper Sandstone in northern Bavaria. Out of 500 wells, 160 had arsenic concentrations in the range 10–150 $\mu g L^{-1}$. The nature of the mineralization in this aquifer was not clearly identified. As yet unidentified areas of mineralization could be quite widespread, although these are likely to be on a local scale.

4. Geothermal Sources

The common occurrence of high concentrations of arsenic in geothermal fluids has been recognized for a long time. Geothermal areas with documented high concentrations include the United States, Japan, New Zealand, Chile, Argentina, Kamchatka, France, and Dominica (references cited in Smedley & Kinniburgh, 2002). One of the largest and best documented geothermal systems is that of Yellowstone National Park in the states of Wyoming, Idaho, and Montana in the United States. Arsenic concentrations up to 7800 $\mu g L^{-1}$ have been found in hot springs and geysers in the region (Thompson & Demonge, 1996). Geothermal inputs have also given rise to high concentrations of arsenic (up to 370 $\mu g L^{-1}$) in waters of the Madison River (Nimick et al., 1998). Other reported geothermal occurrences in the United States include Honey Lake Basin, California (arsenic up to 2600 $\mu g L^{-1}$); Coso Hot Springs, California (up to 7500 $\mu g L^{-1}$); Imperial Valley, California (up to 15,000 $\mu g L^{-1}$); Long Valley, California (up to 2500 $\mu g L^{-1}$); Lassen Volcanic National Park, California (up to 27,000 $\mu g L^{-1}$); Steamboat Springs, Nevada (up to 2700 $\mu g L^{-1}$); and Geyser Bight, Umnak Island, Alaska (up to 3800 $\mu g L^{-1}$) (White et al., 1963; Thompson et al., 1985; Welch et al., 1988, 2000). Geothermal inputs from Long Valley, California, are believed to be responsible for the relatively high concentrations (20 $\mu g L^{-1}$) of arsenic in the Los Angeles Aqueduct which provides the water supply for the city of Los Angeles (Wilkie & Hering, 1998). Geothermal inputs also contribute significantly to the high dissolved arsenic concentrations (up to 20 $mg L^{-1}$) in Mono Lake, California (Maest et al., 1992).

In New Zealand, arsenic concentrations up to 9000 $\mu g L^{-1}$ have been found in geothermal waters (Webster & Nordstrom, 2003). River and lake waters receiving inputs of geothermal water from the Wairakei, Ohaaki, Orakei Korako, and Atiamuri geothermal fields have arsenic concentrations up to 121 $\mu g L^{-1}$ (Robinson et al., 1995). Concentrations diminish significantly downstream from the geothermal input areas.

Arsenic concentrations in the range of 45,000–50,000 $\mu g L^{-1}$ have been found in geothermal waters from the El Tatio system in the Antofagasta region of Chile (Ellis & Mahon, 1977). The geothermal area lies between the volcanoes of the Andes and the Serrania de Tucle. Romero et al. (2003) found concentrations in waters from the Rio Loa and its tributaries in the range of 120–10,000 $\mu g L^{-1}$ as a result of inputs from the El Tatio geothermal system.

Arsenic concentrations in the range of 100–5900 $\mu g L^{-1}$ have been found in geothermal waters from Kamchatka (White et al., 1963). Concentrations in the range of 500–4600 $\mu g L^{-1}$ were also reported in 26 geo-

thermal water samples from five geothermal fields in Kyushu, Japan (Yokoyama et al., 1993).

White et al. (1963) reported arsenic concentrations in geothermal waters from Iceland. While concentrations were high compared to most groundwaters (range 50–120 $\mu g L^{-1}$), these are much lower than the values found in many other geothermal systems described above. This may be related to the fact that the geothermal fluids in the Icelandic volcanic field are associated with magmas of predominantly basaltic composition derived from oceanic mantle, hence having low arsenic concentrations (Webster & Nordstrom, 2003). Typical high-arsenic geothermal fluids are associated with acidic volcanic systems in continental settings. In this case, higher arsenic concentrations may be derived from the interaction of geothermal fluids with the continental crust, particularly argillaceous sediments (Nordstrom, 2002) in which the element is known to be preferentially partitioned. High arsenic concentrations have not been documented in geothermal systems associated with other volcanic provinces of dominantly basaltic composition, whether oceanic or continental (e.g., Hawaii, East African Rift).

Hot springs commonly show a positive correlation between arsenic and chloride. Welch et al. (1988) noted a general relationship between arsenic and salinity in geothermal waters from the United States. Wilkie & Hering (1998) also noted high Cl (and B) concentrations of arsenic-rich geothermal waters in Long Valley, California. High-arsenic geothermal waters are also typically of Na-Cl type in the Kyushu area of Japan (Yokoyama et al., 1993) as are those from the El Tatio geothermal system in Chile. The associations between arsenic and chloride were noted by Webster and Nordstrom (2003) to relate to the similar behavior of these elements during subsurface boiling and phase separation as both partition preferentially into the liquid phase.

IV. MINERAL-WATER INTERACTIONS

A. Adsorbed Arsenic in Sediments

Of the arsenic problem aquifers identified, it appears to be those hosted in young sediments that are most vulnerable to the development of high-arsenic groundwater on a regional scale. In these aquifers, surface reactions are considered to be important controls on the trace-element chemistry of the groundwaters. Arsenic behavior in aquifers, sediments, and soils has commonly been linked to adsorption/desorption reactions (e.g., Korte, 1991; Manning & Goldberg, 1997a; BGS & DPHE, 2001).

The major minerals that adsorb arsenic (as both arsenate and arsenite) in sediments are the metal oxides, particularly those of iron, aluminum, and manganese. Iron oxides are relatively abundant in most sediments and are commonly produced by the weathering of primary minerals. In freshwater sediments and silicate clays, they often constitute about 50% of the iron present (Manning & Goldberg, 1997b). Carbonates may also adsorb arsenic, but their capacity for doing so has not been measured quantitatively and is likely to be relatively small. Of these minerals, the iron oxides are probably the most important adsorbents of arsenic in sandy aquifers because of their relative abundance, strong binding affinity, and high specific surface area, especially the freshly formed amorphous oxides. These oxides are also particularly sensitive to a changing geochemical environment, acid dissolution, and reductive dissolution as well as changes in mineral structure and crystallinity. Aluminum oxides can also be expected to play a significant role in arsenic adsorption when present in quantity (Hingston et al., 1971; Manning & Goldberg, 1997b). Evidence from water treatment suggests that aluminum hydroxides have similar effectiveness to iron hydroxides (on a molar basis) for adsorbing As(V) below pH 7.5, but that iron salts are more efficient at higher pH and for adsorbing As(III) (Edwards, 1994). Iron sulfide minerals such as iron monosulfides and pyrite may also adsorb significant quantities of arsenic.

B. Reduced Sediments and the Role of Iron Oxides

A well-known sequence of reduction reactions occurs when sediments are buried and the environment becomes anaerobic (Berner, 1981; Stumm & Morgan, 1995). Such reactions are common in sediments from a wide variety of environments. The processes causing changes in iron redox chemistry are particularly important because they can directly affect the mobility of arsenic. One of the principal causes of high arsenic concentrations in groundwaters appears to be the reductive dissolution of hydrous iron oxides and/or the release of adsorbed and co-precipitated arsenic. This sequence begins with the consumption of oxygen and an increase in dissolved CO_2 from the decomposition of organic matter. Next, NO_3^- decreases by reduction to NO_2^- and

ultimately to the gases N_2O and N_2. Insoluble manganic oxides dissolve by reduction to soluble Mn^{2+} and hydrous ferric oxides are reduced to Fe^{2+}. These processes are followed by SO_4^{2-} reduction to S^{2-}, then CH_4 production from fermentation and methanogenesis, and finally reduction of N_2 to NH_4^+. During sulfate reduction the sulfide produced reacts with any available iron to produce FeS and ultimately pyrite, FeS_2. Iron is often more abundant than sulfur so that there is excess iron beyond that which can be converted to pyrite. Arsenic(V) reduction would normally be expected to occur after Fe(III) reduction but before SO_4^{2-} reduction.

In sulfate-poor environments, iron from free iron oxides is solubilized as Fe^{2+} under reducing conditions. This gives rise to waters characteristically high in Fe. Groundwaters in such conditions tend to have Fe concentrations of 0.1–30 mg L^{-1}. The reaction is microbially mediated (Lovley & Chappelle, 1995). There is also evidence for solid-state transformations of the iron oxides under reducing conditions. This is reflected by a color change from red/orange/brown colors to gray/green/blue colors. Changes to the magnetic properties have also been documented (Sohlenius, 1996). Direct analysis of the Fe(II) and Fe(III) contents of iron oxides from reduced lake waters and sediments often indicates the presence of a mixed Fe(II)–Fe(III) oxide with an approximate average charge on the iron of 2.5 (Davison, 1993). The fate of iron oxides during reduction is not well understood, in part because they are probably very fine-grained and difficult to observe directly.

"Green rusts" are one possible product of the transformations. These have occasionally been identified or suspected in anoxic soils and sediments but are very unstable under oxidizing conditions (Taylor, 1980; Génin et al., 1998; Cummings et al., 1999). They consist of a range of green-colored Fe(II)–Fe(III) hydroxide minerals with a layered structure and a charge-balancing interlayer counterion, usually carbonate or sulfate. Authigenic magnetite (Fe_3O_4) is another possible product that has been identified in anaerobic sediments (Fredrickson et al., 1998), often with extremely small particle sizes. Magnetite is frequently found in sediments as a residual detrital phase from rock weathering but very fine-grained magnetite is also formed by so-called "magnetotactic" bacteria. Magnetite formation has been established under reducing conditions in the laboratory (Guerin & Blakemore, 1992). However, under strongly reducing conditions magnetite is unstable and in the presence of high concentrations of H_2S, it converts slowly to pyrite on a scale of centuries or more (Canfield & Berner, 1987). At the sediment/water interface in oceans, partial oxidation of primary magnetite can lead to a coating of maghemite, γ-Fe_2O_3. Further burial and reduction leads to the dissolution of the primary magnetite (Torii, 1997).

These studies of iron oxides in reducing environments indicate a lack of understanding of the detailed sequence of events taking place when Fe(III) oxides are subjected to strongly reducing conditions. The changes are evidently substantial and can result in the partial dissolution of the oxides and their transformation to completely new mineral phases. It is not yet clear what impact these transformations have on the adsorbed arsenic load of the original Fe(III) oxides. However, even quite small changes in arsenic binding could have a large impact on porewater arsenic concentrations because of the large solid/solution ratios found in sediments. Therefore, it is likely that understanding the changes to the nature of iron oxide minerals in sedimentary environments is an important part of understanding the processes leading to arsenic mobilization in sedimentary environments.

C. Role of Microbes

It has become increasingly clear in recent years that microbes play an important role in arsenic speciation and release. They can be significant catalysts in the oxidation of arsenite, reduction of arsenate, and methylation and volatilization of arsenic species. The microbiological transformations either provide sources of energy or act as detoxifying mechanisms. A number of chemoautotrophs oxidize As(III) by using oxygen, nitrate, or ferric iron as a terminal electron acceptor and CO_2 as their sole carbon source. Some autotrophs are also capable of As(III) oxidation. Conversely, it has recently been shown that some prokaryotes are capable of the respiratory reduction of As(V) (Oremland et al., 2002). These include several species of eubacteria and a few hyperthermophiles (Archaea).

Arsenic can also be released indirectly as a result of other microbially induced redox reactions. For example, the dissimilatory Fe-reducing bacterium *Shewanella alga* reduces Fe(III) to Fe(II) in scorodite ($FeAsO_4 \cdot 2H_2O$), releasing As(V) in the process (Cummings et al., 1999).

Thermophilic bacteria and cyanobacteria have been recognized in geothermal settings and can affect arsenic speciation and mineral precipitation in such systems (Webster & Nordstrom, 2003). Streams affected by geothermal inputs have also been shown to be influ-

enced by microbial activity. In the geothermally fed waters of Hot Creek, California, Wilkie and Hering (1998) concluded that the oxidation of As(III) was controlled by bacteria attached to macrophytes. In abiotic systems, this oxidation reaction would normally be expected to be slow. In the Hot Creek system, the microbially mediated oxidation proceeded with a pseudo-first-order half-life of just 0.3 hours. Extremophiles such as *Bacillus arsenicoselenatis* have also adapted to the alkaline and saline conditions in the geothermally-influenced Mono Lake of California (Oremland et al., 2002).

V. COMMON FEATURES OF HIGH-ARSENIC GROUNDWATER PROVINCES

A. The Source of Arsenic

In the cases where affected groundwaters are found close to obvious geological or industrial sources rich in arsenic (geothermal springs, drainage from mineralized and mining areas, specific contaminant sources), it is clear that the anomalously high arsenic concentrations in the source region are responsible. The extent of this contamination is usually highly localized because the geochemical conditions within most aquifers do not favor arsenic mobilization on a regional scale. Areas affected by geothermal activity are potentially more widespread because in this case mobilization of arsenic is not required: arsenic is already present in solution and the size of geothermal reservoirs can be large. This probably accounts for why high-arsenic surface waters are normally located in geothermal areas. Perhaps more puzzling is the way in which very high concentrations of arsenic, up to several $mg\,L^{-1}$, are found in groundwaters from areas with apparently near-average source rocks. In aquifers with extensive areas of high-arsenic groundwater, this appears to be the rule rather than the exception. Most of these cases arise in aquifers derived from relatively young sediments, often consisting of alluvium or loess where the total sediment arsenic concentrations are usually in the range of $1–20\,mg\,kg^{-1}$. Recognition of this fact is a recent development and its late appreciation has delayed the discovery of many high-arsenic groundwater provinces. Hitherto, geochemists had concentrated their investigations on the well-recognized, high-arsenic areas associated with mining and geothermal activity (see also Chapter 2, this volume).

Of critical importance is the fact that drinking-water limits for arsenic are very low in relation to the overall abundance of arsenic in the environment. Fortunately, most arsenic is normally retained in the solid phase and does not constitute a problem for potable water supplies. However, it only takes a very small percentage of this "solid" arsenic to dissolve or desorb to give rise to a serious groundwater problem.

B. Mobilization of Arsenic

There appear to be two key factors involved in the formation of high-arsenic groundwaters on a regional scale. First, there must be some form of geochemical trigger which releases arsenic from the aquifer solid phase into the groundwater. Secondly, the released arsenic must remain in the groundwater and not be flushed away. There are a number of possible geochemical triggers. In mining and mineralized areas, oxidation of sulfide ores may be triggered by influxes of oxygen or other oxidizing agents. This may follow a lowering of the water table or change in hydrogeological regime. However, in most arsenic-affected aquifers, the most important trigger appears to be the desorption or dissolution of arsenic from oxide minerals, particularly iron oxides. An important feature of this process is that the initial adjustment to environmental changes is probably quite rapid because adsorption reactions are surface reactions. The rate-limiting factors are probably those that control the major changes in pH, redox condition, and associated water-quality parameters of the aquifer. These are in part related to physical factors such as the rate of diffusion of gases through the sediment, the rate of sedimentation, the extent of microbiological activity, and the rates of chemical reactions. However, many of these are likely to be rapid on a geological time scale. Dissolution reactions are relatively slow but even oxide dissolution is rapid on a geological time scale and can be observed over the course of weeks or even days in flooded soils (Masscheleyn et al., 1991).

A qualification is that if diagenetic changes to the oxide mineral structure take place or if burial of sediment occurs, then there could be a slow release of arsenic over a much longer time scale. Details of the rate of release of arsenic from these sources are not yet clear. It is likely that the rate will diminish with time, with the greatest changes occurring in the early stages. Natural groundwater flushing means that very slow releases of arsenic are likely to be of little consequence because the arsenic released will be removed and not

tend to significantly accumulate. Once the diagenetic readjustment has taken place and the sediments have equilibrated with their new environment, there should be little further release of arsenic. This contrasts with some mineral-weathering reactions which occur in "open" systems and can continue for millions of years—essentially until all of the mineral has dissolved. Seen in this context, the desorption/dissolution of arsenic from metal oxides in young aquifers is essentially a step change responding to a new set of conditions. The geochemical triggers involved could arise for a number of reasons. These are discussed further below.

1. Desorption of Arsenic at High pH Under Oxidizing Conditions

Under the aerobic and acidic to near-neutral conditions typical of many natural environments, arsenic is strongly adsorbed by oxide minerals as the arsenate ion and the concentrations in solution are therefore kept very low. The nonlinear nature of the adsorption isotherm for arsenate (Figure 5) ensures that the amount of arsenic adsorbed is often relatively large, even when dissolved concentrations of arsenic are low. Adsorption protects many natural environments from widespread arsenic toxicity problems. As the pH increases, especially above pH 8.5, arsenic tends to desorb from oxide surfaces thereby increasing the concentration in solution (Dzombak & Morel, 1990). The impact of this is magnified by the high solid/solution ratios typical of aquifers.

Smedley and Kinniburgh (2002) demonstrated the effect of a pH increase on As(V) desorption from hydrous ferric oxide (HFO) using the Dzombak and Morel (1990) diffuse double-layer model. The calculations indicated that for a sandy sediment with 25% porosity containing $1\,g\,Fe\,kg^{-1}$ as HFO, in equilibrium at pH 7 with water having an arsenic concentration of $1\,\mu g\,L^{-1}$ (typical of a river water, for example), increasing the pH under closed-system conditions results in a strong increase in the amount of arsenic desorbed. Above pH 9, the arsenate concentration in solution from this source could exceed $1000\,\mu g\,L^{-1}$.

These calculations assumed that no competing ions existed in the system. In reality, other ions are likely to compete for sorption sites on the HFO and will reduce the arsenic loading on the solid. Smedley and Kinniburgh (2002) demonstrated the reduced arsenic loading on HFO in the presence of phosphorus, but they noted that increasing the pH still had a strong desorbing effect on arsenic. At high pH, phosphate is also released. Other potential competing ions include bicarbonate, silicate, and dissolved organic carbon.

There are several reasons why the pH might increase, but the most important in the present context is the uptake of protons by mineral-weathering and ion-exchange reactions combined with the effect of evaporation in arid and semi-arid regions. This pH increase is commonly associated with the development of salinity and the salinization of soils. Inputs of geothermal waters with high pH may be important in maintaining high arsenic concentrations in some alkaline lakes. Desorption at high pH is the most likely mechanism for the development of groundwater arsenic problems under oxidizing conditions such as those observed in Argentina, Mexico, and parts of the United States, for example, and would account for the observed positive correlation of arsenic concentrations with increasing pH (Figure 6). Increases in pH also induce the desorption of a wide variety of other oxyanions such as phosphate, vanadate, uranyl, molybdate, and borate. This is indeed observed in many groundwaters with high pH (Figure 6) (Smedley et al., 2002). These specifically adsorbed anions all interact with adsorption sites on the oxides in a competitive way and thus influence the extent of binding of each other. The process is not well understood in a quantitative sense. Phosphate, in particular, may play an important role in arsenic binding because it is usually more abundant than arsenic, often by a factor of 50 or more (in molar terms), and is also strongly bound to oxide surfaces. The infurence of Vanadium may also be significant.

The presence of bicarbonate may also promote desorption of arsenate. However, its role is unclear at present. Experimental evidence for the desorption of anionic compounds in the presence of bicarbonate is contradictory (Smedley & Kinniburgh, 2002). Bicarbonate is often the dominant anion in high-arsenic groundwaters and concentrations can be high, frequently exceeding $500\,mg\,L^{-1}$, and occasionally in excess of $1000\,mg\,L^{-1}$ (Table III). Silica may also exert a control on the adsorption of arsenic (Swedlund & Webster, 1998).

The role of dissolved organic carbon (fulvic and humic acids) is uncertain, at least from a quantitative point of view. Humic substances have been shown to reduce As(III) and As(V) sorption by iron oxides under some conditions (Xu et al., 1991; Bowell, 1994) and high-As groundwaters are associated with high humic-acid concentrations in some aquifers (Varsányi et al., 1991; Smedley et al., 2003). However, direct evidence for a causal link between dissolved organic carbon and arsenic desorption does not yet exist.

By contrast, some cations, because of their positive charge, may promote the adsorption of negatively charged arsenate (Wilkie & Hering, 1996). Calcium and magnesium are likely to be the most important cations in this respect because of their abundance in most natural waters and their +2 charge. Ferrous iron (Fe^{2+}) may be important in reduced waters and Al^{3+} in acidic waters.

The aridity described above enables the high pH values to be maintained and minimizes the flushing of any released arsenic. It also allows the buildup of high chloride and fluoride concentrations. Other environments with a high pH (up to pH 8.3), particularly open-system calcareous environments, are likely to be too well-flushed to allow released arsenic to accumulate.

The pH dependence of arsenic adsorption is important but has not yet been measured in detail for any aquifer materials, especially in the presence of typical groundwater compositions. The pH dependence is likely to depend to some extent on the heterogeneity of the aquifer material. Other specifically adsorbed anions, particularly phosphate and perhaps bicarbonate, may also affect the pH dependence of As(V) and As(III) binding.

2. Arsenic Desorption and Dissolution Due to a Change to Reducing Conditions

The onset of strongly reducing conditions, sufficient to enable iron(III) and probably sulfate reduction to take place, appears to be another trigger for the release of arsenic. The most common cause of this is the rapid accumulation and burial of sediments. This occurs in large alluvial systems, especially broad lowland meander belts and braided channels, and in prograding deltas. The organic carbon content of the buried sediment will largely determine the rate at which reducing conditions are created. Freshly produced soil organic matter readily decomposes and the presence of even small quantities can consume all of the dissolved oxygen, nitrate, and sulfate in the system. Solid-phase Fe(III) in minerals may moderate the rate of reduction of the aquifer. Reducing conditions can only be maintained if the diffusion and convection of dissolved oxygen and other oxidants from the surface is less rapid than the consumption. This is facilitated if there is a confining layer of fine-grained material close to the surface. This often occurs in large deltas where fine-grained overbank deposits overlie coarser-grained alluvial deposits.

A change in the redox state of adsorbed arsenic from As(V) to As(III) upon the onset of reducing conditions is likely to be one of the earliest reactions to take place. This changing redox state could have wider repercussions because it will also affect a large number of competing reactions. Phosphate-arsenite competition, for example, is likely to be less important than phosphate-arsenate competition. There is also the potential for arsenite-arsenate competition. Although As(V) is normally more strongly bound than As(III), model calculations suggest that adsorbed phosphate can reverse the relative affinity of As(III) and As(V) at near-neutral pH values (BGS & DPHE, 2001). This has yet to be confirmed experimentally.

3. Changes in the Structure of Oxide Minerals

Disordered and fine-grained iron oxides, which may include HFO, lepidocrocite, schwertmannite, and magnetite, are common products of the early stages of weathering. Freshly-precipitated HFO is extremely fine -grained with cluster sizes of about 5 nm in diameter and a specific surface area of $300\,m^2\,g^{-1}$ or greater. HFO gradually transforms to more ordered structures such as goethite or hematite with larger crystal sizes and reduced surface areas. Goethite typically has specific surface areas of $150\,m^2\,g^{-1}$ or less and those for hematite are even less (Cornell & Schwertmann, 1996). This aging reaction can take place rapidly in the laboratory, but the rate in nature is likely to be inhibited somewhat by the presence of other ions, particularly strongly adsorbed ions such as aluminum, phosphate, sulfate, arsenate, bicarbonate, and silicate (Cornell & Schwertmann, 1996). One consequence of the reduction in surface area is that the amount of As(V) adsorption may decrease on a weight-for-weight basis. If the site density (site nm^{-2}) and binding affinities of the adsorbed ions remain constant, then as the specific surface area of the oxide mineral is reduced, some of the adsorbed ions may be desorbed.

Some of the desorbed ions may also be incorporated into the evolving oxide structure as a solid solution, which results in the reduction of the amount of arsenic released. In addition, if the surface structure changes, it is likely that the binding affinity for both arsenate ions and protons will change because the two are closely related.

Under strongly reducing conditions, it appears that additional processes could operate which may lead to a reduction in the overall adsorption of arsenic. Specifically for iron oxides, some of the surface iron could be reduced from Fe(III) to Fe(II) to produce a mixed-valence oxide perhaps akin to that of a magnetite or a green rust. This would tend to reduce the net positive charge of the surface (or increase its net negative

charge) and would thereby reduce the electrostatic interaction between the surface and anions. This could result in the desorption of arsenic and a corresponding large increase in the concentration of arsenic in solution (BGS & DPHE, 2001).

On balance, laboratory and field evidence suggests that at micromolar concentrations of arsenic, freshly formed HFO binds more arsenic than goethite on a mole of Fe basis (De Vitre et al., 1991) and thus a reduction in affinity appears to be more probable. In Bangladesh, areas with high-arsenic groundwaters tend to correspond with those areas in which the sediments contain a relatively high concentration of oxalate-extractable iron (BGS & DPHE, 2001). This provides indirect support for the importance of iron oxides. It is likely that the soils and sediments most sensitive to arsenic release on reduction and aging are those in which iron oxides are abundant, HFO is initially a major fraction of the iron oxides present, and other arsenic-sorbing minerals are relatively scarce. Although the existing evidence is somewhat contradictory, it tends to suggest that a change from aerobic to anaerobic conditions often results in a net release of arsenic.

4. Mineral Dissolution

Mineral dissolution reactions tend to be most rapid under extremes of pH and Eh. For example, iron oxides dissolve under strongly acidic conditions and under strongly reducing conditions. Minor elements, including arsenic, present either as adsorbed (labile) arsenic or as irreversibly bound (non labile) arsenic will also tend to be released during the dissolution. This can explain, in part at least, the presence of high arsenic concentrations in acid mine drainage and in strongly reducing groundwaters. Reductive dissolution of iron(III) oxides accounts for the high Fe(II) content of anaerobic waters. This process also undoubtedly accounts for some of the arsenic found in reducing groundwaters, but it is probably insufficient to account for all, or even most, of the arsenic released (Smedley & Kinniburgh, 2002). It is likely that arsenic release from iron oxides under reducing conditions involves some combination of reductive dissolution and reductive desorption.

Manganese oxides also undergo reductive desorption and dissolution and thus could contribute to the arsenic load of groundwaters in the same way as iron. High concentrations of dissolved Mn(II) are observed in many reducing high-arsenic groundwaters (e.g., Bangladesh). Manganese(IV) oxide surfaces are also thought to catalyze the oxidation of As(III) (Oscarson et al., 1981).

As described above, one of the most pertinent mineral dissolution processes in respect of arsenic mobilization is the oxidation of sulfide minerals. Pyrite, the most abundant of these minerals, can be an important source of arsenic, especially where it is freshly exposed as a result of excavation by mining or by lowering of the water table. In extreme cases, this can lead to highly acidic groundwaters rich in sulfate, iron, and trace metals. As the dissolved iron is neutralized and oxidized, it tends to precipitate as HFO with resultant adsorption and co-precipitation of dissolved As(V). In this sense, pyrite oxidation is not a very efficient mechanism for releasing arsenic into water.

C. Arsenic Transport Through Aquifers

The geochemical triggers described above may release arsenic into groundwater but are not in themselves sufficient to account for the distribution of high-arsenic groundwaters observed in various parts of the world. The released arsenic must also not have been flushed away or diluted by normal groundwater flow. The rate of arsenic release must be set against the accumulated flushing of the aquifer that has taken place during the period of release. The rocks of most aquifers used for drinking water are up to several hundred million years old and yet contain groundwater that may be at most a few thousand years old. Hence, a large number of pore volumes of fresh water will have passed through the aquifer over its history. This is also the case in most young aquifers with actively flowing groundwater. By contrast, many alluvial and deltaic aquifers are composed of relatively young sediments. Where groundwater flow is slow, these contain relatively old groundwater. The relative ages of aquifer rocks and groundwater are important. High groundwater arsenic concentrations only occur on a regional scale when geochemical conditions capable of mobilizing arsenic are combined with hydrogeological conditions which prevent its loss (see also Chapter 31, this volume).

The Quaternary period has seen considerable changes in climate and global sea level. Variation in groundwater piezometric levels over this period would have induced large variations in base levels of erosion and in groundwater flow regimes and rates. During the last glaciation, about 21,000–13,500 years ago, sea levels would have been up to 130 m below the present mean sea level. This was a worldwide phenomenon and would have affected all then existing coastal aquifers. Conti-

nental and closed basin aquifers on the other hand would have not been affected. The increased hydraulic gradient in coastal aquifers during the glacial period would have resulted in correspondingly large groundwater flows and extensive flushing. The arsenic in these older aquifers would therefore tend to have been flushed away. The deep unsaturated zone would also have led to more extensive oxidation of the shallower horizons with possible increased sorption of arsenic to Fe(III) oxides. Aquifers younger than around 7000 years old, i.e., of Holocene age, will not have been subjected to this increased flushing that occurred during the most recent glaciation.

In Bangladesh, the age of sediment versus depth relationship is important because this has a direct bearing on the extent of aquifer flushing. Many of the shallow sediments in southern Bangladesh are of Holocene age (less than 13,000 years old and many less than 5000 years old). Hence, they will not have experienced the extensive flushing of the last glacial period. The majority of boreholes abstract groundwater from these sediments. Certainly at present, flushing is slow because of the extremely low hydraulic gradients, especially in the south. By contrast, deeper and older sediments, which probably exceed 13,000 years in age, will have been subjected to more extensive flushing. This may account for the low-arsenic groundwaters found in the deep aquifers of Bangladesh. Geochemical factors may also play a role because the evidence shows that while the deep groundwaters are currently reducing, they are less strongly reducing than the shallow aquifers (BGS & DPHE, 2001; van Geen et al., 2003). Certainly, the aquifers in the Pleistocene uplifted alluvial sediments of the Barind and Madhupur Tracts (Figure 3) will have been well flushed since they are at least 25,000–125,000 years old. These sediments invariably yield low-arsenic groundwaters, typically containing less than $0.5\,\mu g\,L^{-1}$ arsenic (Section 111B1a). A complication is that the Bengal Basin is locally rapidly subsiding and accumulating sediments. This adds to the high degree of local and regional variation.

The process of delta development also favors the separation of minerals based on particle size and produces the characteristic upwardly-fining sequences of sand-silt-clay. These lead to confining or semi-confining layers which aid the development of strongly reducing conditions. The youngest, distal part of the deltas will tend to contain the greatest concentration of fine-grained material and this provides an abundant source of arsenic in the form of colloidal-sized oxide materials. Flocculation of colloidal material, including iron oxides, at the freshwater-sea water interface will tend to lead to relatively large concentrations of these colloids in the lower parts of a delta. The larger the delta, and the more rapid the infilling, the lower the hydraulic gradient and the less flushing is likely to have occurred. However, some deltas, even large deltas, may be so old and well-flushed that even the existing low hydraulic gradients will have been sufficient to flush away any desorbed or dissolved arsenic.

Regional flow patterns are not the only important factors. At a local scale, small variations in relief or in drainage patterns may dictate local flow patterns and hence the distribution of arsenic-rich groundwater. Evidence from Argentina, for example, suggests that the highest groundwater arsenic concentrations are found in small-scale topographic depressions where seasonal discharge occurs (Smedley et al., 2002). The same is true in Inner Mongolia (Smedley et al., 2003) and may also be true in Bangladesh. In any case, it is a characteristic of groundwater arsenic problem areas to have a high degree of local-scale variation. This reflects the poor mixing and the low rate of flushing characteristic of the affected aquifers. It is clear that flat low-lying areas, particularly large deltas and inland basins, are particularly prone to potentially high-arsenic groundwaters because they combine many of the risk factors identified above.

VI. Mitigation of High-Arsenic Groundwater Problems

Recognizing that an aquifer may have locally high concentrations of arsenic in the groundwater is one problem, mitigating the problem is a more difficult proposition. This is particularly the case in developing countries such as Bangladesh where the degree of short-range variability in arsenic concentrations is large, where the number of wells in use is immense, and where the technical infrastructure and resources are limited. As international drinking-water limits are also very low, arsenic poses a problem even in developed countries because of the expense of removing arsenic to the concentrations required to comply with regulations. While arsenic-removal plants can be built readily for large municipal water supplies, the problem is much greater for smaller rural supplies, many of which may be privately owned. Clearly, the best means of mitigating arsenic-related chronic health problems is to provide alternative low-arsenic water sources on a long-term basis. Options for mitigation are discussed below. The

best options available will vary from country to country and from aquifer to aquifer, depending on local geological, climatic, social, and economic factors.

A. Identification and Use of Existing Low-Arsenic Wells

Identification of low-arsenic groundwater in an aquifer that is vulnerable to arsenic contamination demands a large-scale water survey and analysis (Kinniburgh & Kosmus, 2002). Identifying regions where the probability of finding high-arsenic groundwater is increased can be done on a reconnaissance basis, but it requires random sampling. On the other hand, as the concentrations of arsenic in a given aquifer are characteristically variable, identifying individual sources of safe water for potable use demands testing of each well. In a country such as Bangladesh with a large reliance on small private tubewell supplies, this task is enormous. This strategy also requires some consideration of the long-term variability in arsenic concentrations in an individual well and therefore ideally requires some form of monitoring. It is unlikely that the concentrations in most wells will change significantly in the short- to medium-term given natural groundwater flow conditions, but changes may take place more rapidly as a result of extensive pumping. The option to identify and use existing low-arsenic wells is likely to involve well sharing in badly affected areas and may require cultural changes. The suitability of this option will vary depending on the percentage of wells affected in a given region and the scale of variation, e.g., the distance to the nearest safe well.

B. Drilling New Wells in Alternative Low-Arsenic Aquifers

Even in parts of the world with recognized groundwater arsenic problems, there are often other aquifers in the region with low-arsenic sources of water. In the Bengal Basin, for example, groundwater from deeper aquifers (>150 m to 200 m) appears to often have low to very low arsenic concentrations. In many problem areas, development of the alternative aquifer may be a solution, albeit at considerable extra cost. However, in the Bengal Basin issues such as sustainability of supply given increased development and the use of groundwater for irrigation are important. Increased abstraction from deeper levels may induce leakage of high-arsenic groundwater from the overlying aquifer or of saline water in the southern coastal areas. In addition, in Bangladesh at least, the deep aquifer does not appear to exist everywhere in the country (BGS & DPHE, 2001). Hence, use of deeper groundwater is not a universal option. It may also require different equipment and skills for the deepest wells, which incur costs perhaps ten to twenty times greater than for small hand-pump tubewells completed in the shallow aquifer.

In Inner Mongolia (Huhhot Basin), deeper aquifers (>100 m) have been developed for potable supplies of groundwater as an alternative to arsenic-enriched shallow sources. However, these deep sources also often have unacceptably high concentrations of arsenic (Smedley et al., 2003). Clearly, it is difficult to generalize and knowledge of the local geology and hydrogeology of a given area is required.

C. Use of Dug Wells

In a number of strongly reducing high-arsenic aquifers, shallow hand-dug wells have been observed to contain low arsenic concentrations (<10 $\mu g L^{-1}$). The Bengal Basin is a notable example (BGS & DPHE, 2001). The low concentrations observed are likely to be due to the maintenance of locally aerated conditions in the aquifer around the well and due to the presence of very young groundwater that has had little opportunity to react with minerals in the shallow aquifer. As such, dug wells provide a potentially suitable alternative source of drinking water. Indeed, as these were traditional sources of water before the advent of borehole technology in the Bengal Basin, this has often been stated as the reason why arsenic-related health problems in the region are a relatively recent phenomenon. Care must be taken to ensure that the water provided from dug wells is bacterially safe. This is often a major drawback of these shallow sources in many parts of the developing world. Another problem in more arid areas is the potential for dug wells to dry out during dry periods. In the Huhhot Basin of Inner Mongolia, dug wells are also not suitable for potable use as many are relatively reducing and can contain high arsenic concentrations, often greater than 50 $\mu g L^{-1}$ (Luo et al., 1997; Smedley et al., 2003).

D. Rainwater Harvesting

Collection and storage of rainwater is another option for providing sources of potable water with very low

concentrations of arsenic and is in use in various parts of the world. In Bangladesh, collection of rainwater is currently being piloted. The method requires that the receptacle chosen to store the rainwater be kept clean and safe from the possibility of bacterial contamination for the duration required for storage. The viability of harvesting rainwater will depend to a major extent on the regional climate, as well as the cost of the receptacle, the presence of a suitable place to locate it, and a suitable roof to capture the rainwater. Even in semi-arid areas such as parts of Argentina, it could provide an option for at least part of the year. In the Bengal Basin, the high annual rainfall means that water availability is less of a problem, although there are still 6–7 months with little or no rainfall.

E. Use of Treated Surface Water

Use of surface water can be on a range of scales from small ponds with attached filters for use by a group of families or a village (as installed commonly in Bangladesh), to major piped and treated water supplies from reservoirs for urban areas. Large schemes require major investment and this is a significant drawback in developing countries. Reservoirs also tend to fill up with silt. Treatment systems on any scale also require maintenance. This option may be the best solution in some circumstances, but it is unlikely to be suitable for all high-arsenic affected regions.

F. Treatment of High-Arsenic Groundwater

When other options are unsuitable, a further possibility is to treat water to remove the high arsenic concentrations. This can also be achieved on a range of scales and with varying degrees of technical sophistication and cost. Treatment is achieved by various methods involving adsorption, ion exchange, or coagulation. The suitability and efficacy of each of these depend on factors including pH, arsenic speciation, and concentrations of other ions (Clifford & Ghurye, 2002). Adsorption techniques most commonly make use of metal oxides (mainly of iron or aluminum). Activated alumina is also an effective medium. Reverse osmosis is practiced in some areas. In Argentina, for example, reverse osmosis is commonly used in urban treatment works and is an effective method for reducing salinity as well as the concentrations of fluoride and arsenic. However, this method is expensive and not suitable for small private supplies in rural areas. Coagulation commonly makes use of alum or ferric chloride, often with an oxidizing agent to oxidize the arsenic to As(V). In developing countries, where treatment has been tried, the methods used are generally the simplest and least expensive, including coagulation with iron salts or alum or adsorption using locally available materials (e.g., brick chips, laterite, iron-oxide coated sand). Various domestic filters have been developed in affected countries such as Bangladesh, India, and China. In reducing high-iron aquifers, passive oxidation is also occasionally used as a partial mitigation measure. This simply involves storing abstracted water for a period to allow oxidation of dissolved Fe(II) and subsequent sedimentation. In the process, arsenic also oxidizes (at least partially) and co-precipitates with, or adsorbs to, freshly forming iron oxides. The effectiveness of this option depends on a number of factors, critically the amount of Fe(II), the ratios of Fe/As and As(III)/As(V), and the time allowed for settling. The treatment methods used in developing countries meet with varying success and require a knowledge of maintenance techniques by the local village community or family. They are, nonetheless, better than no treatment at all and are particularly suitable as short-term measures to remove arsenic and other related elements such as iron and manganese. Clearly, passive oxidation is not an option for groundwaters from oxidizing aquifers such as Argentina or parts of Mexico.

There is also the possibility of *in situ* groundwater treatment whereby the arsenic is removed by promoting its adsorption or precipitation within the aquifer. This could be achieved by both an oxidative route (iron-oxide precipitation) or reductive route (sulfide precipitation) (Welch et al., 2003). These options are currently being explored in Bangladesh and elsewhere.

In summary, the groundwater arsenic problem is complex and in developing countries, where the problem may be large in relation to the resources available to tackle it, there exists no single, simple solution.

VII. CONCLUSIONS

The growing interest in arsenic in groundwater developed over the last few years stems from an increased awareness of its severe and detrimental effects on human health and resultant revisions of recommended and regulatory limits for arsenic in drinking water.

Concern has also increased following the recent recognition of the large scale of arsenic problems currently faced in Bangladesh and elsewhere. This account has attempted to characterize the distribution of arsenic in the environment and to describe the main geochemical controls on its speciation and mobilization.

Natural waters have arsenic concentrations varying over more than four orders of magnitude. Although most have low concentrations ($<10\,\mu g\,L^{-1}$, and often significantly less), where they are higher and the water is used for drinking purposes, they can constitute an important pathway of human exposure to arsenic. Groundwater is probably the source of water most vulnerable to the development of high concentrations because of natural geochemical reactions in aquifers. Well-known high-arsenic groundwater areas occur in Argentina, Chile, China, Hungary, Mexico, Taiwan, and more recently in Bangladesh, West Bengal (India), Nepal, Vietnam, and Myanmar. Many of these areas have developed serious health problems for resident populations and the possibility of more widespread problems in the future is a serious concern. The scale of the problem in terms of populations exposed to arsenic is greatest in the Bengal Basin, with more than 40 million people drinking water containing arsenic above $50\,\mu g\,L^{-1}$, the national standard for arsenic in many of the affected countries.

Such large-scale "natural" groundwater arsenic problem areas tend to be found in two types of environment: strongly reducing aquifers, often derived from alluvial sediment (e.g., Bangladesh, West Bengal, northern China, Hungary) and inland or closed basins in arid or semi-arid areas (e.g., central Argentina, Mexico). Both environments typically contain geologically young sediments and occur in flat, low-lying areas where groundwater flow is sluggish. Aquifers tend to be poorly flushed and any arsenic released from the sediments following burial has been able to accumulate in the groundwater. The arsenic concentrations of the aquifer materials in such problem aquifers appear not to be anomalously high, being typically in the range of 1–$20\,mg\,kg^{-1}$. Arsenic-rich groundwaters may also be found in some geothermal areas and, on a more localized scale, in arsenic-rich mineralized areas, particularly sulfide ore zones and hence areas of mining activity.

The detailed mechanisms leading to the release of arsenic to groundwater are still poorly understood, but there appear to be a number of distinct triggers that can lead to the release of arsenic from mineral sources. The development of strongly reducing conditions at near-neutral pH may lead to the desorption of arsenic from mineral oxides together with the reductive dissolution of iron and manganese oxides, which may also lead to the release of arsenic. These groundwaters typically have abundant Fe(II) and As(III) and in many, sulfate concentrations are low (typically $1\,mg\,L^{-1}$ or less), signifying probable sulfate reduction. Additional large concentrations of phosphate, bicarbonate, silicate, and possibly organic matter can enhance the desorption of arsenic through competition for adsorption sites on metal (especially iron) oxides. Release of arsenic may also be related to the development of high-pH (>8.5) conditions in semi-arid or arid environments, usually as a result of the combined effects of enhanced mineral weathering and high evaporation rates. The pH increase leads to the desorption of adsorbed arsenic (especially As(V) species) and a range of other anion-forming elements such as vanadium, boron, fluoride, molybdenum, selenium, and uranium from oxide minerals. The oxidation of sulfide minerals may also release arsenic to solution, although its fate following release will be critically dependent on the availability of metal oxides which may effectively scavenge the aqueous arsenic and hence limit its dispersion from the site of release.

Although arsenic problems have now been recognized in a number of regions of the world, there are doubtless other areas, principally aquifers, where problems are yet to be recognized. As more widespread water testing, health awareness, and diagnosis programs are undertaken internationally, these problem areas are likely to emerge gradually. Naturally, the best option in identifying any new areas at risk is to test the groundwater directly for arsenic. Where this is not possible, other water-quality data may provide some indication of the likelihood of arsenic problems. The range of water-quality characteristics identified in various provinces in this chapter should help to categorize areas in terms of likely arsenic risk. No single factor is sufficient to identify a problem area but if collectively many of the environmental characteristics and water-quality indicators point toward a potential problem, then this is an indicator for the need for an urgent testing program. Given the high degree of spatial variability in arsenic concentrations observed in many high-arsenic groundwater provinces, the task involved in screening "at-risk" areas may be large. Randomized reconnaissance surveying of the area is a logical first step for assessing the scale and location of problems.

Groundwater provides an important source of drinking water to many millions of people globally. While this chapter has focused on areas where groundwater arsenic concentrations are often high, it must be borne in mind that these are the exceptions. Groundwater

more commonly provides a safe and reliable form of drinking water. Indeed, the proliferation of groundwater use in developing countries over the last few decades has resulted from the need to provide safe sources of drinking water that are protected from the potentially fatal effects of bacterial contamination. In this respect, the use of groundwater for improving community health has been highly successful. With regards to arsenic, most wells in most aquifers are likely to be uncontaminated, even when the groundwaters contain high concentrations of dissolved iron. Therefore it is also important to understand why these groundwaters are not affected. It appears that it is only when a number of critical geochemical and hydrogeological factors are combined that high-arsenic groundwaters occur.

SEE ALSO THE FOLLOWING CHAPTERS

Chapter 22 (Environmental Medicine) · Chapter 23 (Environmental Pathology) · Chapter 31 (Modeling Groundwater Flow and Quality)

FURTHER READING

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