

## 2 Arsenic in groundwaters across the world

### 2.1 IMPORTANCE OF ARSENIC IN DRINKING WATER

Arsenic is a ubiquitous element found in the atmosphere, soils and rocks, natural waters and organisms. It is mobilised in the environment through a combination of natural processes such as weathering reactions, biological activity and volcanic emissions as well as through a range of anthropogenic activities. Most environmental arsenic problems are the result of mobilisation under natural conditions, but man has had an important impact through mining activity, combustion of fossil fuels and through the use of arsenic in pesticides, herbicides, crop desiccants and as an additive to animal feed. Although the use of arsenical products such as weed-killers and wood preservatives has decreased significantly in the last few years, their impact on the environment at least locally, is likely to remain for some years.

Of the various sources of arsenic in the environment, drinking water probably poses the greatest threat to human health. Drinking water is derived from a variety of sources depending on local availability: surface water (rivers, lakes, reservoirs and ponds), groundwater (aquifers) and rain water. These sources are very variable in terms of arsenic risk. Alongside obvious point sources of arsenic contamination, seriously high concentrations are mainly restricted to groundwaters. These are where the greatest number of, as yet unidentified, high-arsenic sources are likely to be found. This chapter therefore focuses on arsenic concentrations in groundwaters and aquifers.

The WHO guideline value for As in drinking water was provisionally reduced in 1993 from  $50 \mu\text{g L}^{-1}$  to  $10 \mu\text{g L}^{-1}$ . The new recommended value is based largely on analytical capability. If the standard basis for risk assessment applied to industrial chemicals were applied to arsenic, the maximum permissible concentration would likely be lower still. The EC maximum admissible concentration (MAC) for As in drinking water is to be reduced to  $10 \mu\text{g L}^{-1}$  in line with current health evidence. The USEPA has also recently introduced a revised maximum contaminant level (MCL) of  $10 \mu\text{g L}^{-1}$  for public water supplies in the USA. The Japanese limit for drinking water is also  $10 \mu\text{g L}^{-1}$ .

Whilst 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 operate at present to the  $50 \mu\text{g L}^{-1}$  standard, in part because of lack of adequate testing facilities for lower concentrations.

Until recently, arsenic was often not on the list of constituents in drinking water routinely analysed by national laboratories, water utilities and NGOs and so the body of information about the distribution of arsenic in drinking water is not as well known as for many other drinking-water constituents. In recent years, it has become apparent that both the WHO guideline value and current national

standards are quite frequently exceeded in drinking-water sources, and often unexpectedly so. Indeed, arsenic along with fluoride, are now recognised as the most serious inorganic contaminants in drinking water on a worldwide basis. In areas of high arsenic concentrations, drinking water provides a potentially major source of arsenic in the diet and so its early detection is of great importance.

### 2.2 SOURCES OF ARSENIC

#### 2.2.1 Minerals

##### *Major arsenic minerals*

Arsenic occurs as a major constituent in more than 200 minerals, including elemental arsenic, arsenides, sulphides, oxides, arsenates and arsenites. A list of some of the most common As minerals is given in Table 2.1. Most are ore minerals and their alteration products. The greatest concentrations of these minerals therefore occur in mineralised areas and are commonly found in close association with the transition metals as well as Cd, Pb, Ag, Au, Sb, P, W and Mo. The most widespread As ore mineral is arsenopyrite, FeAsS. It is generally assumed that arsenopyrite, together with the other dominant As-sulphide minerals realgar and orpiment, are only formed under high temperature conditions in the earth's crust, although there is currently some debate about whether arsenopyrite can form at low temperatures as an authigenic mineral.

##### *Rock-forming minerals*

Though not a major component, arsenic is also often present in varying concentrations in other common rock-forming minerals. As the chemistry of arsenic follows closely that of sulphur, the greatest concentrations of the element tend to occur in sulphide minerals, of which pyrite is the most abundant. Concentrations in pyrite, chalcopyrite and galena can be very variable, even within a given grain, but in some cases reach up to several weight percent (Table 2.2). Arsenian pyrite is a relatively common mineral especially in ore bodies and As concentrations up to almost  $80,000 \text{ mg kg}^{-1}$  have been reported (Table 2.2). Arsenic is also present in the crystal structure of many sulphide minerals as a substitute for sulphur.

Besides being an important component of ore bodies, pyrite is also formed in low-temperature sedimentary environments under reducing conditions (authigenic pyrite). 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. Pyrite commonly forms preferentially in zones of intense reduction such as around buried plant roots or other nuclei of decomposing organic matter. It is often

**Table 2.1.** Major arsenic minerals occurring in nature

Mineral	Composition	Occurrence
Native arsenic	As	Hydrothermal veins
Niccolite	NiAs	Vein deposits and norites
Realgar	AsS	Vein deposits, often associated with orpiment, clays or limestones, also hot-spring deposits
Orpiment	As <sub>2</sub> S <sub>3</sub>	Hydrothermal veins, hot springs, volcanic sublimation product
Cobaltite	CoAsS	High-temperature deposits, metamorphic rocks
Arsenopyrite	FeAsS	The most abundant As mineral, dominantly mineral veins
Tennantite	(Cu,Fe) <sub>12</sub> As <sub>4</sub> S <sub>13</sub>	Hydrothermal veins
Enargite	Cu <sub>3</sub> AsS <sub>4</sub>	Hydrothermal veins
Arsenolite	As <sub>2</sub> O <sub>3</sub>	Secondary mineral formed by oxidation of arsenopyrite, native arsenic and other As minerals
Claudetite	As <sub>2</sub> O <sub>3</sub>	Secondary mineral formed by oxidation of realgar, arsenopyrite and other As minerals
Scorodite	FeAsO <sub>4</sub> ·2H <sub>2</sub> O	Secondary mineral
Annabergite	(Ni,Co) <sub>3</sub> (AsO <sub>4</sub> ) <sub>2</sub> ·8H <sub>2</sub> O	Secondary mineral
Hoernesite	Mg <sub>3</sub> (AsO <sub>4</sub> ) <sub>2</sub> ·8H <sub>2</sub> O	Secondary mineral, smelter wastes
Haematolite	(Mn,Mg) <sub>4</sub> Al(AsO <sub>4</sub> )(OH) <sub>8</sub>	
Conichalcite	CaCu(AsO <sub>4</sub> )(OH)	Secondary mineral
Pharmacosiderite	Fe <sub>3</sub> (AsO <sub>4</sub> ) <sub>2</sub> (OH) <sub>3</sub> ·5H <sub>2</sub> O	Oxidation product of arsenopyrite and other As minerals

present as framboidal grains.

Pyrite is not stable in aerobic systems and oxidises to iron oxides with the release of large amounts of sulphate and acidity as well as many trace elements. The presence of pyrite as a minor constituent in sulphide-rich coals is ultimately responsible for the production of 'acid rain' and acid mine drainage (AMD), and for the presence of arsenic and other trace metal problems around coal mines and areas of intensive coal burning.

High As 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 weight percent values (Table 2.2), particularly where they form as the oxidation products of primary iron sulphide minerals which have an abundant supply of arsenic. Adsorption of arsenate to hydrous iron oxides is particularly strong, even at very low arsenic concentrations (Goldberg, 1986; Manning and Goldberg, 1996; Hiemstra and van Riemsdijk, 1996). Adsorption to hydrous Al and Mn oxides may also be important if these oxides are present in quantity (e.g. Peterson and Carpenter, 1983; Brannon and Patrick, 1987). Arsenic may also be sorbed to the edges of clays and to the surface of calcite (Goldberg and Glaubig, 1988). The degree of adsorption onto these minerals is minor compared to Fe oxides but they are nonetheless common minerals in many sediments. Adsorption reactions are responsible for the relatively low concentrations of arsenic found in most natural waters.

Arsenic concentrations in phosphate minerals are variable but can also reach high values, for example up to 1000 mg kg<sup>-1</sup> in apatite (Table 2.2). However, phosphate minerals are much less abundant than oxide minerals and so make a correspondingly small contribution to the arsenic concentrations of most sediments.

Arsenic can also substitute for Si<sup>4+</sup>, Al<sup>3+</sup>, Fe<sup>3+</sup> and Ti<sup>4+</sup> in many mineral structures and is therefore present in many other rock-forming minerals, albeit at much lower concentrations. Most common silicate minerals contain around 1 mg kg<sup>-1</sup> or less. Carbonate minerals usually contain less than 10 mg kg<sup>-1</sup> (Table 2.2).

## 2.2.2 Rocks, sediments and soils

### *Igneous rocks*

Arsenic concentrations are generally low in most igneous rocks. Ure and Berrow (1982) quoted an average value of 1.5 mg kg<sup>-1</sup> for all rock types (undistinguished). Averages for different types distinguished by silica content (Table 2.3) are slightly higher than this value but generally less than 5 mg kg<sup>-1</sup>. Volcanic glasses are only slightly higher with an average of around 5.9 mg kg<sup>-1</sup> (Table 2.3). Overall, there is relatively little difference between the different rock types.

### *Metamorphic rocks*

Arsenic concentrations in metamorphic rocks tend to reflect the concentrations in their igneous and sedimentary precursors. Most have around 5 mg kg<sup>-1</sup> or less. Pelitic rocks (slates, phyllites) typically have the highest concentrations with on average around 18 mg kg<sup>-1</sup> (Table 2.3).

### *Sedimentary rocks*

The concentration of As in sedimentary rocks is typically in the range 5–10 mg kg<sup>-1</sup> (Webster, 1999), i.e. slightly above average terrestrial abundance. Average sediments are enriched in As relative to igneous rocks. Sands and sandstones tend to have the lowest concentrations, reflecting the low As concentrations of their dominant minerals, quartz and feldspars. Average sandstone As concentrations are around 4 mg kg<sup>-1</sup> (Table 2.3) although Ure and Berrow (1982) gave a lower average figure of 1 mg kg<sup>-1</sup>.

Argillaceous deposits have a broader range and higher average As concentrations than sandstones, typically an average of around 13 mg kg<sup>-1</sup> (Table 2.3; Ure and Berrow, 1982). The higher values reflect the larger proportion of sulphide minerals, organic matter and clays. Black shales have As concentrations typically at the high end of the range, principally because of their high pyrite content. Data given in Table 2.3 suggest that marine argillaceous

deposits have higher concentrations than non-marine deposits. This may also be a reflection of the grain-size distributions, with potential for a higher proportion of fine material in offshore pelagic sediments as well as systematic differences in sulphur and pyrite contents. Sediment provenance is also a likely important factor. Particularly high As concentrations have been determined for shales from mid-ocean settings (Mid-Atlantic Ridge average 174 mg kg<sup>-1</sup>; Table 2.3). Atlantic Ridge gases may in this case be a high-As source.

Arsenic concentrations in coals and bituminous deposits are variable but often high. Samples of organic-rich shale (Kupferschiefer) from Germany have As concentrations of 100–900 mg kg<sup>-1</sup> (Table 2.3). Coal samples have been found with up to 35,000 mg kg<sup>-1</sup>, although generally low concentrations of 2.5–17 mg kg<sup>-1</sup> were reported by Palmer and Klizas (1997).

Carbonate rocks typically have low concentrations, reflecting the low concentrations in the constituent minerals (ca. 3 mg kg<sup>-1</sup>; Table 2.3).

**Table 2.2.** Typical arsenic concentrations in common rock-forming minerals

Mineral	As conc. range (mg kg <sup>-1</sup> )	References
<i>Sulphide minerals:</i>		
Pyrite	100–77000	Baur & Onishi (1969); Arehart et al. (1993); Fleet and Mumin (1997)
Pyrrhotite	5–100	Boyle & Jonasson (1973)
Marcasite	20–600	Dudas (1984)
Galena	5–10000	
Sphalerite	5–17000	
Chalcopyrite	10–5000	
<i>Oxide minerals:</i>		
Haematite	up to 160	
Fe oxide (undifferentiated)	up to 2000	
Fe(III) oxyhydroxide	up to 76000	Pichler et al. (1999)
Magnetite	2.7–41	
Ilmenite	<1	
<i>Silicate minerals:</i>		
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	
<i>Carbonate minerals:</i>		
Calcite	1–8	
Dolomite	<3	
Siderite	<3	
<i>Sulphate minerals:</i>		
Gypsum/anhydrite	<1–6	
Barite	<1–12	
Jarosite	34–1000	
<i>Other minerals:</i>		
Apatite	<1–1000	
Halite	<3	
Fluorite	<2	

Some of the highest observed As concentrations, often several thousand mg kg<sup>-1</sup>, are found in ironstones and Fe-rich rocks. Phosphorites are also relatively enriched in As. In these rocks, concentrations of up to ca. 400 mg kg<sup>-1</sup> have been measured.

#### *Unconsolidated sediments*

Concentrations of As in unconsolidated sediments are not notably different from those in their indurated equivalents, with muds and clays having typically higher concentrations than sands and carbonates. Values are typically 3–10 mg kg<sup>-1</sup>, depending on texture and mineralogy (Table 2.3). High concentrations tend to reflect the amounts of pyrite or Fe oxides present. Increases are also typically found in mineralised areas. Placer deposits in streams can have very high concentrations as a result of the abundance of sulphide minerals.

Average As concentrations for stream sediments in England and Wales are in the range 5–8 mg kg<sup>-1</sup> (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<sup>-1</sup> (range 1.2–2.6 mg kg<sup>-1</sup>), from the Brahmaputra River averaging 2.8 mg kg<sup>-1</sup> (range 1.4–5.9 mg kg<sup>-1</sup>) and from the Meghna River averaging 3.5 mg kg<sup>-1</sup> (range 1.3–5.6 mg kg<sup>-1</sup>).

Cook et al. (1995) found concentrations in lake sediments ranging between 0.9–44 mg kg<sup>-1</sup> (median 5.5 mg kg<sup>-1</sup>) but noted that the highest concentrations were present up to a few kilometres down-slope of mineralised areas. The upper baseline concentration for these sediments is likely to be around 13 mg kg<sup>-1</sup> (90th percentile). They also found concentrations in glacial till of 1.9–170 mg kg<sup>-1</sup> (median 9.2 mg kg<sup>-1</sup>; Table 1.4) and noted the highest concentrations down-ice of mineralised areas (upper baseline, 90th percentile, 22 mg kg<sup>-1</sup>).

Relative arsenic enrichments have been observed in reducing sediments in both nearshore and continental-shelf deposits (Peterson and 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, and were in the range 2.3–8.2 mg kg<sup>-1</sup> (Table 2.3).

#### *Soils*

Baseline concentrations of As in soils are of the order of 5–10 mg kg<sup>-1</sup>. Boyle and Jonasson (1973) quoted an average baseline concentration in soils of 7.2 mg kg<sup>-1</sup> (Table 2.3) and Shacklette et al. (1974) quoted an average of 7.4 mg kg<sup>-1</sup> (901 samples) for American soils. Ure and Berrow (1982) gave a higher average value of 11.3 mg kg<sup>-1</sup>. Peats and bog soils can have higher concentrations (average 13 mg kg<sup>-1</sup>; Table 2.3), principally because of increased prevalence of sulphide mineral phases under the reduced conditions. Acid sulphate soils which are generated by the oxidation of pyrite in sulphide-rich terrains such as pyrite-rich shales, mineral veins and dewatered mangrove swamps

**Table 2.3.** Typical arsenic concentrations in rocks, sediments, soils and other surficial deposits

Rock/sediment type	As conc. average (range) (mg kg <sup>-1</sup> )	No of analyses	Reference
Igneous rocks:			
Ultrabasic rocks (peridotite, dunite, kimberlite etc)	1.5 (0.03–15.8)	40	Baur & Onishi (1969); Boyle & Jonasson (1973);
Basic rocks (basalt)	2.3 (0.18–113)	78	Ure and Berrow (1982);
Basic rocks (gabbro, dolerite)	1.5 (0.06–28)	112	Riedel and Eikmann (1986)
Intermediate (andesite, trachyte, latite)	2.7 (0.5–5.8)	30	
Intermediate (diorite, granodiorite, syenite)	1.0 (0.09–13.4)	39	
Acidic rocks (rhyolite)	4.3 (3.2–5.4)	2	
Acidic rocks (granite, aplite)	1.3 (0.2–15)	116	
Acidic rocks (pitchstone)	1.7 (0.5–3.3)		
Volcanic glasses	5.9 (2.2–12.2)	12	
Metamorphic rocks:			
Quartzite	5.5 (2.2–7.6)	4	Boyle and Jonasson (1973)
Hornfels	5.5 (0.7–11)	2	
Phyllite/slate	18 (0.5–143)	75	
Schist/gneiss	1.1 (<0.1–18.5)	16	
Amphibolite and greenstone	6.3 (0.4–45)	45	
Sedimentary rocks:			
Marine shale/mudstone	3–490		Boyle and Jonasson (1973);
Shale (Mid-Atlantic Ridge)	174 (48–361)		Cronan (1972)
Non-marine shale/mudstone	3.0–12		Welch et al. (1988)
Sandstone	4.1 (0.6–120)	15	Riedel and Eikmann (1986)
Limestone/dolomite	2.6 (0.1–20.1)	40	Baur and Onishi (1969)
Phosphorite	21 (0.4–188)	205	
Iron formations and Fe-rich sediment	1–2900	45	
Evaporites (gypsum/anhydrite)	3.5 (0.1–10)	5	
Coals	0.3–35,000		Belkin et al. (2000)
Bituminous shale (Kupferschiefer, Germany)	100–900		
Unconsolidated sediments:			
Various	3 (0.6–50)		Azcue and Nriagu (1995)
Alluvial sand (Bangladesh)	2.9 (1.0–6.2)	13	This Volume
Alluvial mud/clay (Bangladesh)	6.5 (2.7–14.7)	23	This Volume
River bed sediments (Bangladesh)	1.2–5.9		Datta and Subramanian (1997)
Lake sediments, Lake Superior	2.0 (0.5–8.0)		Allan and Ball (1990)
Lake sediments, British Columbia	5.5 (0.9–44)	119	Cook et al. (1995)
Glacial till, British Columbia	9.2 (1.9–170)		Cook et al. (1995)
World average river sediments	5		Martin and Whitfield (1983)
Stream and lake silt (Canada)	6 (<1–72)	310	Boyle and Jonasson (1973)
Loess silts, Argentina	3–18		Arribère et al. (1997); Smedley et al. (2000a)
Continental margin sediments (argillaceous, some anoxic)	2.3–8.2		Legeleux et al. (1994)
Soils:			
Various	7.2 (0.1–55)	327	Boyle and Jonasson (1973)
Peaty and bog soils	13 (2–36)	14	
Acid sulphate soils (Vietnam)	6–41	25	Gustafsson and Tin (1994)
Acid sulphate soils (Canada)	1.5–45	18	Dudas (1984); Dudas et al. (1988)
Soils near sulphide deposits	126 (2–8000)	193	Boyle and Jonasson (1973)
Contaminated surficial deposits:			
Mining-contaminated lake sediment, British Columbia	342 (80–1104)		Azcue et al. (1994; 1995)
Mining-contaminated reservoir sediment, Montana	100–800		Moore et al. (1988)
Mine tailings, British Columbia	903 (396–2000)		Azcue et al. (1995)
Soils and tailings-contaminated soil, UK	120–52,600	86	Kavanagh et al. (1997)
Tailings-contaminated soil, Montana	up to 1100		Nagorski and Moore (1999)
Industrially polluted inter-tidal sediments, USA	0.38–1260		Davis et al. (1997)
Soils below chemicals factory, USA	1.3–4770		Hale et al. (1997)
Sewage sludge	9.8 (2.4–39.6)		Zhu and Tabatabai (1995)

can also be relatively enriched in As. Dudas (1984) found As concentrations up to 45 mg kg<sup>-1</sup> in the B horizons of acid sulphate soils derived from the weathering of pyrite-rich shales in Canada. Concentrations in the overlying

leached (eluvial, E) horizons were low (1.5–8.0 mg kg<sup>-1</sup>) as a result of volatilisation or leaching of As to greater depths. Gustafsson and Tin (1994) found similarly increased concentrations (up to 41 mg kg<sup>-1</sup>) in acid sulphate soils from

the Mekong delta of Vietnam.

Although the dominant source of As in soils is geological, additional inputs may be derived locally from industrial sources such as smelting and fossil-fuel combustion products and agricultural sources such as pesticides and phosphate fertilisers. Ure and Berrow (1982) quoted concentrations in the range 366–732 mg kg<sup>-1</sup> in orchard soils as a result of the historical application of arsenical pesticides to fruit crops.

Continued irrigation of crops with arsenic-rich groundwater could also significantly enhance the As concentration in the soil since much of the added As can be expected to be retained in the soil layer.

#### *Contaminated surficial deposits*

Arsenic concentrations much higher than baseline values have been found in sediments and soils contaminated by the products of mining activity, including mine tailings and effluent. Concentrations in tailings piles and tailings-contaminated soils can reach up to several thousand mg kg<sup>-1</sup> (Table 2.3). The high concentrations reflect not only increased abundance of primary arsenic-rich sulphide minerals, but also secondary iron arsenates and iron oxides formed as reaction products of the original ore minerals. The primary sulphide minerals are susceptible to oxidation in the tailings pile and the secondary minerals have varying solubility in oxidising conditions in groundwaters and surface waters. Scorodite (FeAsO<sub>4</sub>·2H<sub>2</sub>O) is metastable under most groundwater conditions and tends to dissolve incongruently, forming iron oxides and releasing arsenic into solution (Robins, 1987). Secondary arsenolite (As<sub>2</sub>O<sub>3</sub>) is also relatively soluble. Arsenic bound to iron oxides is relatively immobile, particularly under oxidising conditions.

### 2.2.3 The atmosphere

The concentrations of arsenic in the atmosphere are usually low but as noted above, are increased by inputs from smelting and other industrial operations, fossil-fuel combustion and volcanic activity. Concentrations amounting to around 10<sup>-5</sup>–10<sup>-3</sup> µg m<sup>-3</sup> have been recorded in unpolluted areas, increasing to 0.003–0.18 µg m<sup>-3</sup> in urban areas and greater than 1 µg m<sup>-3</sup> close to industrial plants. Much of the atmospheric arsenic is particulate. Total arsenic deposition rates have been calculated in the range <1–1000 µg m<sup>-2</sup> a<sup>-1</sup> depending on the relative proportions of wet and dry deposition and proximity to contamination sources (Schroeder et al., 1987). Values in the range 38–266 µg m<sup>-2</sup> a<sup>-1</sup> (29–55% as dry deposition) were estimated for the mid-Atlantic coast (Scudlark and Church, 1988).

Airborne arsenic is transferred to water bodies by wet or dry deposition and may therefore increase the aqueous concentration slightly. However, there is little evidence to suggest that atmospheric arsenic poses a real health threat for drinking-water sources. Atmospheric arsenic arising from coal burning has been postulated as a major cause of lung cancer in parts of China (Guizhou Province), but the threat is from direct inhalation of domestic coal-fire smoke together with the consumption of food, especially chillies dried over coal fires, rather than from drinking water

affected by atmospheric inputs of arsenic.

Arsine gas, AsH<sub>3</sub>, like methane, would be expected to be released from strongly reducing soils. Mixing arsenic-rich sludge material from small-scale arsenic removal plants with cow dung has been advocated as one way of dealing with the contaminated sludge. This procedure relies on the strongly reducing conditions created by the dung promoting the reduction of the As and its loss to the atmosphere as arsine gas.

## 2.3 MINERAL-WATER INTERACTIONS

### 2.3.1 Relevance to arsenic mobilisation

As with most trace metals, the concentration of arsenic in natural waters is probably normally controlled by some form of solid-solution interaction. This is most clearly the case for soil solutions, interstitial waters and groundwaters where the solid/solution ratio is large but it is also often true in open bodies of water (oceans, lakes and reservoirs) where the concentration of solid particles is small but still significant. In these open bodies, the particles are of both mineral and biological origin. In most soils and aquifers, mineral-As interactions are likely to dominate over organic matter-As interactions, although organic matter may interact indirectly through its reactions with the surfaces of minerals and its role in controlling redox reactions.

Knowing the types of interaction involved is important because this will govern the response of As to changes in water chemistry. It will also determine the modelling approach required for making predictions about possible future changes and for understanding past changes in arsenic concentrations.

The importance of oxides in controlling the concentration of arsenic in natural waters has been appreciated for a long time (Livesey and Huang, 1981; Matisoff et al., 1982; Korte, 1991; Korte and Fernando, 1991). Clays can also adsorb As(III) and As(V) (Manning and Goldberg, 1997b). Frequently, one of the best correlations between the concentration of As in sediments and other elements is with iron. This is also the basis for the use of iron, aluminium and manganese salts in water treatment, including for arsenic removal (e.g. Edwards, 1994). The As content of residual sludges can be in the range 1,000–10,000 mg kg<sup>-1</sup> (Driehaus et al., 1998; Forstner and Haase, 1998).

Arsenic adsorption onto iron oxides has been quite extensively studied and the data for hydrous ferric oxide (Hfo) in particular has been well documented (Dzombak and Morel, 1990). The extent of adsorption is strongly dependent on the arsenic speciation (and hence redox status), arsenic concentration, pH and the concentration of competing anions such as phosphate. The shapes of the As(III) and As(V) isotherms are very different reflecting the weak electrostatic contribution in the case of As(III) and the strong electrostatic contribution in the case of As(V). The As(III) isotherm resembles a Langmuir isotherm with a near-linear isotherm at low As concentrations and a maximum adsorption at high concentrations (see Chapter 12). The As(V) isotherm like phosphate is strongly nonlinear which means that As(V) loadings can be high even at very low solution As concentrations.

As(III) sorption is practically independent of pH over

the range of pH of interest in groundwaters (pH 6–9) whereas As(V) sorption declines rapidly above pH 8.5 or so. Therefore while As(V) is much more strongly bound at low pH, at about pH 8–9 or above, As(III) binding can be greater than As(V) binding under similar conditions. This rapid decline in As(V) adsorption therefore occurs in a pH range that is found in groundwaters and is one factor that can lead to high As groundwaters.

Groundwaters invariably contain a range of other anions at concentrations exceeding that of As and these can be expected to compete for binding sites. The most relevant are phosphate, silicate, bicarbonate and dissolved organic carbon. All of these can be high in As-rich groundwaters and it can be difficult to differentiate 'cause' from 'effect'. The specific adsorption of positively charged Ca<sup>2+</sup> and Mg<sup>2+</sup> will tend to enhance the adsorption of As(V) thereby tending to counteract the some of the effects of anion competition. In reducing groundwaters, Fe<sup>2+</sup> may also be important.

These competitive interactions can have an important influence on the shape of the arsenic adsorption isotherms and hence on the partitioning and transport of arsenic in groundwater environments. For example, if the oxide surface is dominated by adsorbed phosphate (which is quite likely in many natural environments), then this phosphate will effectively control the electrostatic potential of the surface not the adsorbed As(V). This means that additional As(V) sorption will have little influence on the electrostatics and will lead to an adsorption isotherm that is more like a Langmuir isotherm than a Freundlich isotherm. In effect, the excess phosphate reduces the high loadings expected in low As(V), low phosphate systems. Interactions such as these could therefore play an important role in controlling the mobility of As in natural waters.

While the Dzombak and Morel (1990) Diffuse Layer Model (DLM) and database have been widely used to model As sorption in 'pure' laboratory systems, they have not been so well tested under the more demanding conditions found in natural waters where competition for binding sites can be expected to be intense. Some competition data suggest reasonable predictions under some conditions (Wilkie and Hering, 1996) but the DLM may overestimate some interactions, e.g. As(V)-P competition. The CD-MUSIC model of Hiemstra and van Riemsdijk (1999) looks more promising for describing, and even predicting, the scale of these interactions. However, there is not at present a readily-usable database of sorption parameters for this model. A verified competitive adsorption model and database for the common oxides and groundwater solutes is urgently needed. It would go a long way to enabling many of the complex issues involved in understanding the evolution of arsenic-rich groundwaters to be untangled.

It is difficult to study mineral-water interactions directly in aquifers. Most studies, including those with a bearing on arsenic in groundwater, have been undertaken either in soils, or in lake or ocean sediments and usually from quite shallow depths. There is much to be learned from these studies since the same general principles are expected to apply. One of the most important areas where cross-fertilisation of ideas can occur is in understanding the behaviour of iron oxides in reducing soils and sedi-

ments and the influence of this on the release of arsenic. Korte (1991) speculated some time ago that desorption of arsenic from iron oxides could occur in reducing, alluvial sediments and that this could lead to high-arsenic groundwaters. He anticipated that this could be quite widespread but suggested that it would be most important in small, low yielding alluvial aquifers of local significance (Korte, 1991; Korte and Fernando, 1991) whereas it has in fact turned out to be most problematic in large, productive deltaic aquifers such as those of the Bengal Basin.

### 2.3.2 Arsenic interactions in sediments

The major minerals binding arsenic (as both arsenate and arsenite) in sediments are the metal oxides, particularly those of iron, aluminium and manganese. About 50% of the iron in freshwater sediments is typically in the form of iron oxides and about 20% of the iron is 'reactive' iron. Clays also adsorb arsenic because of the oxide-like character of their edges, as do carbonates. Of these components, adsorption by iron oxides is probably most important in aquifers because of their great abundance and strong binding affinity. Nevertheless, if studies of soil phosphate are a guide, then aluminium oxides can also be expected to play a significant role when present in quantity. Experience from water treatment (Edwards, 1994) suggests that below pH 7.5 aluminium hydroxides are about as effective as iron hydroxides (on a molar Fe-Al basis) for adsorbing As(V) but that iron salts are more efficient at higher pH and for adsorbing As(III). Activated alumina is quite widely used for removing As from water.

The interactions of arsenic with iron oxides have been studied in considerable detail in the laboratory and therefore provide the best insight into the likely behaviour of arsenic-mineral interactions in aquifers. However, most of these laboratory studies, particularly the older studies, have been undertaken at rather high arsenic concentrations and there is a paucity of reliable adsorption data at the low  $\mu\text{g L}^{-1}$  level of relevance to natural waters. In addition, there is uncertainty over the extent to which the Fe oxides most commonly studied in the laboratory reflect the Fe oxides found in nature.

Field data for As(V) adsorption to natural 'diagenetic' Fe oxides (captured in a lake with vertically-installed Teflon sheets) closely paralleled the laboratory data of Pierce and Moore (1982) which was included in the Dzombak and Morel (1990) database (De Vitre et al., 1991). However, it was considerably greater than that calculated using Hingston et al.'s (1971) data for As(V) adsorption on goethite highlighting the great potential of freshly-formed 'amorphous' iron oxides for binding arsenic. Paige et al. (1997) measured the As/Fe ratios during the acid dissolution of a synthetic ferrihydrite containing adsorbed As(V) and concluded that the dissolution was incongruent (i.e. iron and arsenic were not released in the same proportion as found in the bulk mineral) and that the initial As released was probably initially sorbed on the surface of the very small ferrihydrite particles. The same is likely to happen during reductive dissolution. The adsorbed As also slowed down the acid dissolution of the ferrihydrite.

### 2.3.3 Iron and arsenic in reduced sediments

Since one of the principal sources of arsenic in natural waters is believed to be from the release of arsenic from iron oxides following a change to reducing conditions, it is important to understand any changes that take place to the iron oxides themselves. The sequence of processes that occur during the onset of anaerobic conditions has been widely studied in lakes, soils and sediments although usually not from the point of view of arsenic. This sequence begins with the consumption of oxygen and an increase in dissolved  $\text{CO}_2$  from the decomposition of organic matter. Next,  $\text{NO}_3^-$  decreases by reduction to  $\text{NO}_2^-$  and the gases  $\text{N}_2\text{O}$  and  $\text{N}_2$ . Insoluble manganic oxides dissolve by reduction to soluble  $\text{Mn}^{2+}$  and hydrous ferric oxides are reduced to  $\text{Fe}^{2+}$ . These processes are followed by  $\text{SO}_4^{2-}$  reduction to  $\text{S}^{2-}$ , then  $\text{CH}_4$  production from fermentation and methanogenesis, and finally reduction of  $\text{N}_2$  to  $\text{NH}_4^+$ . During sulphate reduction, the consequent sulphide reacts with any available iron to produce  $\text{FeS}$  and ultimately pyrite,  $\text{FeS}_2$ . Iron is often more abundant than sulphur so that there is 'excess iron' beyond that which can be converted to pyrite (Widerlund and Ingri, 1995). Arsenic(V) reduction would normally be expected to occur after Fe(III) reduction but before  $\text{SO}_4^{2-}$  reduction.

Iron from iron oxides is solubilised as  $\text{Fe}^{2+}$  under reducing conditions, giving rise to characteristically high Fe waters which in reducing groundwaters tend to range from 0.1–30  $\text{mg L}^{-1}$  Fe. The reaction is microbially mediated (Lovley and Chappelle, 1995). There is also evidence for solid-state transformations of the iron oxides under reducing conditions. This is most obviously reflected in a colour change from reddish/orange/brown/tan colours to grey/green/blue colours. 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 particle size of these oxides is often extremely small (Canfield, 1989) which makes them difficult to observe with many of the usual imaging techniques. Mössbauer spectroscopy is useful for identifying the form of iron oxides in sediments including anoxic sediments (Boughriet et al., 1997; Drodt et al., 1997).

The exact fate of iron during reduction is not well understood, in part because of the likely fine-grained nature of the minerals produced. Green rusts are one possible product. These were originally referred to as a 'hydrated magnetite' and given a composition ' $\text{Fe}_3(\text{OH})_8$ '. They are layered mixed Fe(II)–Fe(III) hydroxides which contain an interlayer anion to balance the charge, often sulphate or carbonate. Boughriet et al. (1997) suspected the presence of either green-rust-like compounds, Fe(III)-Fe(II)-(CO<sub>3</sub>)(OH) or Fe(II)<sub>x</sub>Ca<sub>1-x</sub>CO<sub>3</sub> solid solutions, in anoxic sediments from the Seine Estuary. They used <sup>57</sup>Fe Mössbauer spectroscopy to characterise the iron. Green rusts have also been identified in anaerobic soils and are thought to play an important role in controlling soil solution Fe concentrations (Genin et al., 1998).

Authigenic magnetite is another possible product in reducing environments (Fredrickson et al., 1998). Magnet-

ite 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 and Blakemore, 1992). However, under strongly reducing conditions magnetite is unstable and in the presence of high concentrations of  $\text{H}_2\text{S}$  slowly converts to pyrite over a period of 100 years or more (Canfield and Berner, 1987). At the sediment/water interface in oceans, partial oxidation of primary magnetite ( $\text{Fe}_3\text{O}_4$ ) can lead to a coating of the iron oxide, maghemite,  $\gamma\text{-Fe}_2\text{O}_3$ . Further burial and reduction leads to the dissolution of the primary magnetite (Torii, 1997).

### 2.3.4 Arsenic release from soils and sediments following reduction

There is considerable evidence from laboratory studies that arsenic is released from soils following flooding and the development of anaerobic conditions (Deuel and Swoboda, 1972; Hess and Blanchard, 1977; McGeehan and Naylor, 1994; McGeehan, 1996; Reynolds et al., 1999). Similar evidence is available from laboratory and field studies of marine and lake sediments. Numerous studies have demonstrated the release of both phosphorus (Mortimer, 1942; Farmer et al., 1994; Slomp et al., 1996) and arsenic below the redox boundary in freshwater and marine sediments (Moore et al., 1988; De Vitre et al., 1991; Sullivan and Aller, 1996).

This release has long been associated with iron-oxide dissolution. Deuel and Swoboda (1972) found that reducing an untreated black clay soil led to the release of As and that the amount released was related to the total arsenic content of the soil and the redox potential. They proposed that the release was primarily due to reduction (and dissolution) of 'ferric arsenates' rather than to changes in the As speciation. Arsenic release occurred rapidly — in less than a week.

A similar response has been noted in strongly reducing reservoir sediments from western Montana, USA (Moore et al., 1988). When redox conditions changed from an oxidising, oxide-dominated environment to a reducing, sulphide-dominated environment at about 65 cm depth there was a dramatic increase in pore water As concentrations from <20  $\mu\text{g L}^{-1}$  to more than 500  $\mu\text{g L}^{-1}$  at 95 cm depth. This increase was ascribed to oxide dissolution. De Vitre et al. (1991) showed that there was a rapid increase in pore water As concentrations (up to about 30  $\mu\text{g L}^{-1}$ ) with depth in a lake sediment and that this was mirrored by an increase in dissolved Fe. Upwardly diffusing  $\text{Fe}^{2+}$  was oxidised near the sediment-water interface and precipitated as an iron oxide which then adsorbed the upwardly diffusing As. Guo et al. (1997) measured the rate of release of As (and other metals) as a metal-spiked sediment was progressively reduced. Arsenic was rapidly released after the Fe and Mn had dissolved, suggesting that dissolution rather than desorption was the controlling process. Selective extractions suggested most of the As in the sediments was associated with Fe and Mn oxides.

A few studies have attempted to differentiate between the oxidation states of arsenic sorbed by sediments. Mass-

cheyn et al. (1991) measured the release of As and other metals following the flooding and reduction of an arsenic-contaminated soil and found that the release of some As occurred before Fe dissolution but that the amount of As released rapidly increased as the amount of iron-oxide dissolution increased. Both As(V) and As(III) were released. Rochette et al. (1998) demonstrated with XANES spectroscopy that reducing conditions can lead to the conversion of As(V) to As(III) in the solid phase of arsenic minerals. Preliminary results based on XANES also indicate a change in solid-state speciation of the As in Bangladesh sediments in going from oxidising to reducing conditions (Foster et al., 2000).

The As concentration in sediments is often too low and/or the particles too small for direct investigation of solid phase arsenic speciation using techniques such as XAFS and PIXE and so selective dissolution has been most widely used. A number of extraction 'schemes' exist which attempt to allocate elements to particular solid phases. Unfortunately, none of these schemes is perfect or universally applicable and there is little consensus on the best techniques to use. The interpretation is particularly difficult for minor and trace constituents which may be released by both dissolution and desorption processes. Nonetheless, these extractants can probe the solid phase in a useful way that reflects to a varying extent the nature of an element in the solid phase, and therefore its potential behaviour or availability. In particular, such techniques are particularly useful for characterising the very fine-grained minerals or organic phases that are presently poorly characterised by direct examination but which nevertheless play an important role in the behaviour of many trace elements.

The usefulness of the various extractants should increase as our quantitative understanding of the dissolution kinetics of typical minerals increases and as the various sorption/desorption reactions involved are quantified. In the meantime, they can serve as a useful guide to the forms of the elements present and to significant variations in such forms, but care has to be taken in interpreting their results in a quantitative and uncritical way.

Gómez-Ariza et al. (1998) have developed a method to speciate solid phase arsenic based on selective extraction of sediments with hydroxylamine hydrochloride, an acidic and reducing extractant that is rather selective for extracting manganese oxides but that also partially extracts iron oxides. Hydroxylamine hydrochloride did not reduce the As(V) during the extraction.

Brannon and Patrick (1987) studied the kinetics of As release and speciation (As(V), As(III), organic) from freshwater sediments when incubated under both oxidising and reducing conditions. This included sediments with and without added As(V). Most of the native and added As was found in the 'moderately reducible' (oxalate-extractable) fraction. During incubation, there was a steady release of As over the three months of the experiments. This was as As(V) under oxidising conditions and as As(III) under anaerobic conditions. There was no concomitant release of Fe (or Al or Mn) indicating that reductive dissolution of iron oxides was not responsible for the As release. Brannon and Patrick (1987) speculated that a change in the structure of the iron oxides may have been important.

McGeehan (1996) was not sure whether the As(V) reduction found in flooded soils occurs in the soil solution or on the soil particles.

Riedel et al. (1997) monitored the release of metals when a column of estuarine sediment was subjected to reducing conditions for several months. Both As and Mn were released following reduction. Widerlund and Ingri (1995) noted that the As concentration in pore water from two sediment cores from the Kalix estuary, Sweden was controlled by the reductive dissolution of iron oxides. The location of the pore water maximum As concentration did not correspond with that of the sediment maximum As concentration.

Azcue and Nriagu (1995) found that the As concentrations in sediment pore waters from a mine-affected lake, Lake Moira, were up to 4–6 times greater than in the lake water. They suggested that this was due to the reductive dissolution of iron oxides. About  $50 \mu\text{g L}^{-1}$  of As was released for each  $\text{mg L}^{-1}$  Fe dissolved.

Manning and Goldberg (1997a) measured As(V) and As(III) adsorption by three Californian soils and found that the soils with the highest citrate-dithionite-bicarbonate extractable Fe and %clay had the greatest affinity for both As(III) and As(V). As(V) sorbed to a greater extent than As(III) at the micromolar As concentrations used suggesting that As would be released when As(V) is reduced to As(III).

Cummings et al. (1999) showed that there can be release of As(V) from hydrous ferric oxide (Hfo) without pre-reduction of the As(V) to As(III). Scorodite, an iron arsenate mineral (Table 2.1), was in part transformed to various ferrous arsenates. They suggested that as the structural  $\text{Fe}^{3+}$  was reduced, sorbed As(V) was released into solution.

All of these studies demonstrate the ability of soils and sediments to release As when subjected to reducing conditions but there is no clear consensus on the precise mechanisms involved, particularly with respect to the roles played by reductive desorption, reductive dissolution and diagenetic changes to the minerals.

### 2.3.5 Transport of arsenic

The transport and adsorption of chemicals are closely related in that adsorption slows down the transport of a chemical compared with the water flow (Appelo and Postma, 1994). In the simplest case of a linear adsorption isotherm, this relationship is straightforward and the partition coefficient,  $K_d$ , defines a constant retardation factor. With non-linear adsorption, which is most likely to be the case for arsenic adsorption, the value of  $K_d$  varies with concentration and is related to the slope of the isotherm. Normally, the  $K_d$  decreases with increasing concentration, leading to less retardation at high concentrations and ultimately to self-sharpening and diffuse fronts. For example, the greater the non-linearity, the longer it will take to flush completely all of the arsenic from an aquifer – the last remaining fraction is removed reluctantly because the binding is so strong at low concentrations.

Since transport is so closely related to the adsorption isotherms, it follows that arsenite and arsenate should travel through an aquifer with different velocities leading



**Figure 2.1.** Documented cases of arsenic problems in groundwater related to natural contamination. Cases include some of the major mining and geothermal occurrences reported in the literature.

to their increased separation along a flow path. This was demonstrated by Gulens et al. (1979) using breakthrough experiments with columns of sand and various groundwaters pumped continuously from piezometers. They studied As(III) and As(V) mobility with groundwaters having a range of Eh's and pH's using radioactive  $^{74}\text{As}$  ( $t_{1/2}=17.7$  d) and  $^{76}\text{As}$  ( $t_{1/2}=26.4$  hr) to monitor the breakthrough of As. They showed that: (i) As(III) moved 5–6 times faster than As(V) under oxidising conditions (pH 5.7); (ii) with a 'neutral' groundwater (pH 6.9), As(V) moved much faster than at pH 5.7 but was still slower than As(III); (iii) with reducing groundwater (pH 8.3), both As(III) and 'As(V)' moved rapidly through the column; (iv) when the amount of As injected was substantially reduced, the mobility of the As(III) and As(V) was greatly reduced.

This chromatographic effect may account in part for the highly variable As(III)/As(V) ratios found in many reducing aquifers. Such a separation is used to advantage to speciate arsenic with various columns. Chromatographic separation during transport will also tend to uncorrelate any correlations found at the source, for example in the As versus Fe relationship, thus complicating a simple interpretation of well water analyses.

There have been few studies of the transport of arsenic in aquifers typical of those contaminated from natural sources. Most studies of arsenic leaching have concerned industrially-contaminated sites. Kuhlmeier (1997a,b) studied the transport of arsenic in highly-contaminated clayey and sandy soils from around an old arsenic herbicide plant in Houston, Texas. He used column experiments to esti-

mate 'apparent'  $K_d$ 's. These were time- and implicitly concentration-dependent and for the sandy soils ranged from  $0.26\text{ L kg}^{-1}$  after one pore volume to  $3.3\text{ L kg}^{-1}$  after 6 pore volumes. They were not too different for the clayey materials. However, the overall As concentrations were very high — the groundwater was heavily contaminated with As ( $408\text{--}464\text{ mg L}^{-1}$ ) mostly with MMAA. The sediment contained only a few  $\text{mg kg}^{-1}$  of inorganic As. Baes and Sharp (1983) gave  $K_d$  values of  $1.0\text{--}8.3\text{ L kg}^{-1}$  (median 3.3) for As(III) binding by soils and  $1.9\text{--}18.0\text{ L kg}^{-1}$  (median 6.7) for As(V).

## 2.4 GROUNDWATER ENVIRONMENTS SHOWING ENHANCED ARSENIC CONCENTRATIONS

### 2.4.1 World distribution of groundwater arsenic problems

A number of large aquifers in various parts of the world have been identified with problems from As occurring at concentrations above  $50\text{ }\mu\text{g L}^{-1}$ , often significantly so. The most noteworthy occurrences are in parts of West Bengal and Bangladesh, Taiwan, northern China, Hungary, Mexico, Chile, Argentina and many parts of the USA but particularly the south-west, (Figure 2.1). Occurrences of mining related As problems have also been recorded in many parts of the world, including Thailand, Ghana, Greece, Austria and parts of the USA (Figure 2.1). Arsenic associated with geothermal waters has also been reported in several areas, including hot springs from parts of the

USA, Japan, Chile, Argentina, France, Dominica, Kamchatka and New Zealand.

Localised groundwater arsenic problems are now being reported from an increasing number of countries and many new cases are likely to be discovered. Until recently, arsenic was not traditionally on the list of elements routinely tested by water quality testing laboratories and so many arsenic-rich sources undoubtedly remain to be identified. The revision of the drinking water standard for arsenic in a number of countries has prompted a reassessment of the situation in many countries. The recent discovery of arsenic contamination on a large scale in Bangladesh has highlighted the need for a rapid assessment of the situation in alluvial aquifers worldwide.

While natural high arsenic groundwaters are not uncommon, they are by no means typical of most aquifers and only exist under special circumstances. These relate to both the geochemical environment and the past and present hydrogeology. Paradoxically, high arsenic groundwaters do not usually appear to be directly related to areas of high arsenic concentrations in the source rocks. This is because of the high solid/solution ratio in aquifers and the low drinking water limits of arsenic – even a rock containing 1 mg As kg<sup>-1</sup> would produce a groundwater with a concentration of some 3–10 mg As L<sup>-1</sup> if all of the arsenic were to dissolve. Therefore only a small fraction of the arsenic needs to dissolve to produce a relatively high-arsenic groundwater.

Distinctive groundwater arsenic problems occur under both reducing and oxidising groundwater conditions; also in both 'wet' and 'arid' environments. Below we discuss the characteristics of the arsenic problems worldwide through a series of type examples. These examples have been ordered according to the type of environment under which they are developed.

## 2.4.2 Reducing environments

### *Bangladesh and West Bengal*

In terms of the population exposed, As problems in groundwater from the alluvial and deltaic aquifers of Bangladesh and West Bengal represent the most serious occurrences identified globally. Concentrations in groundwaters from the affected areas have a very large range from <0.5 µg L<sup>-1</sup> to ca. 3200 µg L<sup>-1</sup>. Resultant health problems were first identified in West Bengal in the late 1980s although the first confirmation in Bangladesh was not made until 1993. Around 6 million in West Bengal are believed to be at risk from drinking water with >50 µg L<sup>-1</sup> As (Table 2.4). Around 5000 patients have been identified with As-related health problems in West Bengal (including skin pigmentation changes) and at least 6000–7000 in Bangladesh.

As with Bangladesh, the affected aquifers in West Bengal are generally shallow (less than 100–150 m deep), of Holocene age and comprise a mixed sequence of micaceous sands, silts and clays deposited by the rivers Ganges and Hoogli and their tributaries. The sediments are derived from the upland Himalayan catchments and from basement complexes of the northern and western parts of West Bengal. In most affected areas, the sediment sequence is

capped by a layer of clay or silt (of variable thickness) which effectively restricts entry of air to the aquifers. This, together with an abundance of recent solid organic matter deposited with the sediments, has resulted in the development of highly reducing aquifer conditions and dominance of As in solution as As(III). As with Bangladesh, deeper groundwaters from the sediment sequence in West Bengal (>100–150 m depth, probably of Pleistocene age) have generally low As concentrations (<10 µg L<sup>-1</sup>).

The characteristic chemical features of the high-arsenic groundwaters of West Bengal are high iron (>0.2 mg L<sup>-1</sup>), manganese (>0.5 mg L<sup>-1</sup>), bicarbonate (>500 mg L<sup>-1</sup>) and often phosphorus (>0.5 mg L<sup>-1</sup>) concentrations, and low chloride (<60 mg L<sup>-1</sup>), sulphate (<1 mg L<sup>-1</sup>), nitrate and fluoride (<1 mg L<sup>-1</sup>) concentrations, with pH values close to or greater than 7 (AIP Steering Committee, 1991; CGWB, 1999). However, the correlations are far from perfect and where good correlations with arsenic are found, these are usually only applicable locally and are therefore of limited value for quantitative prediction of arsenic concentrations at a larger scale. For example, some workers have found a positive correlation between arsenic and iron in localised studies (e.g. Nag et al., 1996), but this is not true of the region as a whole.

As with Bangladesh, the regional distribution of the high-arsenic waters in West Bengal is known to be extremely patchy (AIP Steering Committee, 1991; CSME, 1997), presumably in part because of great variation in sedimentary characteristics and variations in abstraction depth. Estimates of the proportions of tubewells affected in West Bengal are not well-documented and difficult to assess. However, the indications are that the degree of contamination is not as severe in West Bengal as in the worst-affected districts of Bangladesh (e.g. Dhar et al. 1997). Certainly, the overall areal extent of contamination in West Bengal is less than in Bangladesh.

### *Taiwan*

The south-west coastal zone of Taiwan was perhaps the first area to be identified as a problem area for health effects arising from chronic arsenic exposure. Problems have also been identified subsequently in aquifers of NE Taiwan (Hsu et al., 1997). Awareness of the problem began during the 1960s (e.g. Tseng et al., 1968) and arsenic-related health problems have been well-documented by several workers since then (e.g. Chen et al., 1985). Taiwan is the classic area for the identification of black-foot disease but a number of other typical health problems, including internal cancers, have been described.

Kuo (1968) observed As concentrations in groundwater samples from south-west Taiwan ranging between 10 µg L<sup>-1</sup> and 1800 µg L<sup>-1</sup> (mean 500 µg L<sup>-1</sup>, n=126) and found that half the samples analysed had concentrations between 400 µg L<sup>-1</sup> and 700 µg L<sup>-1</sup>. A large study carried out by the Taiwan Provincial Institute of Environmental Sanitation established that 119 townships in the affected area had As concentrations in groundwater of >50 µg L<sup>-1</sup> and 58 townships had >350 µg L<sup>-1</sup> (Lo et al., 1977).

The high As concentrations are found in deep artesian well waters abstracted from sediments which include fine sands, muds and black shale (Tseng et al., 1968). The

groundwaters are therefore likely to be strongly reducing and hence may be analogous to groundwaters in the affected areas of Bangladesh and West Bengal. This is supported by the observation that the As is present largely as As(III) (Chen et al., 1994). However, the hydrogeochemistry of the area is poorly understood in detail. Groundwater from shallow wells in the area have low arsenic concentrations (Guo et al., 1994).

#### *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 on the order of one million with perhaps 150,000 in the Red River delta region. The majority of these are private tubewells. The aquifers exploited are of both Holocene and Pleistocene age.

In the Red River delta region, the Holocene sediments form the shallowest aquifer but these may be only 10–15 m deep and in some cases are entirely absent. Older Pleistocene sediments are then 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 and so the uppermost Holocene aquifer can behave as an unconfined aquifer. Normally the Holocene sediments are separated from the underlying Pleistocene sediments by a clay layer several metres 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 capital city of Hanoi is now largely dependent on groundwater for its public water supply.

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. UNICEF and EAWAG/CEC (Hanoi National University) are now carrying out extensive investigations to assess the scale of the problem. Preliminary results from Hanoi (Berg et al., 2000; Wegelin et al., 2000) indicate that there is a significant arsenic problem in shallow tubewells in the city, particularly in the south. There appears to be a seasonal pattern with significantly higher concentrations in the rainy season. This could be related to the local hydrology since there are significant interactions between the aquifer and the adjacent Red River.

Little is known about the arsenic concentrations in groundwater from the middle and upper parts of the Mekong delta (and into adjacent Cambodia and Laos) and other smaller alluvial aquifers in Vietnam but investigations are presently taking place.

#### *Northern China*

Arsenic occurrence has been found at high concentrations (in excess of the Chinese national standard of  $50 \mu\text{g L}^{-1}$ ) in

groundwaters from Inner Mongolia as well as Xinjiang and Shanxi Provinces (Figure 2.1; Wang, 1984; Wang and Huang, 1994; Niu et al., 1997). The first cases of As poisoning were recognised in Xinjiang Province in the early 1980s. Wang (1984) found As concentrations in groundwaters from the province at up to  $1200 \mu\text{g L}^{-1}$ . Wang and Huang (1994) reported As concentrations of between  $40 \mu\text{g L}^{-1}$  and  $750 \mu\text{g L}^{-1}$  in deep artesian groundwater from the Dzungaria Basin on the north side of the Tianshan Mountains (stretch of ca. 250 km). Arsenic concentrations in artesian groundwater from deep boreholes (up to 660 m) were found to increase with depth. Shallow (non-artesian) groundwaters had observed As concentrations between  $<10 \mu\text{g L}^{-1}$  and  $68 \mu\text{g L}^{-1}$ . The concentration of As in the saline Aibi Lake was reported as  $175 \mu\text{g L}^{-1}$ , while local rivers had concentrations between  $10 \mu\text{g L}^{-1}$  and  $30 \mu\text{g L}^{-1}$ . Artesian groundwater has been used for drinking in the region since the 1960s and chronic health problems have been identified as a result (Wang and Huang, 1994).

In Inner Mongolia, concentrations of As in excess of the Chinese national standard have been identified in groundwaters from aquifers in the Huhhot Basin, Ba Meng Region, and Tumet Plain (e.g. Luo et al., 1997; Ma et al., 1999). These areas include the cities of Boutou and Togto. In the Huhhot Basin, the problem is found in groundwaters from Holocene alluvial and lacustrine aquifers under highly reducing conditions and is worst in the lowest-lying parts of the basin (Smedley et al., 2000b). Concentrations have been found in the groundwaters at up to  $1500 \mu\text{g L}^{-1}$ , with a significant proportion of the As being present as As(III). Shallow groundwaters in the region are commonly saline as a result of evaporative concentration and many have high fluoride concentrations, although these do not generally correlate with high As concentrations. In the affected region, As-related disease has been identified by Luo et al. (1997). Recognised health effects include lung, skin and bladder cancer as well as prevalent keratosis and skin-pigmentation problems.

#### *Hungary and Romania*

Concentrations of As above  $50 \mu\text{g L}^{-1}$  have been identified in groundwaters from alluvial sediments in the southern part of the Great Hungarian Plain and in parts of neighbouring Romania (Figure 2.1). Concentrations up to  $150 \mu\text{g L}^{-1}$  (average  $32 \mu\text{g L}^{-1}$ ,  $n=85$ ) have been recorded by Varsányi et al. (1991). The Great Hungarian Plain, some  $110,000 \text{ km}^2$  in area, consists of a thick sequence of subsiding Quaternary sediments. Groundwaters vary from Ca-Mg- $\text{HCO}_3$ -type in the recharge areas of the basin margins to Na- $\text{HCO}_3$ -type in the low-lying discharge regions. Groundwaters in deep parts of the basin (80–560 m depth) with high As concentrations are reducing with high concentrations of Fe and  $\text{NH}_4$  and many have reported high concentrations of humic acid (up to  $20 \text{ mg L}^{-1}$ ; Varsányi et al., 1991). The groundwaters have highest As concentrations in the lowest parts of the basin, where the sediment is fine grained.

### 2.4.3 Arid oxidising environments

#### *Mexico*

The Lagunera Region of north central Mexico has a well-documented groundwater arsenic problem with significant resulting chronic health problems. The region is arid and groundwater is an important resource for potable supply. Groundwaters from the region are predominantly oxidising with neutral to high pH. Del Razo et al. (1990) quoted pH values for groundwaters in the range 6.3 to 8.9. They found As concentrations in the range  $8 \mu\text{g L}^{-1}$  to  $624 \mu\text{g L}^{-1}$  (average  $100 \mu\text{g L}^{-1}$ ,  $n=128$ ), with half the samples having concentrations greater than  $50 \mu\text{g L}^{-1}$ . They also noted that most (>90%) of the groundwater samples investigated had As present predominantly as As(V). Del Razo et al. (1994) determined the average concentration of As in drinking water from Santa Ana town in the region as  $404 \mu\text{g L}^{-1}$ . The estimated population exposed to As in drinking water with  $>50 \mu\text{g L}^{-1}$  is around 400,000 in Lagunera Region (Del Razo et al., 1990). Groundwaters from the region also have high concentrations of fluoride (up to  $3.7 \text{ mg L}^{-1}$ ; Cebrián et al., 1994).

High As concentrations have also been identified in groundwaters from the state of Sonora in north-west Mexico. Wyatt et al. (1998) found concentrations in the range  $2\text{--}305 \mu\text{g L}^{-1}$  (76 samples) with highest concentrations in groundwaters from the towns of Hermosillo, Etchojoa, Magdalena and Caborca. The As concentrations were also positively correlated with fluoride. Highest observed F concentration in the area was  $7.4 \text{ mg L}^{-1}$ . It is also believed that high arsenic groundwaters have been found in other parts of northern Mexico.

#### *Chile*

Health problems related to As in drinking water were first recognised in northern Chile in 1962. Typical symptoms included skin-pigmentation changes, keratosis, squamous-cell carcinoma (skin cancer), cardiovascular problems and respiratory disease (Zaldivar, 1974). More recently, As 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 As in drinking water. Since exposure was chiefly in the period 1955–1970, this pointed to a long latency period of cancer mortality. Other reported symptoms include impaired resistance to viral infection and lip herpes (Karcher et al., 1999).

High As concentrations have been recorded 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 (Atacama Desert) and water resources are limited. High As concentrations are accompanied by high salinity (due to evaporation) and high B concentrations. Arsenic values below  $100 \mu\text{g L}^{-1}$  in surface waters and groundwaters are apparently quite rare, and concentrations up to  $21,000 \mu\text{g L}^{-1}$  have been found. Karcher et al. (1999) quoted ranges of  $100 \mu\text{g L}^{-1}$  to  $1000 \mu\text{g L}^{-1}$  in raw waters

(average  $440 \mu\text{g L}^{-1}$ ). The As is present in the waters mostly as arsenate. However, the hydrogeochemistry of the aquifers of Chile is as yet poorly understood. The aquifers are composed of volcanogenic sediments though these have not been characterised in detail. In Antofagasta, concentrations of As in the sediments are ca.  $3.2 \text{ mg kg}^{-1}$  (Cáceres et al., 1992). Additional As exposure from smelting of copper ore has also been noted in northern Chile (Cáceres et al., 1992).

Arsenic treatment plants were installed in the towns of Antofagasta and Calama in 1969 to mitigate the problems. Today, the urban population of the major towns are supplied with treated water from the Rivers Toconce and Loa (Karcher et al., 1999) which is transported from the foot of the Andes mountains to the treatment works. However, rural communities still largely rely on untreated water supplies which contain As.

#### *Argentina*

The Chaco-Pampean Plain of central Argentina constitutes perhaps one of the largest regions of high-arsenic groundwaters known, covering around 1 million  $\text{km}^2$ . High concentrations of arsenic have been documented from Córdoba, La Pampa, Santa Fe and Buenos Aires Provinces in particular. Symptoms typical of chronic arsenic poisoning, including skin lesions and some internal cancers, have been recorded in these areas (e.g. Hoppenhayn-Rich et al., 1996). The climate is temperate with increasing aridity towards the west. Groundwaters are derived from Quaternary deposits of loess (mainly silt) with intermixed rhyolitic or dacitic volcanic ash (Nicolli et al., 1989; Nicolli and Merino, 2001; Smedley et al., 1998, 2001a). 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, sometimes many centimetres thick.

Nicolli et al. (1989) found arsenic concentrations in groundwaters from Córdoba in the range  $6\text{--}11500 \mu\text{g L}^{-1}$  (median  $255 \mu\text{g L}^{-1}$ ). Nicolli and Merino (2001) in a study of the Carcarañá River Basin (Córdoba and Santa Fe Provinces) found concentrations in the range  $<10\text{--}720 \mu\text{g L}^{-1}$  (mean  $201 \mu\text{g L}^{-1}$ ) and Smedley et al. (1998) found concentrations for groundwaters in La Pampa Province in the range  $<4\text{--}5280 \mu\text{g L}^{-1}$  (median  $145 \mu\text{g L}^{-1}$ ). The groundwaters often have high salinity and the arsenic concentrations are generally well-correlated with other anion and oxyanion elements (F, V,  $\text{HCO}_3$ , B, Mo). They are also predominantly oxidising and under the pertaining arid conditions, with pronounced silicate and carbonate weathering reactions, often have high pH values (range typically 7.0–8.7). Arsenic is dominantly present as As(V) (Smedley et al., 1998, 2001a). Metal oxides in the sediments (especially Fe and Mn oxides and hydroxides) are thought to be the main source of dissolved arsenic, caused by desorption under high-pH conditions (Smedley et al., 2000a) although derivation from volcanic glass has also been cited as a potential source (Nicolli et al., 1989; Nicolli and Merino, 2001).

## 2.4.4 Mixed oxidising and reducing environments

### *South-western USA*

Many areas have been identified in the USA with arsenic problems in groundwater (Welch et al., 2000). Most of the worst-affected and best-documented cases occur in the south-western states (Nevada, California, Arizona). However, within the last decade, parts of Maine, Michigan, Minnesota, South Dakota, Oklahoma and Wisconsin have been found with concentrations of arsenic exceeding  $10 \mu\text{g L}^{-1}$  and smaller areas of high arsenic groundwaters have been found in many other States. Much water analysis and research has been carried out in the USA, particularly in view of the reduction in the USEPA drinking-water limit and public concern over the possible long-term health effects. Occurrences in groundwater are therefore noted to be widespread, although of those reported, relatively few have significant numbers with concentrations greater than  $50 \mu\text{g L}^{-1}$ . A recent review of the analyses of some 17,000 water analyses from the USA suggested that around 40% exceeded  $1 \mu\text{g L}^{-1}$  and about 5% exceeded  $20 \mu\text{g L}^{-1}$  (percentage above  $50 \mu\text{g L}^{-1}$  unknown; Welch et al., 1999). The As is thought to derive from various sources, including natural dissolution/desorption reactions, geothermal water and mining activity. The natural occurrences of arsenic in groundwater are found under both reducing and oxidising conditions in different areas.

In Nevada, at least 1000 private wells have been found to contain As concentrations in excess of  $50 \mu\text{g L}^{-1}$  (Fontaine, 1994). The city of Fallon, Nevada (population 8000) is served by a groundwater supply with an As concentration of  $100 \mu\text{g L}^{-1}$  which for many years was supplied without treatment. Welch and Lico (1998) reported high As concentrations, often exceeding  $100 \mu\text{g L}^{-1}$  but with extremes up to  $2600 \mu\text{g L}^{-1}$ , in shallow groundwaters from the southern Carson Desert. These are apparently largely present under reducing conditions, having low dissolved-oxygen concentrations and high concentrations of dissolved organic C, Mn and Fe. The groundwaters also have associated high pH ( $>8$ ) and high concentrations of P (locally  $>4 \text{mg L}^{-1}$ ) and U ( $>100 \mu\text{g L}^{-1}$ ; Welch and Lico, 1998). The high As and U concentrations were thought to be due to evaporative concentration of groundwater, together with the influence of redox and desorption processes involving metal oxides.

In groundwaters from the Tulare Basin of the San Joaquin Valley, California, a large range of groundwater As concentrations from  $<1 \mu\text{g L}^{-1}$  to  $2600 \mu\text{g L}^{-1}$  have been found (Fujii and Swain, 1995). Redox conditions in the aquifers appear to be highly variable and high As concentrations are found in both oxidising and reducing conditions. The proportion of As present as As(III) increases in the groundwaters with increasing well depth. The groundwaters from the Basin are often strongly affected by evaporative concentration with resulting high TDS values. Many also have high concentrations of Se (up to  $1000 \mu\text{g L}^{-1}$ ), U (up to  $5400 \mu\text{g L}^{-1}$ ), B (up to  $73,000 \mu\text{g L}^{-1}$ ) and Mo (up to  $15,000 \mu\text{g L}^{-1}$ ; Fujii and Swain, 1995).

Robertson (1989) also noted the occurrence of high As concentrations in groundwaters under oxidising conditions in alluvial aquifers in the Basin and Range Province in Arizona. Arsenic in the groundwater is present predominantly as As(V) and was observed to correlate well with Mo, Se, V, F and pH. Of the 467 samples analysed, 7% had As concentrations greater than  $50 \mu\text{g L}^{-1}$ . Arsenic concentrations in the sediments ranged between  $2\text{--}88 \text{mg kg}^{-1}$ . Oxidising conditions were found to persist in the aquifers down to significant depths (600 m) despite significant groundwater age (up to 10,000 years old). The high arsenic (and other oxyanion) concentrations are a feature of the closed basins of the province.

## 2.4.5 Geothermal sources

Arsenic associated with geothermal waters has been reported in several areas, including hot springs from parts of the USA, Japan, Chile, Kamchatka, New Zealand, France and Dominica (e.g. Welch et al., 1988; Criaud and Fouillac, 1989). As noted above, parts of Salta Province of north-west Argentina also have thermal springs with high As concentrations.

In the USA, occurrences of As linked to geothermal sources have been summarised by Welch et al. (1988). Reported occurrences include Honey Lake Basin, California (As up to  $2600 \mu\text{g L}^{-1}$ ), Coso Hot Springs, California (up to  $7500 \mu\text{g L}^{-1}$ ), Imperial Valley, California (up to  $15,000 \mu\text{g L}^{-1}$ ), Long Valley, California (up to  $2500 \mu\text{g L}^{-1}$ ) and Steamboat Springs, Nevada (up to  $2700 \mu\text{g L}^{-1}$ ). Geothermal waters in Yellowstone National Park also contain As ( $<1\text{--}7800 \mu\text{g L}^{-1}$  in geysers and hot springs) and have given rise to high concentrations (up to  $370 \mu\text{g L}^{-1}$ ) in waters of the Madison River (Nimick et al., 1998). Geothermal inputs from Long Valley, California are believed to be responsible for high concentrations ( $20 \mu\text{g L}^{-1}$ ) of As in the Los Angeles Aqueduct which provides the water supply for the city of Los Angeles (Wilkie and Hering, 1998).

Welch et al. (1988) noted a general relationship between As and salinity in geothermal waters from the USA. Despite a lack of good positive correlation between As and Cl, geothermal waters with As greater than ca.  $1000 \mu\text{g L}^{-1}$  generally had Cl concentrations of  $800 \text{mg L}^{-1}$  or more. Wilkie and Hering (1998) noted the high alkalinity and pH values (average pH 8.3) as well as high Cl and B concentrations of geothermal waters in Long Valley.

Geothermal waters from Kyushu, Japan have been found to have As concentrations in the range  $500\text{--}4600 \mu\text{g L}^{-1}$  (26 samples). The waters are typically of Na-Cl type and the As is present almost entirely present as As(III) (Yokoyama et al., 1993).

Elevated As concentrations have been documented in waters from the geothermal areas of New Zealand. Robinson et al. (1995) found an As concentration in groundwater from the Wairakei geothermal field of  $3800 \mu\text{g L}^{-1}$  and found river and lake waters receiving inputs of geothermal water from the Wairakei, Broadlands, Orakei Korako and Atiamuri geothermal fields to have concentrations up to  $121 \mu\text{g L}^{-1}$ . Concentrations diminished significantly downstream away from the geothermal input areas.

#### 2.4.6 Arsenic mineralisation and mining-related arsenic problems

##### *Thailand*

Probably the worst recorded case of As poisoning related to mining activity is that of Ron Phibun District in Nakhon Si Thammarat Province of southern Thailand. Health problems were first recognised in the area in 1987. Around 1000 people have been diagnosed with As-related skin disorders, particularly in and close to Ron Phibun town (Williams, 1997). The affected area lies within the South-East Asian Tin Belt. Arsenic concentrations have been found at up to 5000  $\mu\text{g L}^{-1}$  in shallow groundwaters from Quaternary alluvial sediment that has been extensively dredged during mining operations. Deeper groundwaters from older limestone aquifers have been found to be less contaminated (Williams et al., 1996) although a few high As concentrations occur, presumably also as a result of contamination from the mine workings. The mobilisation of As is believed to be caused by oxidation of arsenopyrite, exacerbated by the former tin-mining activities. Recent mobilisation in groundwater has occurred during post-mining groundwater rebound (Williams, 1997).

##### *Ghana*

Several workers have reported the effects of mining activity on the environment in Ghana. Ghana is an important gold-mining country and mining has been active since the late 19<sup>th</sup> century. Today, Ghana produces about one third of the world's gold. The most important mining area is the Ashanti Region of central Ghana. As with Ron Phibun District in Thailand, the gold is associated with sulphide mineralisation, particularly arsenopyrite. Arsenic mobilises in the local environment as a result of arsenopyrite oxidation, induced (or exacerbated) by the mining activity. Around the town of Obuasi, high As concentrations have been noted in soils close to the mines and treatment works (Amasa, 1975; Bowell, 1992; 1993). Some high concentrations have also been reported in river waters close to the mining activity (Smedley et al., 1996).

Despite the presence of high As concentrations in the contaminated soils and in bedrocks close to the mines, Smedley et al. (1996) found that many of the groundwaters of the Obuasi area had low As concentrations, with a median concentration in tubewell waters of just 2  $\mu\text{g L}^{-1}$ . Some high concentrations were observed (up to 64  $\mu\text{g L}^{-1}$ ) but these were not generally in the vicinity of the mines or related directly to mining activity. Rather, the higher concentrations were found to be present in relatively reducing groundwaters (Eh 220–250 mV). Oxidising groundwaters,

especially from shallow hand-dug wells, had low As concentrations. This was taken to be due retardation of As by adsorption onto hydrous ferric oxides under the ambient low pH condition of the groundwaters (median pH 5.4 in dug wells; 5.8 in tubewells; Smedley et al., 1996).

##### *United States*

Arsenic contamination from mining activities has been identified in numerous areas of the USA, many of which have been summarised by Welch et al. (1988; 1999). Groundwater from some areas has been reported to have very high As concentrations locally (up to 48,000  $\mu\text{g L}^{-1}$ ). Well-documented cases of As contamination include the Fairbanks gold-mining district of Alaska (Wilson and Hawkins, 1978; Welch et al., 1988), the Coeur d'Alene Pb-Zn-Ag mining area of Idaho, (Mok and Wai, 1990), Leviathan Mine, California (Welch et al., 1988), Kelly Creek Valley, Nevada (Grimes et al., 1995), Clark Fork river, Montana (Welch et al., 2000) and Lake Oahe in South Dakota (Ficklin and Callender, 1989). Some mining areas of the USA have significant problems with acid mine drainage resulting from extensive oxidation of iron sulphides. In these, pH values can be extremely low and iron oxides dissolve and release bound arsenic. Iron Mountain has some extremely acidic mine-drainage waters with negative pHs and As concentrations in the milligram per litre range (Nordstrom et al., 2000).

In Wisconsin, high concentrations of As together with  $\text{SO}_4$  and many other trace metals (Fe, Cu, Co, Cd, Ni, Pb) and acidic conditions have been found in groundwaters affected by oxidation of secondary pyrite cements in sandstone as a result of aquifer dewatering (Schreiber et al., 2000; Weissbach et al., 2000). Arsenic concentrations up to 12  $\text{mg L}^{-1}$  have been recorded, the highest values occurring where water levels fluctuate around the zone of mineralisation. Recently oxidised material is leached into the groundwater during intervals of rising water levels.

##### *Other areas*

Many other areas have increased concentrations of As in soils, sediments and waters as a result of mining activity. Documented cases include the Lavrion region of Greece, associated with lead- and silver-mining activity (Komnitsas et al., 1995), the Zimapán Valley of Mexico, parts of south-west England (Thornton and Farago, 1997), South Africa, Zimbabwe and Bowen Island, British Columbia (Boyle et al., 1998). Although severe contamination of the environment has often been documented in these areas, the impact on groundwaters used for potable supply is usually minor.