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Review

A review of the source, behaviour and distribution of arsenic in natural waters

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Abstract

The range of As concentrations found in natural waters is large, ranging from less than 0.5 μg l^{-1} to more than 5000 μg l^{-1}. Typical concentrations in freshwater are less than 10 μg l^{-1} and frequently less than 1 μg l^{-1}. Rarely, much higher concentrations are found, particularly in groundwater. In such areas, more than 10% of wells may be 'affected' (defined as those exceeding 50 μg l^{-1}) and in the worst cases, this figure may exceed 90%. Well-known high-As groundwater areas have been found in Argentina, Chile, Mexico, China and Hungary, and more recently in West Bengal (India), Bangladesh and Vietnam. The scale of the problem in terms of population exposed to high As concentrations is greatest in the Bengal Basin with more than 40 million people drinking water containing 'excessive' As. These large-scale 'natural' As groundwater problem areas tend to be found in 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 environments tend to contain geologically young sediments and to be in flat, low-lying areas where groundwater flow is sluggish. Historically, these are poorly flushed aquifers and any As released from the sediments following burial has been able to accumulate in the groundwater. Arsenic-rich groundwaters are also found in geothermal areas and, on a more localised scale, in areas of mining activity and where oxidation of sulphide minerals has occurred. The As content of the aquifer materials in major problem aquifers does not appear to be exceptionally high, being normally in the range 1–20 mg kg^{-1}. There appear to be two distinct 'triggers' that can lead to the release of As on a large scale. 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 either to the desorption of adsorbed As (especially As(V) species) and a range of other anion-forming elements (V, B, F, Mo, Se and U) from mineral oxides, especially Fe oxides, or it prevents them from being adsorbed. The second trigger is the development of strongly reducing conditions at near-neutral pH values, leading to the desorption of As from mineral oxides and to the reductive dissolution of Fe and Mn oxides, also leading to As release. Iron (II) and As(III) are relatively abundant in these groundwaters and SO_4 concentrations are small (typically 1 mg l^{-1} or less). Large concentrations of phosphate, bicarbonate, silicate and possibly organic matter can enhance the desorption of As because of competition for adsorption sites. A characteristic feature of high groundwater As areas is the large degree of spatial variability in As concentrations in the groundwaters. This means that it may be difficult, or impossible, to predict reliably the likely concentration of As in a particular well from the results of neighbouring wells and means that there is little alternative but to analyse each well. Arsenic-affected aquifers are restricted to certain environments and appear to be the exception rather than the rule. In most aquifers, the majority of wells are likely to be unaffected, even when, for example, they contain high concentrations of dissolved Fe. © 2002 Published by Elsevier Science Ltd. All rights reserved.

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Contents

1. Introduction

The recent finding that groundwaters from large areas of West Bengal, Bangladesh and elsewhere are heavily enriched with As has prompted a reassessment of the factors controlling the distribution of As in the natural environment and the ways in which As may be mobilised. Arsenic is a ubiquitous element found in the atmosphere, soils and rocks, natural waters and organisms. It is mobilised 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 As problems are the result of mobilisation under natural conditions. However, man has had an important additional impact through mining activity, combustion of fossil fuels, the use of arsenical pesticides, herbicides and crop desiccants and the use of As 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 As in the environment, drinking water probably poses the greatest threat to human health. Airborne As, 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 As risk. Alongside obvious point sources of As 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 As concentrations in groundwaters. However, the authors also review the occurrence of As in a broad range of natural waters since these may indirectly be involved in the formation of As-rich groundwaters and can also provide a useful background against which to view groundwater As concentrations. Furthermore, many of the processes involved in the uptake and release of As are common to a wide range of natural environments.

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 to 10 $\mu g\ l^{-1}$. The new recommended value was based on the increasing awareness of the toxicity of As, particularly its carcinogenicity, and on the ability to measure it quantitatively (WHO, 1993). If the standard basis for risk assessment applied to industrial chemicals were applied to As, the maximum permissible concentration would be lower still. The EC maximum admissible concentration (MAC) for As in drinking water has been reduced to 10 μg l^{-1}. The Japanese limit for drinking water is also 10 μg l^{-1} while the interim maximum acceptable concentration for Canadian drinking water is 25 μg l^{-1}. The US-EPA limit was also reduced from 50 to 10 μg l^{-1} in January 2001 following prolonged debate over the most appropriate limit. However, this rule is now (September 2001) being reconsidered given the high cost implications to the US water industry, estimated at $200 million per year. 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 μg l^{-1} standard, in part because of lack of adequate testing facilities for lower concentrations.

Until recently, As was often not on the list of constituents in drinking water routinely analysed by national laboratories, water utilities and non-governmental organizations (NGOs) and so the body of information about the distribution of As 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, As and F are now recognised as the most serious inorganic contaminants in drinking water on a worldwide basis. In areas of high As concentrations, drinking water provides a potentially major source of As in the diet and so its early detection is of considerable importance.

2. Arsenic in natural waters

2.1. Aqueous speciation

Arsenic is perhaps unique among the heavy metalloids and oxyanion-forming elements (e.g. As, Se, Sb, Mo, V, Cr, U, Re) 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 As 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. Pb^{2+}, Cu^{2+}, Ni^{2+}, Cd^{2+}, Co^{2+}, 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 μg 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.

Relative to the other oxyanion-forming elements, As 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 (SeO_4^{2-}) oxyanion under oxidising conditions but is immobilized under reducing conditions either due to the stronger adsorption of its reduced form, selenite (SeO_3^{2-}), 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 S-rich, reducing environments, many of the trace metals also form insoluble sulphides. Arsenic is distinctive in being relatively mobile under reduced conditions. It can be found at concentrations in the mg l^{-1} range when all other oxyanion-forming elements are present in the μg l^{-1} range.

Redox potential (Eh) and pH are the most important factors controlling As speciation. Under oxidising conditions, $H_2AsO_4^-$ is dominant at low pH (less than about pH 6.9), whilst at higher pH, $HAsO_4^{2-}$ becomes dominant ($H_3AsO_4^0$ and 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 $H_3AsO_3^0$ will predominate (Fig. 1; Brookins, 1988; Yan et al., 2000). The distributions of the species as a function of pH are given in Fig. 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 S, dissolved As-sulphide species can be significant. Reducing, acidic conditions favour precipitation of orpiment (As_2S_3), realgar (AsS) or other sulphide minerals containing coprecipitated As (Cullen and Reimer, 1989). Therefore high-As waters are not expected where there is a high concentration of free sulphide (Moore et al., 1988).

2.2. Abundance and distribution

Concentrations of As in fresh water vary by more than four orders of magnitude (Table 1) depending on the source of As, the amount available and the local geochemical environment. Under natural conditions, the greatest range and the highest concentrations of As are

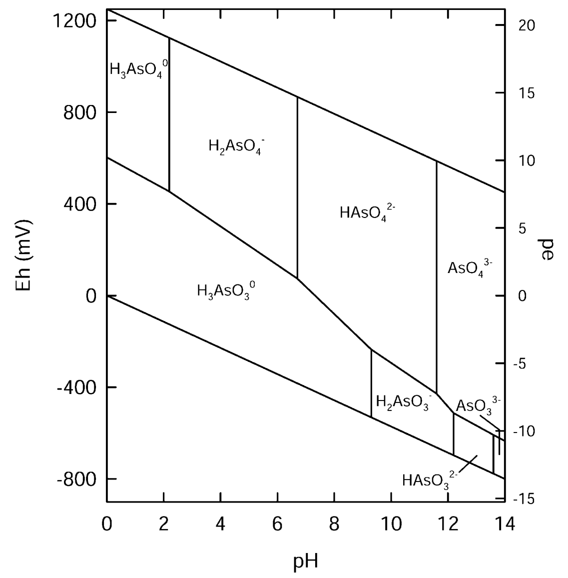

Fig. 1. Eh-pH diagram for aqueous As species in the system As–O_2–H_2O at 25 °C and 1 bar total pressure.

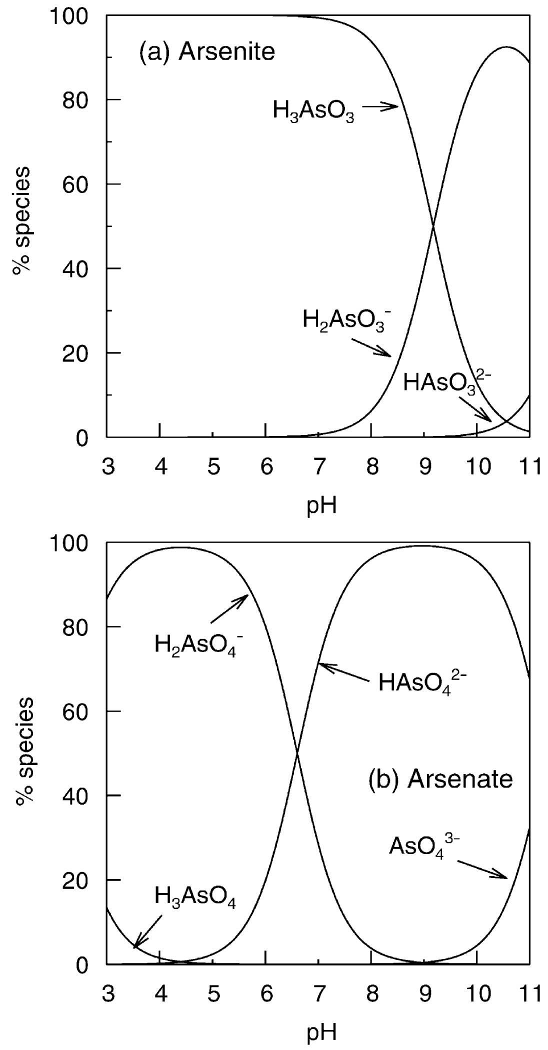

Fig. 2. (a) Arsenite and (b) arsenate speciation as a function of pH (ionic strength of about 0.01 M). Redox conditions have been chosen such that the indicated oxidation state dominates the speciation in both cases.

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 As mobilization and accumulation. The range of concentrations for many water bodies is large and hence 'typical' values are difficult to derive. Many studies of As 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 As 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.

2.2.1. 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 As appears to consist of mainly $As(III)_2O_3$ dust particles (Cullen and Reimer, 1989). Nriagu and Pacyna (1988) estimated that anthropogenic sources of atmospheric arsenic (around 18,800 tonnes a^{-1}) amounted to around 70% of the global atmospheric As flux. While it is accepted that these anthropogenic sources have an important impact on airborne As compositions, their influence on the overall As cycle is not well established.

Baseline concentrations of As in rainfall and snow in rural areas are invariably low at typically less than 0.03 $\mu g\ l^{-1}$ (Table 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 As concentrations of around 0.5 $\mu g\ l^{-1}$ (Table 1), although higher concentrations (average 16 $\mu g\ l^{-1}$) have been found in rainfall collected in Seattle some 35 km downwind of a Cu smelter (Crecelius, 1975). Values given for Arizona snowpacks (Table 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

Table 1
Typical As concentrations in natural waters

Water body and location	As concentration average or range (μg l^{-1})	Reference
Rain water		
Baseline		
Maritime	0.02	Andreae (1980)
Terrestrial (w USA)	0.013–0.032	Andreae (1980)
Coastal (Mid-Atlantic, USA)	0.1 ($<$0.005–1.1)	Scudlark and Church (1988)
Snow (Arizona)	0.14 (0.02–0.42)	Barbaris and Betterton (1996)
Non-baseline:		
Terrestrial rain	0.46	Andreae (1980)
Seattle rain, impacted by copper smelter	16	Crecelius (1975)
River water		
Baseline		
Various	0.83 (0.13–2.1)	Andreae et al. (1983); Froelich et al. (1985); Seyler and Martin (1991)
Norway	0.25 ($<$0.02–1.1)	Lenvik et al. (1978)
South-east USA	0.15–0.45	Waslenchuk (1979)
USA	2.1	Sonderegger and Ohguchi (1988)
Dordogne, France	0.7	Seyler and Martin (1990)
Po River, Italy	1.3	Pettine et al. (1992)
Polluted European rivers	4.5–45	Seyler and Martin (1990)
River Danube, Bavaria	3 (1–8)	Quentin and Winkler (1974)
Schelde catchment, Belgium	0.75–3.8 (up to 30)	Andreae and Andreae (1989)
High-As groundwater influenced:		
Northern Chile	190–21800	Cáceres et al. (1992)
Northern Chile	400–450	Sancha (1999)
Córdoba, Argentina	7–114	Lerda and Prosperi (1996)
Geothermal influenced		
Sierra Nevada, USA	0.20–264	Benson and Spencer (1983)
Waikato, New Zealand	32 (28–36)	McLaren and Kim (1995)
Madison and Missouri Rivers, USA	44 (19–67)	Robinson et al. (1995)
	10–370	Nimick et al. (1998)
Mining influenced		
Ron Phibun, Thailand	218 (4.8–583)	Williams et al. (1996)
Ashanti, Ghana	284 ($<$2–7900)	Smedley et al. (1996)
British Columbia, Canada	17.5 ($<$0.2–556)	Azcue et al. (1994)
Lake water		
Baseline		
British Columbia	0.28 ($<$0.2–0.42)	Azcue et al. (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)
Geothermal influenced		
Western USA	0.38–1000	Benson and Spencer (1983)
Mining influenced		
Northwest Territories, Canada	270 (64–530)	Bright et al. (1996)
Ontario, Canada	35–100	Azcue and Nriagu (1995)
Estuarine water		
Baseline		
Oslofjord, Norway	0.7–2.0	Abdullah et al. (1995)
Saanich Inlet, British Columbia	1.2–2.5	Peterson and Carpenter (1983)

(*continued on next page*)

Table 1 (*continued*)

Water body and location	As concentration average or range (µg l^{-1})	Reference
Rhône Estuary, France	2.2 (1.1–3.8)	Seyler and Martin (1990)
Krka Estuary, Yugoslavia	0.13–1.8	Seyler and Martin (1991)
Mining and industry influenced		
Loire Estuary, France	up to 16	Seyler and Martin (1990)
Tamar Estuary, UK	2.7–8.8	Howard et al. (1988)
Schelde Estuary, Belgium	1.8–4.9	Andreae and Andreae (1989)
Seawater		
Deep Pacific and Atlantic	1.0–1.8	Cullen and Reimer (1989)
Coastal Malaysia	1.0 (0.7–1.8)	Yusof et al. (1994)
Coastal Spain	1.5 (0.5–3.7)	Navarro et al. (1993)
Coastal Australia	1.3 (1.1–1.6)	Maher (1985)
Groundwater		
Baseline UK	<0.5–10	Edmunds et al. (1989)
As-rich provinces (e.g. Bengal Basin, Argentina, Mexico, northern China, Taiwan, Hungary)	10–5000	Das et al. (1995); BGS and DPHE (2001); Nicolli et al. (1989); Smedley et al. (2001a); Del Razo et al. (1990); Luo et al. (1997); Hsu et al. (1997); Varsányi et al. (1991)
Mining-contaminated groundwaters	50–10,000	Wilson and Hawkins (1978);Welch et al. (1988); Williams et al. (1996)
Geothermal water	<10–50,000	Baur and Onishi (1969); White et al., (1963), Ellis and Mahon (1977)
Arsenical herbicide plant, Texas	408,000	Kuhlmeier (1997a,b)
Mine drainage		
Various, USA	<1–34,000	Plumlee et al. (1999)
Iron Mountain	up to 850,000	Nordstrom and Alpers (1999)
Ural Mountains	400,000	Gelova (1977)
Sediment porewater		
Baseline, Swedish Estuary	1.3–166	Widerlund and Ingri (1995)
Baseline, clays, Saskatchewan, Canada	3.2–99	Yan et al. (2000)
Baseline, Amazon shelf sediments	up to 300	Sullivan and Aller (1996)
Mining-contam'd, British Columbia	50–360	Azcue et al. (1994)
Tailings impoundment, Ontario, Canada	300–100,000	McCreadie et al. (2000)
Oilfield and related brine		
Ellis Pool, Alberta, Canada	230	White et al. (1963)
Searles Lake brine, California	up to 243,000	White et al. (1963)

with industrial sources of As, atmospheric precipitation contributes little As to surface and groundwater bodies.

2.2.2. *River water*

Baseline concentrations of As in river waters are also low (in the region of 0.1–0.8 µg l^{-1} but can range up to ca. 2 µg l^{-1}; Table 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 µg l^{-1} in the Krka region of Yugoslavia where the bedrock is As-poor karstic limestone (Table 1). Lenvik et al. (1978) also found low average concentrations of about 0.25 µg 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 0.15–0.45 µg l^{-1} (Table 1).

Relatively high concentrations of naturally-occurring As can occur in some areas as a result of inputs from geothermal sources or high-As groundwaters. Arsenic concentrations in river waters from geothermal areas have been reported typically at around 10–70 µg l^{-1} (e.g. western USA and New Zealand; McLaren and Kim, 1995; Robinson et al., 1995; Nimick et al., 1998; Table 1), although higher concentrations have been found. Nimick et al. (1998) for example found As concentrations up to 370 μg 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 μg l^{-1} in Hot Creek (tributary of the Owens River, California). Some river waters affected by geothermal activity show distinct seasonal variations in As 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. 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 As ranging between 190 and 21,800 μg l^{-1}. The high As concentrations correlated well with salinity. While geothermal inputs are likely to have had an important impact on the chemical compositions of the river waters in this area (Section 5.5), evaporative concentration of baseflow-dominated river water is also likely to be important in the arid conditions. Increased As concentrations (up to 114 μg l^{-1}) have also been reported in river waters from central Argentina where regional groundwater-As concentrations (and pH, alkalinity) are high (Lerda and Prosperi, 1996).

Although bedrock inevitably has an influence on river-water As concentrations, concentrations in rivers with more typical pH and alkalinity values (c. pH 5–7, alkalinity <100 mg l^{-1} as HCO_3) do not show the extremely high concentrations found in groundwaters because of oxidation and adsorption of As 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 <0.5–2.7 μg l^{-1} but with one sample having a high concentration of 29 μg l^{-1} (BGS and DPHE, 2001). The highest value observed is significantly above world-average baseline concentrations (Table 1) but is much lower than some of the values found in the groundwaters.

Significant increases in As concentrations of river waters may also occur as a result of pollution from industrial or sewage effluents. Andreae and Andreae (1989) found concentrations up to 30 μg 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 As in water from most of the catchment was in the range 0.75–3.8 μg l^{-1} and not significantly different from baseline concentrations. Durum et al. (1971) reported As 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 μg l^{-1}, the highest observed concentration, 1100 μg 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 μg l^{-1} upstream of the influence of tailings from gold-mine workings. Downstream, concentrations increased to 23 μg l^{-1}. Azcue et al. (1994) found concentrations up to 556 μg l^{-1} (average 17.5 μg l^{-1}) in streams adjacent to tailings deposits in British Columbia. Williams et al. (1996) and Smedley et al. (1996) noted high As concentrations (typically around 200–300 μg l^{-1}) in surface waters affected respectively by Sn- and Au-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 Fe oxide, for As under oxidising, neutral to mildly acidic conditions.

2.2.3. *Lake water*

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

High As 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 As of 10,000–20,000 μg l^{-1}, 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 As concentrations in some lake waters as a result of varying redox conditions (Aggett and O'Brien, 1985). 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 porewaters at the sediment-water interface. The concentrations were higher in summer when the proportion of As(III) was observed to be higher. Depleted O_2 levels in the bottom lake waters as a result of biological productivity during the summer months are a likely cause of the higher As concentrations in the deeper lake waters.

2.2.4. *Seawater and estuaries*

Average As concentrations in open seawater usually show little variation and are typically around 1.5 μg l^{-1} (Table 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^{-1} under natural conditions. Peterson and Carpenter (1983) found concentrations between 1.2–2.5 μg l^{-1} in waters from Saanich Inlet, British Columbia. Values less than 2 μg l^{-1} were found in Oslofjord, Norway (Abdullah et al., 1995; Table 1). Concentrations are commonly higher when riverine inputs are affected by industrial or mining effluent (e.g. Tamar, Schelde, Loire Estuaries; Table 1) or by geothermal water. Unlike some other trace elements such as B, saline intrusion of seawater into an aquifer is unlikely to lead to a significant increase of As 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 α (Cullen and Reimer, 1989). Several studies have noted variations in the behaviour of As 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^{-1} in fresh waters to 1.8 μg l^{-1} 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 porewaters, coprecipitation with Fe oxides or anthropogenic inputs (e.g. Andreae et al., 1983; Andreae and Andreae, 1989). The flocculation of Fe oxides at the freshwater-saline interface is an important consequence of increases in pH and salinity. This can lead to major decreases in the As flux to the oceans (Cullen and Reimer, 1989).

2.2.5. *Groundwater*

Background concentrations of As in groundwater are in most countries less than 10 μg l^{-1} (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 to 5000 μg l^{-1} (i.e. four orders of magnitude). This range occurs under natural conditions. High concentrations of As are found in groundwater in a variety of environments. These include both oxidising (under conditions of high pH) and reducing aquifers and areas affected by geothermal, mining and industrial activity. Evaporative concentration can also increase concentrations substantially. Most high-As groundwater provinces are the result of natural occurrences of As. Cases of mining-induced As pollution are numerous in the literature but tend to be localised. Cases of industrially-induced As pollution (including that from agriculture) may be severe locally (Table 1) but occurrences are relatively rare. Arsenic occurrences in groundwater are discussed more fully in Section 5.

2.2.6. *Mine drainage*

Under the extremely acid conditions of some acid mine drainage, which can have negative pH values (Nordstrom et al., 2000), high concentrations of a wide range of solutes are found, including Fe and As. The highest reported As concentration of 850,000 μg 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 μg l^{-1} or more) to 340,000 μg l^{-1}, again the highest values being from the Richmond mine. Gelova (1977) also reported an As concentration of 400,000 μg l^{-1} from the Ural Mountains. Dissolved As in acid mine waters is rapidly removed as the Fe is oxidised and precipitated and the As scavenged through adsorption. At Iron Mountain, an efficient neutralization plant removes the As and metals for safe disposal.

2.2.7. *Sediment porewaters*

Some high concentrations of As have been found in porewaters 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 1.3–166 μg l^{-1} in porewaters from the Kalix River estuary of northern Sweden. Yan et al. (2000) found As concentrations in the range 3.2–99 μg l^{-1} in porewaters from clay sediments in Saskatchewan, Canada (Table 1). Increased concentrations have been found in porewaters affected by geothermal inputs. Aggett and Kriegman (1988) found As concentrations up to 6430 μg l^{-1} in anoxic porewaters from New Zealand. Even higher concentrations can be found in porewaters from sediments affected by mining contamination (tailings, mineral-rich deposits). McCreadie et al. (2000) reported As concentrations up to 100,000 μg l^{-1} in porewaters extracted from tailings in Ontario (Table 1). In such cases, high porewater As 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 O_2 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 porewaters 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 As in shallow sediments from the offshore shelf of the Amazon situated far from population centres. They measured porewater 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 50–150 cm beneath the surface, with As concentrations in the peak averaging about 135 $\mu g\ l^{-1}$ and reaching a maximum of 300 $\mu g\ l^{-1}$, 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 (6 M 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.

2.2.8. *Oilfield and other brines*

Only limited data are available for As in oilfield and other brines, but some published accounts suggest that concentrations can be very high. White et al. (1963) reported a dissolved As concentration of 230 $\mu g\ l^{-1}$ in a Na–HCO_3 groundwater from a 1000 m deep oilfield well from Ellis Pool, Alberta, Canada. They also reported a concentration of 5800 $\mu g\ l^{-1}$ As in a Na–Cl-dominated brine from Tisakürt, Hungary. Composite brines from the interstices of salt deposits from Searles Lake, California, have As concentrations up to 243 $mg\ l^{-1}$ (Na 119 $g\ l^{-1}$; White et al., 1963; Table 1).

2.3. *Distribution of arsenic species in water bodies*

Many studies of As speciation in natural waters have been carried out. Most 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 Na borohydride. Some studies also measure the organic As species. The sampling and analytical techniques required are not trivial and not yet well-established (Edwards et al., 1998). Both oxidation of As(III) and reduction of As(V) may occur during storage (Hall et al., 1999). 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 although this may destroy monomethylarsonic acid (MMAA) if present.

In rain water, oxidation states of As present will vary according to the source. This is likely to be dominantly $As(III)_2O_3$ when derived from smelters, coal burning and volcanic sources, although organic species may be derived by volatilization from soils, arsine ($As(-III)H_3$) 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_2 in the atmosphere and reactions with atmospheric SO_2 or O_3 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 $HAsO_4^{2-}$ and $H_2AsO_4^-$ in the pH range of seawater (pH around 8.2; Figs. 1 and 2) and As(III) mainly as the neutral species H_3AsO_3. Relatively high proportions of H_3AsO_3 are found in surface ocean waters (Cullen and Reimer, 1989; Cutter et al., 2001). These coincide with zones of primary productivity. Increases in organic As species have also been recorded in these zones as a result of methylation reactions by phytoplankton.

The relative proportions of As 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. Increased 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 $\mu g\ l^{-1}$) of the dissolved As above the redox front but 87% (1.58 $\mu g\ l^{-1}$) 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 As 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 layer (Maest et al., 1992; Oremland et al., 2000). Rapid oxidation of As(III) occurs as a result of microbial activity during the early stages of lake turnover (Oremland et al., 2000). The As oxidation 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 As 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 As are usually minor in surface waters. In lake waters from Ontario, Azcue and Nriagu (1995) found As(III) concentrations of 7–75 $\mu g\ l^{-1}$, As(V) of 19–58 $\mu g\ l^{-1}$ and only 0.01–1.5 $\mu g\ l^{-1}$ of organic As. Nonetheless, proportions of organic forms of As can increase as a result of methylation reactions catalysed by microbial activity (bacteria, yeasts, algae). The dominant organic forms found are dimethylarsinic acid (DMAA; $(CH_3)_2AsO(OH)$) and monomethylarsonic acid (MMAA; $CH_3AsO(OH)_2$), 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 greatly as a result of variations in the abundance of redox-active solids, especially organic C, the activity of microorganisms and the extent of convection and diffusion of O_2 from the atmosphere. In strongly reducing aquifers (Fe(III)- and SO_4-reducing aquifers), As(III) typically dominates, as expected from the redox sequence. Reducing As-rich groundwaters from Bangladesh have As(III)/As_T ratios varying between 0.1–0.9 but are typically around 0.5–0.6 (DPHE/BGS/MML, 1999; Smedley et al., 2001b). Ratios in reducing groundwaters from Inner Mongolia are typically 0.6–0.9 (Smedley et al., 2001a). Concentrations of organic forms are generally low or negligible in groundwaters (e.g. Chen et al., 1995).

2.4. Impact of redox kinetics on arsenic speciation

Redox reactions are important for controlling the behaviour of many major and minor species in natural waters, including that of As. However, in practice, redox equilibrium is often achieved only slowly and the redox potential tends to be controlled by the major elements (O, C, N, S and Fe). Redox-sensitive minor and trace elements such as As respond to these changes rather than control them. The slow rate of many heterogeneous redox reactions is supported by the studies of Wersin et al. (1991) who estimated that the complete reductive dissolution of Fe(III) oxides in an anoxic Swiss lake sediment would take more than 1 ka. Equilibrium thermodynamic calculations predict that As(V) concentrations should be greater than As(III) concentrations in all but strongly reducing conditions, i.e. where SO_4 reduction is occurring. While this is indeed often found to be the case, 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 O_2, so-called oxygenation, is a particularly slow reaction. For example, 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.

Cherry et al. (1979) suggested that the measured As(V)/As(III) ratios in natural waters, especially groundwaters, might be used as an indicator of the ambient redox (Eh) conditions as the redox changes are sufficiently rapid to occur over periods of years. 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. Measurements of Eh in natural waters using Pt electrodes are known to be problematic (Lindberg and Runnells, 1984). The reliability of the As redox couple as a redox indicator therefore remains to be seen. It is clearly important that where such comparisons are made, the Eh measurements are carried out without disturbing the natural redox environment (Yan et al., 2000). In cases where the aquifer is strongly stratified, groundwater flow induced by pumping during sampling or use may also lead to the mixing of waters with very different redox potentials. 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 $H_2AsO_3^-$ species in solution. They suggested that the half-life for As(III) in natural waters is 1–3 a, although the rate may be greater because of the presence of 'unknown aqueous species' or oxide particles, especially Mn oxides. Certainly there is considerable evidence that Mn 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 Mn-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 O_2 (Scott and Morgan, 1995), the rate being controlled by the rate of a surface reaction. Less is known about the role of Fe oxides in altering the oxygenation kinetics. Photochemical oxidation and reduction may be additional factors in surface waters. Titanium-containing particles may aid the photo-oxidation (Foster et al., 1998).

In the natural environment, the rates of both As(III) oxidation and As(V) reduction reactions are controlled by micro-organisms and can be orders of magnitude greater than under abiotic conditions. For example, sterile water samples have been observed 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 SW USA oxidised rapidly downstream (pseudo first-order half-life calculated at as little as 0.3 h) and they attributed the fast rate to bacterial mediation. The reduction of As(V) to As(III) in Mono Lake was also rapidly being catalysed by bacteria with rate constants ranging from 0.02 to 0.3 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 ($\text{Eh} < 100$ mV) induced by flooding, As(V) is reduced to As(III) in a matter of days or 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 Fe oxides rather than reductive dissolution. Up to 10% 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 a^{-1}.

3. Sources of arsenic

3.1. Minerals

3.1.1. Major arsenic minerals

Arsenic occurs as a major constituent in more than 200 minerals, including elemental As, arsenides, sulphides, oxides, arsenates and arsenites. A list of some of the most common As minerals is given in Table 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, FeAsS. It is generally believed 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) and orpiment has recently been reported to have been formed by microbial precipitation (Newman et al., 1998). Although often present in ore deposits, arsenopyrite is much less abundant than arsenian ('As-rich') pyrite ($Fe(S,As)_2$) which is probably the most important source of As in ore zones (Nordstrom, 2000).

Where arsenopyrite is present in sulphide ores associated with sediment-hosted Au 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 As and thereafter arsenian pyrite. Realgar and orpiment generally form later still. This paragenetic sequence is often reflected by zonation within sulphide

Table 2
Major As minerals occurring in nature

Mineral	Composition	Occurrence
Native arsenic	As	Hydrothermal veins
Niccolite	NiAs	Vein deposits and norites
Realgar	AsS	Vein deposits, often associated with orpiment, clays and limestones, also deposits from hot springs
Orpiment	As_2S_3	Hydrothermal veins, hot springs, volcanic sublimation products
Cobaltite	CoAsS	High-temperature deposits, metamorphic rocks
Arsenopyrite	FeAsS	The most abundant As mineral, dominantly in mineral veins
Tennantite	$(Cu,Fe)_{12}As_4S_{13}$	Hydrothermal veins
Enargite	Cu_3AsS_4	Hydrothermal veins
Arsenolite	As_2O_3	Secondary mineral formed by oxidation of arsenopyrite, native arsenic and other As minerals
Claudetite	As_2O_3	Secondary mineral formed by oxidation of realgar, arsenopyrite and other As minerals
Scorodite	$FeAsO_4.2H_2O$	Secondary mineral
Annabergite	$(Ni,Co)_3(AsO_4)_2.8H_2O$	Secondary mineral
Hoernesite	$Mg_3(AsO_4)_2.8H_2O$	Secondary mineral, smelter wastes
Haematolite	$(Mn,Mg)_4Al(AsO_4)(OH)_8$	
Conichalcite	$CaCu(AsO_4)(OH)$	Secondary mineral
Pharmacosiderite	$Fe_3(AsO_4)_2(OH)_3.5H_2O$	Oxidation product of arsenopyrite and other As minerals

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).

3.1.2. Rock-forming minerals

Though not a major component, As is also often present in varying concentrations in other common rock-forming minerals. As the chemistry of As follows closely that of S, the greatest concentrations of the element tend to occur in sulphide minerals, of which pyrite is the most abundant. Concentrations in pyrite, chalcopyrite, galena and marcasite can be very variable, even within a given grain, but in some cases exceed 10 wt.% (Table 3). Arsenic is present in the crystal structure of many sulphide minerals as a substitute for S. Besides being an important component of ore bodies, pyrite is also formed in low-temperature sedimentary environments under reducing conditions. Such authigenic pyrite plays a very important role in present-day geochemical cycles. It is present in the sediments of many rivers, lakes and the oceans as well as 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 As will also be incorporated. Pyrite is not stable in aerobic systems and oxidises to Fe oxides with the release of large amounts of SO_4, acidity and associated trace constituents, including As. 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, and for the presence of As 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 3), particularly where they form as the oxidation products of primary Fe sulphide minerals, which have an abundant supply of As. Adsorption of arsenate to hydrous Fe oxides is particularly strong and sorbed loadings can be appreciable even at very low As 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 Fe oxides. Adsorption reactions are responsible for the relatively low (and non-toxic) concentrations of As 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^{-1} in apatite (Table 3). However, phosphate minerals are much less abundant than oxide minerals and so make a correspondingly small contribution to the As concentration in most sediments. Arsenic can also substitute for Si^{4+}, Al^{3+}, Fe^{3+} and Ti^{4+} in many mineral structures and is therefore present in many other rock-forming minerals, albeit at much lower concentrations. Most common silicate minerals contain

Table 3
Typical As concentrations in common rock-forming minerals

Mineral	As concentration range (mg kg^{-1})	References
Sulphide minerals:		
Pyrite	100–77,000	Baur and Onishi (1969); Arehart et al. (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	Baur and Onishi (1969)
Sphalerite	5–17,000	Baur and Onishi (1969)
Chalcopyrite	10–5000	Baur and Onishi (1969)
Oxide minerals		
Haematite	up to 160	Baur and Onishi (1969)
Fe oxide (undifferentiated)	up to 2000	Boyle and Jonasson (1973)
Fe(III) oxyhydroxide	up to 76,000	Pichler et al. (1999)
Magnetite	2.7–41	Baur and Onishi (1969)
Ilmenite	<1	Baur and Onishi (1969)
Silicate minerals		
Quartz	0.4–1.3	Baur and Onishi (1969)
Feldspar	<0.1–2.1	Baur and Onishi (1969)
Biotite	1.4	Baur and Onishi (1969)
Amphibole	1.1–2.3	Baur and Onishi (1969)
Olivine	0.08–0.17	Baur and Onishi (1969)
Pyroxene	0.05–0.8	Baur and Onishi (1969)
Carbonate minerals		
Calcite	1–8	Boyle and Jonasson (1973)
Dolomite	<3	Boyle and Jonasson (1973)
Siderite	<3	Boyle and Jonasson (1973)
Sulphate minerals		
Gypsum/anhydrite	<1–6	Boyle and Jonasson (1973)
Barite	<1–12	Boyle and Jonasson (1973)
Jarosite	34–1000	Boyle and Jonasson (1973)
Other minerals		
Apatite	<1–1000	Baur and Onishi (1969), Boyle and Jonasson (1973)
Halite	<3–30	Stewart (1963)
Fluorite	<2	Boyle and Jonasson (1973)

around 1 mg kg^{-1} or less. Carbonate minerals usually contain less than 10 mg kg^{-1} As (Table 3).

3.2. *Rocks, sediments and soils*

3.2.1. *Igneous rocks*

Arsenic concentrations in igneous rocks are generally low. Ure and Berrow (1982) quoted an average value of 1.5 mg kg^{-1} for all igneous rock types (undistinguished). Averages for different types distinguished by silica content (Table 4) are slightly higher than this value but generally less than 5 mg kg^{-1}. Volcanic glasses are only slightly higher with an average of around 5.9 mg kg^{-1} (Table 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 (Nicolli et al., 1989; Smedley et al., 2002). This may relate to the reactive nature of recent acidic volcanic material, especially fine-grained ash and its tendency to give rise to Na-rich high-pH groundwaters (Section 5).

3.2.2. *Metamorphic rocks*

Arsenic concentrations in metamorphic rocks tend to reflect the concentrations in their igneous and sedimentary precursors. Most contain around 5 mg kg^{-1} or less. Pelitic rocks (slates, phyllites) typically have the highest concentrations with on average ca. 18 mg kg^{-1} (Table 4).

3.2.3. *Sedimentary rocks*

The concentration of As in sedimentary rocks is typically in the range 5–10 mg kg^{-1} (Webster, 1999), i.e. slightly above average terrestrial abundance. Average

Table 4
Typical As concentrations in rocks, sediments, soils and other surficial deposits

Rock/sediment type	As concentration average and/or range (mg kg^{-1})	No of analyses	Reference
Igneous rocks			
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	Onishi and Sandell (1955); Baur and Onishi (1969); Boyle and Jonasson (1973); Ure and Berrow (1982); Riedel and Eikmann (1986)
Intermediate (andesite, trachyte, latite)	2.7 (0.5–5.8)	30	
Intermediate (diorite, granodiorite, syenite)	1.0 (0.09–13.4)	39	
Acidic rocks (rhyolite)	4.3 (3.2–5.4)	2	
Acidic rocks (granite, aplite)	1.3 (0.2–15)	116	
Acidic rocks (pitchstone)	1.7 (0.5–3.3)		
Volcanic glasses	5.9 (2.2–12.2)	12	
Metamorphic rocks			
Quartzite	5.5 (2.2–7.6)	4	
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	
Sedimentary rocks			
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 et al. (1988); Belkin et al. (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		
Unconsolidated sediments			
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 Colombia	5.5 (0.9–44)	119	Cook et al. (1995)
Glacial till, British Colombia	9.2 (1.9–170)		Cook et al. (1995)
World average river sediments	5		Martin and Whitfield (1983)
Stream and lake silt (Canada)	6 (<1–72)	310	Boyle and Jonasson (1973)
Loess silts, Argentina	5.4–18		Arribére et al. (1997); Smedley et al. (2002)
Continental margin sediments (argillaceous, some anoxic)	2.3–8.2		Legeleux et al. (1994)
Soils			
Various	7.2 (0.1–55)	327	Boyle and Jonasson (1973)
Peaty and bog soils	13 (2–36)	14	Ure and Berrow (1982)
Acid sulphate soils (Vietnam)	6–41	25	Gustafsson and Tin (1994)
Acid sulphate soils (Canada)	1.5–45	18	Dudas (1984); Dudas et al. (1988)
Soils near sulphide deposits	126 (2–8000)	193	Boyle and Jonasson (1973)
Contaminated surficial deposits			
Mining-contaminated lake sediment, British Colombia	342 (80–1104)		Azcue et al. (1994, 1995)

(*continued on next page*)

Table 4 (*continued*)

Rock/sediment type	As concentration average and/ or range (mg kg^{-1})	No of analyses	Reference
Mining-contaminated reservoir sediment, Montana	100–800		Moore et al. (1988)
Mine tailings, British Colombia	903 (396–2000)		Azcue et al. (1995)
Soils and tailings-contaminated soil, UK	120–52,600	86	Kavanagh et al. (1997)
Tailings-contaminated soil, Montana	up to 1100		Nagorski and Moore (1999)
Industrially polluted inter-tidal sediments, USA	0.38–1260		Davis et al. (1997)
Soils below chemicals factory, USA	1.3–4770		Hale et al. (1997)
Sewage sludge	9.8 (2.4–39.6)		Zhu and Tabatabai (1995)

sediments are enriched in As relative to igneous rocks. Sands and sandstones tend to have the lowest concentrations, reflecting the low As concentrations of their dominant minerals: quartz and feldspars. Average sandstone As concentrations are around 4 mg kg^{-1} (Table 4) although Ure and Berrow (1982) gave a lower average value of 1 mg kg^{-1}.

Argillaceous deposits have a broader range and higher average As concentrations than sandstones, with a typical average of around 13 mg kg^{-1} (Table 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 at the high end of the range, principally because of their enhanced pyrite content. Data given in Table 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 S concentrations. Sediment provenance is also a likely factor. Particularly high As concentrations have been determined for shales from mid-ocean settings (Mid-Atlantic Ridge average 174 mg kg^{-1}; Table 4).

Concentrations in coals and bituminous deposits are variable but often high. Samples of organic-rich shale (Kupferschiefer) from Germany have As concentrations of 100–900 mg kg^{-1} (Riedel and Eikmann, 1986; Table 4). Some coal samples have been found with extremely high concentrations up to 35,000 mg kg^{-1} (Belkin et al., 2000), although generally low concentrations of 2.5–17 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 mg kg^{-1}; Table 4).

Some of the highest observed As concentrations are found in ironstones and Fe-rich rocks. James (1966) collated data for ironstones from various parts of the world and reported As concentrations up to 800 mg kg^{-1} in a chamosite-limonite oolite from the former USSR. Boyle and Jonasson (1973) gave concentrations for Fe-rich rocks up to 2900 mg kg^{-1} (Table 4). Phosphorites are also relatively enriched in As, with values up to ca. 400 mg kg^{-1} having been reported.

3.2.4. Unconsolidated sediments

Concentrations of As in unconsolidated sediments are not notably different from those in their indurated equivalents. Muds and clays usually have higher concentrations than sands and carbonates. Values are typically 3–10 mg kg^{-1}, depending on texture and mineralogy (Table 4). Elevated concentrations tend to reflect the amounts of pyrite or Fe oxides present. Increases are also common 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^{-1} (AGRG, 1978). Similar concentrations have also been found in river sediments where groundwater-As concentrations are high: Datta and Subramanian (1997) found concentrations in sediments from the River Ganges averaging 2.0 mg kg^{-1} (range 1.2–2.6 mg kg^{-1}), from the Brahmaputra River averaging 2.8 mg kg^{-1} (range 1.4–5.9 mg kg^{-1}) and from the Meghna River averaging 3.5 mg kg^{-1} (range 1.3–5.6 mg kg^{-1}).

Cook et al. (1995) found concentrations in lake sediments ranging between 0.9 and 44 mg kg^{-1} (median 5.5 mg kg^{-1}) but noted that the highest concentrations were present up to a few kilometres down-slope of mineralised areas. The upper baseline concentration for these sediments is likely to be around 13 mg kg^{-1} (90th percentile). They also found concentrations in glacial till of 1.9–170 mg kg^{-1} (median 9.2 mg kg^{-1}; Table 4) and noted the highest concentrations down-ice of mineralised areas (upper baseline, 90th percentile, 22 mg kg^{-1}). Relative As 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^{-1} (Table 4).

3.2.5. Soils

Baseline concentrations of As in soils are generally of the order of 5–10 mg kg^{-1}. Boyle and Jonasson (1973) quoted an average baseline concentration in world soils of 7.2 mg kg^{-1} (Table 4) and Shacklette et al. (1974) quoted an average of 7.4 mg kg^{-1} (901 samples) for American soils. Ure and Berrow (1982) gave a higher average value of 11.3 mg kg^{-1}. Peats and bog soils can have higher concentrations (average 13 mg kg^{-1}; Table 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 pyritic shales, mineral veins and dewatered mangrove swamps can also be relatively enriched in As. Dudas (1984) found As concentrations up to 45 mg kg^{-1} 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^{-1}) 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^{-1}) 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^{-1} in orchard soils as a result of the historical application of arsenical pesticides to fruit crops.

3.2.6. 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^{-1} (Table 4). The high concentrations reflect not only increased abundance of primary As-rich sulphide minerals, but also secondary Fe arsenates and Fe oxides formed as reaction products of the original ore minerals. The primary sulphide minerals are susceptible to oxidation in the tailings pile and the secondary minerals have varying solubility in oxidising conditions in groundwaters and surface waters. Scorodite ($FeAsO_4 \cdot 2H_2O$) is a common sulphide oxidation product and its solubility is considered to control As concentrations in such oxidising sulphide environments. Scorodite is metastable under most groundwater conditions and tends to dissolve incongruently, forming Fe oxides and releasing As into solution (Robins, 1987; Krause and Ettel, 1989). In practice, a wide range of Fe–As mineral solubility relationships are found which in part relate to the mineral type (Krause 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 (As_2O_3) is also relatively soluble. Arsenic bound to Fe oxides is relatively immobile, particularly under oxidising conditions.

3.3. The atmosphere

The concentrations of As 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} μg m^{-3} have been recorded in unpolluted areas, increasing to 0.003–0.18 μg m^{-3} in urban areas and greater than 1 μg m^{-3} close to industrial plants (WHO, 2001). Much of the atmospheric As is particulate. Total As deposition rates have been calculated in the range <1–1000 μg m^{-2} a^{-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 μg m^{-2} a^{-1} (29–55% as dry deposition) were estimated for the mid-Atlantic coast (Scudlark and Church, 1988). Airborne As 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 As poses a real health threat for drinking-water sources. Atmospheric As 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 domestic coal fires, rather than from drinking water affected by atmospheric inputs (Finkelman et al., 1999).

4. Mineral–water interactions

4.1. Controls on arsenic mobilisation

As with most trace metals, the concentration of As 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 As concentrations.

The importance of oxides in controlling the concentration of As in natural waters has been appreciated for a long time (Livesey and Huang, 1981; Matisoff et al., 1982) and there has been a wide range of studies to measure the adsorption isotherms on natural and synthetic oxide minerals and to establish the sorption processes at the molecular scale (Table 5). Even so, important uncertainties still remain in relation to the interactions of As(III) and As(V) at environmental concentrations and in the presence of other interacting ions. Frequently, the element which correlates best with As in sediments is Fe. This is also the basis for the use of Fe salts (as well as Al and Mn salts) in water treatment for the removal of As and other elements (e.g. Edwards, 1994). The As content of residual sludges from water treatment can be in the range 1000–10,000 mg kg^{-1} (Forstner and Haase, 1998; Driehaus et al., 1998). Clays can also adsorb As(III) and As(V) (Manning and Goldberg, 1997b) but their role in sediments in terms of As binding is unclear at present.

It is difficult to study mineral-water interactions directly in aquifers. Most studies, including those with a bearing on As 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 of 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 Fe oxides in reducing soils and sediments and the influence of this on the release of As. Matisoff et al. (1982) related reductive dissolution of Fe oxides to the possible release of As in groundwater from an alluvial aquifer in NE Ohio. Korte (1991) and Korte and Fernando (1991) also speculated that desorption of As from Fe oxides could occur in reducing, alluvial sediments and that this could lead to high-As groundwaters.

4.2. Arsenic associations in sediments

The major minerals binding As (as both arsenate and arsenite) in sediments are the metal oxides, particularly those of Fe, Al and Mn (De Vitre et al., 1991; Sullivan and Aller, 1996). About 50% of the Fe in freshwater sediments is in the form of Fe oxides and about 20% of the Fe is 'reactive' Fe. Clays also adsorb As because of the oxide-like character of their edges. The extent of As(V) sorption to, and coprecipitation on, carbonate minerals is unknown but if it behaves like phosphate, it is likely to be strongly retained by these minerals and this may limit As concentrations in groundwaters from limestone aquifers (Millero et al., 2001). Of these mineral components, Fe oxides are probably the most important adsorbents in sandy aquifers because of their greater abundance and the strong binding affinity. Nevertheless, Al oxides can also be expected to play a significant role when present in quantity (Hingston et al., 1971; Manning and Goldberg, 1997b). Experience from water treatment suggests that below pH 7.5, Al hydroxides are about as effective as Fe hydroxides (on a molar basis) for adsorbing As(V) but that Fe salts are more efficient at higher pH and for adsorbing As(III) (Edwards, 1994).

The interactions of As with Fe oxides have been studied in considerable detail in the laboratory and therefore provide the best insight into the likely behavior of As-mineral interactions in aquifers. However, most of these laboratory studies, particularly the older studies, have been undertaken at rather high As concentrations (Hingston et al., 1971) and there is a paucity of reliable adsorption data at the low μg l^{-1} level of relevance to natural waters. In addition, there is uncertainty over the extent to which the Fe oxides most commonly studied in the laboratory reflect the Fe oxides found in 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 et al.'s (1971) data for As(V) adsorption on goethite, highlighting the high affinity for As of freshly-formed 'amorphous' Fe oxides. 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. Fe and As 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.

4.3. Reduced sediments and the role of iron oxides

A well-known sequence of reduction reactions occurs when lakes, fjords, soils, sediments and aquifers become anaerobic (Berner, 1981; Stumm and Morgan, 1995; Langmuir, 1997). The processes causing changes in Fe redox chemistry are particularly important since they can directly affect the mobility of As. One of the principal causes of high As concentrations in subsurface waters is the reductive dissolution of hydrous Fe oxides and/or the release of adsorbed or combined As. This sequence begins with the consumption of O_2 and an increase in dissolved CO_2 from the decomposition of organic matter. Next, NO_3^- decreases by reduction to

Table 5
Studies of As 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 $Al(OH)_3$ (pH 3–10). ‘Adsorption’ exceeded 15 mol kg^{-1} at pH 5. Fitted data to pH dependent Langmuir isotherm	Anderson et al. (1976)
HFO	Kinetics and pH dependence of As(V) and As(III) adsorption on HFO (202 m^2 g^{-1}). Found very high As(V) and As(III) loadings (up to 4–5 mol As kg^{-1}) at the highest concentrations. pH adsorption envelopes at various As_T loadings	Raven et al. (1998)
HFO	Adsorption isotherms for arsenite and arsenate over free concentration range from 10^{-7} to 10^{-3} 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_4 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 two-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 $Fe(O,OH)_6$ octahedra. Saturation at As/Fe mol ratio of 0.68	Waychunas et al. (1996)
HFO	As(III) and As(V) adsorption and OH^- release/uptake on synthetic two-line ferrihydrite. As(V) at pH 9.2 released up to 1 mol OH^- per mol As sorbed whereas As(III) released <0.25 mol As per mol Fe. At pH 4.6, OH^- release was much less for As(V) adsorption and under these conditions there was a net release of H^+ by arsenite. These differences reflect the mechanism of As adsorption and influence the pH dependence of adsorption	Jain et al. (1999)
Granular ‘ferric hydroxide’ (akageneite)	As(V) isotherms given in the sub-μM concentration range; SO_4 competition significant at mM concentrations below pH 7 only; phosphate competition at ‘natural’ groundwater concentrations	Driehaus et al. (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 fitted to Constant Capacitance SCM	Manning et al. (1998)
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^{-1} As)	Matis et al. (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 et al. (1999)

(*continued on next page*)

Table 5 (*continued*)

Mineral	Comment	Reference
Goethite	EXAFS study of As(V) and Cr (VI) adsorption on goethite. Monodentate binding favoured at low surface coverages of As(V), bidentate at high surface coverages	Fendorf et al. (1997)
Manganese oxides	As(III) and As(V) removal by $MnO_2(s)$ is similar, up to say 5 mmol As mol^{-1} Mn at μM As equilibrium solution concentrations. Freundlich isotherm obeyed. As(III) oxidised to As(V). Rapid oxidation (minutes) and adsorption of As(III). Monitored Mn release and effect of pH, Ca, phosphate and sulphate	Driehaus et al. (1995)
Birnessite, cryptomelane and pyrolusite	Studied adsorption of As(III) and As(V) and kinetics of As(III) oxidation in presence of various MnO_2. As(III) adsorption (per unit weight of oxide): cryptomelane > birnessite > pyrolusite whereas for As(V): cryptomelane > pyrolusite > birnessite (not detectable). No isotherms given	Oscarson et al. (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^{-1}) tended to reduce As adsorption. Gives K_d values	Bowell (1994)
Alumina, hematite, quartz and kaolin	As(V) adsorption on natural, low surface area alumina, hematite, quartz and kaolin (0.12–5 $m^2\ g^{-1}$) at pH 3–10. Adsorption decreases with pH; alumina = kaolin > hematite > > quartz. Gives K_d values and isotherms at low concentrations. Some SO_4^{2-} competition especially below pH 7. FA (> 10 mg l^{-1}) generally reduced adsorption at pH 5–7 but not above pH 7 where FA is not adsorbed	Xu et al. (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 K_d (l kg^{-1}) at micromolar concentrations (pH 7) was 2.5–3.5 for As(V) and about 1.5 for As(III). FA decreased adsorption	Xu et al. (1991)

Notes: HFO = hydrous ferric oxide.
SCM = surface complexation model.
EXAFS = extended X-ray absorption fine structure.
XANES = X-ray absorption near-edge structure.
MMAA = monomethylarsonic acid, $CH_3AsO(OH)_2$.
DMAA = dimethylarsinic acid, $(CH_3)_2AsO(OH)$).
FA = fulvic acid.
CD-MUSIC = charge distribution-multisite complexation model.

NO_2^- and the gases N_2O and N_2. Insoluble manganic oxides dissolve by reduction to soluble Mn^{2+} and hydrous ferric oxides are reduced to Fe^{2+}. These processes are followed by SO_4^{2-} reduction to S^{2-}, then CH_4 production from fermentation and methanogenesis, and finally reduction of N_2 to NH_4^+. During SO_4^{2-} reduction, the consequent S^{2-} reacts with any available Fe to produce FeS and ultimately pyrite, FeS_2. Iron is often more abundant than S so that there is 'excess Fe' 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_4^{2-} reduction.

In SO_4^{2-}-poor environments, Fe from free Fe oxides is solubilized as Fe^{2+} under reducing conditions. This gives rise to characteristically high-Fe waters. Groundwaters in such conditions tend to have Fe concentrations of 0.1–30 mg l^{-1}. The reaction is microbially mediated (Lovley and Chappelle, 1995). There is also evidence for solid-state transformations of the Fe 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 Fe 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 Fe of 2.5 (Davison, 1993). The exact fate of Fe 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 Fe 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 '$Fe_3(OH)_8$'. Boughriet et al. (1997) suspected the presence of either green-rust-like compounds, Fe(III)–Fe(II)–$(CO_3)(OH)$ or $Fe(II)_xCa_{1-x}CO_3$ solid solutions, in anoxic sediments from the Seine Estuary. They used ^{57}Fe Mössbauer spectroscopy to characterize the Fe. 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_3O_4), 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_2S, it slowly converts to pyrite over a period of 100a or more (Canfield and Berner, 1987). At the sediment/water interface in oceans, partial oxidation of primary magnetite (Fe_3O_4) can lead to a coating of maghemite, γ-Fe_2O_3. Further burial and reduction leads to the dissolution of the primary magnetite (Torii, 1997).

These studies of 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 Fe oxide minerals in sedimentary environments is an important aspect in understanding the processes leading to As mobilisation in sedimentary environments.

4.4. Arsenic release from soils and sediments following reduction

There is considerable evidence from laboratory studies that As 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 P (Mortimer, 1942; Farmer et al., 1994; Slomp et al., 1996) and As (Aggett and O'Brien, 1985; Moore et al., 1988; De Vitre et al., 1991; Azcue and Nriagu, 1995; Widerlund and Ingri, 1995) below the redox boundary in sediments. This release has long been associated with Fe 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 As 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 porewater As concentrations (up to about 30 μg l^{-1}) with depth in a lake sediment and that this was mirrored by an increase in dissolved Fe. Upwardly diffusing Fe^{2+} was oxidised near the sediment-water interface and precipitated as an Fe oxide which then adsorbed the upwardly diffusing As. As noted in Section 2.2.7, much larger As concentrations, up to a peak of 6430 μg l^{-1}, have been measured in porewaters from shallow, anoxic lake sediments in the geothermal region of New Zealand (Aggett and Kriegman, 1988). This dissolved As, mostly As(III), diffused across the sediment-lake water interface and accumulated along with dissolved Fe and Mn in the hypolimnion until turnover. On the other hand, recent studies of As profiles in Crowley Lake, California, a lake affected by large inputs of As in surface water affected by geothermal sources, suggest that As is not released from the sediments. Rather it is taken up by the sediments, probably in solid sulphide phases (Kneebone and Hering, 2000).

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 desorption 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 As sorbed by sediments. Masscheleyn et al. (1991) measured the release of As and other metals following the flooding and reduction of an As-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 Fe-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 As 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).

There is now considerable evidence that high-As groundwaters can be associated with reducing conditions, particularly in alluvial and deltaic environments. The Bengal Basin is the most notable example. While the precise mechanisms responsible for this remain uncertain, it is possible that both reductive desorption and reductive dissolution of As from oxides and clays play a role. At the near-neutral pH of many groundwaters, As(III) is expected to be less strongly sorbed than As(V) and so some desorption of As may occur as a result of the onset of strongly reducing conditions following sediment burial (DPHE/BGS/MML, 1999, Vol. S4). Recent experiments with synthetic Fe and Al oxides have demonstrated the desorption of As following reduction of As(V) to As(III) (Zobrist et al., 2000). Dissolution of the oxides was not necessary for As release.

4.5. Speciation of elements in sediments and the role of selective extraction techniques

The As concentration in sediments is normally too low and/or the particles too small for direct investigation of solid phase As speciation using techniques such as XAFS and PIXE and so selective dissolution has been most widely used. A number of chemical extraction 'schemes' have been devised which attempt to allocate elements to particular solid phases but few of these are specifically designed for speciating solid phase As. Gómez-Ariza et al. (1998) developed a method to speciate solid-phase As based on selective extraction of sediments with hydroxylamine hydrochloride, an acidic and reducing extractant that is rather selective for extracting Mn oxides but that also extracts small amounts of Fe oxides. Hydroxylamine hydrochloride did not reduce the As(V) during the extraction.

Keon et al. (2001) have described a more comprehensive 8-step sequential extraction scheme that attempts to partition sediment As into various forms. The scheme uses: (i) 1 M $MgCl_2$ (for ionically-bound As); (ii) 1 M NaH_2PO_4 (strongly adsorbed); (iii) 1 M HCl (acid volatile sulphides, carbonates, Mn oxides and very amorphous Fe oxyhydroxides); (iv) 0.2 M oxalate/oxalic acid (amorphous Fe oxyhydroxides); (v) 0.05 M Ti(III)–citrate-EDTA-bicarbonate (crystalline Fe oxyhydroxides); (vi) 10 M HF (arsenic oxides and silicates); (vii) 16 M HNO_3 (pyrite and amorphous As_2S_3) and (viii) hot 16 M $HNO_3 + 30\%$ H_2O_2 (orpiment and other recalcitrant minerals). About 90% of the As in a selection of highly-contaminated sediments from the Wells G&H Superfund site in the Aberjona catchment was found to be in the (ii)–(iv) fractions described above.

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 3-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 Fe oxides was not responsible for the As release. Brannon and Patrick (1987) speculated that a change in the structure of the Fe 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 3 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). Arsenic(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 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.

Aggett and Roberts (1986) found a good correlation between the release of both As and phosphate from New Zealand lake sediments with that of EDTA-extractable Fe. They concluded that the As was primarily associated with amorphous Fe oxides and they suggested that because of the relative constancy of the Fe/As ratio during dissolution, the As had probably been coprecipitated with the Fe oxide rather than being adsorbed to it.

Acid ammonium oxalate has been widely used for extracting 'amorphous Fe oxides' and has been extensively used on sediments from Bangladesh (BGS and DPHE, 2001). There was a good overall correlation between extractable As and Fe but many other elements were also correlated with the extractable Fe since this tended to be most abundant in the fine-grained sediments. Nevertheless, the amount of oxalate-extractable Fe and As of the aquifer sediments appeared to separate low-As groundwater areas from high-As areas. Acid ammonium oxalate is less selective with reducing sediments compared with oxidising sediments since mixed valence Fe minerals such as magnetite are also dissolved to a considerable extent. It also can dissolve appreciable amounts of clays, as reflected by the extensive release of Mg, Al and Si.

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.

Alkaline extractants, particularly bicarbonate solutions at various pH values (e.g. 7.6, 8.5 and 10), have been widely used to assess the plant availability of soil phosphate. These have not yet been applied to the extraction of As, specifically As(V), although Gustafsson and Jacks (1995) used 0.5 M NaOH. This usually extracted some 1/2 to 2/3 of the 'total' As(V) from the mineral horizons of some Swedish forest soils.

Unfortunately, none of the selective extraction schemes is perfect or universally applicable and there is little consensus on the best techniques to use. There are no recognised procedures for solid phase As speciation, although a number of traditional approaches have been used on an ad hoc basis and new approaches are the subject of current research (Keon et al., 2001). The interpretation of results for many of these extractions is difficult for minor and trace constituents which may be released by dissolution, codissolution 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 useful for characterising 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 in the natural environment.

4.6. 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, 1994). In the simplest case of a linear adsorption isotherm, this relationship is straightforward and the partition coefficient, K_d, defines a constant retardation factor. With a non-linear adsorption isotherm, the value of K_d varies with concentration and is related to the shape of the isotherm. Normally, the K_d decreases with increasing concentration, leading to less retardation at high concentrations and ultimately to self-sharpening fronts and diffuse tails during transport. This means that it is difficult to flush As completely from an aquifer.

Since the transport of a solute is closely related to the extent of adsorption and the nature of the adsorption isotherm, it follows that arsenate and arsenite, which have different adsorption isotherms, should travel through an aquifer with different velocities. This will lead 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}As (half-life = 17.7 days) and ^{76}As (half-life = 26.4 h) 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 condition (i) but was still slower than As(III); (iii) with reducing groundwater at 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 As 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 further complicating a simple interpretation of well water analyses.

A number of experimental investigations of As adsorption reported in the literature, most commonly for pure Fe and Al oxides, allow K_d values to be estimated for a range of adsorbents (Table 6). The K_ds thus derived, here mostly calculated for pH 7, have a large range, spanning around 6 orders of magnitude. All other things being equal, K_ds tend to decrease with increasing As concentration reflecting some nonlinearity in the sorption isotherm. As expected, under similar conditions, K_ds are often greater for As(V) than for As(III) but this is not always the case. Values are highest for HFO which in part reflects the large adsorption capacity of HFO. High K_d values are also found for Mn oxides (birnessite). Experiments with Mn oxides by Driehaus et al. (1995) suggest that values are high for both As(V) and As(III), although in practice, much of the As(III) was probably oxidised to As(V) during the experiment by the Mn(IV) oxide (Oscarson et al., 1981; 1983). There is a need for more high-quality data on the sorption of As(V) and As(III) at low As concentrations (1–100 μg l^{-1}) including experiments carried out in the presence of competing anions and using aquifer solids rather than synthetic minerals.

A few field-based investigations have been carried out on natural and contaminated systems which allow K_d values for As sorption to be determined directly. Kuhlmeier (1997a,b) studied the transport of As in highly-contaminated clayey and sandy soils from around an

Table 6
Solid-solution partition coefficients (K_ds) calculated from experimental data at or near pH 7 for a range of oxides and clays

Material	Components	K_d (l kg^{-1})	pH	Comments	Reference
Alumina (α-Al_2O_3)	As(III)	42	7	$^{a}c = 37$ μg l^{-1}, $I = 0.1$ M	Xu et al. (1991), Fig. 2
Alumina (α-Al_2O_3)	As(V)	760	7	$c = 3.8$ μg l^{-1}, $I = 0.1$ M	Xu et al. (1988), Fig. 3
Alumina (α-Al_2O_3)	As(V)	520	7	$c = 1200$ μg l^{-1}, $I = 0.01$ M	Anderson et al. (1976), Fig. 2
Amorphous aluminium hydroxide	As(III)	230	7	$c = 4$ μg l^{-1}	Manning and Goldberg (1997a), Fig. 1
Gibbsite	As(V)	133	7	$c = 16$ mg l^{-1}	Hingston et al. (1971), Fig. 3a
Gibbsite	As(V)	32	7	$c = 16$ mg/l + 5.5 mg l^{-1} P	Hingston et al. (1971), Fig. 3c + b
Goethite	As(V)	192	7	$c = 4.9$ mg l^{-1}, $I = 0.1$ M	Hingston et al. (1971), Fig. 2
Goethite	As(V) + P	54	7	$c = 66$ mg l^{-1}, + 74 mg l^{-1} P, $I = 0.1$ M	Hingston et al. (1971), Fig. 4
Goethite (natural)	As(III)	32	7	$c = 40$ μg l^{-1}	Bowell (1994), Fig. 2
Goethite (natural)	As(V)	1800	7	$c = 1.5$ μg l^{-1}	Bowell (1994), Fig. 2
Haematite	As(V)	34	7	$c = 48$ μg l^{-1}, $I = 0.1$ M	Xu et al. (1988), Fig. 3
Haematite (natural)	As(III)	21	7	$c = 48$ μg l^{-1}	Bowell (1994), Fig. 2
Haematite (natural)	As(V)	25	7	$c = 45$ μg l^{-1}	Bowell (1994), Fig. 2
HFO	As	7000		$c = 50$ μg l^{-1}	Thirunavukukkarasu et al. (2001), Fig. 3
HFO	As(III)	120,000	7	$c = 310$ μg l^{-1}, $I = 0.1$ M	Swedlund and Webster (1999), Fig. 1a
HFO	As(III)	670,000	7	$c = 27$ μg l^{-1}, $I = 0.01$ M	Pierce and Moore (1982), Fig. 1
HFO	As(III)	7340	7	$c = 18900$ μg l^{-1}, $I = 0.01$ M	Pierce and Moore (1982), Fig. 3
HFO	As(III)	520,000	7	$c = 30$ μg l^{-1}, $I = 0.01$ M; possibly partial oxidation during experiment	Wilkie and Hering (1996), Fig. 1
HFO	As(III) + Si	13,000	7	$c = 1690$ μg l^{-1}, $Si_T = 62$ mg l^{-1}, $I = 0.1$ M	Swedlund and Webster (1998), Fig. 1a
HFO	As(V)	> 1,000,000	7	$c < 50$ μg l^{-1}, $I = 0.1$ M	Swedlund and Webster (1998), Fig. 1b
HFO	As(V)	460,000	7	$c = 32$ μg l^{-1} $I = 0.01$ M	Pierce and Moore (1982), Fig. 5
HFO	As(V)	120,000	7	$c = 160$ μg l^{-1} $I = 0.01$ M	Pierce and Moore (1982), Fig. 5
HFO	As(V)	37,000	7	$c = 850$ μg l^{-1} $I = 0.01$ M	Pierce and Moore (1982), Fig. 5
HFO	As(V)	66,000	7	$c = 19500$ μg l^{-1} $I = 0.01$ M	Pierce and Moore (1982), Fig. 7
HFO	As(V) + Si	8,100	7	$c = 2130$ μg l^{-1}, $Si_T = 62$ mg l^{-1}, $I = 0.1$ M	Swedlund and Webster (1998), Fig. 1b
HFO (granular)	As(V)	2,100,000	6	50 μg l^{-1}	Driehaus et al. (1998), Fig. 1
Iron-oxide-coated sand	Oxidn state uncertain	600	?	$c = 50$ μg l^{-1}	Thirunavukukkarasu et al. (2001), Fig. 2
Lepidocrocite (natural)	As(III)	35	7	$c = 39$ μg l^{-1}	Bowell (1994), Fig. 2
Lepidocrocite (natural)	As(V)	1000	7	$c = 2.7$ μg l^{-1}	Bowell (1994), Fig. 2

(*continued on next page*)

Table 6 (*continued*)

Material	Components	K_d (l kg^{-1})	pH	Comments	Reference
Birnessite (δ-MnO_2)	"As(III)"	46,000	7	$c = 75$ μg l^{-1}, $I = 0.01$ M; As(III) probably all oxidised during experiment	Driehaus et al. (1995), Fig. 1
Birnessite (δ-MnO_2)	As(V)	57,500	7	$c = 75$ μg l^{-1}, $I = 0.01$ M	Driehaus et al. (1995), Fig. 1
Quartz	As(V)	2	7	$c = 71$ μg l^{-1}, $I = 0.1$ M	Xu et al. (1988), Fig. 3
Illite	As(III)	98	7	$c = 9$ μg l^{-1}	Manning and Goldberg (1997a), Fig. 1
Kaolinite	As(III)	19	7	$c = 20$ μg l^{-1}	Manning and Goldberg (1997a), Fig. 1
Kaolinite	As(V)	760	7	$c = 3.8$ μg l^{-1}, $I = 0.1$ M	Xu et al. (1988), Fig. 3
Wyoming Bentonite	As(III)	30	7	$c = 17$ μg l^{-1}	Manning and Goldberg (1997a), Fig. 1

[a] c = final dissolved As concentration; I = ionic strength.

old As herbicide plant in Houston, Texas. He used column experiments to estimate 'apparent' K_d values. These were time- and implicitly concentration-dependent and for the sandy soils ranged from 0.26 l kg^{-1} after one void volume to 3.3 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 mg l^{-1}), mostly as MMAA. The sediment contained only a few mg kg^{-1} of inorganic As.

Baes and Sharp (1983) gave K_d values of 1.0–8.3 l kg^{-1} (median 3.3) for As(III) binding by soils and 1.9–18.0 l kg^{-1} (median 6.7) for As(V). The authors have estimated K_ds for 3 Californian soils (pH 5.7–7.1) at an equilibrium concentration of 50 μg l^{-1} to range from 5–52 l kg^{-1} for As(III) and 10–80 for As(V) (Manning and Goldberg, 1997a, Fig. 4).

Data from Sullivan and Aller (1996) indicate that K_d values calculated for sediment profiles from the Amazon Shelf are in the approximate range 11–5000 l kg^{-1}. High-As porewaters were mostly from the zones with low K_d values (typically <100 l kg^{-1}). The concentrations of reactive solid As derived from an acid leach were in the approximate range 1–13 mg kg^{-1} and the authors gave an average total sediment As concentration of 12 mg kg^{-1}. Smedley et al. (2000) also estimated K_d for loess sediments bearing high-As groundwaters from La Pampa, Argentina. They estimated a low value, close to 1 l kg^{-1}, using coupled porewater and oxalate-extract data. Arsenic concentrations of the analysed sediments were in the range 3–18 mg kg^{-1}.

Calculated sorption and retardation factors, based on the Dzombak and Morel (1990) diffuse double layer model and database for HFO, indicate highly variable K_ds depending on: the HFO (and other active oxide) content of the sediment, As speciation, As concentration, pH and concentration of competitors such as phosphate (DPHE/BGS/MML, 1999, Vol. S3 and S4). Inferred K_ds from these calculations for Bangladesh sediments range from about 1 l kg^{-1} for As(V) under 'high P-low Fe' conditions to more than 200 l kg^{-1} under 'low P-high Fe' conditions. Broadly similar values are inferred for As(III) sorption under comparable conditions—the presence of high phosphate concentrations is calculated to severely reduce As(V) sorption but not As(III) sorption. Coupled studies of sediment and groundwater chemistry in piezometers (10–50 m depth) in 3 high-As groundwater locations in Bangladesh (BGS and DPHE, 2001) suggest that the K_ds for As are low, approximately 2–6 l kg^{-1}. These values have been derived by assuming that the sorbed As can be equated to the oxalate-extractable As and so are likely to represent an upper estimate.

Values obtained for K_d from these field studies in areas having high-As groundwaters generally suggest that it is, for whatever reason, the low K_d values that are responsible for the high dissolved As concentrations, rather than high absolute concentrations of As in the sediment. The K_d values given in Table 6 are in many cases much higher than found in natural sediments, even after allowing for the relatively minor concentration (a few percent) of Fe oxides in most sediments. There is some evidence that use of the surface complexation model and database of Dzombak and Morel (1990) can lead to an overestimation of sorption when applied to natural sediments (Kent et al., 1995). This may reflect a difference between the natural Fe oxides found in sediments and synthetic HFO used for most laboratory studies or other factors such as the presence of competing ions in the natural sediments. Certainly it would be difficult to infer the location of high-As groundwaters from an analysis of total sediment As concentrations alone.

5. Groundwater environments with high arsenic concentrations

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 μg l^{-1}, often significantly so. The most noteworthy occurrences are in parts of Argentina, Bangladesh, Chile, China, Hungary, India (West Bengal), Mexico, Romania, Taiwan, Vietnam and many parts of the USA, particularly the SW (Fig. 3). Some of the better documented cases are summarised in Table 7. These include natural sources of enrichment as well as mining-related sources. Recent reconnaissance surveys of groundwater quality in other areas such as parts of Nepal, Myanmar and Cambodia have also revealed concentrations of As in some sources exceeding 50 μg l^{-1}, although documentation of the affected aquifers is so far limited. 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.

Localised groundwater As problems are now being reported from an increasing number of countries and many new cases are likely to be discovered. Until recently, As was not traditionally on the list of elements routinely tested by water-quality testing laboratories and so many high-As water sources may have been missed. Revision of drinking-water regulations and guidelines for As has prompted a reassessment of the situation in many countries. The recent discovery of As enrichment on a large scale in Bangladesh has highlighted the need for a rapid assessment of the situation in alluvial aquifers worldwide. As described above, As 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 sometimes being in the mg l^{-1} 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 Ghana, Greece, Thailand and the USA (Fig. 3).

While high-As groundwaters (with As 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-As groundwaters are not necessarily related to areas of high As concentrations in the source rocks. Distinctive groundwater As problems occur under both reducing and oxidising groundwater conditions; also under both humid/temperate and arid climates. Below, the authors discuss the characteristics of the As problems worldwide through a series of type examples. These have been ordered according to the environment under which they are developed.

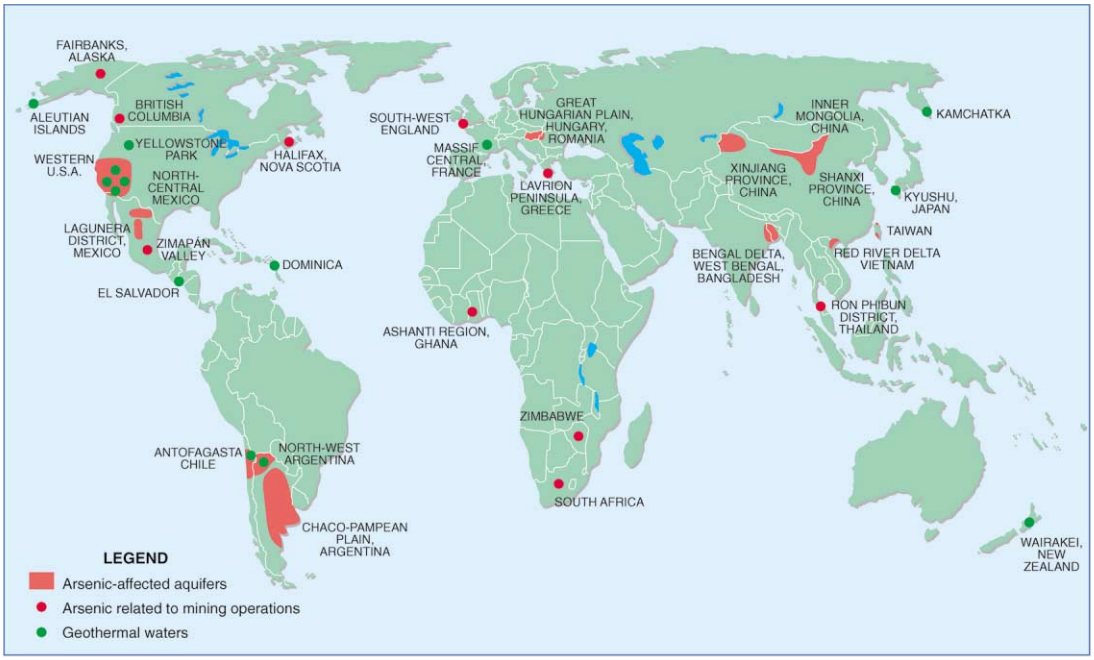

Fig. 3. Distribution of documented world problems with As in groundwater in major aquifers as well as water and environmental problems related to mining and geothermal sources. Areas in blue are lakes.

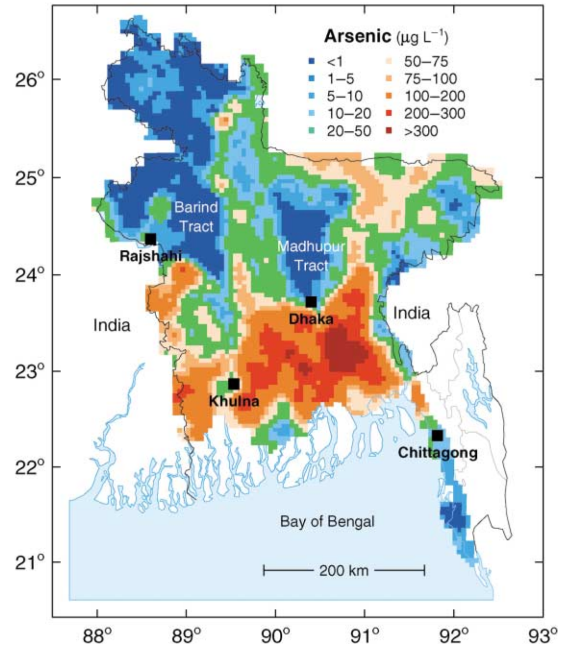

Fig. 4. Smoothed map showing the distribution of As in groundwater from shallow (<150 m) tubewells in Bangladesh.

5.2. Reducing environments

5.2.1. 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 to ca. 3200 μg l^{-1} (DPHE/BGS/MML, 1999; CGWB, 1999; BGS and DPHE, 2001). Some 27% of shallow (<150 m deep) wells in Bangladesh contain more than 50 μg l^{-1} As (BGS and DPHE, 2001). The worst-affected area is in the SE of Bangladesh (Fig. 4) where in some districts more than 90% of wells are affected. Resultant health problems were first identified in West Bengal in the 1980s but the first diagnosis in Bangladesh was not made until 1993. Up to around 30–35 million people in Bangladesh are estimated to be exposed to As in drinking water at concentrations above 50 μg l^{-1} (BGS and DPHE, 2001) and up to 6 million in West Bengal (Table 7). Skin disorders including hyper/hypopigmentation changes and keratosis are the most common external manifestations, although skin cancer has also been identified. 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 As-related health problems is also not known but could be appreciable.

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 these 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 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 aquifer sediments are capped by a layer of clay or silt (of variable thickness) which effectively restricts entry of air to the aquifers. This, together with the presence of recent solid organic matter deposited with the sediments, has resulted in the development of highly reducing conditions which favour the mobilisation of As. The mobilisation has probably occurred by a complex combination of redox changes

Table 7
Summary of documented cases of naturally-occurring As problems in world groundwaters (includes some mining cases)

Country/region	Area (km^2)	Population exposed[a]	Concentration ranges (μg l^{-1})	Aquifer type	Groundwater conditions	Reference
Bangladesh	150,000	ca. 3×10^7	<0.5–2500	Holocene alluvial/deltaic sediments. Abundance of solid organic matter	Strongly reducing, neutral pH, high alkalinity, slow groundwater flow rates	DPHE/BGS/MML (1999); BGS and DPHE (2001)
West Bengal	23,000	6×10^6	<10–3200	As Bangladesh	As Bangladesh	CGWB (1999); PHED/UNICEF (1999)
China:		5.6×10^6				Sun et al. (2001)
Taiwan	4000	?10^5 (formerly)	10–1820	Sediments, including black shale	Strongly reducing, artesian conditions, some groundwaters contain humic acid	Kuo (1968), Tseng et al. (1968)
Inner Mongolia (Tumet Plain including Huhhot Basin (HB); Ba Men, Bayingao, Hexi)	4300 (HB) ?30,000 total	? ca. 10^5 in HB	<1–2400	Holocene alluvial and lacustrine sediments	Strongly reducing conditions, neutral pH, high alkalinity. Deep groundwaters often artesian, some have high concentrations of humic acid	Luo et al. (1997), Zhai et al. (1998), Ma et al. (1999), Sun et al. (1999), Smedley et al. (2001a)
Xinjiang (Tianshan Plain)	38,000	? 500 diagnosed	40–750	Holocene alluvial plain	Reducing, deep wells (up to 660 m) are artesian	Wang and Huang (1994)
Shanxi				Alluvial plain	?Reducing	Sun et al. (1999)
Red River delta, Vietnam	1200 identified	$>10^6$	1–3050	Holocene alluvial/deltaic sediments	Reducing, high Fe, Mn, NH$_4$, high alkalinity	Berg et al. (2001)
Hungary, Romania (Danube Basin)	110,000	29,000	<2–176	Quaternary alluvial plain	Reducing groundwater, some artesian. Some high in humic acid	Varsányi et al. (1991), Gurzau and Gurzau (2001)
Argentina (Chaco-Pampean Plain)	10^6	2×10^6	<1–5300 (7500 in some porewaters)	Holocene and earlier loess with rhyolitic volcanic ash	Oxidising, neutral to high pH, high alkalinity. Groundwaters often saline. As mainly present as As(V), accompanied by high B, V, Mo, U. Also high As concentrations in some river waters	Nicolli et al. (1989), Sancha and Castro (2001), Smedley et al. (2002)
Northern Chile (Antofagasta)	125,000	500,000	100–1000	?Quaternary volcanogenic sediment	Generally oxidising. Arid conditions, high salinity, high B. Also high-As river waters	Cáceres et al. (1992), Karcher et al. (1999); Sancha and Castro (2001)
South-west USA:		3.5x10^5 (total)				Smith et al. (1992)
Basin and 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)

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Table 7 (*continued*)

Country/region	Area (km^2)	Population exposed[a]	Concentration ranges (μg l^{-1})	Aquifer type	Groundwater conditions	Reference
Tulare Basin, San Joaquin Valley, California	5000		<1–2600	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)	Welch and Lico (1998)
Salton Sea Basin					Some saline groundwaters, with high U	Welch and Lico (1998)
Mexico (Lagunera)	32,000	4×10^5	8–620	Volcanic sediments	Oxidising, neutral to high pH, As mainly as As(V)	Del Razo et al. (1990)
Some problem areas related to mining activity and mineralised areas						
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 et al. (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 et al. (1988)
Moira Lake, Ontario, Canada	100		50–3000	Mine tailings	Ore mining (Au, haematite, magnetite, Pb, Co)	Azcue and Nriagu (1995)
Coeur d'Alene, Idaho, USA			up to 1400	Valley-fill deposits	River water and groundwater affected by Pb-Zn-Ag mining	Welch et al. (1988), Mok and Wai (1990)
Lake Oahe, South Dakota, USA			up to 2000	Lake sediments	Arsenic in sediment porewaters from Au mining in the Black Hills	Ficklin and Callender (1989)
Bowen Island, British Colombia	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 et al. (1998)
Northern Bavaria, Germany	2500		<10–150	Upper Triassic Keuper Sandstone with mineralisation (uncharacterized)	Variable SO_4 concentrations, usually low NO_3, low dissolved O_2 concentrations	Heinrichs and Udluft (1999)

[a] Exposed refers to population drinking water with As >50 μg l^{-1} (drinking-water standard of most countries).

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 Fe oxides, reductive dissolution of the oxides themselves and likely changes in Fe-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 As concentrations: less than 5 μg l^{-1} and usually less than 0.5 μg l^{-1} (BGS and DPHE, 2001). Also wells from the older Plio-Pleistocene sediments of the Barind and Madhupur Tracts have low As concentrations (Fig. 4). It is a fortunate fact that both Calcutta and Dhaka draw their water from older sediments and do not have an As problem. Dhaka is sited at the southern tip of the Madhupur Tract (Fig. 4). Dug wells also generally have low As concentrations, typically <10 μg l^{-1} (BGS and DPHE, 2001).

The characteristic chemical features of the high-As groundwaters of the Bengal Basin are high Fe (>0.2 mg l^{-1}), Mn (>0.5 mg l^{-1}), HCO_3^- (>500 mg l^{-1}) and often P (>0.5 mg l^{-1}) concentrations, and low Cl^- (<60 mg l^{-1}), SO_4^{2-} (<1 mg l^{-1}), NO_3^- and F^- (<1 mg l^{-1}) concentrations, with pH values close to or greater than 7. Measured redox potentials are typically less than 100 mV (PHED, 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 As are found, these are only applicable locally and are of limited value for quantitative prediction of As concentrations, even at a village scale. For example, some workers have found a positive correlation between As and Fe 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 SO_4 concentrations (BGS and DPHE, 2001). This association suggests that As mobilisation is effected under the most strongly reducing conditions, coincident with SO_4^{2-} reduction. Some of the groundwaters of Bangladesh are sufficiently reducing for CH_4 generation to have taken place.

Arsenic speciation studies have revealed a large range in the relative proportions of dissolved arsenate and arsenite present in the groundwaters (e.g. Das et al., 1995; Acharyya, 1997). The modal proportion of arsenite appears to be between 50 and 60% of the total As (BGS and DPHE, 2001). This may reflect lack of redox equilibrium in the aquifer or a mixed groundwater from a strongly stratified aquifer. Low As concentrations are most common in groundwaters from northern Bangladesh and the aquifers in Plio-Pleistocene sediments of the uplifted Barind and Madhupur Tracts of north-central Bangladesh.

The regional distribution of the high-As waters in West Bengal and Bangladesh is known to be extremely patchy (PHED, 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 enrichment is not as severe in West Bengal as in the worst-affected (SE) districts of Bangladesh (e.g. Dhar et al. 1997). Certainly, the overall areal extent of enrichment in West Bengal is less than in Bangladesh.

The As-affected groundwaters in the Bengal Basin are associated with sediments having total As concentrations in the range <2–20 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 3 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 As 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 ^3H, 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 a study area in western Bangladesh was ‘modern’ since it contained 83% modern C (pmc) or greater, indicating an age of the order of decades. Shallow groundwaters collected 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 2 ka. Deep groundwaters analysed from southern Bangladesh were even older with ^{14}C activities of 28 pmc or less, suggesting the presence of palaeowaters with ages of the order of 2–12 ka.

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 5–10 ka. 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 parts of Bangladesh and means that deep wells, often more than 200 m deep, may need to be constructed to obtain fresh water. As mentioned above, these almost always have low As concentrations. Other potential sources of low-As water in the region are surface water (rivers and ponds), rainwater and dug-well water.

5.2.2. Taiwan

Arsenic problems in groundwaters in Taiwan were first recognised during the 1960s (e.g. Tseng et al., 1968) and chronic As-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 blackfoot disease but a number of other typical health problems, including internal cancers, have been described. High As concentrations in groundwater have been recognised in both the SW (Tseng et al., 1968) and NE (Hsu et al., 1997) of the island.

Kuo (1968) observed As concentrations in groundwater samples from SW Taiwan ranging between 10 and 1800 $\mu g\ l^{-1}$ (mean 500 $\mu g\ l^{-1}$, $n=126$) and found that half the samples analysed had concentrations between 400 and 700 $\mu g\ l^{-1}$. 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 $>50\ \mu g\ l^{-1}$ and 58 townships had $>350\ \mu g\ l^{-1}$ (Lo et al., 1977). In north-eastern Taiwan, Hsu et al. (1997) found As concentrations in some groundwaters exceeding 600 $\mu g\ l^{-1}$, with an average of 135 $\mu g\ l^{-1}$ (377 samples).

In the SW, 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 NE 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, a hypothesis 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 samples taken from shallow open dug wells are observed to have low As concentrations (Guo et al., 1994).

5.2.3. Northern China

Arsenic has been found at high concentrations (in excess of the Chinese national standard of 50 $\mu g\ l^{-1}$) in groundwaters from Inner Mongolia as well as Xinjiang and Shanxi Provinces (Fig. 2; Wang, 1984; Wang and Huang, 1994; Niu et al., 1997; Smedley et al., 2001a). The first cases of As poisoning were recognised in Xinjiang Province in the early 1980s. Wang (1984) found As concentrations up to 1200 $\mu g\ l^{-1}$ in groundwaters from the province. Wang and Huang (1994) reported As concentrations of between 40 and 750 $\mu g\ l^{-1}$ 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 $<10\ \mu g\ l^{-1}$ (the detection limit) and 68 $\mu g\ l^{-1}$. The concentration of As in the saline Aibi Lake was reported as 175 $\mu g\ l^{-1}$, while local rivers had concentrations of between 10 and 30 $\mu g\ l^{-1}$. Artesian groundwater has been used for drinking in the region since the 1960s and chronic health problems have been identified as a result (Wang and Huang, 1994).

In Inner Mongolia, concentrations of As in excess of 50 $\mu g\ l^{-1}$ have been identified in groundwaters from aquifers in the Ba Men region and the Tumet Plain, which includes the Huhhot Basin (e.g. Luo et al., 1997; Ma et al., 1999). These areas include the towns 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., 2001a). Concentrations up to 1500 $\mu g\ l^{-1}$ have been found in the groundwaters, with a significant proportion (60–90%) of the As being present as As(III). Some shallow dug wells also have groundwater with relatively high As concentrations (up to 556 $\mu g\ l^{-1}$; Smedley et al., 2001a). Shallow groundwaters in parts of the region are saline as a result of evaporative concentration exacerbated by irrigation and many have high F^- 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.

5.2.4. Vietnam

The aquifers of the large deltas of the Mekong and Red Rivers are now widely exploited for drinking water. The total number of tubewells in Vietnam is unknown but could be of the order of one million, with perhaps 150,000 in the Red River delta region. The majority of these are private tubewells. The capital city, Hanoi, is now largely dependent on groundwater for its public water supply. The aquifers exploited are of both Holocene and Pleistocene age. In parts of the Red River delta region, Holocene sediments form the shallow aquifer which may be only 10–15 m deep. Where absent, older Pleistocene sediments are exposed at the surface. Unlike Bangladesh, even when the Holocene sediments are present, there is not always a layer of fine silt-clay at the surface. Normally the Holocene sediments are separated from the underlying Pleistocene sediments by a clay layer several 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 Fe, Mn and NH_4. 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 As concentrations in groundwater in Vietnam until recently. UNICEF and EAWAG/CEC (Hanoi National University) have been carrying out extensive investigations to assess the scale of the problem. Results from Hanoi (Wegelin et al., 2000; Berg et al., 2001) indicate that there is a significant As problem in shallow tubewells in the city, particularly in the south. Concentrations in the range 1–3050 μg l^{-1} (average 159 μg l^{-1}) were reported by Berg et al. (2001). There appears to be a large seasonal variation with significantly lower concentrations having been found at most investigated sites during sampling in May (early 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 As 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.

5.2.5. Hungary and Romania

Concentrations of As above 50 μg l^{-1} have been identified in groundwaters from alluvial sediments in the southern part of the Great Hungarian Plain (Fig. 3) of Hungary and neighbouring parts of Romania. Concentrations up to 150 μg l^{-1} (average 32 μg l^{-1}, 85 samples) have been found by Varsányi et al. (1991). The Plain, some 110,000 km^2 in area, consists of a thick sequence of subsiding Quaternary sediments. Groundwaters vary from Ca–Mg–HCO_3-type in the recharge areas of the basin margins to Na–HCO_3-type in the low-lying discharge regions. Groundwaters in deep parts of the basin (80–560 m depth) with high As concentrations are reducing with high concentrations of Fe and NH_4 and many have reported high concentrations of humic acid (up to 20 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. Gurzau and Gurzau (2001) reported As concentrations up to 176 μg l^{-1} in the associated aquifers of neighbouring Romania (Table 7).

5.3. Arid oxidising environments

5.3.1. Mexico

The Lagunera Region of north central Mexico has a well-documented As problem in groundwater with significant resulting chronic health problems. The region is arid and groundwater is an important resource for potable supply. Groundwaters are predominantly 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 to 624 μg l^{-1} (average 100 μg l^{-1}, $n = 128$), with half the samples having concentrations greater than 50 μg l^{-1}. They also noted that most (>90%) of the groundwater samples investigated had 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 μg l^{-1}. The estimated population exposed to As in drinking water with >50 μg l^{-1} is around 400,000 in Lagunera Region (Del Razo et al., 1990). Groundwaters from the region also have high concentrations of F^- (up to 3.7 mg l^{-1}; Cebrián et al., 1994).

High As concentrations have also been identified in groundwaters from the state of Sonora in NW Mexico. Wyatt et al. (1998) found concentrations in the range 2–305 μg 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 F. The highest observed F concentration in the area was 7.4 mg l^{-1}. The reasons for the correlation in this case are uncertain. It is also believed that high-As groundwaters have been found in other parts of northern Mexico.

5.3.2. 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 μg 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 reported in surface waters and groundwaters from Administrative Region II (incorporating the cities of Antofagasta, Calama and Tocopilla) of northern Chile (Cáceres et al., 1992). The region is arid (Atacama Desert) and water resources are limited. High As concentrations are accompanied by high salinity and high B concentrations. This in part relates to evaporation but is also thought to be significantly affected by geothermal inputs from the El Tatio geothermal field. Arsenic concentrations below 100 μg l^{-1} in surface waters and groundwaters are apparently quite rare, and concentrations up to 21,000 μg l^{-1} have been found. Karcher et al. (1999) quoted ranges of 100 μg l^{-1} to 1000 μg l^{-1} in raw waters (average 440 μg l^{-1}). The affected waters of Chile are taken to be predominantly oxidising (with dissolved O_2 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 volcanic rocks and sediments, but the As sources are not well-characterised. In Antofagasta, concentrations of As in the sediments are ca. 3.2 mg kg^{-1} (Cáceres et al., 1992). Additional As exposure from smelting of Cu ore has also been noted in northern Chile (Cáceres et al., 1992).

Arsenic treatment plants were installed in the towns of Antofagasta and Calama in 1969 to mitigate the problems. Today, the urban 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.

5.3.3. Argentina

The Chaco-Pampean Plain of central Argentina constitutes perhaps one of the largest regions of high-As groundwaters known, covering around 1×10^6 km^2. High concentrations of As have been documented from Córdoba, La Pampa, Santa Fe, Buenos Aires and Tucumán Provinces in particular. Symptoms typical of chronic As 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. The high-As groundwaters are from Quaternary deposits of loess (mainly silt) with intermixed rhyolitic or dacitic volcanic ash (Nicolli et al., 1989; Smedley et al., 1998, 2002). The sediments display abundant evidence of post-depositional diagenetic changes under semi-arid conditions, with common occurrences of calcrete in the form of cements, nodules and discrete layers, sometimes many centimetres thick.

Nicolli et al. (1989) found As concentrations in groundwaters from Córdoba in the range 6–11500 μg l^{-1} (median 255 μg l^{-1}). Nicolli and Merino (2002) in a study of the Carcarañá River Basin (Córdoba and Santa Fe Provinces) found concentrations in the range <10–720 μg l^{-1} (mean 201 μg l^{-1}). Smedley et al. (1998, 2002) found concentrations for groundwaters in La Pampa Province in the range <4–5280 μg l^{-1} (median 145 μg l^{-1}). Nicolli et al. (2001) found concentrations in groundwaters from Tucumán Province of 12–1660 μg l^{-1} (median 46 μg l^{-1}). The groundwaters often have high salinity and the As concentrations are generally well-correlated with other anion and oxyanion elements (F, V, HCO_3, B, Mo). They are also predominantly oxidising with low dissolved Fe and Mn concentrations. Under the arid conditions, silicate and carbonate weathering reactions are pronounced and the groundwaters often have high pH values. Smedley et al. (2002) found pH values typically of 7.0–8.7; Nicolli et al. (2001) found pH values of 6.3–9.2. Arsenic is dominantly present as As(V) (Smedley et al., 2002). Metal oxides in the sediments (especially Fe and Mn oxides and hydroxides) are thought to be the main source of dissolved As, caused by desorption under high-pH conditions (Smedley et al., 1998, 2002), although the direct dissolution of volcanic glass has also been cited as a potential source (Nicolli et al., 1989).

5.4. Mixed oxidising and reducing environments

5.4.1. South-western USA

Many areas have been identified in the USA with As 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 As exceeding 10 μg l^{-1} and smaller areas of high As 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-proposed reduction in the US-EPA drinking-water maximum contaminant level 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 μg l^{-1}. A recent review of the analyses of some 17,000 water analyses from the USA concluded that around 40% exceeded 1 μg l^{-1} and about 5% exceeded 20 μg l^{-1} (percentage above 50 μg 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 As 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 μg l^{-1} (Fontaine, 1994). The city of Fallon, Nevada (population 8000) is served by a groundwater supply with an As concentration of 100 μg 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 μg l^{-1} but with extremes up to 2600 μg l^{-1}, in shallow groundwaters from the southern Carson Desert. These are largely present under reducing conditions, having low dissolved-O_2 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 mg l^{-1}) and U (>100 μg 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 μg l^{-1} to 2600 μg 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 μg l^{-1}), U (up to 5400 μg l^{-1}), B (up to 73,000 μg l^{-1}) and Mo (up to 15,000 μg 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 O_2 values of the groundwaters were in the range 3–7 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 μg l^{-1}. Arsenic concentrations in the sediments ranged between 2 and 88 mg kg^{-1}. Oxidising conditions (with dissolved O_2 present) were found to persist in the aquifers down to significant depths (600 m) despite significant groundwater age (up to 10 ka old). The high As (and other oxyanion) concentrations are a feature of the closed basins of the province.

5.5. Geothermal sources

As noted above, As associated with geothermal waters has been reported in several parts of the world, including hot springs from parts of the USA, Japan, New Zealand, Chile, 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 NW 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, 2000). Reported occurrences include Honey Lake Basin, California (As up to 2600 μg l^{-1}), Coso Hot Springs, California (up to 7500 μg l^{-1}), Imperial Valley, California (up to 15,000 μg l^{-1}), Long Valley, California (up to 2500 μg l^{-1}) and Steamboat Springs, Nevada (up to 2700 μg l^{-1}). Geothermal waters in Yellowstone National Park also contain high concentrations of As. Thompson and Demonge (1996) reported concentrations of <1–7800 μg l^{-1} in geysers and hot springs; values up to 2830 μg l^{-1} were reported by Ball et al. (1998). These geothermal sources have given rise to high concentrations of As (up to 370 μg l^{-1}) in waters of the Madison River (Nimick et al., 1998). Geothermal waters at Lassen Volcanic National Park, California have As concentrations ranging up to 27,000 μg l^{-1} (Thompson et al., 1985). An As concentration of 3800 μg l^{-1} has also been reported from Geyser Bight, Umnak Island, Alaska (White et al., 1963). Geothermal inputs from Long Valley, California are believed to be responsible for relatively high concentrations (20 μg 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 mg l^{-1}) in Mono Lake, California (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 μg l^{-1} mostly had Cl concentrations of 800 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 5 geothermal fields in Kyushu, Japan, As concentrations have been reported in the range 500–4600 μg 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).

Robinson et al. (1995) found an As concentration in waste geothermal brine from the main drain at the Wairakei geothermal field in New Zealand of 3800 μg l^{-1}. River and lake waters receiving inputs of geothermal water from the Wairakei, Broadlands, Orakei Korako and Atiamuri geothermal fields have As concentrations up to 121 μg l^{-1}, although concentrations are reported to diminish significantly downstream away from the geothermal input areas.

High As concentrations have 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 (Na–Cl solutions with Na concentrations in the range 2000–5000 mg l^{-1}). Arsenic concentrations of the waters are reported to be in the range 45,000–50,000 μg l^{-1} (Ellis and Mahon, 1977). White et al. (1963) also reported As concentrations in the range 50–120 μg l^{-1} for thermal waters from Iceland and in the range 100–5900 μg l^{-1} for thermal waters from Kamchatka.

5.6. Sulphide mineralisation and mining-related arsenic problems

5.6.1. Thailand

Probably the worst case of As poisoning related to mining activity known is that of Ron Phibun District in Nakhon Si Thammarat Province of southern Thailand. Health problems were first recognised in the area in 1987. By the late 1990s, around 1000 people had 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 SE Asian Tin Belt. Arsenic concentrations up to 5000 μg l^{-1} have been found in shallow groundwaters from Quaternary alluvial sediment that has been extensively dredged during Sn-mining operations. Deeper groundwaters from an older limestone aquifer 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 Sn-mining activities. The recent appearance in groundwater has occurred during post-mining groundwater rebound (Williams, 1997).

5.6.2. Ghana

Ghana is an important Au-mining country and mining has been active since the late 19th century. Today, Ghana produces about one third of the world's Au. The most important mining area is the Ashanti Region of central Ghana. As with Ron Phibun District in Thailand, the Au 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 μg l^{-1}. Some higher concentrations were observed (up to 64 μg 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, 1996; Smedley et al., 1996).

5.6.3. 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 μg l^{-1}). Well-documented cases of As contamination include the Fairbanks Au-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 Fe sulphide minerals. In these, pH values can be extremely low and Fe oxides, produced from the oxidation reaction, dissolve and release bound As. Iron Mountain has some extremely acidic mine-drainage waters with negative pH values and As concentrations in the mg l^{-1} range (Nordstrom et al., 2000).

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 μg 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 a^{-1} 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).

5.6.4. Other areas

Many other areas have increased concentrations of As in water, soils, sediments and vegetation as a result of local mineralisation, exacerbated by mining activity. Documented cases include the Lavrion region of Greece, associated with Pb and Ag mining (Komnitsas et al., 1995), the Zimapán Valley of Mexico (Armienta et al., 1997), parts of SW England (Thornton and Farago, 1997), South Africa and Zimbabwe (Jonnalagadda and Nenzou, 1996). Although severe contamination of the environment has often been documented in these areas, the impact on groundwaters used for potable supply is usually minor.

Increased concentrations of dissolved As have also been found in parts of the world with local mineralisation which has not been mined. Boyle et al. (1998) recorded concentrations up to 580 μg l^{-1} in groundwaters from an area of sulphide mineralisation in Bowen Island, British Colombia. Heinrichs and Udluft (1999) found often high concentrations in groundwater from the Upper Triassic Keuper Sandstone in northern Bavaria. Out of 500 wells, 160 had As concentrations in the range 10–150 μg l^{-1}. The nature of the mineralisation in this aquifer was not clearly identified. As yet unidentified areas of mineralisation could be quite widespread, although these are likely to be on a local scale.

6. Common features of groundwater arsenic problem areas

6.1. A hydrogeochemical perspective

Historically, as new sources of high As groundwaters have been found, treatment plants have been built and the problem has receded from public attention. Although much recent research has been carried out in the USA, there have been few detailed hydrogeochemical and hydrogeological studies in the As-affected aquifers from many other parts of the world. Despite this, sufficient is already known that it is useful to attempt to bring together some of the common features and to speculate about the critical factors that can lead to high-As groundwaters. This will help to focus future scientific studies and should provide some guidance to water providers who have to undertake a rapid assessment of water supplies for As. It is helpful to consider the formation of high-As groundwaters in terms of the 3 major factors involved, namely, the source of the As, its mobilisation, and its subsequent transport (or lack of it).

6.2. The source of arsenic

In the cases where affected groundwaters are found close to obvious geological or industrial sources rich in As (geothermal springs, drainage from mineralised and mining areas, specific contaminant sources), it is clear that the anomalously high As 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 As mobilisation on a regional scale. Areas affected by geothermal activity are potentially more widespread since in this case mobilisation of As is not an issue: As is already present in solution and the size of geothermal reservoirs can be large. Perhaps more puzzling is the way in which exceptionally high concentrations of As, up to several mg l^{-1}, are found in groundwaters from areas with apparently near-average source rocks. In aquifers with extensive high-As groundwater, 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 kg^{-1}. Recognition of this fact is a recent development and its late appreciation has delayed the discovery of many high-As groundwater provinces.

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

6.3. Arsenic 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 As from the aquifer solid phase into the groundwater. Secondly, the released As must remain in the groundwater and not be flushed away. There are a number of possible geochemical triggers. In mining and mineralised areas, oxidation of sulphide ores may be triggered by influxes of O_2 or other oxidising agents. However, in most As-affected aquifers, the most important trigger appears to be the desorption/dissolution of As from oxide minerals, particularly Fe oxides. An important feature of this process is that the initial adjustment is probably quite rapid since it involves a shift from one point on the adsorption isotherm to another 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 are likely to be 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 or even days in flooded soils (Ponnamperuma et al., 1967; Masscheleyn et al., 1991).

A qualification is that if diagenetic changes to the oxide mineral structure are important (see below) or if burial of sediment is important, then there could be a slow release of As over a much longer time scale. Details of the rate of release of As 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 in the early stages. Natural groundwater flushing means that very slow releases of As are likely to be of little consequence since the As 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 As. 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 As from metal oxides in young aquifers is essentially a step change responding to a new set of conditions. As discussed above, 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 the authors speculate what these might be. Some model calculations of their possible impact are given in BGS and DPHE (2001).

6.3.1. Desorption at high pH under oxidising conditions

Under the aerobic and acidic to near-neutral conditions typical of many natural environments, As is very strongly adsorbed by oxide minerals as the arsenate ion. The highly non-linear nature of the adsorption isotherm for arsenate ensures that the amount of As adsorbed is relatively large, even when dissolved concentrations of As are low. Adsorption protects many natural environments from widespread As toxicity problems. As pH increases, especially above pH 8.5, As desorbs from the oxide surfaces, thereby increasing the concentration of As in solution. The impact of this is magnified by the high solid/solution ratios typical of aquifers (3–10 kg l^{-1}).

It is possible to demonstrate this effect with some model calculations. The Dzombak and Morel (1990) diffuse double layer model (DLM) for hydrous ferric oxide (HFO), and its accompanying thermodynamic database, provides a simple means of calculating the amount of As adsorbed under various conditions. If we assume that a sandy sediment with 25% porosity contains 1 g Fe kg^{-1} as HFO and that it is initially in equilibrium at pH 7 with a river water containing 1 μg l^{-1} of As and 0.05 mol l^{-1} NaCl, then according to the DLM, HFO has an As loading of almost 15,000 mg kg^{-1}. This is equivalent to 23 mg As kg^{-1} sediment. If the pH is then raised while maintaining a constant total As concentration in the sediment plus porewater, equivalent to evolution within a ‘closed’ system, then desorption of As occurs (Fig. 5). There is a sharp increase in porewater As concentration above pH 8.5. Above pH 9, the As(V) concentration can exceed 1000 μg l^{-1}. An ionic strength of 0.05 M is greater than found in most river waters but is useful for maintaining a constant ionic strength in the calculations. Normally the effects of changes in ionic strength are relatively small. This system assumes no competing anions in solution.

More realistically, other anions (e.g. phosphate, bicarbonate and silicate) in the river water will compete for sorption sites on the HFO and thereby reduce the initial As loading. If we assume for example that the river water also contains 10 μg l^{-1} phosphate-P, then the initial As loading is reduced to 5600 mg kg^{-1} HFO. However, while this reduces the As release at high pH to some extent, the pH effect is still strong (Fig. 5). Phosphate (and other adsorbed anions) are also released along with As at high pH. At pH 9, the calculated total P concentration in the above example is 13 mg l^{-1}.

There are several reasons why the pH might increase but the most important in the present context is the uptake of protons by mineral weathering and ion-exchange reactions, combined with the effect of evaporation in arid and semi-arid regions. This pH increase is commonly associated with the development of salinity and the salinisation of soils. Inputs of high-pH geothermal waters may be important in maintaining high As

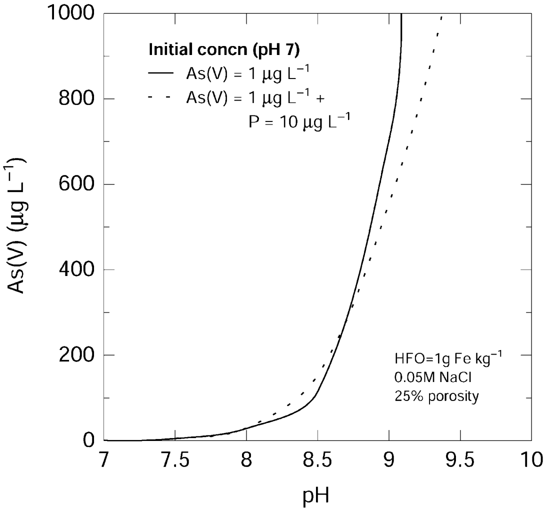

Fig. 5. Calculated increase in As concentration when the pH of a sediment containing 1 g kg^{-1} Fe as HFO is increased from its initial value of pH 7 under closed-system conditions.

concentrations in some alkaline lakes. Desorption at high pH is the most likely mechanism for the development of groundwater-As problems under the oxidising conditions and would account for the observed positive correlation of As concentrations with increasing pH (e.g. Robertson, 1989; Smedley et al., 2002).

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 (Smedley et al., 2002). 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 As binding since it is invariably more abundant than As, often by a factor of 50 or more (in molar terms), and is also strongly bound to oxide surfaces. At pH 7, arsenate is as strongly sorbed as phosphate (Hingston et al., 1971). The role of HCO_3^-, often the major anion in As-affected groundwaters, in promoting the desorption of arsenate is unclear at present. Wilkie and Hering (1996) did not find any large effects of 1 mM HCO_3 on As(V) or As(III) sorption by HFO at pH 6 and 9 (but greatest for As(III) at pH 9). Recent studies have shown that a high p_{CO_2} (and implicitly HCO_3 concentration) significantly reduces the binding of chromate, another strongly sorbed anion, by goethite (Villalobos et al., 2001). Bicarbonate concentrations in high-As groundwaters usually exceed 300 mg l^{-1} (5 mM) (Smedley et al., 1998; 2001a BGS and DPHE, 2001) and can exceed 1000 mg l^{-1} (16 mM). Hence, experiments need to be extended to these high concentrations to verify the role of HCO_3 in sorption processes.

The role of dissolved organic C (fulvic and humic acids) is also uncertain, at least from a quantitative point of view. Humic substances have been shown to reduce As(III) and As(V) sorption by Fe oxides under some conditions (Xu et al., 1991; Bowell, 1994) and high-As groundwaters are associated with high humic-acid concentrations in some aquifers (Smedley et al., 2001a). However, direct evidence for a causal link between dissolved organic C and As desorption does not yet exist.

Some cations, because of their positive charge, may promote the adsorption of negatively charged arsenate (Wilkie and Hering, 1996). Calcium and Mg are likely to be the most important cations in this respect because of their abundance in most natural waters and their +2 charge. Divalent Fe may be important in reduced waters and Al in acidic 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 As. It also allows the build-up of high Cl and F 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 As to have accumulated. Since calcium arsenate is highly insoluble, it is also likely that arsenate will be strongly sorbed by calcium carbonate minerals, although this has not been demonstrated.

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 HCO_3, may also significantly affect the pH dependence of As(V) and As(III) binding. High pH values cannot explain the development of high As concentrations in reducing environments such as Bangladesh since groundwaters in reducing environments normally have a near-neutral pH.

6.3.2. Arsenic desorption and dissolution due to a change to reducing conditions

The onset of strongly reducing conditions, sufficient to enable Fe(III) and probably SO_4 reduction to take place, appears to be another trigger for the release of As. 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. The organic C 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 O_2, NO_3 and SO_4. Reducing conditions can only be maintained if the diffusion and convection of dissolved O_2 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 overlie coarser-grained alluvial deposits.

While the detailed reactions (in surface chemical terms) that 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 As concentrations under reducing conditions are to be made.

In the absence of other specifically adsorbed anions, As(III) adsorption by Fe oxides is practically independent of pH. This contrasts sharply with that of As(V) as described above. In the 'real world', some pH dependence in As(III) adsorption will be induced by secondary interactions arising from the pH dependence of other specifically adsorbed and competing ions such as phosphate and even As(V).

6.3.3. *Reduction in surface area of oxide minerals*

Disordered and fine-grained Fe oxides, which may include HFO, lepidocrocite, schwertmannite and magnetite, are commonly formed in the early stages of weathering. Freshly-precipitated HFO is extremely fine-grained with cluster sizes of about 5 nm diameter and a specific surface area of 600 $m^2\ g^{-1}$ or greater. HFO gradually transforms (crystallises) to more ordered forms such as goethite or hematite with correspondingly large crystal sizes and reduced surface areas. This 'ageing' reaction can take place rapidly in the laboratory but the rate in nature is likely to be somewhat inhibited by the presence of other ions, particularly by strongly adsorbed ions such as Al, PO_4, SO_4, AsO_4, HCO_3 and silicate (Cornell and Schwertmann, 1996).

One consequence of this reduction in surface area is that the amount of As(V) adsorption may decrease on a weight for weight basis. If the site density (site nm^{-2}) and binding affinities of the adsorbed ions remain constant, then as the specific surface area of an oxide mineral is reduced, some of the adsorbed ions will be desorbed. The specific surface area of HFO on which the DLM was calibrated by Dzombak and Morel (1990) was taken as 600 $m^2\ g^{-1}$. Aged products, such as goethite typically have specific surface areas of 150 $m^2\ g^{-1}$ or less and even less for hematite (Cornell and Schwertmann, 1996).

Assuming that the site density remains unchanged during ageing and the binding affinity of As(V) and protons also remains unchanged, it is possible to calculate the effect that a reduction in surface area might have. If we assume similar initial conditions to the pH example given above, i.e. HFO in equilibrium with a solution containing 1 μg As(V) l^{-1} and a sediment with 25% porosity and a HFO concentration equivalent to 1g Fe kg^{-1}, then these calculations show that there is a marked increase in As concentration in solution when the surface area is reduced to below 300 $m^2\ g^{-1}$ (Fig. 6).

Assuming that the HFO was also initially in equilibrium with 10 μg l^{-1} phosphate-P increases the effect somewhat. These calculations are strongly dependent on the shape of the adsorption isotherm and the initial As loading, and are therefore sensitive to all the interactions that control the isotherm. For example, for As(III) which has a close-to-linear isotherm at typical groundwater concentrations, the effect of a reduction in surface area is less dramatic and is closer to a linear function of the surface-area reduction.

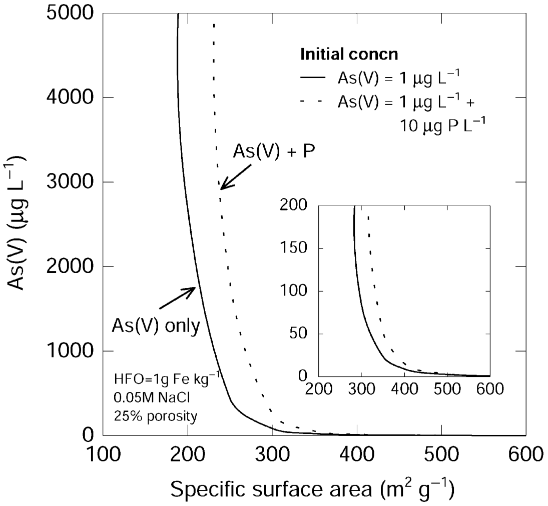

Fig. 6. Calculated increase in As concentration when the specific surface area of HFO in a sediment containing 1 g kg^{-1} Fe as HFO is reduced from its initial value of 600 $m^2\ g^{-1}$ under closed-system conditions.

6.3.4. *Reduction in binding strength between arsenic and mineral surfaces*

While the calculations outlined above are useful in the sense that they give some indication of possible surface area effects, they make important and unverified assumptions, and are almost certainly an oversimplification of reality. For example, some of the desorbed ions are likely to be incorporated into the evolving oxide structure as a solid solution. This will reduce the amount of As released. Also, if the surface structure changes, then it is likely that the binding affinity of arsenate ions and protons will also change since the binding affinity is closely related to surface structure. For example, Kinniburgh et al. (1977) found that while aged HFO gels had a significantly reduced proton buffer capacity, and by implication a reduced specific surface area, the binding of trace Zn^{2+} increased on ageing, implying that the binding affinity of Zn increased with increasing crystallisation of the gel and that this more than compensated for the reduction in specific surface area, i.e. the isotherm changed from a low-affinity isotherm to a high-affinity isotherm.

Under strongly reducing conditions, it appears that additional processes could operate which may lead to a reduction in the overall adsorption of As. Specifically for Fe oxides, some of the surface Fe could be reduced from Fe(III) to Fe(II) to produce a mixed-valence oxide perhaps akin to that of a magnetite or a green rust. This would tend to reduce the net positive charge of the surface (or increase its net negative charge) and would thereby reduce the electrostatic interaction between the surface and anions. This could result in the desorption of As and a corresponding large increase in the concentration of As in solution (BGS and DPHE, 2001).

On balance, laboratory and field evidence suggests that at micromolar As concentrations, freshly-formed HFO binds more As than goethite on a mole of Fe basis (De Vitre et al., 1991) and so a reduction in affinity appears to be more probable. In Bangladesh, areas with high-As groundwaters tended to correspond with those areas in which the sediments contain a relatively high concentration of oxalate-extractable Fe (BGS and DPHE, 2001). This provides indirect support for the importance of Fe oxides. Some early work (Khalid et al., 1977) also showed that the sorption of phosphate by reduced soils was less than that for their oxidised equivalents but that this was only true at low (near natural) phosphate loadings. It can be speculated that the soils and sediments most sensitive to arsenic release on reduction and ageing are those in which Fe oxides are abundant, in which HFO is a major fraction of the Fe oxides present, and in which other As-sorbing minerals are relatively scarce. While the existing evidence is somewhat contradictory, it tends to suggest that a change from aerobic to anaerobic conditions often results in a net release of As.

6.3.5. Mineral dissolution

Mineral dissolution reactions tend to be most rapid under extremes of pH and Eh. Iron oxides dissolve under strongly acidic conditions and under strongly reducing conditions. Minor elements, including As, present either as adsorbed (labile) As or as irreversibly-bound (non-labile) As will also tend to be released during this dissolution. This can explain, in part at least, the presence of high As concentrations in acid mine drainage and in strongly reducing groundwaters. The reductive dissolution of Fe(III) oxides has been extensively discussed in the context of estuarine, lake and river particles and sediments (Davison, 1993; Lovley and Chapelle, 1995). It accounts for the high Fe(II) content of anaerobic waters, and the ubiquity of Fe in the environment means that waters with near-neutral pH and high Fe are invariably anaerobic waters. While this process undoubtedly accounts for some of the As found in reducing groundwaters, it does not appear to be sufficient to account for all, or even most, of the As released. Congruent dissolution of a typical Fe oxide without any precipitation of secondary Fe phases would only release a few, or a few tens, of μg As l^{-1} which is far less that that found in many As-rich reducing groundwaters. The precise sequence of events that occurs during the reductive dissolution of Fe(III) oxides containing adsorbed and coprecipitated As is complex and has not been studied in detail. It is even more complex than for phosphate release because of the variable oxidation state of As. The reduction of both the Fe(III) oxide and the As(V) are microbially catalysed and the relative rates depend on the viability and nutrient supply of the specific microbial strains involved (Ehrlich, 1996). Reductive dissolution cannot of course explain the occurrence of high-As oxidising groundwaters.

Manganese oxides also undergo reductive desorption and dissolution and so could contribute to the As load of groundwaters in the same way as Fe. Certainly many of the reducing groundwaters of Bangladesh contain high concentrations of Mn (DPHE/BGS/MML, 1999; BGS and DPHE, 2001). 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 As to groundwater, or its uptake from groundwater.

Sulphide oxidation, particularly pyrite oxidation, can also be an important source of As 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 SO_4, Fe and trace metals. As the dissolved Fe is neutralised, 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.

6.4. Transport—historical groundwater flows

The geochemical triggers described above may release As into groundwater but are not alone sufficient to account for the distribution of high-As groundwaters observed. The additional factor is that the released As 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, being up to about 400 ka (Collon et al., 2000). The water moves slowly through this aquifer and over its 2.5 Ga history, there have been many pore volumes of fresh water flushed through the system. Any desorbed As 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 As *and* the hydrogeological regime to preserve it are both operating that we see high groundwater As concentrations on a regional scale.

It is also necessary to consider historical groundwater 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 ka (Pirazzoli, 1996). Sea levels reflect global climate patterns. Between about 120 ka ago and 18 ka ago, the sea level steadily declined (with a few fluctuations) as glaciers expanded. The last glaciation was at a maximum some 21–13.5 ka 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 As 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 13.5–7 ka ago, warming occurred and sea levels rapidly rose to their existing levels. Therefore aquifers that are younger than some 7 ka 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 As has taken place. The other important factor is the partitioning of As between the aquifer solid phase and the groundwater. This determines the ease with which As is flushed out and is related to the slope of the adsorption isotherm (Appelo and Postma, 1994). In simple cases, this can be expressed by the partition coefficient, K_d. The greater the K_d, the greater the capacity of the sediment to withstand changes and the slower the As 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, As concentration and speciation, phosphate concentration and so on. In practice, the adsorption isotherms are usually non-linear, which means that the K_d varies with concentration. This leads to more complex transport behaviour but the same general principles apply. In aquifers with high-As groundwater, the K_d will be less than under 'normal' oxidised conditions since a reduced K_d is precisely the reason for the development of As problems in aquifers. There have so far been no reliable studies of K_d values applicable to As-affected aquifers. The greater the quantity of As involved, the more strongly it is adsorbed and the slower the rate of groundwater movement, the longer that high-As groundwaters will persist.

As described above, the number of pore volumes that have passed through the aquifer is a function of the groundwater flow velocity integrated over the time since sediment burial. In Bangladesh, the age of sediment vs 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 ka old, even less than 5 ka old, and so will not have experienced the extensive flushing of the last glacial period. These sediments are from where the majority of the tubewells abstract water. 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 ka old, will have been subjected to more extensive flushing. This may account for the 'As-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 (Fig. 4) will have been well flushed since they are at least 25–125 ka old. These sediments invariably yield low-As groundwaters, typically containing less than 0.5 $\mu g\ l^{-1}$ As. 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.

Regional flow patterns are not the only important factors. At a local scale, small variations in relief or in drainage patterns may dictate local flow patterns and hence the distribution of As-rich groundwater. For example, there is evidence from Argentina that the highest groundwater As concentrations are found in the slightly lower areas where seasonal discharge occurs (Smedley et al., 2002). The same is true in Inner Mongolia (Smedley et al., 2001a) and may also be true in Bangladesh. In any case, it is a characteristic of groundwater As problem areas that there is a high degree of local-scale variation. This reflects the poor mixing and low rate of 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-As 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. These lead to confining or semi-confining layers which aid the development of strongly reducing conditions. The youngest, distal part of the deltas will tend to contain the greatest concentration of fine-grained material and this provides an abundant source of As in the form of colloidal-sized oxide materials. Flocculation of colloidal material, including Fe 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 will have been sufficient to flush away any desorbed or dissolved As.

6.5. Future developments in arsenic research

It is necessary to know how As 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 As 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 As. The concentration profile of a non-reactive solute such as Cl can help to establish this. Age-related tracers such as ^{3}H, ^{14}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 that take place. This refers principally to the nature of the adsorption–desorption isotherms and the mechanisms of reductive dissolution of Fe and Mn 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 porewaters 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.

Calculations of the rate of movement of As 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 investigations of the interaction of As 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 As and Fe speciation, changes in mineral surface chemistry and the kinetics and stoichiometry of Fe and As release.

6.6. Identification of 'at risk' aquifers

This review has outlined some of the factors that are likely to be responsible for the development and persistence of As-rich groundwaters. These can be summarised in the form of various 'risk' factors that can help to identify groundwater provinces which deserve the highest priority for As testing (Fig. 7). These factors relate to the nature of the environment, particularly in relation to the source of As and the hydrogeology of the aquifer, as well as to the possible processes that can lead to the mobilisation of As. The best option is obviously to test the groundwater directly for As enrichment but where this is not possible, other water-quality data may provide some indication of the likelihood of arsenic enrichment. No single factor is sufficient to identify a problem area but if collectively many of the environmental characteristics and water-quality indicators point towards this, then some kind of testing should be undertaken as a matter of priority. A stratified random survey is the best approach with the stratification going across geological or landform types. Fig. 7 can only be used to identify susceptible provinces, not individual wells.

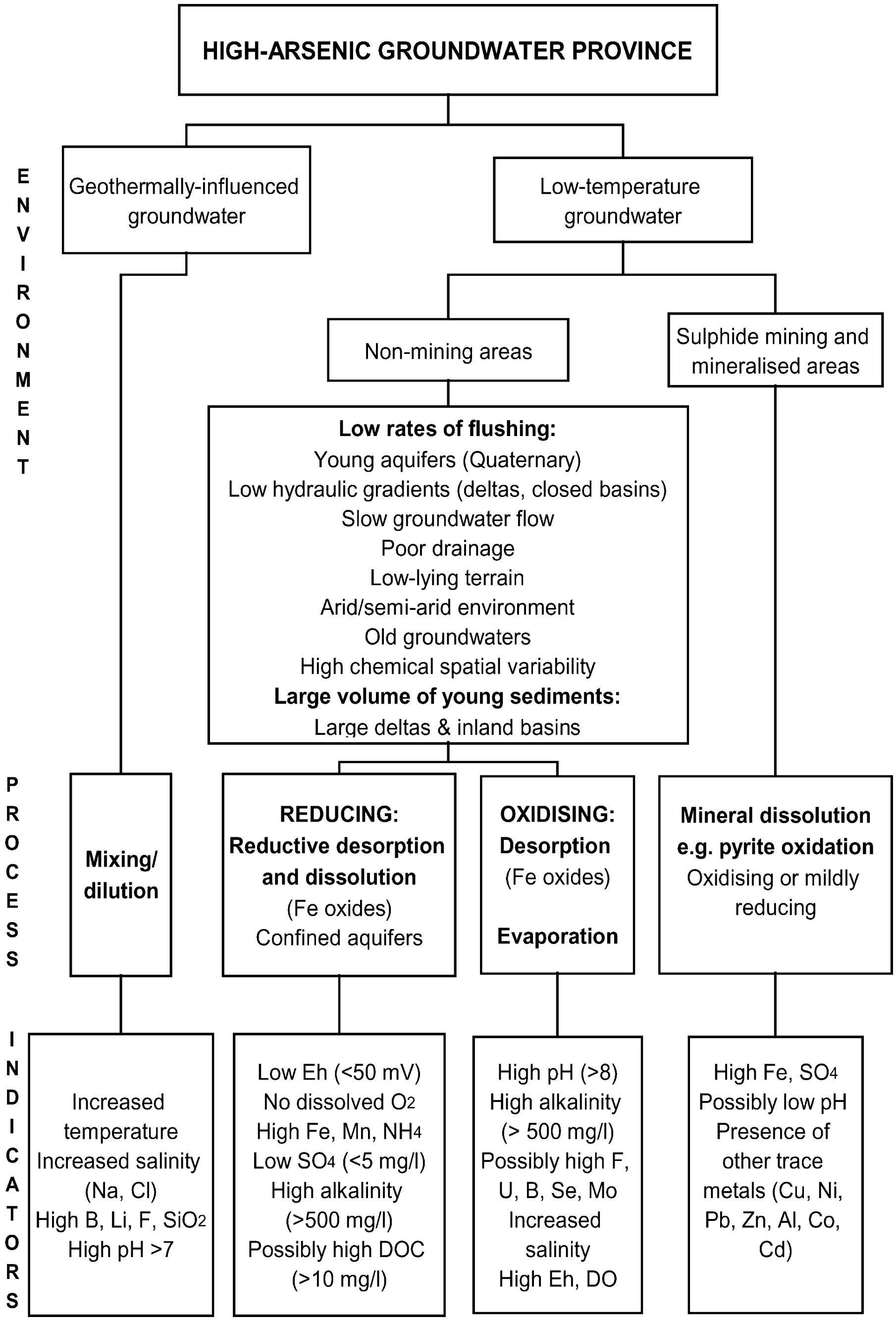

Fig. 7. Classification of groundwater environments prone to As problems from natural sources. Not all the indicators of low rates of flushing necessarily apply to all environments.

7. Concluding remarks

Much research has been carried out on As, particularly in the last few years, as a response to the growing evidence of the element's detrimental health effects, to reductions in regulatory limits for As, and to the recognition of the scale of arsenic enrichment in Bangladesh and elsewhere. This review has attempted to characterise the distribution of As in the environment, and to describe the main geochemical controls on its speciation and mobilisation. The documented As-rich areas are also summarised and the main types of environment under which As concentrations in waters are expected to be problematic are highlighted. Doubtless there are other areas of the world, principally aquifers, with as yet unrecognised problems. As widespread As testing, health awareness and diagnosis improve internationally, these are likely to emerge gradually.

For many water providers, including non-governmental organisations working in rural communities in developing countries, As represents a new and poorly understood threat. It is almost certain that there will have been little or no As testing and there is likely to be a general lack of understanding of the issues involved. In some cases, such as Bangladesh, the size of the As testing programme required is unprecedented in scale. In other cases, there is a lack of appreciation of a potential problem, or the lack of suitable facilities for testing As. A rapid, randomised testing programme will establish if there is an extensive As problem. It is far more difficult to identify each affected well in view of the high degree of spatial variability in arsenic concentrations usually found in high-As areas.

Groundwater provides drinking water to more than 1.5 billion people daily and to many more in times of surface water scarcity (DFID, 2001). While this review has focussed on areas where groundwater As concentrations may be excessively high, it must not be forgotten that this is the exception rather than the rule. Groundwater frequently provides a perfectly safe and reliable form of drinking water. The challenge therefore is to locate existing affected wells as quickly as possible, to provide an alternative source of safe drinking water, and to ensure that new sources are not As-rich. In most aquifers, most wells are likely to be unaffected by As enrichment, even when the groundwaters contain high concentrations of dissolved Fe. Therefore it is also necessary to understand why these groundwaters are not affected. It appears that it is only when a number of critical factors are combined that high-As groundwaters are found.

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

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References

Abdullah, M.I., Shiyu, Z., Mosgren, K., 1995. Arsenic and selenium species in the oxic and anoxic waters of the Oslofjord, Norway. Mar. Pollut. Bull. 31, 116–126.

Acharyya, S.K., 1997. Arsenic in groundwater—geological overview. In: Consultation on Arsenic in Drinking Water and Resulting Arsenic Toxicity in India and Bangladesh. Proc. WHO conference, New Delhi, May 1997.

AGRG, 1978. The Wolfson Geochemical Atlas of England and Wales. Clarendon Press, Oxford.

Aggett, J., Kriegman, M.R., 1988. The extent of formation of arsenic(III) in sediment interstitial waters and its release to hypolimnetic waters in Lake Ohakuri. Water Res. 22, 407–411.

Aggett, J., O'Brien, G.A., 1985. Detailed model for the mobility of arsenic in lacustrine sediments based on measurements in Lake Ohakuri. Environ. Sci. Technol. 19, 231–238.

Aggett, J., Roberts, L.S., 1986. Insight into the mechanism of accumulation of arsenate and phosphate in hydro lake sediments by measuring the rate of dissolution with ethylenediaminetetraacetic acid. Environ. Sci. Technol. 20, 183–186.

Allan, R.J., Ball, A.J., 1990. An overview of toxic contaminants in water and sediments of the Great Lakes. Part I. Water Pollut. Res. J. Can. 25, 387–505.

Amasa, S.K., 1975. Arsenic pollution at Obuasi goldmine, town and surrounding countryside. Environ. Health Perspect. 12, 131–135.

Anderson, M.A., Ferguson, J.F., Gavis, J., 1976. Arsenate adsorption on amorphous aluminum hydroxide. J. Colloid Interface Sci. 54, 391–399.

Andreae, M.O., 1979. Arsenic speciation in seawater and interstitial waters: the influence of biological-chemical interactions on the chemistry of a trace element. Limnol. Oceanog. 24, 440–452.

Andreae, M.O., 1980. Arsenic in rain and the atmospheric mass balance of arsenic. J. Geophys. Res. 85, 4512–4518.

Andreae, M.O., Andreae, T.W., 1989. Dissolved arsenic species in the Schelde estuary and watershed, Belgium. Estuar. Coast. Shelf Sci. 29, 421–433.

Andreae, M.O., Byrd, T.J., Froelich, O.N., 1983. Arsenic, antimony, germanium and tin in the Tejo estuary, Portugal: modelling of a polluted estuary. Environ. Sci. Technol. 17, 731–737.

Appelo, C.A.J., Postma, D., 1994. Geochemistry, Groundwater and Pollution. AA Balkema, Rotterdam.

Arehart, G.B., Chryssoulis, S.L., Kesler, S.E., 1993. Gold and arsenic in iron sulfides from sediment-hosted disseminated gold deposits-implications for depositional processes. Econ. Geol. Bull. Soc. Econ. Geol. 88, 171–185.

Armienta, M.A., Rodriguez, R., Aguayo, A., Ceniceros, N., Villasenor, G., Cruz, O., 1997. Arsenic contamination of groundwater at Zimapan, Mexico. Hydrogeol. J. 5, 39–46.

Arribére, M.A., Cohen, I.M., Ferpozzi, L.H., Kestelman, A.J., Casa, V.A., Guevara, S.R., 1997. Neutron activation analysis of soils and loess deposits, for the investigation of the origin of the natural arsenic-contamination in the Argentine Pampa. Radiochim. Acta 78, 187–191.

Azcue, J.M., Nriagu, J.O., 1995. Impact of abandoned mine tailings on the arsenic concentrations in Moira Lake, Ontario. J. Geochem. Explor. 52, 81–89.

Azcue, J.M., Murdoch, A., Rosa, F., Hall, G.E.M., 1994. Effects of abandoned gold mine tailings on the arsenic concentrations in water and sediments of Jack of Clubs Lake, BC. Environ. Technol. 15, 669–678.

Azcue, J.M., Mudroch, A., Rosa, F., Hall, G.E.M., Jackson, T.A., Reynoldson, T., 1995. Trace elements in water, sediments, porewater, and biota polluted by tailings from an abandoned gold mine in British Columbia, Canada. J. Geochem. Explor. 52, 25–34.

Baes, C.F., Sharp, R.D., 1983. A proposal for estimation of soil leaching and leaching constants for use in assessment models. J. Environ. Qual. 12, 17–28.

Ball, J.W., Nordstrom, D.K., Jenne, E.A., Vivit, D.V., 1998. Chemical Analyses Of Hot Springs, Pools, Geysers, And Surface waters from Yellowstone National Park, Wyoming, and Vicinity, 1974–1975. USGS Open-File Rep. 98–182.

Barbaris, B., Betterton, E.A., 1996. Initial snow chemistry survey of the Mogollon Rim in Arizona. Atmos. Environ. 30, 3093–3103.

Baur, W.H., Onishi, B.-M.H., 1969. Arsenic. In: Wedepohl, K.H. (Ed.), Handbook of Geochemistry. Springer-Verlag, Berlin. pp. 33-A-1–33-0-5.

Belkin, H.E., Zheng, B., Finkelman, R.B., 2000. Human health effects of domestic combustion of coal in rural China: a causal factor for arsenic and fluorine poisoning. In: 2nd World Chinese Conf. Geological Sciences, Extended Abstr., August 2000, Stanford Univ., pp. 522–524.

Belzile, N., Tessier, A., 1990. Interactions between arsenic and iron oxyhydroxides in lacustrine sediments. Geochim. Cosmochim. Acta 54, 103–109.

Benson, L.V., Spencer, R.J., 1983. A Hydrochemical Reconnaissance Study of the Walker River Basin, California and Nevada. USGS Open File Rep., 83–740. United States Geological Survey, Denver.

Berg, M., Tran, H.C., Nguyen, T.C., Pham, H.V., Schertenleib, R., Giger, W., 2001. Arsenic contamination of groundwater and drinking water in Vietnam: a human health threat. Environ. Sci. Technol. 35, 2621–2626.

Berner, R., 1981. A new geochemical classification of sedimentary environments. J. Sed. Petrol. 51, 359–365.

BGS, DPHE, 2001. Arsenic contamination of groundwater in Bangladesh. In: Kinniburgh, D.G., Smedley, P.L. (Eds.), British Geological Survey (Technical Report, WC/00/19. 4 Volumes). British Geological Survey, Keyworth.

Boughriet, A., Figueiredo, R.S., Laureyns, J., Recourt, P., 1997. Identification of newly generated iron phases in recent anoxic sediments: Fe-57 Mössbauer and microRaman spectroscopic studies. Journal of the Chem. Soc.-Faraday Trans. 93, 3209–3215.

Bowell, R.J., 1992. Supergene gold mineralogy at Ashanti, Ghana: implications for the supergene behaviour of gold. Mineral. Mag. 56, 545–560.

Bowell, R.J., 1993. Mineralogy and geochemistry of tropical rain forest soils: Ashanti, Ghana. Chem. Geol. 106, 345–348.

Bowell, R.J., 1994. Sorption of arsenic by iron-oxides and oxyhydroxides in soils. Appl. Geochem. 9, 279–286.

Boyle, D.R., Turner, R.J.W., Hall, G.E.M., 1998. Anomalous arsenic concentrations in groundwaters of an island community, Bowen Island, British Columbia. Environ. Geochem. Health 20, 199–212.

Boyle, R.W., Jonasson, I.R., 1973. The geochemistry of As and its use as an indicator element in geochemical prospecting. J. Geochem. Explor. 2, 251–296.

Brannon, J.M., Patrick, W.H., 1987. Fixation, transformation, and mobilization of arsenic in sediments. Environ. Sci. Technol. 21, 450–459.

Bright, D.A., Dodd, M., Reimer, K.J., 1996. Arsenic in sub-Arctic lakes influenced by gold mine effluent: the occurrence of organoarsenicals and 'hidden' arsenic. Sci. Tot. Environ. 180, 165–182.

Brookins, D.G., 1988. Eh-pH Diagrams for Geochemistry. Springer-Verlag, Berlin.

Cáceres, L., Gruttner, E., Contreras, R., 1992. Water recycling in arid regions—Chilean case. Ambio 21, 138–144.

Canfield, D.E., 1989. Reactive iron in sediments. Geochim. Cosmochim. Acta 53, 619–632.

Canfield, D.E., Berner, R.A., 1987. Dissolution and pyritization of magnetite in anoxic marine sediments. Geochim. Cosmochim. Acta 51, 645–659.

Cebrián, M.E., Albores, M.A., Garciá-Vargas, G., Del Razo, L.M., Ostrosky-Wegman, P., 1994. Chronic arsenic poisoning in humans. In: Nriagu, J.O. (Ed.), Arsenic in the Environment, Part II: Human Health and Ecosystem Effects. John Wiley, New York, pp. 93–107.

CGWB, 1999. High Incidence of Arsenic in Groundwater in West Bengal. Central Ground Water Board, India, Ministry of Water Resources, Government of India.

Chen, C.J., Chuang, Y.C., Lin, T.M., Wu, H.Y., 1985. Malignant neoplasms among residents of a blackfoot disease-endemic area in Taiwan: high-arsenic artesian well water and cancers. Cancer Res. 45, 5895–5899.

Chen, S.L., Dzeng, S.R., Yang, M.H., Chlu, K.H., Shieh, G.M., Wal, C.M., 1994. Arsenic species in groundwaters of the Blackfoot disease areas, Taiwan. Environ. Sci.Technol. 28, 877–881.

Chen, S.L., Yeh, S.J., Yang, M.H., Lin, T.H., 1995. Trace element concentration and arsenic speciation in the well water of a Taiwan area with endemic Blackfoot disease. Biol. Trace Elem. Res. 48, 263–274.

Cherry, J.A., Shaikh, A.U., Tallman, D.E., Nicholson, R.V., 1979. Arsenic species as an indicator of redox conditions in groundwater. J. Hydrol. 43, 373–392.

Choprapawon, C., Rodcline, A., 1997. Chronic arsenic poisoning in Ronpibool Nakhon Sri Thammarat, the Southern Province of Thailand. In: Abernathy, C.O., Calderon, R.L., Chappell, W.R. (Eds.), Arsenic Exposure and Health Effects. Chapman and Hall, London, pp. 69–77.

Collon, P., Kutschera, W., Loosli, H.H., Lehmann, B.E., Purtschert, R., Love, A., Sampson, L., Anthony, D., Cole, D., Davids, B., Morrissey, D.J., Sherrill, B.M., Steiner, M., Pardo, R.C., Paul, M., 2000. Kr-81 in the Great Artesian Basin, Australia: a new method for dating very old groundwater. Earth Planet. Sci. Lett. 182, 103–113.

Cook, S.J., Levson, V.M., Giles, T.R., Jackaman, W., 1995. A comparison of regional lake sediment and till geochemistry surveys—a case-study from the Fawnie Creek area, Central British Columbia. Explor. Min. Geol. 4, 93–110.

Cornell, R.M., Schwertmann, U., 1996. The Iron Oxides: Structure, Properties, Reactions, Occurrence and Uses. VCH, Weinheim.

Crecelius, E.A., 1975. The geochemical cycle of arsenic in Lake Washington and its relation to other elements. Limnol. Oceanog. 20, 441–451.

Criaud, A., Fouillac, C., 1989. The distribution of arsenic(III) and arsenic(V) in geothermal waters: Examples from the Massif Central of France, the Island of Dominica in the Leeward Islands of the Caribbean, the Valles Caldera of New Mexico, USA, and southwest Bulgaria. Chem. Geol. 76, 259–269.

Cronan, D.S., 1972. The mid-Atlantic Ridge near 45°N, XVII: Al, As, Hg, and Mn in ferriginous sediments from the median valley. Can. J. Earth Sci. 9, 319–323.

CSME, 1997. Geology And Geochemistry Of Arsenic Occurrences In Groundwater Of Six Districts of West Bengal. Report of the Centre for Study of Man and Environment, Calcutta.

Cullen, W.R., Reimer, K.J., 1989. Arsenic speciation in the environment. Chem. Rev. 89, 713–764.

Cummings, D.E., Caccavo, F., Fendorf, S., Rosenzweig, R.F., 1999. Arsenic mobilization by the dissimilatory Fe(III)-reducing bacterium Shewanella alga BrY. Environ. Sci. Technol. 33, 723–729.

Cutter, G.A., Cutter, L.S., Featherstone, A.M., Lohrenz, S.E., 2001. Antimony and arsenic biogeochemistry in the western Atlantic Ocean. Deep-Sea Res. Part II—Topical Stud. Oceanog. 48, 2895–2915.

Das, D., Chatterjee, A., Mandal, B.K., Samanta, G., Chakraborti, D., Chanda, B., 1995. Arsenic in ground-water in 6 districts of West Bengal, India—the biggest arsenic calamity in the world. 2. Arsenic concentration in drinking-water, hair, nails, urine, skin-scale and liver-tissue, biopsy of the affected people. Analyst 120, 917–924.

Datta, D.K., Subramanian, V., 1997. Texture and mineralogy of sediments from the Ganges-Brahmaputra-Meghna river system in the Bengal basin, Bangladesh and their environmental implications. Environ. Geol. 30, 181–188.

Davis, A., de Curnou, P., Eary, L.E., 1997. Discriminating between sources of arsenic in the sediments of a tidal waterway, Tacoma, Washington. Environ. Sci. Technol. 31, 1985–1991.

Davison, W., 1993. Iron and manganese in lakes. Earth Sci. Rev. 34, 119–163.

Del Razo, L.M., Arellano, M.A., Cebrián, M.E., 1990. The oxidation states of arsenic in well-water from a chronic arsenicism area of northern Mexico. Environ. Pollut. 64, 143–153.

Del Razo, L.M., Hernández, J.L., García-Vargas, G.G., Ostrosky-Wegman, P., Cortinas de Nava, C., Cebrián, M.E., 1994. Urinary excretion of arsenic species in a human population chronically exposed to arsenic via drinking water. A pilot study. In: Chappell, W.R., Abernathy, C.O., Cothern, C.R. (Eds.), Arsenic Exposure and Health, 91–100. Science and Technology Letters, Northwood.

Deuel, L.E., Swoboda, A.R., 1972. Arsenic solubility in a reduced environment. Soil Sci. Soc. Am. Proc. 36, 276–278.

De Vitre, R., Belzile, N., Tessier, A., 1991. Speciation and adsorption of arsenic on diagenetic iron oxyhydroxides. Limnol. Oceanog. 36, 1480–1485.

DFID, 2001. Addressing the Water Crisis: Healthier And More Productive Lives For People. UK Department for International Development, London.

(special issue). Curr. Sci. 734859.

DPHE/BGS/MML, 1999. Groundwater Studies for Arsenic Contamination in Bangladesh. Phase I: Rapid Investigation Phase. BGS/MML Technical Report to Department for International Development, UK), 6 volumes.

Driehaus, W., Jekel, M., Hildebrandt, U., 1998. Granular ferric hydroxide-a new adsorbent for the removal of arsenic from natural water. J. Water Supp. Res. Technol.-Aqua 47, 30–35.

Driehaus, W., Seith, R., Jekel, M., 1995. Oxidation of arsenate(III) with manganese oxides in water-treatment. Water Res. 29, 297–305.

Drodt, M., Trautwein, A.X., Konig, I., Suess, E., Koch, C.B., 1997. Mössbauer spectroscopic studies on the iron forms of deep-sea sediments. Physics and Chemistry of Minerals 24, 281–293.

Dudas, M.J., 1984. Enriched levels of arsenic in post-active acid sulfate soils in Alberta. Soil Sci. Soc. Am. J. 48, 1451–1452.

Dudas, M.J., Warren, C.J., Spiers, G.A., 1988. Chemistry of arsenic in acid sulfate soils of northern Alberta. Comm. Soil Sci. Plant Anal. 19, 887–895.

Durum, W.H., Hem, J.D., Heidel, S.G., 1971. Reconnaissance of Selected Minor Elements in Surface Waters of the United States, October 1970. US Geol. Surv. Circ. 643.

Dzombak, D.A., Morel, F.M.M., 1990. Surface Complexation Modelling- Hydrous Ferric Oxide. John Wiley, New York.

Eary, L.E., Schramke, J.A., 1990. Rates of inorganic oxidation reactions involving dissolved oxygen. In: Melchior, D.C., Bassett, R.L. (Eds.), Chemical Modeling of Aqueous Systems II. ACS Symposium Series. American Chemical Society, Washington, DC, pp. 379–396.

Edmunds, W.M., Cook, J.M., Kinniburgh, D.G., Miles, D.L., Trafford, J.M., 1989. Trace-element Occurrence in British Groundwaters. Res. Report SD/89/3, British Geological Survey, Keyworth.

Edwards, M., 1994. Chemistry of arsenic removal during coagulation and Fe–Mn oxidation. J. Am. Water Works Assoc. 86, 64–78.

Edwards, M., Patel, S., McNeill, L., Chen, H.W., Frey, M., Eaton, A.D., Antweiler, R.C., Taylor, H.E., 1998. Considerations in As analysis and speciation. J. Am. Water Works Assoc. 90, 103–113.

Ellis, A.J., Mahon, W.A.J., 1977. Chemistry and Geothermal Systems. Academic Press, New York.

Erhlich, H.L., 1996. Geomicrobiology, 3rd ed. Marcel Dekker, New York.

Farmer, J.G., Baileywatts, A.E., Kirika, A., Scott, C., 1994. Phosphorus fractionation and mobility in Loch Leven sediments. Aquat. Conserv.-Mar. Freshwater Ecosys. 4, 45–56.

Fendorf, S., Eick, M.J., Grossel, P., Sparks, D.L., 1997. Arsenate and chromate retention mechanisms on goethite. 1. Surface structure. Environ. Sci. Technol. 31, 315–320.

Ficklin, W. H. and Callender, E., 1989. Arsenic geochemistry of rapidly accumulating sediments, Lake Oahe, South Dakota. In: Mallard, G. E. and Ragone, S. E. (Eds.), US Geol. Surv. Water Resour. Investig. Rep. 88–4420. U.S. Geol. Surv. Toxic Substances Hydrology Program—Proc. Tech. Meeting, Phoenix, Arizona, 26–30 September 1988, pp. 217–222.

Finkelman, R.B., Belkin, H.E., Zheng, B., 1999. Health impacts of domestic coal use in China. Proc. Nat. Acad. Sci., USA 96, 3427–3431.

Fleet, M.E., Mumin, A.H., 1997. Gold-bearing arsenian pyrite and marcasite and arsenopyrite from Carlin Trend gold deposits and laboratory synthesis. Am. Mineral. 82, 182–193.

Fontaine, J.A., 1994. Chapter 28. Regulating arsenic in Nevada drinking water supplies: past problems, future challenges. In: Chappell, W.R., Abernathy, C.O., Cothern, C.R. (Eds.), Arsenic Exposure and Health. Science and Technology Letters, Northwood, pp. 285–288.

Forstner, U., Haase, I., 1998. Geochemical demobilization of metallic pollutants in solid waste-implications for arsenic in waterworks sludges. J. Geochem. Explor. 62, 29–36.

Foster, A.L., Breit, G.N., Welch, A.L., Whitney, J.W., Islam, M. Nazrul, Islam, H. Khairul, Alam M.K., Islam, M.S., 2000. In-situ Identification of Arsenic Species in Soil and Aquifer Sediment from Ramrail, Brahmanbaria, Bangladesh. Presentation at AGU Fall meeting, 15–19 December 2000, San Francisco, California.

Foster, A.L., Brown, G.E., Parks, G.A., 1998. X-ray absorption fine-structure spectroscopy study of photocatalyzed, heterogeneous As(III) oxidation on kaolin and anatase. Environ. Sci. Technol 32, 1444–1452.

Fredrickson, J.K., Zachara, J.M., Kennedy, D.W., Dong, H., Onstott, T.C., Hinman, N.W., Li, S.-M., 1998. Biogenic iron mineralization accompanying the dissimilatory reduction of hydrous ferric oxide by a groundwater bacterium. Geochim. Cosmochim. Acta 62, 3239–3257.

Froelich, P.N., Kaul, L.W., Byrd, J.T., Andreae, M.O., Roe, K.K., 1985. Arsenic, barium, germanium, tin, dimethyl-sulfide and nutrient biogeochemsitry in Charlotte Harbour, Florida, a phosphorus-enriched estuary. Estuar. Coast. Shelf Sci. 20, 239–264.

Fujii, R., Swain, W.C., 1995. Areal Distribution of Selected Trace Elements, Salinity, and Major Ions in Shallow Ground Water, Tulare Basin, Southern San Joaquin Valley, California. US Geol. Surv. Water-Resour. Investig. Rep. 95–4048.

Gelova, G.A., 1977. Hydrogeochemistry of Ore Elements. Nedra, Moscow.

Génin, J.-M.R., Bourrié, G., Trolard, F., Abdelmoula, M., Jaffrezic, A., Refait, P., Maitre, V., Humbert, B., Herbillon, A., 1998. Thermodynamic equilibria in aqueous suspensions of synthetic and natural Fe(II)-Fe(III) green rusts: occurrences of the mineral in hydromorphic soils. Environ. Sci. Technol. 32, 1058–1068.

Ghosh, M.M., Yuan, J.R., 1987. Adsorption of inorganic arsenic and organoarsenicals on hydrous oxides. Environ. Prog. 6, 150–157.

Goldberg, S., 1986. Chemical modeling of arsenate adsorption on aluminum and iron oxide minerals. Soil Sci. Soc. Am. J. 50, 1154–1157.

Goldberg, S., Glaubig, R.A., 1988. Anion sorption on a calcareous, montmorillonitic soil—arsenic. Soil Sci. Soc. Am. J. 52, 1297–1300.

Gómez-Ariza, J.L., Sanchez Rodas, D., Giraldez, I., 1998. Selective extraction of iron oxide associated arsenic species from sediments for speciation with coupled HPLC-HG-AAS. Journal of Anal. Atom. Spectrom. 13, 1375–1379.

Grimes, D.J., Ficklin, W.H., Meier, A.L., McHugh, J.B., 1995. Anomalous gold, antimony, arsenic, and tungsten in ground water and alluvium around disseminated gold deposits along the Getchell Trend, Humboldt County, Nevada. J. Geochem. Explor. 52, 351–371.

Guerin, W.F., Blakemore, R.P., 1992. Redox cycling of iron supports growth and magnetite synthesis by *Aquaspirillum magnetotacticum*. Appl. Environ. Microbiol. 58, 1102–1109.

Gulens, J., Champ, D.R., Jackson, R.E., 1979. Influence of redox environments on the mobility of arsenic in ground water. In: Jenne, E.A. (Ed.), Chemical Modelling in Aqueous Systems. American Chemical Society, pp. 81–95.

Guo, H.R., Chen, C.J., Greene, H.L., 1994. Arsenic in drinking water and cancers: a brief descriptive view of Taiwan studies. In: Chappell, W.R., Abernathy, C.O., Cothern, C.R. (Eds.), Arsenic Exposure and Health. Science and Technology Letters, Northwood, pp. 129–138.

Guo, T.Z., DeLaune, R.D., Patrick, W.H., 1997. The influence of sediment redox chemistry on chemically active forms of arsenic, cadmium, chromium, and zinc in estuarine sediment. Environ. Internat 23, 305–316.

Gurzau, E.S., Gurzau, A.E., 2001. Arsenic in drinking water from groundwater in Transylvania, Romania: In: Chapell, W.R., Abernathy, C.O., Calderon, R.L. (Eds.), Arsenic Exposure and Health Effects IV. Elsevier, Amsterdam, pp. 181–184.

Gustafsson, J.P., Jacks, G., 1995. Arsenic geochemistry in forested soil profiles as revealed by solid-phase studies. Appl. Geochem. 10, 307–315.

Gustafsson, J.P., Tin, N.T., 1994. Arsenic and selenium in some Vietnamese acid sulfate soils. Sci. Tot. Environ. 151, 153–158.

Hale, J.R., Foos, A., Zubrow, J.S., Cook, J., 1997. Better characterization of arsenic and chromium in soils: a field-scale example. J. Soil Contam. 6, 371–389.

Hall, G.E.M., Pelchat, J.C., Gauthier, G., 1999. Stability of inorganic arsenic(III) and arsenic(V) in water samples. J. Anal. Atom. Spectrom 14, 205–213.

Hasegawa, H., 1997. The behavior of trivalent and pentavalent methylarsenicals in Lake Biwa. Appl. Organometal. Chem. 11, 305–311.

Hasegawa, H., Matsui, M., Okamura, S., Hojo, M., Iwasaki, N., Sohrin, Y., 1999. Arsenic speciation including 'hidden' arsenic in natural waters. Applied Organometal. Chem. 13, 113–119.

Hess, R.E., Blanchar, R.W., 1977. Dissolution of arsenic from waterlogged and aerated soil. Soil Sci. Soc. Am. J. 41, 861–865.

Heinrichs, G., Udluft, P., 1999. Natural arsenic in Triassic rocks: a source of drinking-water contamination in Bavaria, Germany. Hydrogeol. J. 7, 468–476.

Hiemstra, T., van Riemsdijk, W.H., 1996. A surface structural approach to ion adsorption: the charge distribution, CD. Model. J. Colloid Interface Sci. 179, 488–508.

Hiemstra, T., van Riemsdijk, W.H., 1999. Surface structural ion adsorption modeling of competitive binding of oxyanions by metal hydroxides. J. Colloid Interface Sci. 210, 182–193.

Hingston, F.J., Posner, A.M., Quirk, J.P., 1971. Competitive adsorption of negatively charged ligands on oxide surfaces. In: Discussions of the Faraday Society, No. 52. The Faraday Society, London, pp. 334–342.

Hopenhayn-Rich, C., Biggs, M.L., Fuchs, A., Bergoglio, R., Tello, E.E., Nicolli, H., Smith, A.H., 1996. Bladder-cancer mortality associated with arsenic in drinking water in Argentina. Epidemiol. 7, 117–124.

Howard, A.G., Apte, S.C., Comber, S.D.W., Morris, R.J., 1988. Biogeochemical control of the summer distribution and speciation of arsenic in the Tamar estuary. Estuar. Coast. Shelf Sci. 27, 427–443.

Howard, A.G., Hunt, L.E., Salou, C., 1999. Evidence supporting the presence of dissolved dimethylarsinate in the marine environment. Appl. Organometal. Chem. 13, 39–46.

Hsu, K.-H., Froines, J.R., Chen, C.-J., 1997. Studies of arsenic ingestion from drinking water in northeastern Taiwan: chemical speciation and urinary metabolites. In: Abernathy, C.O., Calderon, R.L., Chappell, W.R. (Eds.), Arsenic Exposure and Health Effects. Chapman Hall, London, pp. 190–209.

Jain, A., Raven, K.P., Loeppert, R.H., 1999. Arsenite and arsenate adsorption on ferrihydrite: surface charge reduction and net OH^- release stoichiometry. Environ. Sci. Technol. 33, 1179–1184.

James, H.L., 1966. Chemistry of the iron-rich sedimentary rocks. Data of Geochemistry. USGS Prof. Pap. 440-W.

Johnson, D.L., Pilson, M.E.Q., 1975. The oxidation of arsenite in seawater. Environ. Lett. 8, 157–171.

Jonnalagadda, S.B., Nenzou, G., 1996. Studies on arsenic-rich mine dumps. 1. Effect on the surface soil. J. Environ. Sci. Health Part A—Environ. Sci. Toxic Hazard. Subst. Control 31, 1909–1915.

Karcher, S., Cáceres, L., Jekel, M., Contreras, R., 1999. Arsenic removal from water supplies in Northern Chile using ferric chloride coagulation. J. Chart. Inst. Water Environ. Manag. 13, 164–169.

Kavanagh, P.J., Farago, M.E., Thornton, I., Braman, R.S., 1997. Bioavailability of arsenic in soil and mine wastes of the Tamar Valley, SW England. Chem. Spec. Bioavail. 9, 77–81.

Kent, D.B., Davis, J.A., Anderson, L.C.D., Rea, B.A., 1995. Transport of chromium and selenium in a pristine sand and gravel aquifer: role of adsorption processes. Water Resour. Res. 31, 1041–1050.

Keon, N.E., Swartz, C.H., Brabander, D.J., Harvey, C., Hemond, H.F., 2001. Validation of an arsenic sequential extraction method for evaluating mobility in sediments. Environ. Sci. Technol. 35, 2778–2784.

Khalid, R.A., Patrick, W.H., DeLaune, R.D., 1977. Phosphorus sorption characteristics of flooded soils. Soil Sci. Soc. Am. 41, 305–310.

Kinniburgh, D.G., Sridhar, K., Jackson, M.L., 1977. Specific adsorption of zinc and cadmium by iron and aluminum hydrous oxides. In: Hanford, W.A. (Ed.), The Fifteenth Hanford Life Sciences Symposium on Biological Implications of Metals in the Environment, 29 September–1 October 1975. USERDA, Natl Technical Information Service, 1977, Springfield, VA.

Klumpp, D.W., Peterson, P.J., 1979. Arsenic and other trace elements in the waters and organisms of an estuary in SW England. Environ. Pollut. 19, 11–20.

Kneebone, P.E., Hering, J.G., 2000. Behavior of arsenic and other redox sensitive elements in Crowley Lake, CA: a reservoir in the Los Angeles Aqueduct system. Environ. Sci. Technol. 34, 4307–4312.

Komnitsas, K., Xenidis, A., Adam, K., 1995. Oxidation of pyrite and arsenopyrite in sulphidic spoils in Lavrion. Miner. Engineer 12, 1443–1454.

Korte, N., 1991. Naturally occurring arsenic in groundwaters of the midwestern United States. Environ. Geol. Water Sci. 18, 137–141.

Korte, N.E., Fernando, Q., 1991. A review of arsenic(III) in groundwater. Crit. Rev. Environ. Control 21, 1–39.

Krause, E., Ettel, V.A., 1989. Solubilities and stabilities of ferric arsenate compounds. Hydrometal. 22, 311–337.

Kuhlmeier, P.D., 1997a. Partitioning of arsenic species in fine-grained soils. J. Air Waste Manag. Assoc. 47, 481–490.

Kuhlmeier, P.D., 1997b. Sorption and desorption of arsenic from sandy soils: Column studies. J. Soil Contam. 6, 21–36.

Kuhn, A., Sigg, L., 1993. Arsenic cycling in eutrophic Lake Greifen, Switzerland—influence of seasonal redox processes. Limnol. Oceanog. 38, 1052–1059.

Kuo, T.-L., 1968. Arsenic content of artesian well water in endemic area of chronic arsenic poisoning. Rep. Inst. Pathol. National Taiwan Univ. 20, 7–13.

Langmuir, D., 1997. Aqueous Environmental Geochemistry. Prentice Hall, New Jersey.

Legeleux, F., Reyss, J.L., Bonte, P., Organo, C., 1994. Concomitant enrichments of uranium, molybdenum and arsenic in suboxic continental-margin sediments. Oceanolog. Acta 17, 417–429.

Lenvik, K., Steinnes, E., Pappas, A.C., 1978. Contents of some heavy metals in Norwegian rivers. Nord. Hydrol. 9, 197–206.

Lerda, D.E., Prosperi, C.H., 1996. Water mutagenicity and toxicology in Rio Tercero, Cordoba, Argentina. Water Res. 30, 819–824.

Lindberg, R.D., Runnells, D.D., 1984. Ground water redox reactions: an analysis of equilibrium state applied to Eh measurements and geochemical modeling. Sci. 225, 925–927.

Livesey, N.T., Huang, P.M., 1981. Adsorption of arsenate by soils and its relation to selected chemical properties and anions. Soil Sci. 131, 88–94.

Lo, M.-C., Hsen, Y.-C., Lin, K.-K., 1977. Second Report on the Investigation of Arsenic Content in Underground Water in Taiwan. Taiwan Provincial Institute of Environmental Sanitation, Taichung, Taiwan.

Lovley, D.R., Chapelle, F.H., 1995. Deep subsurface microbial processes. Rev. Geophys. 33, 365–381.

Luo, Z.D., Zhang, Y.M., Ma, L., Zhang, G.Y., He, X., Wilson, R., Byrd, D.M., Griffiths, J.G., Lai, S., He, L., Grumski, K., Lamm, S.H., 1997. Chronic arsenicism and cancer in Inner Mongolia - consequences of well-water arsenic levels greater than 50 $\mu g\ l^{-1}$. In: Abernathy, C.O., Calderon, R.L., Chappell, W.R. (Eds.), Arsenic Exposure and Health Effects. Chapman Hall, London, pp. 55–68.

Ma, H.Z., Xia, Y.J., Wu, K.G., Sun, T.Z., Mumford, J.L., 1999. Arsenic exposure and health effects in Bayingnormen, Inner Mongolia. In: Chappell, W.R., Abernathy, C.O., Calderon, R.L. (Eds.), Arsenic Exposure and Health Effects. Elsevier, Amsterdam, pp. 127–131.

Maest, A.S., Pasilis, S.P., Miller, L.G., Nordstrom, D.K., 1992. Redox geochemistry of arsenic and iron in Mono Lake, California, USA. In: Kharaka, Y.K., Maest, A.S. (Eds.), Proc. 7th Internat. Symp. Water-Rock Interaction. A. A. Balkema, Rotterdam, pp. 507–511.

Maher, B.A., Taylor, R.M., 1988. Formation of ultrafine-grained magnetite in soils. Nature 336, 368–370.

Maher, W.A., 1985. Arsenic in coastal waters of South Australia. Water Res. 19, 933–934.

Manning, B.A., Fendorf, S.E., Goldberg, S., 1998. Surface structures and stability of arsenic(III) on goethite: spectroscopic evidence for inner-sphere complexes. Environ. Sci. Technol. 32, 2383–2388.

Manning, B.A., Goldberg, S., 1996. Modeling competitive adsorption of arsenate with phosphate and molybdate on oxide minerals. Soil Sci. Soc. Am. J. 60, 121–131.

Manning, B.A., Goldberg, S., 1997a. Arsenic(III) and arsenic(V) adsorption on three California soils. Soil Sci. 162, 886–895.

Manning, B.A., Goldberg, S., 1997b. Adsorption and stability of arsenic(III) at the clay mineral-water interface. Environ. Sci. Technol. 31, 2005–2011.

Martin, J.-M., Whitfield, M., 1983. The significance of the river input of chemical elements to the ocean. In: Wong, C.S., Boyle, E., Bruland, K.W., Burton, J.D., Goldberg, E.D. (Eds.), Trace Metals in Seawater. Plenum Press, New York, pp. 265–296.

Masscheleyn, P.H., DeLaune, R.D., Patrick, W.H., 1991. Effect of redox potential and pH on arsenic speciation and solubility in a contaminated soil. Environ. Sci. Technol. 25, 1414–1419.

Matis, K.A., Zouboulis, A.I., Malamas, F.B., Afonso, M.D.R., Hudson, M.J., 1997. Flotation removal of As(V) onto goethite. Environ. Pollut. 97, 239–245.

Matis, K.A., Zouboulis, A.I., Zamboulis, D., Valtadorou, A.V., 1999. Sorption of As(V) by goethite particles and study of their flocculation. Water Air Soil Pollut. 111, 297–316.

Matisoff, G., Khourey, C.J., Hall, J.F., Varnes, A.W., Strain, W.H., 1982. The nature and source of arsenic in northeastern Ohio groundwater. Ground Water 20, 446–456.

McCreadie, H., Blowes, D.W., Ptacek, C.J., Jambor, J.L., 2000. Influence of reduction reactions and solid-phase composition on porewater concentrations of arsenic. Environ. Sci. Technol. 34, 3159–3166.

McGeehan, S.L., 1996. Arsenic sorption and redox reactions: Relevance to transport and remediation. J. Environ. Sci. Health Part A-Environ. Sci. Engineer. Toxic Hazard. Subst. Control 31, 2319–2336.

McGeehan, S.L., Naylor, D.V., 1994. Sorption and redox transformation of arsenite and arsenate in two flooded soils. Soil Sci. Soc. Am. J. 58, 337–342.

McLaren, S.J., Kim, N.D., 1995. Evidence for a seasonal fluctuation of arsenic in New Zealand's longest river and the effect of treatment on concentrations in drinking water. Environ. Pollut. 90, 67–73.

Millero, F., Huang, F., Zhu, X.R., Liu, X.W., Zhang, J.Z., 2001. Adsorption and desorption of phosphate on calcite and aragonite in seawater. Aquat. Geochem. 7, 33–56.

Mok, W., Wai, C.M., 1990. Distribution and mobilization of arsenic and antimony species in the Coeur D'Alene River, Idaho. Environ. Sci. Technol. 24, 102–108.

Moore, J.N., Ficklin, W.H., Johns, C., 1988. Partitioning of arsenic and metals in reducing sulfidic sediments. Environ. Sci. Technol. 22, 432–437.

Mortimer, C.H., 1942. The exchange of dissolved substances between mud and water in lakes. Parts III and IV, summary and references. J. Ecol. 30, 147–201.

Nag, J.K., Balaram, V., Rubio, R., Alberti, J., Das, A.K., 1996. Inorganic arsenic species in groundwater: a case study from Purbasthali, Burdwan, India. J. Trace Elem. Med. Biol. 10, 20–24.

Nagorski, S.A., Moore, J.N., 1999. Arsenic mobilization in the hyporheic zone of a contaminated stream. Water Resourc. Res. 35, 3441–3450.

Navarro, M., Sanchez, M., Lopez, H., Lopez, M.C., 1993. Arsenic contamination levels in waters, soils, and sludges in southeast spain. Bull. Environ. Contam. Toxicol. 50, 356–362.

Newman, D.K., Ahmann, D., Morel, F.M.M., 1998. A brief review of microbial arsenate respiration. Geomicrobiol. 15, 255–268.

Nicolli, H.B., Merino, M.H., 2002. High contents of F, As and Se in groundwater of the Carcarañá river basin, Argentine Pampean Plain. Environ. Geol., in press.

Nicolli, H.B., Suriano, J.M., Peral, M.A.G., Ferpozzi, L.H., Baleani, O.A., 1989. Groundwater contamination with arsenic and other trace-elements in an area of the Pampa, province of Córdoba, Argentina. Environ. Geol. Water Sci. 14, 3–16.

Nicolli, H.B., Tineo, A., García, J.W., Falcón, C.M., Merino, M.H., 2001. Trace-element quality problems in groundwater from Tucumán, Argentina. In: Cidu, R. (Ed.), Water-Rock Interaction 2001. Vol. 2. Swets & Zeitlinger, Lisse, pp. 993–996.

Nimick, D.A., Moore, J.N., Dalby, C.E., Savka, M.W., 1998. The fate of geothermal arsenic in the Madison and Missouri Rivers, Montana and Wyoming. Water Resour. Res. 34, 3051–3067.

Niu, S., Cao, S., Shen, E., 1997. The status of arsenic poisoning in China. In: Abernathy, C.O., Calderon, R.L., Chappell, W.R. (Eds.), Arsenic Exposure and Health Effects. Chapman Hall, London, pp. 78–83.

Nordstrom, D.K., 2000. An overview of arsenic mass poisoning in Bangladesh and West Bengal, India. In: Young, C. (Ed.), Minor Elements 2000: Processing and Environmental Aspects of As, Sb, Se, Te, and Bi. Society for Mining, Metallurgy and Exploration, pp. 21–30.

Nordstrom, D.K., Alpers, C.N., 1999. Negative pH, efflorescent mineralogy, and consequences for environmental restoration at the Iron Mountain Superfund Site, California. Proc. Nat. Acad. Sci., USA 96, 3455–3462.

Nordstrom, D.K., Alpers, C.N., Ptacek, C.J., Blowes, D.W., 2000. Negative pH and extremely acidic mine waters from Iron Mountain California. Environ. Sci. Technol. 34, 254–258.

Nriagu, J.O., Pacyna, J.M., 1988. Quantitative assessment of worldwide contamination of air, water, and soils by trace metals. Nature 333, 134–139.

Onishi, H., Sandell, E.B., 1955. Geochemistry of arsenic. Geochim. Cosmochim. Acta 7, 1–33.

Oremland, R.S., Dowdle, P.R., Hoeft, S., Sharp, J.O., Schaefer, J.F., Miller, L.G., Blum, J.S., Smith, R.L., Bloom, N.S., Wallschlaeger, D., 2000. Bacterial dissimilatory reduction of arsenate and sulfate in meromictic Mono Lake, California. Geochim. Cosmochim. Acta 64, 3073–3084.

Oscarson, D.W., Huang, P.M., Defosse, D., Herbillion, A., 1981. Oxidative power of Mn(IV) and Fe(III) oxides with respect to As(III) in terrestrial and aquatic environments. Nature 291, 50–51.

Oscarson, D.W., Huang, P.M., Liaw, W.K., Hammer, U.T., 1983. Kinetics of oxidation of arsenite by various manganese dioxides. Soil Sci. Soc. Am. J. 47, 644–648.

Paige, C.R., Snodgrass, W.J., Nicholson, R.V., Scharer, J.M., 1997. An arsenate effect on ferrihydrite dissolution kinetics under acidic oxic conditions. Water Res. 31, 2370–2382.

Palmer, C.A., Klizas, S.A., 1997. The Chemical Analysis Of Argonne Premium Coal Samples. US Geol. Surv. Bull. 2144, US Geological Survey, Reston, USA.

Peterson, M.L., Carpenter, R., 1983. Biogeochemical processes affecting total arsenic and arsenic species distributions in an intermittently anoxic Fjord. Mar. Chem. 12, 295–321.

Peterson, M.L., Carpenter, R., 1986. Arsenic distributions in porewaters and sediments of Puget Sound, Lake Washington, the Washington coast and Saanich Inlet, B.C. Geochim. Cosmochim. Acta 50, 353–369.

Pettine, M., Camusso, M., Martinotti, W., 1992. Dissolved and particulate transport of arsenic and chromium in the Po River, Italy. Sc. Tot. Environ. 119, 253–280.

PHED, 1991. Arsenic Pollution in Groundwater in West Bengal. Report of Arsenic Investigation Project to the National Drinking Water Mission, Delhi, India.

PHED/UNICEF, 1999. Joint Plan of Action to Address Arsenic Contamination of Drinking Water. Government of West Bengal and UNICEF. Public Health Engineering Department, Government of West Bengal.

Pichler, T., Veizer, J., Hall, G.E.M., 1999. Natural input of arsenic into a coral reef ecosystem by hydrothermal fluids and its removal by Fe(III) oxyhydroxides. Environ. Sci. Technol. 33, 1373–1378.

Pierce, M.L., Moore, C.B., 1982. Adsorption of arsenite and arsenate on amorphous iron hydroxide. Water Res. 16, 1247–1253.

Pirazzoli, P.A., 1996. Sea-level Changes: The Last 20 000 Years. John Wiley, Chichester.

Plumlee, G.S., Smith, K.S., Montour, M.R., Ficklin, W.H., Mosier, E.L., 1999. Geologic controls on the composition of natural waters and mine waters draining diverse mineral-deposit types. In: Environmental Geochemistry of Mineral Deposits. Part B: Case Studies. Chapter 19, pp. 373–432 (Chapter 19).

Ponnamperuma, F.N., Tianco, E.M., Loy, T., 1967. Redox equilibria in flooded soils: I. The iron hydroxide systems. Soil Sci. 103, 371–382.

Quentin, K.E., Winkler, H.A., 1974. Occurrence and determination of inorganic polluting agents. Z. für Bakteriol. und Hygiene 158, 514–523.

Raven, K.P., Jain, A., Loeppert, R.H., 1998. Arsenite and arsenate adsorption on ferrihydrite: kinetics, equilibrium, and adsorption envelopes. Environ. Sci. Technol. 32, 344–349.

Reuther, R., 1992. Geochemical mobility of arsenic in a flow-through water-sediment system. Environ. Technol. 13, 813–823.

Reynolds, J.G., Naylor, D.V., Fendorf, S.E., 1999. Arsenic sorption in phosphate-amended soils during flooding and subsequent aeration. Soil Sci. Soc. Am. J. 63, 1149–1156.

Riedel, F.N., Eikmann, T., 1986. Natural occurrence of arsenic and its compounds in soils and rocks. Wissensch. Umwelt 3–4, 108–117.

Riedel, G.F., 1993. The annual cycle of arsenic in a temperate estuary. Estuaries 16, 533–540.

Riedel, G.F., Sanders, J.G., Osman, R.W., 1997. Biogeochemical control on the flux of trace elements from estuarine sediments: water column oxygen concentrations and benthic infauna. Estuar. Coast. Shelf Sci. 44, 23–38.

Rittle, K.A., Drever, J.I., Colberg, P.J.S., 1995. Precipitation of arsenic during bacterial sulfate reduction. Geomicrobiol. J. 13, 1–11.

Robertson, F.N., 1989. Arsenic in groundwater under oxidizing conditions, south-west United States. Environ. Geochem. Health 11, 171–185.

Robins, R.G., 1987. Solubility and stability of scorodite, $FeAsSO_4 \cdot 2H_2O$: discussion. Am. Mineral. 72, 842–844.

Robinson, B., Outred, H., Brooks, R., Kirkman, J., 1995. The distribution and fate of arsenic in the Waikato River System, North Island, New Zealand. Chem. Spec. Bioavail. 7, 89–96.

Rochette, E.A., Li, G.C., Fendorf, S.E., 1998. Stability of arsenate minerals in soil under biotically generated reducing conditions. Soil Sci. Soc. Am. J. 62, 1530–1537.

Sancha, A.M., 1999. Full-scale application of coagulation processes for arsenic removal in Chile: a successful case study. In: Chappell, W.R., Abernathy, C.O., Calderon, R.L. (Eds.), Arsenic Exposure and Health Effects. Elsevier, Amsterdam, pp. 373–378.

Sancha, A.M., Castro, M.L., 2001. Arsenic in Latin America: occurrence, exposure, health effects and remediation. In: Chapell, W.R., Abernathy, C.O., Calderon, R.L. (Eds.), Arsenic Exposure and Health Effects IV. Elsevier, Amsterdam, pp. 87–96.

Schreiber, M.J., Simo, J., Freiberg, P., 2000. Stratigraphic and geochemical controls on naturally occurring arsenic in groundwater, eastern Wisconsin, USA. Hydrogeol. J. 8, 161–176.

Schroeder, W.H., Dobson, M., Kane, D.M., Johnson, N.D., 1987. Toxic trace-elements associated with airborne particulate matter—a review. Internat. J. Air Pollut. Control Hazard. Waste Manag. 37, 1267–1285.

Scott, M.J., Morgan, J.J., 1995. Reactions at oxide surfaces. 1. Oxidation of As(III) by synthetic birnessite. Environ. Sci. Technol. 29, 1898–1905.

Scudlark, J.R., Church, T.M., 1988. The atmospheric deposition of arsenic and association with acid precipitation. Atmos. Environ. 22, 937–943.

Seyler, P., Martin, J.-M., 1989. Biogeochemical processes affecting arsenic species distribution in a permanently stratified lake. Environ. Sci. Technol. 23, 1258–1263.

Seyler, P., Martin, J.-M., 1990. Distribution of arsenite and total dissolved arsenic in major French estuaries: dependence on biogeochemical processes and anthropogenic inputs. Mar. Chem. 29, 277–294.

Seyler, P., Martin, J.-M., 1991. Arsenic and selenium in a pristine river-estuarine system: the Krka, Yugoslavia. Mar. Chem. 34, 137–151.

Shacklette, H.T., Boerngen, J.G., Keith, J.R., 1974. Selenium, fluorine, and arsenic in superficial materials of the conterminous United States. US Geol. Surv., Circ. 692. US Government Printing Office, Washington DC.

Slomp, C.P., Epping, E.H.G., Helder, W., van Raaphorst, W., 1996. A key role for iron-bound phosphorus in authigenic apatite formation in North Atlantic continental platform sediments. J. Mar. Res. 54, 1179–1205.

Smedley, P.L., 1996. Arsenic in rural groundwater in Ghana. J. Afr. Earth Sci. 22, 459–470.

Smedley, P.L., Edmunds, W.M., Pelig-Ba, K.B., 1996. Mobility of arsenic in groundwater in the Obuasi area of Ghana. In: Appleton, J.D., Fuge, R., McCall, G.J.H. (Eds.), Environmental Geochemistry and Health, Geol. Soc. Spec. Publ. 113. Geological Society, London, pp. 163–181.

Smedley, P.L., Nicolli, H.B., Barros, A.J., Tullio, J.O., 1998.

Origin and mobility of arsenic in groundwater from the Pampean Plain, Argentina. In: Arehart, G.B., Hulston, J.R. (Eds.), Water-Rock Interaction. Proc. 9th Internat. Symp., Taupo, New Zealand, 1998. Balkema, Rotterdam, pp. 275–278.

Smedley, P.L., Macdonald, D.M.J., Nicolli, H.B., Barros, A.J., Tullio, J.O., Pearce, J.M., 2000. Arsenic and other quality problems in groundwater from northern La Pampa Province, Argentina. British Geological Survey Technical Report, WC/99/36. British Geological Survey, Keyworth.

Smedley, P.L., Zhang, M., Zhang, G., Luo, Z., 2001a. Arsenic and other redox-sensitive elements in groundwater from the Huhhot Basin, Inner Mongolia. In: Cidu, R. (Ed.), Water-Rock Interaction 2001, Vol. 1. Swets & Zeitlinger, Lisse, pp. 581–584.

Smedley, P.L., Kinniburgh, D.G., Huq, I., Luo, Z., Nicolli, H.B., 2001b. International perspective on naturally occurring arsenic problems in groundwater. In: Chappell, W.R., Abernathy, C.O., Calderon, R.L. (Eds.), Arsenic Exposure and Health Effects IV. Elsevier, Amsterdam, pp. 9–25.

Smedley, P.L., Nicolli, H.B., Macdonald, D.M.J., Barros, A.J., Tullio, J.O., 2002. Hydrogeochemistry of arsenic and other inorganic constituents in groundwaters from La Pampa, Argentina. Appl. Geochem. 17, 259–284.

Smith, A.H., Goycolea, M., Haque, R., Biggs, M.L., 1998. Marked increase in bladder and lung cancer mortality in a region of northern Chile due to arsenic in drinking water. Am. J. Epidemiol. 147, 660–669.

Smith, A.H., Hopenhayn-Rich, C., Bates, M.N., Goeden, H.M., Hertz-Picciotto, I., Duggan, H.M., Wood, R., Kosnett, M.J., Smith, M.T., 1992. Cancer risks from arsenic in drinking water. Environ. Health Perspect. 97, 259–267.

Smith, A.H., Lingas, E.O., Rahman, M., 2000. Contamination of drinking-water by arsenic in Bangladesh: a public health emergency. Bull. WHO. 78, 1093–1103.

Smith, S.L., Jaffe, P.R., 1998. Modeling the transport and reaction of trace metals in water-saturated soils and sediments. Water Resour. Res. 34, 3135–3147.

Sohlenius, G., 1996. Mineral magnetic properties of late Weichselian-Holocene sediments from the northwestern Baltic proper. Boreas 25, 79–88.

Sonderegger, J.L., Ohguchi, T., 1988. Irrigation related arsenic contamination of a thin, alluvial aquifer, Madison River Valley, Montana, USA. Environ. Geol. Water Sci. 11, 153–161.

Stewart, F. H., 1963. Data of Geochemistry, 6th ed. Chap. Y. Marine Evaporites. US Geol. Surv. Prof. Pap. 440-Y.

Stumm, W., Morgan, J.J., 1995. Aquatic Chemistry: Chemical Equilibria and Rates in Natural Waters. Wiley-Interscience, New York.

Sullivan, K.A., Aller, R.C., 1996. Diagenetic cycling of arsenic in Amazon shelf sediments. Geochim. Cosmochim. Acta 60, 1465–1477.

Sun, G.F., Dai, G.J., Li, F.J., Yamauchi, H., Yoshida, T., Aikawa, H., 1999. The present situation of chronic arsenism and research in China. In: Chappell, W.R., Abernathy, C.O., Calderon, R.L. (Eds.), Arsenic Exposure and Health Effects. Elsevier, Amsterdam, pp. 123–126.

Sun, G.F., Pi, J.B., Li, B., Guo, X.Y., Yamauchi, H., Yoshida, T., 2001. Progresses on researches of endemic arsenism in China: population at risk, intervention actions, and related scientific issues. In: Chapell, W.R., Abernathy, C.O., Calderon, R.L. (Eds.), Arsenic Exposure and Health Effects IV. Elsevier, Amsterdam, pp. 79–85.

Swedlund, P.J., Webster, J.G., 1998. Arsenic removal from geothermal bore waters: the effect of monosilicic acid. In: Arehart, G.B., Hulston, J.R. (Eds.), Water-Rock Interaction. Proc. 9th Internat. Symp., Taupo, New Zealand, 1998. Balkema, Rotterdam, pp. 947–950.

Taylor, R.M., 1980. Formation and properties of Fe(II)–Fe(III) hydroxycarbonate and its possible significance in soil formation. Clay Minerals 15, 369–382.

Thirunavkukkarasu, O.S., Viraraghavan, T., Subramanian, K.S., 2001. Removal of arsenic in drinking water by iron oxide-coated sand and ferrihydrite - Batch studies. Water Qual. Res. J. Can. 36, 55–70.

Thompson, J.M., Demonge, J. M., 1996. Chemical Analyses of Hot Springs, Pools, and Geysers from Yellowstone National Park, Wyoming and Vicinity, 1980–1993. US Geol. Surv. Open File Rep. 96–68.

Thompson, J.M., Keith, T.E.C., Consul, J.J., 1985. Water chemistry and mineralogy of Morgan and Growler hot springs, Lassen KGRA, California. Transactions of the Geothermal Research Council 9, 357–362.

Thornton, I., Farago, M., 1997. The geochemistry of arsenic. In: Abernathy, C.O., Calderon, R.L., Chappell, W.R. (Eds.), Arsenic Exposure and Health Effects. Chapman Hall, London, pp. 1–16.

Torii, M., 1997. Low-temperature oxidation and subsequent downcore dissolution of magnetite in deep-sea sediments, ODP Leg 161, Western Mediterranean. J. Geomag. Geoelect. 49, 1233–1245.

Tseng, W.P., Chu, H.M., How, S.W., Fong, J.M., Lin, C.S., Yeh, S., 1968. Prevalence of skin cancer in an endemic area of chronic arsenicism in Taiwan. J. Nat. Cancer Inst. 40, 453–463.

Umitsu, M., 1993. Late Quaternary sedimentary environments and landforms in the Ganges Delta. Sed. Geol. 83, 177–186.

Ure, A., Berrow, M., 1982. Chapter 3. The elemental constituents of soils. In: Bowen, H.J.M. (Ed.), Environmental Chemistry. Royal Society of Chemistry, London, pp. 94–203.

Varsányi, I., Fodré, Z., Bartha, A., 1991. Arsenic in drinking water and mortality in the southern Great Plain, Hungary. Environ. Geochem. Health 13, 14–22.

Villalobos, M., Trotz, M.A., Leckie, J.O., 2001. Surface complexation modeling of carbonate effects on the adsorption of Cr(VI), Pb(II), and U(VI) on goethite. Environ. Sci. Technol. 35, 3849–3856.

Wang, G., 1984. Arsenic poisoning from drinking water in Xinjiang. Chin. J. Prevent. Med. 18, 105–107.

Wang, L., Huang, J., 1994. Chronic arsenism from drinking water in some areas of Xinjiang, China. In: Nriagu, J.O. (Ed.), Arsenic in the Environment, Part II: Human Health and Ecosystem Effects. John Wiley, New York, pp. 159–172.

Waslenchuk, D.G., 1979. The geochemical controls on arsenic concentrations in southeastern United States rivers. Chem. Geol. 24, 315–325.

Waychunas, G.A., Fuller, C.C., Rea, B.A., Davis, J.A., 1996. Wide angle X-ray scattering, WAXS study of "two-line" ferrihydrite structure: Effect of arsenate sorption and counterion variation and comparison with EXAFS results. Geochim. Cosmochim. Acta 60, 1765–1781.

Webster, J.G., 1999. Arsenic. In: Marshall, C.P., Fairbridge, R.W. (Eds.), Encyclopaedia of Geochemistry. Chapman Hall, London, pp. 21–22.

Webster, J.G., Nordstrom, D.K., Smith, K.S., 1994. Transport and natural attenuation of Cu, Zn, As, and Fe in the acid mine drainage of Leviathan and Bryant Creeks. In: Alpers, C.N., Blowes, D.W. (Eds.), Environmental Geochemistry of Sulphide Oxidation. Am. Chem. Soc. Symp. Ser., 550. ACS, Washington DC, pp. 244–260.

Wegelin, M., Gechter, D., Hug, S., Mahmud, A., 2000. SORAS—a simple arsenic removal process. In: 'Water, Sanitation, Hygiene: Challenges of the Millennium', 26th WEDC Conference, Dhaka, 5–9 November, 2000, pp. 379–382.

Welch, A.H., Lico, M.S., 1998. Factors controlling As and U in shallow ground water, southern Carson Desert, Nevada. Appl. Geochem. 13, 521–539.

Welch, A.H., Helsel, D.R., Focazio, M.J., Watkins, S.A., 1999. Arsenic in ground water supplies of the United States. In: Chappell, W.R., Abernathy, C.O., Calderon, R.L. (Eds.), Arsenic Exposure and Health Effects. Elsevier, Amsterdam, pp. 9–17.

Welch, A.H., Lico, M.S., Hughes, J.L., 1988. Arsenic in ground-water of the Western United States. Ground Water 26, 333–347.

Welch, A.H., Westjohn, D.B., Helsel, D.R., Wanty, R.B., 2000. Arsenic in ground water of the United States: occurrence and geochemistry. Ground Water 38, 589–604.

Wersin, P., Hohener, P., Giovanoli, R., Stumm, W., 1991. Early diagenetic influences on iron transformations in a fresh water lake sediment. Chem. Geol. 90, 233–252.

White, D.E., Hem, J.D., Waring, G.A., 1963. Data of Geochemistry, 6th ed. M. Fleischer, (Ed). Chapter F. Chemical Composition of Sub-Surface Waters. US Geol. Surv. Prof. Pap. 440-F.

WHO, 1993. Guidelines for drinking-water quality. Volume 1: Recommendations, 2nd ed. WHO, Geneva.

WHO, 2001. Environmental Health Criteria 224: Arsenic compounds 2nd edition. World Health Organisation, Geneva.

Widerlund, A., Ingri, J., 1995. Early diagenesis of arsenic in sediments of the Kalix River estuary, Northern Sweden. Chem. Geol. 125, 185–196.

Wilkie, J.A., Hering, J.G., 1996. Adsorption of arsenic onto hydrous ferric oxide: Effects of adsorbate/adsorbent ratios and co-occurring solutes. Colloids Surfaces A-Physicochem. Engineer. Aspects 107, 97–110.

Wilkie, J.A., Hering, J.G., 1998. Rapid oxidation of geothermal arsenic(III) in streamwaters of the eastern Sierra Nevada. Environ. Sci. Technol. 32, 657–662.

Williams, M., 1997. Mining-related Arsenic Hazards: Thailand Case-study. Summary Report. Brit. Geol. Surv. Tech. Rep., WC/97/49.

Williams, M., Fordyce, F., Paijitprapapon, A., Charoenchaisri, P., 1996. Arsenic contamination in surface drainage and groundwater in part of the southeast Asian tin belt, Nakhon Si Thammarat Province, southern Thailand. Environ. Geol. 27, 16–33.

Wilson, F.H., Hawkins, D.B., 1978. Arsenic in streams, stream sediments and ground water, Fairbanks area, Alaska. Environ. Geol. 2, 195–202.

Wyatt, C.J., Fimbres, C., Romo, L., Mendez, R.O., Grijalva, M., 1998. Incidence of heavy metal contamination in water supplies in Northern Mexico. Environ. Res. 76, 114–119.

Xu, H., Allard, B., Grimvall, A., 1988. Influence of pH and organic substance on the adsorption of As(V) on geologic materials. Water Air Soil Pollut. 40, 293–305.

Xu, H., Allard, B., Grimvall, A., 1991. Effects of acidification and natural organic materials on the mobility of arsenic in the environment. Water Air Soil Pollut. 57–8, 269–278.

Yan, X.-P., Kerrich, R., Hendry, M.J., 2000. Distribution of arsenic(III), arsenic(V) and total inorganic arsenic in porewaters from a thick till and clay-rich aquitard sequence, Saskatchewan, Canada. Geochim. Cosmochim. Acta 64, 2637–2648.

Yokoyama, T., Takahashi, Y., Tarutani, T., 1993. Simultaneous determination of arsenic and arsenious acids in geothermal water. Chem. Geol. 103, 103–111.

Yusof, A.M., Ikhsan, Z.B., Wood, A.K.H., 1994. The speciation of arsenic in seawater and marine species. J. Radioanal. Nucl. Chem.-Articles 179, 277–283.

Zaldivar, R., 1974. Arsenic contamination of drinking water and foodstuffs causing endemic chronic poisoning. Beitr. zur Pathol. 151, 384–400.

Zhai, C., Dai, G., Zhang, Z., Gao, H., Li, G., 1998. An environmental epidemiological study of endemic arsenic poisoning in Inner Mongolia. In: Abstr. 3rd Internat. Conf. Arsenic Exposure and Health Effects, San Diego, 1998, p. 17.

Zhu, B.J., Tabatabai, M.A., 1995. An alkaline oxidation method for determination of total arsenic and selenium in sewage sludges. J. Environ. Qual. 24, 622–626.

Zobrist, J., Dowdle, P.R., Davis, J.A., Oremland, R.S., 2000. Mobilization of arsenite by dissimilatory reduction of adsorbed arsenate. Environ. Sci. Technol. 34, 4747–4753.