

# Chapter 1. Source and behaviour of arsenic in natural waters

Pauline L Smedley and David G Kinniburgh

British Geological Survey, Wallingford, Oxon OX10 8BB, U.K.

1.1	Importance of arsenic in drinking water .....	2
1.2	Artenic in natural waters .....	2
1.2.1	Abundance and distribution .....	2
1.2.2	Aqueous speciation of arsenic.....	2
1.2.3	Redox and kinetics.....	13
1.3	Sources of arsenic .....	14
1.3.1	Minerals .....	14
1.3.2	Rocks, sediments and soils.....	17
1.3.3	The atmosphere .....	22
1.4	Mineral-water interactions .....	22
1.4.1	Relevance to arsenic mobilisation .....	22
1.4.2	Artenic interactions in sediments.....	26
1.4.3	Iron in reduced sediments and aquifers .....	27
1.4.4	Artenic release from soils and sediments following reduction .....	28
1.4.5	Transport of arsenic .....	29
1.5	Groundwater environments showing enhanced arsenic concentrations.....	30
1.5.1	World distribution of groundwater arsenic problems .....	30
1.5.2	Reducing environments .....	35
1.5.3	Arid oxidising environments.....	40
1.5.4	Mixed oxidising and reducing environments .....	43
1.5.5	Geothermal sources .....	44
1.5.6	Artenic mineralisation and mining-related arsenic problems .....	45
1.6	Common features of groundwater arsenic problem areas .....	46
1.6.1	A hydrogeochemical perspective.....	46
1.6.2	The source term.....	46
1.6.3	The necessary geochemical trigger .....	47
1.6.4	The hydrogeological dimension – aquifer flushing .....	52
1.7	Outstanding questions and further needs .....	54
1.7.1	Field analytical methods for arsenic determination.....	54
1.7.2	Surveys of groundwater quality.....	55
1.7.3	Will the problem groundwaters get better or worse with time? .....	55
1.7.4	Transport under natural flow conditions .....	56
1.7.5	Interaction of arsenic with sediments .....	56
1.8	Strategy for locating arsenic problems in groundwater.....	57
1.9	Non-technical Summary .....	59
	Acknowledgments.....	61

## 1.1 Importance of arsenic in drinking water

Arsenic (As) 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, the use of arsenical pesticides, herbicides and crop desiccants and the use of arsenic as an additive to livestock feed, particularly for poultry. Although the use of arsenical products such as pesticides and herbicides has decreased significantly in the last few decades, their use for wood preservation is still common. The impact on the environment of the use of arsenical compounds, at least locally, will remain for some years.

Of the various sources of arsenic in the environment, drinking water probably poses the greatest threat to human health. Airborne arsenic, particularly through occupational exposure, has also given rise to known health problems in some areas.

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, high concentrations are mainly found in groundwaters. These are where the greatest number of, as yet unidentified, sources are likely to be found. This review therefore focuses on the factors controlling arsenic concentrations in groundwaters.

Following the accumulation of evidence for the chronic toxicological effects of As in drinking water, recommended and regulatory limits of many authorities are being reduced. 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 be lower still. The US-EPA limit was also reduced from  $50 \mu\text{g l}^{-1}$  to  $10 \mu\text{g l}^{-1}$  in January 2001 following prolonged debate over the most appropriate limit. The EC maximum admissible concentration (MAC) for As in drinking water is also to be reduced to  $10 \mu\text{g l}^{-1}$ . The Japanese limit for drinking water is  $10 \mu\text{g l}^{-1}$  and the interim maximum acceptable concentration for Canadian drinking water is  $25 \mu\text{g l}^{-1}$ .

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 and 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.

## 1.2 Arsenic in natural waters

### 1.2.1 Aqueous speciation

Arsenic is perhaps unique among the heavy metalloids and oxyanion-forming elements (e.g. arsenic, selenium, antimony, molybdenum, vanadium, chromium, uranium, rhenium) in its sensitivity to mobilisation at the pH values typically found in groundwaters (pH 6.5–8.5) and under both oxidising and reducing conditions. Arsenic can occur in the environment in several oxidation states

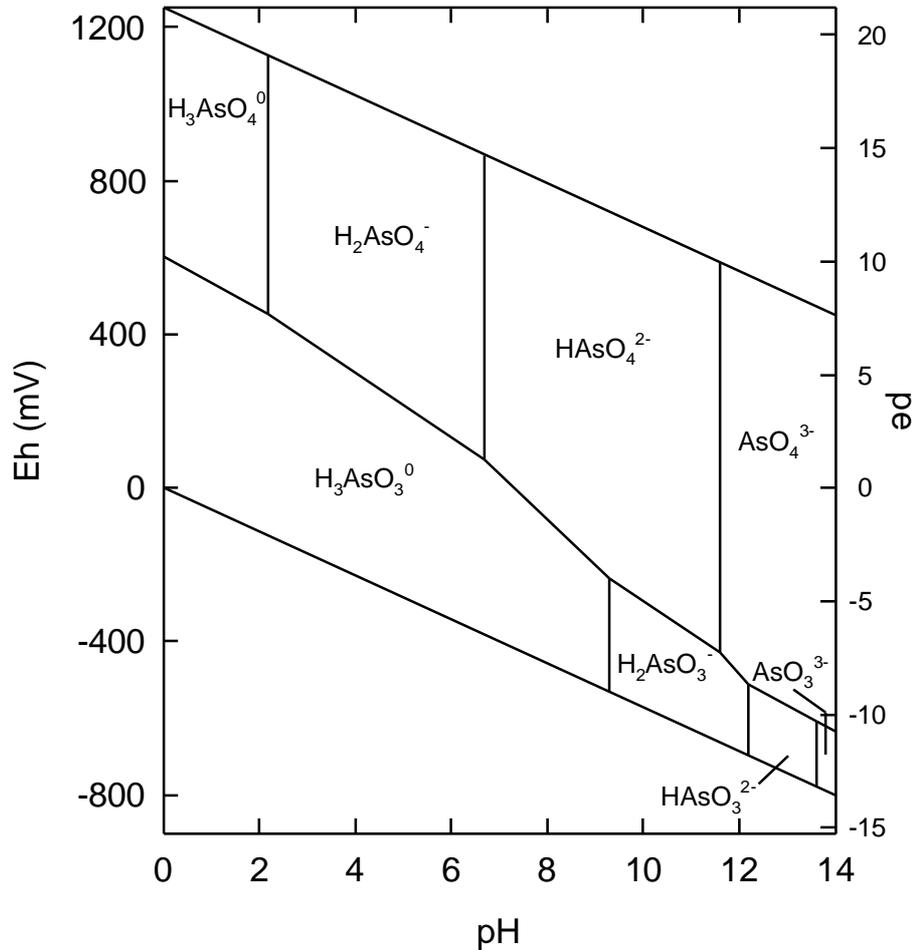
(-3, 0, +3 and +5) but in natural waters is mostly found in inorganic form as oxyanions of trivalent arsenite (As(III)) or pentavalent arsenate (As(V)). Organic arsenic forms may be produced by biological activity, mostly in surface waters, but are rarely quantitatively important. Organic forms may however occur where waters are significantly impacted by industrial pollution.

Most toxic trace metals occur in solution as cations (e.g.  $\text{Pb}^{2+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Cd}^{2+}$ ,  $\text{Co}^{2+}$ ,  $\text{Zn}^{2+}$ ) which generally become increasingly insoluble as the pH increases. At the near-neutral pH typical of most groundwaters, the solubility of most trace-metal cations is severely limited by precipitation as, or coprecipitation with, an oxide, hydroxide, carbonate or phosphate mineral, or more likely by their strong adsorption to hydrous metal oxides, clay or organic matter. In contrast, most oxyanions including arsenate tend to become less strongly sorbed as the pH increases (Dzombak and Morel, 1990). Under some conditions at least, these anions can persist in solution at relatively high concentrations (tens of  $\mu\text{g l}^{-1}$ ) even at near-neutral pH values. Therefore the oxyanion-forming elements such as Cr, As, U and Se are some of the most common trace contaminants in groundwaters.

However, relative to the other oxyanion-forming elements, arsenic is among the most problematic in the environment because of its relative mobility over a wide range of redox conditions. Selenium is mobile as the selenate ( $\text{SeO}_4^{3-}$ ) oxyanion under oxidising conditions but is immobilized under reducing conditions either due to the stronger adsorption of its reduced form, selenite ( $\text{SeO}_3^{3-}$ ), or due to its reduction to the metal. Chromium can similarly be mobilized as stable Cr(VI) oxyanion species under oxidising conditions, but forms cationic Cr(III) species in reducing environments and hence behaves like other trace cations (i.e. is relatively immobile at near-neutral pH values). Other oxyanions such as molybdate, vanadate, uranyl and rhenate also appear to be less mobile under reducing conditions. In sulphur-rich, reducing environments, many of the trace metals also form insoluble sulphides. By contrast, arsenic is perhaps unique in being relatively mobile under reduced conditions. It can be found at concentrations in the  $\text{mg l}^{-1}$  range when all other oxyanion-forming metals are present in the  $\mu\text{g l}^{-1}$  range.

Redox potential (Eh) and pH are the most important factors controlling arsenic speciation. Under oxidising conditions,  $\text{H}_2\text{AsO}_4^-$  is dominant at low pH (less than about pH 6.9), whilst at higher pH,  $\text{HAsO}_4^{2-}$  becomes dominant ( $\text{H}_3\text{AsO}_4^0$  and  $\text{AsO}_4^{3-}$  may be present in extremely acidic and alkaline conditions respectively). Under reducing conditions at pH less than about pH 9.2, the uncharged arsenite species  $\text{H}_3\text{AsO}_3^0$  will predominate (Figure 1.1; Brookins, 1988; Yan *et al.*, 2000). The distributions of the species as a function of pH are given in Figure 1.2. In practice, most studies in the literature report speciation data without consideration of the degree of protonation. In the presence of extremely high concentrations of reduced sulphur, dissolved arsenic-sulphide species can be significant. Reducing, acidic conditions favour precipitation of orpiment ( $\text{As}_2\text{S}_3$ ), realgar ( $\text{AsS}$ ) or other sulphide minerals containing coprecipitated arsenic. Therefore high arsenic waters are not expected where there is a high concentration of free sulphide (Moore *et al.*, 1988). Thioarsenite species will be more important at neutral and alkaline pH in the presence of very high sulphide concentrations.

**Figure 1.1 Eh-pH diagram of aqueous arsenic species in the system As–O<sub>2</sub>–H<sub>2</sub>O at 25°C and 1 bar total pressure**



PENDING

**Figure 1.2 Arsenic speciation (arsenite and arsenate) against pH**

### 1.2.2 Abundance and distribution

Concentrations of arsenic in fresh water vary by more than four orders of magnitude (Table 1.1) depending on the source of arsenic, the amount available and the local geochemical environment. Under natural conditions, the greatest range and the highest concentrations of arsenic are found in groundwaters as a result of the strong influence of water-rock interactions and the greater tendency in aquifers for the physical and geochemical conditions to be favourable for arsenic mobilization and accumulation. The range of concentrations for many water bodies is large and hence

'typical' values are difficult to derive. Many studies of arsenic reported in the literature have also preferentially targeted known problem areas and hence reported ranges are often extreme and unrepresentative of natural waters as a whole. Nonetheless, the following compilation of data for ranges of arsenic concentrations found in various parts of the hydrosphere and lithosphere gives a broad indication of the expected concentration ranges and their variation in the environment.

#### *Atmospheric precipitation*

Arsenic enters the atmosphere through inputs from wind erosion, volcanic emissions, low-temperature volatilisation from soils, marine aerosols and pollution and is returned to the earth's surface by wet and dry deposition. The most important anthropogenic inputs are from smelter operations and fossil-fuel combustion. The arsenic appears to consist of mainly  $\text{As(III)}_2\text{O}_3$  dust particles (Cullen and Reimer, 1989). Nriagu and Pacyna (1988) estimated that anthropogenic sources of atmospheric arsenic (around 18,800 tonnes  $\text{yr}^{-1}$ ) amounted to around 30% of the global atmospheric arsenic flux. While it is accepted that these anthropogenic sources have an important impact on airborne arsenic compositions, their influence on the overall arsenic cycle is not well established.

Baseline concentrations of arsenic in rainfall and snow in rural areas are invariably low at typically less than  $0.03 \mu\text{g l}^{-1}$  (Table 1.1). Concentrations in areas affected by smelter operations, coal burning and volcanic emissions are generally higher. Andreae (1980) found rainfall potentially affected by smelting and coal burning to have arsenic concentrations of around  $0.5 \mu\text{g l}^{-1}$  (Table 1.1), although higher concentrations (average  $16 \mu\text{g l}^{-1}$ ) have been found in rainfall collected in Seattle some 35 km downwind of a copper smelter (Crecelius, 1975). Values given for Arizona snowpacks (Table 1.1; Barbaris and Betterton, 1996) are also probably slightly above baseline concentrations because of potential inputs of airborne As from smelters, power plants and soil dust. In general however, sources of airborne As in most industrialized nations are limited as a result of air-pollution control measures. Unless significantly contaminated with industrial sources of As, atmospheric precipitation contributes little As to surface and groundwater bodies.

#### *River water*

Baseline concentrations of arsenic in river waters are also low (in the region of  $0.1\text{--}0.8 \mu\text{g l}^{-1}$  but up to ca.  $2 \mu\text{g l}^{-1}$ ; Table 1.1). They vary according to the composition of the surface recharge, the contribution from baseflow and the bedrock lithology. Concentrations at the low end of the range have been found in rivers draining As-poor bedrocks. Seyler and Martin (1991) found average river concentrations as low as  $0.13 \mu\text{g l}^{-1}$  in the Krka region of Yugoslavia where the bedrock is As-poor karstic limestone (Table 1.1). Lenvik *et al.* (1978) also found low average concentrations of about  $0.25 \mu\text{g l}^{-1}$  in rivers draining basement rocks in Norway, the lowest being in catchments on Precambrian rocks. Waslenchuk (1979) found concentrations in river waters from the south-eastern USA in the range  $0.15\text{--}0.45 \mu\text{g l}^{-1}$  (Table 1.1).

<b>Water body and location</b>	<b>Arsenic concentration average or range (<math>\mu\text{g l}^{-1}</math>)</b>	<b>Reference</b>
<b>Rain water:</b>		
<i>Baseline:</i>		
Maritime	0.02	Andreae (1980)
Terrestrial (w USA)	0.013–0.032	Andreae (1980)
Coastal (Mid-Atlantic, USA)	0.1 (<0.005–1.1)	Scudlark and Church (1988)
Snow (Arizona)	0.14 (0.02–0.42)	Barbaris and Betterton (1996)
<i>Non-baseline:</i>		
Terrestrial rain	0.46	Andreae (1980)
Seattle rain, impacted by copper smelter	16	Creelius (1975)
<b>River water:</b>		
<i>Baseline:</i>		
Various	0.83 (0.13–2.1)	Andreae <i>et al.</i> (1983); Froelich <i>et al.</i> (1985); Seyler and Martin (1991)
Norway	0.25 (<0.02–1.1)	Lenvik <i>et al.</i> (1978)
South-east USA	0.15–0.45	Waslenchuk (1979)
USA	2.1	Sonderegger and Ohguchi (1988)
Dordogne, France	0.7	Seyler and Martin (1990)
Po River, Italy	1.3	Pettine <i>et al.</i> (1992)
Polluted European rivers	4.5–45	Seyler and Martin (1990)
River Danube, Bavaria	3 (1–8)	Quentin and Winkler (1974)
Schelde catchment, Belgium	0.75–3.8 (up to 30)	Andreae and Andreae (1989)
High-As groundwater influenced: Northern Chile Northern Chile	190–21800 400–450	Cáceres <i>et al.</i> (1992) Sancha (1999)
Córdoba, Argentina	7–114	Lerda and Prosperi (1996)
<i>Geothermal influenced:</i> Sierra Nevada, USA Waikato, New Zealand Madison and Missouri Rivers, USA	0.20–264 32 (28–36) 44 (19–67) 10–370	Benson and Spencer (1983) McLaren and Kim (1995) Robinson <i>et al.</i> (1995) Nimick <i>et al.</i> (1998)
<i>Mining influenced:</i> Ron Phibun, Thailand	218 (4.8–583)	Williams <i>et al.</i> (1996)

<b>Water body and location</b>	<b>Arsenic concentration average or range (<math>\mu\text{g l}^{-1}</math>)</b>	<b>Reference</b>
Ashanti, Ghana	284 (<2–7900)	Smedley <i>et al.</i> (1996)
British Columbia, Canada	17.5 (<0.2–556)	Azcue <i>et al.</i> (1994)
<b>Lake water:</b>		
<i>Baseline</i> British Columbia	0.28 (<0.2–0.42)	Azcue <i>et al.</i> (1994; 1995)
Ontario	0.7	Azcue and Nriagu (1995)
France	0.73–9.2 (high Fe)	Seyler and Martin (1989)
Japan	0.38–1.9	Baur and Onishi (1969)
Sweden	0.06–1.2	Reuther (1992)
<i>Geothermal influenced:</i> Western USA	0.38–1000	Benson and Spencer (1983)
<i>Mining influenced:</i> Northwest Territories, Canada Ontario, Canada	270 (64–530) 35–100	Bright <i>et al.</i> (1996) Azcue and Nriagu (1995)
<b>Estuarine water:</b>		
<i>Baseline</i>		
Oslofjord, Norway	0.7–2.0	Abdullah <i>et al.</i> (1995)
Saanich Inlet, British Columbia	1.2–2.5	Peterson and Carpenter (1983)
Rhône Estuary, France	2.2 (1.1–3.8)	Seyler and Martin (1990)
Krka Estuary, Yugoslavia	0.13–1.8	Seyler and Martin (1991)
<i>Mining and industry influenced</i> Loire Estuary, France Tamar Estuary, UK Schelde Estuary, Belgium	up to 16 2.7–8.8 1.8–4.9	Seyler and Martin (1990) Howard <i>et al.</i> (1988) Andreae and Andreae (1989)
<b>Seawater:</b>		
Deep Pacific and Atlantic Coastal Malaysia Coastal Spain Coastal Australia	1.0–1.8 1.0 (0.7–1.8) 1.5 (0.5–3.7) 1.3 (1.1–1.6)	Cullen and Reimer (1989) Yusof <i>et al.</i> (1994) Navarro <i>et al.</i> (1993) Maher (1985)
<b>Groundwater:</b>		
Baseline UK	<0.5–10	Edmunds <i>et al.</i> (1989)
As-rich provinces (e.g. Bengal Basin, Argentina, Mexico, northern China, Taiwan, Hungary)	10–5000	See section 1.5

<b>Water body and location</b>	<b>Arsenic concentration average or range (<math>\mu\text{g l}^{-1}</math>)</b>	<b>Reference</b>
Mining-contaminated groundwaters	50–5000	See section 1.5.6
Geothermal water	<10–50,000	Baur and Onishi (1969), White <i>et al.</i> , (1963), Ellis and Mahon (1977)
Arsenical herbicide plant, Texas	408,000	Kuhlmeier (1997)
<b>Mine drainage:</b>		
Various, USA	<1–34,000	Plumlee <i>et al.</i> (1999)
Iron Mountain	up to 850,000	Nordstrom and Alpers (1999)
Ural Mountains	400,000	Gelova (1977)
<b>Sediment pore water:</b>		
Baseline, Swedish Estuary	1.3–166	Widerlund and Ingri (1995)
Baseline, clays, Saskatchewan, Canada	3.2–99	Yan <i>et al.</i> (2000)
Baseline, Amazon shelf sediments	up to 300	Sullivan and Aller (1996)
Mining-contam'd, British Columbia	50–360	Azcue <i>et al.</i> (1994)
Tailings impoundment, Ontario, Canada	300–100,000	McCreadie <i>et al.</i> (2000)
<b>Oilfield and related brine:</b>		
Ellis Pool, Alberta, Canada	230	White <i>et al.</i> (1963)
Searles Lake brine, California	up to 243,000	

Relatively high concentrations of naturally-occurring arsenic can occur in some areas as a result of inputs from geothermal sources or high-arsenic groundwaters. Arsenic concentrations in river waters from geothermal areas have been reported typically at around 10–70  $\mu\text{g l}^{-1}$  (e.g. western USA and New Zealand; McLaren and Kim, 1995; Robinson *et al.*, 1995; Nimick *et al.*, 1998; Table 1.1), although higher concentrations have been found. Nimick *et al.* (1998) for example found arsenic concentrations up to 370  $\mu\text{g l}^{-1}$  in Madison River water (Wyoming and Montana) as a result of geothermal inputs from the Yellowstone geothermal system. Wilkie and Hering (1998) also found concentrations in the range 85–153  $\mu\text{g l}^{-1}$  in Hot Creek (tributary of the Owens River, California). Some river waters affected by geothermal activity show distinct seasonal variations in arsenic concentration. Concentrations in the Madison River have been noted to be highest during low-flow conditions. This has been attributed to a greater contribution of geothermal water during times of low flow and dilution from spring runoff at times of high flow (Nimick *et al.*, 1998). In the Waikato river system of New Zealand, As maxima were found in the summer months. These increases were linked to temperature-controlled microbial reduction of As(V) to As(III) with consequent increased mobility of As(III) (McLaren and Kim, 1995).

Increased concentrations are also reported in some river waters from arid areas where the surface water is dominated by river baseflow, i.e. by water flowing into the surface water from the surrounding rocks. The resulting surface waters often have a high pH and alkalinity. For example, in surface waters from the Loa River Basin of northern Chile (Antofagasta area, Atacama desert), Cáceres *et al.* (1992) found concentrations of naturally-occurring arsenic ranging between 190–21,800  $\mu\text{g l}^{-1}$ . The high arsenic concentrations correlated well with salinity and were presumably related to evaporative concentration of baseflow-dominated river water. Increased arsenic concentrations (up to 114  $\mu\text{g l}^{-1}$ ) have also been reported in river waters from central Argentina where regional groundwater-arsenic concentrations (and pH, alkalinity) are high (Lerda and Prospero, 1996).

Although bedrock inevitably has an influence on river-water arsenic concentrations, concentrations in rivers with more typical pH and alkalinity values (c. pH 5–7, alkalinity  $<100 \text{ mg l}^{-1}$  as  $\text{HCO}_3$ ) do not show the extremely high concentrations found in groundwaters because of oxidation and adsorption of arsenic species onto the river sediments as well as dilution by surface recharge and runoff. Arsenic concentrations in seven river water samples from Bangladesh have been reported in the range  $<0.5\text{--}2.7 \mu\text{g l}^{-1}$  but with one sample having a high concentration of  $29 \mu\text{g l}^{-1}$  (BGS and DPHE, 2001). The highest value observed is significantly above world-average baseline concentrations (Table 1.1) but is much lower than some of the values found in the groundwaters (Section 1.5).

Significant increases in arsenic concentrations of river waters may also occur as a result of pollution from industrial or sewage effluents. Andreae and Andreae (1989) found concentrations of up to  $30 \mu\text{g l}^{-1}$  in water from the River Zenne, Belgium which is affected by inputs from urban and industrial sources, particularly sewage. However, the concentration of arsenic in water from most of the catchment was in the range  $0.75\text{--}3.8 \mu\text{g l}^{-1}$  and not significantly different from baseline concentrations. Durum *et al.* (1971) reported arsenic concentrations in 727 samples of surface waters from the United States. While 79% of the samples had As concentrations below the (rather high) detection limit of  $10 \mu\text{g l}^{-1}$ , the highest observed concentration,  $1,100 \mu\text{g l}^{-1}$ , was found in Sugar Creek, South Carolina, downstream of an industrial complex.

Arsenic can also be derived from mine wastes and mill tailings. Azcue and Nriagu (1995) found baseline concentrations in the Moira River, Ontario of  $0.7 \mu\text{g l}^{-1}$  upstream of the influence of tailings from gold-mine workings. Downstream, concentrations increased to  $23 \mu\text{g l}^{-1}$ . Azcue *et al.* (1994) found concentrations up to  $556 \mu\text{g l}^{-1}$  (average  $17.5 \mu\text{g l}^{-1}$ ) in streams adjacent to tailings deposits in British Columbia. Williams *et al.* (1996) and Smedley *et al.* (1996) noted high arsenic concentrations (typically around  $200\text{--}300 \mu\text{g l}^{-1}$ ) in surface waters affected respectively by tin- and gold-mining activities. Though often involving notable increases above baseline concentrations, such anomalies tend to be relatively localised around the pollution source, principally because of the strong adsorption affinity of oxide minerals, especially iron oxide, for arsenic under oxidising, neutral to mildly acidic conditions.

#### *Lake water*

Concentrations of arsenic in lake waters are typically close to or lower than those found in river water. Baseline concentrations have been found at  $<1 \mu\text{g l}^{-1}$  in Canada (Azcue and Nriagu, 1995; Azcue *et al.*, 1995). As with river waters, increased concentrations are found in lake waters affected by geothermal water and by mining activity. Ranges of typically  $100\text{--}500 \mu\text{g l}^{-1}$  have been reported in some mining areas and up to  $1000 \mu\text{g l}^{-1}$  in geothermal areas (Table 1.1). Arsenic concentrations in mining-affected lake waters are not always high however, as removal from solution can be achieved effectively by adsorption onto iron oxides under neutral to mildly acidic conditions. Azcue *et al.* (1994), for example, found arsenic concentrations in Canadian lake waters affected by mining effluent similar to those not affected by mining effluent, in each case about  $0.3 \mu\text{g l}^{-1}$ .

High arsenic concentrations are also found in some alkaline closed-basin lakes as a result of extreme evaporation and/or geothermal inputs. Mono Lake in the California, USA, for example, has

concentrations of dissolved arsenic of 10–20 mg l<sup>-1</sup>, with pH values in the range 9.5–10 as a result of inputs from geothermal springs and the weathering of volcanic rocks followed by evaporation (Maest *et al.*, 1992).

There is also much evidence for stratification of arsenic concentrations in some lake waters. Azcue and Nriagu (1995) found that concentrations increased with depth (up to 10 m) in lake waters from Ontario, probably because of an increasing ratio of As(III) to As(V) with depth and an influx of mining-contaminated sediment pore waters at the sediment-water interface. The concentrations were higher in summer when the proportion of As(III) was observed to be higher. Depleted oxygen levels in the bottom lake waters as a result of biological productivity during the summer months are a likely cause of the higher arsenic concentrations in the deeper lake waters.

#### *Seawater and estuaries*

Average arsenic concentrations in open seawater usually show little variation and are typically around 1.5 µg l<sup>-1</sup> (Table 1.1).

Concentrations in estuarine water are more variable as a result of varying river inputs and salinity or redox gradients but are also usually low, at typically less than 4 µg l<sup>-1</sup> under natural conditions. Peterson and Carpenter (1983) found concentrations between 1.2–2.5 µg l<sup>-1</sup> in waters from Saanich Inlet, British Columbia. Values less than 2 µg l<sup>-1</sup> were found in Oslofjord, Norway (Abdullah *et al.*, 1995; Table 1.1). Concentrations are commonly higher when riverine inputs are affected by industrial or mining effluent (e.g. Tamar, Schelde, Loire Estuaries; Table 1.1) or by geothermal water. Unlike some other trace elements such as boron, saline intrusion of seawater into an aquifer is unlikely to lead to a significant increase of arsenic in the affected groundwater.

Arsenate shares many chemical characteristics with phosphate and hence in oxic marine and estuarine waters, depletions in phosphate in biologically productive surface waters are mirrored by depletions in arsenate. Arsenate concentration minima often coincide with photosynthetic maxima evidenced by high concentrations of chlorophyll a (Cullen and Reimer, 1989).

Several studies have noted variations in the behaviour of arsenic during estuarine mixing. Some have reported conservative behaviour. In the unpolluted Krka Estuary of Yugoslavia, Seyler and Martin (1991) observed a linear increase in total As with increasing salinity ranging from 0.13 µg l<sup>-1</sup> in fresh waters to 1.8 µg l<sup>-1</sup> offshore (i.e. seawater value). However, other studies have observed non-conservative behaviour (departures from simple mixing) in estuaries due to processes such as diffusion from sediment pore waters, coprecipitation with iron oxides or anthropogenic inputs (e.g. Andreae *et al.*, 1983; Andreae and Andreae, 1989). The flocculation of iron oxides at the freshwater-saline interface is important as a result of increases in pH and salinity. This can lead to major decreases in the arsenic flux to the oceans (Cullen and Reimer, 1989).

#### *Groundwater*

Background concentrations of arsenic in groundwater are in most countries less than 10 µg l<sup>-1</sup> (e.g. Edmunds *et al.*, 1989 for the UK; Welch *et al.*, 2000 for the USA) and sometimes substantially lower. However, values quoted in the literature show a very large range from <0.5–5000 µg l<sup>-1</sup> (i.e. four orders of magnitude). This range occurs under natural conditions. High concentrations of arsenic are found in groundwater in a variety of environments. This includes both oxidising (under conditions of high pH) and reducing aquifers and in areas affected by geothermal, mining and industrial activity. Evaporative concentration can also increase concentrations substantially. Most high-arsenic groundwater provinces are the result of natural occurrences of arsenic. Cases of mining-induced arsenic pollution are numerous in the literature but tend to be localised. Cases of industrially-induced arsenic pollution (including that from agriculture) may be severe locally (Table 1.1) but occurrences are relatively rare. Groundwater provinces with naturally-occurring As problems are discussed in more detail in Section 1.5.

### *Mine drainage*

Under the extremely acid conditions of some acid mine drainage (AMD), which can have negative pH values (Nordstrom *et al.*, 2000), high concentrations of a wide range of solutes are found, including iron and arsenic. The highest reported arsenic concentration of  $850,000 \mu\text{g l}^{-1}$  is from an acid seep in the Richmond mine at Iron Mountain, California (Nordstrom and Alpers, 1999). In a compilation of some 180 samples of mine drainage from the USA, Plumlee *et al.* (1999) reported concentrations ranging from detection limits ( $<1 \mu\text{g l}^{-1}$  or more) to  $340,000 \mu\text{g l}^{-1}$ , again the highest values being from the Richmond mine. Gelova (1977) also reported an arsenic concentration of  $400,000 \mu\text{g l}^{-1}$  from the Ural Mountains. Dissolved arsenic in acid mine waters is rapidly removed as the iron is oxidised and precipitated and the arsenic scavenged through adsorption. At Iron Mountain, an efficient neutralization plant removes the arsenic and other metals for safe disposal.

### *Sediment pore waters*

Some high concentrations of As have been found in pore waters extracted from unconsolidated sediments and often form sharp contrasts to the concentrations observed in overlying surface waters (e.g. Belzile and Tessier, 1990). Widerlund and Ingri (1995) found concentrations in the range  $1.3\text{--}166 \mu\text{g l}^{-1}$  in pore waters from the Kalix River estuary of northern Sweden. Yan *et al.* (2000) found As concentrations in the range  $3.2\text{--}99 \mu\text{g l}^{-1}$  in pore waters from clay sediments in Saskatchewan, Canada (Table 1.1). Even higher concentrations can be found in pore waters from sediments affected by mining contamination (tailings, mineral-rich deposits). McCreadie *et al.* (2000) reported As concentrations up to  $100,000 \mu\text{g l}^{-1}$  in porewaters extracted from tailings in Ontario (Table 1.1). In such cases, high pore water arsenic concentrations are most likely to be linked to the strong redox gradients that occur below the sediment-water interface often over depth scales of centimeters. Burial of fresh organic matter and the slow diffusion of oxygen through the sediment leads to reducing conditions just below the sediment-water interface. This encourages the reduction of As(V) and desorption from Fe and Mn oxides, as well as reductive dissolution of these minerals. There is much evidence for cycling of As between shallow sediment pore waters and overlying surface waters in response to temporal variations in redox conditions.

Sullivan and Aller (1996) carried out an elegant study of the cycling of arsenic in shallow sediments from the offshore shelf of the Amazon situated far from population centres. They measured pore water As and Fe concentration profiles as well as sediment As and Fe(II) concentrations. There was frequently a well-correlated peak in dissolved As and Fe concentrations some 50 cm to 150 cm beneath the surface with As concentrations in the peak averaging about  $135 \mu\text{g l}^{-1}$  and reaching a maximum of  $300 \mu\text{g l}^{-1}$ , much greater than from marine coastal environments. The dissolved As/Fe molar ratio varied but was typically about 1:300. Dissolved As varied inversely with easily-leachable (6M HCl) As in the sediment and increased directly with solid-phase Fe(II). In these sediments, Fe oxides were believed to be a much more important source of As than Mn oxides.

### *Oilfield and other brines*

Only limited data are available for arsenic in oilfield and other brines, but some published accounts suggest that concentrations can be very high. White *et al.* (1963) reported a dissolved arsenic concentration of  $230 \mu\text{g l}^{-1}$  in a sodium-bicarbonate groundwater from a 1000 m deep oilfield well from Ellis Pool, Alberta, Canada. They also reported a concentration of  $5800 \mu\text{g l}^{-1}$  arsenic in a sodium-chloride-dominated brine from Tisakürt, Hungary. Composite brines from the interstices of salt deposits from Searles Lake, California, have arsenic concentrations up to  $243 \text{ mg l}^{-1}$  (Na  $119 \text{ g l}^{-1}$ ; White *et al.*, 1963; Table 1.1).

## **1.2.3 Distribution of arsenic species in water bodies**

Most studies of arsenic speciation in natural waters attempt to separate the inorganic species into As(III) and As(V) usually by chromatographic separation or by making use of the relatively slow reduction of As(V) by sodium borohydride. Some studies also measure the organic arsenic species

too. The sampling and analytical techniques required are far from trivial and not yet well-established (Edwards *et al.*, 1998). Separation of species may be carried out in the field to avoid the problem of preserving species for later laboratory analysis. Alternatively, preservation with HCl and ascorbic acid has been successful.

In rain water, oxidation states will vary according to the arsenic source. This is likely to be dominantly As(III)<sub>2</sub>O<sub>3</sub> when derived from smelters, coal burning and volcanic sources, although organic species may be derived by volatilization from soils, arsine (As(-III)H<sub>3</sub>) may derive from landfills and reducing soils such as peats and arsenate may be derived from marine aerosols. Reduced forms will undergo oxidation by O<sub>2</sub> in the atmosphere and reactions with atmospheric SO<sub>2</sub> or O<sub>3</sub> are likely (Cullen and Reimer, 1989).

In oxic seawater, the As is typically dominated by As(V), though some As(III) is invariably present and becomes of increasing importance in anoxic bottom waters. Ratios of As(V)/As(III) are typically in the range 10–100 in open seawater (Andreae, 1979; Peterson and Carpenter, 1983; Pettine *et al.*, 1992). Arsenic(V) should exist mainly as HAsO<sub>4</sub><sup>2-</sup> and H<sub>2</sub>AsO<sub>4</sub><sup>-</sup> in the pH range of seawater (pH around 8.2; Figures 1.1. and 1.2) and As(III) will exist mainly as the neutral species H<sub>3</sub>AsO<sub>3</sub>. Relatively high proportions of H<sub>3</sub>AsO<sub>3</sub> are found in surface waters. These coincide with zones of primary productivity. Increases in organic arsenic species have also been recorded in these zones as a result of methylation reactions by phytoplankton (Cullen and Reimer, 1989).

The relative proportions of arsenic species are more variable in estuarine waters because of variable redox and salinity, and terrestrial inputs (Howard *et al.*, 1988; Abdullah *et al.*, 1995). However, they are still dominated by As(V). Andreae and Andreae (1989) found As(V)/As(III) ratios varying between 5–50 in the Schelde Estuary of Belgium with the lowest ratios in anoxic zones where inputs of industrial effluent had an impact. Elevated proportions of As(III) also result from inputs of mine effluent (Klumpp and Peterson, 1979). Seasonal variations in As concentration and speciation have been noted in estuaries (Riedel, 1993). In seasonally anoxic estuarine waters, variations in the relative proportions of As(III) and As(V) can be large. Peterson and Carpenter (1983) found a distinct crossover in the proportions of the two species with increasing depth in response to the onset of anoxic conditions in the estuarine waters of Saanich Inlet of British Columbia. Arsenic(III) represented only 5% (0.10 μg l<sup>-1</sup>) of the dissolved As above the redox front but 87% (1.58 μg l<sup>-1</sup>) below it. In marine and estuarine waters, organic forms are usually less abundant but are nonetheless often detected (e.g. Riedel, 1993; Howard *et al.*, 1999). Concentrations of these will depend on abundance and species of biota present and on temperature.

In lake and river waters, As(V) is also generally the dominant species (e.g. Seyler and Martin, 1990; Pettine *et al.*, 1992), though significant seasonal variations in speciation as well as absolute concentration have been found. Concentrations and relative proportions of As(V) and As(III) vary according to changes in input sources, redox conditions and biological activity. The presence of As(III) may be maintained in oxic waters by biological reduction of As(V), particularly during summer months. Higher relative proportions of As(III) have been found in river stretches close to inputs of As(III)-dominated industrial effluent (Andreae and Andreae, 1989) and in waters with a component of geothermal water.

Proportions of As(III) and As(V) are particularly variable in stratified lakes where redox gradients can be large and seasonally variable (Kuhn and Sigg, 1993). As with estuarine waters, distinct changes in arsenic speciation occur in lake profiles as a result of redox changes. For example, in the stratified, hypersaline and hyperalkaline Mono Lake (California, USA), there is a predominance of As(V) in the upper oxic layer and of As(III) in the reducing part (Maest *et al.*, 1992; Oremland *et al.*, 2000). Rapid oxidation of As(III) occurs during the early stages of lake turnover as a result of microbial activity (Oremland *et al.*, 2000). This occurs before Fe(II) oxidation.

Unlike Mono Lake, speciation of As in lakes does not necessarily follow that expected from thermodynamic considerations. Recent studies have shown that arsenite predominates in the oxidised

epilimnion of some stratified lakes whilst arsenate may persist in the anoxic hypolimnion (Kuhn and Sigg, 1993; Newman *et al.*, 1998). Proportions of arsenic species may also vary according to the availability of particulate Fe and Mn oxides (Pettine *et al.*, 1992; Kuhn and Sigg, 1993).

Organic forms of arsenic are usually minor in surface waters. In lake waters from Ontario, Azcue and Nriagu (1995) found As(III) concentrations of 7–75  $\mu\text{g l}^{-1}$ , As(V) of 19–58  $\mu\text{g l}^{-1}$  and only 0.01–1.5  $\mu\text{g l}^{-1}$  of organic As. Nonetheless, proportions of organic forms of arsenic can increase as a result of methylation reactions catalysed by microbial activity (bacteria, yeasts, algae). The dominant organic forms found are dimethylarsinic acid (DMAA;  $(\text{CH}_3)_2\text{AsO}(\text{OH})$ ) and monomethylarsonic acid (MMAA;  $\text{CH}_3\text{AsO}(\text{OH})_2$ ), where As is present in both cases in the pentavalent oxidation state. Proportions of these two species have been noted to increase in summer as a result of increased microbial activity (e.g. Hasegawa, 1997). The organic species may also be more prevalent close to the sediment-water interface (Hasegawa *et al.*, 1999).

In groundwaters, the ratio of As(III) to As(V) can vary enormously as a result of large variations in aquifer redox conditions, redox gradients and history. In strongly reducing aquifers (Fe(III)- and sulphate-reducing), As(III) typically dominates. Reducing arsenic-rich groundwaters from Bangladesh have As(III)/As<sub>T</sub> ratios varying between 0.1–0.9 but are typically around 0.5–0.6 (DPHE/BGS/MML, 1999). Ratios in reducing groundwaters from Inner Mongolia are typically 0.7–0.9 (Smedley *et al.*, 2000b). Concentrations of organic forms are generally low or negligible in groundwaters (e.g. Chen *et al.*, 1995).

#### 1.2.4 Redox and kinetics

Redox reactions are important for controlling the behaviour of many major and minor species in natural waters, including that of arsenic. However, in practice, redox equilibrium is often achieved only slowly. For example, Wersin *et al.* (1991) estimated that the complete reductive dissolution of Fe(III) oxides in an anoxic Swiss lake sediment would take more than 1000 years. Equilibrium thermodynamic calculations predict that As(V) should dominate over As(III) in all but strongly reducing conditions, i.e. at least sulphate-reducing conditions (Section 1.2.1). However, such theoretical behaviour is not necessarily followed quantitatively in natural waters where different redox couples can point to different implied redox potentials (Eh values) reflecting thermodynamic disequilibrium (Seyler and Martin, 1989; Eary and Schramke, 1990; Kuhn and Sigg, 1993). In Oslofjord, Norway, As(III) was found under oxidising conditions (Abdullah *et al.*, 1995). Also, in oxygenated seawater, the As(V)/As(III) ratios should be of the order of  $10^{15}$ – $10^{26}$  (Andreae, 1979) whereas measured ratios of 0.1–250 have been found largely supported by biological transformations (Johnson and Pilson, 1975; Cullen and Reimer, 1989). Oxidation of As(III) by dissolved oxygen, so-called oxygenation, is a particularly slow reaction. Johnson and Pilson (1975) gave half-lives for the oxygenation of As(III) in seawater ranging from several months to a year.

Other studies have demonstrated the stability of As(V)/As(III) ratios over periods of days or weeks during water sampling when no particular care was taken to prevent oxidation again suggesting relatively slow oxidation rates. Andreae (1979) found stable ratios in seawater for up to 10 days (4°C). Cherry *et al.* (1979) found from experimental studies that the As(V)/As(III) ratios were stable in anoxic solutions for up to 3 weeks but that gradual changes occurred over longer timescales. They also suggested that the measured As(V)/As(III) ratios in natural waters might be used as an indicator of the ambient redox (Eh) conditions, particularly in groundwater where equilibration times are long. Yan *et al.* (2000) have also concluded that the As(V)/As(III) ratio may be used as a reliable redox indicator for groundwater systems. However, this optimism may be unfounded since Welch *et al.* (1988) found that the Eh calculated from the As(V)-As(III) couple neither agreed with that from the Fe(II)-Fe(III) and other redox couples nor with the measured Eh. Therefore, the reliability of the arsenic redox couple as a redox indicator remains to be seen. It is clearly important that where such comparisons are made, reliable Eh measurements are carried out (Yan *et al.*, 2000). Perhaps the most that can be said at present is that the existence of As(III) implies reducing conditions somewhere in the system.

Laboratory studies show that the kinetics of oxygenation of As(III) are slowest in the slightly acid range, around pH 5 (Eary and Schramke, 1990) which is why water samples are often acidified to about this pH to preserve their *in situ* speciation. Eary and Schramke (1990) also gave an empirical rate equation for the reaction over the pH range 8–12.5. This was based on the concentration (activity) of the  $\text{H}_2\text{AsO}_3^-$  species in solution. They suggested that the half-life for As(III) in natural waters is 1–3 years although the rate may be greater because of the presence of ‘unknown aqueous species’ or oxide particles, especially manganese oxides. Certainly there is considerable evidence that manganese oxides can increase the rate of As(III) oxidation with half-lives being reduced to as little as 10–20 min in the presence of manganese-oxide particles (Oscarson *et al.*, 1981; Scott and Morgan, 1995). This is used to advantage in the removal of As(III) from drinking water (Driehaus *et al.*, 1995). The rate of oxidation is independent of the concentration of dissolved oxygen (Scott and Morgan, 1995), the rate being controlled by the rate of a surface reaction. Less is known about the role of iron oxides in altering the oxygenation kinetics. Photochemical oxidation and reduction may be additional factors in surface waters. Ti-containing particles may aid the photo-oxidation (Foster *et al.*, 1998).

As with most redox reactions in the natural environment, both the oxidation of arsenite and the reduction of arsenate can be bacterially catalysed. Sterile water samples have been noted to be less susceptible to speciation changes than non-sterile samples (Cullen and Reimer, 1989). Wilkie and Hering (1998) found that As(III) in geothermal waters input to streams in south-west USA oxidised rapidly downstream (pseudo first-order half-life calculated at as little as 0.3 hours) and attributed the fast rate to bacterial mediation. The reduction of As(V) to As(III) in Mono Lake was also rapidly catalysed by bacteria with rate constants ranging from 0.02 to 0.3  $\text{day}^{-1}$  (Oremland *et al.*, 2000). Methylated As species are also readily oxidised chemically and biologically (Abdullah *et al.*, 1995).

Less is known about the rate of solid-phase reduction of As(V) to As(III) but there have been some studies with soils and sediments. The evidence from soils is that under moderately reducing conditions ( $E_h < 100 \text{ mV}$ ) induced by flooding, As(V) is reduced to As(III) in a matter of days or several weeks and adsorbed As(V) is released as As(III) (Masscheleyn *et al.*, 1991; Reynolds *et al.*, 1999). Masscheleyn *et al.* (1991) found from laboratory experiments that some of the As was released before Fe, implying reductive desorption from iron oxides rather than reductive dissolution. Up to 10 per cent of the total As in the soil eventually became soluble. Smith and Jaffé (1998) modelled As(V) reduction in benthic sediments as a first order reaction with respect to arsenate with a rate coefficient of  $125 \text{ yr}^{-1}$ .

### 1.3 Sources of arsenic

#### 1.3.1 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 1.2. Most are ore minerals or their alteration products. However, these minerals are relatively rare in the natural environment. The greatest concentrations of these minerals occur in mineralised areas and are found in close association with the transition metals as well as Cd, Pb, Ag, Au, Sb, P, W and Mo. The most abundant As ore mineral is arsenopyrite,  $\text{FeAsS}$ . It is generally accepted 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. However, authigenic arsenopyrite has been reported in sediments by Rittle *et al.* (1995). Although often present in ore deposits, arsenopyrite is much less abundant than arsenian (‘arsenic-rich’) pyrite ( $\text{Fe}(\text{S},\text{As})_2$ ) which is probably the most important source of As in ore zones (Nordstrom, 2000).

**Table 1.2 Major arsenic minerals occurring in nature**

<b>Mineral</b>	<b>Composition</b>	<b>Occurrence</b>
Native arsenic	As	Hydrothermal veins
Niccolite	NiAs	Vein deposits and norites
Realgar	AsS	Vein deposits, often associated with orpiment, clays and limestones, also deposits from hot springs
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

Where arsenopyrite is present in sulphide ores associated with sediment-hosted gold deposits, it tends to be the earliest-formed mineral, derived from hydrothermal solutions and formed at temperatures typically of 100°C or more. This is followed by the formation of rarer native arsenic and thereafter arsenian pyrite. Realgar and orpiment generally form later still. This paragenetic sequence is often reflected by zonation within sulphide minerals, with arsenopyrite cores zoning out to arsenian pyrite and realgar-orpiment rims. Oxides and sulphates are formed at the latest stages of ore mineralisation (Arehart *et al.*, 1993).

#### *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 10 weight percent (Table 1.3). Arsenic is present in the crystal structure of many sulphide minerals as a substitute for sulphur.

**Table 1.3. Typical arsenic concentrations in common rock-forming minerals**

Mineral	As concentration range (mg kg <sup>-1</sup> )	References
<b>Sulphide minerals:</b>		
Pyrite	100–77,000	Baur and Onishi (1969); Arehart <i>et al.</i> (1993); Fleet and Mumin (1997)
Pyrrhotite	5–100	Boyle and Jonasson (1973);
Marcasite	20–126,000	Dudas (1984); Fleet and Mumin (1997)
Galena	5–10,000	
Sphalerite	5–17,000	
Chalcopyrite	10–5000	
<b>Oxide minerals:</b>		
Haematite	up to 160	
Fe oxide (undifferentiated)	up to 2000	
Fe(III) oxyhydroxide	up to 76,000	Pichler <i>et al.</i> (1999)
Magnetite	2.7–41	
Ilmenite	<1	
<b>Silicate minerals:</b>		
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	
<b>Carbonates minerals:</b>		
Calcite	1–8	
Dolomite	<3	
Siderite	<3	
<b>Sulphate minerals:</b>		
Gypsum/anhydrite	<1–6	
Barite	<1–12	
Jarosite	34–1000	

**Other minerals:**

Apatite	<1–1000	
Halite	<3–30	Stewart (1963)
Fluorite	<2	

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 of 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 sometimes present in a characteristic form as framboidal pyrite. During the formation of this pyrite, it is likely that some of the soluble arsenic will also be incorporated.

Pyrite is not stable in aerobic systems and oxidises to iron oxides with the release of large amounts of sulfate, acidity and associated trace constituents including arsenic. The presence of pyrite as a minor constituent in sulfide-rich coals is ultimately responsible for the production of ‘acid rain’ and acid mine drainage (AMD), and for the presence of arsenic 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 sorbed species. Concentrations in Fe oxides can also reach weight percent values (Table 1.3), 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 and sorbed loadings can be appreciable even at very low arsenic concentrations in solution (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 on the surface of calcite (Goldberg and Glaubig, 1988), a common mineral in many sediments. However, these loadings are much smaller on a weight basis than for the iron oxides. Adsorption reactions are responsible for the relatively low (and non-toxic) 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 1.3). However, phosphate minerals are much less abundant than oxide minerals and so make a correspondingly small contribution to the arsenic load 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 1.3).

### 1.3.2 Rocks, sediments and soils

#### *Earth's crust*

Few estimates exist for the concentration of arsenic in the earth's crust. However, the concentration is generally taken to be low. Onishi and Sandell (1955) gave the average arsenic concentration of the lithosphere as about 2 mg kg<sup>-1</sup>.

**Table 1.4. Typical arsenic concentrations in rocks, sediments, soils and other surficial deposits**

Rock/sediment type	As concentration average and/or range (mg kg <sup>-1</sup> )	No of analyses	Reference
<b>Igneous rocks:</b>			
Ultrabasic rocks (peridotite, dunite, kimberlite etc)	1.5 (0.03–15.8)	40	
Basic rocks (basalt)	2.3 (0.18–113)	78	
Basic rocks (gabbro, dolerite)	1.5 (0.06–28)	112	
Intermediate (andesite, trachyte, latite)	2.7 (0.5–5.8)	30	Onishi and Sandell (1955); Baur and Onishi (1969); Boyle and Jonasson (1973); Ure and Berrow (1982); Riedel and Eikmann (1986)
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	
<b>Metamorphic rocks:</b>			
Quartzite	5.5 (2.2–7.6)	4	
Hornfels	5.5 (0.7–11)	2	
Phyllite/slate	18 (0.5–143)	75	Boyle and Jonasson (1973)
Schist/gneiss	1.1 (<0.1–18.5)	16	
Amphibolite and greenstone	6.3 (0.4–45)	45	
<b>Sedimentary rocks:</b>			
Marine shale/mudstone	3–15 (up to 490)		
Shale (Mid-Atlantic Ridge)	174 (48–361)		
Non-marine shale/mudstone	3.0–12		
Sandstone	4.1 (0.6–120)	15	Onishi and Sandell (1955); Baur and Onishi (1969); Boyle and Jonasson (1973); Cronan (1972); Riedel and Eikmann (1986); Welch <i>et al.</i> (1988); Belkin <i>et al.</i> (2000)
Limestone/dolomite	2.6 (0.1–20.1)	40	
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		
Bituminous shale (Kupferschiefer, Germany)	100–900		

Rock/sediment type	As concentration average and/or range (mg kg <sup>-1</sup> )	No of analyses	Reference
<b>Unconsolidated sediments:</b>			
Various	3 (0.6–50)		Azcue and Nriagu (1995)
Alluvial sand (Bangladesh)	2.9 (1.0–6.2)	13	BGS and DPHE (2001)
Alluvial mud/clay (Bangladesh)	6.5 (2.7–14.7)	23	BGS and DPHE (2001)
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 <i>et al.</i> (1995)
Glacial till, British Columbia	9.2 (1.9–170)		Cook <i>et al.</i> (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	5.4–18		Arribére <i>et al.</i> (1997); Smedley <i>et al.</i> (2000a)
Continental margin sediments (argillaceous, some anoxic)	2.3–8.2		Legeleux <i>et al.</i> (1994)
<b>Soils:</b>			
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 <i>et al.</i> (1988)
Soils near sulphide deposits	126 (2–8000)	193	Boyle and Jonasson (1973)
<b>Contaminated surficial deposits:</b>			
Mining-contaminated lake sediment, British Columbia	342 (80–1104)		Azcue <i>et al.</i> (1994; 1995)
Mining-contaminated reservoir sediment, Montana	100–800		Moore <i>et al.</i> (1988)
Mine tailings, British Columbia	903 (396–2000)		Azcue <i>et al.</i> (1995)
Soils and tailings-contaminated soil, UK	120–52,600	86	Kavanagh <i>et al.</i> (1997)
Tailings-contaminated soil, Montana	up to 1100		Nagorski and Moore (1999)
Industrially polluted inter-tidal sediments, USA	0.38–1260		Davis <i>et al.</i> (1997)
Soils below chemicals factory, USA	1.3–4770		Hale <i>et al.</i> (1997)
<b>Sewage sludge</b>	9.8 (2.4–39.6)		Zhu and Tabatabai (1995)

### *Igneous rocks*

Arsenic concentrations in igneous rocks are generally similar to those found in the crust. Ure and Berrow (1982) quoted an average value of  $1.5 \text{ mg kg}^{-1}$  for all rock types (undistinguished). Averages for different types distinguished by silica content (Table 1.4) are slightly higher than this value but generally less than  $5 \text{ mg kg}^{-1}$ . Volcanic glasses are only slightly higher with an average of around  $5.9 \text{ mg kg}^{-1}$  (Table 1.4). Overall, there is relatively little difference between the different igneous rock types. Despite not having exceptional concentrations of As, volcanic rocks, especially ashes, are often implicated in the generation of high-As waters. This may relate to the reactive nature of recent acidic volcanic material, especially fine-grained ash and its tendency to give rise to sodium-rich high-pH groundwaters (Section 1.5.3).

### *Metamorphic rocks*

Arsenic concentrations in metamorphic rocks tend to reflect the concentrations in their igneous and sedimentary precursors. Most contain around  $5 \text{ mg kg}^{-1}$  or less. Pelitic rocks (slates, phyllites) typically have the highest concentrations with on average ca.  $18 \text{ mg kg}^{-1}$  (Table 1.4).

### *Sedimentary rocks*

The concentration of As in sedimentary rocks is typically in the range  $5\text{--}10 \text{ mg kg}^{-1}$  (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  $4 \text{ mg kg}^{-1}$  (Table 1.4) although Ure and Berrow (1982) gave a lower average figure of  $1 \text{ mg kg}^{-1}$ .

Argillaceous deposits have a broader range and higher average As concentrations than sandstones, typically an average of around  $13 \text{ mg kg}^{-1}$  (Table 1.4; Ure and Berrow, 1982). The higher values reflect the larger proportion of sulphide minerals, oxides, organic matter and clays. Black shales have As concentrations typically at the high end of the range principally because of their enhanced pyrite content. Data given in Table 1.4 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. Marine shales tend to contain higher sulphur concentrations. 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  $174 \text{ mg kg}^{-1}$ ; Table 1.4). Atlantic Ridge gases may in this case be a high-As source.

Concentrations in coals and bituminous deposits are variable but often high. Samples of organic-rich shale (Kupferschiefer) from Germany have As concentrations of  $100\text{--}900 \text{ mg kg}^{-1}$  (Table 1.4). Some coal samples have been found with extremely high concentrations up to  $35,000 \text{ mg kg}^{-1}$  (Belkin *et al.*, 2000) although generally low concentrations of  $2.5\text{--}17 \text{ mg kg}^{-1}$  were reported by Palmer and Klizas (1997).

Carbonate rocks typically have low concentrations, reflecting the low concentrations of the constituent minerals (ca.  $3 \text{ mg kg}^{-1}$ ; Table 1.4).

Some of the highest observed As concentrations, often several thousand  $\text{mg kg}^{-1}$ , are found in ironstones and Fe-rich rocks. Phosphorites are also relatively enriched in As (values up to ca.  $400 \text{ mg kg}^{-1}$  having been measured).

### *Unconsolidated sediments*

Concentrations of As in unconsolidated sediments are not notably different from those in their indurated equivalents, 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 1.4). Elevated 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 in the range 2.3–8.2 mg kg<sup>-1</sup> (Table 1.1).

### *Soils*

Baseline concentrations of As in soils are generally of the order of 5–10 mg kg<sup>-1</sup>. Boyle and Jonasson (1973) quoted an average baseline concentration in world soils of 7.2 mg kg<sup>-1</sup> (Table 1.4) 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 1.4), 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 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 lower levels. Gustafsson and Tin (1994) found similarly elevated 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, and hence dependent to some extent on the concentration in the parent rock material, 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.

### *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 1.4). 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 ( $\text{FeAsO}_4 \cdot 2\text{H}_2\text{O}$ ) is a common sulphide oxidation product and its solubility is considered to control arsenic concentrations in such oxidising sulphide environments. Scorodite is metastable under most groundwater conditions and tends to dissolve incongruently, forming iron oxides and releasing arsenic into solution (Robins, 1987; Kraus and Ettel, 1989). However, in practice, a wide range of Fe-As solubility relationships are found which in part relate to the mineral type (Kraus and Ettel, 1989). There is some confusion in the analysis of these solubility relationships between congruent dissolution, incongruent dissolution and sorption/desorption reactions. Secondary arsenolite ( $\text{As}_2\text{O}_3$ ) is also relatively soluble. Arsenic bound to iron oxides is relatively immobile, particularly under oxidising conditions.

### 1.3.3 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  $10^{-5}$ – $10^{-3}$   $\mu\text{g m}^{-3}$  have been recorded in unpolluted areas, increasing to 0.003–0.18  $\mu\text{g m}^{-3}$  in urban areas and greater than 1  $\mu\text{g m}^{-3}$  close to industrial plants (PCS/WHO, 2001). Much of the atmospheric arsenic is particulate. Total arsenic deposition rates have been calculated in the range  $<1$ – $1000$   $\mu\text{g m}^{-2} \text{yr}^{-1}$  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  $\mu\text{g m}^{-2} \text{yr}^{-1}$  (29–55% as dry deposition) were estimated for the mid-Atlantic coast (Scudlark and Church, 1988). Concentrations in atmospheric precipitation are given in Section 1.2.1.

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 invoked 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 and especially from consumption of foods dried over coal fires, rather than from drinking water affected by atmospheric inputs (Finkelman *et al.*, 1999).

## 1.4 Mineral-water interactions

### 1.4.1 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 can be of mineral and biological origin. It is likely that in most soils and aquifers, mineral-As interactions are likely to dominate over organic matter-As interactions, although organic matter may interact to some extent through its reactions with the surfaces of minerals.

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 (see Box 1.1).

### Box 1.1. Mineral-water interactions

Mineral-water interactions can be divided into two broad types from a geochemical point of view: *precipitation-dissolution* reactions and *adsorption-desorption* reactions. *Precipitation-dissolution* reactions involve the growth or erosion of a mineral structure and so only involve structural ions, i.e. those elements included in the chemical formula of the mineral. The solubility of minerals can in principle be described quite well by a solubility product, although this may vary with the particle size and crystallinity of the mineral. Also the rate of dissolution or precipitation can be very slow and so thermodynamic equilibrium is often not attained in practical time-scales.

*Adsorption-desorption* reactions involve the binding of chemicals to the surface of minerals (or other solids) and are described by adsorption (or desorption) isotherms. *Ion exchange* is a special type of surface reaction in which one ion (e.g.  $\text{Ca}^{2+}$ ) replaces another ion or ions of equivalent charge (e.g.  $2 \text{Na}^+$ ). An *adsorption* or *exchange isotherm* relates the concentration of a chemical in *solution* to its concentration on a *surface*. Generally, the greater the concentration of a chemical in solution, the greater its concentration bound to the surface. The actual concentration on the surface depends on the chemical involved and with what else it is competing for space on the surface. There is always a preference for the binding of some ions over others but it is normal in nature for a wide variety of ions to be adsorbed at once. This competition for binding sites means that the amount of an ion adsorbed may be quite sensitive to the concentration of other ions present, i.e. the water quality. As a result, there are many complex formulae to describe adsorption-desorption and ion exchange reactions in the natural environment. Being surface reactions, these reactions tend to be rapid, certainly by geological time-scales.

*Coprecipitation* is also a common natural process whereby minor constituents are incorporated or scavenged into a mineral structure as it forms, e.g. arsenic can be coprecipitated during the formation of pyrite. Also, both phosphate and arsenic are coprecipitated during the formation of iron oxides. The term coprecipitation does not imply any particular mechanism and in practice both adsorption and precipitation may occur at the same time. The reverse process, which may be called *codissolution*, is also likely to be important for the release of trace metals in the natural environment. Coprecipitation often leads to *solid solutions* in which the mixing of components extends into the bulk mineral structure. Solid solutions are very common in nature since mineral precipitation tends to occur from highly 'impure' natural waters. Solid solutions occur most commonly between ions of similar size and character. If the composition of the solution from which the solid solution is forming changes during formation, then the resulting mineral may be 'zoned', i.e. its composition may vary from core to rim.

Adsorption reactions (e.g. on iron oxides) tend to apply to a broad range of ions since they are only based on the formation of a two-dimensional surface structure. Coprecipitation reactions are more selective and precipitation reactions even more so. The relatively unspecific nature of adsorption and coprecipitation reactions means that trace elements in nature are subject to a wide range of interactions that are often difficult to quantify, and therefore to model. This applies to the reactions that affect arsenic.

Precipitation-dissolution and adsorption-desorption reactions are not entirely unrelated processes and in practice, the distinction is not always that clear. For example, arsenic which forms highly insoluble arsenic-sulfide minerals will tend to adsorb strongly to other sulphide minerals such as pyrite ( $\text{FeS}_2$ ).

The importance of oxides in controlling the concentration of arsenic in natural waters has been appreciated for a long time (Table 1.5) (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, aluminum 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  $\text{mg kg}^{-1}$  (Forstner and Haase, 1998; Driehaus *et al.*, 1998).

**Table 1.5 Studies of arsenic adsorption by metal oxides**

Mineral	Comment	Reference
Aluminium oxides	As(V) and As(III) adsorption on activated alumina: pH dependence, kinetics, column breakthrough. Regeneration by desorbing with NaOH. Modelling with pH-dependent Langmuir isotherm (for As) and surface complexation model (for protons).	Ghosh and Yuan (1987)
'Amorphous' aluminium hydroxide	As(V) on precipitated Al(OH) <sub>3</sub> (pH 3–10). 'Adsorption' exceeded 15 mol kg <sup>-1</sup> at pH 5. Fitted data to pH dependent Langmuir isotherm.	Anderson <i>et al.</i> (1976)
Hfo	Kinetics and pH dependence of As(V) and As(III) adsorption on Hfo (202 m <sup>2</sup> g <sup>-1</sup> ). Found very high As(V) and As(III) loadings (up to 4–5 mol As kg <sup>-1</sup> ) at the highest concentrations. pH adsorption envelopes at various As <sub>T</sub> loadings.	Raven <i>et al.</i> (1998)
Hfo	Adsorption isotherms for arsenite and arsenate over free concentration range from 10 <sup>-7</sup> M to 10 <sup>-3</sup> M (pH 4–10). Fitted to Langmuir isotherm at low concentrations and linear isotherm at higher concentrations. Dzombak and Morel (1990) fitted this data to their diffuse double layer model.	Pierce and Moore (1982)
Hfo	Sorption of As(V) and As(III) on Hfo at As concentrations of environmental significance (low micromolar range) and pH 4–9. Compared results with Dzombak and Morel (1990) model predictions – generally reasonable agreement. SO <sub>4</sub> decreased adsorption of As(V) and As(III), especially at low pH, while Ca increased As(V) adsorption at high pH. 1 mM bicarbonate did not affect either As(V) or As(III) adsorption greatly.	Wilkie and Hering (1996)
Hfo	A wide angle X-ray scattering (and EXAFS) study of 2-line ferrihydrite coprecipitated with varying amounts of As(V) suggested that the As reduced crystallite size because of the formation of strongly bound inner sphere complex between As(V) and edge sharing Fe(O,OH) <sub>6</sub> octahedra. Saturation at As/Fe mole ratio of 0.68.	Waychunas <i>et al.</i> (1996)
Hfo	As(III) and As(V) adsorption and OH <sup>-</sup> release/uptake on synthetic two-line ferrihydrite. As(V) at pH 9.2 released up to 1 mol OH <sup>-</sup> per mol As sorbed whereas As(III) released <0.25 mol As per mol Fe. At pH 4.6, OH <sup>-</sup> release was much less for As(V) adsorption and under these conditions there was a net release of H <sup>+</sup> by arsenite. These differences reflect the mechanism of As adsorption and influence the pH dependence of adsorption.	Jain <i>et al.</i> (1999)
Granular 'ferric hydroxide' (akageneite)	As(V) isotherms given in the sub-μM concentration range; SO <sub>4</sub> competition significant at mM concentrations below pH 7 only; phosphate competition at 'natural' groundwater concentrations.	Driehaus <i>et al.</i> (1998)
Goethite	An EXAFS and XANES study of As(III) adsorption to a synthetic goethite suggested bidentate inner sphere binding. One plot of As(III) and As(V) pH adsorption envelopes. As(III) data	Manning <i>et al.</i> (1998)

Mineral	Comment	Reference
	fitted to Constant Capacitance SCM.	
Goethite	Batch adsorption of As(V) on synthetic goethite. Used Mo blue analysis for As. Shows pH edge at about pH 9. Data fitted Langmuir isotherm presumably at constant pH (up to 60 mg l <sup>-1</sup> As).	Matis <i>et al.</i> (1997)
Goethite	Successfully applied the CD-MUSIC surface complexation model to literature data for anion adsorption to goethite including As(V)–P competition. The CD-MUSIC is the most promising of the SCMs for modelling complex natural systems.	Hiemstra and van Riemsdijk (1999)
Goethite	As(V) adsorption on synthetic goethite primarily for a study of impact on flocculation and electrokinetics. No isotherms. Final pH varied but not defined.	Matis <i>et al.</i> (1999)
Hematite		Fendorf <i>et al.</i> (1997)
Manganese oxides	As(III) & As(V) removal by MnO <sub>2</sub> (s) is similar, up to say 5 mmol As mol <sup>-1</sup> Mn at μM As equilibrium solution concentrations. Freundlich isotherm obeyed. As(III) oxidised to As(V). Rapid (minutes) oxidation and adsorption of As(III). Monitored Mn release and effect of pH, Ca, phosphate and sulphate.	Driehaus <i>et al.</i> (1995)
Birnessite, cryptomelane and pyrolusite	Studied adsorption of As(III) and As(V) and kinetics of As(III) oxidation in presence of various MnO <sub>2</sub> . As(III) adsorption (per unit weight of oxide): cryptomelane>birnessite>pyrolusite whereas for As(V): Cryptomelane>pyrolusite>birnessite (not detectable). No isotherms given.	Oscarson <i>et al.</i> (1983)
Goethite, hematite and lepidocrocite	Batch adsorption of As(V), As(III), MMAA and DMAA on natural minerals (coarse-grained and very low He-Ar surface area). As adsorption: generally goethite > lepidocrocite > hematite (pH 2–12, maximum often pH 5–8). At pH 7 on goethite, As(III) > MMAA > DMAA > As(V) (?). FA (up to 50 mg l <sup>-1</sup> ) tended to reduce As adsorption. Gives Kd values.	Bowell (1994)
Alumina, hematite, quartz and kaolin	As(V) adsorption on natural, low surface area alumina, hematite, quartz and kaolin (0.12–5 m <sup>2</sup> g <sup>-1</sup> ) at pH 3–10. Adsorption decreases with pH; alumina = kaolin > hematite >> quartz. Gives Kd values and isotherms at low concentrations. Some SO <sub>4</sub> <sup>2-</sup> competition especially below pH 7. FA (>10 mg l <sup>-1</sup> ) generally reduced adsorption at pH 5–7 but not above pH 7 where FA is not adsorbed.	Xu <i>et al.</i> (1988)
Alumina	On natural alumina, adsorption was As(V) > As(III) > MMAA = DMAA (pH > 6). Maximum adsorption at pH 5 for As(V) and pH 7 for As(III). As(V) but not As(III) adsorption decreased rapidly above pH 6. Log Kd (l kg <sup>-1</sup> ) at micromolar concentrations (pH 7) was 2.5–3.5 for As(V) and about 1.5 for As(III). FA decreased adsorption.	Xu <i>et al.</i> (1991)

Notes: Hfo= Hydrous ferric oxide or ferrihydrite

SCM = Surface Complexation Model

EXAFS = Extended X-ray absorption fine structure

XANES = X-ray absorption near-edge structure

MMAA = monomethylarsonic acid,  $\text{CH}_3\text{AsO}(\text{OH})_2$

DMAA = dimethylarsinic acid,  $(\text{CH}_3)_2\text{AsO}(\text{OH})$

FA = fulvic acid

CD-MUSIC = Charge Distribution - Multisite Complexation model

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 learnt from the studies with soils and sediments since the same general principles are expected to apply. One of the most important areas where cross-fertilization of ideas can occur is in understanding the behaviour of iron oxides in reducing soils and sediments and the influence of this on the release of arsenic. Matisoff *et al.* (1982) related reductive dissolution of iron oxides to the possible release of arsenic in groundwater from an alluvial aquifer in north-east Ohio. Korte (1991) also speculated that desorption of arsenic from iron oxides could occur in reducing, alluvial sediments and that this could lead to high-arsenic groundwaters.

#### 1.4.2 Arsenic interactions in sediments

The major minerals binding arsenic (as both arsenate and arsenite) in sediments are the metal oxides, particularly those of iron, aluminum and manganese. About 50% of the iron in freshwater sediments is 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 sandy aquifers because of their greater abundance and the 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 basis) for adsorbing As(V) but that iron salts are more efficient at higher pH and for adsorbing As(III). Arsenic(V), like phosphate, is expected to be strongly adsorbed by calcium carbonate minerals and this may limit As concentrations in groundwater from limestone aquifers.

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 behavior 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 iron oxides most commonly studied in the laboratory reflect the iron oxides found in the field.

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's (1971) data for As(V) adsorption on goethite highlighting the high affinity of freshly-formed 'amorphous' iron oxides for arsenic. Paige *et al.* (1997) measured the As/Fe ratios during the acid dissolution of a synthetic ferrihydrite containing sorbed 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 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.

### 1.4.3 Iron in reduced sediments and aquifers

The processes causing changes in iron redox chemistry need to be understood because they directly affect the mobility of arsenic. One of the principal causes of high arsenic concentrations in subsurface waters is the reductive dissolution of hydrous iron oxides and/or the release of adsorbed or combined arsenic. A sequence of reduction reactions occurs when lakes, fjords, soils, sediments and aquifers become anaerobic (Stumm and Morgan, 1995). This sequence begins with the consumption of oxygen and an increase in dissolved CO<sub>2</sub> from the decomposition of organic matter. Next, NO<sub>3</sub><sup>-</sup> decreases by reduction to NO<sub>2</sub><sup>-</sup> and the gases N<sub>2</sub>O and N<sub>2</sub>. Insoluble manganic oxides dissolve by reduction to soluble Mn<sup>2+</sup> and hydrous ferric oxides are reduced to Fe<sup>2+</sup>. These processes are followed by SO<sub>4</sub><sup>2-</sup> reduction to S<sup>2-</sup>, then CH<sub>4</sub> production from fermentation and methanogenesis, and finally reduction of N<sub>2</sub> to NH<sub>4</sub><sup>+</sup>. During sulphate reduction, the consequent sulphide reacts with any available iron to produce FeS and ultimately pyrite, FeS<sub>2</sub>. 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 SO<sub>4</sub><sup>2-</sup> reduction.

In sulphate-poor environments, iron from free iron oxides is solubilized as Fe<sup>2+</sup> under reducing conditions. This gives rise to characteristically high-Fe waters, which in groundwaters tend to range from 0.1–30 mg l<sup>-1</sup> 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 exact fate of iron during reduction is not well understood, in part because it is probably very fine-grained and difficult to observe directly. Mössbauer spectroscopy is a useful technique for identifying the form of iron oxides in sediments, including anoxic sediments (Boughriet *et al.*, 1997; Drodt *et al.*, 1997).

'Green rusts' are one possible product of the transformations. These have occasionally been identified or suspected in anoxic soils and sediments (Taylor, 1980; Boughriet *et al.*, 1997; Cummings *et al.*, 1999). They consist of a range of green-coloured Fe(II)-Fe(III) hydroxide minerals with a layered structure and a charge-balancing interlayer counterion, usually carbonate or sulphate. Green rusts were originally referred to as 'hydrated magnetite' and given a composition 'Fe<sub>3</sub>(OH)<sub>8</sub>'. 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 characterize 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 (Fe<sub>3</sub>O<sub>4</sub>), is another possible product which has been identified in anaerobic sediments (Fredrickson *et al.*, 1998), often with extremely small particle sizes (Maher and Taylor, 1988; Canfield, 1989). Magnetite is frequently found in sediments as a residual detrital phase from rock weathering but very fine-grained magnetite is also formed by so-called 'magnetotactic' bacteria. Magnetite formation has been established under reducing conditions in the laboratory (Guerin and Blakemore, 1992). However, under strongly reducing conditions magnetite is unstable and in the presence of high concentrations of H<sub>2</sub>S, it 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 (Fe<sub>3</sub>O<sub>4</sub>) can lead to a coating of maghemite, γ-Fe<sub>2</sub>O<sub>3</sub>. Further burial and reduction leads to the dissolution of the primary magnetite (Torii, 1997).

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

#### 1.4.4 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 Blanchar, 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 sediments (Moore *et al.*, 1988; De Vitre *et al.*, 1991; Azcue and Nriagu, 1995; Widerlund and Ingri, 1995).

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 in less than a week.

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 trace elements) as a spiked sediment was progressively reduced. Arsenic was rapidly released after the Fe and Mn had dissolved suggesting that dissolution rather than desorption was the dominant process, or at least that dissolution and adsorption occurred simultaneously. Selective extractions suggested that most of the As in the sediments was associated with Fe and Mn oxides. 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.

A few studies have attempted to differentiate between the oxidation states of arsenic sorbed by sediments. Masscheleyn *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 normally 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.

Gómez-Ariza *et al.* (1998) 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 extracts small amounts of 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, a steady release of As was observed over a three-month period, with As(V) occurring under oxidising conditions and As(III) under reducing 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 that occurs in flooded soils occurs in the soil solution or on the soil particles.

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 percent 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 under reducing conditions when As(V) is reduced to As(III).

Cummings *et al.* (1999) found that As(V) was released from hydrous ferric oxide (Hfo) under reducing conditions without any pre-reduction of As(V) to As(III). Scorodite, a ferric arsenate mineral (Table 1.2), was also in part transformed to various ferrous arsenates. Therefore, the reduction of As(V) to As(III) may follow the initial release of As into solution rather than initiate it.

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/or diagenetic changes to the mineral structure.

None of the extraction 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.

#### **1.4.5 Transport of arsenic**

The transport of chemicals and adsorption are closely related in that adsorption slows down the transport of a chemical compared with the water flow (Appelo and Postma, 1992). 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 bit 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 arsenate and arsenite should travel through an aquifer with different velocities leading to their increased separation along a flow path. This was demonstrated by Gulens *et al.* (1979) using breakthrough experiments with columns of sand (containing 0.6% Fe and 0.01% Mn) and various groundwaters pumped continuously from piezometers. They studied As(III) and As(V) mobility with groundwaters having a range of Eh and pH values 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 under (i) 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 in analytical chemistry 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 derived 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 estimate ‘apparent’ Kd values. These were time- and implicitly concentration-dependent and for the sandy soils ranged from  $0.26 \text{ l kg}^{-1}$  after one void volume to  $3.3 \text{ l kg}^{-1}$  after 6 void 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 (408–464  $\text{mg l}^{-1}$ ), mostly as MMAA. The sediment contained only a few  $\text{mg kg}^{-1}$  of inorganic As. Baes and Sharp (1983) gave Kd values of 1.0–8.3  $\text{l kg}^{-1}$  (median 3.3) for As(III) binding by soils and 1.9–18.0  $\text{l kg}^{-1}$  (median 6.7) for As(V).

## 1.5 Groundwater environments showing enhanced arsenic concentrations

### 1.5.1 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  $50 \mu\text{g l}^{-1}$ , often significantly so. The most noteworthy occurrences are in parts of Argentina, Bangladesh, Chile, northern China, Hungary, India (West Bengal), Mexico, Romania, Taiwan (China) and many parts of the USA, particularly the south-west (Figure 1.3). Some of the better documented cases are summarised in Table 1.6. These include natural sources of contamination as well as mining-related sources. Arsenic associated with geothermal waters has also been reported in several areas, including hot springs from parts of Argentina, Japan, New Zealand, Chile, Kamchatka, Iceland, France, Dominica and the USA.

PENDING

### Figure 1.3 Map of documented world arsenic problems

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 intended 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.

As described above, arsenic problems also occur in some areas where sulphide-mining activity is prevalent, the As being released from sulphide minerals as they are oxidised as a result of

mining operations. In mining areas, As problems can be severe with concentrations in affected waters often being in the milligram-per-litre range. However, unlike As occurrences in major aquifers, the problems in these areas are typically localised, rather than of widespread occurrence. Mining-related As problems in water have been identified in many parts of the world, including Austria, Ghana, Greece, India (Madhya Pradesh), South Africa, Thailand and the USA (Fig. 1.3).

**Table 1.6 Summary of documented cases of naturally-occurring As problems in world groundwaters (includes some mining cases)**

Country/ Region	Area (km <sup>2</sup> )	Population exposed*	Concentration ranges (µg l <sup>-1</sup> )	Aquifer type	Groundwater conditions	Reference
Bangladesh	150,000	ca. 3x10 <sup>7</sup>	<0.5 to 2500	Holocene alluvial/ deltaic sediments. Abundance of solid organic matter	Strongly reducing, neutral pH, high alkalinity, slow groundwater flow rates	DPHE/BGS/MML (1999)
West Bengal	23,000	6x10 <sup>6</sup>	<10 to 3200	As Bangladesh	As Bangladesh	CGWB (1999); POA (1999)
China:		5.6x10 <sup>6</sup>				Sun et al. (2000)
Taiwan	4000	?10 <sup>5</sup> (formerly)	10 to 1820	Sediments, including black shale	Strongly reducing, artesian conditions, some groundwaters contain humic acid	Kuo (1968), Tseng <i>et al.</i> (1968)
Inner Mongolia (Huhhot Basin (HB), Bayingao, Hexi, Ba Meng, Tumet Plain)	4300 (HB), ?30,000 total	? ca. 10 <sup>5</sup> in HB	<1 to 2400	Holocene alluvial and lacustrine sediments	Strongly reducing conditions, neutral pH, high alkalinity. Deep groundwaters often artesian, some have high concentrations of humic acid	Luo <i>et al.</i> (1997), Zhai <i>et al.</i> (1998), Ma <i>et al.</i> (1999), Sun <i>et al.</i> (1999), Smedley <i>et al.</i> (2000b, 2001b)
Xinjiang (Tianshan Plain)	38,000	? (500 diagnosed)	40 to 750	Holocene alluvial plain	Reducing, deep wells (up to 660 m) are artesian	Wang and Huang (1994)
Shanxi				Alluvial plain	?Reducing	Sun <i>et al.</i> (1999)
Hungary, Romania (Danube Basin)	110,000	29,000	<2 to 176	Quaternary alluvial plain	Reducing groundwater, some artesian. Some high in humic acid	Varsányi <i>et al.</i> (1991); Gurzau (2000)
Argentina (Chaco-Pampean Plain)	10 <sup>6</sup>	2x10 <sup>6</sup>	<1 to 5300 (7800 in some porewaters)	Holocene and earlier loess with rhyolitic volcanic ash	Oxidising, neutral to high pH, high alkalinity. Groundwaters often saline. As(V), accompanied by high B, V, Mo, U. Also high As concentrations in some river waters	Nicolli <i>et al.</i> , 1989; Nicolli and Merino (2001); Smedley <i>et al.</i> (2001a); Sancha and Castro (2000)
Northern Chile (Antofagasta)	125,000	500,000	100 to 1000	?Quaternary volcanogenic sediment	Generally oxidising. Arid conditions, high salinity, high B. Also high-As river waters	Cáceres <i>et al.</i> (1992), Karcher <i>et al.</i> (1999); Sancha and Castro (2000)
South-west USA:		3.5x10 <sup>5</sup> (tot)				Smith <i>et al.</i> (1992)
Basin & Range, Arizona	200,000		up to 1300	Alluvial basins, some evaporites	Oxidising, high pH. As (mainly As(V)) correlates positively with Mo, Se, V, F	Robertson (1989)

Country/ Region	Area (km <sup>2</sup> )	Population exposed*	Concentration ranges (µg l <sup>-1</sup> )	Aquifer type	Groundwater conditions	Reference
Tulare Basin, San Joaquin Valley, California	5000		<1 to 2600	Holocene and older basin- fill sediments	Internally-drained basin. Mixed redox conditions. Proportion of As(III) increases with well depth. High salinity in some shallow groundwaters. High Se, U, B, Mo	Fujii and Swain (1995)
Southern Carson Desert, Nevada	1300		up to 2600	Holocene mixed aeolian, alluvial, lacustrine sediments, some thin volcanic ash bands	Largely reducing, some high pH. Some with high salinity due to evaporation. Associated high U, P, Mn, DOC (Fe to a lesser extent) Some saline groundwaters, with high U	Welch and Lico (1998)
Salton Sea Basin						Welch and Lico (1998)
Mexico (Lagunera)	32,000	4x10 <sup>5</sup>	8 to 620	Volcanic sediments	Oxidising, neutral to high pH, As mainly as As(V)	Del Razo <i>et al.</i> (1990)
<b>Some problem areas related to mining activity and mineralised areas</b>						
Thailand (Ron Phibun)	100	?15,000	1 to 5000	Dredged Quaternary alluvium (some problems in limestone), tailings	Oxidation of disseminated arsenopyrite due to former tin mining, subsequent groundwater rebound	Williams <i>et al.</i> (1996), Williams (1997)
Greece (Lavrion)				Mine tailings	Mining	
Fairbanks, Alaska, USA			up to 10,000	Schist, alluvium, mine tailings	Gold mining, arsenopyrite, possibly scorodite	Wilson and Hawkins (1978); Welch <i>et al.</i> (1988)
Moira Lake, Ontario, Canada	100		50–3000	Mine tailings	Ore mining (gold, haematite, magnetite, lead, cobalt)	Azcue and Nriagu (1995)
Coeur d'Alene, Idaho, USA			up to 1400	Valley-fill deposits	River water and groundwater affected by lead- zinc-silver mining	Welch <i>et al.</i> (1988), Mok and Wai (1990)
Lake Oahe, South Dakota, USA			up to 2000	Lake sediments	As in sediment porewaters from gold mining in the Black Hills	Ficklin and Callender (1989)
Bowen Island, British Columbia	50		0.5–580	Sulphide mineral veins in volcanic country rocks	neutral to high-pH groundwaters (up to 8.9), As correlated with B, F	Boyle <i>et al.</i> (1998)

\* Exposed refers to population drinking water with As >50 µg l<sup>-1</sup> (drinking-water standard of most countries)

While natural high-arsenic groundwaters (with arsenic above drinking-water standards) 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 to the past and present hydrogeology. Paradoxically, high-arsenic groundwaters are not necessarily related to areas of high arsenic concentrations in the source rocks.

Distinctive groundwater arsenic problems occur under both reducing and oxidising groundwater conditions; also in both 'wet' and 'dry' 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.

### **1.5.2 Reducing environments**

#### *Bangladesh and India (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  $<0.5 \mu\text{g l}^{-1}$  to ca.  $3200 \mu\text{g l}^{-1}$  (DPHE/BGS/MML, 1999; CGWB, 1999). Resultant health problems were first identified in West Bengal in the late 1980s but the first diagnosis in Bangladesh was not made until 1993. Between 30 and 36 million people in Bangladesh are estimated to be exposed to As in drinking water at concentrations above  $50 \mu\text{g l}^{-1}$  (BGS and DPHE, 2001) and up to 6 million in West Bengal (Table 1.6). Skin disorders including hyper/hypopigmentation changes and keratosis are the most common external manifestations, although skin cancer has also been identified (see Chapter 4). Around 5000 patients have been identified with As-related health problems in West Bengal (including skin pigmentation changes) although some estimates put the number of patients with arsenicosis at more than 200,000 (Smith *et al.*, 2000). The number in Bangladesh is not known but must be many times greater than in West Bengal. The instance of internal arsenic-related health problems is not known but could be appreciable.

### **Box 1.3. The Bangladesh groundwater arsenic problem**

The map of Bangladesh shows quite clearly the regional pattern of arsenic contamination of the groundwater based on the analysis of water from 3500 wells. The blue and green areas are below the Bangladesh drinking-water standard ( $50 \mu\text{g l}^{-1}$ ) while the blue areas are below the WHO guideline value ( $10 \mu\text{g l}^{-1}$ ). The worst-affected area is in southern Bangladesh especially the south-east. Water from the southern-most coastal region has low arsenic concentrations because the water is drawn from wells greater than 200 m depth in order to avoid salinity problems in the shallower horizons. Most of the other wells are from a depth of 15–80 m. While many wells in northern Bangladesh have acceptably low arsenic concentrations, there are occasional, highly localised 'hot spots' as shown by the red dots. The concentration of arsenic in these hot spots can exceed  $2000 \mu\text{g l}^{-1}$ .

MAP PENDING

West Bengal and Bangladesh rely heavily on groundwater for public drinking-water supply. Groundwater development has been actively encouraged in the region over the last few decades by government and other agencies as a means of providing an alternative to polluted surface water and thereby reducing the incidence of water-borne diseases. There has also been a rapid increase in the number of private tubewells and now the number of private tubewells exceeds the number of public tubewells. In this sense, the increase in use of groundwater has been very successful. The identification of chronic health problems related to As was unforeseen and has taken a number of years to become apparent.

The affected aquifers 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 Ganges, Brahmaputra and Meghna river systems and their precursors. 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 which favour the mobilisation of As. The mobilisation has probably occurred by a complex combination of redox changes brought on by rapid burial of the alluvial and deltaic sediments, including reduction of the solid-phase As to As(III), desorption of As from iron oxides, reductive dissolution of the oxides themselves and likely changes in iron-oxide structure and surface properties following the onset of reducing conditions (BGS and DPHE, 2001). Deep wells, tapping depths greater than 150–200 m, almost invariably have low arsenic concentrations, less than  $5 \mu\text{g l}^{-1}$  and usually less than  $0.5 \mu\text{g l}^{-1}$  (BGS and DPHE, 2001). Also wells from the older Plio-Pleistocene sediments of the Barind and Madhupur Tracts have low arsenic concentrations. It is a fortunate fact that both Calcutta and Dhaka draw their water from older sediments and do not have an arsenic problem. Dhaka is sited at the southern tip of the Madhupur Tract (BGS and DPHE, 2001).

The characteristic chemical features of the high-arsenic groundwaters are high iron ( $>0.2 \text{ mg l}^{-1}$ ), manganese ( $>0.5 \text{ mg l}^{-1}$ ), bicarbonate ( $>500 \text{ mg l}^{-1}$ ) and often phosphorus ( $>0.5 \text{ mg l}^{-1}$ ) concentrations, and low chloride ( $<60 \text{ mg l}^{-1}$ ), sulphate ( $<1 \text{ mg l}^{-1}$ ), nitrate and fluoride ( $<1 \text{ mg l}^{-1}$ ) concentrations, with pH values close to or greater than 7. Measured redox potentials are typically less than 100 mV (AIP Steering Committee, 1991; CGWB, 1999; DPHE/BGS/MML, 1999; BGS and DPHE, 2001). However, the correlations between dissolved elements are usually far from perfect and where good correlations with arsenic are found, these are only applicable locally and are of limited value for quantitative prediction of arsenic concentrations, even at a village scale. For example, some workers have found a positive correlation between arsenic and iron in village studies (e.g. Nag *et al.*, 1996), but this is not true of Bangladesh and West Bengal as a whole. One commonly observed relationship in the groundwaters is a general negative correlation between As and  $\text{SO}_4$  concentrations (BGS and DPHE, 2001). This association suggests that As mobilisation is effected under the most

strongly reducing conditions, coincident with sulphate reduction. Some of the groundwaters of Bangladesh are sufficiently reducing for methane generation to have taken place.

The worst-affected areas of Bangladesh are to the south and east of Dhaka (Fig. 1.3) where in some villages, more than 90% of the wells have arsenic concentrations above  $50 \mu\text{g l}^{-1}$ . The groundwaters are predominantly reducing, as evidenced by the major-element chemistry described above. Arsenic speciation studies have revealed a large range in the relative proportions of dissolved arsenate and arsenite (e.g. Das *et al.*, 1995; Acharyya, 1997). The modal proportion of arsenite appears to be between 50% and 60% of the total arsenic (BGS and DPHE, 2001). This may reflect lack of redox equilibrium in the aquifer or a mixed groundwater from a strongly stratified aquifer.

The regional distribution of the high-arsenic waters in West Bengal and Bangladesh is known to be extremely patchy (AIP Steering Committee, 1991; CSME, 1997; BGS and DPHE, 2001), 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), where in some instances more than 90% of tubewells investigated exceed the Bangladesh and Indian drinking-water standard for arsenic ( $50 \mu\text{g l}^{-1}$ ; BGS and DPHE, 2001). Certainly, the overall areal extent of contamination in West Bengal is less than in Bangladesh.

The arsenic-affected groundwaters in the Bengal Basin are associated with sediments having total arsenic concentrations in the range  $<2\text{--}20 \text{ mg kg}^{-1}$ , i.e. not exceptional by world-average values. This is not surprising given the scale of the problem. These sediments are derived from the drainage systems of three major rivers (Ganges, Brahmaputra and Meghna) which are themselves sourced from a wide area of the Himalaya. Therefore, while it could be argued that the source of much of the arsenic in the Bengal Basin sediments is derived from specific mineralised areas in the source region, these are likely to be so widespread as to be academic and of little practical relevance.

Isotopic evidence suggests that some groundwater from the Bengal Basin has had a long residence time in the aquifers. In Bangladesh, BGS and DPHE (2001) found that tritium, an indicator of modern groundwater, was usually detectable at a few TU in the shallowest groundwaters but deeper groundwaters usually had lower concentrations, typically  $<0.4$  TU. Such low concentrations are indicative of older groundwater, with a large proportion having been recharged prior to the 1960s. Radiocarbon data also suggest the presence of old groundwater at some sites. Groundwater from 10–40 m depth in groundwaters from western Bangladesh was ‘modern’ (83 pmc or greater) indicating an age of the order of decades. Shallow groundwaters from south-central Bangladesh were also modern (78 pmc or greater), although groundwater from 150 m was notably older (51 pmc) with a model age of about 2000 years. Deep groundwaters analysed from southern Bangladesh were even older with  $^{14}\text{C}$  activities of 28 pmc or less, suggesting the presence of palaeowaters with ages of 2,000–12,000 years.

The reasons for the distinction between groundwater As concentrations in the shallow and deep aquifers of the Bengal Basin are not yet well-understood. Differences between the sediments at depth may occur in terms of absolute As concentrations and in the oxidation states and binding properties of the As to the sediments. However, it is also possible that the history of groundwater movement and aquifer flushing in the Bengal Basin has been important in generating the differences in dissolved As concentrations between the shallow and deep aquifers. Older, deeper sediments have been subject to longer periods of groundwater flow, aided by greater hydraulic heads during the Pleistocene period when glacial sea levels around the Bangladesh landmass were up to 130 m lower than today (e.g. Umitsu, 1993). Flushing of the deeper older aquifers with groundwater is therefore likely to have been much more extensive than in the Holocene sediments deposited during the last 5000–10000 years. Hence, much of the As in the deep sediments may have previously been flushed away.

Salinity becomes a problem in the near-coastal parts of the aquifers in southern Bangladesh as a result of saline intrusion (BGS and DPHE, 2001). This affects the usability of the shallow aquifer in Bangladesh and means that deep wells, often more than 200 m deep, need to be constructed to obtain fresh water. As mentioned above, these almost always have low arsenic concentrations.

#### *Taiwan (China)*

The south-west coastal zone of Taiwan, China was perhaps the first area to be identified as a problem area for health effects arising from chronic arsenic exposure. Arsenic problems are also documented in north-eastern parts of the island (Hsu *et al.*, 1997). Awareness of the arsenic 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  $10 \mu\text{g l}^{-1}$  and  $1800 \mu\text{g l}^{-1}$  (mean  $500 \mu\text{g l}^{-1}$ ,  $n=126$ ) and found that half the samples analysed had concentrations between  $400 \mu\text{g l}^{-1}$  and  $700 \mu\text{g l}^{-1}$ . 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  $>50 \mu\text{g l}^{-1}$  and 58 townships had  $>350 \mu\text{g l}^{-1}$  (Lo *et al.*, 1977). In north-eastern Taiwan, Hsu *et al.* (1997) found As concentrations in groundwaters in the range  $<10$  to  $>600 \mu\text{g l}^{-1}$  with an average of  $135 \mu\text{g l}^{-1}$  (377 samples).

In the south-west, the high As concentrations are found in groundwaters from deep artesian wells (mostly 100–280 m) abstracted from sediments which include fine sands, muds and black shale (Tseng *et al.*, 1968). Groundwaters abstracted from the north-east of Taiwan are also artesian, but of shallower depth (typically in the range 16–40 m; Hsu *et al.*, 1997). In each area, the groundwaters are likely to be strongly reducing and hence may be analogous to groundwaters in the affected areas of Bangladesh and India (West Bengal). This is supported by the observation that the As is present largely as As(III) (Chen *et al.*, 1994). However, both the geochemistry of the groundwaters and the mineral sources in Taiwan are poorly defined at present. Groundwater from shallow open dug wells in the area have low arsenic concentrations (Guo *et al.*, 1994).

#### *Northern China*

Arsenic 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 (Fig. 1.2; Wang, 1984; Wang and Huang, 1994; Niu *et al.*, 1997; Smedley *et al.*, 2001). 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 (from Aibi Lake in the west to Mamas River in the east, a 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 of 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).

#### **Box 1.4: Arsenic in groundwater of the Huhhot Basin, Inner Mongolia, China**

High arsenic concentrations in groundwaters and associated health problems have been identified in several parts of northern China, especially Inner Mongolia (e.g. Ba Meng, Tumet Plain, Huhhot Basin, Baiyingao), Xinjiang and Shanxi Provinces.

One of the worst-affected areas is the Huhhot Basin. Huhhot, the capital city of Inner Mongolia, lies within an alluvial basin bounded by mountains to the north, east and south. The alluvial sediments are of Holocene age and are composed of a mixed sequence of sands, silts and clays derived from a former lake and marginal alluvial fan deposits eroded from the surrounding mountains. Groundwater is important in the rural areas of the basin, both for irrigation and domestic supply and has been abstracted from dug wells since the 1930s. Today, groundwater is abstracted from tubewells using both motorised pumps and hand pumps.

The groundwater is derived from varying depths but mostly from a shallow (less than around 50 m) aquifer and a deeper aquifer (100–400 m). Both aquifers are in parts contaminated with arsenic. The observed range of total arsenic concentrations in groundwater varies from  $<1 \mu\text{g l}^{-1}$  to  $1400 \mu\text{g l}^{-1}$ . The arsenic-rich groundwaters are highly reducing with low nitrate and high ammonium concentrations. Concentrations of arsenic are highest in the low-lying part of the basin where conditions are most reducing and groundwater flow is most sluggish. Like Bangladesh, the arsenic is present in both oxidised (arsenate) and reduced (arsenite) forms, although arsenite is dominant. The deep groundwaters often also have high concentrations of dissolved humic materials and can contain high concentrations of fluoride (up to  $7 \text{ mg l}^{-1}$ ) though this is not correlated with arsenic. In a study by Smedley *et al.* (2001), about 40% of the wells sampled had arsenic concentrations exceeding the WHO guideline value of  $10 \mu\text{g l}^{-1}$ . Many of the people in the region drinking high-arsenic groundwater have visible skin lesions. Currently, about 200 cases of arsenic-related disease have been identified in the basin including various cancers, lung cancer being the most common.

**Figures: Map of Huhhot Basin with As concentrations; location map of China**

**PENDING**

In Inner Mongolia, concentrations of As in excess of the Chinese national standard ( $50 \mu\text{g l}^{-1}$ ) 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.*, 2001b). 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). Some shallow dug wells also have groundwater with relatively high As concentrations (up to  $556 \mu\text{g l}^{-1}$ ; Smedley *et al.*, 2001b). Shallow groundwaters in parts of the region are saline as a result of evaporative concentration exacerbated by irrigation and many have high fluoride concentrations, although the F does not generally correlate with As. 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.

#### *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 capital city, Hanoi, is now largely dependent on groundwater for its public water supply. 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. 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 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.

#### *Hungary*

Concentrations of As above  $50 \mu\text{g l}^{-1}$  have been identified in groundwaters from alluvial sediments associated with the River Danube in the southern part of the Great Hungarian Plain (Fig. 1.2). Concentrations up to  $150 \mu\text{g l}^{-1}$  (average  $32 \mu\text{g l}^{-1}$ , 85 samples) have been found by Varsányi *et al.* (1991). The 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.

### **1.5.3 Arid oxidising environments**

#### *Mexico*

The Lagunera Region of north central Mexico has a well-documented arsenic problem in groundwater with significant resulting chronic health problems. The region is arid and groundwater is an important resource for potable supply. Groundwaters 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 at concentrations of the order of  $500 \mu\text{g l}^{-1}$  (Smith *et al.*, 1998). 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 concentrations 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 affected waters of Chile are taken to be predominantly oxidising (with dissolved oxygen present), largely because the As is reported to be present in the waters as arsenate (Thornton and Farago, 1997 and references cited therein). However, the geochemistry of the aquifers of Chile is as yet poorly understood. The aquifers are composed of volcanogenic sediments, but 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) and geothermal sources are also recognised (Section 1.5.5).

Arsenic treatment plants were installed in the towns of Antofagasta and Calama in 1969 to mitigate the problems. Today, the urban populations 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 (Box 1.5). Symptoms typical of chronic arsenic poisoning, including skin lesions and some internal cancers, have been recorded in these areas (e.g. Hopenhayn-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, 1997; Smedley *et al.*, 1998). 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.

### Box 1.5. Arsenic in La Pampa, Argentina

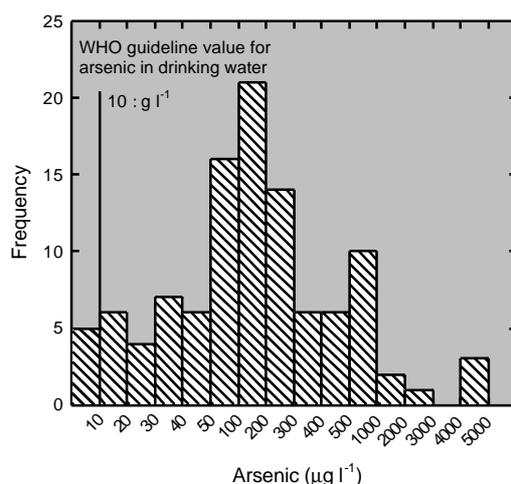
The population of La Pampa Province in central Argentina relies heavily upon groundwater for drinking and agricultural production. Water-quality problems from high arsenic concentrations are common. Concentrations in groundwater from wells and boreholes (having depths in the range 6–140 m) have been found by Smedley *et al.* (1998) ranging between <4 and 5300  $\mu\text{g l}^{-1}$ . The concentrations are log-normally distributed, with a median of 145  $\mu\text{g l}^{-1}$ . The spatial variability of arsenic concentrations is large and there is no distinct regional trend in the distribution of high-arsenic groundwaters. Of the groundwaters sampled, 95% were found to exceed the WHO guideline value for arsenic in drinking water. The high concentrations have been linked with development of skin lesions and internal cancers.

Arsenic is not the only element of health concern: high salinity, as well as fluoride (0.03–29  $\text{mg l}^{-1}$ ) and many other trace elements (uranium, boron, vanadium, molybdenum and nitrate) also occur in many of the groundwaters. Dental fluorosis from chronic exposure to fluoride is common but the health effects of other trace elements present in the drinking water are unknown.

Groundwaters from La Pampa are oxidising with typically high dissolved-oxygen concentrations and low concentrations of dissolved iron and manganese. Groundwater pHs are neutral to alkaline (up to 8.7). Groundwater arsenic is dominated by As(V), As(III) rarely exceeds 5% of the total present. Total arsenic correlates positively with pH, alkalinity ( $\text{HCO}_3^-$ ) and with fluoride and vanadium and weaker positive correlations are also observed between arsenic and beryllium as well as boron. These occur in solution as anion (fluoride) and oxyanion (arsenate, vanadate, borate and molybdate) species. High salinity is caused by groundwater evaporation under arid conditions; high pH and alkalinity derive by extensive silicate and carbonate weathering reactions. These characteristics are particularly pronounced in low-lying depressions which act as local groundwater-discharge areas (ponding) during rainy periods and sites of evaporation during dry periods.

Concentrations of arsenic in the aquifer sediments are similar to average values for silty and sandy sediments. Measured total concentrations range between 3  $\text{mg kg}^{-1}$  and 18  $\text{mg kg}^{-1}$ , with finer-grained sediments being at the higher end of the range. Arsenic bound to amorphous oxides (iron, manganese, aluminum) ranges between 0.5  $\text{mg kg}^{-1}$  and 9.6  $\text{mg kg}^{-1}$  (mean 2  $\text{mg kg}^{-1}$ ) and represents around 10–50% of the total present. Of this fraction, roughly half (0.02  $\text{mg kg}^{-1}$  to 4.7  $\text{mg kg}^{-1}$ , mean 1.0  $\text{mg kg}^{-1}$ ) appears to be associated with the manganese oxides. This suggests that much of the arsenic present in the sediments is relatively labile. Much of the remaining arsenic appears to be bound to more crystalline iron-oxide minerals. Mobilisation of arsenic together with the other anionic and oxyanion species can be achieved readily by desorption from iron, manganese and possibly aluminium oxides in the sediments under the ambient conditions of high pH and alkalinity. The aquifer is also composed of young Quaternary loess sediments (silts and fine sands) with low regional hydraulic gradients and presumed slow groundwater-flow rates. Aquifer flushing rates, and rates of removal of problem elements, are therefore thought to be have been low.

Figures: map of La Pampa, location map of Argentina and histogram.



MAP PENDING

Nicolli *et al.* (1989) found arsenic concentrations in groundwaters from Córdoba in the range 6–11500  $\mu\text{g l}^{-1}$  (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 <10–720  $\mu\text{g l}^{-1}$  (mean

201  $\mu\text{g l}^{-1}$ ) and Smedley *et al.* (1998) found concentrations for groundwaters in La Pampa Province in the range <4–5280  $\mu\text{g l}^{-1}$  (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 with low dissolved Fe and Mn concentrations 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). 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.*, 1998) although the direct dissolution of volcanic glass has also been cited as a potential source (Nicolli *et al.*, 1989; Nicolli and Merino, 2001).

#### 1.5.4 Mixed oxidising and reducing environments

##### *South-western USA*

Many areas have been identified in the USA with arsenic problems in groundwater. Most of the worst-affected and best-documented cases occur in the south-western states (Nevada, California, Arizona). However, within the last decade, aquifers in 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 long-planned reduction in the US-EPA 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 of sources 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 be derived from various sources, including natural dissolution/desorption reactions, geothermal water and mining activity. The natural occurrences of arsenic in groundwater occur under both reducing and oxidising conditions in different areas. Concentration by evaporation is thought to be an important process in the more arid 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 has been supplied without treatment other than chlorination. 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 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, combined 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. Dissolved oxygen values of the groundwaters were found to be in the range 3–7  $\text{mg l}^{-1}$ . Arsenic in the

groundwater was found from a limited number of samples to be present predominantly as As(V). The dissolved As correlated well with Mo, Se, V, F and pH, the latter being in the range 6.9–9.3. 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 (with dissolved oxygen present) 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.

### 1.5.5 Geothermal sources

Arsenic associated with geothermal waters has been reported in several areas, including hot springs from parts of the USA, Japan, New Zealand, Iceland, Kamchatka, France and Dominica (e.g. White *et al.*, 1963; Welch *et al.*, 1988; Criaud and Fouillac, 1989). Parts of Salta and Jujuy Provinces in 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 high concentrations of As ( $<1\text{--}7800 \mu\text{g l}^{-1}$  in geysers and hot springs; Thompson and Demonge, 1996; values up to  $2830 \mu\text{g l}^{-1}$  reported by Ball *et al.*, 1998). As noted in Section 1.2.1, these 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 waters at Lassen Park, California have arsenic concentrations ranging up to  $27,000 \mu\text{g l}^{-1}$  (Thompson *et al.*, 1985). An arsenic concentration of  $3800 \mu\text{g l}^{-1}$  has also been reported for Geysir Bight, Umnak Island, Alaska (White *et al.*, 1963). Geothermal inputs from Long Valley, California are believed to be responsible for relatively 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). Geothermal inputs also contribute significantly to the high dissolved As concentrations (up to  $20 \text{ mg l}^{-1}$ ) in Mono Lake, California (Section 1.2.2; Maest *et al.*, 1992).

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 As-rich geothermal waters in Long Valley.

Of 26 geothermal water samples analysed from five geothermal fields in Kyushu, Japan, As concentrations have been reported in the range  $500\text{--}4600 \mu\text{g l}^{-1}$ . The waters are typically of Na-Cl type and the As is present in all but one sample overwhelmingly as As(III) (Yokoyama *et al.*, 1993).

Increased 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  $121 \mu\text{g l}^{-1}$ , although concentrations diminished significantly downstream away from the geothermal input areas.

High arsenic concentrations have also been found in geothermal waters from the El Tatio system in the Antofagasta region of Chile. The geothermal area lies in a basin (altitude 4250 m) between the volcanoes of the Andes and the Serrania de Tucle. The geothermal waters are highly saline (sodium-chloride solutions with sodium concentrations in the range  $2000\text{--}5000 \text{ mg l}^{-1}$ ). Arsenic concentrations of the waters are reported to be in the range  $45,000\text{--}50,000 \mu\text{g l}^{-1}$  (Ellis and Mahon, 1977).

White *et al.* (1963) also reported arsenic concentrations in the range 50–120  $\mu\text{g l}^{-1}$  for thermal waters from Iceland and in the range 100–5900  $\mu\text{g l}^{-1}$  for thermal waters from Kamchatka.

### 1.5.6 Sulphide 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; Choprapawon and Rodcline, 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 tin-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. The recent appearance 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 (Webster *et al.*, 1994), 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 oxides. 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 pH values and As concentrations in the milligram-per-litre range (Nordstrom *et al.*, 2000; Section 1.2.1).

In Wisconsin, As and other trace-element problems in groundwater have arisen as a result of the oxidation of sulphide minerals (pyrite and marcasite) present as a discrete secondary cement horizon in the regional Ordovician sandstone aquifer. Concentrations of As up to 12,000  $\mu\text{g l}^{-1}$  have been reported in the well waters (Schreiber *et al.*, 2000). The oxidation appears to have been promoted by groundwater abstraction which has led to the lowering of the piezometric surface at a rate of around 0.6 m year<sup>-1</sup> since the 1950s with partial dewatering of the aquifer. The high As concentrations are observed where the piezometric surface intersects, or lies close to, the sulphide cement horizon (Schreiber *et al.*, 2000).

#### *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.

### **1.6 Common features of groundwater arsenic problem areas**

#### **1.6.1 A hydrogeochemical perspective**

Historically, as new sources of high arsenic groundwaters have been found, treatment plants have been built and the problem has receded from public attention. With the exception of a number of recent studies in the USA, there have been few detailed hydrogeochemical and hydrogeological studies of the arsenic-affected areas. Therefore much remains uncertain about the detailed mechanisms by which high-arsenic groundwaters have formed.

However, as described above, sufficient is already known that it is useful to attempt to bring together the common features and to speculate about the critical factors that could lead to high-As groundwaters. This will help to focus future scientific studies and should provide some guidance to those water undertakers who have to undertake a rapid assessment of their supplies for arsenic. It is helpful to consider the formation of high-arsenic groundwaters in terms of the three major factors involved, namely, the source of the arsenic, its mobilisation, and its subsequent transport (or lack of it).

#### **1.6.2 The source of arsenic**

In the cases where affected groundwaters are found close to obvious geological or industrial sources rich in arsenic (geothermal springs, drainage from mineralised and mining areas, specific contaminant sources), it is clear that the anomalously high arsenic concentrations in the source region are responsible. The extent of this contamination is usually highly localised because the geochemical conditions within most aquifers do not favour arsenic mobilisation on a regional scale. However, in areas strongly affected by geothermal activity, high-arsenic groundwaters may be more widespread as a result of the large source of arsenic and the fact that the source arsenic is already in solution.

Perhaps more puzzling is the way by which exceptionally high concentrations of arsenic – up to several mg  $\text{l}^{-1}$  – are found in groundwaters from areas with apparently near-average source rocks. In the extensive high groundwater arsenic areas, this appears to be the rule rather than the exception. Most of these cases arise in aquifers derived from relatively young aquifer materials, often consisting of alluvium or loess where the total As concentrations in the sediments are usually in the range 1–20 mg  $\text{kg}^{-1}$ . A recognition of this fact is a recent development and its late appreciation has delayed the discovery of many high-arsenic groundwater provinces.

A critical point is that the drinking-water limit for arsenic is very low in relation to the overall abundance of arsenic in the natural environment (Section 1.5.1 and Box 1.6). Fortunately, most of this arsenic is normally immobilized by various minerals, particularly iron oxides, and so is not available for abstraction. However, it only takes a small percentage of this 'solid' arsenic to dissolve or desorb to give rise to a serious groundwater problem. This can provide an explanation for both the oxidizing and reducing high-arsenic environments described in Section 1.5. An abundant source of iron oxides with its surface-bound and coprecipitated arsenic provides a ready source of arsenic that may be released given an appropriate change in geochemical conditions.

### **Box 1.6. Why is arsenic such a problem in some 'natural' groundwaters?**

#### **Importance of the very high solid/solution ratio in aquifers**

One of the paradoxes of arsenic and groundwater is that extensive arsenic problems are found in areas in which the aquifer sediments themselves appear to have near-to-average arsenic concentrations, i.e. in the range 2–10 mg kg<sup>-1</sup>. While the detailed mechanisms for the evolution of high-arsenic groundwaters are not yet well understood, sufficient is already known to provide some insight into the reasons for this. Firstly, because of the high solid/solution ratios found in soils and aquifers (3–6 kg l<sup>-1</sup>) and the low absolute value of the drinking water limit for arsenic, even small changes in the distribution of arsenic between solid and solution are important. Secondly, in many soils and aquifers, much of the arsenic appears to be associated with secondary minerals such as iron, aluminium and manganese oxides, probably in large part as adsorbed arsenic species. This form is particularly sensitive to changes in the environment and it only takes a small change in the amount of arsenic adsorbed to change the concentration of arsenic in the groundwater significantly. For example, if it assumed that say 1 mg kg<sup>-1</sup> of the sediment arsenic is present in a labile form, in the event of complete dissolution or desorption, this would produce up to 3000–6000 µg As l<sup>-1</sup> in the groundwater, many times the WHO guideline value.

#### **The triggers for change**

There appear to be two main drivers leading to a change in the amount of arsenic adsorbed. Firstly, it is well known that an increase in pH leads to the release of many anions adsorbed onto iron, aluminium and manganese oxides, including that of arsenate but less so arsenite (see Box 1.2). For arsenate, a change from pH 7 to pH 8.5 or above can be critical. Such a change frequently occurs in arid and semi-arid areas as a result of evaporation in inland (closed) basins. These pH changes normally occur under oxidising conditions.

Secondly, a change from oxidising conditions to reducing conditions may promote the desorption of arsenic. This is likely to reflect changes in the oxidation state of arsenic in groundwater: changing from strongly sorbed arsenate under oxidising conditions to less strongly sorbed arsenite under reducing conditions. Changes in the oxide minerals themselves also appear to be important, including possible changes to their structure and surface properties as well as partial dissolution in the case of iron and manganese oxides. Again these changes occur under conditions that are not uncommon in aquifers, especially in young alluvial aquifers where a ready supply of organic carbon from the constituent sediments readily consumes any free oxygen.

However, these changes alone are not enough. An additional and critical factor is the extent to which the aquifer has been flushed. In closed basins, there is little flushing and a wide variety of chemicals accumulate, often including fluoride, phosphate, uranium, vanadium and selenium as well as arsenic. In aquifers with more active groundwater flow, any arsenic released by the above processes will eventually be flushed away and there is unlikely to be substantial further release since the sediments will have re-equilibrated with the new environment. Therefore present-day arsenic problem areas are most likely to be found in areas where the amount of flushing has been low either due to their young age or to very slow groundwater movement. The very low hydraulic gradients found in large delta regions, such as the Bengal Basin, are ideal for minimising the extent of flushing and hence preserving high arsenic concentrations in groundwater.

### **1.6.3 Mobilisation – the necessary geochemical trigger**

There appear to be two key factors involved in the formation of high-As groundwaters on a regional scale: firstly, there must be some form of geochemical trigger which releases arsenic from the aquifer solid phase into the groundwater. Secondly, the released arsenic must remain in the groundwater and not be flushed away.

There are a number of possible geochemical triggers but the most important appears to be the desorption/dissolution of arsenic from oxide minerals, particularly iron oxides. An important feature of this process is that the initial adjustment is probably quite rapid since it involves a shift in the adsorption isotherm from one point on the isotherm to another point and adsorption reactions, being surface reactions, are usually rapid. The rate limiting factors are probably those controlling the major changes in pH, Eh and associated water quality parameters of the aquifer. These are in part related to physical factors such as the rate of diffusion of gases through the sediment and the rate of sedimentation, in part due to the extent of microbiological activity and in part related to the rates of chemical reactions. However, many of these factors can be seen as being rapid on a geological time scale (tens of thousands of years and longer). Dissolution reactions are slower but even oxide dissolution is rapid on a geological time scale and can be observed in a matter of weeks in paddy soils.

A qualification is that if diagenetic changes to the mineral structure are important (see below) or if burial to a certain depth is important, then there could be a slow release of arsenic over a much longer time scale. Details of the rate of release of arsenic and how this varies with time are not yet clear. It is likely that the rate will diminish with time with the greatest changes occurring early on. Natural groundwater flushing means that very slow releases of arsenic are likely to be of little consequence since the arsenic released will not tend to accumulate to a significant extent.

A corollary of this hypothesis is that once the diagenetic readjustment has taken place and the sediments have equilibrated with their new environment, there should be little further release of arsenic – this contrasts with some mineral-weathering reactions which occur in ‘open’ systems and can continue for millions of years until all of the mineral has dissolved. Seen in this context, the desorption/dissolution of arsenic in young aquifers is essentially a step change responding to a new set of conditions. As discussed above (Section 1.4), the type of reactions that may occur can be seen today most clearly where they occur at a small spatial scale and over a short time scale, for example, across a redox boundary in a lake sediment. The geochemical triggers involved could arise for a number of possible reasons. Below we speculate what these might be. Some model calculations of their possible impact are given in BGS and DPHE (2001).

#### *Desorption at high pH under oxidising conditions*

Under aerobic and acidic to near-neutral conditions, arsenic is very strongly adsorbed by oxide minerals as the arsenate ion (Box 1.2). The highly non-linear nature of the adsorption isotherm for arsenate ensures that the amount of arsenic adsorbed is relatively large, even at low solution concentrations. In a simple system with no competing anions, hydrous ferric oxide (Hfo) can have an As loading of nearly 15,000 mg kg<sup>-1</sup> when in equilibrium with 1 µg As(V) l<sup>-1</sup> at pH 7. This adsorption reaction protects many natural environments from widespread As toxicity problems. As the pH increases, especially above pH 8.5, arsenic desorbs from the oxide surfaces, thereby increasing the concentration of arsenic in solution. The impact of this is magnified by the high solid/solution ratios typical of aquifers (3–10 kg l<sup>-1</sup>).

There are several reasons why the pH might increase but the most important in the present context is the uptake of protons by mineral weathering reactions combined with the effect of evaporation in arid and semi-arid regions. This pH increase is commonly associated with the development of salinity and the salinisation of soils. Inputs of high-pH geothermal waters may be important in maintaining high As concentrations in some alkaline lakes. Desorption at high pH is the most likely mechanism for the development of groundwater-arsenic problems under the oxidising conditions described in Section 1.5.3 and would account for the observed positive correlation of arsenic concentrations with increasing pH.

### Box 1.2. Adsorption of arsenic by iron oxides

The adsorption of arsenic by iron oxides is a very important natural process that is to a large extent responsible for preventing widespread arsenic toxicity problems in nature. Arsenic is very strongly adsorbed by iron oxides, especially under oxidising and slightly acidic conditions. This is often the basis for the removal of arsenic during water treatment. The amount of adsorption is described by the *adsorption isotherm* which relates the concentration of arsenic adsorbed to its concentration in solution. Once this is known for a wide range of conditions then many properties can be calculated, including the percentage of arsenic adsorbed as a function of pH (see Figure), the likely efficiency of arsenic removal plants and the extent of retardation of arsenic during movement through soils and aquifers.

Adsorption isotherms are either *linear* or *non-linear*. A linear isotherm means that the amount of a species adsorbed is directly proportional to its concentration in solution. The isotherms for the two forms of arsenic, arsenate and arsenite, are very different including their pH dependence (see Figure). The arsenate isotherm is highly non-linear, the arsenite isotherm less so. An important consequence of the highly non-linear adsorption for arsenate is that even at the  $\mu\text{g l}^{-1}$  level of arsenic in solution, the arsenic loading on the oxide can be appreciable corresponding to thousands of mg As/kg in the case of hydrous ferric oxide (Hfo). The loading on more crystalline iron oxides such as goethite and hematite is somewhat lower because of their lower surface area, but is still appreciable.

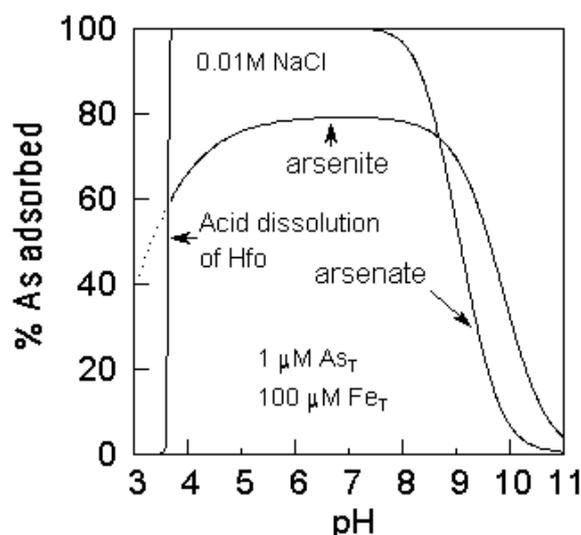


Figure showing the pH dependence of arsenate and arsenite adsorption on hydrous ferric oxide (Hfo) calculated according to the Dzombak and Morel (1990) diffuse double-layer model. Arsenate is very strongly adsorbed below pH 8 while arsenite is more strongly bound than arsenate at pH values greater than about 9. Therefore desorption of arsenic can occur either from an increase in pH from say 8.0 to 9.0 or from a change in oxidation state from arsenate to arsenite. Unfortunately, applying these observations to the 'real world' is not so straightforward: the presence of other specifically adsorbed ions such as phosphate changes these relationships. Also natural iron oxides may differ significantly from Hfo.

While there have been many studies of arsenic adsorption important for understanding the groundwater arsenic problem remain unclear, including the best mathematical formulation of the isotherm and how adsorption changes with pH and redox status. The most popular basis at present for calculating the amount of arsenic adsorbed by iron oxides is the diffuse double-layer model of Dzombak and Morel (1990) and its associated database but this model cannot account for the competitive interactions found in nature very well and the database is based on a limited amount of experimental data. The CD-MUSIC model of Hiemstra and van Riemsdijk (1999) is more promising but is more complex and at present is not coded into the popular geochemical modelling packages.

As such a pH increase induces the desorption of a wide variety of oxyanions, other oxyanions such as phosphate, vanadate, uranyl and molybdate will also tend to accumulate. There is evidence that this is indeed the case (Box 1.5). These specifically-adsorbed anions all interact with the adsorption sites on the oxides in a competitive way and so influence, in a complex way, the extent of binding of each other. This is not well understood in a quantitative sense. Phosphate in particular may play an important role in arsenic binding since it is invariably more abundant than arsenic, often by a factor of 50 or more (in molar terms), and is also strongly bound to oxide surfaces. Phosphate is as strongly bound as arsenate. The role of bicarbonate, often the major anion in arsenic-affected

groundwaters, in promoting the desorption of arsenate is unclear at present, as is the role of dissolved organic carbon (fulvic and humic acids). Some cations, because of their positive charge, may promote the adsorption of negatively charged arsenate (Wilkie and Hering, 1996). Calcium is likely to be the most important cation in this respect because of its abundance in most natural waters and its +2 charge. Divalent Fe may be important in reduced waters. Silica also exerts a control on the sorption of As (Swedlund and Webster, 1998).

The aridity described above enables the high pH values to be maintained and minimises the flushing of the arsenic. It also allows the build-up of high chloride and fluoride concentrations. Other high-pH environments (up to pH 8.3), particularly open-system calcareous environments, are likely to be too well flushed to allow any released arsenic to have accumulated. Arsenate may also be sorbed by carbonate minerals. The pH dependence of adsorption is critical but has not yet been measured in detail for any aquifer materials especially in the presence of typical groundwater compositions. The pH dependence is likely to depend to some extent on the heterogeneity of the aquifer material. Other specifically adsorbed anions, particularly phosphate and perhaps bicarbonate, may also significantly affect the pH dependence of As(V) and As(III) binding. High pH values cannot explain the development of high arsenic concentrations in reducing environments such as Bangladesh since groundwaters in reducing environments normally have a near-neutral pH.

#### *Desorption and dissolution due to a change to reducing conditions*

The onset of strongly reducing conditions – sufficient to enable iron(III) and probably sulphate reduction to take place – appears to be a second trigger for the release of arsenic. The most common cause of this is the rapid accumulation and burial of sediments. This occurs in river valleys, especially in broad valleys with wide meandering river channels carrying heavy sediment loads. Large, rapidly advancing deltas are an extreme case. Aeolian deposition of extensive deposits of loess can provide the necessary conditions. The organic carbon content of the buried sediment will largely determine the rate at which reducing conditions are created. Freshly-produced soil organic matter readily decomposes and it does not take much of this to use up all of the dissolved oxygen, nitrate and sulphate. Reducing conditions can only be maintained if the diffusion and convection of dissolved oxygen and other oxidants from the surface is less rapid than their consumption. This is helped if there is a confining layer of fine-grained material close to the surface. This often occurs in large deltas where fine-grained overbank deposits overly coarser-grained alluvial deposits.

#### **Change in arsenic speciation**

While the detailed reactions (in surface chemical terms) which occur when reduction takes place are not well understood, the change from normally strongly adsorbed As(V) to normally less strongly adsorbed As(III) may be one of the first reactions to take place, although not all the evidence supports this (e.g. De Vitre *et al.*, 1991). A change in the redox state of the adsorbed ions could have wider-ranging repercussions since it will also affect the extent to which other anions can compete for adsorption sites. Phosphate-arsenite competition, for example, is likely to be less important than phosphate-arsenate competition. There is also the potential for arsenite-arsenate competition. Model calculations suggest that adsorbed phosphate can reverse the relative affinity of As(III) and As(V) at near neutral pH values (BGS and DPHE, 2001). These complexities are poorly understood at present but are important if reliable quantitative predictions of arsenic concentrations under reducing conditions are to be made.

#### **Reduction in surface area of oxide minerals**

Freshly-precipitated metal oxides, particularly iron oxides, are often highly disordered and gradually transform to more ordered forms. Such disordered and fine-grained iron oxides, which may include Hfo, lepidocrocite, schwertmannite and magnetite, are commonly formed in the early stages of weathering. Furthermore, cycling between oxidized and reduced states of Fe in shallow sediments, with the aid of sulphide-sulphate cycling, may serve to keep the iron oxides in a 'reactive' state (Canfield, 1989). Once the oxides are more deeply buried and subject to groundwater flow, especially with oxidising water, they are likely to transform to the more stable forms of goethite and hematite.

There is ample evidence that this ageing reaction can take place rapidly in the laboratory but the rate of the reaction in nature is likely to be somewhat inhibited by the presence of other ions, particularly strongly adsorbed ions such as aluminium, phosphate, sulphate, arsenate and silicate (Cornell and Schwertmann, 1996).

All other things being equal, if the surface area of an oxide mineral is reduced, then adsorbed ions will be desorbed into solution. Some will be re-adsorbed, depending on the shape of the adsorption isotherm, the solid/solution ratio and the extent of inclusion within the evolving solid phase but the concentration in solution will tend to increase. Such reductions in surface area are well-established for Hfo which has a specific surface area of 100–600 m<sup>2</sup> g<sup>-1</sup> compared with a much smaller specific surface area for its aged products, typically 150 m<sup>2</sup> g<sup>-1</sup> or less for goethite and much less still for hematite (Cornell and Schwertmann, 1996).

#### **Reduction in binding strength between arsenic and the mineral surfaces**

It is perhaps not unreasonable to speculate that the diagenetic reactions that take place once a sediment is buried not only lead to a reduction in specific surface area but could also lead to a reduction in the binding strength of the adsorbed arsenic. This could arise from the mineral transformations described in section 1.4.3. However, it is also possible that the adsorption affinity (i.e. the intrinsic binding constant) could actually *increase* following crystallisation. This would tend to offset changes taking place due to a reduction in surface area. On balance, laboratory and field evidence suggests that at micromolar As concentrations freshly-formed Hfo does bind more arsenic than goethite on a mole of Fe basis (De Vitre *et al.*, 1991).

Under strongly reducing conditions, it appears that additional processes could operate which may lead to a reduction in the overall adsorption of arsenic. Specifically for iron oxides, some of the surface iron centers could be reduced from Fe<sup>3+</sup> to Fe<sup>2+</sup> to produce a mixed valence oxide perhaps akin to that of a magnetite or a green rust-type compound (section 1.3.4). This would tend to reduce the net positive charge of the surface (or increase its net negative charge) and would thereby reduce the electrostatic interaction between the surface and anions. This could result in the desorption of arsenic and a corresponding increase in the concentration of arsenic in solution.

#### **The role of mineral dissolution**

Mineral dissolution reactions would release both adsorbed As and irreversibly bound As located within the mineral structure. The most likely candidate for such a reaction is the reductive dissolution of iron oxides and this has been extensively discussed in the context of estuarine, lake and river sediments. Such a reaction accounts for the high ferrous iron content of anaerobic waters. While this undoubtedly accounts for some of the release of arsenic in reducing groundwaters, it does not appear to be sufficient to account for all of the arsenic released. In a few reducing groundwaters in Bangladesh, for example, the dissolved arsenic concentration is greater than that of iron (on a weight basis). If congruent dissolution alone were responsible for the arsenic release, this would require either the extensive precipitation of secondary iron phases (most likely carbonates or sulphides) or the chromatographic separation of iron and arsenic as a result of groundwater movement. Congruent dissolution of a typical iron oxide without any precipitation of secondary iron phases would only release a few µg As l<sup>-1</sup>. Reductive dissolution cannot of course explain the high-arsenic oxidising groundwaters.

The sequence of events that occur during the reductive dissolution of iron(III) oxides containing adsorbed and coprecipitated arsenic is complex and has not been studied in detail. Incongruent dissolution of arsenic from iron oxides probably occurs at the same time as desorption reactions. It is even more complex than for phosphate because of the added complication of the variable oxidation state of arsenic. The reduction of both the oxide and the arsenic are microbially catalyzed and the relative rates depend on the viability and nutrient supply of the specific microbial strains involved (Ehrlich, 1996).

Manganese oxides also undergo reductive desorption and dissolution and so could contribute to the arsenic load of groundwaters in the same way as iron. Certainly many of the reducing groundwaters of Bangladesh contain high concentrations of manganese (DPHE/BGS/MML, 1999). The Mn oxide surfaces also readily catalyse the oxidation of As(III) (Oscarson *et al.*, 1981). It is not known whether or not the dissolution of carbonate minerals (calcite, dolomite, siderite), which are common minerals in aquifers, contribute significantly to the release of arsenic to groundwater, or its uptake from groundwater.

Sulphide oxidation, particularly pyrite oxidation, can also be an important source of arsenic especially where these minerals are freshly exposed as a result of a lowering of the water table. This can occur locally in and around mines and on a more regional scale in aquifers. In extreme cases, this can lead to highly acidic groundwaters rich in sulphate, iron and trace metals. As the dissolved iron is neutralized, it tends to precipitate as a hydrous ferric oxide (sometimes schwertmannite) with a resultant adsorption and coprecipitation of dissolved As(V). In this sense, pyrite oxidation is not a very efficient mechanism for releasing As to surface and groundwaters.

#### **1.6.4 Transport – the hydrogeological dimension**

The geochemical triggers described above may release arsenic into groundwater but are not alone sufficient to account for the distribution of high-arsenic groundwaters observed. The additional factor is that the released arsenic must not have been flushed away or diluted by normal groundwater flow. This also places a time dimension on the problem since the rate of release must be set against the accumulated flushing of the aquifer that has taken place during the period of release. The rocks of most aquifers used for drinking water are several hundred million years old and yet contain groundwater that may be only a few thousand years old or younger. This implies that many pore volumes of fresh water have passed through the aquifer over its history.

The oldest fresh groundwaters are found in the Great Artesian Basin of Australia and are up to one million years old. The water moves slowly through this aquifer – at a rate of about  $0.1 \text{ m yr}^{-1}$  – and over its 2.5 billion year history, there have been many pore volumes of fresh water flushed through the system. Any desorbed arsenic will have long since disappeared. The same is true of most young aquifers with actively flowing groundwater. On the other hand, many deltaic and alluvial aquifers are characterised by relatively young sediments and often relatively old groundwater. The relative ages of the aquifer rocks and of the groundwater are important. It is only when the geochemical trigger to mobilise arsenic *and* the hydrogeological regime to preserve it are both operating that we see high groundwater arsenic concentrations on a regional scale.

It is also necessary to consider historical water flows which may have been very different from the present-day flows. One of the more significant ‘recent’ events is the global change in sea levels that has occurred over the last 130,000 years (Pirazzoli, 1996). Sea levels broadly respond to the amount of ice stored in glaciers and so reflect global climate patterns. Between about 120,000 years ago and 18,000 years ago, the sea-level steadily declined (with a few ups and downs) as glaciers expanded. The last glaciation was at a maximum some 21,000–13,500 years ago with sea levels being up to 130 m below present mean sea-level. This was a worldwide phenomenon and would have affected all then existing coastal aquifers. Continental and closed basin aquifers on the other hand would have been unaffected. The hydraulic gradient in coastal aquifers would therefore have been much greater than at present which would have resulted in correspondingly large groundwater flows and extensive flushing. The arsenic in these older aquifers would therefore tend to have been flushed away. The deep unsaturated zone would also have led to more extensive oxidation of the shallower horizons with possible increased sorption of As to Fe(III) oxides. Relics of these high flows are seen in the extensive fissure formation in some of the world’s older carbonate aquifers.

Between some 13,500–7000 years ago, warming occurred and sea levels rapidly rose to their existing levels. Therefore aquifers that are younger than some 7,000 years old will not have been subjected to this increased flushing that occurred during the most recent glaciation.

The time taken to flush an aquifer depends on many factors (Appelo and Postma, 1994). A critical factor is the number of pore volumes of 'fresh' water that have passed through the aquifer since the initial release of arsenic has taken place. The other important factor is the partitioning of arsenic between the aquifer solid phase and the groundwater. This determines how easy it is to flush out the arsenic and is related to the slope of the adsorption isotherm (Appelo and Postma, 1994). In simple cases, this can be expressed by a partition coefficient or  $K_d$ . The greater the  $K_d$ , the greater the capacity of the sediment to withstand changes and the slower the arsenic will tend to be flushed from the aquifer. The  $K_d$  depends on many factors both relating to the aquifer material itself and to the chemistry of the groundwater, i.e. its pH, arsenic concentration and speciation, phosphate concentrations and so on. In practice, the adsorption isotherms are usually non-linear which means that the  $K_d$  varies with concentration which leads to more complex transport but the same general principles apply. The  $K_d$  will be less than under 'normal' oxidised conditions since a reduced  $K_d$  is precisely the reason for the arsenic problem in the first place. There have so far been no reliable studies of  $K_d$  values applicable to arsenic-affected aquifers. The greater the quantity of arsenic involved, the more strongly it is adsorbed and the slower the rate of groundwater movement, the longer that high-arsenic groundwaters will persist.

As described above, the number of pore volumes that have passed through the aquifer is itself a function of the groundwater flow velocity integrated over the time since sediment burial. In Bangladesh, the age of sediment–depth relationship is particularly important since this has a direct bearing on the extent of flushing. Many of the shallow sediments in southern Bangladesh are less than 13,000 years old, even less than 5,000 years old, and so will not have experienced the extensive flushing of the last glacial period. These are where the majority of the tubewells are situated. Certainly at present flushing is slow because of the extremely small hydraulic gradients especially in southern Bangladesh. However, deeper and older sediments, which may exceed 13,000 years old, will have been subjected to more extensive flushing. This may account for the 'arsenic-free' groundwaters found in the deep aquifers of Bangladesh. Geochemical factors may also play a role since the evidence is that while the deep groundwaters are currently reducing, they are less strongly reducing than the shallow aquifers. Certainly, the aquifers in the Pleistocene uplifted alluvial sediments of the Barind and Madhupur Tracts will have been well flushed since they are at least 25,000–125,000 years old. These sediments invariably yield low-As groundwaters, typically containing less than  $0.5 \mu\text{g l}^{-1}$  arsenic. A complication is that the Bengal Basin is locally rapidly subsiding and filling in with sediments. This adds to the high degree of local and regional variation.

Not only are the regional flow patterns important. At a local scale, small variations in relief or in drainage patterns may dictate local flow patterns and hence the distribution of arsenic-rich groundwater. For example, there is evidence from Argentina that the highest groundwater arsenic concentrations are found in the slightly lower areas where seasonal discharge occurs. The same is true in Inner Mongolia and may also be true in Bangladesh. In any case, it is a characteristic of groundwater arsenic problem areas that there is a high degree of local-scale variation. This reflects the poor mixing and low flushing characteristic of the affected aquifers.

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

While we have attempted to explain some of the factors that give rise to high-arsenic groundwaters, we are aware that much remains unknown about exactly how such waters are formed and that our generalizations may not apply universally. They should serve as hypotheses to be tested and amended by further detailed field and laboratory investigations.

## **1.7 Outstanding questions and further needs**

### **1.7.1 Field analytical methods for arsenic determination**

In view of the characteristic high degree of spatial variation of groundwater arsenic concentrations in arsenic-affected areas, the analysis of each water supply is the only certain way of determining its potability.

In countries such as Bangladesh which have a very large number of wells to be tested and in which the existing laboratory-testing infrastructure is not able to cope with the demand, a rapid field testing programme is necessary. Carrying out such a programme is a major organisational challenge and reliable field tests are critical to the success of such a programme. The less need for retesting in a laboratory the better since this involves difficult sample tracking and could result in confusion and could even discredit the field testing programme. If field testing is to be carried out, then ideally it should be capable of giving a reliable result first time. Of course, all analytical results have an uncertainty or error associated with them and this should be monitored through some form of quality control programme. It also means that there is inevitably some uncertainty in the classification of wells with concentrations close to the standard value.

Most of the current field test kits are based on the Gutzeit method which involves the reduction of As(III) and As(V) by zinc to give arsine gas which is then used to produce a stain on mercuric bromide paper. Hydrogen sulphide gas is removed with zinc acetate-treated glass wool. There have been many studies of the sensitivity and reliability of these kits, particularly in India and Bangladesh. The early kits were usually good at detecting high-As waters (say greater than  $100 \mu\text{g l}^{-1}$ ) but often were found to have rather poor reliability at lower concentrations. Ideally a field test kit for arsenic should be:

- sensitive and reliable – it should be quantitative at the  $5\text{--}200 \mu\text{g l}^{-1}$  level and have a precision that is about the same as, or slightly better than, the short-term variability observed in the field, say  $\pm 20$  percent or  $\pm 5 \mu\text{g l}^{-1}$  for low concentrations;
- robust – it should be able to maintain a good performance for long periods under actual field conditions assuming reasonable care is taken;
- simple to use – it should be designed to be as simple as possible to use by field workers with the minimum of technical training and supervision;
- affordable – it must not be so expensive as to preclude its use either in terms of capital or recurrent costs;
- safe to use – it must not pose a hazard to the user or environment even after heavy use.

A number of improvements have been made to the early kits and several promising kits are now either in production or in development. Perhaps the most promising is a field-test kit being developed by Professor Walter Kosmus of Karl-Franzens University of Graz, Austria. This is a logical development of the standard Gutzeit kit in that it: (i) replaces zinc with sodium borohydride and thus removes the problem of obtaining low-As zinc; (ii) uses solid tablets instead of liquid chemicals and thus avoids the need for carrying strong acids or sodium borohydride solution in the field; (iii) has a simple, robust and easy-to-make straight-through arsine generator; (iv) forces all of the arsine gas through a smaller portion of mercury bromide-treated filter paper to ensure maximum sensitivity and

precision; (v) uses a separate, small calculator-style device to measure the stain developed photometrically; (vi) determines total arsenic, and (vii) is relatively stable and easily calibrated.

The challenge with all such devices is to reduce their costs sufficiently to enable them to be widely used where needed.

### **1.7.2 Surveys of groundwater quality**

The first priority must be to carry out reconnaissance regional surveys of all possible high arsenic areas where there is currently little or suitable data. This should be done on as close to a stratified-random basis as possible with the stratification based on a knowledge of local geology and the desire to get a reasonably uniform coverage. Suspect areas should then be sampled in more detail.

Aside from its primary role as part of a public health programme, high density village-scale testing of wells for arsenic will also lead to a better understanding of the causes of the arsenic problem and ultimately will help to guide any future development of groundwater resources. Therefore an important task is the careful recording of well details and combining this with the test results into some form of database. Ideally the geographic coordinates of a well should be recorded to within 10 m or so that reliable large-scale maps can be made. Ordinary GPS devices can now usually give coordinates to better than about  $\pm 10$  m and can certainly aid this mapping.

In arsenic problem areas, detailed studies should be undertaken to provide a sounder basis for understanding the causes of the problem and its variation in space and time. These could include a more comprehensive range of water quality parameters including all of the major, and a range of minor, constituents. Age-related parameters such as  $^3\text{H}$  and  $^{14}\text{C}$  should also be measured. Studies should be made of the local geology and hydrogeology including water level monitoring, pumping tests, and studies of the mineralogy, sedimentology, chemical composition and adsorption behaviour of the aquifer materials. Either purpose-built piezometers or suitable production wells should be monitored for changes in arsenic and other water quality parameters with time. Such studies are expensive and are not warranted unless the scale of the problem is large. As experience is gained and the processes better understood, some of these studies may become unnecessary.

Perhaps one of the lessons from Bangladesh is that surprises can still happen and that in any new large-scale groundwater development, a broad-ranging 'water quality' survey should be carried out before full-scale development takes place. 'Water quality' here is taken to include a wide range of parameters not just those on the existing lists of statutory 'health-related' parameters. For the inorganic elements, recent advances in analytical methodology mean that this should now be possible in most well-equipped water quality laboratories. For the organics, particularly the anthropogenic persistent organic compounds, this is less straightforward but still possible albeit very expensive. The scope of such broad and open-ended surveys should be commensurate with the anticipated scale of the groundwater development.

### **1.7.3 Will the problem groundwaters get better or worse with time?**

The answer to this question is probably 'better' but over a long time and on a timescale that is not relevant to the present exploitation. High arsenic groundwaters tend to be found in aquifers of Holocene age, i.e. aquifers in which the sediments have been deposited in the last ten thousand years. With time, the high concentrations of arsenic will be flushed away in the normal groundwater flow. The actual timescale depends on many factors that are poorly understood. The arsenic concentration in an individual well could increase before it decreases as arsenic is transported through the aquifer.

The influence of time is also connected to the relationship between the depth of well and the arsenic concentration since deeper sediments tend to be older. In Bangladesh, the deeper aquifer (below about 150–200 m depth) where studied appears to be essentially arsenic-free at present. Most of the problems are confined to the shallow aquifer, particularly over the depth interval 12–70 m beneath ground level. The past is not necessarily a good guide to the future – the extensive flushing of

aquifers that took place during the last glaciation and the preceding period of globally low sea levels will have led to unusually high hydraulic gradients and relatively rapid flushing. At present sea levels are rising as a result of global warming further reducing hydraulic gradients. Of more importance in the Bengal Basin context is the extent to which present and future exploitation of both shallow and deep aquifers for domestic supply and for irrigation might impact on the present good quality of groundwater from the deep aquifer. There is the possibility that heavy pumping of the deep aquifer may draw contaminated shallow groundwater down to the deep aquifer especially in the absence of a confining layer of clay at intermediate depths. There is also the possibility that poor well construction may lead to the rapid movement of contaminated water to depth.

Significant changes in arsenic transport in groundwater may occur locally due to the influence of mining, groundwater pumping and irrigation. Mining in hardrock areas may in effect create a new aquifer with extensive fracturing, adits and other drainage channels. The water table is also often lowered by drainage or pumping and this can induce air entry and enhanced oxidation.

#### **1.7.4 Transport under natural flow conditions**

It is necessary to know how arsenic moves in an aquifer to predict how concentrations might change in the future. Arsenic, like any other solute, moves in response to the flow of groundwater and its interaction with the aquifer solid phase. Adsorption or precipitation reactions will tend to retard movement relative to that of the groundwater whereas the co-transport of chemicals, including phosphate from fertilisers, that enhance the release of arsenic could lead to its more rapid movement through the aquifer, albeit limited by the rate of flow of the groundwater. Establishing the basic groundwater flow patterns within an aquifer is a prerequisite to understanding the movement of arsenic. The concentration profile of a non-reactive solute such as chloride can help to establish this. Age-related tracers such as  $^3\text{H}$ ,  $^{14}\text{C}$  and CFCs can also help as well as basic hydrogeological investigations of the aquifer.

Aside from the basic hydrogeology of the aquifer, it is also important to understand quantitatively the solid-solution interactions which take place. This refers principally to the nature of the adsorption-desorption isotherms and the mechanisms of reductive dissolution of iron and manganese oxides. It is likely that what is conveniently called 'reductive dissolution' is in fact a mixture of desorption, dissolution and structural rearrangement of the oxides themselves. A two-stranded approach is required: firstly, a detailed characterisation of sediments and associated pore waters is needed from a variety of aquifers, both affected and not affected, akin to that undertaken by limnologists and oceanographers when studying their sedimentary environments. In reduced aquifers, special care should be taken to avoid oxidation of the sediment. Secondly, these field studies need to be backed up by new theoretical advances in modelling the relevant surface chemical reactions of the oxides and sediments particularly in reducing environments. This will involve both modelling and laboratory work. There are probably some important scientific discoveries yet to be made!

#### **1.7.5 Interaction of arsenic with sediments**

Calculations of the rate of movement of arsenic through an aquifer depend on knowing the appropriate solid-solution partition coefficient ( $K_d$ ), or more particularly, on knowing the nature of the adsorption isotherm and in being able to predict how the partitioning changes with changes in groundwater chemistry. Therefore there is a need for laboratory studies of the interaction of arsenate, and if appropriate of arsenite also, with the affected aquifer materials. These will need to be carried out under conditions as close as possible to those found in the field including reducing conditions if appropriate. This can be difficult.

These studies need to be backed up by laboratory studies of the interaction of arsenic with model oxide materials to establish better models for competitive adsorption of both arsenate and arsenite with other common anions and cations. It is likely that this will lead to the development of new models, or at least to a refinement of existing ones. Any new adsorption models need to be incorporated into a groundwater solute transport package.

Reductive dissolution of oxides with adsorbed As is poorly understood and needs careful experimental investigations to establish the sequence of events in terms of changes in arsenic and iron speciation, changes in mineral surface chemistry and the kinetics and stoichiometry of Fe and As release.

### **1.8 Strategy for locating arsenic problems in groundwater**

The greatest challenge facing many water utilities and water providers in terms of the arsenic problem is the large number of wells that may not have been analysed for arsenic and that need to be tested. The challenge is to identify and mitigate any contaminated wells as soon as possible, and if there is going to be a substantial delay, the most seriously contaminated should be tackled first. Therefore a major task is to identify rapidly the most contaminated wells.

For many water providers, including NGOs in rural communities in developing countries, arsenic represents a new and poorly understood threat. There is almost certainly a general lack of understanding of the variation of arsenic concentrations in their area. In some cases, such as West Bengal (India) and Bangladesh, the scale of the testing programme required is unprecedented. In other cases, there is a lack of knowledge of the potential problem, or the lack of suitable facilities for testing. A rapid testing programme carried out in some randomised manner will establish if an extensive arsenic problem exists. It is far more difficult to identify every actual contaminated well in view of the high degree of spatial variability usually found in arsenic-contaminated areas. This is especially true where there is an extensive network of rural wells. Figure 1.4 helps to identify 'at risk' areas for priority testing. It can only be used to identify susceptible provinces, not individual wells.

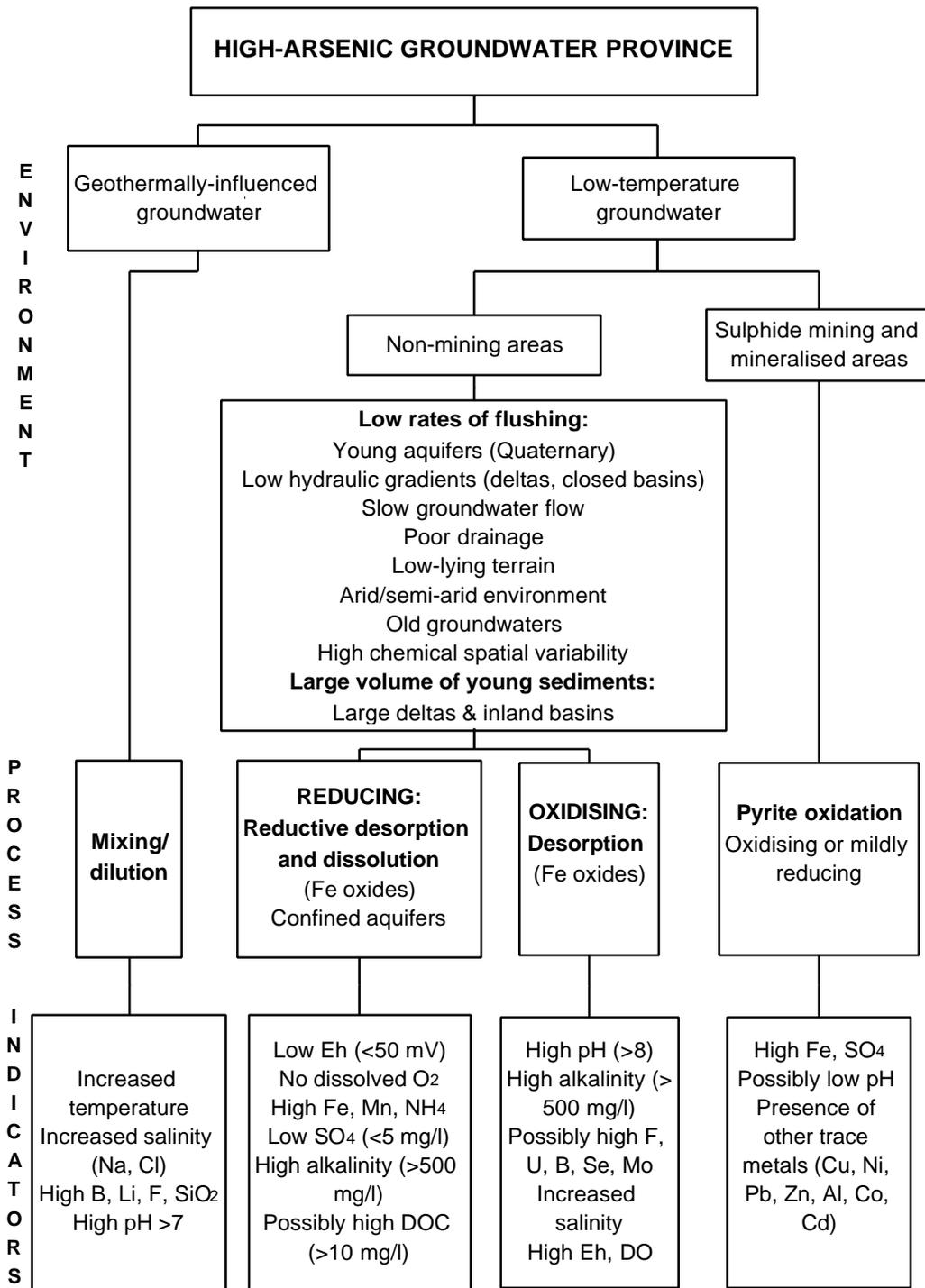


Figure 1.4 Flow diagram to aid locating possible high-arsenic groundwaters

## 1.9 Non-technical Summary

### Arsenic in the environment

- Arsenic is a well-known poison. It has featured in history as a poison for killing people both in fact and in fiction. It was once a popular poison because it conveniently left no easily detectable trace. The analysis was difficult, and remains so.
- Arsenic is not that rare. Small amounts are found in all rocks, soils and sediments and arsenic can be detected at low concentrations in most natural waters – rain, rivers, lakes, groundwater and seawater. Occasionally it is present at much higher concentrations and this is of concern where the water is being used for drinking water or irrigation. Groundwater presents a particular risk since this is where most of the naturally high concentrations of arsenic have been found and groundwater is often used as a source of drinking water.

### The scale of the problem

- Well-known cases of arsenic poisoning from natural arsenic in the drinking water have been found in Taiwan, Chile, Argentina, Mexico, China and more recently in West Bengal (India) and Bangladesh. The scale of the problem in terms of population exposed to high arsenic concentrations is greatest in the Bengal Basin with perhaps 40 million people drinking water containing ‘excessive’ arsenic. Many of the worst problems occur in poor countries without the necessary infrastructure to be able to respond rapidly.
- The problem in Bangladesh was undetected for many years because of the lack of suitable arsenic testing laboratories within the country. The problem is made worse by the very large number of wells present. An estimate of 6–11 million wells has been made. Most of these are operated by hand-pumps and obtain their water from depths of 10–70 metres.

### National drinking-water standards

- Each country defines the maximum amount of arsenic that it permits in drinking water. This is usually done formally through a national drinking-water standard. The WHO has set its provisional guideline value at  $10 \mu\text{g l}^{-1}$  but many countries have yet to adopt this standard in their legislation.
- The standard currently adhered to in India, Bangladesh and most of the countries which have groundwater arsenic problems is  $50 \mu\text{g l}^{-1}$  although the US-EPA and EC limits have both recently been reduced to  $10 \mu\text{g l}^{-1}$ . The chronic or long-term toxicity of arsenic is believed to be such that if the standard basis for risk assessment that is applied to industrial chemicals were applied to arsenic, the maximum permissible concentration would be lower still.

### The nature and causes of the problem

- The range of arsenic concentrations found in natural waters is unusually large, ranging from less than  $0.5 \mu\text{g l}^{-1}$  to more than  $5000 \mu\text{g l}^{-1}$ , i.e. a range of greater than ten thousand times. Typical concentrations in freshwater are less than  $10 \mu\text{g l}^{-1}$  and often less than  $1 \mu\text{g l}^{-1}$ . Rarely, much higher concentrations are found and this gives rise to arsenic problem areas. In such areas, the percentage of ‘affected’ wells (defined as those exceeding  $50 \mu\text{g l}^{-1}$ ) may exceed 10 percent of all wells and even in the worst cases, may exceed 90 percent of wells.
- These large-scale ‘natural’ arsenic groundwater problem areas are found all over the world but they tend to be confined to two types of environment: firstly, inland or closed basins in arid or semi-arid areas, and secondly, strongly reducing aquifers often derived from alluvium. Both types of susceptible environments tend to contain very young sediments and to be in low-lying, flat areas where groundwater flow is sluggish. Historically, these are poorly flushed aquifers and any arsenic released from the sediments has therefore been able to

accumulate in the groundwater. Arsenic-contaminated groundwaters are also found in geothermal areas and, on a more localised scale, in areas of mining activity or where sulphide oxidation has occurred. There are likely to be other known problems in mining areas related to acid mine drainage (AMD) and the generally metal-rich waters. In most cases, these mineralized sources do not pose a major threat to drinking water supplies.

- Similarly, sources of geothermal water are usually well known and suitably monitored.
- Although the way in which the high-arsenic groundwaters are formed is not well understood in detail, some general features are emerging. These are listed below:
  - the arsenic content of the aquifer materials does not appear to be exceptionally high – it is normally in the range 2–10 mg kg<sup>-1</sup>;
  - there appear to be two distinct ‘triggers’ that can lead to the release of arsenic from the aquifer material into the pore water. The first is the development of high pH (>8.5) conditions in semi-arid or arid environments usually as a result of the combined effects of mineral weathering and high evaporation rates. This pH change leads to the desorption of adsorbed arsenic (especially arsenate species) from natural mineral oxides, or prevents arsenic from being adsorbed in the first place. The second trigger is the development of strongly reducing conditions at near neutral pH values, leading to the reductive desorption of arsenic from natural mineral oxides and to the reductive dissolution of iron and manganese oxides also leading to arsenic release. These are both responses to a change in the geochemical environment;
  - there is as yet little direct evidence to support these arsenic release mechanisms for aquifers but the circumstantial evidence is strong. Detailed observations from other related environments such as lake and ocean sediments and soils, and from laboratory experiments with pure minerals, also lends credence to them;
  - high concentrations of phosphate, bicarbonate, silicate and possibly organic matter, either individually or in combination, can enhance the mobility of arsenic in water through competition for adsorption sites;
  - there is also potential for release of arsenic into groundwaters through the oxidation of sulphide minerals, particularly pyrite, brought about by aeration of the aquifer, for example by ‘over-abstraction’ of groundwater. However, compared with the ‘iron-oxide reduction hypothesis’, the ‘pyrite oxidation hypothesis’ is not an efficient mechanism for releasing arsenic because of the readsorption of As by the iron(III) oxides that invariably precipitates further along the flow path.

#### **The future**

- Very little is known about how long it will take to flush out the arsenic released by the processes described above in specific aquifers. This is likely to depend on the past, present and future groundwater flows, and hence on the detailed palaeohydrogeology of the aquifer, and on the sediment chemistry. It is almost certainly longer than the timescales of relevance to the present groundwater As problems;
- the extent of flushing of an aquifer since the original deposition of the aquifer ‘rocks’ is clearly critical — the greater this is, the less likely it is that there will be an arsenic problem. This means that deeper, older aquifers will tend to suffer fewer problems (all other things being equal). Groundwater flows were greater than at present during the last glacial period (21,000–7,000 years ago) when sea levels were much lower and so aquifers laid down before this are less likely to be severely affected;

- while we suspect that the arsenic problem will gradually disappear under natural groundwater flow, this may take many thousands of years and in the meantime, some wells may increase in arsenic concentration and some may decrease. Some of the arsenic may return via baseflow to be re-adsorbed by iron(III) oxides in the river sediments. The quantities of arsenic involved in affected aquifers are very large and there is little possibility of completely flushing it out in the short-term by pumping;
- a characteristic feature of high groundwater arsenic areas is the large degree of spatial variability – the well-to-well variability is usually large which means that it may be difficult to predict what the concentration of arsenic is likely to be in a particular well from the results of neighbouring wells. This means that in affected areas there is little alternative but to analyse each well separately for arsenic. Affected aquifers are the exception rather than the rule. In most aquifers, the majority of wells are likely to be unaffected even when they contain high concentrations of dissolved iron.

### **Acknowledgments**

We thank Kirk Nordstrom, Don Runnells, Alan Welch and Rick Johnstone for thorough and constructive reviews. We also thank the Department for International Development (UK) and the World Health Organisation for support in preparing this review. The maps of Argentina and China are courtesy of the University of Texas at Austin map library. The review is published with the permission of the Director, British Geological Survey (NERC).