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Arsenic in Groundwater: A Summary of Sources and the Biogeochemical and Hydrogeologic Factors Affecting Arsenic Occurrence and Mobility

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1. Introduction

1.1. World-wide occurrences of arsenic-contaminated groundwater – Forms and toxicity

Arsenic (As) is a metalloid element (atomic number 33) with one naturally occurring isotope of atomic mass 75, and four oxidation states (-3, 0, +3, and +5) (Smedley and Kinniburgh, 2002). In the aqueous environment, the +3 and +5 oxidation states are most prevalent, as the oxyanions arsenite (H_3AsO_3 or H_2AsO_3^- at pH ~9-11) and arsenate (H_2AsO_4^- and HAsO_4^{2-} at pH ~4-10) (Smedley and Kinniburgh, 2002). In soils, arsine gases (containing As^3) may be generated by fungi and other organisms (Woolson, 1977).

The different forms of As have different toxicities, with arsine gas being the most toxic form. Of the inorganic oxyanions, arsenite is considered more toxic than arsenate, and the organic (methylated) arsenic forms are considered least toxic (for a detailed discussion of toxicity issues, the reader is referred to Mandal and Suzuki (2002)). Arsenic is a global health concern due to its toxicity and the fact that it occurs at unhealthful levels in water supplies, particularly groundwater, in more than 70 countries (Ravenscroft et al., 2009) on six continents.

1.2. Health effects and standards

Despite its use in medicines for nearly 2,500 years (Mandal and Suzuki, 2002; Cullen, 2008) As has long been recognized as a toxic and often lethal substance. Chronic exposure to As can cause harm to the human cardiovascular, dermal, gastrointestinal, hepatic, neurological, pulmonary, renal and respiratory systems (ATSDR, 2000) and reproductive system (Mandal and Suzuki, 2002). Research on health effects is summarized and discussed by

Mandal and Suzuki (2002) and Ng et al. (2003). A compilation of their reviews is found in Table 1.

System	Health effects
Cardiovascular	Heart attack, cardiac arrhythmias, thickening of blood vessels, loss of circulation leading to gangrene of extremities, hypertension
Dermal	Hyperpigmentation, abnormal skin thickening, narrowing of small arteries leading to numbness (Raynaud's Disease), squamous and basal-cell cancer
Gastrointestinal	Heartburn, nausea, abdominal pain
Hematological	Anemia, low white-blood-cell count (leucopenia)
Hepatic	Cirrhosis, fatty degeneration, abnormal cell growth (neoplasia)
Neurological	Brain malfunction, hallucinations, memory loss, seizures, coma, peripheral neuropathy
Pulmonary	Chronic cough, restrictive lung disease, cancer
Respiratory	Laryngitis, tracheal bronchitis, rhinitis, pharyngitis, shortness of breath, perforation of nasal septum
Renal	Hematuria, proteinuria, shock, dehydration, cortical necrosis, cancer of kidneys and bladder
Reproductive	Spontaneous abortions, still-births, congenital malformations of fetus, low birth weight

Table 1. Summary of effects of chronic arsenic exposure on human health. (Data from Mandal and Suzuki, 2002, and Ng et al., 2003, and references therein.)

The carcinogenic properties of As were suspected as early as the late 19th Century (Smith et al., 2002). Arsenic is now widely recognized and regulated as a carcinogen (ATSDR, 2000; National Research Council, 1999; USEPA, 2001). Consequently, the occurrence of As in waters at concentrations that exceed existing standards for drinking-water supplies has become of increasing concern, leading to recommended or legislated decreases in concentrations of As in drinking water in many countries. In 1993, the World Health Organization provisionally recommended a decrease from 50 µg/L to 10 µg/L (WHO, 1993). The United States (USA) federal standard, the European Union (EU) Drinking Water Directive (98/83/EC), the New Zealand Drinking Water Standard, the Japanese standard, and recent laws in many Latin American countries (Argentina, Bolivia, Brazil, Chile, Colombia, Costa Rica, El Salvador, Guatemala, Honduras, Nicaragua, and Panama) now place 10 µg/L as the drinking water maximum contaminant level (MCL) (Bundschuh et al., 2012; Robinson et al., 2004; Rowland et al., 2011; Smedley and Kinniburgh, 2002; USEPA, 2001). Mexico has adopted 25 µg/L as a standard (Bundschuh et al., 2012), whereas Australia has instituted a standard of 7 µg/L (NHMRC, 1996) and the State of New Jersey in the USA adopted an As MCL of 5 µg/L in 2006 (NJDEP, 2009). Some developing countries (Bangladesh, for example) have maintained the earlier 50 µg/L MCL standard (Ng et al., 2003). Many instances of As concentrations in groundwater that far exceed standards have been reported throughout much of the world

(Smedley, 2008) and the number of countries in which groundwater is found to be contaminated by As has increased substantially over the past 80 years. This chapter presents a brief overview of the history of groundwater As contamination and summarizes information about the sources, occurrence and mobility of As in groundwater. A compilation of worldwide hazardous waste sites is beyond the scope of the chapter, and only a few examples will be presented. Information on As occurrence reported in previous important summaries and discussions (e.g., Bhattacharya et al., (eds) 2007; Smedley and Kinniburgh, 2002; Welch and Stollenwerk, (eds.) 2003) is presented in addition to recent findings from the past decade.

1.3. Chronology of discoveries of geogenic arsenic contamination

Currently (2012), As contamination of groundwater resources has been identified in many parts of the world, although recognition of the widespread nature of the problem has been advanced only relatively recently. Despite localized inputs of As from human activities, much of the contamination of groundwater with As is shown to arise from geogenic sources and affected groundwater has been found in countries on nearly every continent or major land mass. To date, none has been reported for Greenland, and Antarctica (Figure 1).

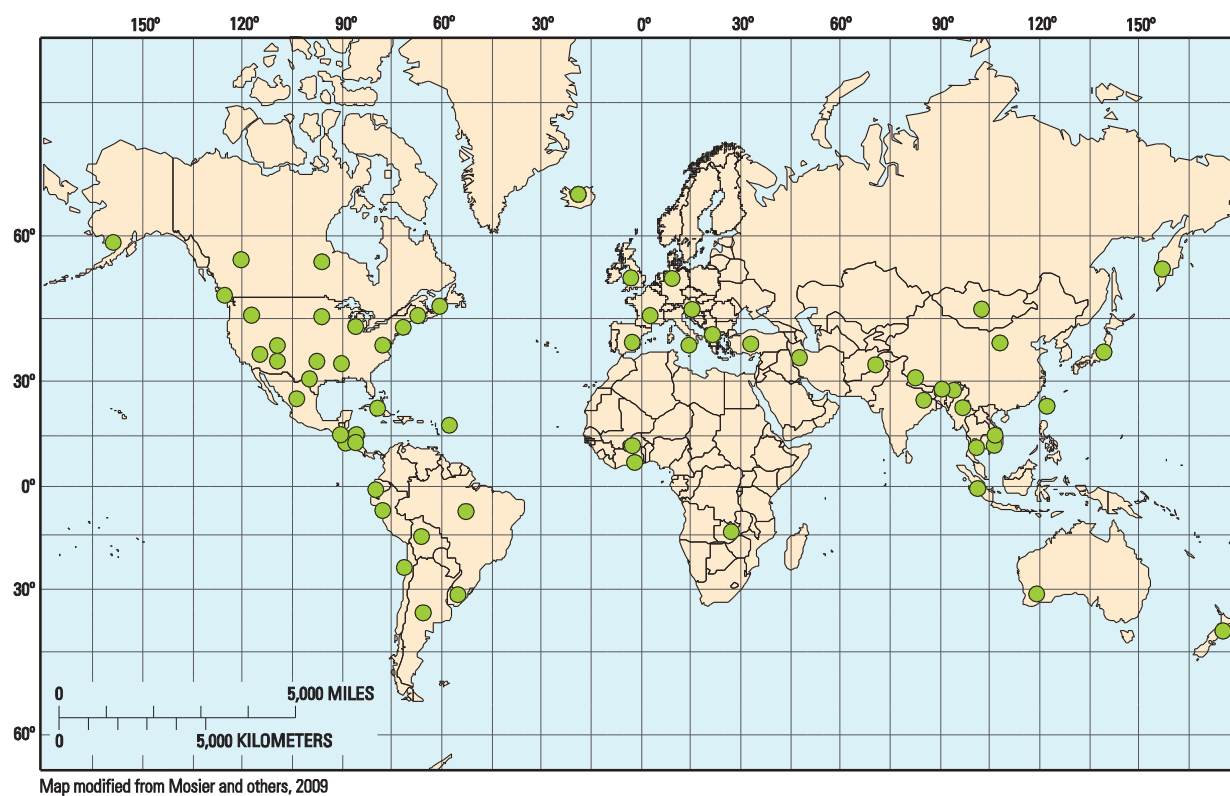


Figure 1. Countries, states, provinces, or areas mentioned in this chapter in which arsenic concentrations in groundwater, including geothermal waters and water contaminated by mining, exceed 10 micrograms per liter (the World Health Organization (WHO) recommended standard (WHO, 1993)). Arsenic concentrations at most locations shown exceed 50 micrograms per liter. Locations of dots are spatially generalized and do not indicate precise locations of arsenic-contaminated waters.

The discoveries of As contamination of groundwater have occurred over a span of nearly 100 years, the most recent within the last decade. Observations of health problems first led to the realization that As was being inadvertently ingested. Arsenic poisoning in humans in Argentina was recognized as early as 1913, and attributed to the drinking of groundwater (Bundschuh et al., 2012, and reference therein). A possible connection between skin cancers and drinking water was recognized in Taiwan during the 1930s (Chen et al., 1994). In the 1940s, As contamination of well water in the Pannonian Basin in Romania and adjacent Hungary was discovered (Gurzau and Pop, 2012; Mukherjee et al., 2006). Recognition of similar occurrences in other European countries such as southwestern England, Germany, Greece, and Spain followed, and groundwaters with As concentrations that exceed standards are now observed in more than 70 countries worldwide (Nordstrom, 2002; Ravenscroft et al., 2009).

During the mid-20th century, instances of As contamination of groundwater were reported for the western USA and Alaska (Welch et al., 1988; Mueller et al., 2001), but were not fully recognized in the states of Oklahoma, Texas, and Arkansas and in the Midwest and Northeastern parts of the country until the 1980s (Ayotte et al., 2003; Ayotte et al., 1999; Haque et al., 2008; Peters, 2008; Peters and Burkert, 2007; Scanlon et al., 2009; Sharif et al., 2008; Welch et al., 2000 and references therein). Most recently, groundwater containing As in excess of USA Federal and State MCLs was found in parts of the Atlantic Coastal Plain (Barringer et al., 2010; Drummond and Bolton, 2010; Haque et al., 2008; Mumford et al., 2012; Pearcy et al., 2011). In Canada, As-contaminated groundwaters in New Brunswick and Nova Scotia were noted in the 1970s (Bottomley, 1984), and instances in western Canada were noted in the 1960s and 1980s (Wang and Mulligan, 2006a).

In West Bengal, India, cases of arsenic poisoning were first noted in 1983-84, according to Rahman et al. (2005), although Mandal and Suzuki place 1978 as the time when arsenicosis (skin lesions) and groundwater contamination were first noticed in West Bengal. Since the 1980s, extensive sampling of well water in West Bengal has revealed levels of As that exceed 50 µg/L — concentrations in some samples exceeding 1000 µg/L (Rahman et al., 2005). In 1983-84, several patients treated for arsenicosis in West Bengal came from neighboring Bangladesh. Sampling in Bangladesh during the early 1990s of waters from tube wells (installed two decades earlier to provide what was thought to be safe, pathogen-free drinking water) revealed elevated concentrations of As (Smith et al., 2000).

Continued sampling throughout West Bengal showed concentrations ranging from <1 to 2,500 µg/L (Nordstrom, 2002). Although the population exposed to As-contaminated water in West Bengal was ultimately estimated to have been about 6,000,000, the exposed population in Bangladesh has been estimated to be about five times that number (Nordstrom, 2002), making the contamination in Bangladesh the arsenic-related public health problem of the greatest magnitude yet observed. Following the early discoveries in West Bengal and Bangladesh, well-water sampling in Vietnam, Cambodia, and Pakistan also identified contamination of groundwater with As (Agusa et al., 2006; Berg et al., 2001; Chanpiwat et al., 2011; Hoang et al., 2010; Luu et al., 2009; Nickson et al., 2005; Smedley, 2008; Sthiannopkao et al., 2008;), as well as in 1999, Nepal (Gurung et al., 2005), and in 2000, Myanmar (Tun, 2003).

Health problems attributed to As exposure were first noted within a district in a province of Thailand in 1987. Sampling indicated As at concentrations in groundwater that exceeded 5,000 $\mu\text{g/L}$ with about 15,000 people thought to have been exposed (Nordstrom, 2002; Smedley, 2008). Sampling of well waters during the 1990s and later in northern parts of China, including Inner Mongolia, have shown groundwater As concentrations that range widely, from <1 to about 2,400 $\mu\text{g/L}$ (Nordstrom, 2002; Smedley, 2008). In Japan, As levels were found to be high in geothermal waters and springs as early as the 1950s (Noguchi and Nakagawa, 1969), and As contamination of groundwater was noted in 1994. Exposure to As from industrial sources was noted as early as the 1950s (Mukherjee et al., 2006). In 1981 in Iran, chronic arsenic poisoning was noticed and subsequent well-water sampling revealed concentrations exceeding 1,000 $\mu\text{g/L}$ (Mukherjee et al., 2006).

Arsenic contamination of both surface water and groundwater also is found in many Latin American countries, but the full extent of the problem is not yet clear (Bundschuh et al., 2012). Groundwater concentrations in Argentina are reported to range as high as about 15,000 $\mu\text{g/L}$ (Bundschuh et al., and references therein). High levels of As were found in waters in Chile and Mexico in the 1950s and 60s (Bundschuh et al., 2012; Rosas et al., 1999). In northern Chile, As concentrations in groundwater ranged from 20 to 5,000 $\mu\text{g/L}$, and there is strong evidence from hair, skin, bones and funerary preparations (clay, paint) of Chinchorro culture mummies that the population there was exposed to high levels of As more than 7,000 years ago (Bundschuh et al., 2012), and, presumably, has been ever since. Concentrations of As in groundwater in Mexico generally are not reported to reach the higher levels found in Argentina except for a geothermal area in Michoacán, where 24,000 $\mu\text{g/L}$ are reported (Bundschuh et al., 2012, and references therein). In mined areas of Mexico, leaching from tailings piles have contributed As to groundwater (Carillo-Chávez et al., 2000; Méndez and Armienta, 2003). Arsenic-contaminated surface water and groundwater subsequently was recognized in parts of Peru in the 1970s (Bundschuh et al., 2010). Although As contamination of waters in Argentina, Chile, Mexico and Peru was known from the early and mid-20th century, surface water and (or) groundwaters (and geothermal waters) containing geogenic As at contaminant levels were discovered in alluvial, metasedimentary, volcanic, and metavolcanic aquifers only since the late 1990s in Bolivia, Brazil, Columbia, Cuba, Ecuador, El Salvador, Guatemala, Honduras, Nicaragua, and Uruguay (Bundschuh et al., 2012).

In Africa, the occurrence of high concentrations of As in groundwater from wells in a village in Burkina Faso was first noticed in the 1970s, but more extensive sampling did not occur until several decades later (Smedley, 2008). Arsenic-related skin diseases were noted in the region, and, although many wells yielded water with As concentrations < 10 $\mu\text{g/L}$, concentrations as high as 1,600 $\mu\text{g/L}$ were found (Smedley et al., 2007). Effects of mining on soils and waters in other African countries (Ghana and Zambia) have been studied only recently (e.g., Howell et al., 1994; Nakayama et al., 2011; Smedley and Kinniburgh (2002); As contamination of groundwater has been reported in Ghana. Arsenic contamination of well water was discovered during the drought in Perth, Australia in 2002 (Appleyard et al., 2006).

2. Sources of arsenic

2.1. Anthropogenic sources

Sources of As that arise from human activities include mining and processing of ores and manufacturing using As-bearing sulfides. Smelters in numerous countries, including Canada, Chile, Italy, South Africa, the USA, and the former USSR have processed metal ores (mainly copper, but also zinc, gold, and tin) that contain As. The smelting process, both recent and ancient, has released As to the air and soils both locally and globally (Matschullat, 2000). Elevated As levels in precipitation and in soils surrounding smelters have frequently been documented (e.g., Ball et al., 1983; Beaulieu and Savage, 2005; Carpenter et al., 1978). Disposal of mining wastes has caused As contamination of groundwater in numerous places, including in Thailand, Ghana, and Turkey (Gunduz et al., 2010; Smedley and Kinniburgh, 2002; Smedley, 2008). In southwestern England, mineral deposits and mineral processing (tin, copper, with accessory As minerals) are recognized sources of As to soils and groundwater (Brunt et al., 2004; Camm et al., 2004; Palumbo-Roe et al., 2007). In southeastern Europe (Serbia, Bosnia, Poland), and in Spain, mining activities left a legacy of arsenic that has contaminated soils and waters (Dangic, 2007; Gomez et al., 2006; Karczewska et al., 2007). Groundwater contamination in mined areas is also found in parts of the western USA and Canada (Moncur et al., 2005; Welch et al., 2000).

Arsenic compounds have been used in the manufacture of numerous products. Arsenic has been used in glass production and by the wood-preservation industry. The latter industry has been, through the end of the 20th century, the most active user of such compounds in the USA (Welch et al., 2000), but the industry's voluntary reduction of the use of chromated copper arsenate (CCA) since 2003 has resulted in a more limited availability of CCA treated wood and products (Brooks, 2008). Contamination of soils and surface-water bodies has resulted from use of CCA-treated wood (Khan et al., 2006; Rice et al., 2002).

The use of inorganic arsenical pesticides has waned in recent years owing to bans in the 1980s and 90s (Welch et al., 2000), but, in the past, manufacture and use of arsenical pesticides were important contributors of As to the environment (e.g., Barringer et al., 1998; Barringer et al., 2001; USEPA, 2011). Inorganic arsenicals have been used on a variety of crops (citrus, cotton, tobacco, and potatoes) and on fruit trees; (Walsh and Keeney, 1975; Welch et al., 2000). The use of lead-arsenate pesticides in orchards has prompted concern that additions of phosphate fertilizers could displace arsenate sorbed to soil particles, mobilizing As to groundwater (e.g. Davenport and Peryea, 1991). Manufacture of pesticides has been responsible for As contamination of soil, surface water, and groundwater. Examples of contamination caused by former pesticide manufacture are found in India and in the USA (Barringer et al., 1998; Mukherjee et al., 2006; USEPA, 2011). Soil contamination by As may also occur in areas where soils are amended with chicken and swine manure. Such fertilizers can contain As due to use of chicken and swine feeds containing the growth additive Roxarsone, an organic arsenical (4-hydroxy-3-nitrophenylarsonic acid) (Hileman, 2007; O'Day, 2006).

There have been military uses of As, and attempts to recycle As-bearing materials. Arsenic was used in chemical warfare agents, most recently in the first half of the 20th century (Krüger et al., 2007). In the 1930s, concern over disposal of stockpiles of As compounds led to experiments with incorporating As in cement which was then used to coat pilings and other wooden structures (van Sicken and Gerry, 1936). One ounce of white arsenic was added to 12 pounds of sand and 3 pounds of cement, water was added and the slurry was applied to wood pilings by air gun. To the authors' knowledge, no studies of the effects of this practice on the environment have been published. Arsenic currently is used in various electronic devices, and improper disposal and lack of care in recycling these materials also can add As to the environment (Brooks, 2008).

Anthropogenic sources of As can affect the quality of surface water through groundwater discharge and runoff (Hemond, 1995; Martin and Pederson 2002). In the case of pesticides, the effect can be through direct applications to water bodies for control of nuisance vegetation (Kobayashi and Lee, 1978; Tanner and Clayton, 1990; Durant et al., 2004). Although groundwater contamination does exist at various sites affected by agricultural, industrial or military releases, for example (e.g., Hemond, 1995; Krüger et al. 2007; USEPA, 2011), contamination introduced at the land surface does not always move to groundwater. Owing to the affinity of As for soil constituents such as metal oxides and hydroxides (mainly iron (Fe), aluminum (Al), and manganese (Mn)) and clays (Goldberg and Glaubig, 1988; Manning and Goldberg, 1996), the As can be attenuated in the intervening soils by sorption to Fe hydroxides or clays, or by precipitation reactions, such as formation of As- or Fe-sulfides in anoxic soils (e.g., Brunt et al., 2004; Cancès et al, 2008).

2.2. Geologic sources

2.2.1. Arsenic minerals

For most known areally extensive instances of As contamination of groundwater, the sources of the As have been shown to be geogenic (Smedley and Kinniburgh, 2002). A summary table of the worldwide occurrence of As in groundwater (Nordstrom, 2002) indicates that mining of arsenic and metal ores and natural geologic sources of As dominate the environmental conditions listed for inputs of As to groundwater.

There are about 24 As-bearing minerals that are commonly found in hydrothermal veins, ore deposits, and rocks. Most primary As minerals are sulfides, of which arsenopyrite is the most common (Ehrlich and Newman, 2009). Secondary minerals tend to be less common arsenates and oxides. WHO (2001) provides a list of these minerals, which also can be found tabulated in Mandal and Suzuki (2002, p. 203). Arsenic in crustal rocks also has an affinity for, and is associated with, pyrite or Fe hydroxides and oxides (Nordstrom, 2002) for which chemical formulas are FeS_2 , FeOOH , Fe_2O_3 , and Fe_3O_4 , respectively. The As content of crustal rocks varies widely; Smedley and Kinniburgh, 2002, p. 531) compile and tabulate those results. Concentrations of As in water associated with crustal rocks are described below.

2.2.2. Geothermal activity, volcanic and plutonic rocks, and mineralized zones

Geothermally active zones occur along plate boundaries, in tectonic rift areas such as those in East Africa and at seafloor spreading centers, such as in Iceland, and at “hot spots” where mantle-derived plumes ascend, such as in Hawaii and Yellowstone National Park, USA. Arsenic is one of a suite of incompatible elements (these do not fit easily into the lattices of common rock-forming minerals), which include antimony (Sb), boron (B), fluoride (F), lithium (Li), mercury (Hg), selenium (Se) and thallium (Tl). Together with hydrogen sulfide, these elements are ubiquitous in high-temperature geothermal settings (Webster and Nordstrom, 2003). Concentrations of arsenic are high mainly in geothermal waters that leach continental rocks; geothermal waters in basaltic rocks, such as in Iceland, contain lesser amounts of As. Arsenic in hot geothermal fluids was shown to be derived mainly from leaching of host rocks at Yellowstone National Park, in Wyoming, USA (Stauffer and Thompson, 1984), rather than derived from magmas. The As in the hot fluid is present as As(III) in arsenious acid (H_3AsO_3); in low-sulfide fluids, the arsenite in the arsenious acid is oxidized to arsenate as the rising fluid mixes with cold oxygenated groundwater or encounters the atmosphere. In high sulfide solutions, As may be present as thioarsenate complexes (Webster and Nordstrom, 2003; Planer-Friedrich et al., 2007).

In the western USA, there are As inputs to groundwater and surface water from geothermal fluids in and near Yellowstone National Park (e.g., Ball et al., 1998, 2002; Nimick et al., 1998) and in other western mineralized areas (Welch et al., 1988). Groundwater associated with volcanics (tuffs and rhyolites) in California contain As at concentrations ranging up to 48,000 $\mu\text{g/L}$, with As-bearing sulfide minerals as the main source of As (Welch et al., 1988, and references therein). Geothermal waters on Dominica in the Lesser Antilles also contain concentrations of As $>50 \mu\text{g/L}$ (McCarthy et al., 2005).

In general, because arsenic is an incompatible element, it accumulates in differentiated magmas, and is commonly found at higher concentrations in volcanic rocks of intermediate (andesites) to felsic (rhyolites) composition than in mafic (basaltic) rocks—as shown for the western USA (Welch et al., 1988; Welch et al., 2000). In Maine and New Hampshire, USA, where As-contaminated groundwater is present, pegmatites, granites and metamorphic rocks (granofels) were found to have substantial As contents—up to 60, 46 and 39 mg/kg, respectively (Peters, 2008; Peters et al., 1999; Peters and Blum, 2003). Weathering of pegmatite veins in Connecticut, USA, was thought to contribute As to groundwater (Brown and Chute, 2002). Although the As content of mafic rocks can be relatively low, fractured ultramafic rocks in Vermont, USA, contribute up to 327 $\mu\text{g/L}$ of As to groundwater (Ryan et al., 2011).

Leached from surrounding rocks, As in hot springs from geothermal fields in New Zealand is found at concentrations that range to 4,800 $\mu\text{g/L}$ (Brown and Simmons, 2003). Acidic (pH 1.2) geothermal springs in Japan contained As at 2,600 $\mu\text{g/L}$ (Noguchi and Nakagawa, 1969). Arsenic in these springs precipitated out as As sulfides and lead (Pb) As sulfides in surface-water sediments. The As contents of the sediments ranged from about 5 to 56 wt. % (Noguchi and Nakagawa, 1969).

In Latin America, volcanic and geothermal activity along the Pacific tectonic plate boundaries produces As-rich waters and gases in springs and fumaroles. In sodium-chloride (Na-Cl)-rich waters, As concentrations can reach about 50,000 $\mu\text{g/L}$ at the El Tatio geothermal field in Chile (Lopez et al, 2012). Arsenic concentrations in waters of geothermal fields in Mexico vary; 250 to 73,600 $\mu\text{g/L}$ are reported, where the host rocks through which these waters have risen include sandstones and shales, lava flows and pyroclastics, and metamorphosed carbonate rocks, basalts and hornblende andesites (Lopez et al., 2012).

In the coastal volcanic areas of Central and South American countries, rocks are mainly andesitic or rhyolitic in composition. Arsenic concentrations in the geothermal springs throughout these areas vary widely—concentrations of several thousand micrograms per liter are reported, but none are reported as high as the highest concentration in a Mexican geothermal field (see above). Where springs and fumaroles discharge water and gases to a lake in the Bolivian Altiplano, however, As concentrations in the lake water are reported as high as 4,600,000 $\mu\text{g/L}$, the As apparently being contributed by oxidation of sulfide deposits (Lopez et al., 2012).

Dissolution of volcanic glasses in ash layers and leaching of loess-type deposits in the Chaco-Pampean plain of Argentina have resulted in groundwater As concentrations that range from <10 to 5,300 $\mu\text{g/L}$ (Nicolli, et al., 2012) where the potentially affected rural population numbers several million people. Mining of various metals (gold, copper, silver) in Latin America has played an important role in mobilizing As from the geologic materials and exacerbating contamination of groundwater resources (McClintock et al., 2012).

In Europe, groundwaters containing As at concentrations that exceed 50 $\mu\text{g/L}$ are found in geothermal fields of the Massif Central in France, and in Greece, (Brunt et al., 2004; Karydakos et al., 2005). Iceland, where As concentrations in groundwater can exceed 10 $\mu\text{g/L}$ (Arnórsson, 2003) sits astride the Mid-Atlantic Ridge, and is subject to outpourings of basaltic lava that typically contain less As than do more silicic lavas (Onishi and Sandell (1955; Baur and Onishi, 1969; Ure and Berrow, 1982). In geothermal systems of northern and northeastern Spain, the As concentrations are high and deposit As-rich minerals (Navarro et al., 2011); the Caldes de Malavella field in northern Spain contributes substantial As to groundwater—50-80 $\mu\text{g/L}$ in springs, and from <1 to 200 $\mu\text{g/L}$ in groundwater (Piqué et al., 2010). Groundwaters (including brines) contained As concentrations ranging from 1.6 to 6,900 $\mu\text{g/L}$ in the Phlegraean Fields in southern Italy (Aiuppa et al., 2006). Quaternary volcanic rocks with hydrothermal activity on the island of Ischia (offshore from Naples, Italy) impart As to groundwater at concentrations that range up to 3,800 $\mu\text{g/L}$ (Aiuppa, et al., 2006; Daniele, 2004).

In the Mid-East, in northwestern Iran, As concentrations in thermal waters and hot springs are as high as 3,500 and 890 $\mu\text{g/L}$, respectively, in the area of Mt. Sabalan, a stratavolcano (Haeri et al, 2011). In western Anatolia, in Turkey, natural leaching, aided by pumping and discharge of waste geothermal fluids from an active geothermal system, has mobilized As from metamorphic, igneous and sedimentary rocks to groundwater in a shallow alluvial aquifer, where highest As concentrations in groundwater and geothermal waters were 561 and 594 $\mu\text{g/L}$, respectively (Gunduz and Simsek (2008).

Groundwater in early Proterozoic silicic volcanics and granites of the Chhattisgarh Basin of India contains As at concentrations that exceed 10 $\mu\text{g/L}$. The As is perhaps emplaced there by hydrothermal fluids (Acharyya, 2002).

2.2.3. Sedimentary and meta-sedimentary bedrock

Arsenic is found in coals, with the content of some coals from southwestern China being highest—826 to 2,578 mg/kg is reported (Nriagu et al., 2007) and up to 32,000 mg/kg is listed by Wang et al., (2006). In Germany, the As content of bituminous shales ranges from 100 to 900 mg/kg (Smedley and Kinniburgh, 2002). The As contents of American coals are reported to range as high as 2,200 mg/kg (Wang et al., 2006), but the mean concentration for more than 7000 samples is about 24 mg/kg (Kolker et al., 2006). Pyrite is the main source of As in coals with high As content, whereas in lower As coals, the As tends to be associated with the organic material (Yudovich and Ketris, 2005). In Pennsylvania, USA, As concentrations in water discharging from abandoned anthracite mines ranged from <0.03 to 15 $\mu\text{g/L}$ and from abandoned bituminous mines, from 0.10 to 64 $\mu\text{g/L}$, with 10% of samples exceeding the USEPA MCL of 10 $\mu\text{g/L}$ (Cravotta, 2008).

In Wisconsin, USA, As concentrations of water in sandstone and dolomite aquifers were as high as 100 $\mu\text{g/L}$. Oxidation of pyrite hosted by these formations was the likely source of the As, the transport of which was, in some instances, retarded by its association with Fe oxyhydroxides (Burkel and Stoll, 1999; Thornburg and Sahai, 2004). In the adjacent State of Michigan, USA, As concentrations in groundwater reached 220 $\mu\text{g/L}$ in another sandstone aquifer (Haack and Rachol, 2000). In Australia, a combination of increased water withdrawals during development and declining recharge due to drought caused oxidation of pyrite in sedimentary aquifers, resulting in As contamination of well water (Appleyard et al., 2006). In England, groundwater from a sandstone aquifer contained As at concentrations that spanned 10 to 50 $\mu\text{g/L}$; the As content of the sandstone ranged from 5 to 15 mg/kg. Desorption at pH of about 8 appeared to be the mechanism for As release to groundwater (Kinniburgh et al., 2006). Water from wells completed in a Mesozoic Era sandstone in northern Bavaria also contained As at concentrations from 10 to 150 $\mu\text{g/L}$ (Heinrichs and Udluft, 1999), although the mineralogy contributing the As was not identified.

In the Piedmont of Pennsylvania and New Jersey, USA, groundwater in Mesozoic age aquifers of red and black shale, mudstone, and siltstone contains elevated levels of As—domestic well waters from Pennsylvania contained up to 65 $\mu\text{g/L}$ (Peters and Burkert, 2007), whereas in New Jersey the highest concentration measured recently was 215 $\mu\text{g/L}$ (Serfes, 2005). Pyrites in the reduced black shales and mudstones are a major source of As, with measured As contents of 3,000 and 40,000 mg/kg in some samples (Serfes, 2005). Arsenic (as arsenate) is also released from the red shales by desorption as pH rises above 6.5 (Serfes, 2005). These Piedmont rocks also contain hornfels along contacts with diabase intrusions, some of which contain mineralization by copper (Cu), As, and uranium (U). Typical As-bearing minerals in the Piedmont rocks include arsenopyrite (FeAsS), cobaltite ($(\text{Ni}, \text{Co}, \text{Fe})\text{AsS}$), alloclasite ($(\text{Co}, \text{Fe})\text{AsS}$), gersdorffite (NiAsS), erythrite ($\text{Co}_3(\text{AsO}_4)_2 \cdot 8\text{H}_2\text{O}$), and safflorite ($(\text{Co}, \text{Fe}, \text{Ni})\text{As}_2$) (Senior and Sloto, 2006).

In Taiwan, groundwater from artesian wells completed in black shales, muds and fine sands is contaminated with As. In northern Bavaria, mineralized sandstone yields As-contaminated groundwater (Smedley and Kinniburgh, 2002).

Carbonate rocks typically contain low concentrations of As (Baur and Onishi, 1969; Smedley and Kinniburgh, 2002), although some limestones may contain As-bearing pyrite (e.g. Price and Pichler, 2006). Because arsenate can substitute for phosphate in minerals, phosphorite deposits can contain substantial amounts of As—up to about 400 mg/kg is reported (Smedley and Kinniburgh, 2002). Barringer et al. (2011) report 19.5 to 56.6 mg/kg of As in phosphorite deposits in the Coastal Plain of New Jersey, USA.

The As content of meta-sedimentary rocks varies widely, with the contents of gneisses and quartzites generally < 10 mg/kg, and higher As contents for slates and phyllites —up to 143 mg/kg (Boyle and Jonasson, 1973). In the New England states of northeastern USA, groundwater contamination with As was found to be prevalent in water from wells completed in formations containing metapelite rocks (schists, phyllites, slates), particularly those rocks adjacent to intrusive bodies. In New England, meta-shales contain As-bearing minerals pyrrhotite, cobaltite, and arsenopyrite, and supergene minerals include orpiment (As₂S₃) and loellingite (FeAs₂) (Foley et al., 2002). Mineralization in a Proterozoic marble in New Jersey, USA, has resulted in zinc ores and, in addition to arsenopyrite and loellingite, a variety of uncommon As-bearing minerals. Past mining activities have contributed to the release of As from the bedrock to shallow groundwater; concentrations ranged from 2.02 to 22.0 µg/L in water discharging to the area's major river, the Wallkill River (Barringer et al., 2007). In mineralized meta-sedimentary rocks containing sulfide minerals in Fairbanks, Alaska, USA, groundwater contains As at concentrations that range from <3 µg/L to 1,670 µg/L (Mueller et al., 2001).

2.2.4. Alluvial and coastal plain unconsolidated sediments

The sediments shed from the Himalayas have formed the extensive alluvial plain and delta through which the Ganges, Brahmaputra and Meghna Rivers flow and which form aquifers in India (West Bengal Delta Region) and adjacent Bangladesh. To the east, the deltas of the Mekong and Red Rivers form aquifers in Vietnam and adjacent Cambodia and Laos. Arsenic released from these sediments has caused the most widespread contamination in the world, with populations of many millions affected by drinking As-laden well water. The largest number of people (about 35 million) exposed to As contamination is in Bangladesh, and about 6 million in neighboring West Bengal, India (Nordstrom, 2002). The As contents of these young sediments are not extremely high—about 1 to 15 mg/kg, but vary with depth (Smedley, 2008). The concentrations of As in groundwater range, however, from undetectable to several thousand µg/L, with a survey of about 3,200 wells in Bangladesh by researchers from the United Kingdom (UK) and Bangladesh finding that As concentrations in about 27% of samples exceeded 50 µg/L, the Bangladeshi Drinking Water Standard (Smedley, 2008). In local areas, the percentage of affected wells was higher; in central Bangladesh, As in water from about 75% of 6000 wells exceeded 50 µg/L (van Geen et al., 2003). The sediments of Holocene age are micaceous sands, silts, and clays. Reduced, gray sediments of the upper aquifer, where As

concentrations in groundwater are high, are underlain by brown, oxidized sediments where As concentrations in groundwater are low. In some places the two layers are separated by a thick clay layer (Harvey et al., 2002). The mineralogy of both layers, where the clay was absent, was found to be similar for part of the Bengal Basin near Dhaka, Bangladesh. Minerals included quartz, plagioclase and potassium feldspar, micas (biotite, muscovite, and phlogopite), chlorite, and amphibole; carbonaceous material was sparse. Trace amounts of siderite were present in the reduced sediments, but not in the deeper, oxidized sediments (Stollenwerk et al., 2007). In the shallow aquifer in West Bengal, organic carbon is present as petroleum-related compounds (Rowland et al., 2006).

In Cambodia, Vietnam, and Laos, As in young deltaic sediments of the Mekong and Red River basins has also contaminated groundwater, again exposing several million people to unhealthy levels of As ($>1,000 \mu\text{g/L}$ in some cases) in drinking water (Agusa et al., 2006; Berg et al., 2001; Chanpiwat et al., 2011; Hoang et al., 2010; Luu et al., 2009; Sthiannopkao et al., 2008). The aquifers are composed of quartz sands and clays that host Fe oxide and hydroxide phases, also possibly manganese (Mn) oxides, and organic matter is present. Siderite, pyrite, and orpiment are also found in sediments of the Mekong delta (Quicksall et al., 2008) and siderite, ilmenite, vivianite, gibbsite and boehmite are reported for the Red River delta sediments (Eiche et al., 2008).

In the Pannonian Basin of Hungary and Romania, Quaternary sediments of fluvial and eolian origin have contributed As to groundwater; the sediments are composed of sands and loess. Quartz, feldspar, carbonates (calcite and dolomite, muscovite, chlorite, clays, and humic substances are reported and fine particles of Fe hydroxides are indicated (Varsányi and Kovács, 2006). Other Fe-bearing minerals, from which As may be released, are reported to include goethite, limonite, pyrite, and siderite (Rowland et al., 2011).

Alluvial and lacustrine sediments in the Huhhot Basin of Inner Mongolia form two aquifers, separated by a clay confining layer; some boreholes completed in the deeper aquifer are artesian. The sediments are more fine-grained in the low-lying parts of the basin and it is in these sediments that reducing conditions are present and As concentration in groundwater are highest ($1,500 \mu\text{g/L}$). Organic matter is found in the aquifers and dissolved organic carbon concentrations in groundwater are high (Smedley et al., 2003).

The Atlantic Coastal Plain is located along the east coast of the USA. In addition to quartz-rich deposits of near-shore origin, the Coastal Plain is composed partly of sediments of marine origin that contain the mineral glauconite, the As contents of which are high (up to 130 mg/kg) in some formations (Dooley, 2001). In the state of Maryland, USA, in an aquifer composed of these marine sediments, As concentrations in groundwater exceed $10 \mu\text{g/L}$ and have been found as high as $80 \mu\text{g/L}$ (Pearcy et al, 2011). Farther north, in the state of New Jersey, As concentrations in water from an observation well in a glauconite-bearing aquifer were $110 \mu\text{g/L}$ (dePaul and Szabo, 2007), and water from several domestic wells in similar aquifers in the same region has exceeded the state MCL of $5 \mu\text{g/L}$. In shallow groundwater discharging to New Jersey Coastal Plain streams underlain by the glauconitic sediments, As concentrations have exceeded the MCL, ranging as high as $89.2 \mu\text{g/L}$. The sediments below the streambeds also contain other phyllosilicates (illite, smectites, muscovite, biotite, chlorite) and quartz. In addition to the glauconite sands, associated phosphorite deposits were found

to contain As up to 56.6 mg/kg and siderite that precipitated in sediments beneath a streambed contained 184 mg/kg of As (Barringer et al., 2011; Mumford et al., 2012).

Glauconite sands and clays of Pliocene and Miocene age, overlain by younger non-glauconitic sands, clays, thin coal beds and peats, are also present in the lowlands of south Sumatra, Indonesia. Arsenic concentrations exceeded the WHO guidelines in water from several wells completed in both the glauconitic formations and the younger sediments, with the higher concentrations found in water from the youngest (Holocene) sediments (Winkel et al., 2008). Glauconitic sediments are found on several continents (Barringer et al., 2010) and the recent findings in the Atlantic Coastal Plain and Sumatra indicate that these marine sediments, in addition to all the aquifers in other geologic settings, can now also be considered a potential source of As-contaminated groundwater.

3. Biogeochemical factors

3.1. Oxidation

Oxidation of As-bearing sulfides has been proposed as a mechanism for releasing As from geologic materials (Smedley, 2008). Although originally proposed as a mechanism for As release from the alluvial sediments of West Bengal and Bangladesh, the presence of sulfide minerals in those aquifers is rare and appears limited to biogenic framboidal pyrite, and pyrite in woody peat, and on magnetite (Acharyya, 2002). Oxidation of sulfides in mined areas throughout the world is a well-known phenomenon that has led to high concentrations of As in soils, surface water and groundwater; examples of such occurrences include western Canada, the western USA, and the Bolivian Altiplano (Lopez et al., 2012; Moncur et al., 2005; Welch et al., 2000). Sulfide oxidation has also resulted in high As concentrations (up to 215 µg/L) in groundwater in the eastern USA, in parts of the Piedmont rocks in Pennsylvania and New Jersey (Peters and Burkert, 2007; Serfes, 2005), where an As-oxidizing bacterium was involved in the mobilization of As (Rhine et al., 2008). A broad diversity of microorganisms oxidizes dissolved arsenic for different reasons including dissimilatory respiration, detoxification, and energy needs (Santini and Ward, 2012).

3.2. Reduction

Because of the magnitude of the contamination in West Bengal and Bangladesh, these two regions have received substantial attention from the research community. In general, reductive dissolution of Fe hydroxides and release of sorbed As explains much of the observed mobilization of As from sediments to groundwater (e.g., Nickson et al., 2000; Zheng et al., 2004). Organic matter in the alluvial aquifers is likely an important component of the reduction process. Field and experimental studies have shown that metal-reducing microbes can enhance mobilization of As, and that oxidation of the organic matter drives the redox reactions whereby Fe hydroxides are reductively dissolved and sorbed As released (Islam et al., 2004; McArthur et al., 2004). Arsenic also is released from Mn oxides as they reductively dissolve, but may not remain in the groundwater, instead resorbing to Fe hydroxides (McArthur et al., 2004). Other

studies indicate that As could also be released from biotite into Bangladeshi groundwater (Hopf et al., 2001; Seddique et al., 2008).

Reductive dissolution of Fe hydroxides has been proposed as a viable mechanism for As release in many other affected aquifers as well—for example, in Croatia, Inner Mongolia, northern China, and the eastern and southeastern USA (Barringer et al., 2010; Barringer et al., 2011; Guo et al., 2010; Haque et al., 2008; Mumford et al., 2012; Percy et al., 2011; Sharif et al., 2008; Ujevic et al., 2010; Xie et al., 2008). Although less intensely studied than Bengal Basin sediments, release of As from Fe oxides appears to be an important mechanism in the Inner Mongolian sediments (Smedley, 2008).

3.3. Microbially mediated reactions

Given the similarities to the shallow aquifers in Cambodia, Vietnam, Laos, and Myanmar, much of what has been found in West Bengal and Bangladesh may apply to the aquifers in those countries as well. A study of indigenous bacteria in Cambodian sediments indicated arsenic-respiring bacteria that reduce As(V) (arsenate) to As(III) (arsenite) were fueled by inputs of organic carbon (Lear et al., 2007), similar to findings for bacteria in West Bengal sediments. Additionally, results of experiments showed microbially mediated reduction of As(V), and Fe, and release from minerals (clay, glauconite sands, oxides and hydroxides) (Campbell et al., 2006; Dong et al., 2003; Hopf et al., 2009; Kostka et al., 1999; McLean et al., 2006; Percy et al., 2011), demonstrating the involvement of microbes in the reduction-oxidation (redox) reactions.

The bacteria involved in the reactions involve several groups. Iron-reducing bacteria of the genus *Geobacter* can reduce Fe in minerals such as hydroxides (Lloyd and Oremland, 2006), thus leading to dissolution of the hydroxides and sorbed As release. *Geobacter* bacteria have been investigated as As reducers; although *G. uraniumreducens* contains genes for As respiration, it was not conclusively shown to respire As, and *G. sulfurreducens* did not reduce As enzymatically (Islam et al., 2005; Lear et al., 2007). Bacteria known as dissimilatory arsenate respiring prokaryotes (DARPs) are identified as arsenic reducers, which means that As(V) serves as the terminal electron acceptor in dissimilatory reduction of arsenate. In the glauconitic sediments of the New Jersey Coastal Plain, USA, amplification of the arsenic respiratory reductase gene (*arrA*) followed by alignment and gene sequencing revealed clones with close (99%) similarity to *Alkaliphilus oremlandii* (CP000453) (formerly *Clostridium* species strain OhLAs)—a known arsenate-respiring bacterium (Mumford et al., 2012). Also using molecular techniques, an arsenate-respiring proteobacterium *Sulfurospirillum* sp. strain NP4 was identified by Lear et al. (2007) in Cambodian sediments. The bacterium *Desulfotomaculum auripigmentum* reduces As(V) to As(III) as well as sulfate to sulfide, and precipitates orpiment (Newman et al. 1997; Ehrlich and Newman, 2009)

It should be noted, however, that not all microbial reduction of arsenate is the result of bacterial respiration. Many bacteria detoxify arsenate by reducing it to arsenite and expelling it (Oremland and Stolz, 2005) and, in some cases, by methylating and expelling it (Bentley and Chasteen, 2002). Presence of dimethylarsinate and monomethylarsonate in groundwater, as was found in shallow groundwater in glauconitic sediments of the New Jersey Coastal Plain, probably was indicative of such microbial activity (Mumford, et al., 2012). In experiments, As

was mobilized from apatite by the bacterium *Burkholderia fungorum*, which utilizes phosphorus from the apatite (Mailloux et al., 2009). There is apatite present in the sediments released from the Himalayas to the alluvial aquifers of South East Asia, and there are apatite-rich phosphorite beds in the glauconitic New Jersey Coastal Plain. In addition to reductive dissolution of iron hydroxides releasing sorbed As, arsenate reduction by As-respirers and other As-reducing bacteria, As may also be released by the mechanism suggested by Mailloux et al. (2009) in some aquifers.

Conditions that support microbial sulfate reduction are reported for the aquifers of the West Bengal, Mekong, and Red River deltas. Where such conditions exist, there is the potential for precipitation of sulfide minerals that could remove As as well as Fe from solution. Buschmann and Berg (2009) found As concentrations to be lower in groundwater from zones where sulfate (SO_4^{2-}) and Fe reduction were occurring in the aquifers of the Bengal, Mekong, and Red River deltas. They suggest such conditions, which could result in precipitation of insoluble sulfides, are a control on As levels in groundwater. Some of the chemical reactions that likely affect As mobility are shown in Table 2.

Reaction description	Equation	Reference
Oxidation of pyrite	$\text{FeS}_2 + 15/4 \text{O}_2 + 7/2 \text{H}_2\text{O} \rightarrow \text{Fe}(\text{OH})_3 + 2\text{H}_2\text{SO}_4$ $10\text{FeS}_2 + 30\text{NO}_3^- + 20 \text{H}_2\text{O} \rightarrow 10 \text{Fe}(\text{OH})_3 + 15 \text{N}_2 + 15 \text{SO}_4^{2-} + 5 \text{H}_2\text{SO}_4$	Welch et al., (2000)
Oxidation of arsenopyrite	$\text{FeAsS}(\text{S}) + 11/4 \text{O}_2(\text{aq}) + 3/2 \text{H}_2\text{O}(\text{aq}) \rightarrow \text{Fe}^{2+}(\text{Aq}) + \text{SO}_4^{2-}(\text{aq}) + \text{H}_3\text{AsO}_3(\text{aq})$	Morin & Calas, (2006)
Oxidation of arsenite	$\text{H}_3\text{AsO}_3 + 1/2 \text{O}_2(\text{aq}) \rightarrow \text{H}_2\text{AsO}_4^- + \text{H}^+$	Morin & Calas, (2006)
Reductive dissolution of Fe hydroxides (release of sorbed arsenate not shown)	$4\text{Fe}^{\text{III}}\text{OOH} + \text{CH}_2\text{O} + 7\text{H}_2\text{CO}_3 \rightarrow 4\text{Fe}^{\text{II}} + 8\text{HCO}_3^- + 6\text{H}_2\text{O}$	Nriagu et al. (2007)
Reduction of sulfate, formation of sulfide	$2\text{CH}_2\text{O} + \text{SO}_4^{2-} \rightarrow 2\text{HCO}_3^- + \text{H}_2\text{S}$	Nriagu et al., (2007)
Oxidation of organic carbon (lactate) and reduction of As(V)	$\text{CH}_3\text{-CHOH-COO}^- + 2\text{HAsO}_4^{2-} + 3\text{H}^+ \rightarrow \text{CH}_3\text{COO}^- + 2\text{HAsO}_2 + 2\text{H}_2\text{O}$ $2\text{H}_2\text{O} + \text{HCO}_3^-$	Saltikov et al., (2003)
Microbially mediated precipitation of orpiment	$2\text{HAsO}_2 + 3\text{HS}^- + 3\text{H}^+ \rightarrow \text{As}_2\text{S}_3 + 4\text{H}_2\text{O}$	Ehrlich and Newman(2009)
Incongruent dissolution of glauconite (with release of arsenic not shown)	$\text{K}_2(\text{Fe}_{1-x}\text{Mg}_x)_2\text{Al}_6(\text{Si}_4\text{O}_{10})_3(\text{OH})_{12(\text{s})} + 3/2 \text{O}_2(\text{g}) + 6\text{H}^+ \rightarrow \text{K}^+$ $+ 2x\text{Mg}^{+2}(\text{aq}) + 6\text{SiO}_2(\text{aq}) + 2(1-x).\text{Fe}(\text{OH})_{3(\text{s})} + 3/2 \text{Al}_4(\text{Si}_4\text{O}_{10})(\text{OH})_{8(\text{s})}$	Chapelle and Knobel (1983)

Table 2. Reactions involved in, or affecting, reduction, oxidation, and (or) precipitation of arsenic in water and sediments.

3.4. Sources, sinks, electron donors, and competitive ions

Aqueous sulfide was measured in As-rich groundwater discharging to a New Jersey Coastal Plain, USA, stream (Barringer et al., 2010), but sulfide minerals (pyrite) were rare or not present in cores of streambed sediments. Siderite (FeCO_3) was found, however, more than a meter deep in the sediments and, judging from the As content (184 mg/kg), the siderite is an effective sink for As released to the shallow groundwater (Mumford et al., 2012). Siderite apparently forms when bacteria respire organic matter, creating bicarbonate (HCO_3^-), in an Fe-rich, reducing environment with circumneutral to alkaline pH (Fredrickson et al., 1998). Siderite is reported for parts of the Southeast Asian alluvial aquifers, and presumably acts as an As sink there as well, because Islam et al., (2005) found both arsenate (As(V)) and arsenite (As(III)) sorbed effectively to the siderite in their experiments. Jönsson and Sherman (2008), however, found that the binding of As(III) with siderite is weak. Clearly, however, siderite plays a role in removing one or both of the prevalent As species from solution. Whether siderite remains a permanent sink for As is not known; it would seem possible that biogeochemical conditions in an aquifer could change such that sorbed As would be released back into solution.

In the microbial release of As from geologic materials to groundwater, the presence of organic matter is seen as a critical factor, as it is an electron donor that fuels microbial activity. Organic acids also may compete with As species, along with oxyanions such as phosphate, molybdate, sulfate, and silicate, for binding sites on solids (Wang and Mulligan, 2006b). Nevertheless, the main role of organic matter in As release appears to be that it provides the necessary substrate to bacterial communities for growth and activity – as part of the process in which it is oxidized by bacteria, the organic matter also may produce quinone-like moieties that act as electron shuttles in the resulting redox reactions (Mladenov, et al., 2010).

In the studies of the biogeochemistry of the Southeast Asian aquifers, the source of the organic matter was a matter of controversy. Buried peat was suggested as the source (McArthur et al., 2004), whereas Harvey et al. (2002) indicated that young carbon from the land surface moved to depth by irrigation pumping accounted for the organic matter in the redox reactions. (It may be that both sources are operative in different places.) Rowland et al., (2006, 2007) found naturally occurring hydrocarbons in West Bengal and Cambodian aquifers that could promote the microbial activity involved in arsenic release. Héry et al., (2010) point out that very low organic carbon contents (i.e. $\leq 1\%$) in sediments is sufficient to stimulate the microbially mediated reactions that result in metal and arsenic reduction in the aquifers.

Organic matter can come from anthropogenic sources as well as natural sources. Barringer et al. (2010) indicated that the likely source of organic matter in the glauconitic system they studied came from wastewater discharged for many years from farming and other subsequent activities. The issue of whether anthropogenic inputs from agricultural practices have contributed organic matter to shallow groundwater in West Bengal and Bangladesh has received much debate (Farooq et al., 2010; Neumann et al., 2009; Sengupta et al., 2008) and it is not entirely resolved. It has been noted, however, at various contamination sites, that petroleum leaks, organic-rich leachates from landfills, as well as inputs of organic carbon for remediation purposes has led to mobilization of As (Hering et al., 2009). Thus it is clear that inputs of organic carbon from both natural and anthropogenic activities can supply electrons and stimulate the

microbially mediated processes that lead to As release from geologic materials into groundwater.

4. Hydrogeologic factors

4.1. Residence time

Several biogeochemical processes that release As from geologic materials have been identified, as presented in the previous section. Smedley and Kinniburgh (2002) point out that whether released As remains at problematic levels in groundwater depends not only on whether there are biogeochemical reactions that retard the transport of As, but also upon the hydrologic and hydrogeologic properties of the aquifer, such as flow velocity and dispersion. If the kinetics of As release are slow, and groundwater residence time is short, then As concentrations may not increase to the point where groundwater would be considered contaminated. Conversely, if reactions that mobilize As are rapid and residence time is long, then As can accumulate in groundwater such that concentrations become hazardous—as seen in Bangladesh, for example. Eventually, if the biogeochemical conditions that lead to release and mobilization of As continue to be present (within a geologic timeframe), then the source could become exhausted.

4.2. Seasonal changes in recharge

Natural fluctuations can affect the fate and transport of As within groundwater systems. Seasonal fluctuations in recharge could, during periods of high precipitation, bring dilution to shallow groundwater, but also transport surficially derived materials to the aquifer. As mentioned above, the transport of dissolved organic matter from agricultural land in the Bengal Delta has been suggested to fuel bacterial activity that releases As from the aquifer materials, and, in that region, seasonal (monsoon) rainfall has an important effect on recharge rates and the transmission of land-derived substances to depth in the aquifers. On a much smaller scale, As concentrations in shallow groundwater that discharges to Coastal Plain streams in New Jersey, USA, varies with season and hydrologic conditions. Increased recharge during springtime results in more diluted shallow groundwater and low As concentrations, whereas hot, dry weather results in decreased recharge and higher As concentrations. Where clay lenses underlie the stream channel shallow groundwater levels above the clay decline during warm, dry periods, and some stream segments may ultimately lose water to groundwater. Thus, in some stream segments seasonal hydrologic conditions control As-rich groundwater discharges to the stream. In other segments, As-rich groundwater may discharge on a relatively constant basis with higher concentrations of As being present during warm dry weather (Barringer et al., 2010).

4.3. Effects of pumping

Pumping-induced changes to hydraulic gradients can alter flow paths at regional and local scales and can lead to introduction of contaminants to otherwise potable water. For As-

contaminated well water in Bangladesh, the contamination is found in the shallower of two aquifers. Although water of the deeper aquifer is generally free of As contamination, the replacement of shallow tube wells with wells in the deep aquifer was thought to have the potential to transport contamination downward to low-As ground water (Ravenscroft et al, 2001; Harvey et al., 2002; van Geen et al., 2003).

Pumping also can result in changes in redox conditions along a flow path. As suggested by Peters and Blum (2003), anoxic water can be drawn upward to oxic zones near the wellhead, resulting in disequilibrium between As species. The converse is also possible—anoxic waters could be introduced by pumping to oxic zones such that Fe(III) in ferric hydroxides is reduced, hydroxides are dissolved, and sorbed As is released. Or, in cases where As is released under anoxic conditions, introduction of oxic water through pumping could slow or terminate the reaction. An example of pumping-induced changes in redox conditions is found at the individual borehole scale in eastern Wisconsin, USA. In a field experiment, longer periods between pumping episodes allowed longer periods of anoxia, which resulted in higher concentrations of As in groundwater (Ayotte et al., 2011). Pumping also could move constituents such as organic carbon from the surface to depth, where the carbon could stimulate microbially mediated redox reactions such as Fe reduction that leads to As release from aquifer materials. Pumping could also move higher pH water into a zone of lower pH water, creating an environment in which As sorbed to aquifer materials can desorb.

Flow rates at the individual borehole scale can also be sufficiently rapid that contact time between groundwater and aquifer material is minimized, and reactions releasing As may be relatively slow. Limited contact time is thought to be the explanation for lower dissolved constituents, including As, in water from wells with high yield compared with those with low yield and higher dissolved constituents in the Hungarian Pannonian Basin (Varsányi and Kovács, 2006). Similar results are reported for a well in a sandstone aquifer in Wisconsin, USA, where reducing conditions developed with no pumping and As concentrations increased (indicating dissolution of Fe hydroxides and As release), whereas rapid well purging introduced oxic conditions to water near the well bore (Gotkowitz et al., 2004).

5. Conclusions

Arsenic contamination of groundwater resources has been identified in many parts of the world. In some cases, as in geothermal fields, the impact of As on drinking-water supplies may not be great, but there are parts of the world where groundwater is a major drinking-water source for millions of people, many of which are in poverty and have limited ability to solve the problem of a contaminated water source. Since the discoveries of widespread groundwater contamination with As, considerable effort has been expended to find suitable, inexpensive methods for removing As. A discussion of those efforts, and the results, is beyond the scope of this chapter; the reader is directed to Feenstra et al. (2007) for an overview of As removal methods.

Geogenic sources of As are numerous—within the various geologic materials, the most common occurrences of As appear to be in sulfides (mainly pyrite) and as sorbed species on Fe hydroxides, although As also appears within some silicate and carbonate rocks. The main processes involved in As release to groundwater are reduction of Fe hydroxides, reduction of As within minerals and as a sorbed species, competitive sorption with other oxyanions, and sulfide oxidation. Increasingly, studies show that these processes can be mediated by microbes.

Although major geologic sources of arsenic include alluvial materials, mineralized sedimentary and metasedimentary rocks and volcanic rocks and related deposits, recent findings indicating that As also is released from glauconitic sediments suggests that not all geologic sources and conditions for the release of As to groundwater have yet been identified. Further, it is apparent from some studies that human activities can increase the rates and amounts of As mobilized and dissolved in groundwater through inputs of organic carbon, and from water withdrawals and other changes to natural hydrologic systems. Thus, while there are human efforts to mitigate the As contamination of drinking-water supplies, there are also human activities that exacerbate the problem. The more fully we understand how, when, and where As is mobilized from geologic materials, or from anthropogenic releases to the environment, the more effectively we can find solutions to this major contamination problem.

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