Arsenic in groundwater and the environment

P. L. Smedley and D.G. Kinniburgh

British Geological Survey

Citation:

Smedley, P. L. and Kinniburgh, D.G. 2013. Chapter 12: Arsenic in groundwater and the environment. In: Essentials of Medical Geology, Second Edition. Eds: Selinus, O., Alloway, B., Centeno, J.A., Finkelman, R.B., Fuge, R., Lindh, U. and Smedley, P.L. Springer, pp 279-310.

Introduction

Awareness of the problems associated with arsenic in drinking water and the environment has grown significantly over the last two decades or so and today an enormous literature exists documenting its occurrence, behaviour and impacts in many places across the globe. The mobilisation of arsenic in the environment occurs through a complex combination of natural biogeochemical reactions and human interactions. Most recognised problems are generated by mobilisation and transport under natural conditions, but mobilisation has also been caused, or exacerbated, by mining, fossil-fuel combustion and use of synthetic arsenical compounds (pesticides, herbicides, crop desiccants and arsenic-based additives in livestock feed). Arsenical pesticides and herbicides have been used much less over the last few decades, and more recent restrictions have been imposed on the use of arsenic in wood preservation (e.g. European Communities' Directive 2003/2/EC), but the legacy of such sources may still pose a localised threat to the environment.

Human exposure to arsenic occurs through a number of pathways, including air, food, water and soil. The relative impacts of these vary depending on local circumstances but of the potential pathways, drinking water poses one of the greatest threats to human health as borne out by the large number of documented case histories from around the world. The concentrations of arsenic in drinking water are very variable, depending on nature of source (surface water, groundwater, rainwater) and local conditions, and observed ranges vary over several orders of magnitude. Excepting localised sources of anthropogenic contamination, the highest aqueous arsenic concentrations are usually found in groundwaters because of the high solid/solution ratios found in aquifers. Groundwaters therefore pose the greatest overall threat to health. Groundwaters with arsenic concentrations sufficiently high to be detrimental to humans, or with already detectable health impacts have been reported in Argentina, Bangladesh, Burkina Faso, Cambodia, Chile, China, India, Hungary, Laos, Mexico, Nepal, Romania, Spain, Taiwan, Thailand and Vietnam and occasional problems are found in many other countries.

Some of the groundwater arsenic problems have been recognised for a considerable time. Probably the earliest cases of health effects from arsenic contamination of drinking water were recognised in a mining area of Poland in the 1890s. Here, contamination of water supplies by oxidation of arsenic-bearing sulphide minerals produced localised health problems (see Tseng et al., 1968). In central Argentina, arsenic-related health problems were first documented in 1917 and problems in Taiwan were also first identified in the 1910s. In each of these cases, solutions to the problems were sought primarily through engineering which for the most part provided alternative supplies of surface water or of treated water. As a result, geochemical investigations into the processes controlling the arsenic mobilisation in these areas were not carried out until much more recently and awareness of the problems observed in impacted regions such as the Bengal Basin, Cambodia and Vietnam have developed many years later.

European and US EPA regulations implement the current recommended WHO provisional guideline value for arsenic in drinking water of 10 µg L^{-1}. However, many countries continue to use the WHO pre-1993 guideline value of 50 µg L^{-1} as their national standard, in part because of the difficulties of testing low concentrations and in part due to difficulties with compliance. Concentrations of 10 µg L^{-1} and 50 µg L^{-1} are therefore both still used as reference points for the testing and reporting of arsenic.

This chapter reports the current state of knowledge on the occurrence of arsenic in natural waters and their host rocks across the world and attempts to describe what are currently understood to be the main biogeochemical processes that control its mobilisation in the environment.

Sources of arsenic in the natural environment

Minerals

Arsenic occurs as a major constituent in more than 200 minerals, including elemental arsenic, arsenides, sulphides, oxides, arsenates and arsenites. Most are ore minerals or their alteration products. These minerals are relatively rare in the natural environment. Among the most common occurrences in ore zones are arsenian pyrite ($Fe(S,As)_2$), arsenopyrite (FeAsS), löllingite ($FeAs_2$), realgar (AsS), orpiment (As_2S_3), cobaltite (CoAsS), niccolite (NiAs) and scorodite ($FeAsO_4.2H_2O$). Arsenian pyrite ($Fe(As,S)_2$) is probably the most important source of arsenic in ore zones (Deditius et al., 2008; Savage et al., 2000) and concentrations in excess of 10 weight % (up to 19 weight %) As have been reported (e.g. Barker et al., 2009; Blanchard et al., 2007; Reich and Becker, 2006). Reich and Becker (2006) concluded from first-principles calculations that pyrite and marcasite polymorphs can contain up to 6 weight % As in solid solution, beyond which unmixing to separate pyrite/marcasite and arsenopyrite occurs. The oxidation state of As in arsenian pyrite is most typically As^{1-} in substitution for S, although recent occurrences of As^{3+}-bearing pyrite ($(Fe,As)S_2$) have been documented in some hydrothermal gold deposits, signalling precipitation in more oxidising conditions than in the more common As^{1-} form (Chouinard et al., 2005; Deditius et al., 2008).

Other rock-forming sulphide minerals, including chalcopyrite and galena, also contain often high concentrations of arsenic (Table 1) as well as a range of other trace elements (transition metals, Cd, Pb, Ag, Au, Sb, P, W and Mo). Zonation of trace elements within sulphide grains is common.

Besides being an important component of ore bodies, pyrite is also formed in low-temperature sedimentary environments under sulphide-reducing conditions. Such authigenic pyrite plays an important role in present-day geochemical cycles, being present in the sediments of rivers, lakes, oceans and aquifers. Authigenic realgar has also been observed in shallow aquifer sediments (O'Day et al., 2004). In sulphidic solutions, soluble arsenic will likely be incorporated into pyrite through surface arsenite adsorption (Bostick and Fendorf, 2003). Pyrite is unstable in aerobic systems and oxidises to form iron oxides with release of associated arsenic. A lower stability of arsenian pyrite compared to low-As pyrite also potentially favours As release (Blanchard et al., 2007; Savage et al., 2000). The presence of pyrite in mineralised veins is responsible for the production of acid mine drainage, and for the common presence of arsenic problems around coal mines and areas of intensive coal burning.

Arsenic is also found in large concentrations in many oxide minerals and hydrous metal oxides, either as part of the mineral structure or as adsorbed species. Concentrations in Fe oxides can reach several weight percent (Table 1), particularly where they form as the oxidation products of primary As-bearing iron sulphide minerals. Adsorption of arsenic to hydrous iron oxides is particularly strong, depending on redox speciation, pH, solute compositions and iron-oxide form; adsorbed loadings can be great even where concentrations in solution are low. Adsorption to hydrous Al and Mn oxides may also be important if present in quantity (Goldberg, 1986; Stollenwerk, 2003). Sorption to the edges of clays may occur, although the loadings are much smaller on a weight basis than for the iron oxides (Smedley and Kinniburgh, 2002).

Concentrations in phosphate minerals can be relatively high, for example up to 1000 mg kg^{-1} in apatite (Table 1). However, phosphate minerals are much less abundant than oxide minerals and so make a correspondingly small contribution to the arsenic concentration in most sediments. Arsenic tends to be present at much smaller concentrations in the common rock-forming minerals, although low concentrations are invariably present. Most common silicate minerals (including quartz, feldspar, micas, amphiboles) contain around 1 mg kg^{-1} or less (Table 1). Concentrations of arsenic in carbonate minerals are also usually low, of the order of a few mg kg^{-1}, although Di Benedetto et al. (2006) found up to 257 mg kg^{-1} in Italian travertines.

Rocks, sediments and soils

Arsenic occurs ubiquitously but at variable concentrations in rocks, unconsolidated sediments and soils. Average crustal abundance is around 1.5 mg kg^{-1}. Igneous rocks usually have concentrations of around 5 mg/kg or less. Volcanic glasses have on average around 6 mg kg^{-1} (Smedley and Kinniburgh, 2002). Metamorphic rocks tend to have concentrations that reflect those of their igneous and sedimentary precursors. Most also contain around 5 mg kg^{-1} or less. Pelitic rocks (slates, phyllites) typically have the highest concentrations (Table 2), with on average of around 18 mg kg^{-1}.

Concentrations in sedimentary rocks are typically in the range 5–10 mg kg^{-1} (Webster, 1999). Average sediments are enriched in arsenic relative to igneous and metamorphic rocks because they contain greater quantities of minerals with high adsorbed arsenic loads. Of the sediments, sands and sandstones have lower concentrations which reflect the dominance of low-arsenic minerals (i.e. quartz and feldspars). Average sandstone arsenic concentrations are around 4 mg kg^{-1}.

Argillaceous deposits have a broader range of concentrations than sandstones (Table 2), being on average around 13 mg kg^{-1}. Higher values reflect the larger proportion of sulphide minerals, oxides, organic matter and clays present. Black shales have concentrations at the upper end of the range, principally because of their enhanced pyrite content (Table 2). Marine clays appear to have higher concentrations than non-marine equivalents. This may also be due to a higher proportion of pyrite in offshore pelagic sediments.

German organic-rich shales have arsenic concentrations of 100–900 mg kg^{-1} (Riedel and Eikmann, 1986). Some coal samples have very high concentrations, up to 35,000 mg kg^{-1} (Belkin et al., 2000) (Table 2), although lower concentrations of 2.5–17 mg kg^{-1} are more typical. Some of the highest observed arsenic concentrations are found in ironstones and Fe-rich rocks. Concentrations of arsenic up to 2900 mg kg^{-1} have been reported for such rocks (Table 2, references in Smedley and Kinniburgh, 2002). Phosphorites are also relatively enriched in arsenic, with concentrations up to ca. 400 mg kg^{-1}. Data for carbonate rock types usually indicate relatively low arsenic concentrations (Tables 1, 2).

Unconsolidated sediments have compositions which do not differ significantly from their indurated equivalents. Much evidence indicates that muds and clays have higher concentrations than most sands and carbonates. Values are typically 3–10 mg kg^{-1}, depending on texture and mineralogy (Table 2). High concentrations reflect abundance of pyrite or iron oxides. There is often a significant positive correlation between the iron and arsenic concentrations in sediments. High concentrations are also common in mineralised areas. Placer deposits in streams can have concentrations reflecting the abundance of sulphide minerals. Average arsenic concentrations for stream sediments in England and Wales have been reported in the range 5–8 mg kg^{-1} (Table 2, references in Smedley and Kinniburgh, 2002), although a higher median value (13.4 mg kg^{-1}) has been computed from a more recent survey in eastern England (BGS data, unpublished). In the Bengal Basin, river sediments with concentrations averaging 2.0 mg kg^{-1}, 2.8 mg kg^{-1} and 3.5 mg kg^{-1} were found for samples from the Ganges, Brahmaputra and Meghna rivers respectively (Datta and Subramanian, 1997).

Cook et al. (1995) found concentrations in Canadian lake sediments ranging between 0.9–44 mg kg^{-1} but noted that the highest concentrations were present up to a few kilometres down-slope of mineralised areas. They also found concentrations in glacial till of 1.9–170 mg kg^{-1} (Table 2) and noted the highest concentrations down-ice of mineralised areas.

In soils, concentrations of arsenic are of the order of 5–15 mg kg^{-1}, with an average of 7.2 mg kg^{-1} quoted for world soils and 7.4 mg kg^{-1} for American soils (Table 2, references in Smedley and Kinniburgh, 2002). Peats and bog soils can have higher concentrations (average 13 mg kg^{-1}; Table 2), but this is principally because of an increased prevalence of sulphide mineral phases under the reduced conditions. Shotyk (1996) found up to 9 mg As kg^{-1} in peat profiles and in a profile with lower mineral content, i.e. purer peat, the As content was 1 mg kg^{-1} or lower.

Acid sulphate soils can be generated by the oxidation of pyrite in sulphide-rich terrains including mineralised areas and dewatered mangrove swamps and as such can be relatively enriched in arsenic. Acid sulphate soils from Canada have arsenic concentrations up to 45 mg kg^{-1} (Dudas, 1984). Gustafsson and Tin (1994) found similarly high concentrations (up to 41 mg kg^{-1}) in acid sulphate soils from the Mekong delta of Vietnam.

Additional arsenic inputs to soils may be derived locally from industrial sources such as smelting and fossil-fuel combustion products and agricultural sources such as pesticides and phosphate fertilisers. Concentrations in the range 366–732 mg kg^{-1} have been found in orchard soils following historical application of arsenical pesticides to fruit crops (Table 2). Long-term use of phosphate fertilisers may also add arsenic to soil.

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

Arsenic in groundwater

Aqueous speciation

Analytical capability for aqueous arsenic species has developed rapidly and modern automated hyphenated chromatographic techniques (e.g. Bednar et al., 2004) have improved on traditional methods using hydride generation, repeat measurements and determination of species by difference. Sensitive detection can be achieved with methods such as ICP-MS and this coupled with field-based (solid-phase extraction) or laboratory-based (e.g. HPLC) techniques allows for the direct measurement of aqueous organic forms alongside the more abundant inorganic As(III) and As(V). Field-based measurements counteract potential problems with instability in sample storage although significant problems with matrix effects using solid-phase extraction (Bednar et al., 2004) mean that this technique can be unsuitable for analysis of e.g. SO_4-rich acid minewaters, saline geothermal waters or alkaline, SO_4- and oxyanion-rich groundwaters, at least without large sample dilutions.

Arsenic can occur in the environment in a number of oxidation states (-3, -1, 0, +3 and +5) but in natural waters is found principally in inorganic form as arsenite (As(III)) or arsenate (As(V)), depending on redox conditions. Arsenic can form aqueous complexes with carbonate ligands, and As(III) with reduced sulphur (thioarsenites), which may be significant in some groundwaters.

Organic arsenic species produced by microbiological methylation reactions may be present in surface waters and may even dominate in organic-rich soil solutions, but are rarely present in quantity in groundwaters (Bednar et al., 2004; Chen et al., 1995; Das et al., 1995; Del Razo et al., 1990; Kondo et al., 1999; Lin et al., 1998). Exceptions potentially occur locally in cases of industrial or agricultural pollution. In practice concentrations of organic compounds in soil solutions rarely exceed a few micrograms per litre (Huang and Matzner, 2006).

The ratio of As(III) to As(V) in groundwaters depends upon the abundance of the redox-active solids, including organic carbon and iron/manganese oxide, the flux of potential oxidants (oxygen, nitrate and sulphate) and on microbial activity. In geothermal systems, As(III) usually forms the main solute component but this can oxidise rapidly in surface conditions when mixed with surface water and especially when facilitated by bacteria (Wilkie and Hering, 1998). Arsenic(III) also dominates in strongly reducing aquifers, typified by Fe(III) and sulphate reduction, as expected from the redox sequence (Berg et al., 2007; BGS and DPHE, 2001; Chen et al., 1994; Das et al., 1995; Postma et al., 2007; Smedley et al., 2003; Stollenwerk et al., 2007; Tandukar et al., 2005; van Geen et al., 2006; Zheng et al., 2005). By contrast, in oxidising systems, solute arsenic is dominated by As(V) (Altamirano Espinoza and Bundschuh, 2009; Bhattacharya et al., 2005; Del Razo et al., 1990; Robertson, 1989; Smedley et al., 2007; Smedley et al., 2002). The strong oxidising capacity of Mn oxides has been well-documented and implicated in arsenic redox speciation in several systems (Amirbahman et al., 2006; Oscarson et al., 1981a; Oscarson et al., 1981b; Ying et al., 2011).

In natural systems, thermodynamic equilibrium in As species is often not achieved although abundant evidence indicates that reaction kinetics can be accelerated significantly by microbial activity, which have been shown to both oxidise arsenite (Hering and Kneebone, 2002; Wilkie and Hering, 1998) and reduce arsenate (Oremland and Stolz, 2003).

Sorption plays a key role in arsenic speciation and iron oxides in particular have a strong control on aqueous concentrations. Fig. 1 shows pe-pH predominance diagrams for the As-Fe system. Fig. 1a and 1b both show the redox and pH sensitivity of both aqueous As and Fe, with a range of protonated and hydrolysed species present over the natural pH range. Iron tends to be insoluble in oxic, near-neutral pH systems and forms a variety of iron oxides depending on the precise conditions and their evolution. Hydrous ferric oxide (HFO), a high-surface-area form of iron oxide, often forms when Fe is precipitated rapidly. This oxide is able to adsorb As on its surface and the adsorbed As (HFO-As) can become the dominant form of As (Fig. 1c). HFO is subject to both acid dissolution at low pH and reductive dissolution at low pe (Fig. 1(c)) which result in the release of As to solution. At high pH, As is desorbed from HFO due to increasing electrostatic repulsion of the negatively charged oxide surface and the AsO_4^{3-} species, again leading to higher concentrations in solution. HFO tends to transform slowly to more stable forms of iron oxide with lower specific surface area, such as goethite, with time. Goethite still has a significant adsorption affinity for As, albeit somewhat different from HFO due to the different crystal structure. Goethite is less prone than HFO to both acid dissolution and reductive dissolution and so the Goethite-As field occupies a correspondingly large area on the predominance diagram at low pH and low pe (Fig 1(d)). However, the lower specific surface area of goethite compared with HFO means that adsorption is not so great at high pH and so in goethite-dominated systems the aqueous As species tend to predominate at high pH.

Although these predominance diagrams illustrate some important geochemical interactions of Fe and As, they by no means tell the whole story. There are many other important interactions that have been omitted from these diagrams. For example, reduced iron oxides such as magnetite can form at low pe and these too will tend to adsorb As (Dixit and Hering, 2003). Also, significant concentrations of sulphide may be present in reduced systems leading to the potential formation of pyrite and other Fe-S minerals, again with scope for the adsorption of As on the mineral surface or the incorporation of As into the mineral structure as a solid solution. Nonetheless, the diagrams go some way to explaining observed occurrences of high-arsenic groundwater in some strongly reducing aquifers and at extremes of pH.

Arsenic abundance and distribution in groundwater

Aquifers have high solid:solution ratios, typically 3–20 kg L^{-1} and as a result, groundwaters within them are especially vulnerable to water-rock interaction and arsenic release. In addition, aquifers more often have the physical and chemical conditions favourable for arsenic mobilisation and transport than is the case in surface waters. Despite this, the occurrence of high arsenic concentrations in groundwaters is the exception rather than the rule. Background concentrations in groundwater are in most countries less than 10 µg L^{-1} and often substantially lower. Nonetheless, values quoted in the literature show a very large range from <0.5–15,000 µg L^{-1}, i.e. more than four orders of magnitude.

Mobilisation of arsenic in solution is favoured especially under oxidising conditions at high pH and under strongly reducing conditions. Evaporative concentration can also increase arsenic (and other element) concentrations substantially and may be important in some arid areas. Additional arsenic problems are encountered in some geothermal areas and in many areas of sulphide mineralisation and mining. Documented cases of industrial arsenic pollution (including those from agriculture) also exist. While these may be severe locally, occurrences are relatively rare and can usually be anticipated.

Investigations worldwide have revealed a number of major aquifers with significant groundwater arsenic problems. The hydrogeological and geochemical conditions in these affected aquifers vary, although some common unifying features are apparent. Particular areas of risk are large alluvial and delta plains and sedimentary inland basins, the latter especially in arid and semi-arid areas. Geologically young (Quaternary) aquifers are particularly prone to developing and preserving high-arsenic groundwater. Alluvial and delta plains with recognised groundwater arsenic problems include the Bengal Basin (Bangladesh, India), Mekong Valley (Cambodia, Laos, Vietnam), Yellow River Plain (China), Terai (Nepal), Red River delta (Vietnam), Chianan and Lanyang Plains (Taiwan) and Great Hungarian Plain (Hungary and Romania). Those from inland and closed basins include the Chaco-Pampean Plain (Argentina), and other plains of Chile, Mexico and south-western USA (Fig. 2). In many of these areas, significant numbers of wells have arsenic concentrations of several hundreds of micrograms per litre, with occasional sources in the milligram-per-litre range. Arsenic-related health problems have been recognised in the resident populations in numerous areas. Reconnaissance surveys of groundwater quality in other areas such as parts of Burma and Pakistan have also revealed small numbers of wells with concentrations of arsenic above drinking-water limits. Documentation of the affected aquifers of Burma is so far limited. The regions of the world having major aquifers with recognised arsenic problems are outlined below and categorised in terms of their environmental conditions. Distributions of arsenic in the environment related to geothermal activity as well as mining and mineralisation are also described.

Alluvial plains and deltas

Bengal Basin (Bangladesh, India)

The change from use of surface water or dug-well water to groundwater accessed by hand-pumped tubewells began in India and Bangladesh during the 1960s and accelerated significantly from the 1980s onwards. This led to a vast increase in the access of rural populations to what was considered a superior and safe source of drinking water from the readily available groundwater resources contained in the shallow aquifers. The discovery in 1983 in West Bengal (Garai et al., 1984) and in 1993 in Bangladesh (BGS and DPHE, 2001) of problems with arsenic in the groundwater changed the situation significantly. Access of rural populations to improved supplies of drinking-water was down from the 90% coverage in the early 1990s to 68% in 2004 (Rosenboom, 2004). The discoveries led to the instigation of major programmes of well testing and resource assessment, health surveillance, water-supply mitigation, and research.

Concentrations of arsenic in the groundwaters of the Bengal Basin span some four orders of magnitude, with occasional extremes above 1 mg L^{-1}. Recognised health problems include skin disorders and internal cancers. The high arsenic concentrations occur in groundwaters within unconsolidated grey micaceous alluvial and deltaic Holocene sands and silts associated with the Ganges, Brahmaputra and Meghna river systems. The presence of poorly-permeable surficial overbank deposits (BGS and DPHE, 2001; Chakraborti et al., 2001; McArthur et al., 2004; van Geen et al., 2008), particularly in the lower sections of the basin, together with both solid organic matter and DOC in the groundwater, has resulted in development of strongly reducing aquifer conditions, aided by microbial reactions. Groundwater compositions are typified by high concentrations of dissolved Fe, Mn, HCO_3, NH_4, P and DOC as well as high As, and low concentrations of NO_3 and SO_4, though the correlations between these parameters are often poor. Methane has also been detected in some groundwaters (Ahmed et al., 1998). Many studies have observed that dissolved arsenic concentrations peak in the typical depth range 15–50 m (BGS and DPHE, 2001; Harvey et al., 2002; Klump et al., 2006; McArthur et al., 2004; Zheng et al., 2005), although high concentrations (>50 ug L^{-1}) are observed at depths up to about 150 m below surface.

A national survey of arsenic in groundwater (BGS and DPHE, 2001), using some 3500 groundwater samples, found that 27% of samples from the Holocene shallow aquifer (<150 m depth) contained arsenic at concentrations exceeding 50 µg L^{-1}, and 46% exceeded 10 µg L^{-1} (Fig. 3). Subsequent arsenic analyses from the Bangladesh Arsenic Mitigation and Water Supply Program (BAMWSP, 2005) showed that of almost 5 million tube wells tested nationally by the mid 2000s, some 30% had arsenic concentrations above 50 µg L^{-1}. The results from these two datasets compare reasonably well. Each demonstrates a very variable distribution of arsenic regionally across Bangladesh, with the greatest proportion of exceedances occurring in groundwaters from the southern and south-eastern parts of the country.

A UNICEF/DPHE survey of groundwaters from southern Bangladesh (Rosenboom, 2004), found of some 317,000 tubewells tested, 66% contained arsenic with concentrations above 50 µg L^{-1}; 10% had <10 µg L^{-1}. Van Geen et al. (2003b) also found, from a survey of 6000 tube wells in Araihazar, south-central Bangladesh, that some 75% of tube wells (depth range 15–30 m) had arsenic concentrations above 50 µg L^{-1}. The higher percentage exceedances of these studies reflect their location in some of the worst-affected areas.

The BGS and DPHE (2001) study estimated, on the basis of the population at the time (125 million estimate), that up to 35 million people were drinking groundwater with arsenic concentrations above 50 µg L^{-1}, and 57 million were drinking water with concentrations above 10 µg L^{-1}. This represents by far the most severely affected population recognised globally. Figures will have been modified somewhat by subsequent mitigation efforts although this is to be offset by population growth (161 million 2012 estimate).

In India, the first evidence of arsenic-related health problems emerged in West Bengal (Bhattacharya et al., 1997; Chowdhury et al., 1997; Das et al., 1994), where it is estimated that about 6.5 million people are drinking water with arsenic concentrations greater than 50 µg L^{-1} (Mukherjee et al., 2006). High-arsenic groundwaters have subsequently also been identified in alluvial aquifers in the states of Bihar, Tripura, Uttar Pradesh, Jharkhand and Assam (Chakraborti et al., 2003; Mukherjee et al., 2006). Sedimentary aquifers potentially at risk from high arsenic concentrations in groundwater also occur in the neighbouring states of Meghalaya and Mizoram. In 2003, the Indian Bureau of Standards revised the national limit for arsenic in drinking water from 50 µg L^{-1} to 10 µg L^{-1}, in recognition of the severity of groundwater arsenic health problems in the country.

High-arsenic groundwaters have been found in up to nine districts of West Bengal, the five worst affected being Malda, Murshidabad, Nadia, 24 North Parganas and 24 South Parganas (Chakraborti et al., 2004; McArthur et al., 2004; Rahman et al., 2001). These cover up to 38 000 km^2. High arsenic concentrations occur typically in the depth range 10–80 m (McArthur et al., 2004). Chakraborti et al. (2001) found from 90,000 water analyses in the Holocene aquifers of West Bengal that some 34% exceeded 50 µg L^{-1} and 55% exceeded 10 µg L^{-1}.

In both Bangladesh and West Bengal, groundwaters from older Pleistocene aquifers usually have low arsenic concentrations (<10 µg L^{-1}). These sediments, dominantly orange-brown and more oxic than the overlying Holocene deposits, occur at variable depths. BGS and DPHE (2001) distinguished the aquifers using a 150-m depth cut-off, although van Geen et al. (2003b) documented Pleistocene deposits in the Araihazar area of Bangladesh at depths as shallow as 30 m (range 30–120 m). Pleistocene deposits also occur at surface within the distinct structural units of the Madhupur and Barind Tracts of Bangladesh (BGS and DPHE, 2001) and give rise to the low mapped arsenic concentrations in shallow groundwaters there (Fig. 3).

Dug wells also usually have low arsenic concentrations, and offer a potential alternative supply of drinking water. However, Rosenboom (2004) found that 11% of shallow dug wells tested in the UNICEF/DPHE survey had concentrations above 50 µg L^{-1}. Dug wells are also more prone to bacterial contamination and sustainability problems during the dry season.

Arsenic in the Holocene aquifer sediments typically has concentrations in the range <1–20 mg/kg (BGS and DPHE, 2001; Chakraborti et al., 2001; Swartz et al., 2004) which are not unusual by world standards. The arsenic has been found or postulated to occur in association with Fe(III)- or mixed Fe(II)–Fe(III) oxides (BGS and DPHE, 2001; Harvey et al., 2002; Horneman et al., 2004; McArthur et al., 2001; Swartz et al., 2004), phyllosilicate minerals (Breit et al., 2001) and sulfide minerals (Nickson et al., 2000; Polizzotto et al., 2006). Most studies concur that iron oxides are an important control on arsenic mobilisation in the Bengal Basin groundwaters, although opinions are divided on the precise mechanisms involved. Competition for adsorption sites between dissolved arsenic species and other constituents such as phosphate is also likely to exert a control. Paucity of sulphate in the groundwaters over large parts of the region appears contributory to the limited sequestration of arsenic by iron sulphide under the strongly reducing conditions.

Redox changes in the aquifers involve reduction of As(V) to As(III) with resultant changes in sorption behaviour. Reductive dissolution of iron oxide and reductive desorption of arsenic are processes likely to result in increased solute arsenic concentrations, exacerbated by competition for binding sites between arsenic and especially phosphate. Such reactions appear to be only part of a complex sequence of diagenetic transformations in the sediments arising from the onset of reducing conditions. Reactions involve changes in iron oxide structure, redox status and surface properties over time, with transformation to phases such as magnetite as well as precipitation of siderite and vivianite having been invoked (e.g. BGS and DPHE, 2001; Horneman et al., 2004; Swartz et al., 2004). Microbial mediation of the redox reactions and arsenic cycling has been demonstrated (Islam et al., 2004).

Several studies have found much higher ratios of Fe(II)/FeT in the Holocene Bengal sediments compared to the underlying Pleistocene deposits (Horneman et al., 2004; Polizzotto et al., 2006; van Geen et al., 2006). Iron oxides in the latter appear dominanted by goethite and haematite and explain the prominent colour change from grey to orange-brown in passing from the Holocene to the Pleistocene sediments (e.g. van Geen et al., 2003b). Holocene sediments have also been found to contain much higher concentrations of phosphate-extractable (van Geen et al., 2006; Zheng et al., 2005) and oxalate-extractable (BGS and DPHE, 2001) arsenic and iron than Pleistocene aquifer sediments, which point to an increased proportion of labile arsenic in Holocene deposits. Nonetheless, some studies have concluded that conditions in the Holocene aquifers are too strongly reducing to be consistent with in-situ Fe(III) reduction to Fe(II) and propose that arsenic is released instead from iron oxides in surficial soils and sediments and transported to depth as a plume by groundwater flow (Polizzotto et al., 2006; Polizzotto et al., 2005).

The nature of organic matter involved in the redox cycling is also a matter of debate. Peat deposits (McArthur et al., 2001) and peaty strata marginal to peat basins (McArthur et al., 2004) have been invoked as important sources of organic matter to drive the redox reactions. Others cite the importance of disseminated organic matter in the sediments and dissolved in water (BGS and DPHE, 2001). In these cases, rapid rates of sedimentation accommodate the organic carbon and can prevent its rapid oxidation. Others have concluded that introduction of anthropogenic carbon through drawdown induced by groundwater pumping has been responsible for catalysing the reduction reactions within the aquifers (Harvey et al., 2006; Harvey et al., 2002), although this conclusion has not been universally accepted (e.g. Klump et al., 2006; van Geen et al., 2003a). In West Bengal, the lack of detectable thermotolerant coliforms in high-arsenic groundwaters has also been used as an argument against anthropogenic organic matter being the driver for iron reduction and arsenic release at depth (McArthur et al., 2004).

Groundwater flow and flushing has doubtless had an impact on arsenic mobilisation and distributions, both under natural conditions and by modern groundwater pumping (Michael and Voss, 2008). Natural hydraulic gradients in the aquifers are low and groundwater flow strongly controlled by local permeability variations. Groundwater arsenic concentrations show a relationship with surface soil and sediment texture, which suggests a larger degree of aquifer recharge, and flushing, in areas with higher surface permeability (van Geen et al., 2006). It is also likely that longer-term groundwater flow throughout the Quaternary has resulted in flushing of Pleistocene relative to Holocene deposits, especially since palaeo-head gradients would have been greater during pre-Holocene glacial lowstand periods (BGS and DPHE, 2001). However, major abstractions of groundwater over the last few decades, particularly that for irrigation use, have changed flow patterns significantly. Many recent studies have shown that shallow groundwaters (<30 m or so) in the Bengal Basin often have short residence times, on the scale of years to decades (e.g. Klump et al., 2006), likely induced by pumping. Pumping-induced flow and mixing have the potential to either increase or decrease solute arsenic concentrations with time.

In recent years, many studies have focussed on the sustainability of the Pleistocene low-arsenic aquifer in respect of potential drawdown of contaminated water following increased abstraction. Modelling has concluded that the groundwater arsenic concentrations in the deep aquifer are likely to remain low provided abstraction is limited to domestic use by hand-pumps, partly because of the comparatively small volumes involved and partly due to the instigation of a hydraulic barrier in the shallow aquifer by irrigation pumping from there (Burgess et al., 2010; Michael and Voss, 2008).

Nepal

Groundwater is abundant in the Quaternary alluvial sediments of the lowland Terai region of southern Nepal and is an important resource for domestic and agricultural use. Groundwater from tubewells supplies some 11 million people (Chitrakar and Neku, 2001). Both shallow and deep aquifers occur throughout most of the Terai region, the deep aquifer being artesian. Quaternary alluvium also infills several intermontaine basins in Nepal, most notably that of the Kathmandu Valley of central Nepal.

A number of surveys of groundwater quality in the Terai region have revealed the presence of arsenic in samples from shallow tubewells (<50 m depth) (Gurung et al., 2005) and some 500,000 people are believed to be exposed to drinking water with arsenic concentrations greater than 50 µg L^{-1} (Pokhrel et al., 2009). Arsenicosis problems have been identified in some areas (Maharjan et al., 2007). By 2004, some 245,000 tubewells had been tested for arsenic, of which 3% were found to exceed 50 µg L^{-1}, the highest observed concentration being 400 µg L^{-1} (Tandukar et al., 2005). From testing in 17 of the 20 Terai districts, the Nepal Red Cross Society (NRCS), also found 3% of groundwater sources sampled having concentrations above 50 µg L^{-1}, the highest observed concentration being 205 µg L^{-1}. The worst-affected districts are Rautahat, Nawalparasi, Parsa and Bara in the central area of the Terai. Other surveys have revealed the occurrence of high-arsenic groundwaters in the River Bagmati area. Concentrations in the Kathmandu Valley appear mostly low (Gurung et al., 2007; Pant, 2011).

The high arsenic concentrations in the Terai occur in anaerobic groundwaters with characteristics similar to those found in the Holocene aquifers of the Bengal Basin (high Fe, Mn, NH_4, DOC and low SO_4, NO_3). Dissolved arsenic is dominated by As(III) (Bhattacharya et al., 2003; Tandukar et al., 2005). Deeper tubewells in the Terai appear to have lower arsenic concentrations (generally <10 µg L^{-1}).

Taiwan

Health prolems due to arsenic in groundwater were first reported in Taiwan between 1910 and 1920 (Chen and Liu, 2007) although awareness of the link with drinking water was delayed until the 1960s (Tseng et al., 1968). Blackfoot disease (BFD, a peripheral vascular disorder with similarities to gangrene) is a well-publicised health problem of the region and is most likely linked to past occurrence of arsenic in the drinking water, although the high humic-acid concentration in groundwaters of the region has been cited as an additional causal factor (Lu et al., 1990). A number of other diseases, including internal cancers, have also been described. High groundwater arsenic concentrations have been recognised in both the south-west Chianan Plain (Chen and Liu, 2007; Tseng et al., 1968) and north-east Lanyang Plain (Hsu et al., 1997; Lewis et al., 2007), although BFD occurrence appears restricted to the south-west (Lewis et al., 2007).

Groundwater samples from Chianan Plain have arsenic concentrations in the range 10–1800 µg L^{-1} with a significant number being more than 400 µg L^{-1} (Chen and Liu, 2007). These occur in groundwaters from deep artesian wells (mostly 80–250 m) abstracted from late Pleistocene alluvial and deltaic sediments. The groundwaters are strongly reducing with evidence of dissolved sulphide and CH_4 in some samples. Groundwaters from the top 50–80 m are also reducing but are saline with SO_4 concentrations of 2700–6000 mg L^{-1}, associated with marine deposition and subsequent evaporation (Chen and Liu, 2007). Groundwaters abstracted from Lanyang are also artesian, but of shallower depth (typical range 16–40 m) (Hsu et al., 1997). Here, arsenic concentrations reach up to 600 µg L^{-1} (Hsu et al., 1997). In each area, the groundwaters are strongly reducing, dissolved As being dominated by As(III) (Chen et al., 1994). Groundwater samples taken from shallow open dug wells have low arsenic concentrations (Guo et al., 1994).

Cambodia, Laos and Vietnam

The discovery of high concentrations of arsenic in groundwaters from Cambodia, Laos and Vietnam is, perhaps surprisingly, relatively recent. Development of groundwater from tubewells in these countries has increased significantly since the 1990s (Berg et al., 2006; Chanpiwat et al., 2011; Polya et al., 2005) and this recent change is perhaps responsible for the delayed recognition. High arsenic concentrations are found in groundwater from Holocene sediments. These are deposited by the Mekong River in all three countries, the Red River in Vietnam and the Bassac River (Buschmann et al., 2007) and the Tonle Sap (Berg et al., 2007) in Cambodia.

In Cambodia, 10 affected provinces have been identified but the most severely impacted is Kandal Province where extremes up to 3500 µg L^{-1} have been reported (Berg et al., 2007; Buschmann et al., 2007; Sampson et al., 2008). Berg et al. (2006) found 20% of samples analysed exceeding 50 µg L^{-1}. The groundwaters occur mainly in groundwater from wells >16 m deep (Polya et al., 2005). In Laos, more limited data are available but concentrations along the Mekong Valley have been reported in the range <0.5–278 µg L^{-1} (Chanpiwat et al., 2011).

In Vietnam, aquifers in both the Mekong delta and Red River delta are exploited for water supply and the total number of tubewells in use could be of the order of one million (Berg et al., 2007). Aquifers exploited are of both Holocene and Pleistocene age. In the Vietnamese Mekong delta, the shallow aquifer is affected by salinity and cannot be used for drinking water. Groundwater for irrigation and drinking is therefore abstracted from depths of 150–250 m from Neogene deposits. Holocene aquifers in the northern Vietnamese part of the Mekong delta, upstream of the zone affected by saline intrusion, have arsenic concentrations in the range <1–845 µg L^{-1} (Berg et al., 2007).

In the Red River delta, concentrations up to 3000 µg L^{-1} occur (Berg et al., 2007; Nguyen et al., 2009) in an area which includes the city of Hanoi, particularly the southern part. Holocene sediments up to about 30 m thick form the shallow aquifer, below which, Pleistocene sands and gravels occur. These are separated in places by a clay layer several metres thick, although ‘windows’ exist which allow hydraulic continuity between the two. Holocene sand deposits are largely capped by surficial confining overbank clays (typically some 2–10 m thick) (Postma et al., 2007). Both Holocene and Pleistocene aquifers are used for water supply. It is estimated that around one million people are drinking water in the delta area with an As concentration greater than 50 µg L^{-1} (Winkel et al., 2011).

Arsenic-affected groundwaters in these countries are reducing (with high concentrations of Fe, Mn and DOC; dissolved As overwhelmingly dominated by As(III)) (Chanpiwat et al., 2011; Rowland et al., 2007). In Vietnam, high concentrations of NH_4 and CH_4 are also found in some areas (Berg et al., 2007; Postma et al., 2007). As elsewhere in Asia, arsenic mobilisation in the Holocene aquifers has been linked to reductive dissolution of iron oxides in the sediments. In the Red River delta, these have been taken to be relatively crystalline oxide phases such as haematite or goethite (Postma et al., 2007). As in Bangladesh however, there are proponents of the origin of the arsenic lying in surface soils and sediments with subsequent transport to the Holocene aquifer (Polizzotto et al., 2008). In an extensive survey of groundwater in the Red River delta, Winkel et al. (2011) have documented the drawdown of As from the Holocene to the Pleistocene aquifer as a result of long-term heavy abstraction of groundwater.

To date, limited numbers of arsenicosis patients have been recognized in Cambodia, probably due to relatively recent introduction of tubewell water as a source of drinking water (Berg et al., 2007). However, the first cases were diagnosed (Kandal Province) in 2006 (Sampson et al., 2008). Few cases have been reported in Vietnam and to the best of our knowledge no arsenic-health problems have been documented in Laos.

Northern China

Arsenic (concentrations in excess of the Chinese national standard of 50 µg L^{-1}) has been found in groundwaters from a number of areas in northern China, including Xinjiang, Shanxi, Jilin and Liaoning Provinces as well as Inner Mongolia (Fig. 2) (Bian et al., 2012; Deng et al., 2009; Ning et al., 2007; Smedley et al., 2003; Xie et al., 2009). The earliest problems were recognised in Xinjiang Province where concentrations of 40–750 µg L^{-1} were found in deep artesian groundwater (wells to 660 m deep) from the Quaternary Dzungaria (Junggar) Basin (Wang and Huang, 1994). Under artesian conditions, As concentrations increased with depth; shallow (non-artesian) groundwaters had concentrations between <10–68 µg L^{-1}.

In the Datong and Jinzhong Basins of Shanxi Province, arsenic concentrations up 4400 µg L^{-1} have been found (Guo et al., 2003; Xie et al., 2009; Xie et al., 2008). Datong Basin groundwaters have highest observed concentrations in the depth range 15–60 m (Xie et al., 2008), present under usually strongly reducing conditions (Xie et al., 2009). Groundwaters from the Hetao Plain of Inner Mongolia also have high concentrations, up to 1350 µg L^{-1} (Guo et al., 2001), being highest in boreholes with a depth range of 15–30 m (open dug wells of 3–5 m depth had low concentrations).

In the Huhhot Basin, part of the Tumet Plain of Inner Mongolia, arsenic also occurs in strongly reducing groundwaters from mainly Holocene alluvial and lacustrine aquifers. Problems are worst in the lowest-lying parts of the basin (Smedley et al., 2003). These groundwaters also have characteristically high concentrations of dissolved Fe, Mn, DOC, HCO_3 and NH_4 and low concentrations of nitrate and sulphate (Luo et al., 1997; Smedley et al., 2003). The arsenic, at concentrations up to 1500 µg L^{-1}, is again dominated by As(III). Unlike the Bengal Basin, deep pre-Holocene aquifers also have relatively high, though less extreme, arsenic concentrations (up to 300 µg L^{-1}). Many of these waters have associated high concentrations of humic acid which may have an impact on arsenic mobilisation, as well as health effects. Unusually, groundwater from several hand-dug wells in the low-lying part of the Huhhot Basin also has relatively high arsenic concentrations, up to 550 µg L^{-1}. This may owe to the maintenance of relatively reducing conditions at shallow depths as a result of high organic content (solid and dissolved) (Smedley et al., 2003).

Documented health problems derive especially from Xinjiang Province and Inner Mongolia. The problems are manifested by skin lesions, including melanosis and hyperkeratosis, vascular disorders and lung, skin and bladder cancer.

Hungary and Romania

Concentrations of arsenic above 50 µg L^{-1} have been identified in groundwaters from alluvial sediments in the southern part of the Great Hungarian Plain (part of the Pannonian Basin) of Hungary and neighbouring parts of Romania (Fig. 2). Concentrations up to 150 µg L^{-1} (average 32 µg L^{-1}) 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 arsenic concentrations are reducing and many have reported high concentrations of dissolved organic matter (humic acid quoted as up to 20 mg L^{-1}) (Varsányi et al., 1991). The groundwaters have largest arsenic concentrations in the lowest parts of the basin, where the sediment is fine-grained. Gurzau and Gurzau (2001) reported concentrations up to 176 µg L^{-1} in the associated aquifers of neighbouring Romania.

Inland basins in arid and semi-arid areas

Mexico

In terms of arsenic occurrence, the Principal aquifer of Comarca Lagunera in the states of Coahuila and Durango is the best-documented region in Mexico. The population exposed to arsenic in drinking water with >50 µg L^{-1} has been estimated at around 400,000 (Del Razo et al., 1990). Health problems related to arsenic were first recognized there in the early 1960s and symptoms include melanosis, keratosis and skin cancer. Groundwater from a large number of wells has been found with arsenic concentrations well in excess of the national standard for drinking water (currently 25 µg L^{-1}). Concentrations have been found in the range 3–740 µg L^{-1}, around half being above 50 µg L^{-1} (Del Razo et al., 1990; Del Razo et al., 1994; IMTA, 1992; Rosas et al., 1999). Highest concentrations are found in the San Pedro, Tlahualilo and Francisco I. Madero areas (Fig. 4). The region has been subject to heavy groundwater abstraction and water levels have fallen significantly over the last century. The water table lies more than 100 m below surface in the centre of the depression.

The groundwaters of Comarca Lagunera 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 also noted that most (>90%) of the groundwater samples investigated had arsenic present predominantly as As(V). The groundwater also has high concentrations of fluoride (up to 3.7 mg L^{-1}) (Cebrián et al., 1994). The high arsenic concentrations occur in the low-lying parts of the basin which act as zones of groundwater discharge. Being an internal drainage basin the discharge area contains groundwater with significant residence times; radiocarbon dating and supporting stable-isotopic measurements reveal groundwater model ages up to 30,000 years in the low-lying areas (Brouste et al., 1997) (Fig. 4). Convergent flow within the discharge zones likely facilitates accumulation of solutes such as arsenic.

Arsenic problems have also been identified in groundwaters from the states of Sonora and Chihuahua in northern Mexico. Wyatt et al. (1998) found concentrations in Sonora in the range 2–305 µg L^{-1} and observed similar correlations with fluoride, which reached up to 7.4 mg L^{-1}. In Chihuahua, arsenic concentrations reached 650 µg L^{-1} in saline and F-rich groundwater from wells up to 250 m deep (Junta Municipal, 2000).

Chile

Health problems related to arsenic in drinking water were first recognised in northern Chile in 1962. Symptoms included skin-pigmentation changes, keratosis, skin cancer, cardiovascular problems and respiratory disease. More recently, chronic arsenic ingestion has been linked to lung and bladder cancer. Arsenic exposure dated back from the period 1955–1970. Both surface waters and groundwaters from Administrative Region II (incorporating the cities of Antofagasta, Calama and Tocopilla) of northern Chile (Cáceres et al., 1992) have high concentrations. The region is arid, being part of the Atacama Desert, and water resources are limited. High As concentrations are accompanied by high salinity and concentrations of boron and lithium. This in part relates to evaporation but is also significantly affected by geothermal inputs from the El Tatio geothermal field. Arsenic concentrations below 100 µg L^{-1} in surface waters and groundwaters are apparently quite rare, and concentrations up to 21,000 µg L^{-1} have been found. Karcher et al. (1999) quoted ranges of 100 µg L^{-1} to 1000 µg L^{-1} in untreated surface waters and groundwaters (average 440 µg L^{-1}).

The affected groundwaters of Chile are predominantly oxidising with As(V) the dominant species. The aquifers are composed of volcanic rocks and volcanogenic sediments, but the arsenic sources are not well-characterised. In Antofagasta, concentrations of arsenic in sediments are ca. 3.2 mg kg^{-1} (Cáceres et al., 1992). Sediments from the Rio Loa and its tributaries have much higher concentrations (26–2000 mg kg^{-1}) as a result of geothermal inputs from the river system (Romero et al., 2003). Additional exposure to arsenic from the smelting of copper ore has also been noted in northern Chile (Cáceres et al., 1992).

Argentina

The Chaco-Pampean Plain of central Argentina constitutes perhaps one of the largest regions of high-arsenic groundwaters known, covering around 1 million km^2. High concentrations of arsenic have been found in parts of the provinces of Córdoba, La Pampa, Santa Fe, Buenos Aires, Tucumán, San Luis, Chaco and Santiago Del Estero. An estimated two million people live in these As-affected areas (Castro de Esparza, 2009). Symptoms typical of chronic arsenic poisoning, including skin lesions and some internal cancers, have been recorded (Bates et al., 2004; Hopenhayn-Rich et al., 1996). The high-arsenic groundwaters are mostly from Quaternary deposits of silt-grade loess, with intermixed rhyolitic or dacitic volcanic ash (Nicolli et al., 2010; Nicolli et al., 1989; Smedley et al., 2002). The sediments display abundant evidence of post-depositional diagenetic changes under semi-arid climatic conditions, with common occurrences of palaeosols and calcrete.

A large range of As concentrations is observed in the groundwaters, with many samples exceeding 1000 µg L^{-1}. Nicolli et al. (1989) reported concentrations in groundwaters from Córdoba in the range 6–11,500 µg L^{-1} (median 255 µg L^{-1}). Smedley et al. (2002) found concentrations in La Pampa Province in the range <4–5280 µg L^{-1} (median 145 µg L^{-1}). Nicolli et al. (2010) found concentrations in Tucumán Province of 11–1660 µg L^{-1} (median 46 µg L^{-1}). Blanes et al. (2011) reported concentrations up to 1070 µg L^{-1} in groundwater from Chaco Province, Bhattacharya et al. (2006) found concentrations of 7–15,000 µg L^{-1} in Santiago Del Estero and Farías et al. (2003) found concentrations of 10–593 µg L^{-1} in groundwater from four Pampean provinces.

The groundwaters from the Chaco-Pampean loess plain have a large salinity range, with often high pH and alkalinity and are predominantly oxidising. Smedley et al. (2002) found pH values of 7.0–8.7 in groundwaters from La Pampa; Nicolli et al. (2010) found values of 6.3–9.2 in Tucumán. The high-As Pampean groundwaters are usually of Na-HCO$_3$ type. Under the overwhelmingly oxic conditions of the groundwaters, As(V) usually dominates (Bhattacharya et al., 2006; Smedley et al., 2002). Generation of the Na-HCO$_3$ high-pH waters is achieved through silicate hydrolysis (e.g. albite weathering), carbonate reaction and associated ion exchange.

Arsenic mobility in the Chaco-Pampean groundwaters is likely controlled to a large extent by pH-dependent sorption to metal oxides in the sediments. Positive correlations between dissolved As and pH in the groundwaters (Fig. 5) are consistent with weaker sorption of As(V) to iron oxide surfaces at high pH (Bhattacharya et al., 2005; Smedley et al., 2002). Presence of Mn(IV) oxides, along with low concentrations of solid organic carbon (Sracek et al., 2009) are likely contributory in maintaining oxic conditons through the aquifer.

A unifying feature of the Chaco-Pampean loess sediments is the presence of rhyolitic volcanic ash either intermixed with the sediments or in thin discrete layers. The components of the ash may constitute the ultimate sources of the dissolved As, though linkages are lost through subsequent weathering and redistribution. Dissolved As is also generally well-correlated with other anion and oxyanion elements (F, V, HCO_3, Mo and B; Fig. 5), some of these elements having very high concentrations. Volcanic ash may also be the ultimate source of these oxyanion species (Nicolli et al., 1989).

Nicaragua

Alluvial aquifers of the Sébaco Valley of western Nicaragua contain groundwater with occasional high As concentrations. Altmirano Espinoza and Bundschuh (2009) reported concentrations in the range 10–122 µg L^{-1} and cited an earlier (2005) UNICEF survey in Jinotega municipality in which concentrations up to 1200 µg L^{-1} were found. In the village of El Zapote, a well drilled in 1994 and tested for As in 1996 had a recorded concentration of 1320 µg L^{-1}. Residents drinking the water displayed skin and respiratory disorders (Gomez et al., 2009) and the well was closed in 1996. The groundwater in the El Zapote well derived from Tertiary volcanic rocks which also form the precursors of the Quaternary alluvial aquifer in the valley. The groundwaters of the Sébaco Valley have pHs in the range 6–8, are oxic, and arsenic is dominantly As(V) (Altamirano Espinoza and Bundschuh, 2009). The higher-As groundwaters appear to be of Na-HCO_3 composition. Morales et al. (2009) also found high As concentrations in groundwater from neighbouring Esteli Department, with observed concentrations up to 115 µg L^{-1}, an apparent positive correlation between As and pH and similar dominance of As(V).

Spain

Cenozoic aquifers of the Duero Basin of north-central Spain have recently been found to contain arsenic with concentrations up to 613 µg L^{-1}. Sediments are mixed, carbonate-rich alluvial and lacustrine deposits and water sources within them include springs, shallow wells and boreholes up to 500 m deep (Gomez et al., 2006). Groundwaters are mainly oxic but with variable redox potentials and often high salinity and SO_4 concentrations. Groundwater pH ranges from 5.9–10.6 and the highest arsenic concentrations generally occur in waters with pH>8. Correlations have been found between arsenic and both vanadium and tungsten and, in shallow wells, also with uranium which reaches concentrations up to 216 µg L^{-1}. Concentrations of boron are also high in some (Gomez et al., 2006).

South-west USA

Concentrations of arsenic in most groundwaters of the USA are low. From some 20,000 analyses of groundwater samples taken from public-supply wells across the USA, Focazio et al. (2000) found that 11% exceeded 10 µg L^{-1} and 2% exceeded 50 µg L^{-1} (55% contained 1 µg L^{-1} or less). However, high concentrations have been found in several states, as shown for example by the USGS map of groundwater arsenic occurrence (Ryker, 2001). Some of the most widespread and best-documented cases occur in the south-western states of Nevada, California and Arizona. Other aquifers in Maine, Michigan, Minnesota, South Dakota, Oregon, Texas, Oklahoma and Wisconsin have groundwater with concentrations of arsenic exceeding 10 µg L^{-1} (e.g. Ayotte et al., 2006; Focazio et al., 2000; Scanlon et al., 2009; Schreiber et al., 2000; Welch et al., 2000). From the high-arsenic areas, various sources and processes have been cited, including natural dissolution/desorption reactions, geothermal water and mining activity. High concentrations occur under both reducing and oxidising conditions in different areas. Evaporative concentration is thought to be an important process in the more arid areas. Human influences including effects of groundwater pumping have also been cited as causal in arsenic mobilisation (Ayotte et al., 2011).

In Nevada, arsenic concentrations over 100 µg/L have been found in a large number of private groundwater supplies (Fontaine, 1994). Concentrations exceeding 100 µg L^{-1} with extremes up to 2600 µg L^{-1} have also been found in shallow groundwaters from the southern Carson Desert (Welch et al., 1988). These are largely present under reducing conditions. The groundwaters also have associated high pH (>8) and high concentrations of phosphorus (some >4 mg L^{-1}) and uranium (>100 µg L^{-1}), concluded to be largely concentrated by evaporation, combined with the influence of redox and desorption processes involving metal oxides.

In California, a large range of arsenic concentrations (<1–2600 µg L^{-1}) has been found in groundwater from the Tulare Basin of the San Joaquin Valley (Fujii and Swain, 1995). Redox conditions are variable and high arsenic concentrations are found in both oxidising and reducing conditions. The proportion of groundwater arsenic present as As(III) increases with increasing well depth. The groundwaters from the Basin are often strongly affected by evaporation with resulting high concentrations of total dissolved solids. 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).

In Arizona, Robertson (1989) also noted the occurrence of high arsenic concentrations in some groundwaters under oxidising conditions (dissolved oxygen 3–7 mg L^{-1}) in alluvial aquifers of the Basin and Range Province. Only limited analysis of arsenic species was carried out, but results obtained suggested that the arsenic was present predominantly as As(V). The dissolved arsenic correlated positively with pH, Mo and V as well as Se and F. Groundwater pH values were in the range 6.9–9.3. Arsenic concentrations in the sediments of the Basin and Range Province were in the range 2–88 mg kg^{-1}. Oxidising conditions persist in the aquifers down to significant depths (600 m) despite the groundwaters having very long residence times (up to 10,000 years). The high arsenic (and other oxyanion) concentrations are a feature of the closed basins of the province.

Sulphide mineralisation and mining-related arsenic problems

Arsenic problems have long been recognised in association with zones of ore mineralisation as a result of the high concentrations of arsenic in sulphide minerals. Oxidation of the sulphide minerals, exacerbated by mining activity, potentially leads to the release of arsenic and transition and heavy metals. Oxidation reactions are catalysed by bacteria, notably *Thiobacillus ferrooxidans*, *Thiobacillus thiooxidans* and *Leptospirillum ferrooxidans* (Schrenk et al., 1998). Oxidation releases SO_4 and associated trace elements and generates acidity which maintains high aqueous concentrations of many released trace metals. One of the highest arsenic concentrations ever reported, 850,000 µg L^{-1}, is from a mine seep at Iron Mountain, California (Nordstrom and Alpers, 1999). Plumlee et al. (1999) also found arsenic concentrations in USA mine drainage ranging up to 340,000 µg L^{-1}.

Under oxidising conditions, iron released during pyrite oxidation typically precipitates as an iron(III) oxide. Trace elements likewise coprecipitate with, or adsorb onto, these iron oxides. Water is also neutralised in the presence of carbonate minerals. As a result, many mine waters have near-neutral pH values (e.g. Welch et al., 2000) and many have relatively low iron and arsenic concentrations. The considerable capacity of iron oxides to adsorb arsenic means that even in areas where high dissolved arsenic concentrations occur, they are usually restricted to the local area around the zone of oxidation, typically a few kilometres or less. Nonetheless, contamination of soils, sediments and vegetation in mining and mineralised areas can be substantial.

Most mining-impacted water sources are not used for potable supply, although a few notable exceptions exist and have given rise to localised health problems. Arsenic health problems related to mining activity have been well-documented in Ron Phibun District in Nakhon Si Thammarat Province of southern Thailand. The area lies within the South-East Asian Tin Belt and has been mined for several generations. Arsenic-related health problems were first recognised there in 1987. By the late 1990s, around 1000 people had been diagnosed with skin disorders, particularly in and close to Ron Phibun town (Williams, 1997). Arsenic concentrations up to 5000 µg L^{-1} have been found in shallow groundwaters from Quaternary alluvial sediments that have been extensively dredged during mining operations. Deeper groundwaters from an older limestone aquifer were apparently less contaminated (Williams et al., 1996), although a few high arsenic concentrations occurred, presumably also as a result of contamination from the mine workings. The mobilisation of arsenic is related to the oxidation of arsenopyrite, exacerbated by the former tin-mining activities. The recent appearance in groundwater has occurred during post-mining groundwater rebound (Williams, 1997).

A relatively recent discovery has also been made of arsenic-related health problems in northern Burkina Faso. In rural boreholes close to the town of Ouahigouya, concentrations of As in the range <0.5–1630 µg L^{-1} have been documented following recognition of occurrences of melanosis, keratosis and skin cancer in some village populations. The highest concentrations occurred in boreholes in close proximity to mineralised veins containing arsenoprite and other sulphide minerals which are hosted within Precambrian (Birimian) metamorphic rocks (Smedley et al., 2007) (Fig. 6). The arsenic was overwhelmingly present as As(V), signifying oxidation of the original As-hosting sulphide minerals. Although mining for gold takes place in Burkina Faso, this is chiefly on a small (artisanal) scale and there is no evidence that the mining operations per se have been responsible for the arsenic mobilisation. During the 1970s, health problems of suspected drinking water origin were also identified in a village close to the town of Mogtedo in central Burkina Faso. High concentrations of As (200–1600 µg L^{-1}) were found in three borehole samples. The residents were relocated and further investigations of As in Birkinabé groundwater ceased until the renewed interest during the mid 2000s.

Environmental arsenic damage has also been documented in geologically analogous areas of neighbouring Ghana, where gold mining occurs on a much larger scale in the Ashanti Region. To date, there is little evidence of detrimental effects on human health through drinking-water exposure. Gold reserves have long been mined in the region where the gold is also associated with sulphide mineralisation, particularly arsenopyrite. Around the town of Obuasi, high arsenic concentrations have been found in soils close to the mines and treatment works. Some high concentrations were also found in river waters close to the mining activity. However, many of the groundwaters had low arsenic concentrations and the highest observed were not proximal to mining activity but appeared to be natural occurrences under mildy reducing aquifer conditions.

Arsenic contamination from mining activities has been identified in numerous areas of the USA (Welch et al., 2000). Groundwater from some areas has very high arsenic concentrations locally (up to 48,000 µg L^{-1}). Well-documented cases include the Fairbanks gold-mining district of Alaska, the Coeur d'Alene Pb-Zn-Ag mining area of Idaho, Bunker Hill mine in Idaho, Leviathan Mine in California, Mother Lode in California, Kelly Creek Valley in Nevada, Clark Fork river area in Montana and Lake Oahe in South Dakota.

Elsewhere, documented cases of mining-related arsenic contamination include the Zimapán Valley (Mexico), Baja California (Mexico), Lavrion (Greece), Minas Gerais (Brazil), Styria (Austria), Zloty Stok (Poland), Oruro Province (Bolivia), west Devon (England), eastern Zimbabwe, Korea, Sarawak (Malaysia) (Smedley and Kinniburgh, 2002) and Aznalcollar (Spain) (Fig. 2). Doubtless, arsenic problems also exist in many other undocumented mining areas.

Increased concentrations of dissolved arsenic have also been found in parts of the world with local mineralisation which has not been mined. In Wisconsin, USA, arsenic 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 arsenic up to 12,000 µg L^{-1} have been found in the well waters (Schreiber et al., 2000). The oxidation appears to have been promoted by groundwater abstraction which has led to the lowering of the piezometric surface at a rate of around 0.6 m year^{-1} since the 1950s, resulting in a partial dewatering of the aquifer. The high arsenic concentrations were observed where the piezometric surface intersects, or lies close to, the sulphide cement horizon. Boyle et al. (1998) also recorded naturally high arsenic concentrations (up to 580 µg L^{-1}) in groundwaters from an area of sulphide mineralisation in Bowen Island, British Colombia.

Geothermal sources

The common occurrence of high concentrations of arsenic in geothermal fluids has been recognised for a long time. Geothermal areas with documented high concentrations include the USA, Japan, New Zealand, Chile, Argentina, Equador, Kamchatka, France, Italy and Dominica (Fig. 2). One of the largest and best-documented geothermal systems is that of Yellowstone National Park, USA where arsenic concentrations up to 7800 µg L^{-1} have been found in hot springs and geysers (Thompson and Demonge, 1996). Geothermal inputs have also given rise to high concentrations of arsenic (up to 370 µg L^{-1}) in waters of the Madison River, USA (Nimick et al., 1998). Others include Honey Lake Basin, California (arsenic 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}), Lassen Volcanic National Park, California (up to 27,000 µg L^{-1}), Steamboat Springs, Nevada (up to 2700 µg L^{-1}) and Geyser Bight, Umnak Island, Alaska (up to 3800 µg L^{-1}) (Welch et al., 2000). Geothermal inputs from Long Valley, California are believed responsible for the relatively high concentrations (20 µg L^{-1}) of arsenic in the Los Angeles Aqueduct which supplies water for the city of Los Angeles (Wilkie and Hering, 1998). Geothermal inputs also contribute significantly to the high dissolved arsenic concentrations (up to 20 mg L^{-1}) in Mono Lake, California (Maest et al., 1992).

In New Zealand, geothermal waters occur with arsenic concentrations up to 9000 µg L^{-1} (Webster, 2003). River and lake waters receiving inputs from the Wairakei, Ohaaki, Orakei Korako and Atiamuri geothermal fields have concentrations up to 121 µg L^{-1} (Robinson et al., 1995). Concentrations diminish significantly downstream from the geothermal inputs.

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

In Papallacta Lake, Equador, arsenic of geothermal origin has a range between 1090–7850 µg L^{-1}. The lake is fed by the Tambo River which in turn receives inflows from hot springs along its route. Speciation of As in water from two hot springs which were Fe-rich and highly reducing showed a dominance of inorganic As(III) (Cumbal et al., 2009). In contrast, two cool springs with higher redox potentials showed a dominance of As(V). The variations indicate oxidation of discharging geothermal fluids over time and mixing with oxygenated surface water.

Arsenic concentrations in the range 100–5900 μg L^{-1} have been also been found in geothermal waters from Kamchatka (White et al., 1963) and in the range 500–4600 μg L^{-1} in geothermal fields from Kyushu, Japan (Yokoyama et al., 1993).

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

Hot springs commonly show a positive correlation between arsenic and chloride (e.g. Welch et al., 1988; Wilkie and Hering, 1998). This association was noted by Webster and Nordstrom (2003) to relate to their similar behaviour during sub-surface boiling and phase separation as both elements partition preferentially into the liquid phase.

Mineral-water interactions

Adsorbed arsenic in sediments

Of the arsenic problem aquifers identified, it appears to be those hosted in young sediments that are most vulnerable to the development of high-arsenic groundwater on a regional scale. In these, surface reactions are important controls on the trace-element chemistry of the groundwaters. The major minerals which adsorb arsenic (as both arsenate and arsenite) in sediments are the metal oxides, particularly those of iron, aluminium and manganese. Iron oxides are relatively abundant in most sediments and are commonly produced by the weathering of primary minerals. In freshwater sediments and silicate clays, they often constitute about 50% of the iron present (Manning and Goldberg, 1997). In sandy aquifers, the iron oxides are probably the most important adsorbents of arsenic because of their relative abundance, strong binding affinity and high specific surface area, especially the freshly-formed amorphous oxides. These are also particularly sensitive to a changing geochemical environment, acid dissolution and reductive dissolution, as well as to changes in mineral structure and crystallinity. Although the affinity for arsenate adsorption is strong, arsenite has been shown to adsorb more strongly to HFO and goethite than arsenate under alkaline conditions (pH>7) (Dixit and Hering, 2003). Aluminium oxides can be expected to play a significant role in arsenic adsorption when present in quantity (Manning and Goldberg, 1997). Iron sulphide minerals (FeS, FeS_2) may also adsorb significant quantities of arsenic and it is likely the limited supply of SO_4 in reducing groundwater that restricts the removal of arsenic from solution in many of the high-arsenic aquifers of south-east Asia (O'Day et al., 2004).

The role of carbonates as arsenic sorbents has also been investigated recently. Experiments by So et al. (2008) and Alexandratos (2007) found that arsenate sorbs readily to calcite surfaces, the affinity depending on alkalinity, pH and ionic strength. Experiments by Goldberg and Glaubig (1988) also observed adsorption of As(V) on calcite, and Romero et al. (2004) speculated that calcite retarded arsenate in the carbonate aquifer of Zimapán, Mexico. By contrast, So et al. (2008) found that arsenite did not sorb significantly to calcite. These observations suggest that calcite would have little effect on arsenic mobility in reducing conditions but could be important in carbonate aquifers under oxic conditions.

Reduced sediments and the role of iron oxides

A recognised sequence of reduction reactions occurs when sediments are buried and the environment becomes anaerobic (Berner, 1981). Such reaction sequences are common in sediments from a wide variety of environments (e.g. Postma et al., 2007). The processes causing changes in iron redox chemistry are particularly important since they can directly affect the mobility of arsenic. The reductive dissolution of hydrous iron oxides and/or the release of adsorbed and coprecipitated arsenic are key to this process. The redox sequence begins with the consumption of oxygen and an increase in dissolved CO_2 from the decomposition of organic matter. NO_3^- decreases by reduction to NO_2^- and ultimately to the gases N_2O and N_2. Insoluble manganese(IV) oxides dissolve by reduction to soluble Mn^{2+} and hydrous ferric oxides are reduced to Fe^{2+}. Subsequent reactions involve SO_4^{2-} reduction to S^{2-}, then CH_4 production from fermentation and methanogenesis, and finally reduction of N_2 to NH_4^+. The position of As(V) reduction in the sequence relative to Fe reduction has been disputed but is expected before SO_4^{2-} reduction. During sulphate reduction, the sulphide produced reacts with any available iron to produce FeS and ultimately pyrite, FeS_2. Iron is often more abundant than sulphur so that excess iron results beyond that which can be converted to pyrite. In the presence of carbonate or phosphate, dissolved Fe(II) may precipitate as siderite (e.g. Postma et al., 2007) or vivianite (Swartz et al., 2004), each of which has potential to remove As from solution (Islam et al., 2005b).

There is also evidence for solid-state transformations of the iron oxides under reducing conditions. This is reflected by a change from red/orange/brown to grey/green/blue coloration. Analysis of the Fe(II) and Fe(III) contents of iron oxides from reduced lake and aquifer sediments often indicate the presence of mixed Fe(II)-Fe(III) oxides (Davison, 1993; Fendorf et al., 2010). Green rusts have been identified or suspected in anoxic soils and sediments (Cummings et al., 1999; O'Day et al., 2004; Taylor, 1980). These consist of a range of green-coloured mixed Fe(II)-Fe(III) hydroxide minerals. Authigenic magnetite (Fe_3O_4) has also been identified in anaerobic sediments, formed by microbial transformations (Cummings et al., 2000; Fredrickson et al., 1998). Magnetite formation has also been established under reducing conditions in the laboratory (Benner et al., 2002; Dixit and Hering, 2003; Guerin and Blakemore, 1992; Islam et al., 2005b). Under strongly reducing conditions magnetite is unstable and eventually dissolves. In the presence of high concentrations of H_2S, magnetite converts slowly to pyrite on a scale of centuries or more.

These studies of iron oxides in reducing environments indicate the complexities involved in the 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, as well as to changes in their arsenic sorptive capacities. Even quite small changes in arsenic binding could have a large impact on porewater arsenic concentrations because of the large solid/solution ratio found in sediments. Therefore, understanding the changes to the nature of iron oxide minerals in sedimentary environments is an important part of understanding the processes leading to arsenic mobilisation in sedimentary environments.

Role of microbes

It has become increasingly clear that microbes play an important role in arsenic speciation and mobilisation. They can be significant catalysts in the oxidation of arsenite, respiration of arsenate and methylation and volatilisation reactions (Lloyd and Oremland, 2006; Oremland and Stolz, 2005; Oremland et al., 2004). The microbiological transformations either provide sources of energy or act as detoxifying mechanisms. A number of chemoautotrophs oxidise As(III) by using oxygen, nitrate or ferric iron as a terminal electron acceptor and CO_2 as their sole carbon source. Some heterotrophs are also capable of As(III) oxidation using organic carbon. Conversely, many prokaryotes (e.g. *Bacillus selentireducens* and *Bacillus arsenicoselantis*) are capable of As(V) respiration or As(III) oxidation (Oremland et al., 2002; Oremland and Stolz, 2003; Pederick et al., 2007). Arsenic can also be released indirectly as a result of other microbially-induced redox reactions. For example, the dissimilatory Fe-reducing bacterium *Shewanella alga* reduces Fe(III) to Fe(II) in scorodite ($FeAsO_4.2H_2O$), releasing As(V) in the process (Cummings et al., 1999). The Fe(III)-reducing bacteria *Geobacter* and *Geothrix* have also been shown to affect arsenic cycling in reduced aquifer sediments (Islam et al., 2005a; Islam et al., 2005b).

Thermophilic bacteria and cyanobacteria have been recognised in geothermal settings and affect arsenic speciation and mineral precipitation in such systems (Webster and Nordstrom, 2003). Streams affected by geothermal inputs may also be influenced by microbial activity. In geothermally-fed waters of Hot Creek, California, Wilkie and Hering (1998) concluded that the oxidation of As(III) was bacterially-controlled and that in abiotic systems, this oxidation reaction was much slower. Extremophiles have also adapted to the alkaline and saline conditions in the geothermally-influenced Mono Lake of California (Oremland et al., 2002; Oremland et al., 2004).

Organic matter plays a key role in many microbial reactions in sediments and the type of organic matter present affects its reactivity and hence bioavailability. Organic matter has been shown to act both as an energy source for Fe- and As-reducing bacteria and as an electron shuttle enhancing microbial reactions (Islam et al., 2005a; Rowland et al., 2007).

Common features of high-arsenic groundwater provinces

The sources of arsenic

In the cases where affected groundwaters are found close to obvious geological or industrial sources rich in arsenic (geothermal springs, drainage from mineralised and mining areas, specific contaminant sources), it is clear that the anomalously high arsenic concentrations in the source region are responsible. The extent of this contamination is usually highly localised because the geochemical conditions within most aquifers do not favour arsenic mobilisation on a regional scale. Areas affected by geothermal activity are potentially more widespread since in this case mobilisation of arsenic is not required: arsenic is already present in solution and the size of geothermal reservoirs can be large. This probably accounts for why high-arsenic surface waters are normally located in geothermal areas. Perhaps more remarkable is the way in which very high concentrations of arsenic, up to several mg L^{-1}, are found in groundwaters from areas with unremarkable concentrations of arsenic in the source rocks. In aquifers with extensive areas of high-arsenic groundwater, this appears to be the rule rather than the exception. Most of these cases arise in aquifers derived from relatively young sediments, often consisting of alluvium or loess where the total sediment arsenic concentrations are typically in the range 1–20 mg kg^{-1} (e.g. BGS and DPHE, 2001; Postma et al., 2007; Swartz et al., 2004).

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

Mobilisation of arsenic

Two key factors appear to be involved in the formation of high-As groundwaters on a regional scale: firstly, some form of geochemical trigger releases arsenic from the aquifer solid phase into the groundwater. Secondly, the released arsenic remains in the groundwater and must not be flushed away. There are a number of possible geochemical triggers. In mining and mineralised areas, oxidation of sulphide ores is triggered by influxes of oxygen or other oxidising agents. This may follow a lowering of the water table or change in hydrogeological regime or excavation by mining. In most arsenic-affected aquifers, the most important trigger appears to be the desorption or dissolution of arsenic from oxide minerals, particularly iron oxides. An important feature of this process is that the initial adjustment to environmental changes is probably quite rapid since adsorption reactions are surface reactions. The rate-limiting factors are probably those that control the major changes in pH, redox condition and associated water-quality parameters of the aquifer. These are in part related to physical factors such as the rate of diffusion of gases through the sediment, the rate of sedimentation, the extent of microbiological activity and the rates of chemical reactions. Many of these are likely to be rapid on a geological time scale. Dissolution reactions are relatively slow but even oxide dissolution is rapid on a geological time scale and can be observed over the course of weeks or even days in flooded soils (Masscheleyn et al., 1991). A qualification is that if diagenetic changes to the oxide mineral structure take place or if burial of sediment occurs, there could be a slow release of arsenic over a much longer time scale. The rates of release are likely to be most rapid initially and to diminish over time. Once the diagenetic readjustment has taken place and the sediments have equilibrated with their new environment, there should be little further release of arsenic.

The geochemical triggers involved in arsenic mobilisation could arise for a number of reasons. These are discussed further below.

Desorption of arsenic at high pH under oxidising conditions

Under the aerobic and acidic to near-neutral conditions typical of many natural environments, arsenic is strongly adsorbed by oxide minerals as the arsenate ion and the concentrations in solution are low. The non-linear nature of the adsorption isotherm for arsenate (Dzombak and Morel, 1990) ensures that the amount of arsenic adsorbed is often relatively large, even when dissolved concentrations of arsenic are low. With an increase in pH, especially above pH 8.5, arsenate tends to desorb from oxide surfaces, thereby increasing the concentration in solution (Dzombak and Morel, 1990). The impact of this is magnified by the high solid/solution ratios typical of unconsolidated aquifers.

The presence of other ions in the system can further impact on dissolved arsenic concentrations because other ions such as phosphate compete for sorption sites on the oxide (e.g. HFO, goethite) and will reduce the arsenic loading on the solid surface. At high pH, phosphate is also released (Dzombak and

Morel, 1990). Other potential competing ions include bicarbonate, silicate and vanadium (Appelo et al., 2002; Smedley et al., 2005; Swedlund and Webster, 1999). Bicarbonate is often the dominant anion in high-arsenic groundwaters and concentrations can be high, frequently exceeding 500 mg L^{-1}, and occasionally above 1000 mg L^{-1} (Table 3). Concentrations of silica can also be high in some oxic arid groundwaters; high concentrations of vanadium are more unusual but have been found for example in Argentina (Smedley et al., 2005; Smedley et al., 2002).

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, together with the effect of evaporation in arid and semi-arid regions. A 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 arsenic concentrations in some alkaline lakes. Desorption at high pH is the most likely mechanism for the development of groundwater-arsenic problems under oxidising conditions such as those observed in Argentina, Mexico and parts of the USA for example, and would account for the observed positive correlation of arsenic concentrations with increasing pH (e.g. Fig. 5). Increases in pH also induce the desorption of a wide variety of other oxyanions including those of V, U, Mo and B which are observed in many high-pH groundwaters (Fig. 5) (Bhattacharya et al., 2005; Smedley et al., 2005; Smedley et al., 2002). These specifically-adsorbed anions all interact with adsorption sites on the oxides in a competitive way and so influence the extent of binding of each other.

By contrast, some cations, because of their positive charge, may promote the adsorption of negatively charged arsenate (Wilkie and Hering, 1996). Calcium and magnesium are likely to be the most important cations in this respect because of their abundance in most natural waters and their +2 charge. Changes in surface charge and sorption capacity due to Ca/Na ion exchange have been implicated recently in the mobilisation of arsenate in the Southern High Plains aquifer, Texas (Scanlon et al., 2009). Other cations could also have an influence: Fe^{2+} may be important in reduced waters and Al^{3+} in acidic waters.

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

Arsenic desorption and dissolution due to a change to reducing conditions

The onset of strongly reducing conditions, sufficient to enable iron(III) and probably sulphate reduction to take place is another well-documented trigger for the release of arsenic. Arsenic may be released by reductive dissolution, or reductive desorption, or a combination of the two. No clear relationship between dissolved concentrations of Fe(II) or As are expected as a result (Pedersen et al., 2006). Such processes occur in large alluvial systems, especially broad lowland meander belts and braided channels, and in prograding deltas. Microbial reactions are key and the organic carbon content and reactivity in the buried sediment can determine the rate at which reducing conditions are created (Postma et al., 2007; Rowland et al., 2007). Freshly-produced soil organic matter is reactive and readily decomposes; the presence of even small quantities can consume all of the available electron acceptors (e.g. dissolved oxygen, nitrate and sulphate) in the system. Solid-phase Fe(III) in minerals may moderate the rate of reduction. Reducing conditions are maintained as long as the diffusion and convection of dissolved oxygen and other oxidants from the surface is less rapid than their consumption. This is facilitated if there is a confining layer of fine-grained material close to the surface. This commonly occurs in large deltas where fine-grained overbank deposits overlie coarser-grained alluvial deposits.

A change in the redox state of adsorbed arsenic from As(V) to As(III) also occurs during the diagenetic process. Arsenite is found as a dominant redox state in many reducing sediments (e.g. Rowland et al., 2005). Some studies have found As reduction coinciding with Fe(III) reduction (Herbel and Fendorf, 2005). Others have concluded that reductive dissolution of iron oxides precedes the reduction of As(V) to As(III) (Islam et al., 2004).

The changing As redox state will also affect a large number of competing reactions. Phosphate-arsenite competition, for example, is likely to be less important than phosphate-arsenate competition. Competition with HCO_3 and organic matter is possible (Appelo et al., 2002; Stachowicz et al., 2007). There is also the potential for arsenite-arsenate competition.

Changes in the structure of oxide minerals

Disordered and fine-grained iron oxides, including HFO, lepidocrocite, schwertmannite and magnetite, are common products of the early stages of weathering. Freshly-precipitated HFO is extremely fine-grained with a specific surface area of 300 $m^2 g^{-1}$ or more. HFO gradually transforms to more ordered structures such as goethite or haematite with larger crystal sizes and reduced surface areas. Goethite typically has specific surface areas of 150 $m^2 g^{-1}$ or less and those for haematite are even less (Cornell and Schwertmann, 1996). This ageing reaction can take place rapidly in the laboratory but the rate in nature may be inhibited by the presence of other ions, particularly strongly adsorbed ions such as aluminium, phosphate, sulphate, arsenate, bicarbonate and silicate (Cornell and Schwertmann, 1996). A reduction in surface area ultimately decreases the amount of As(V) adsorption possible on a weight-for-weight basis. If the site density (site nm^{-2}) and binding affinities of the adsorbed ions remain constant, then as the specific surface area of the oxide mineral is reduced, some of the adsorbed ions may be desorbed (Dixit and Hering, 2003).

Under strongly reducing conditions, additional processes could operate which lead to a change in the binding affinity for arsenic. In iron oxides, some of the surface iron could be reduced from Fe(III) to

Fe(II) to produce a mixed-valence oxide such as magnetite. This has been shown to have variable effects on arsenic release, especially depending on microbiological interactions. Several studies have shown that biotransformation of fresh iron oxides can lead to a net reduction in the release of As, at least in the short term until specific surface area is reduced to a point where As binding sites are diminished or reductive dissolution of the oxide occurs (Herbel and Fendorf, 2006; Kocar et al., 2006; Pedersen et al., 2006; Tufano and Fendorf, 2008). Herbel and Fendorf (2006) observed that in experiments with HFO reduction, *Sulfospirillium barnesii*, a bacterium capable of both Fe(III) and As(V) reduction, induced high concentrations of Fe(II) which were capable of transforming ferrihydrite to goethite and magnetite, and although As was released initially, release diminished upon mineral transformation. Nonetheless, laboratory and field evidence suggests that at micromolar concentrations of arsenic, freshly-formed HFO binds more arsenic than the more crystalline goethite on a mole of Fe basis (de Vitre et al., 1991) and so a reduction in affinity is more likely overall (Dixit and Hering, 2003; Herbel and Fendorf, 2005).

In most soils and sediments, total As concentrations tend to correlate with total Fe. In Bangladesh, areas with high-As groundwaters tend to correspond with areas in which the sediments contain relatively large amounts of phosphate- or oxalate-extractable iron (BGS and DPHE, 2001; van Geen et al., 2006; Zheng et al., 2005). These observations provide indirect support for the importance of labile iron oxides in releasing arsenic to solution. It is likely that the soils and sediments most sensitive to arsenic release on reduction and ageing are those in which iron oxides are abundant, in which HFO is initially a major fraction of the iron oxides present, and in which other arsenic-sorbing minerals are absent or scarce.

Mineral dissolution

Mineral dissolution reactions tend to be most rapid under extremes of pH and Eh. For example, iron oxides dissolve under strongly acidic conditions and under strongly reducing conditions. Minor elements, including arsenic, present either as adsorbed (labile) arsenic or as irreversibly-bound (non-labile) arsenic will also tend to be released during the dissolution. This can explain, at least in part, the presence of high arsenic concentrations in acid mine drainage and in strongly reducing groundwaters. Reductive dissolution of iron(III) oxides accounts for the high Fe(II) content of anaerobic waters.

As described above, one of the most pertinent mineral dissolution processes in respect of arsenic mobilisation is the oxidation of sulphide minerals. Pyrite, the most abundant of these minerals, can be an important source of arsenic, especially where it is freshly exposed by mining or by lowering of the water table. In extreme cases, this can lead to highly acidic groundwaters rich in sulphate, iron and trace metals. As the dissolved iron is neutralised and oxidised, it precipitates as HFO with resultant adsorption and coprecipitation of dissolved As(V). In this sense, pyrite oxidation is not a very efficient mechanism for releasing arsenic into water.

Arsenic transport through aquifers

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

The Quaternary period has seen considerable changes in climate and global sea level. Variation in groundwater piezometric levels over this period would have induced large variations in base levels of erosion and in groundwater flow regimes and rates. During the last glaciation, some 21,000–13,500 years ago, sea levels would have been 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 not have been affected. The increased hydraulic gradient in coastal aquifers during the glacial period would have resulted in correspondingly large groundwater flows and extensive flushing. The arsenic in groundwater in these older aquifers would therefore tend to have been flushed away. The deep unsaturated zone would also have led to more extensive oxidation of the shallower horizons with possible increased sorption of arsenic to Fe(III) oxides. Aquifers younger than around 7,000 years old, i.e. of Holocene age, will not have been subjected to this increased flushing. Such conditions are applicable to the southern Asian aquifers where Holocene high-As aquifers overlie older Pleistocene aquifers with low As concentrations. Differing flushing histories are likely contributory, in combination with different aquifer redox characteristics (grey vs red-brown aquifer sands), to the differing aqueous As distributions observed.

The evidence suggests that in the Bengal Basin, Pleistocene aquifers have thus far been largely protected from contamination by As-rich groundwater from the overlying Holocene aquifers by clay aquitards that separate the two. However, that could change if drawdown of groundwater is induced by heavy pumping of the deep aquifer (Michael and Voss, 2008). Such drawdown appears to have already affected the Pleistocene aquifer of the Red River delta of Vietnam, where intervening clay aquitards are thinner or in places absent (Winkel et al., 2011) and the aquifer is contaminated in places as a result of a century of heavy groundwater abstraction. Perhaps even more vulnerable are the currently low-As zones identified in Holocene deposits as lateral flow induced by pumping is more favourable than vertical flow in the stratified sediments (Fendorf et al., 2010).

At a local scales, small variations in relief or in drainage patterns may dictate local flow patterns and hence the distribution of arsenic-rich groundwater. Low-lying areas favour deposition of fine-grained deposits and are prone to flooding, under which reducing conditions can prevail and groundwater flow is restricted. Small-scale topographic depressions can also be the locations of seasonal discharge which restrict arsenic flushing. Such accumulations of dissolved As in topographic depressions have been observed for example in Argentina, China, Bangladesh, Hungary and Mexico (Nath et al., 2010; Smedley et al., 2002; Smedley et al., 2003; Varsányi et al., 1991). It is clear that flat low-lying areas, particularly large deltas and inland basins, are prone to potentially high-arsenic groundwaters since they combine many of the risk factors identified above.

Concluding remarks

This account has attempted to characterise the distribution of arsenic in the environment, and to describe the main geochemical controls on its speciation and mobilisation. We have also summarised the documented arsenic-rich areas and highlighted the main types of environment under which arsenic concentrations in waters are expected to be problematic. Doubtless there are other areas of the world where arsenic problems are yet to be recognised. However, increased awareness of the need for testing, increased health surveillance and increased recognition of the various risk factors associated with high-arsenic water mean that these are likely to be diminished in number. There are however, other areas where problems have been recognised but the scale is yet to be determined.

Environmental research has progressed significantly since the first aquifers were mapped or cases of arsenicosis recognised, although uncertainties remain in some of the key biogeochemical processes involved. On a simple level, mobilisation of arsenic relates to changes in speciation and mineral solubility as a result of pH and redox changes in aquifers and the environment. But the processes involve a complex interplay of microbial interactions, ageing and diagenesis of metal oxides, ion competitive effects, mineral solubilities, presence of multiple minerals, nature and reactivity of organic matter, and flow.

One of the greatest hindrances to development is the enormous degree of spatial heterogeneity in aqueous As concentrations recognised in many if not all affected aquifers, often seemingly in aquifers with unremarkable concentrations of solid-phase arsenic. Such heterogeneity, on various scales, requires major testing and monitoring operations and hinders prediction of water quality for future drilling programmes. In the efforts to provide alternative sources of low-arsenic water to affected populations, significant challenges also exist to avoid risk substitution. Such risks include lesssustainable supplies, bacterial and other contamination of surface sources or future arsenic contamination of thus-far low-arsenic aquifers.

Groundwater provides an important source of drinking water to many millions of people globally. While this chapter has focused on areas where groundwater arsenic concentrations are often high, it is to be remembered that these are the exceptions. Groundwater more commonly provides a safe and reliable form of drinking water. In reducing exposure to the potentially fatal effects of faecal contamination, the use of groundwater for improving community health in developing countries has been highly successful. With regards to arsenic, most wells in most aquifers are likely to be uncontaminated, even when the groundwaters contain high concentrations of dissolved iron. It is also important to understand why these groundwaters are not affected. It appears that it is only when a number of critical geochemical and hydrogeological factors are combined that high-arsenic groundwaters occur.

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List of figures

Figure 1. pe-pH predominance diagrams for the As-Fe system. (a) aqueous As species only; (b) aqueous Fe species only; (c) As species where hydrous ferric oxide (HFO) has been allowed to precipitate when stable and sorb As, and (d) the same as (c) except that goethite has been assumed to be the stable iron-oxide mineral. Adsorbed species concentrations have been calculated using the CD-MUSIC model. Where appropriate, total concentrations of Fe = 3e-3 M and As = 1e-4 M. A background concentration of 0.1M NaCl was assumed in all cases. No reduced Fe minerals such as magnetite have been allowed to precipitate. All calculations were made by Phreeqc and plotted using PhreePlot.

Figure 2. Occurrence of documented arsenic problems in groundwater (arsenic >50 µg L^{-1}) in major aquifers and environmental problems related to mining and geothermal sources.

Figure 3. Smoothed contour map of arsenic concentrations in shallow groundwater (<150 m) from Bangladesh and histograms of the distributions of arsenic in three special study areas (BGS and DPHE, 2001). Low concentrations indicated in blue in northern Bangladesh denote the locations of the Tista Fan, and Madhupur and Barind Tracts.

Figure 4. a) Distributions of arsenic in the groundwaters of Comarca Lagunera, Mexico (data from IMTA (1992). b) Groundwater bodies distinguished by residence time (data from Brouste et al., 1997).

Figure 5. Variations in total arsenic concentration with pH, HCO_3, F, vanadium, boron, molybdenum and uranium in groundwater from La Pampa and Tucumán provinces, Argentina (data from Nicolli et al., 2010; Smedley et al., 2002; Warren, 2001).

Figure 6. Map of the distribution of arsenic in groundwater from the Ouahigouya area of Burkina Faso (from Smedley et al., 2007). High concentrations are associated closely with zones of sulphide mineralisation, which are also subject to artisanal gold mining.

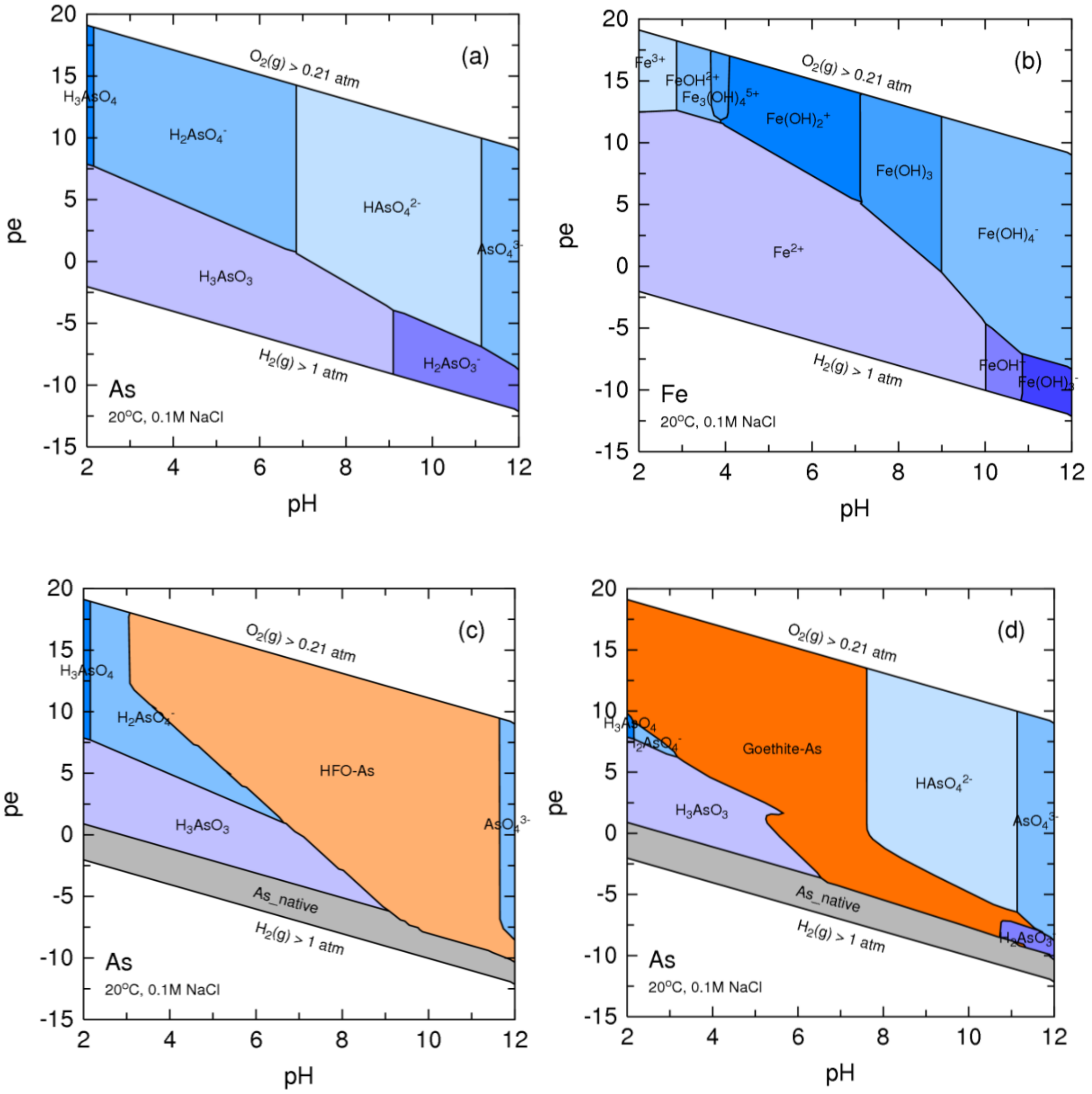
(a)
$O_2(g) > 0.21$ atm
H_3AsO_4
$H_2AsO_4^-$
$HAsO_4^{2-}$
AsO_4^{3-}
H_3AsO_3
$H_2AsO_3^-$
$H_2(g) > 1$ atm
As
20°C, 0.1M NaCl
pe
pH
20
15
10
5
0
-5
-10
-15
2
4
6
8
10
12
(b)
$O_2(g) > 0.21$ atm
Fe^{3+}
$FeOH^{2+}$
$Fe_3(OH)_4^{5+}$
$Fe(OH)_2^+$
$Fe(OH)_3$
$Fe(OH)_4^-$
Fe^{2+}
$FeOH^+$
$Fe(OH)_3^-$
$H_2(g) > 1$ atm
Fe
20°C, 0.1M NaCl
(c)
$O_2(g) > 0.21$ atm
H_3AsO_4
$H_2AsO_4^-$
HFO-As
AsO_4^{3-}
H_3AsO_3
As_native
$H_2(g) > 1$ atm
As
20°C, 0.1M NaCl
(d)
$O_2(g) > 0.21$ atm
H_3AsO_4
$H_2AsO_4^-$
Goethite-As
$HAsO_4^{2-}$
AsO_4^{3-}
H_3AsO_3
As_native
$H_2AsO_3^-$
$H_2(g) > 1$ atm
As
20°C, 0.1M NaCl

Figure 1.


Fairbanks, Alaska
Aleutian Islands
Coeur D'Alene
British Columbia
Lake Oahe
Wisconsin
Yellowstone Park
Western U.S.A.
Clark Fork River
Halifax, Nova Scotia
New England
Don Pedro, California
North-Central Mexico
Baja California
Comarca Lagunera, Mexico
Zimapán Valley
Dominica
El Salvador
Nicaragua
Equador
Bolivia
North-West Argentina
Antofagasta Chile
Minas Gerais, Brazil
Chaco-Pampean Plain, Argentina
Iceland
Poland
England
Styria, Austria
Great Hungarian Plain, Hungary,Romania
Massif Central, France
Asturias
Italy
Aznalcollar
Lavrion Peninsula, Greece
Burkina Faso
Ghana
Serengeti, Tanzania
Zimbabwe
Inner Mongolia, China
Kamchatka
Xinjiang Province, China
Shanxi Province, China
Gubong, Korea
Indus Plain, Pakistan
Terai, Nepal
Tibet
Kyushu, Japan
Bengal Basin, Bangladesh, India
Taiwan
Rajnandgaon, India
Red River Delta Vietnam
Irrawaddy Delta, Myanmar
Mekong Valley, Laos, Cambodia, Vietnam
Ron Phibun, Thailand
Sarawak
Wairakei, New Zealand
LEGEND
Arsenic-affected aquifers
Arsenic related to mining and mineralisation
Geothermal waters

Figure 2.

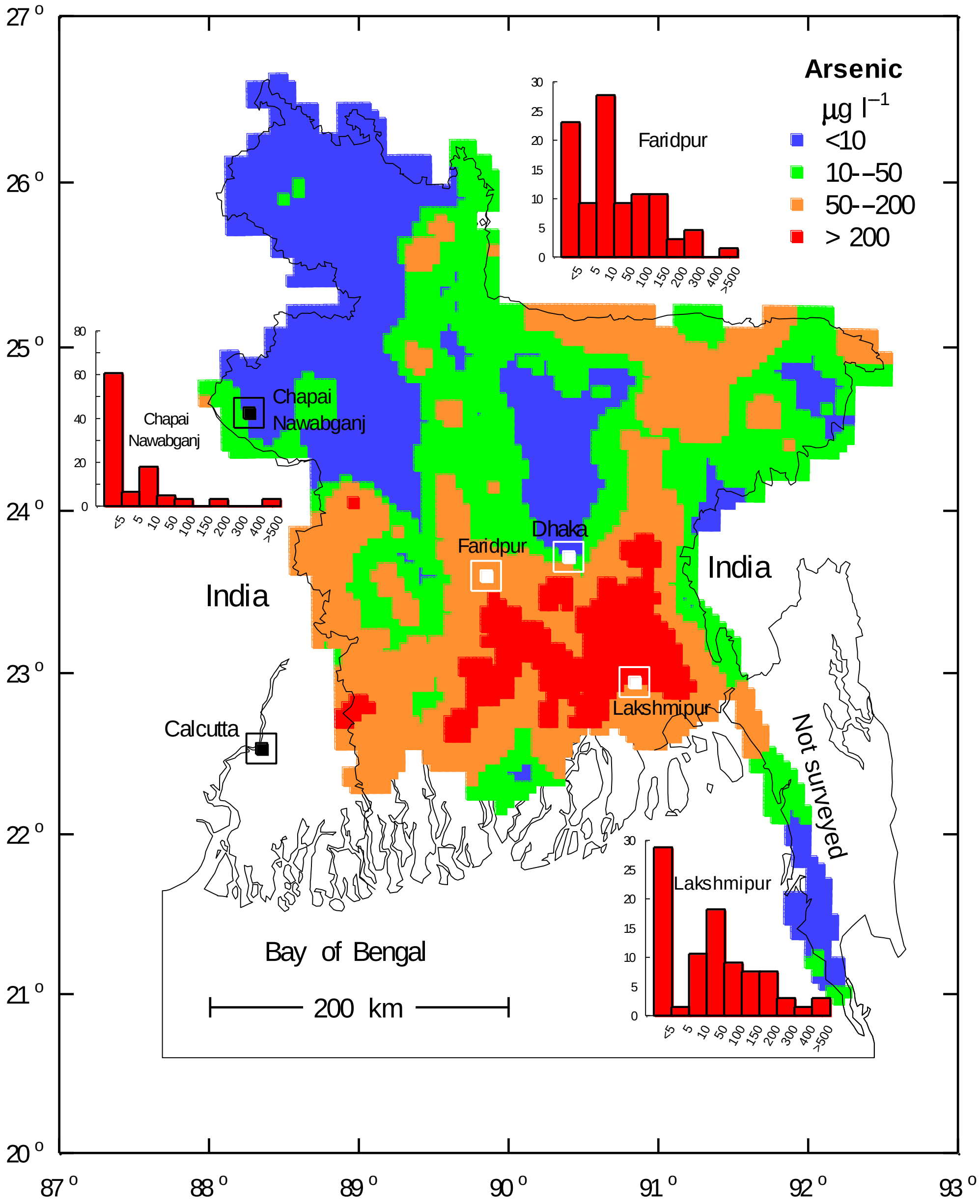
Arsenic
µg l⁻¹
<10
10--50
50--200
> 200
Faridpur
Chapai Nawabganj
Dhaka
Faridpur
Lakshmipur
Calcutta
India
India
Not surveyed
Bay of Bengal
200 km
27°
26°
25°
24°
23°
22°
21°
20°
87°
88°
89°
90°
91°
92°
93°
<5
5
10
50
100
150
200
300
400
>500

Figure 3.

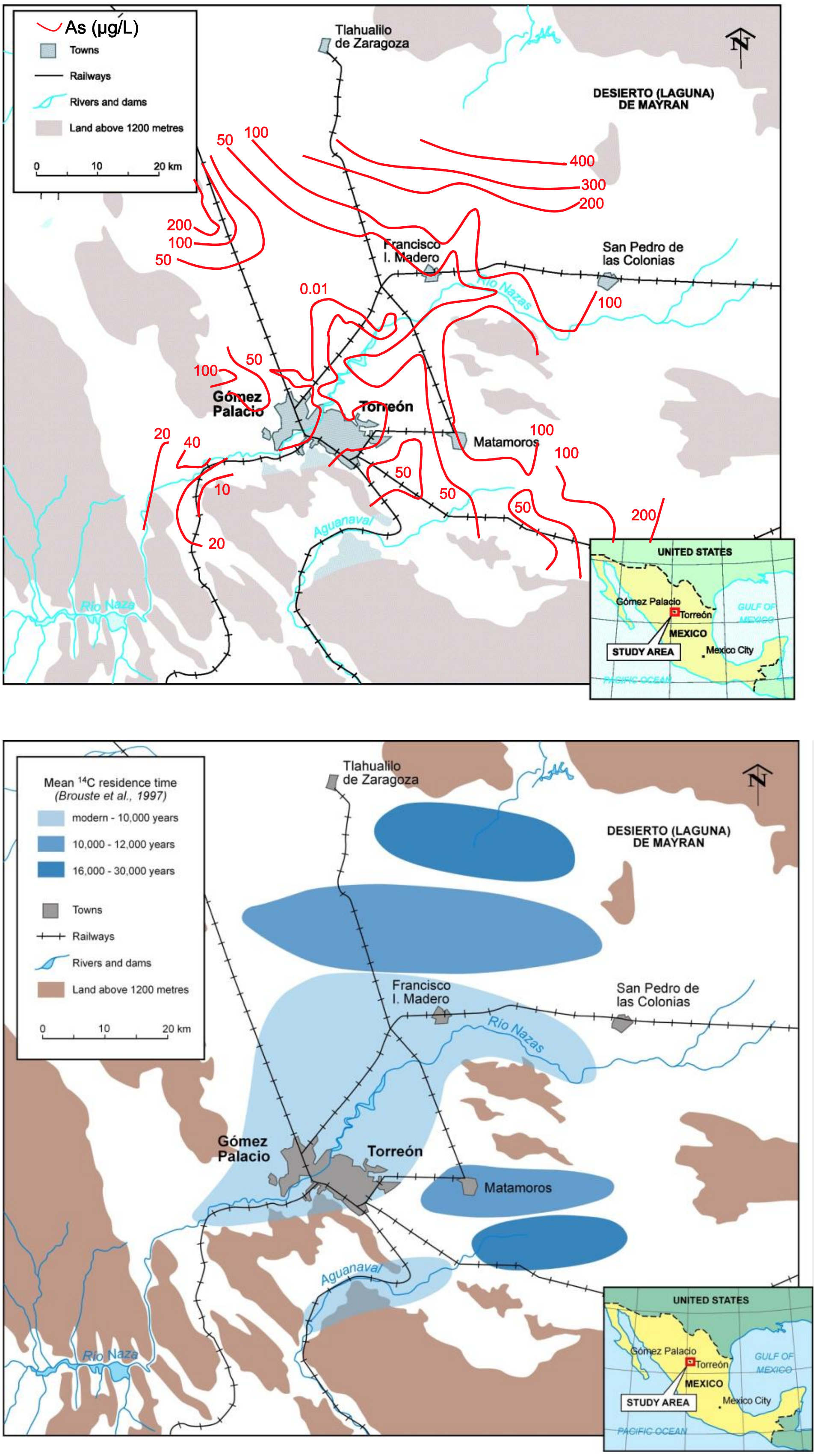
As (µg/L)
Towns
Railways
Rivers and dams
Land above 1200 metres
0
10
20 km
Tlahualilo de Zaragoza
DESIERTO (LAGUNA) DE MAYRAN
400
300
200
50
100
200
100
50
Francisco I. Madero
San Pedro de las Colonias
0.01
100
Rio Nazas
50
100
Gómez Palacio
Torreón
Matamoros
20
40
100
100
10
50
50
50
200
20
Aguanaval
Rio Naza
UNITED STATES
Gómez Palacio
Torreón
MEXICO
GULF OF MEXICO
STUDY AREA
Mexico City
PACIFIC OCEAN
Mean 14C residence time (Brouste et al., 1997)
modern - 10,000 years
10,000 - 12,000 years
16,000 - 30,000 years
Towns
Railways
Rivers and dams
Land above 1200 metres
0
10
20 km
Tlahualilo de Zaragoza
DESIERTO (LAGUNA) DE MAYRAN
Francisco I. Madero
San Pedro de las Colonias
Rio Nazas
Gómez Palacio
Torreón
Matamoros
Aguanaval
Rio Naza
UNITED STATES
Gómez Palacio
Torreón
MEXICO
GULF OF MEXICO
STUDY AREA
Mexico City
PACIFIC OCEAN

Figure 4.

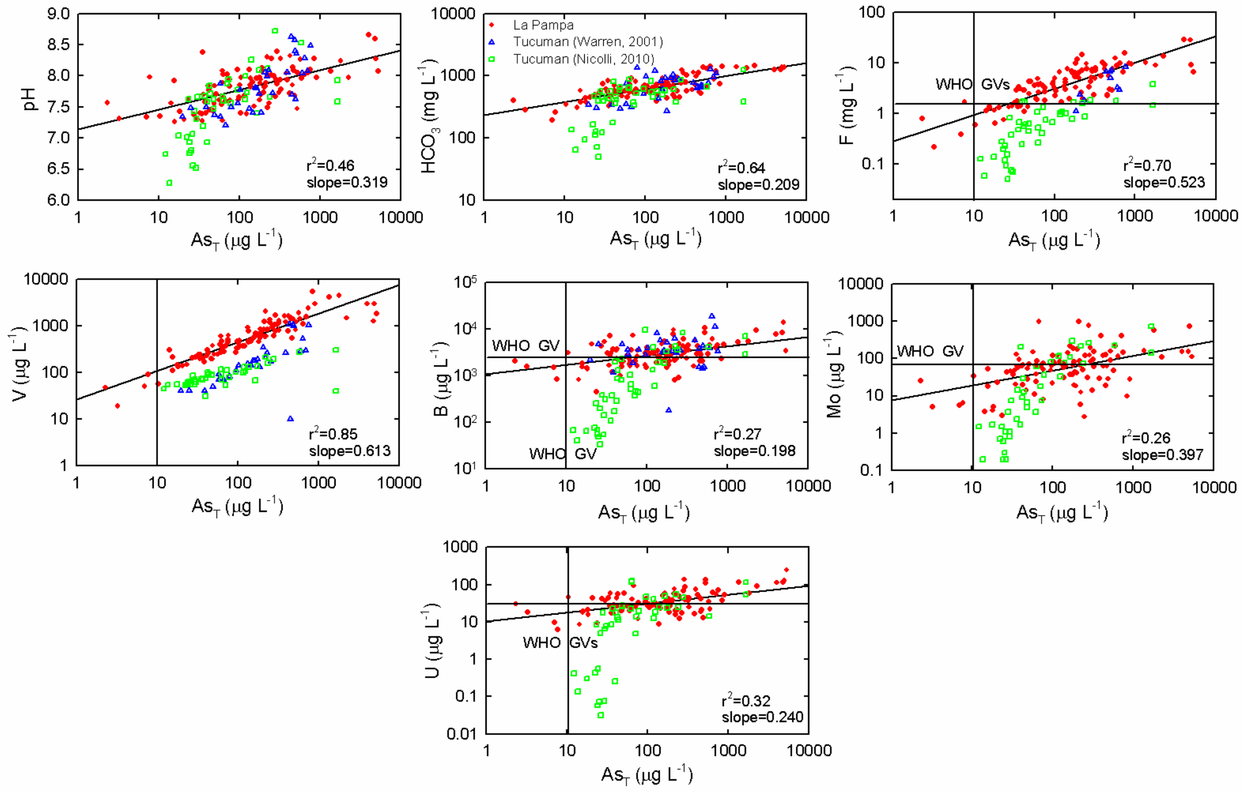
pH
9.0
8.5
8.0
7.5
7.0
6.5
6.0
r²=0.46
slope=0.319
As_T (µg L⁻¹)
1
10
100
1000
10000
La Pampa
Tucuman (Warren, 2001)
Tucuman (Nicolli, 2010)
HCO3 (mg L⁻¹)
r²=0.64
slope=0.209
F (mg L⁻¹)
WHO GVs
r²=0.70
slope=0.523
V (µg L⁻¹)
r²=0.85
slope=0.613
B (µg L⁻¹)
WHO GV
WHO GV
r²=0.27
slope=0.198
Mo (µg L⁻¹)
WHO GV
r²=0.26
slope=0.397
U (µg L⁻¹)
WHO GVs
r²=0.32
slope=0.240
0.01
0.1

Figure 5.

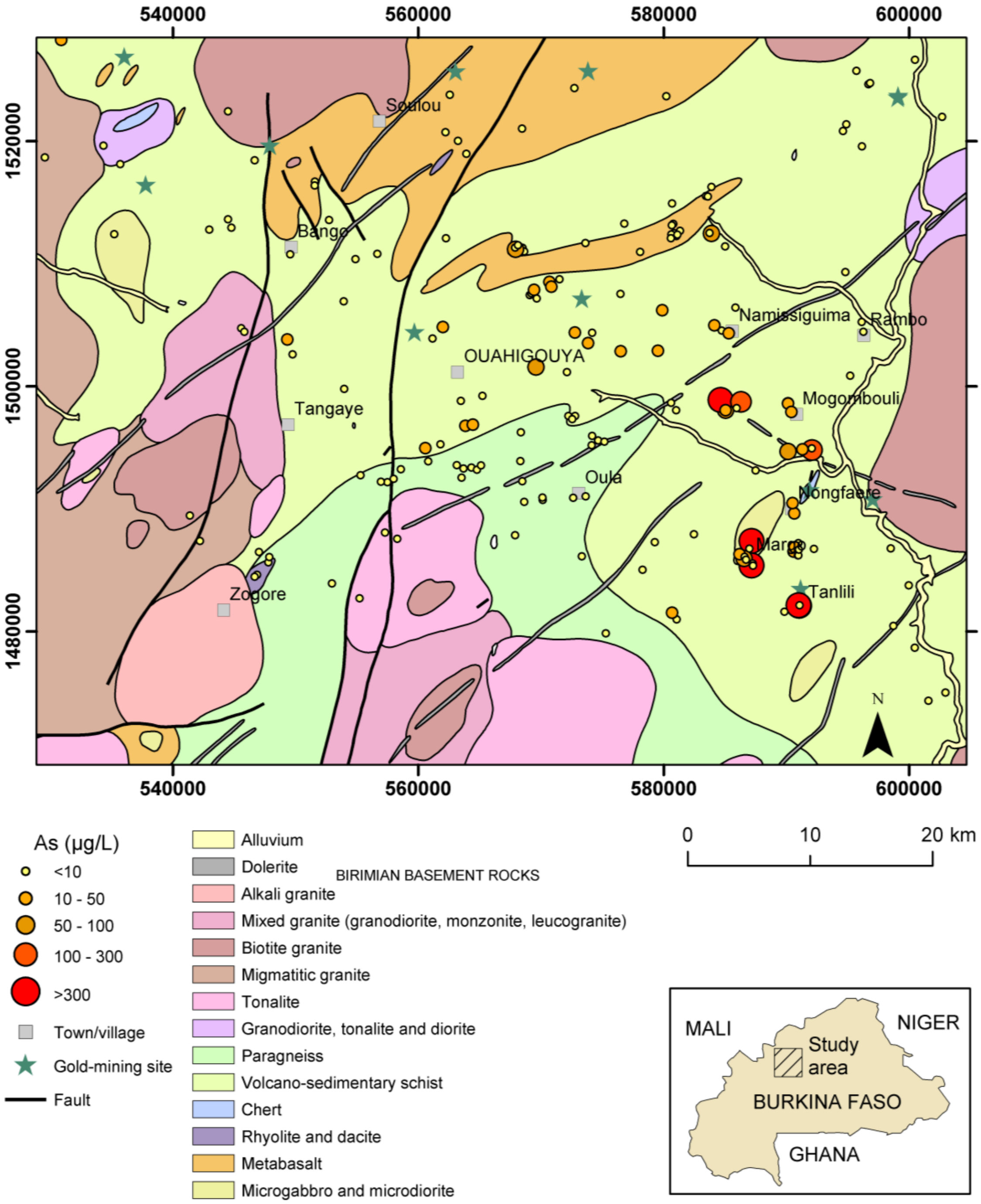
540000
560000
580000
600000
1520000
1500000
1480000
Soulou
Bango
Namissiguima
Rambo
OUAHIGOUYA
Tangaye
Mogombouli
Oula
Nongfaere
Margo
Zogore
Tanlili
N
As (µg/L)
<10
10 - 50
50 - 100
100 - 300
>300
Town/village
Gold-mining site
Fault
Alluvium
Dolerite
BIRIMIAN BASEMENT ROCKS
Alkali granite
Mixed granite (granodiorite, monzonite, leucogranite)
Biotite granite
Migmatitic granite
Tonalite
Granodiorite, tonalite and diorite
Paragneiss
Volcano-sedimentary schist
Chert
Rhyolite and dacite
Metabasalt
Microgabbro and microdiorite
0
10
20 km
MALI
NIGER
Study area
BURKINA FASO
GHANA

Figure 6.

Tables

Table 1. Typical ranges of arsenic concentrations in rock-forming and accessory minerals (Barker et al., 2009; Di Benedetto et al., 2006; Savage et al., 2005; Smedley and Kinniburgh, 2002 and references therein).

Mineral	Arsenic concentration range (mg kg^{-1})
Sulphide minerals:	
Pyrite	100–130,000
Pyrrhotite	5–100
Marcasite	20–126,000
Galena	5–10,000
Sphalerite	5–17,000
Chalcopyrite	10–5000
Oxide minerals:	
Haematite	up to 160
Fe(III) oxyhydroxide	up to 76,000
Magnetite	2.7–41
Ilmenite	<1
Silicate minerals:	
Quartz	0.4–1.3
Feldspar	<0.1–2.1
Biotite	1.4
Amphibole	1.1–2.3
Olivine	0.08–0.17
Pyroxene	0.05–0.8
Carbonate minerals:	
Calcite	1–260
Dolomite	<3
Siderite	<3
Sulphate minerals:	
Gypsum/anhydrite	<1–6
Barite	<1–12
Jarosite	34–2000
Other minerals:	
Apatite	<1–1000
Halite	<3–30
Fluorite	<2

Table 2. Typical ranges of arsenic concentrations in rocks, sediments, soils and other superficial deposits (from sources summarised in Smedley and Kinniburgh, 2002).

Rock/sediment type	As concentration range (mg kg^{-1})
Igneous rocks	
Ultrabasic rocks	0.03–15.8
Basic rocks	0.06–113
Intermediate rocks	0.09–13.4
Acidic rocks	0.2–15
Metamorphic rocks	
Quartzite	2.2–7.6
Hornfels	0.7–11
Phyllite/slate	0.5–143
Schist/gneiss	<0.1–18.5
Amphibolite and greenstone	0.4–45
Sedimentary rocks	
Marine shale/mudstone	3–15 (up to 490)
Shale (Mid-Atlantic Ridge)	48–361
Non-marine shale/mudstone	3.0–12
Sandstone	0.6–120
Limestone/dolomite	0.1–20.1
Phosphorite	0.4–188
Iron formations and Fe-rich sediment	1–2900
Evaporites (gypsum/anhydrite)	0.1–10
Coals	0.3–35,000
Unconsolidated sediments	
Alluvial sand (Bangladesh)	1.0–6.2
Alluvial mud/clay (Bangladesh)	2.7–14.7
River bed sediments (Bangladesh)	1.2–5.9
Lake sediments	0.5–44
Glacial till	1.9–170
World average river sediments	5
Stream and lake silt	<1–72
Stream sediment, England & Wales	5–8
Loess silts, Argentina	5.4–18
Continental margin sediments	2.3–8.2
Soils	
Mixed soils	0.1–55
Peaty and bog soils	2–36
Peat	up to 9
Acid sulphate soils	1.5–45
Soils near sulphide deposits	2–8000
Contaminated superficial deposits	
Mining-contaminated lake sediment	80–1104
Mining-contaminated reservoir sediment	100–800
Mine tailings	396–2000
Soils and tailings-contaminated soil	120–52,600
Industrially polluted inter-tidal sediments	0.38–1260
Orchard soils	366–732
Soils below chemicals factory	1.3–4770

Table 3. Summary of documented high-arsenic groundwater provinces and their typical chemical and hydrogeological characteristics.

Groundwater environment/aquifer type	Examples	Typical aquifer conditions	Typical chemical features of high-arsenic groundwaters	Likely mechanisms of arsenic mobilisation
Strongly reducing groundwater	Alluvial/deltaic aquifers of the Bengal Basin, Mekong Valley, northern China, Taiwan, Nepal, Great Hungarian Plain	Young (Quaternary) sediments, often slow groundwater flow, low-lying parts of aquifers; rapidly accumulated sediments	High Fe (>1 mg L^{-1}), Mn (>0.5 mg L^{-1}), NH_4-N (>1 mg L^{-1}), high HCO_3 (>500 mg L^{-1}); low NO_3-N (<1 mg L^{-1}), low SO_4 (<5 mg L^{-1}). Often high P (>0.5 mg L^{-1}). Sometimes high concentrations of dissolved organic matter, including humic acid. Arsenic dominated by As(III)	Reductive desorption of As from metal oxides and reductive dissolution of Fe oxides. Competition between arsenic and other anionic species (especially P)
Oxic groundwater, high pH	Inland basins or closed basins (arid and semi-arid areas): Argentina, Mexico, parts of Nicaragua, western USA, Chile, Spain	Young (Quaternary) sediments, slow groundwater flow, low-lying parts of aquifers; often (not always) volcanic components present	pH typically >8, high HCO_3 (>500 mg L^{-1}), low Fe, Mn, often correspondingly high F, U, B, V, Mo, Se. Some groundwaters have high salinity due to evaporation. Arsenic dominated by As(V)	Desorption of As and other oxyanion-forming elements from metal oxides, especially of Fe and Mn; volcanic ash may be ultimate source for some locations
Geothermally-influenced groundwater	Parts of Kamchatka, Chile, Argentina, Equador, western USA, Japan, New Zealand	Any aquifers affected by geothermal inputs, especially in rift zones	High Si, B, Li, often high salinity (Na, Cl); high pH (>7); increased groundwater temperature; As speciation variable	Mixing of fresh groundwater with geothermal solutions
Groundwater from sulphide mineralised/mining areas	Parts of Burkina Faso, Canada, USA, Thailand, Korea, Poland, Greece, Ghana, Zimbabwe, England	Groundwater in fractures in crystalline rocks or alluvial placer deposits	Oxidising or mildly reducing conditions possible; high SO_4 concentrations (typically hundreds of mg L^{-1} or higher); acidic (unless buffered by carbonate minerals); often increased concentrations of other trace metals (Ni, Pb, Zn, Cu, Cd). Arsenic speciation variable	Oxidation of sulphide minerals