4: Sources and distribution of arsenic in groundwater and aquifers

Pauline L Smedley

Introduction

A rapid growth in research on arsenic occurrence and behaviour in the environment has occurred over the last decade or so. Today, environmental arsenic problems have been recognised and documented in numerous countries across the world, in a range of geological and climatic settings. Arsenic can be mobilised naturally in water and soils through weathering reactions and microbiological activity. Its mobilisation can also be initiated or exacerbated through anthropogenic activities such as metal mining and groundwater abstraction, and in some cases through the use of arsenical pesticides in agriculture and wood preservation. The relative roles of these processes vary from region to region although most workers would accept the dominant role played by natural biogeochemical processes in the mobilisation of As in waters from the areas of the world that have been worst affected.

Drinking water constitutes a major, and possibly dominant, pathway of exposure to As in humans. The WHO provisional guideline value for As in drinking water is 10 µg/L, having reduced from 50 µg/L in 1993. Most industrialised countries also take 10 µg/L as a statutory limit although most developing nations continue to use the pre-1993 WHO guideline value as a national standard because of difficulties with analytical detection and compliance.

Although the concentrations of As in drinking water are usually low, in some circumstances they can reach far in excess of these statutory drinking-water limits and thus cause a potentially severe threat to health. Groundwaters are generally more vulnerable to As contamination than surface waters because of the interaction of groundwater with aquifer minerals and the increased potential in aquifers for the generation of the physicochemical conditions favourable for As release. Indeed, the majority of the world's recognised As-related health problems are linked with long-term use of groundwater for drinking. Some of the best-documented and most severe cases of As-contaminated groundwater occur in aquifers from Asia (e.g. parts of Bangladesh, China, India, Nepal) and South America (e.g. Argentina, Mexico).

A significant amount of the research carried out over the last decade has focused on characterising the occurrence and speciation of As in affected regions across the world and investigating the processes controlling As mobility in groundwaters and aquifers. This chapter describes the key features of high-As groundwater provinces with examples taken from a range of geological and climatic settings, and outlines some of the main biogeochemical processes involved.

Arsenic occurrence in groundwater

Aqueous speciation

Arsenic occurs in the environment in several oxidation states but in water is mostly found as the inorganic forms, arsenite (+3) and arsenate (+5). Organic forms of As are rarely significant in groundwaters but may become more important in waters affected by industrial pollution.

Under oxic conditions at thermodynamic equilibrium, aqueous As is dominated by arsenate oxyanions ($H_2As(V)O_4^-$ or $HAs(V)O_4^{2-}$ depending on pH conditions). Under reducing conditions and over a wide range of pH values, the uncharged arsenite species $H_3AsO_3^0$ predominates (Figure 4.1). However, in natural systems thermodynamic equilibrium is often not achieved because of slow As redox kinetics (e.g. Eary and Schramke, 1990). Much recent evidence suggests that redox kinetics can be significantly accelerated by microbial activity which has been implicated in both the oxidation of arsenite (Wilkie and Hering, 1998; Hering and Kneebone, 2002; Katsoyiannis et al., 2004) and the dissimilatory reduction of arsenate (Oremland and Stolz, 2003). Oxidation of As(III) is also well known to be catalysed by Mn oxides (Oscarson et al., 1981; Driehaus et al., 1995; Katsoyiannis et al., 2004; Amirbahman et al., 2006). Arsenite oxidation rates are pH-dependent, the reaction being slowest in acidic conditions (Eary and Schramke, 1990; Amirbahman et al., 2006). Dissolved As-S species can occur in strongly reducing environments although precipitation of As sulphide minerals limits the concentrations of dissolved As in conditions where sulphide concentrations are high.

Sorption plays an important role in As speciation. Amorphous iron oxides in particular are well-known to have strong sorption capacities for As and therefore exert a strong influence on As mobility (Dzombak and Morel, 1990). Figure 4.2 shows the predominant species in the system As-Fe-H_2O where sorption of As species onto hydrous ferric oxide (Hfo) is taken into consideration. The diagram is subject to the deficiencies of current As thermodynamic databases but illustrates the strong adsorptive capacity of Hfo for As (especially arsenate) at near-neutral pH under oxic to mildly reducing conditions. Under oxic conditions, aqueous As species have increased importance at both high and low pH, the former related to electrostatic repulsion from negatively charged oxide surfaces and the latter to Hfo instability and dissolution. Under strongly reducing conditions, aqueous arsenite is a predominant species over a wide pH range, again linked to Hfo instability. The system illustrated in Figure 4.2 does not consider sulphide species. The strong tendency for sorption to iron oxides at near-neutral pH in oxic conditions is a significant factor in defining the low-As status of most natural groundwaters. The distribution of predominant species shown in Figure 4.2 also goes some way to explaining the high As concentrations observed in some groundwaters under strongly reducing conditions and at extremes of pH.

World distribution of high-As groundwaters

Although the occurrence of several cases of high As concentrations in groundwaters have by now been well-documented, it should be stressed that the concentrations of As in groundwater are usually low or very low. Most groundwaters have concentrations below the WHO provisional guideline value for drinking water of 10 µg/L and many have concentrations below analytical detection limits. In an investigation of some 20,000 groundwater samples from public-supply wells in the USA, Focazio et al. (2000) found that 11% exceeded 10 µg/L and 2% exceeded 50 µg/L, while 55% contained 1 µg/L or less (the detection limit of the method used). Similarly, from some 1200 groundwater analyses from various aquifers in England & Wales reported by Shand et al. (2007), 6% had concentrations exceeding 10 µg/L and 1% had more than 50 µg/L while 68% had concentrations of 1 µg/L or less. This distribution is largely because of the normally strong partitioning of As to solid

minerals, especially iron oxides, under the pH and redox conditions of most groundwaters.

Exceedances of As above drinking-water limits can and do occur in groundwaters from many aquifers of varying lithology. Indeed, the toxicity of As is such that only very small mass transfers of As to water are required for this to be achieved. Increased testing of groundwaters for As in recent years has resulted in the recognition of many examples. However, the occurrence of very high aqueous As concentrations, perhaps one to two orders of magnitude higher than the WHO guideline value, or high concentrations occurring on a regional scale, tend to be associated with a small number of specific geological and hydrogeochemical environments.

Areas of sulphide mineralisation have long been associated with environmental As problems. Sulphide minerals can contain very high concentrations of As and oxidation of the minerals during weathering can lead to As release. Rates of mineral dissolution in such mineralised areas may be enhanced by mining activity and As contamination can be particularly severe in water associated with mine wastes and mine drainage. Geothermal environments may be regarded as the precursors of mineralised areas and geothermal fluids can also contain very high concentrations of As.

A map of the distribution of documented cases of As contamination in groundwater and the environment is given in Figure 4.3 (updated from Smedley and Kinniburgh, 2002). Many of these cases are related to areas of mineralisation and associated mining activity. Examples include several parts of the USA and Canada, northern Burkina Faso, the Lavrion area of Greece, Chattisgarh in India, the Zimapán region of Mexico, Ron Phibun District of Thailand, and parts of south-west England (Thornton, 1994; Komnitsas et al., 1995; Williams et al., 1996; Chakraborti et al., 1999; Pandey et al., 2002; Armienta et al., 2005; Smedley et al., 2007). Some high-As areas are also associated with the occurrence of geothermal fluids. Examples include parts of the USA (Wilkie and Hering, 1998), central America (Criaud and Fouillac, 1989), Japan and New Zealand (Swedlund and Webster, 1998). Contamination of local soils and waters can be severe in such mineralised or geothermal areas, at least locally. Some, though not all, have had an adverse effect on human health through contamination of drinking water.

Other areas with recognised high-As groundwaters are not associated with obvious mineralisation or geothermal activity. Some of these occur in regionally extensive aquifers which can be a major source of drinking water for large populations. Such affected aquifers are found in parts of Argentina, Chile, Mexico, USA, Hungary, Romania, Bangladesh, India, Nepal, Burma, Cambodia, Pakistan, China and Vietnam (Figure 4.3). In several of these aquifers, high As concentrations have only been discovered through the identification of health problems. Some have been identified relatively recently as a result of randomised groundwater testing programmes.

Many differences exist in hydrogeological and geochemical conditions between these regions, but some notable similarities are also apparent. The majority of the recognised high-As groundwater provinces are in young unconsolidated sediments, usually of Quaternary, and often of Holocene, age (<12,000 years). The affected aquifers tend to be in inland closed basins in arid or semi-arid settings (e.g. Argentina, Mexico, south-west USA) (Robertson, 1989; Rosas et al., 1999; Smedley et al., 2002) or large alluvial and deltaic plains (e.g. Bengal delta, Yellow River Plain, Irrawaddy

delta, Red River delta, Mekong valley) (e.g. Chatterjee et al., 1995; Berg et al., 2001; Smedley et al., 2003; van Geen et al., 2003; Polya et al., 2005). The groundwaters with high As concentrations tend to occur under oxic, high pH conditions or under strongly reducing conditions. Some documented case studies from these terrains are described below.

Arsenic in mining and mineralised areas

Arsenic occurs as a major constituent in more than 200 minerals, most of them ore minerals or their weathering products. They include elemental arsenic, arsenides, sulphides, oxides, arsenates and arsenites. These As minerals are relatively rare in nature but are concentrated in some ore zones. The most abundant As ore minerals are arsenopyrite (FeAsS) and arsenian pyrite (Fe(S,As)$_2$). Other As-bearing sulphides in mineralised areas include realgar (AsS) and orpiment (As$_2$S$_3$). Arsenic is also present at high concentrations in the more common sulphide minerals, the most abundant of which is pyrite (FeS$_2$). Concentrations in pyrite, chalcopyrite, galena and marcasite can be very variable but potentially reach several weight % (Table 4.1). High concentrations of As, up to several weight %, can also be found in many oxide minerals and hydrous metal oxides (Table 4.1), especially when formed as weathering products of primary sulphide minerals. Iron sulphides and iron oxides together constitute the most important mineral sources of As in groundwaters and it follows that environmental As problems can arise in mineralised areas where these are particularly concentrated.

Arsenic-related health problems in mineralised areas can arise through exposure to high-As soils and waste piles, release of As to the atmosphere through intensive coal burning (e.g. Ding et al., 2001), or contamination of drinking water.

Ron Phibun District, Thailand

Health problems linked to As in drinking water were first recognised in residents of Ron Phibun District, Nakhon Si Thammarat Province in Thailand (Figure 4.1) in 1987. Over 1000 people in the area were diagnosed with As-related skin disorders, including keratosis and melanosis, particularly in and close to Ron Phibun town (Williams, 1997). At the time of first recognition of the problems, some 15,000 people were thought to be drinking water with more than 50 µg/L As (Fordyce et al., 1995).

The affected area lies within the South-East Asian Tin Belt where primary Sn-W-As mineralisation and alluvial placer tin deposits were mined for over 100 years. Legacies of the mining operations included arsenopyrite and pyrite-rich waste piles, and waste from ore dressing plants and panning. Waste piles from former bedrock mining contained up to 30% As (Williams et al., 1996). Alluvial soils also contain up to 0.5% As (Fordyce et al., 1995).

High As concentrations have been found in both surface waters and shallow groundwaters from the area around the mining activity as a result of natural oxidation of arsenopyrite, mining activity and release following post-mining groundwater rebound (Figure 4.4) (Williams, 1997). Williams et al. (1996) reported concentrations of As in the surface waters reaching up to 580 µg/L. Shallow groundwaters (<15 m deep) from alluvial and colluvial deposits were reported to have extremely high As

4

concentrations, reaching up to 5100 µg/L with 39% of samples having more than 50 µg/L. Conditions in the shallow aquifer were noted to be generally oxic with nitrate concentrations (as N) up to 8.9 mg/L, low Fe concentrations (<0.4 mg/L) and dissolved As being present dominantly as As(V).

Deeper groundwaters from an underlying carbonate aquifer (well depth >15 m) had generally lower As concentrations, although 15% of samples exceeded 50 µg/L (Williams et al., 1996). The presence of more reducing conditions may be responsible for the observed high As concentrations in some of the deeper groundwaters, though leakage of high-As groundwater from the overlying aquifer is also possible.

As a result of the severe health and environmental problems, mining activity in the area has ceased and remediation measures have included transportation of mine waste to confined local landfill (Wattanasen et al., 2006).

Burkina Faso

Although investigations in the 1970s revealed the occurrence of high As concentrations in groundwater from three boreholes from one village in central Burkina Faso (de Jong and Kikietta, 1981), little investigation of As concentrations in groundwater has taken place in the country until relatively recently. Over the last few years, surveys have revealed the presence of high concentrations of As in some groundwaters from northern Burkina Faso and more extensive testing programmes are ongoing.

High groundwater As concentrations have been found in the provinces of Yatenga and Zondoma, close to the town of Ouahigouya in northern Burkina Faso (COWI, 2004; Smedley et al., 2007) (Figure 4.5). Skin disorders (melanosis, keratosis and skin tumours) have also been reported in the region (Oudedraogo, 2006). The As is found in groundwater from Lower Proterozoic (Birimian) volcano-sedimentary rocks which host gold and associated sulphide mineralisation. Gold mining has expanded significantly in Burkina Faso since the 1980s, although production is artisanal. The sulphide minerals present in the mineral veins include pyrite, arsenian pyrite and chalcopyrite which are highly altered, as are the host schists. A prominent mineralised zone runs with a NE–SW orientation in the Mogombouli–Nongfaere–Margo–Tanlili area (Figure 4.5).

Groundwater in the Ouahigouya area is abstracted from hand-pumped boreholes, typically 50–120 m deep, or from more traditional shallow dug wells. Smedley et al. (2007) reported from a study of 45 groundwater samples from the area that most had As concentrations of less than the WHO guideline value of 10 µg/L, although a large range from <0.5 to 1630 µg/L was observed. The high concentrations were found exclusively in borehole waters, concentrations in sampled dug wells being less than 10 µg/L. High concentrations of As in the groundwater appear to be strongly associated with this mineralised zone.

From available data, the groundwater appears to be mainly oxic, with dissolved oxygen present in most samples and median nitrate concentrations of 2.1 and 1.1 mg/L (as N) in groundwater from dug wells and boreholes respectively (Table 4.2). As with the Ron Phibun shallow groundwaters, dissolved As occurs dominantly

5

as As(V) (Figure 4.6). The source of the As in the Ouahigouya area is most likely to be the oxidised sulphide minerals and secondary iron oxides in the mineralised zones.

Arsenic in geothermal waters

High concentrations of As have also long been associated with some geothermal fluids. Geothermal systems are found in diverse tectonic settings including active plate margins (e.g. the Pacific Rim), continental and oceanic hot spots (e.g. Yellowstone, Hawaii respectively) and within-plate rift zones (e.g. the East African Rift) (Webster and Nordstrom, 2003). High As concentrations have been found in geothermal fluids from continental plate margins (e.g. Alaska, Japan, Kamchatka, New Zealand, Philippines) and some continental hotspots (e.g. Yellowstone) but are generally not associated with oceanic hotspots or within-plate rift zones. Stauffer and Thomson (1984) found As concentrations up to 10,000 µg/L and Thompson and Demonge (1996) found concentrations up to 7800 µg/L in hot springs and geysers from Yellowstone National Park. Geothermal brines from the Wairakei geothermal field in New Zealand have As concentrations up to 3800 µg/L (Robinson et al., 1995). White et al. (1963) reported concentrations up to 5900 µg/L in thermal waters from Kamchatka. In contrast, concentrations in the range <0.03–10 µg/L were found in geothermal waters from Iceland (Arnorsson, 2003) and <10–70 µg L^{-1} in geothermal waters from Hawaii (Webster and Nordstrom, 2003). The reasons for the differences in As concentrations in geothermal fluids between these tectonic settings are not fully understood. They may be partially related to the fact that basaltic rocks, which constitute the likely As sources in oceanic settings, have comparatively low As concentrations (ca. 0.05–0.2 mg/kg compared to around 1 mg/kg for more evolved rhyolites, Arnorsson, 2003). Potentially more importantly, increased loads of dissolved As can be derived by leaching from continental crustal material which is present in convergent plate margin and continental hotspot settings.

High concentrations of As in geothermal areas are more commonly reported in surface waters than groundwaters (e.g. Nimick et al., 1998; Wilkie and Hering, 1998), although some groundwaters have been affected (Welch et al., 2000).

High-As geothermal waters are often associated with a characteristic suite of other trace constituents, including Li, B, F, Hg, Sb, Se, Th, and H_2S. Positive correlations with Cl and salinity have also often been reported (Webster and Nordstrom, 2003).

Arsenic in young sedimentary aquifers

In recent years it has become increasingly apparent that some of the most extensive and serious groundwater As problems occur not in areas influenced by metalliferous mineralisation or geothermal activity, but in seemingly ordinary sedimentary aquifers. Indeed, this is one of the most significant reasons why As problems in regions such as the Bengal Basin were not recognised earlier. An important discovery of recent years has been that the sediments composing these aquifers do not tend to contain unusually high As concentrations. Average As concentrations in soils and sediments are in the approximate range 5–10 mg/kg. This compares for example with concentrations of 1–15 mg/kg found in sediments of the Bengal Basin (BGS and DPHE, 2001), 3–29 mg/kg found in the Huhhot Basin of China (Smedley et al., 2003) and 0.6–33 mg/kg in the Red River Basin of Vietnam (Berg et al., 2001). All of these areas are characterised by high groundwater As concentrations. Arsenic release to groundwater

in such areas must therefore occur by a combination of special geochemical and hydrogeological conditions rather than extraordinary As-rich sources.

Many minerals may be involved in the release of As to groundwater and it is often very difficult in a given aquifer to distinguish the principal As mineral sources. There is also a problem in distinguishing between primary and secondary sources. However, it is widely recognised that metal oxides, particularly iron oxides, can and do play an important role in the cycling of As in sedimentary aquifers. The release of As from iron oxides under reducing conditions has been widely documented (e.g. Deuel and Swoboda, 1972; de Vitre et al., 1991; Widerlund and Ingri, 1995). It is also recognised that many of As problems in young sedimentary aquifers occur under strongly reducing conditions. Recent investigations have shown that release of significant concentrations of As can occur under oxidising conditions in aquifers where pH values rise sufficiently high to promote desorption of As(V) from metal-oxide surfaces, or at least inhibit sorption to such surfaces. Some well-documented case studies from both reducing and oxic high-pH aquifer settings are outlined below.

Aquifers in reducing conditions

Bangladesh

The most serious of the world's recognised groundwater As problems without doubt occurs in Bangladesh. The region has been the subject of intensive water testing, hydrogeological and epidemiological investigation, patient identification and treatment and mitigation effort since the groundwater As problem was first recognised by the national government and others in 1993.

The high-As groundwaters of the region are mainly from aquifers of Holocene age which comprise unconsolidated grey micaceous sands, silts and clays deposited as alluvial and deltaic sediments associated with the Ganges, Brahmaputra and Meghna rivers. The sediments are derived from the upland Himalayan catchments and from basement complexes of the northern and western parts of West Bengal. Many studies have observed that the highest concentrations of As in the shallow Holocene aquifer of Bangladesh occur at depths typically around 15–50 m (BGS and DPHE, 2001; Harvey et al., 2002; Klump et al., 2006). Concentrations of As in excess of 1000 µg/L have been found in some shallow groundwaters from the region, although these are relatively rare.

A random national survey of As in groundwater (BGS and DPHE, 2001), using laboratory data for 3208 groundwater samples from the shallow Holocene aquifer (<150 m depth), found that 27% of samples had As concentrations greater than the national standard for As in drinking water of 50 µg/L; 46% exceeded 10 µg/L. A map of smoothed groundwater As distributions is given in Figure 4.7. More recent data from the Bangladesh Arsenic Mitigation and Water Supply Program (BAMWSP, 2005) showed that of almost 5 million boreholes tested nationally using field-test kits, some 30%, had As concentrations greater than 50 µg/L. Each dataset produced for Bangladesh groundwaters demonstrates a very variable distribution of As regionally across the country, with the greatest proportion of exceedances in groundwaters from the south and south-east (Figure 4.7).

In some parts of southern Bangladesh, the majority of boreholes have concentrations greater than 50 µg/L. A recent UNICEF/DPHE survey of groundwaters from 15 upazilas in southern Bangladesh (Rosenboom, 2004) found that of 316,951 boreholes tested, 66% had As concentrations greater than 50 µg/L. In 574 villages tested in the survey, groundwater from every single borehole had concentrations exceeding 50 µg/L. Van Geen et al. (2003) also found, from a survey of 6000 boreholes in Araihazar upazila of central Bangladesh, that some 75% of the shallow boreholes deriving water from Holocene sediments (depth range 15–30 m) had As concentrations above 50 µg/L. The BGS and DPHE (2001) survey also found some villages in southern Bangladesh where more than 90% of the boreholes had As concentrations greater than 50 µg/L.

The results clearly indicate a problem that is very large. BGS and DPHE (2001) estimated, on the basis of the population at the time, that up to 35 million people were drinking groundwater with As concentrations above 50 µg/L and up to 57 millions were drinking water with greater than 10 µg/L. Mitigation efforts have gone some way to reducing the exposure, although this is offset somewhat by the rapid population growth rate and the continuing installation of new boreholes. Many millions of people in the country still remain without access to low-As water.

A combination of the presence of poorly-permeable sediment horizons, particularly as overbank deposits in the upper part of the Holocene sequence and a relative abundance of co-deposited fresh organic matter leads to often poor hydraulic circulation and the generation of strongly reducing conditions in many parts of the aquifers. The groundwaters of the region typically have high concentrations of Fe, Mn and HCO_3 and often high NH_4-N and DOC concentrations, as well as low concentrations of SO_4 and NO_3-N (Table 4.3) (BGS and DPHE, 2001; Harvey et al., 2002; van Geen et al., 2003). In some areas, conditions are even sufficiently reducing for methane generation and 'flaring' wells have been recognised (Ahmed et al., 1998). Such reducing conditions favour the mobilisation of As.

Arsenic speciation studies suggest that a large range in the relative proportions of dissolved As(V) and As(III) exists in the groundwaters of Bangladesh (Acharyya, 1997; Ohno et al., 2005; Bhattacharya et al., 2006a). BGS and DPHE (2001) found the modal proportion of As(III) to be between 50% and 60% of the total As (Figure 4.8). However, detailed studies of groundwaters with high As concentrations have generally shown a strong dominance of As(III) (≥70%) (e.g. Zheng et al., 2005).

Arsenic has been found in the sediments in association with mixed Fe(II)-Fe(III) oxides (Bhattacharya et al., 1997; BGS and DPHE, 2001; Harvey et al., 2002; Horneman et al., 2004; Swartz et al., 2004), phyllosilicate minerals (Breit et al., 2001) and sulphide minerals (e.g. Nickson et al., 2000; Polizzotto et al., 2006). There is as yet little overall consensus on the detailed mechanisms involved in As mobilisation in the Bangladesh aquifers, although most workers would agree that the iron oxides exert a significant control in the process. Under the ambient strongly reducing conditions, dissolution of sulphide minerals is unlikely to be a major release mechanism on a regional scale.

Huhhot Basin, Inner Mongolia, China

Drinking-water related As problems have been recognised in several parts of northern China and a number of studies have documented arsenicosis symptoms among resident populations (Ma et al., 1999; Yu et al., 2007). In Inner Mongolia, high As concentrations have been found in groundwaters from the Ba Men region and Tumet Plain, part of which includes the Huhhot Basin (Luo et al., 1997; Ning et al., 2007).

The Huhhot Basin (area around 80 x 60 km, Figure 4.9) lies on the southern edge of the Gobi Desert and experiences an arid climate with average annual precipitation of around 440 mm. The basin inclines gently south-westwards and is composed of up to 1500 m of poorly-consolidated sediments, a large thickness of which are Quaternary (Smedley et al., 2003). The Quaternary sediments consist largely of coarse-grained alluvial-fan deposits on the basin margins, but with finer-grained lacustrine deposits in the lower-lying parts of the basin further south-west.

Residents in the region depend heavily on groundwater for domestic supply and agriculture. In recent years, traditional dug wells have largely been replaced as drinking-water sources by hand-pumped boreholes which mainly abstract groundwater at shallow levels (typically <30 m). Groundwater is also present within a discrete, deeper aquifer (typically >100 m depth) which is separated from the shallow aquifer by clay layers. Boreholes tapping this deeper aquifer are often artesian in the central parts of the basin.

Smedley et al. (2003) found from a study of 73 samples taken from the Huhhot Basin that groundwaters have a large range of As concentrations: <1–1480 µg/L in the shallow aquifer and <1–308 µg/L in the deep aquifer. They reported that 25% of shallow sources and 57% of deep sources had As concentrations greater than 50 µg/L. Unlike Bangladesh, the deep aquifer is actually more severely affected than the shallow aquifer. The regional distributions of As in the groundwaters from the shallow and deep aquifers combined are shown in Figure 4.9. Groundwaters from the basin margins within the coarser-grained deposits are oxic and have universally low dissolved As concentrations. High As concentrations are generally restricted to the low-lying part of the basin where the sediments are finer-grained and the groundwaters strongly reducing (Smedley et al., 2003). As with Bangladesh, these high-As groundwaters also typically have high concentrations of dissolved Fe, Mn, NH_4-N, P and DOC and low concentrations of SO_4 and NO_3-N (Table 4.4). The aquifer characteristics of the Huhhot Basin clearly have many similarities with those of Bangladesh although high DOC concentrations (often with discoloured waters reflecting an abundance of humic substances) are a particular feature of this region.

The sediments in the Huhhot Basin have been less well studied than those of Bangladesh, but available evidence suggests that here too, iron oxides are likely to have played an important role in the cycling of As in the aquifers. Positive correlations between sediment As and Fe concentrations and the presence of a relatively high proportion of oxalate-extractable As in the aquifer sediments (Smedley et al., 2003) supports this conclusion. The generation of high alkalinity values, as well as depleted $\delta^{13}C$ ratios (to -21 ‰) in some of the high-As groundwaters also suggests that organic matter has been an important factor in the development of the strongly reducing conditions found in the aquifers (Smedley et al., 2003). The high

concentrations of dissolved organic matter may also have played a role in maintaining As in soluble form.

Aquifers in alkaline oxidizing conditions

Chaco-Pampean Plain, Argentina

The Chaco-Pampean Plain covers a vast area of around 1 million square kilometres in central Argentina and represents perhaps the largest high-As groundwater province known. The region experiences a temperate climate with aridity increasing towards the west. Average annual rainfall in La Pampa province in central Argentina is around 600 mm. High-As groundwaters in the region are from shallow aquifers formed in Quaternary deposits of loess (mainly silt) with intermixed rhyolitic or dacitic volcanic ash. These often occur within closed basins (Nicolli et al., 1989; Smedley et al., 2002; Smedley et al., 2005; Bhattacharya et al., 2006b). Investigations carried out in the provinces of Córdoba, La Pampa and Santiago del Estero have shown that many groundwaters from the loess aquifers not only contain high concentrations of As, but also a number of other potentially toxic trace elements including F, V, B, U, Se and Mo. Groundwater salinity is also often high in many of the groundwaters of the region (Nicolli et al., 1989; Smedley et al., 2002; Bhattacharya et al., 2006b).

Groundwaters from La Pampa province are oxic and have neutral to alkaline pH (pH around 7.0–8.7; Table 4.5) (Smedley et al., 2002). The high-As waters are typically of Na-HCO_3 type. Dissolved As is dominated by As(V) (Figure 4.10). Arsenic correlates positively with pH, alkalinity (HCO_3), F and V and weaker positive correlations have been observed with Be, B and U. High salinity is related to evaporation in the semi-arid climatic conditions and high pH and alkalinity are derived dominantly by silicate-weathering reactions. Bhattacharya et al. (2006b) found a more varied range of redox conditions in groundwaters from Santiago del Estero province although conditions there were also mostly oxic with dissolved As being dominated by As(V). The median groundwater As concentration in their study was 54 µg/L (40 samples).

Concentrations of arsenic in the loess sediments of Córdoba were found in the range 5.51–37.3 mg/kg (Nicolli et al., 1989) and those from La Pampa were in the range 3–18 mg/kg (Smedley et al., 2005). Similarly, 7M HNO_3 extracts of Quaternary sediments from Santiago del Estero province were in the range 2.5–7.3 mg/kg (Bhattacharya et al., 2006b). Rhyolitic ash present in the loess deposits may constitute a significant primary source of the As and associated trace elements in the groundwaters (Nicolli et al., 1989), but Fe and Mn oxides in the loess sediments are also likely to play a role in controlling the concentrations of As in the groundwaters. Adsorption of As(V) and other oxyanion species to Fe oxides is likely to be important at neutral pH but less strong under alkaline (pH>8) conditions (Smedley et al., 2002). Therefore, an increase in pH can lead to the release of As, and other co-adsorbed anions, to groundwater.

Mechanisms of arsenic release

Oxidation of sulphide minerals

Numerous primary sulphide minerals occur in association with gold and base-metal deposits in mineralised zones. These minerals include Fe sulphides such as pyrite and arsenopyrite, complex copper sulphides such as enargite and tennantite, as well as the

As sulphides orpiment and realgar. Dissolution of these minerals, particularly the more abundant Fe sulphides, has been recognised as a cause of high concentrations of aqueous As in many mineralised areas of the world. All these minerals oxidise readily in contact with the atmosphere and release As and other potentially toxic trace elements. The As released is repartitioned between water and secondary minerals, including schwertmannite, scorodite and the iron oxides. The oxidation reactions can lead to severe degradation of water quality, particularly in areas strongly affected by mining activity. However, aqueous As is strongly attenuated by adsorption to iron oxides, especially under the acidic and oxidising conditions prevalent in the vicinity of the mineral transformations. High As concentrations in surface waters and groundwaters are therefore typically of localised occurrence.

Release from iron oxides under reducing conditions

In many of the world's recognised high-As aquifers, the generation of reducing conditions appears to have played a critical role in triggering the release of As to groundwater. The presence of organic matter in the system drives a complex series of redox reactions, involving progressive and sequential loss of dissolved oxygen, production of CO_2 from the oxidation of organic carbon, reduction of nitrate, Mn(IV) and Fe(III) and subsequently reduction of SO_4 and possibly production of CH_4. The reductive dissolution of Fe oxides during this process can be responsible for release of As to water. As part of the redox reaction sequence, As(V) is also reduced to As(III). This species is normally less strongly adsorbed to Fe oxides and may therefore trigger a further net release of As from adsorption sites as reduction proceeds (Figure 4.2). The importance of microbial activity in catalysing As release in aquifers has been increasingly recognised in recent years (Oremland et al., 2002; Islam et al., 2004). Several species of microbes have been found to be capable of dissimilatory arsenate reduction and a number of others use arsenate reduction as a detoxification mechanism (Hoeft et al., 2002).

Another potentially important process in the sediments is diagenesis of the iron oxides themselves. This may involve a change in oxide structure (bulk and surface) and oxidation state, which can affect the affinity of the minerals concerned for As binding. A change under reducing conditions from Fe(III) forms to mixed Fe(II)/Fe(III) oxides such as magnetite or green rust has been recognised in Bangladesh and elsewhere (Lovley et al., 1990; BGS and DPHE, 2001; Benner et al., 2002; Horneman et al., 2004).

The role of competitive sorption has been stressed by many studies. Phosphate is a well-known competitor for arsenate on Fe-oxide binding sites (Manning and Goldberg, 1996) and is often present at relatively high concentrations in reducing high-As groundwaters such as those in Bangladesh (BGS and DPHE, 2001), West Bengal (McArthur et al., 2004) and China (Smedley et al., 2003). Phosphate concentrations are sometimes in excess of 1 mg/L and almost always in excess of the concentrations of dissolved As. Bicarbonate, also often present at very high concentrations in high-As groundwaters, has likewise been implicated as a potential competitor for As (Appelo et al., 2002; Charlet et al., 2007). Silica may exert a control on the sorption of As(V) and As(III) (Swedlund and Webster, 1998; Rochette et al., 2000) although its effect was considered less significant for groundwaters in West Bengal by Charlet et al. (2007). The competitive impact of dissolved organic carbon species such as fulvic and humic acids is unclear at present.

The nature and origin of the organic carbon that acts as a driver for redox reactions in high-As aquifers has been much debated. Peat deposits (McArthur et al., 2001) and peaty strata marginal to peat basins (McArthur et al., 2004) have been implicated. Alternatively, disseminated organic matter in the sediments and water have been cited as likely carbon sources (BGS and DPHE, 2001). The introduction of anthropogenic organic carbon through drawdown induced by groundwater pumping has also been proposed as a driver for As release (Harvey et al., 2002; Harvey et al., 2006).

Release of arsenic at high pH

As noted above, under aerobic and near-neutral pH conditions characteristic of many aquifers, adsorption of arsenic to Fe oxides as arsenate is normally strong. Aqueous As concentrations in aquifers are therefore usually low. However, at high pH the adsorption capacity for As(V) is reduced. There are a number of reasons why groundwater pH might increase, but among the most important are uptake of protons by mineral-weathering and ion-exchange reactions, evaporation and inputs from geothermal sources. Uptake of protons during mineral weathering and evaporation can be significant processes in arid and semi-arid regions. Observed pH increases in such environments are commonly associated with the development of groundwater and soil salinity. Inputs of high-pH geothermal waters may be important in maintaining high As concentrations in some alkaline lakes.

The generation of high groundwater pH, especially above pH 8.5, is thought to be an important criterion for the mobilisation of As(V) since sorption to Fe oxides is less favourable under such conditions (Figure 4.2). Such processes are likely to have been responsible for maintaining high groundwater As concentrations in oxidising Quaternary sedimentary aquifers in the semi-arid inland basins of Argentina (Smedley et al., 2002), south-western USA (Robertson, 1989) and Mexico (Rosas et al., 1999) for example. As such a pH increase induces the desorption of a wide variety of oxyanions, other solute oxyanions such as vanadate, uranyl, phosphate and molybdate may also accumulate, as has been observed in some areas (Smedley et al., 2002; Bhattacharya et al., 2006b). As with reducing high-As groundwaters, specific adsorption of these anionic species to oxide binding sites can reduce the load of sorbed As(V). Vanadate has been proposed as a particularly important competitor for As in the oxic Pampean aquifer of Argentina (Smedley et al., 2005). By contrast, some cations, because of their positive charge, may promote the adsorption of negatively charged arsenate (Wilkie and Hering, 1996). Calcium is likely to be the most important cation in this respect because of its abundance in most natural waters and its +2 charge. Aluminium and manganese oxides can also adsorb As to some extent and although less well studied in high-As groundwater contexts, these may be additional sources of or sinks for As in some aquifers.

Variations in groundwater flow

A high degree of spatial variability in arsenic concentrations both areally and with depth has been noted in many of the recognised high-As groundwaters (BGS and DPHE, 2001; Smedley et al., 2002; van Geen et al., 2003; Charlet et al., 2007). Variations in groundwater flow are likely to have been a factor in generating the chemical variations observed. Considerable heterogeneity in sediment texture and composition on a scale of centimetres to metres has been observed in Holocene Bangladesh sediments for instance (BGS and DPHE, 2001) and can be responsible for

large variations in permeability and flow. Low-flow horizons occur in low-lying parts of deltas and the insides of river meanders. These have often been associated with occurrences of localised As 'hotspots'. The accumulation of fine-grained, iron-oxide rich deposits may also be favoured in such low-flow zones.

Lack of aquifer flushing has been considered important in maintaining high groundwater As concentrations in both reducing aquifers and oxic, high-pH aquifers. In the latter case, arid climatic conditions enable high pH values to be maintained as well as restricting groundwater flow. High As concentrations are less likely to occur in well-flushed aquifers.

Impact of man's activities

One question that has not been fully answered by the various studies on As in groundwater carried out to date is the extent to which man's activities have contributed to the As problems in different aquifers. In some sulphide mining areas, man has clearly had a major impact by excavating ore minerals, accumulating and redistributing waste piles and pumping mine effluent. This is particularly the case where mining activity is large-scale and long-term. However, in areas where mining activity is small-scale (e.g. artisanal) and/or initiated relatively recently, the impact is likely to be much smaller. Such is the case in northern Burkina Faso where Smedley et al. (2007) concluded that there was no evidence for the high groundwater As concentrations observed being affected significantly by human activity.

In sedimentary high-As aquifers the impacts of anthropogenic activity are also poorly-defined. Groundwater pumping will have an inevitable effect on groundwater flow and mixing both within and between aquifers and will mean that some changes to the aquifer systems can be expected in the medium to long term. Other potential impacts include inputs of anthropogenic organic carbon and phosphorus to the land surface and seasonal waterlogging of soils due to rice production. The significance of such processes is difficult to quantify for any given region.

Studies in the Bengal Basin during the 1990s concluded that high-As groundwaters there were the result of recent over-pumping of groundwater for rice irrigation which were considered to cause dewatering of the sediments and resultant oxidation of sulphide minerals (e.g. Das et al., 1996). Subsequent studies in the region have dismissed this as a significant mechanism as strongly reducing conditions prevail in the affected parts of the aquifers. Many workers have attributed the redox transformations in the Bengal aquifers to reactions with naturally-occurring organic carbon in a natural process which may have been going on for many thousands of years (BGS and DPHE, 2001; McArthur et al., 2001; McArthur et al., 2004). Harvey et al. (2002) attributed the process to more recent introductions of anthropogenic carbon from the land surface from pollutants, although the evidence for this has been disputed (e.g. Klump et al., 2006).

A number of retrospective studies have suggested that groundwater As concentrations in Bangladesh are higher in older boreholes. DPHE/BGS/MML (1999) suggested that an increase in the percentage of boreholes exceeding 50 μg/L occurred as a function of well age, although possible causes of such changes were not discussed. Variations with well age could occur for example as a result of time-varied changes in spatial or depth distribution of boreholes, which may have responded to increased intelligence

on As spatial distributions since the mid 1990s. However, in Bangladesh, no obvious spatial or depth relationship is discernible from available groundwater-quality data (dataset of BGS and DPHE, 2001).

Van Geen et al. (2003) suggested on the basis of regression of As concentrations as a function of year of borehole installation that small increases occurred with well age over all depth intervals investigated in Araihazar upazila of central Bangladesh. Rosenboom (2004) also found that median As concentrations in boreholes from southern Bangladesh were higher where well age was >25 years old than those of <25 years. They found no significant change in spatial distribution of wells with time, although deep (low-As) tubewells were not present among the older wells in the dataset and shallow dug wells constituted a larger proportion of the old wells.

The results of these studies do not provide strong evidence that groundwater As concentrations in Bengal Basin boreholes have increased with time. However, they do raise some interesting questions about temporal variability and reiterate the need for detailed long-term monitoring. The analysis of survey-type data in this way often involves large numbers of samples and invariably explains only a small proportion of the total variance. A critical analysis needs to be undertaken to ensure that any so-called 'statistically significant' trends are indeed truly significant. Division of the Bangladesh groundwater As data from the BGS and DPHE (2001) database into districts (Figure 4.11) suggests that As concentrations in most districts do not show significant trends as a function of well age, although a few exceptions occur. A closer examination of the local circumstances is needed to establish whether a real temporal variation exists at these sites.

Conclusions

The concentrations of As in natural waters, including groundwater, are usually low. Most are below the WHO provisional guideline value for As in drinking water of 10 µg/L and many below 1 µg/L. Investigations in the last few years have shown that As mobilisation can occur in many aquifers and concentrations can exceed the low drinking-water thresholds in diverse hydrogeological conditions. However, very high As concentrations in groundwater, potentially orders of magnitude greater than threshold values, and extensive areas affected by high-As groundwater tend to be found in a rather limited number of settings.

This chapter has described some of the key features of these settings. They include areas of metalliferous mineralisation and mining, particularly in connection with gold occurrence, areas of geothermal activity, and major alluvial/deltaic plains and inland basins composed of young (Quaternary) sediments. High-As groundwaters in young sedimentary aquifers occur in response to the generation of specific geochemical conditions, among the most important of which appear to be the development of conditions which are either strongly reducing or oxic and high-pH. Although these two cases are geochemically very different, they each favour As mobility in part through the reduced capacity of metal oxides to adsorb As under such conditions. Lack of flushing of groundwater from an aquifer can also be a factor in maintaining high groundwater As concentrations. Low-lying sedimentary basins and delta plains are typically areas of such slow groundwater movement.

The extent to which anthropogenic activity has affected the distributions of As in groundwater in sedimentary aquifers is not well-established although the evidence for a significant deleterious effect on As concentrations is not compelling. Impacts are potentially diverse and include modification of groundwater flow regimes and inputs of chemical pollutants that can affect As speciation. Pumping-induced groundwater mixing will inevitably modify the chemistry of groundwater in a given aquifer over time but such changes could feasibly lead to decreased As concentrations in places as well as increased ones. Further investigations are required for any given aquifer to establish the magnitude of any impacts.

Although the most important triggers for As release in aquifers have become increasingly well-established in recent years, newly discovered areas of contamination are still emerging as a result of increased groundwater testing. Fortunately, new examples on the scale of Bangladesh As contamination have not emerged. However, the discovery of high As concentrations in groundwaters and associated health problems in a mineralised area of Burkina Faso as recently as 2004 reiterates the need for continued reconnaissance testing, especially in areas that are recognised to be potentially at risk.

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Tables

Table 4.1 Ranges of arsenic concentrations in various minerals (data sources: Stewart, 1963; Baur and Onishi, 1969; Boyle and Jonasson, 1973; Dudas, 1984; Arehart et al., 1993; Fleet and Mumin, 1997; Pichler et al., 1999; Paktunc et al., 2006).

Mineral	Arsenic concentration range (mg/kg)
Sulphide minerals	
Pyrite	100–120,000
Pyrrhotite	5–100
Marcasite	20–276,000
Galena	5–10,000
Sphalerite	5–17,000
Chalcopyrite	10–5000
Oxide minerals	
Haematite	up to 29,000
Iron(III) oxyhydroxide	up to 76,000
Magnetite	2.7–41
Maghemite	up to 186,000
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	1–8
Dolomite	<3
Siderite	<3
Sulphate minerals	
Gypsum/anhydrite	<1–6
Barite	<1–12
Jarosite	34–1000
Others	
Apatite	<1–1000
Halite	<3–30
Fluorite	<2

Table 4.2. Summary statistical data for selected chemical constituents in groundwater from the Ouahigouya area of Burkina Faso (after Smedley et al., 2007).

Parameter	Units	Range (n=9)	Median	Range (n=36)	Median
		Wells		Boreholes	
pH		5.2–7.0	5.7	5.8–7.8	7.1
DO	mg/L	1.4–4.5	3.3	<0.1–5.8	0.8
SEC	µS/cm	40–201	65	54–1770	369
SO_4	mg/L	<0.2–33	0.38	<0.2–657	6.8
NO_3-N	mg/L	<0.05–5.5	2.1	<0.05–22	1.05
Fe	mg/L	0.009–0.11	0.03	0.005–0.69	0.008
Mn	µg/L	1.5–1450	18	0.2–99	1.1
As	µg/L	<0.5 – 6.1	1.5	<0.5 – 1630	15

Table 4.3. Statistical summary of chemistry of groundwater from shallow boreholes (<100 m) in Faridpur, central Bangladesh (see Figure 4.7 for location) (after BGS and DPHE, 2001).

Parameter	Units	Range (n=59)	Median
pH		6.4–7.4	6.9
DO	mg/L	<0.1–1.4	<0.1
SEC	µS/cm	344–1400	749
SO_4	mg/L	<0.2–64	<0.2
HCO_3	mg/L	200–848	536
NO_3-N	mg/L	<0.3–4.9	<0.3
NH_4-N	mg/L	<0.06–17.6	1.02
DOC	mg/L	0.1–13.0	1.9
Fe	mg/L	0.05–20	5.6
Mn	mg/L	0.04–4.2	0.69
P	mg/L	<0.2–5	1.5
As	µg/L	<0.5–1460	39

Table 4.4. Statistical summary of groundwater chemistry (boreholes and wells) in the Huhhot Basin, China (Smedley et al., 2003).

Parameter	Units	Range (n=73)	Median
pH		7.0–8.6	7.8
DO	mg/L	<0.1–9.8	0.4
SEC	µS/cm	463–4350	841
SO_4	mg/L	<0.2–1007	34.6
HCO_3	mg/L	182–1150	389
NO_3-N	mg/L	<0.01–34.3	1.13
NH_4-N	mg/L	<0.01–18	0.02
DOC	mg/L	0.3–30.6	3.6
Fe	mg/L	<0.01–4.51	0.07
Mn	mg/L	<0.001–1.29	0.026
P	mg/L	<0.05–3.10	0.18
As	µg/L	<1–1480	5.4

Table 4.5. Statistical summary of selected chemical constituents in groundwater from La Pampa, Argentina (after Smedley et al., 2002).

Parameter	Units	Range (n=108)	Median
pH		7.0–8.7	7.9
SEC	µS/cm	773–17500	2610
DO	mg/L	0.8–9.9	6.1
Cl	mg/L	8.5–4580	192
HCO_3	mg/L	195–1440	653
SO_4	mg/L	6.8–3200	290
As_T	µg/L	<4–5300	150
As(III)	µg/L	<3–110	4.2
Fe	mg/L	<0.006–1.1	0.055
Mn	µg/L	<1–79	2
B	mg/L	0.46–13.8	3.0
F	mg/L	0.03–29	3.8
Mo	µg/L	2.7–990	62

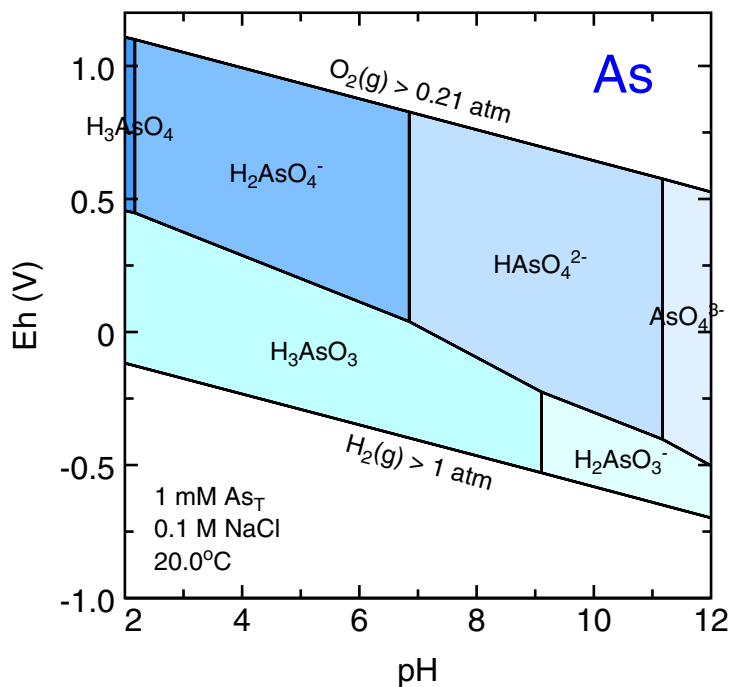|			
U	µg/L	6.2–250	31
V	mg/L	0.02–5.4	0.56

Figures

Figure 4.1. Eh-pH diagram of aqueous As species in a system containing As and NaCl at 20°C and 1 bar total pressure. The speciation calculations were performed using PHREEQC (Parkhurst and Appelo, 1999; Kinniburgh and Cooper, 2004).
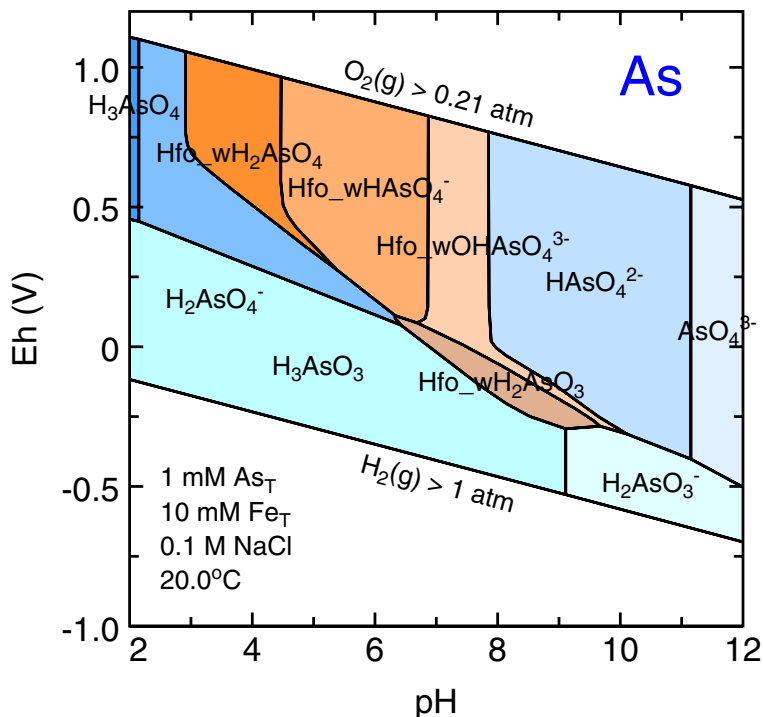

Figure 4.2. Eh-pH diagram for an As-Fe system in which hydrous ferric oxide (Hfo: $(Fe(OH)_3(a))$ precipitates and adsorbs As(V) and As(III) species. Under strongly reducing conditions, Hfo does not precipitate and so cannot adsorb As. The speciation calculations were performed using PHREEQC (Parkhurst and Appelo, 1999;

Kinniburgh and Cooper, 2004) and the Diffuse-Double-Layer model of Dzombak and Morel (Dzombak and Morel, 1990).

Figure 4.3. Summary of the world distribution of documented problems with As in groundwater (>50 µg/L) and the environment (updated from Smedley and Kinniburgh, 2002).
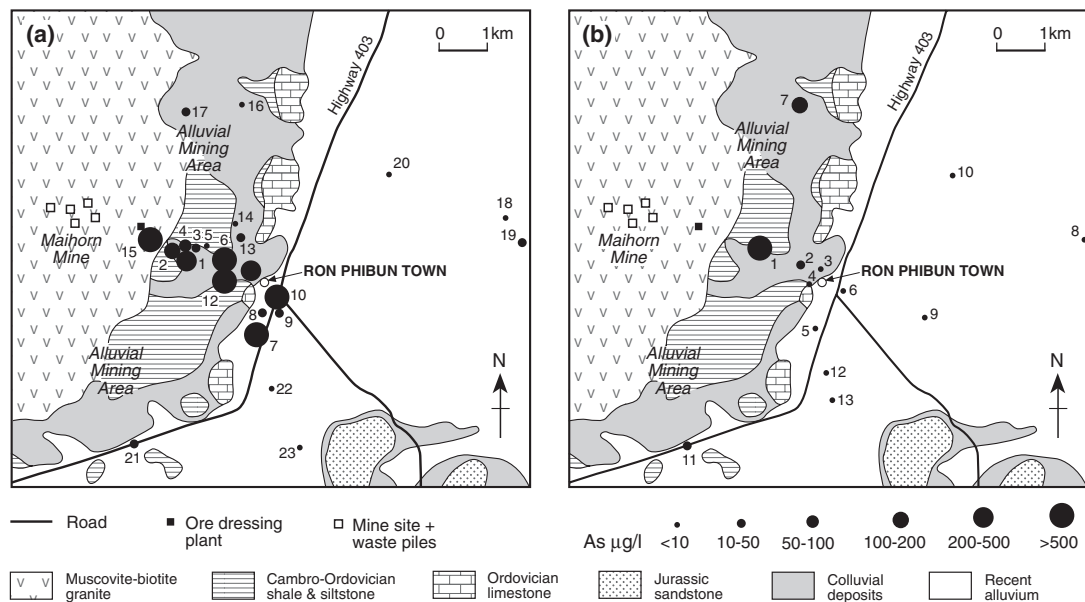
Figure 4.4. Simplified geological map of Ron Phibun area, peninsular Thailand, showing the distribution of As in groundwaters (from Williams et al., 1996). The distributions are (a) As in groundwaters from shallow boreholes in an alluvial aquifer (<15 m depth), (b) As in groundwaters from deeper boreholes (>15 m) in a carbonate aquifer. Sample numbers refer to data given in Williams et al. (1996).

28
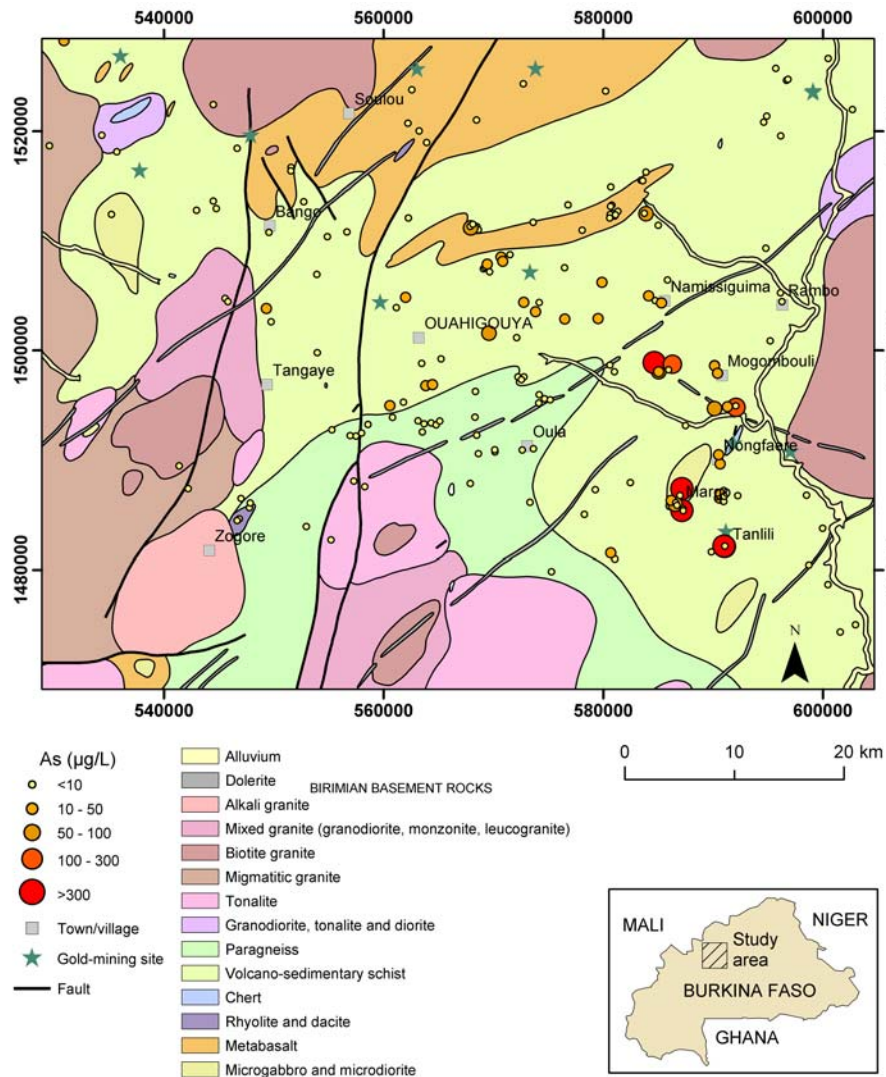
Figure 4.5. Geological map of the Ouahigouya area, northern Burkina Faso, showing the concentrations of As in sampled boreholes and dug wells (data from COWI, 2004; Smedley et al., 2007).
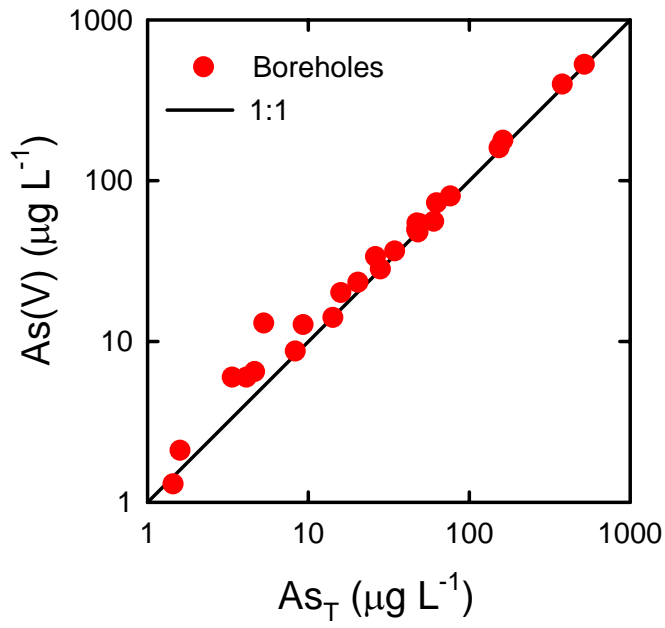
Figure 4.6. Relationship between As(V) and total As in waters from boreholes in the Ouahigouya area of Burkina Faso (after Smedley et al., 2007).
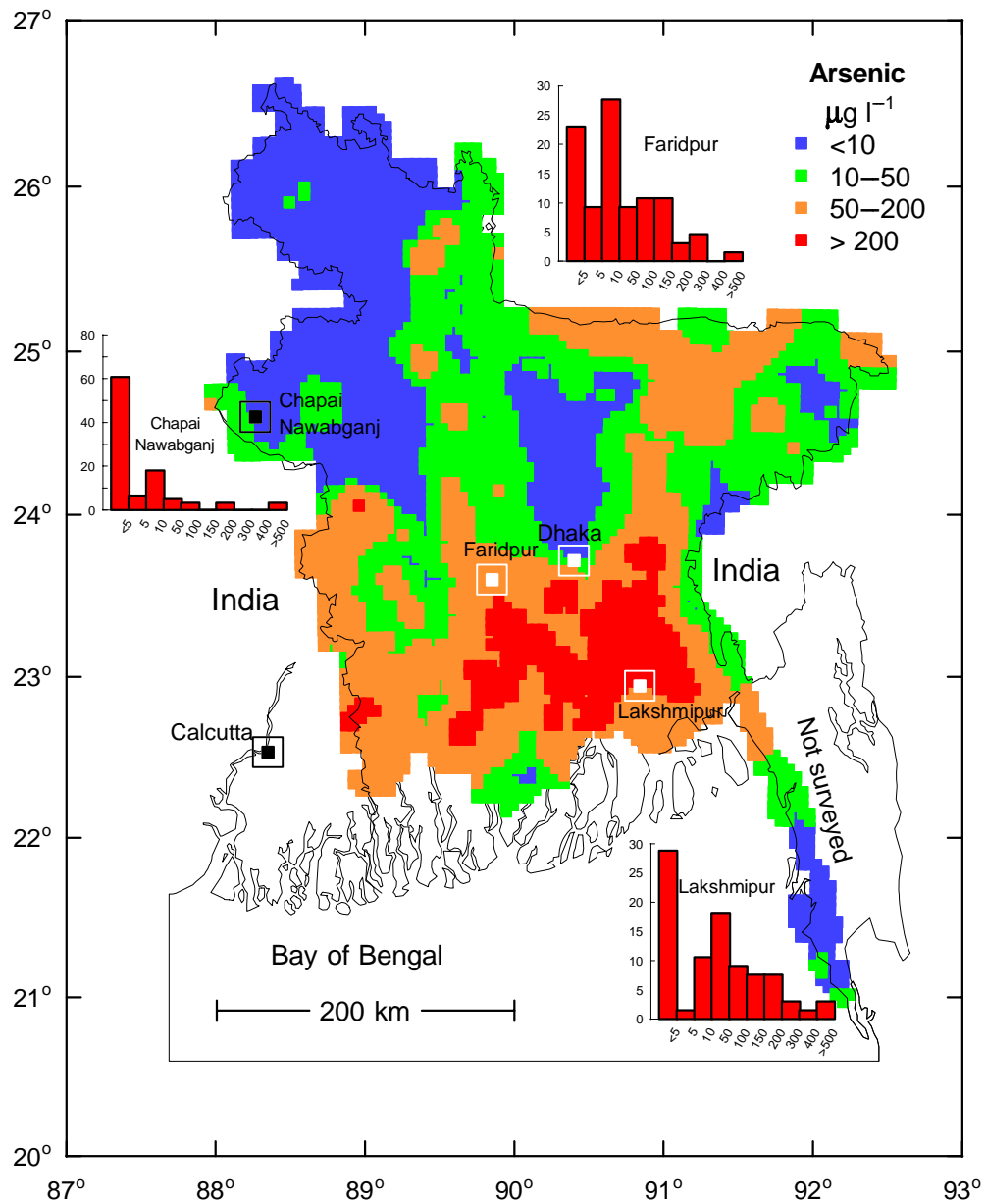
Figure 4.7. Smoothed map of As distributions in groundwater in Bangladesh showing the locations of special study areas described in detail by BGS and DPHE (2001) and histograms of As concentrations in each area. Arsenic distributions based on 3208 groundwater samples from the shallow aquifer (<150 m depth).
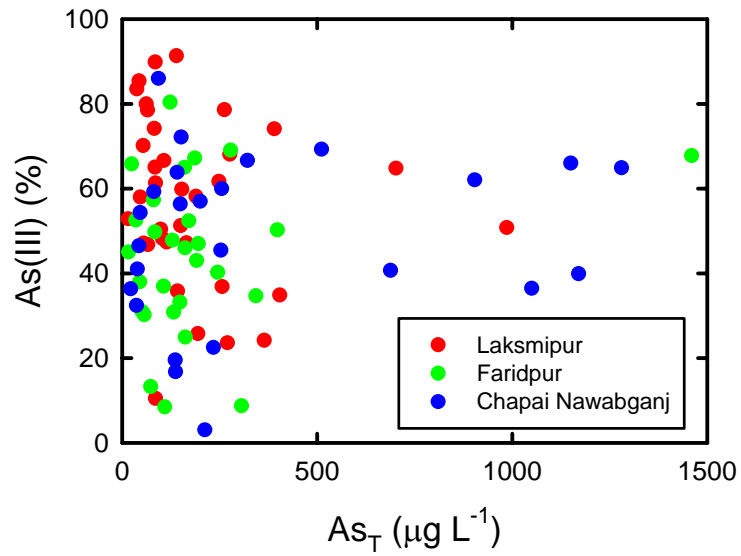
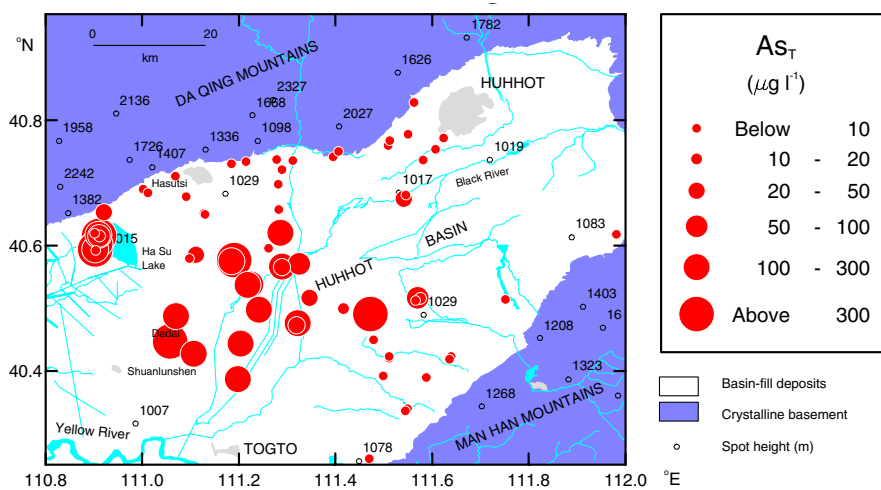Figure 4.8. Percentage of As present as As(III) in groundwaters from three special study areas in Bangladesh.

Figure 4.9. Distribution of total As in groundwaters from the Huhhot Basin of Inner Mongolia (after Smedley et al., 2003).
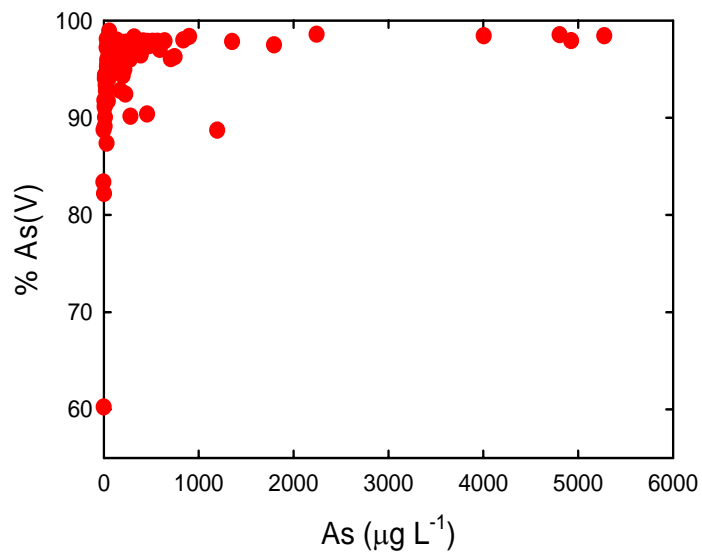
Figure 4.10. Relationship between As(V) and total As in groundwaters from La Pampa province of Argentina (after Smedley et al., 2002).
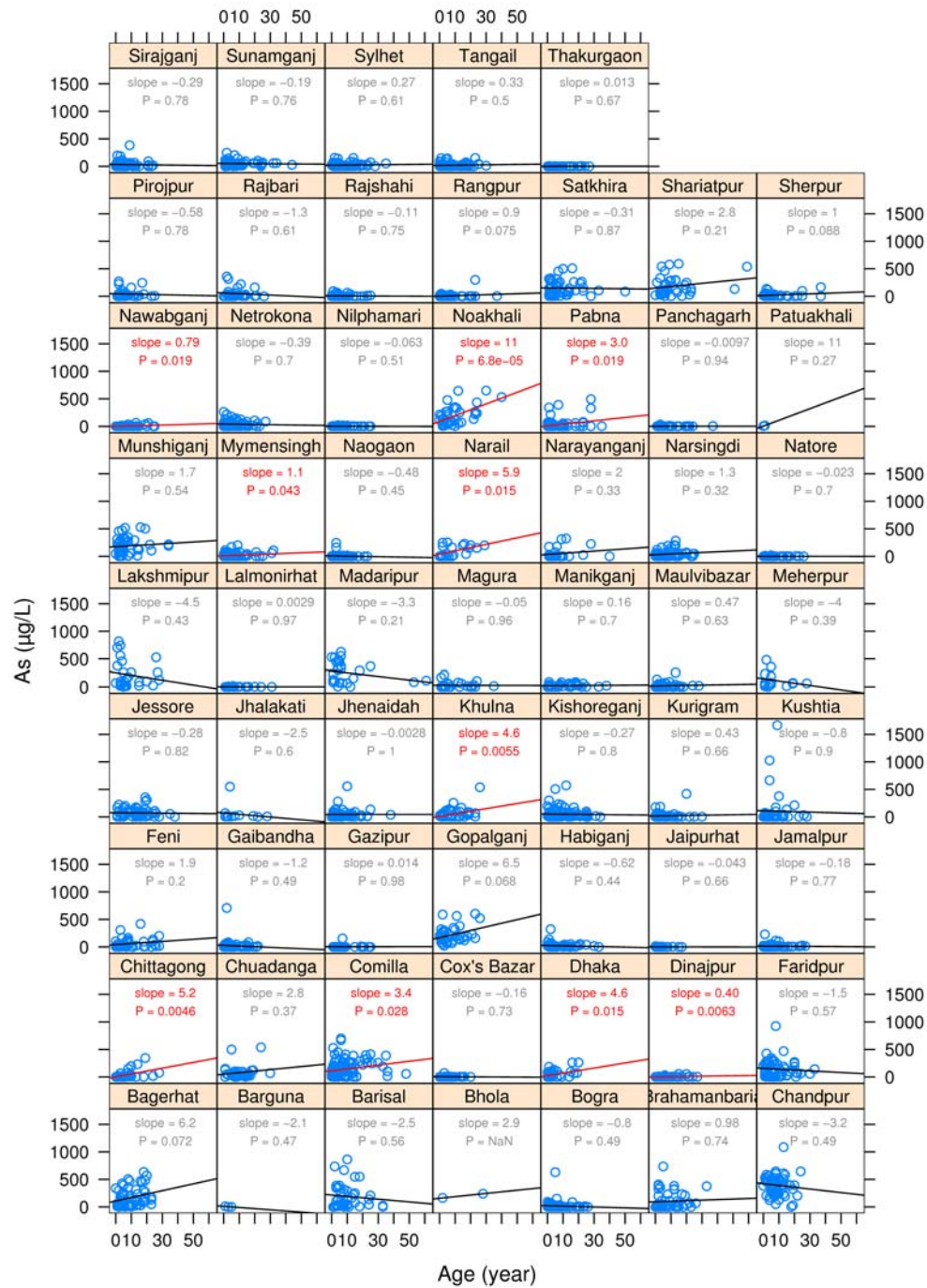
Figure 4.11. Relationship between groundwater As concentration and borehole age in Bangladesh, divided by district. Linear regression has been performed on each data subset and values of slope are given for each district. Statistically significant trends (p <0.01) are highlighted in red. Dataset from BGS and DPHE (2001) (3173 samples, borehole depth <150 m).

34