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Arsenic in Groundwaters from Major Aquifers: Sources, Effects and Potential Mitigation

DFID Summary Report – Project R6491



British Geological Survey
Keyworth
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Arsenic in Groundwaters from Major Aquifers: Sources, Effects and Potential Mitigation

Summary Report – Project R6491

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EXECUTIVE SUMMARY

Arsenic in drinking water poses a serious threat to human health. Natural contamination of water with arsenic occurs over a range of geochemical conditions. In aquifers, mobilisation can occur under strongly reducing (anaerobic) conditions, or under oxidising conditions where groundwater pHs are high. Arsenic is also mobilised in water in areas of sulphide mining and geothermal areas. The greatest potential problems are associated with major aquifers which may be regionally extensive and may affect many millions of people if they are relied upon for drinking water.

High concentrations of arsenic have been found in groundwaters from many parts of the world, including the Bengal Basin (Bangladesh, West Bengal), Inner Mongolia and other parts of northern China, Taiwan, Mexico, Chile, Argentina, Hungary and Romania and parts of the western USA.

In the affected areas of Argentina, northern Chile and Mexico, climatic conditions are arid or semi-arid and geochemical reactions generate often Na-HCO₃ dominated groundwaters with high pH values (commonly greater than 8). Some are saline as a result of evaporation. The aquifers are typically aerobic with arsenic present dominantly as arsenate (As(V)). The sources of arsenic are considered to be mainly iron oxides, but manganese or aluminium oxides may be additional sources. Mobilisation occurs by desorption from oxide surfaces under high-pH conditions.

In the affected regions of Bangladesh and West Bengal, Taiwan, Inner Mongolia, Hungary and Romania, groundwater conditions are generally highly reducing with no dissolved oxygen and often high iron, manganese and ammonium concentrations. Groundwaters are usually fresh where rainfall is high but salinity may increase in some shallow groundwaters where the climate is arid (e.g. Inner Mongolia) or in coastal areas affected by saline intrusion. Groundwater pHs in these areas are usually near-neutral. Some, though not all, have high concentrations of humic acid. In these groundwaters, arsenic is present as both As(III) and As(V), though the former often dominates.

Arsenic problems in groundwaters from western USA occur under either reducing or oxidising conditions. Many arsenic problems in the USA are also mining-related and some are geothermal.

Investigations of groundwaters have been carried out in three major aquifers where arsenic problems are recognised: northern La Pampa Province of Argentina, the Huhhot Basin of Inner Mongolia and three study areas in Bangladesh. In each region, the investigations have characterised the spatial distributions of arsenic and other inorganic constituents, the nature of the arsenic source and the mechanisms of mobilisation in the groundwaters. Suitable mitigation measures have also been considered.

Groundwaters from La Pampa are oxidising. The arsenic is present almost entirely as As(V). Arsenic concentrations in pumped groundwaters often have high arsenic concentrations, 95% in excess of the WHO guideline value for arsenic in drinking water of 10 µg l⁻¹. Concentrations up to 5.3 mg l⁻¹ were found. The groundwaters are often also affected by high salinity and high concentrations of bicarbonate, fluoride, vanadium, boron, molybdenum, selenium, nitrate and uranium. Many of the groundwaters have high pH values (>8) and arsenic, fluoride, bicarbonate, vanadium in particular correlate positively with pH. Shallow groundwaters, especially where the water table is close to the ground surface, have increased salinity as a result of evaporation. Localised topographic depressions are often the sites of locally-high arsenic concentrations as these represent aquifer discharge zones with limited groundwater movement. Arsenic in porewaters from one such zone was found at up to 7.8 mg l⁻¹. The high concentrations are not related to evaporation. High dissolved arsenic concentrations are also correlated with increased arsenic concentrations in the sediments. Arsenic mobilisation is believed to be caused by pH-dependent desorption from oxide minerals in the aquifer.

Groundwaters from northern La Pampa exemplify a large part of the Chaco-Pampean Plain of Argentina, covering a large area of some 10^6 km². Groundwater quality in the region is poorly characterised as a whole but serious contamination with arsenic and the other constituents is suspected to be regionally extensive as a result of similar geological and hydrogeological conditions.

By contrast, groundwaters with high arsenic concentrations from Bangladesh are typically highly reducing, with low sulphate concentrations indicating sulphate reduction. Arsenic concentrations have been found at up to $2400 \mu\text{g l}^{-1}$ and the arsenic is present as both As(III) and As(V) in variable proportions. The distribution of high-arsenic groundwaters is extremely patchy. The arsenic problems are restricted to shallow groundwaters from the Holocene alluvial aquifer. Deep groundwaters from >150 m depth usually have low arsenic concentrations. High-arsenic groundwaters have been found in large parts of Bangladesh, including isolated 'hotspots'. The worst arsenic problems, with the highest average concentrations, occur to the southern and eastern parts of Bangladesh, in the low-lying parts of the Bengal delta where sediments are largely fine-grained and relatively enriched in iron oxides.

In the Huhhot Basin of Inner Mongolia, Holocene aquifers consist of alluvial and lake sediments. Groundwater compositions progress from being aerobic and containing dissolved oxygen and nitrate on the basin margins, towards becoming increasingly reducing down the groundwater flow gradient. In the low-lying parts of the basin, sulphate reduction has occurred under the reducing conditions. Arsenic concentrations are low in the oxidising groundwaters but are high in the reducing waters where sulphate reduction has occurred. Analysed concentrations of arsenic reach up to $1500 \mu\text{g l}^{-1}$ in the shallow groundwaters (<100 m) and up to $308 \mu\text{g l}^{-1}$ in the deep groundwaters (>100 m). Deep groundwaters are often artesian and many contain high concentrations of humic acid (up to 64 mg l^{-1}). In the high-arsenic waters, As(III) is usually the dominant form. Some of the shallow groundwaters also have high concentrations of fluoride (up to 3.5 mg l^{-1}).

The arsenic provinces in Argentina, Bangladesh and Inner Mongolia share the characteristics of young age of aquifer sediments (i.e. Quaternary, thousands to tens of thousands of years old) and slow groundwater flow rates. Hence, in each case the sediments have had little opportunity for removal of arsenic and other trace elements by groundwater flushing.

Understanding of the geochemical conditions under which arsenic problems have arisen in the documented cases throughout the world leads to the conclusion that other parts of the world with similar geological and hydrogeological conditions may be similarly affected but not yet recognised. These include some of the large Holocene alluvial/deltaic plains where reducing conditions occur. Examples are the Red River and Mekong deltas of Vietnam and bordering Cambodia, the Irrawaddy delta of Burma, the Nile delta of Egypt and the Indus Valley of Pakistan, as well as inland alluvial basins such as the Yellow River Plain. In addition, geological conditions similar to those in central Argentina exist in parts of Paraguay and Uruguay.

Large deltas and alluvial plains are amongst the most densely populated places on earth. As the aquifers are usually highly productive in these areas, groundwater is also often heavily used. Presence of arsenic problems in the groundwaters can therefore have very serious consequences for human health. Rapid reconnaissance surveys need to be undertaken in these 'at risk' areas to establish the scales of arsenic contamination.

RECOMMENDATIONS

Recent experience with arsenic has shown that there can be natural groundwater-quality problems in areas previously thought to have good quality. Following this experience, water providers need to make careful reassessments of groundwaters in individual countries to identify 'at risk' aquifers. Although geochemical studies have shown that a number of other chemical constituents in water can be useful indicators of potential arsenic problems, these cannot be used reliably to predict the concentrations of arsenic in individual wells. Therefore, there is no substitute for measuring arsenic itself. A number of recommendations are proposed for water providers and policy makers as guidance for identifying potential problems and providing a basis for appropriate mitigation strategies:

- identify 'at risk' aquifers in a given country using experience of other affected areas (young sediments, large alluvial and delta plains; sulphide mining areas; geothermal areas; see Figure 6.1);
- identify laboratories suitable for arsenic analysis within a given country and develop arsenic-testing capability;
- promote the development of better field-test kits that are both reliable and sufficiently sensitive to measure concentrations down to around $5 \mu\text{g l}^{-1}$ for mass screening of large numbers of wells. Provide adequate training in their use;
- carry out rapid reconnaissance surveys of arsenic in identified aquifers on a *random* basis using the local infrastructure. The density of the survey need not be high (commensurate with the scale of groundwater abstraction and the size of the aquifer at risk);
- create a central water-quality database and map the data. Use GPS to locate sites;
- depending on the capabilities and aquifer type, test for other constituents of potential health concern (e.g. Fe, Mn, NO_3 , F, B, U, Mo, Se, salinity), at least on a subset of samples;
- resample identified problem areas at a higher density, possibly every well used for drinking water;
- consider a strategy for longer-term monitoring of arsenic;
- given individual situations, consider the most appropriate approaches to mitigation and act upon them.

1. INTRODUCTION

Most natural waters have low concentrations of arsenic, typically less than $10 \mu\text{g l}^{-1}$. However, high concentrations can occur under a range of geochemical and hydrogeological conditions and long-term use of high-arsenic waters for potable supply can be seriously detrimental to health. Groundwaters are generally more vulnerable to arsenic contamination than surface waters because of natural geochemical processes and the high solid:solution ratios in aquifers.

Arsenic problems are especially of concern in developing countries where technologies and financial resources are often not available to enable water treatment before use. However, the problem has become more serious in both developed and developing nations because of moves to reduce statutory drinking-water limits for arsenic in response to toxicological data. The current WHO guideline value for arsenic in drinking water is $10 \mu\text{g l}^{-1}$ although many countries still use the pre-1993 WHO guideline value of $50 \mu\text{g l}^{-1}$ as their national standard. Some still have no national standard. Pressure to reduce national standard values is likely to increase as a result of the reduction of both the US-EPA MCL (maximum contaminant level) and the EC MAC (maximum admissible concentration) for arsenic in drinking water. A value of $5 \mu\text{g l}^{-1}$ has been recommended by the US-EPA and a value of $10 \mu\text{g l}^{-1}$ is due to be incorporated into the EC regulations by the end of 2000.

The detrimental effects of arsenic in drinking water are well established. Arsenic is toxic and carcinogenic. Chronic ingestion has been associated with a number of problems, particularly skin disorders, the most common being pigmentation changes and keratosis. Additional reported symptoms include other more serious dermatological problems (e.g. skin cancer), cardiovascular (blackfoot disease, Raynaud's syndrome, hypertension), neurological, respiratory and hepatic diseases as well as diabetes mellitus (e.g. Gorby, 1994). A number of internal cancers have also been linked with arsenic in drinking water, particularly lung, bladder, and prostate cancer (e.g. Smith et al., 1992; 1998). Clinical symptoms of arsenic poisoning and their relative prevalence seem to vary between affected regions. Many studies have shown a dose-response relationship for various symptoms (e.g. Tseng et al. 1968; Hopenhayn-Rich et al., 1996).

Latency periods of several years to tens of years have been noted for the development of arsenic-related health problems, a factor which in part explains why many of the problems have only recently emerged, despite several years of groundwater use (Albores et al., 1979; Cebrián et al., 1983; 1994). Latency periods are likely to vary as a result of several factors, including arsenic dose, length of exposure, gender and general health and nutrition.

Many of the advanced and most serious clinical symptoms are incurable. Others can be treated and mild symptoms can go into remission provided a supply of low-arsenic drinking water can be provided at a relatively early stage. Provision of arsenic-free alternative sources is therefore an important priority for exposed populations.

In the developing countries where arsenic-related health problems exist, the problems have generally arisen over the last few years or decades as a result of development of groundwater resources for potable use. These were developed as a positive alternative to traditional surface-water sources which suffer from bacteriological contamination and can be the causes of severe water-borne diseases. Groundwater has been highly successful in reducing the incidence of such bacterial diseases but problems from natural contamination by inorganic constituents has, until now, often gone unmonitored. Arsenic and fluoride are the two most severe of these inorganic contaminants.

This report summarises the hydrogeochemical investigations carried out in three of the worst-affected groundwater arsenic provinces in the world: Argentina, Bangladesh and Inner Mongolia. More detailed accounts of these areas are listed on page iv.

2. ARSENIC IN GROUNDWATER AND THE ENVIRONMENT

2.1 Arsenic in minerals

Although minerals containing arsenic as a major constituent are rare, more than 200 such minerals exist in nature, including elemental arsenic, arsenides, sulphides, oxides, arsenates and arsenites. Most are ore minerals and their alteration products. The greatest concentrations of these therefore occur in mineralised areas associated with basement rocks and active volcanic areas. In these, As is commonly found in close association with the transition metals as well as Cd, Pb, Ag, Au, Sb, P, W and Mo. The most abundant and widespread arsenic ore mineral is arsenopyrite, FeAsS. Arsenopyrite, together with the other dominant As-sulphide minerals realgar and orpiment, are only formed under high-temperature conditions in the earth's crust.

Arsenic is also often present in varying concentrations in other common rock-forming minerals. As the chemistry of arsenic follows closely that of sulphur, the greatest concentrations of the element tend to occur in sulphide minerals, of which pyrite (FeS₂) is the most abundant. Concentrations in pyrite, chalcopyrite (CuFeS₂) and galena (PbS) can be very variable, even within a given grain, but in some cases reach up to several weight percent (Table 2.1). Pyrite is an important component of ore bodies and is formed in low-temperature sedimentary environments under anaerobic conditions. Sedimentary (authigenic) pyrite plays a very important role in present-day geochemical cycles and is present in the sediments of many rivers, lakes and the oceans, as well as many aquifers.

High arsenic concentrations are also found in many oxide minerals and hydrous metal oxides, either as part of the mineral structure or as adsorbed species. Concentrations in iron oxides can also reach weight percent values (Table 2.1), particularly where they form as the oxidation products of primary iron sulphide minerals which have an abundant supply of arsenic. Sorption of arsenate to hydrous iron oxides is particularly strong (Goldberg, 1986; Manning and Goldberg, 1996). Sorption to hydrous Al and Mn oxides may also occur if these oxides are present in quantity (e.g. Peterson and Carpenter, 1986; Manning and Goldberg, 1996). Arsenic may also be sorbed to the edges of clays and on the surface of calcite. These sorption reactions are responsible for the relatively low (and non-toxic) concentrations of arsenic found in most natural waters.

Arsenic concentrations in phosphate minerals are variable but can also reach high values, for example up to 1000 mg kg⁻¹ in apatite. However, phosphate minerals are much less abundant than oxide minerals and so make a correspondingly small contribution to the arsenic content of most sediments. Arsenic can also substitute for Si⁴⁺, Al³⁺, Fe³⁺ and Ti⁴⁺ in many mineral structures and is therefore present in many other rock-forming minerals, albeit at much lower concentrations. Most common silicate minerals contain around 1 mg kg⁻¹ or less. Carbonate minerals usually contain less than 10 mg kg⁻¹ (Table 2.1).

The most important arsenic-bearing minerals are therefore the sulphide and oxide minerals. These have strong controls on arsenic mobilisation and retardation in the environment. Those minerals containing arsenic as a major element may cause local environmental problems, but are quantitatively less significant.

2.2 Hydrogeochemistry of arsenic

Arsenic is perhaps unique among the heavy metalloids in its capacity to mobilise at the pH values of natural groundwaters and over a wide range of redox conditions. Arsenic can occur in the environment in several oxidation states (-3 to +5) but in natural waters is mostly found as an oxyanion, as arsenite (As(III)) or arsenate (As(V)). Most other toxic trace metals occur in solution as cations (e.g. Pb²⁺, Cu²⁺, Ni²⁺, Cd²⁺, Co²⁺, Zn²⁺) and hence solubilise preferentially in acidic conditions. Selenium is

Table 2.1. Arsenic concentrations in the major rock-forming minerals (Smedley and Kinniburgh, 2000)

Mineral	As concentration range (mg kg ⁻¹)	Mineral	As concentration range (mg kg ⁻¹)
Sulphide minerals:		Carbonate minerals:	
Pyrite	100–10000	Calcite	1–8
Pyrite (gold ores)	300–54000	Dolomite	<3
Pyrrhotite	5–100	Siderite	<3
Marcasite	20–600	Sulphate minerals:	
Galena	5–10000	Gypsum/anhydrite	<1–6
Sphalerite	5–17000	Barite	<1–12
Chalcopyrite	10–5000	Jarosite	34–1000
Oxide minerals:		Other minerals:	
Haematite	up to 160	Apatite	<1–1000
Fe oxide (undiff'd)	up to 2000	Halite	<3
Fe(III) oxyhydroxide	up to 76000	Fluorite	<2
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		

mobile as an oxyanion under oxidised conditions, but is immobilised as Se metal under reducing conditions. Chromium can also be mobilised as a dissolved oxyanion under oxidising conditions, but forms cation species (Cr³⁺) in reducing environments and hence behaves like other trace cations. These factors, together with the high toxicity of As, render the element one of the most serious problems for potable groundwater quality.

The arsenate form of arsenic is dominant in oxidising conditions, whilst arsenite is more abundant in reducing conditions. It is generally accepted that most of the arsenic in natural waters is present in inorganic form. Organic arsenicals (e.g. monomethylarsonic acid, MMAA, and dimethylarsinic acid, DMAA) are known to be produced by reactions involving bacteria and algae. These have been observed, albeit in small quantities, in some river waters and porewaters but are less significant in groundwaters.

As noted above, mobility of As in water is limited principally by adsorption onto iron oxides and hydroxides, as well as possibly oxides of aluminium and manganese. Iron oxides in particular have long been recognised as effective arsenic scavengers and indeed, precipitation of these is used as an effective water-treatment technology for removal of As from water (e.g. Wilkie and Hering, 1996). Adsorption is controlled strongly by both pH and As speciation (As(III) or As(V); Dzombak and Morel, 1990). Adsorption to iron oxides is less strong at high pH (>7) and As(V) is generally more strongly bound than As(III). The sorption capacity of the poorly ordered amorphous iron oxides is greater than the more structured forms (goethite, haematite) due to the larger surface area and hence increased availability of binding sites in amorphous forms (Dzombak and Morel, 1990). Arsenic can also be mobilised under reducing conditions by the reductive dissolution of the iron oxides themselves. Binding efficiency may be affected by competition effects from other dissolved constituents. Presence of dissolved phosphate in particular has been shown to compete with arsenic (especially As(V)), for binding sites on iron oxides and hydroxides (e.g. Livesey and Huang, 1981; Manning and Goldberg, 1996).

2.3 World distribution of arsenic problems

Cases of serious contamination of water with arsenic can exist in mineralised areas where sulphide minerals are concentrated. In such areas, contamination is often made worse by mining activities which accelerate sulphide oxidation. Arsenic problems also exist in areas affected by geothermal activity (Figure 2.1). Whilst these two types of conditions can produce serious problems with often very high concentrations of arsenic in water, they tend to be localised to the area of mining or geothermal activity and are usually easily recognised. Far more serious potentially, are the problems from arsenic in groundwaters from major aquifers which can be regionally very extensive and may affect large numbers of people if they are used significantly for potable supply.

A number of large aquifers worldwide have been identified with problems from arsenic occurring at concentrations above $50 \mu\text{g l}^{-1}$, often significantly so. The most noteworthy occurrences are in parts of West Bengal and Bangladesh, Taiwan, northern China, Argentina, Chile, Mexico, Hungary, Romania and parts of south-west USA (Figure 2.1). Many of the occurrences affect aquifers over large areas and can therefore have a potentially severe impact on human health. It is unfortunate that many of the occurrences are in parts of the developing world where infrastructure and economy is least well able to mitigate the problems and hence raw groundwater is commonly used for drinking without treatment.

2.3.1 Natural occurrences in aquifers

Bangladesh and West Bengal

In terms of the population exposed, arsenic problems in groundwater from the alluvial and deltaic aquifers of Bangladesh and West Bengal represent the most serious occurrences identified globally. Concentrations in groundwaters from the affected areas have a very large range from $<0.5 \mu\text{g l}^{-1}$ to around $3200 \mu\text{g l}^{-1}$ (e.g. DPHE/BGS/MML, 1999; CGWB, 1999; Table 2.2). Several health problems have been identified in affected populations. Skin disorders including pigmentation changes and keratosis are the most common manifestations, although skin cancer has also been identified. Several thousand patients have been identified with arsenic-related skin lesions.

The affected aquifers are generally shallow (less than 100–150 m deep), of Holocene age and comprise mixed alluvial and deltaic sands, silts and clays associated with the Ganges, Hugli, Brahmaputra and Meghna river systems. The groundwaters are typically strongly reducing. Deeper groundwaters from the sediment sequence (>100 –150 m depth, probably of Pleistocene age) have generally low arsenic concentrations ($<10 \mu\text{g l}^{-1}$).

Taiwan

Taiwan was perhaps the first area arsenic-affected area to be identified. Awareness of the problem began during the 1960s and health problems have been well-documented (e.g. Tseng et al., 1968; Chen et al., 1985). The region has been the focus of much epidemiological work over the last 30 years. Taiwan is the classic area for the identification of blackfoot disease but other peripheral vascular disorders as well as cardiovascular disease, neurological problems, diabetes and internal cancers have also been identified.

Kuo (1968) observed arsenic concentrations in groundwater from south-west Taiwan in the range 10 – $1800 \mu\text{g l}^{-1}$ (mean $500 \mu\text{g l}^{-1}$, $n=126$). Chen et al. (1995) found concentrations in the range 437 – $897 \mu\text{g l}^{-1}$ (mean $671 \mu\text{g l}^{-1}$). The high concentrations are present in deep (100–280 m) artesian groundwaters from sediments which include black shale (Tseng et al., 1968). The groundwaters are therefore likely to be strongly reducing. This is supported by the fact that the As is present largely as As(III) and the groundwaters commonly have high Fe and Mn and low Se concentrations (Chen et al., 1994; 1995). Some of the groundwaters appear to contain methane (Tseng et al., 1968) as well as humic substances. Groundwater from shallow wells has low arsenic concentrations (Guo et al., 1994).

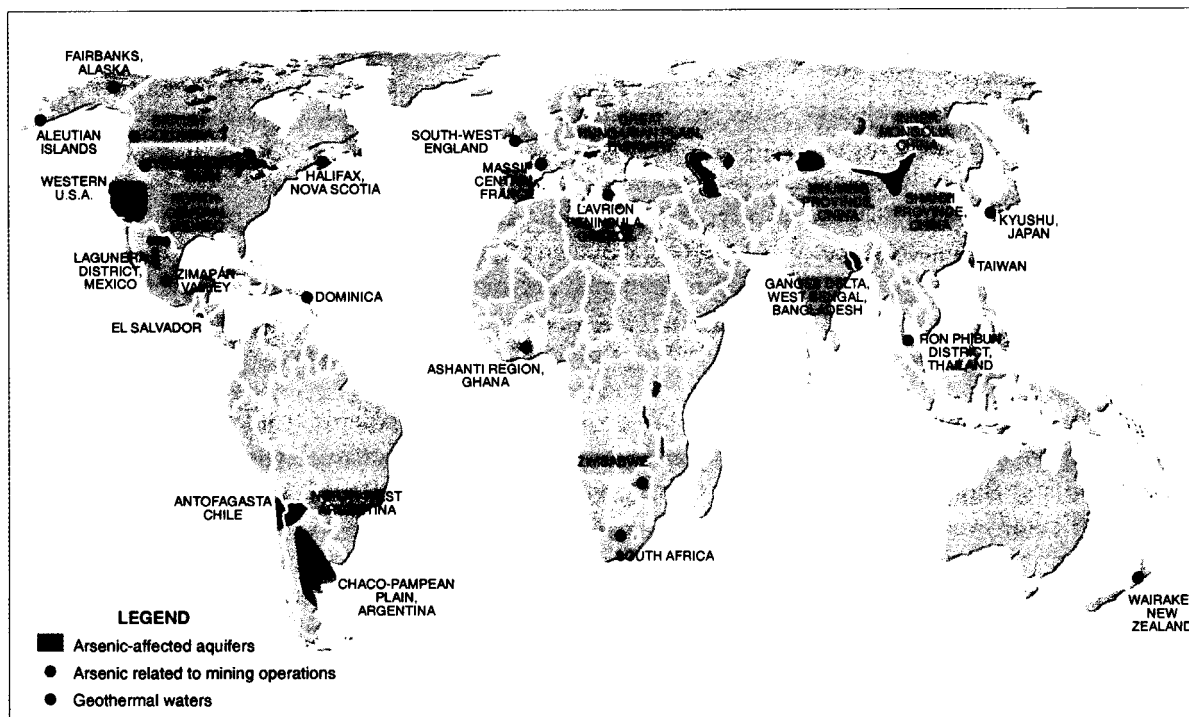


Figure 2.1. Distribution of documented world problems with arsenic in groundwater in major aquifers as well as mining-related problems and geothermal sources

Northern China

Arsenic occurrence has been found at high concentrations in groundwaters from Inner Mongolia as well as Xinjiang and Shanxi Provinces (Figure 2.1; Wang, 1984; Wang and Huang, 1994; Niu et al., 1997). The first cases of arsenic poisoning were recognised in Xinjiang Province in the early 1980s. Wang (1984) found concentrations up to $1200 \mu\text{g l}^{-1}$ in the groundwaters. Wang and Huang (1994) reported arsenic concentrations of between $40 \mu\text{g l}^{-1}$ and $750 \mu\text{g l}^{-1}$ in deep artesian groundwater (up to 660 m) from the Dzungaria Basin on the north side of the Tianshan Mountains (extending over a distance of some 250 km). Arsenic concentrations were found to increase with depth. Shallow (non-artesian) groundwaters had observed As concentrations between $<10 \mu\text{g l}^{-1}$ and $68 \mu\text{g l}^{-1}$.

In Inner Mongolia, high concentrations of As have been identified in groundwaters from aquifers in the Huhhot Basin, Ba Meng Region, and Tumet Plain. These areas include the cities of Boutou and Togto. In the affected region, As-related disease has been identified by Luo et al. (1997). Recognised health effects include lung, skin and bladder cancer as well as prevalent keratosis and skin-pigmentation problems.

Hungary and Romania

Concentrations of arsenic up to $150 \mu\text{g l}^{-1}$ have been found in groundwaters from alluvial sediments in the southern part of the Great Hungarian Plain (Figure 2.1; Varsányi et al., 1991). The plain consists of a thick sequence of subsiding Quaternary sediments. Groundwaters in deep parts of the basin (80–560 m depth) with high As concentrations are reducing with high concentrations of Fe and NH_4 and many have reported high concentrations of humic acid (up to 20mg l^{-1} ; Varsányi et al., 1991). The groundwaters have highest arsenic concentrations in the lowest parts of the basin, where the sediment is fine-grained. High arsenic concentrations have also recently been identified in groundwaters from neighbouring Romania (Gurzau, 2000).

Table 2.2. Summary of documented cases of naturally-occurring As problems in world groundwaters (includes some mining cases)

Country/ Region	Area (km ²)	Population exposed*	Concentration ranges ($\mu\text{g l}^{-1}$)	Aquifer type	Groundwater conditions	Reference
Bangladesh	150,000	ca. 3×10^7	<0.5 to 2500	Holocene alluvial/ deltaic sediments. Abundance of solid organic matter	Strongly reducing, neutral pH, high alkalinity, slow groundwater flow rates	DPHE/BGS/MML (1999)
West Bengal	23,000	6×10^6	<10 to 3200	As Bangladesh	As Bangladesh	CGWB (1999); POA (1999)
China:						
Taiwan	4000	? 10^5 (formerly)	10 to 1820	Sediments, including black shale	Strongly reducing, artesian conditions, some groundwaters contain humic acid	Kuo (1968), Tseng et al. (1968)
Inner Mongolia (Huhhot Basin (HB), Bayingao, Hexi, Ba Meng, Tumet Plain)	4300 (HB) ?30,000 total	? ca. 10^5 in HB	<1 to 2400	Holocene alluvial and lacustrine sediments	Strongly reducing conditions, neutral pH, high alkalinity. Deep groundwaters often artesian, some have high concentrations of humic acid	Luo et al. (1997), Ma et al. (1999), Zhai et al. (1998), Sun et al. (1999), this study
Xinjiang (Tianshan Plain)	38,000	? (500 diagnosed)	40 to 750	Holocene alluvial plain	Reducing, deep wells (up to 660 m) are artesian	Wang and Huang (1994)
Shanxi				Alluvial plain	?Reducing	Sun et al. (1999)
Hungary (Danube Basin)	110,000	29,000	<2 to 150	Quaternary alluvial plain	Reducing groundwater, some high in humic acid	Varsányi et al. (1991)
Argentina (Chaco- Pampean Plain)	10^6	? 5×10^6	<1 to 11500 (up to 7800 in porewaters)	Holocene and earlier loess with rhyolitic volcanic ash	Oxidising, neutral to high pH, high alkalinity. Groundwaters often saline. As(V), accompanied by high B, V, Mo, U. Also high As concentrations in some river waters	Nicolli et al., 1989; Nicolli and Merino (2000), this study
Northern Chile (Antofagasta)	125,000		100 to 1000	?Quaternary volcanicogenic sediment	Generally oxidising. Arid conditions, high salinity, high B. Also high-As river waters	Cáceres et al. (1992), Karcher et al. (1999)
South-west USA:		3×10^5 (tot)				
Basin & Range, Arizona	200,000		up to 1300	Alluvial basins, some evaporites	Oxidising, high pH. As (mainly As(V)) correlates positively with Mo, Se, V, F	Robertson (1989)

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

*Exposed refers to population drinking water with As $>50 \mu\text{g l}^{-1}$ (drinking-water standard of most countries)

Mexico

The best-documented region of Mexico with arsenic-related health problems is the arid Lagunera Region of north central Mexico. Groundwaters from the region are predominantly oxidising with neutral to alkaline pH (6.3 to 8.9, Del Razo et al., 1990). Arsenic concentrations have been found in the range $8 \mu\text{g l}^{-1}$ to $624 \mu\text{g l}^{-1}$ (average $100 \mu\text{g l}^{-1}$, $n=128$; Del Razo et al., 1990). Most of the groundwaters have As dominantly present as As(V). Some groundwaters also have high concentrations of fluoride (up to 3.7 mg l^{-1} ; Cebrián et al., 1994).

High As concentrations have also been identified in groundwaters from the state of Sonora in north-west Mexico. Wyatt et al. (1998) found concentrations in the range $2\text{--}305 \mu\text{g l}^{-1}$. The arsenic concentrations were also positively correlated with fluoride, observed fluoride concentrations being up to 7.4 mg l^{-1} .

Western USA

Much research has been carried out on As in groundwater in the USA. Occurrences in groundwater are therefore noted to be widespread, although exceedances are often reported relative to lower guideline values than reported in other affected countries. Welch et al. (1999) noted increased concentrations in groundwaters from parts of Maine, Michigan, Minnesota, South Dakota, Oklahoma and Wisconsin. Of 17,000 water analyses, they found that around 40% exceeded $1 \mu\text{g l}^{-1}$ (percentage above $50 \mu\text{g l}^{-1}$ unknown). The As is thought to derive from various sources, including natural dissolution/desorption reactions, geothermal water and mining activity. The main areas where naturally-high concentrations of As occur in groundwater in the USA are in the south-western states (e.g. Nevada, California, Arizona, Utah). These areas include some localised mining- and geothermal-related As occurrences, but many of the affected groundwaters are from alluvial basins which occur under a range of redox conditions.

Welch and Lico (1998) reported high As concentrations (often exceeding $100 \mu\text{g l}^{-1}$, but with extremes up to $2600 \mu\text{g l}^{-1}$) in shallow groundwaters from the southern Carson Desert of Nevada. These are apparently largely present under reducing conditions, having low dissolved-oxygen concentrations and high concentrations of dissolved organic C, Mn and Fe. The high As concentrations were thought to be due to evaporative concentration of groundwater, together with the influence of redox and desorption processes involving metal oxides.

In groundwaters from the Tulare Basin of the San Joaquin Valley, California, redox conditions in the aquifers are highly variable and increased arsenic concentrations are found in both reducing and oxidising conditions. The proportion of As present as As(III) is also variable but increases in different wells with depth. The groundwaters from the Basin are often strongly affected by evaporative concentration with resulting high concentrations of dissolved solids (Fujii and Swain, 1995).

High groundwater arsenic concentrations occur in alluvial aquifers under oxidising conditions in the Basin & Range Province in Arizona (Robertson, 1989). Dissolved arsenic is present predominantly as As(V) and is observed to correlate well with Mo, Se, V, F and pH. Oxidising conditions apparently persist in the aquifers down to significant depths (600 m) despite significant groundwater age (up to 10,000 years old; Robertson, 1989).

Argentina

Large parts of the Chaco-Pampean Plain of central Argentina are known to have groundwaters with high concentrations of As. Nicolli et al. (1989) found that 84% of samples investigated in Córdoba Province had concentrations greater than $50 \mu\text{g l}^{-1}$. Nicolli and Merino (2000) found that 89% of groundwaters investigated in the Carcarañá River Basin (Córdoba and Santa Fe Provinces) exceeded $50 \mu\text{g l}^{-1}$ (most falling in the range $50\text{--}250 \mu\text{g l}^{-1}$). The aquifers are Quaternary loess deposits with

some volcanic ash. Groundwaters are neutral to slightly alkaline (pH up to 8.3) and many are saline with high alkalinity and associated high concentrations of F, V, U, Mo and Se. River waters in the region have also been found to have high As and V concentrations (Lerda and Prosperi, 1996).

High As concentrations have also been identified in groundwaters from north-west Argentina. The Andean village of San Antonio de los Cobres in Salta Province has groundwaters with As concentrations in the range 200–500 $\mu\text{g l}^{-1}$. The cause is uncertain but sulphide minerals are known to be present in the volcanic bedrocks and thermal springs have been found with reported As concentrations up to 10 mg l^{-1} (Vahter et al., 1995). Thermal springs discharge to surface waters and these also have high As concentrations (up to 800 $\mu\text{g l}^{-1}$).

Chile

Health problems related to As in drinking water were first recognised in northern Chile in 1962. Typical symptoms included skin-pigmentation changes, keratosis, skin cancer, cardiovascular problems and respiratory disease (Zaldivar, 1974). More recently, As ingestion has been linked to lung and bladder cancer (Smith et al., 1998) and other symptoms have been reported (Karcher et al., 1999). High As concentrations have been recorded in surface waters and groundwaters from Administrative Region II (incorporating the cities of Antofagasta, Calama and Tocopilla) of northern Chile (Cáceres et al., 1992). The region is arid and water resources are limited. The aquifers are composed of volcanogenic sediments. High groundwater As concentrations are accompanied by high salinity (due to evaporation) and high B concentrations. Arsenic values below 100 $\mu\text{g l}^{-1}$ in surface waters and groundwaters are apparently quite rare, and concentrations up to 21,000 $\mu\text{g l}^{-1}$ have been found. The As is present in waters mostly as As(V).

2.3.2 Mining and mineralised areas

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

Some As problems have also been reported in Ghana. Ghana is an important gold-producing country and mining has taken place since the late 19th century. The most important mining area is the Ashanti Region. The gold is associated with sulphide mineralisation, particularly arsenopyrite. Arsenic has mobilised as a result of arsenopyrite oxidation, induced or made worse by the mining activity. Around the town of Obuasi, high concentrations have been found in soils close to the mines and treatment works (Amasa, 1975; Howell, 1992; 1993). Some high concentrations have also been reported in river waters close to the mines (Smedley et al., 1996a).

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

from shallow hand-dug wells, had low concentrations as a result of sorption of arsenic onto ferric hydroxides under the low pH conditions of the groundwaters (median pH 5.4 in dug wells; 5.8 in tubewells; Smedley et al., 1996a; b).

Arsenic contamination from mining activities has been identified in numerous areas of the USA, many of which have been summarised by Welch et al. (1988). Groundwater from some areas has very high As concentrations locally (up to 48,000 $\mu\text{g l}^{-1}$). Documented cases include the Fairbanks mining district of Alaska (Wilson and Hawkins, 1978; Welch et al., 1988), the Coeur d'Alene mining area of Idaho, (Mok and Wai, 1990), Leviathan Mine, California (Welch et al., 1988), Kelly Creek Valley, Nevada (Grimes et al., 1995), Iron Mountain, California (Nordstrom et al., 2000) and Lake Oahe in South Dakota (Ficklin and Callender, 1989; Table 2.2).

Other documented cases of mining-related contamination include the Lavrion region of Greece (Komnitsas et al., 1995), the Zimapán Valley of Mexico, parts of south-west England (Thornton and Farago, 1997), among others.

Arsenic problems have also been recognised in mineralised areas where sulphide minerals undergo natural oxidation. Boyle et al. (1998) found As concentrations of 0.5–580 $\mu\text{g l}^{-1}$ in groundwaters close to sulphide mineral veins in volcanic rocks from Bowen Island, British Columbia. Schreiber et al. (2000) also recorded arsenic concentrations in groundwaters from Wisconsin up to 12,000 $\mu\text{g l}^{-1}$ where affected by oxidation of pyrite and marcasite by periodic dewatering of the aquifers.

2.3.3 Geothermal sources

Arsenic associated with geothermal waters has been reported in several parts of the world, including hot springs from parts of the USA, Japan, New Zealand, Chile, El Salvador, Kamchatka, France, Dominica and Argentina (e.g. Ellis and Mahon, 1977; Welch et al., 1988; Criaud and Fouillac, 1989).

In the USA, reported occurrences include Honey Lake Basin, California (As up to 2600 $\mu\text{g l}^{-1}$), Coso Hot Springs, California (up to 7500 $\mu\text{g l}^{-1}$), Imperial Valley, California (up to 15000 $\mu\text{g l}^{-1}$), Long Valley, California (up to 2500 $\mu\text{g l}^{-1}$) and Steamboat Springs, Nevada (up to 2700 $\mu\text{g l}^{-1}$) (Welch et al., 1988). Geothermal waters in Yellowstone National Park also contain As and have given rise to high concentrations (up to 370 $\mu\text{g l}^{-1}$) in waters of the Madison and Missouri Rivers (Nimick et al., 1998). Geothermal inputs from Long Valley, California are believed to be responsible for high concentrations (20 $\mu\text{g l}^{-1}$) of As in the Los Angeles Aqueduct which provides the water supply for the city of Los Angeles (Wilkie and Hering, 1998).

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

In New Zealand, Robinson et al. (1995) found As in groundwater from the Wairakei geothermal field at a concentration of 3800 $\mu\text{g l}^{-1}$. River and lake waters receiving inputs of geothermal water from the Wairakei, Broadlands, Orakei Korako and Atiamuri geothermal fields were found to have concentrations up to 121 $\mu\text{g l}^{-1}$, although they diminished significantly downstream away from the geothermal input areas. Although severe contamination of the environment has often been documented in these areas, the impact on groundwaters used for potable supply is usually minor.

3. LA PAMPA, ARGENTINA

3.1 Background

The Province of La Pampa in central Argentina lies within the Chaco-Pampean Plain, a vast area of around $1.2 \times 10^6 \text{ km}^2$ extending from the Paraguay border in the north of the country to the Patagonian Plateau in the south and to the east of the Andean Cordillera. Groundwater is a vital resource and is relied upon heavily for potable supply and agriculture. However, significant quality problems occur from high concentrations of harmful elements such as As, F, $\text{NO}_3\text{-N}$, B, Mo and U as well as high salinity. Arsenic constitutes one of the most severe health threats. Symptoms typical of chronic arsenic poisoning, including skin lesions and some internal cancers, have been recorded in some of the areas. Occurrence of high fluoride concentrations in the drinking water has also given rise to dental fluorosis. The extent of the groundwater-quality problems is not well-defined, but is believed to cover large parts of the Chaco-Pampean Plain.

A hydrogeochemical investigation has been carried out in northern La Pampa Province, in an area covering around $110 \text{ km} \times 70 \text{ km}$ (Figure 3.1). The investigation has included sampling of over 100 groundwater sources used for potable supply, agriculture and domestic purposes. Two shallow boreholes (30 m depth) were also drilled in the eastern part of the study area to i) investigate porewater quality and variations with depth, ii) investigate sediment chemistry and determine likely mineral sources of arsenic and iii) relate porewater chemistry to sediment chemistry to determine the main arsenic mobilisation processes. Results have been assessed to determine the nature and scale of arsenic and other water-quality problems in La Pampa and to provide recommendations on the most appropriate mitigation measures. The study is described in more detail by Smedley et al. (2000a, b).

3.2 Geology and hydrogeology

Shallow aquifers of the area are composed of Quaternary loess deposits which comprise mainly brown silts and fine sands with some volcanic material (ash, including glass and pumice). The sediments have been altered diagenetically and have abundant calcrete and occasional manganese-oxide nodules and cements. Wells and boreholes in the study area range in depth from around 150 m in the west to $<20 \text{ m}$ in the east, as a result of topographic variation. Most abstract groundwater from the Pampean loess aquifer. The aquifer is unconfined as a result of the presence of relatively coarse-grained, sandy deposits in the topmost horizons.

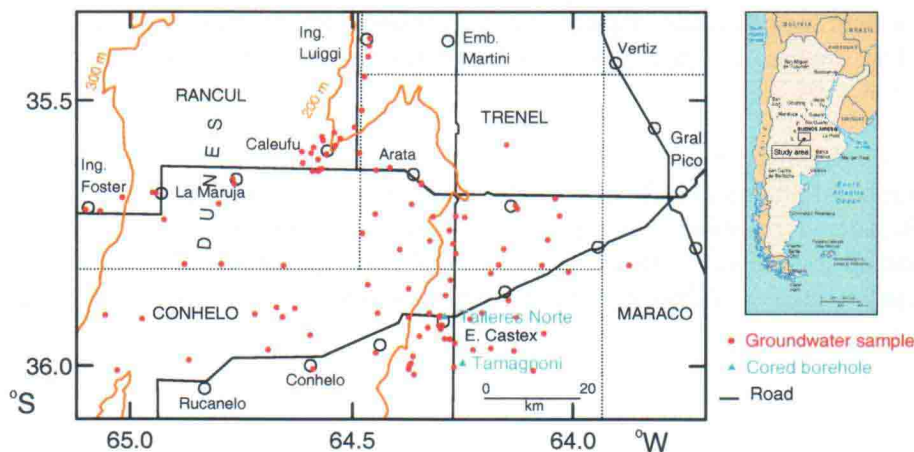


Figure 3.1. Sketch map of the study area of northern La Pampa

The annual groundwater recharge has been estimated as 30 mm in the study area and as 60–100 mm beneath the sand dunes in the western part (Smedley et al., 2000a). These estimates are rather low, considering that there are no major discharge zones within the area. It is likely that much of the rainfall is evaporated or transpired and does not infiltrate below the root zone. As a result of the semi-arid climatic conditions, low recharge totals and lack of significant topographic variation, groundwater flow in the aquifer is considered to be very slow. The travel time for groundwater to flow a distance of 100 km (i.e. from the west to the east of the study area) is estimated to be in the order of 10^4 years.

Groundwater flow in localised topographic depressions is of particular hydrogeological and geochemical significance. Where the water table intersects or is close to the surface, groundwater discharge is likely for at least part of the year. Such depressions are the sites of evaporation from the soil or water surface and in extreme cases, encrustations of evaporated salts can occur along the depression margins.

Depressions may also be zones of recharge where the water table does not rise to the ground surface and where rainfall is sufficiently intense to cause runoff and ponding of water. Localised zones of recharge underlying depressions are characterised by relatively fresh groundwater of low salinity (Bannert, 1974). The appropriate scenario for a given area will depend on the position of the water table in relation to the ground surface and may vary seasonally and with longer-term climatic variation.

A model of groundwater flow (Figure 3.2) involves regional flow from the higher regions of the west towards the east. Superimposed on this are shallow flow cells which occur in zones of higher recharge where pockets of younger groundwater are found. To the east, the terrain levels out and groundwater recharge is more diffuse. Here, groundwater in discharge zones can experience localised evaporation. Discharge zones may also cause deeper, regionally-flowing, groundwaters to be brought nearer to the

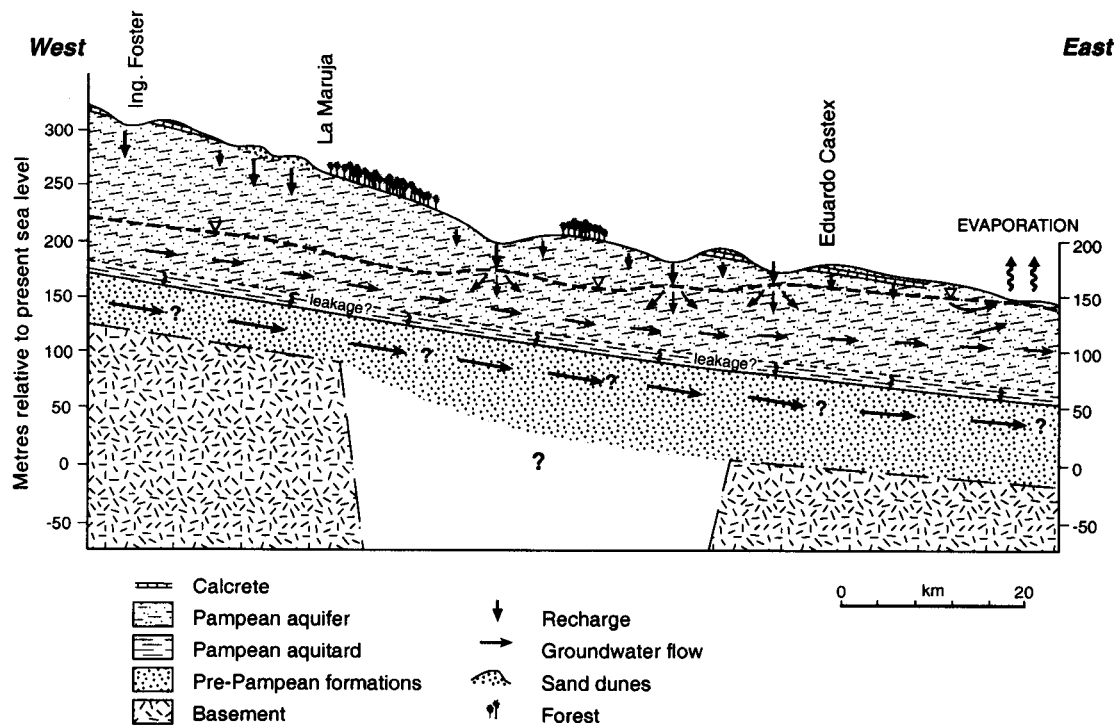


Figure 3.2. Model of groundwater flow in the Pampean aquifer of northern La Pampa. Regional flow follows the topographic gradient but shallow flow cells are set up as a response to local topographic variations. Depressions can act as small-scale groundwater discharge zones and can have a major impact on groundwater chemistry

Table 3.1. Summary of groundwater quality in northern La Pampa

Determinand	Units	Min	Max	Median	Mean	n
Well depth	m	6.0	140	29.1	42	103
Water level	m	2.1	129	14.1	28	93
Temperature	°C	16.1	29.1	19.8	20.6	108
pH		6.99	8.66	7.85	7.82	108
Eh	mV	131	492	325	327	102
Dissolved oxygen	mg l ⁻¹	0.8	9.9	6.1	5.9	106
SEC	µS cm ⁻¹	773	17520	2610	3341	108
Ca	mg l ⁻¹	1.55	599	20.9	45.1	108
Mg	mg l ⁻¹	2.01	521	21.5	45.3	108
Na	mg l ⁻¹	120	3100	543	667	108
K	mg l ⁻¹	3.3	70.6	11.8	14.8	108
Cl	mg l ⁻¹	8.5	4580	192	458	108
SO ₄	mg l ⁻¹	6.80	3170	285	432	108
HCO ₃	mg l ⁻¹	195	1440	653	716	108
NO ₃ -N	mg l ⁻¹	<0.2	144	9.06	19.35	108
NO ₂ -N	mg l ⁻¹	<0.003	0.169	0.003	0.011	108
NH ₄ -N	mg l ⁻¹	<0.01	0.14	<0.02	0.01	108
Si	mg l ⁻¹	21.1	39.2	29.2	29.6	108

SEC: specific electrical conductance

surface. Water-balance calculations for the aquifer suggest that a significant proportion of groundwater flow occurs within deeper, more permeable, aquifers below the loess (Figure 3.2).

3.3 Summary of groundwater chemistry

Groundwaters from sampled wells and boreholes have very variable chemical compositions. Sodium-bicarbonate waters are dominant. Salinity is high in many with concentrations of total dissolved solids (TDS) up to 11400 mg l⁻¹ (Table 3.1). Groundwaters also typically have high alkalinity (up to 1440 mg l⁻¹ as HCO₃) and a large range of concentrations of total As: As_T (<4–5300 µg l⁻¹), F (0.03–29 mg l⁻¹), B (0.5–13.8 mg l⁻¹), V (0.02–5.4 mg l⁻¹), Mo (2.7–991 µg l⁻¹) and U (6.2–248 µg l⁻¹; Table 3.2). Of the groundwaters investigated, 95% exceed 10 µg l⁻¹ (the WHO guideline value for As in drinking water) and 73 % exceed 50 µg l⁻¹ (the Argentine national standard). In addition, 83 % exceed the WHO guideline value for F (1.5 mg l⁻¹), 99 % for B (0.3 mg l⁻¹), 39 % for Mo (70 µg l⁻¹) and 100 % for U (2 µg l⁻¹). A limited number of Se analyses also indicate some groundwaters have high concentrations (up to 40 µg l⁻¹).

The groundwaters are universally oxidising with high dissolved-oxygen concentrations and redox

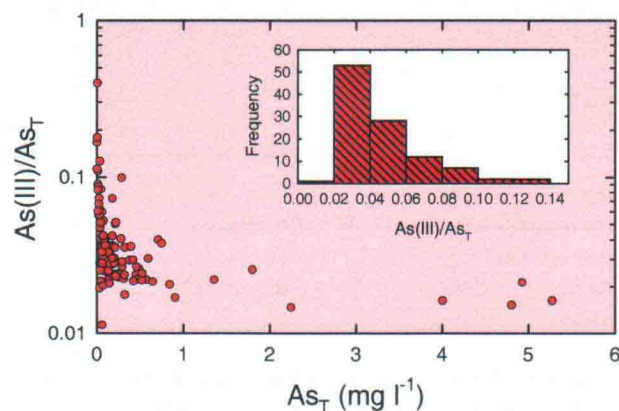


Figure 3.3. As(III)/As_T ratio against As_T concentration in the groundwaters from La Pampa

Table 3.2. Trace-element data for the Pampean groundwaters. Subscript T: total concentrations

	Units	Min	Max	Median	Mean	n
As(III)	$\mu\text{g l}^{-1}$	<3	105	4.2	10.7	108
As _T	$\mu\text{g l}^{-1}$	<4	5280	149	414	108
Fe _T	$\mu\text{g l}^{-1}$	<6	1160	55.0	125	108
Mn	$\mu\text{g l}^{-1}$	<1	79	2.0	5.17	108
Ba	$\mu\text{g l}^{-1}$	5.0	259	36	45	108
Sr	mg l^{-1}	0.066	13.3	0.595	1.27	108
V	mg l^{-1}	0.019	5.43	0.558	0.837	108
B	mg l^{-1}	0.46	13.8	2.97	3.47	108
P _T	mg l^{-1}	<0.2	0.70	<0.2	0.191	108
F	mg l^{-1}	0.034	29.2	3.84	5.24	108
Br	mg l^{-1}	0.055	11.6	0.67	1.18	108
I	$\mu\text{g l}^{-1}$	17.4	730	121	159	108
Se	$\mu\text{g l}^{-1}$	<2	40	8	12	34
Be	$\mu\text{g l}^{-1}$	<0.01	0.40	0.01	0.05	107
Al	$\mu\text{g l}^{-1}$	2.88	991	16.1	55.1	107
Cr	$\mu\text{g l}^{-1}$	0.40	20.4	2.30	2.98	107
Co	$\mu\text{g l}^{-1}$	<0.03	1.28	0.13	0.21	107
Ni	$\mu\text{g l}^{-1}$	<0.15	18.7	0.88	1.96	107
Cu	$\mu\text{g l}^{-1}$	0.41	88.6	7.10	11.96	107
Zn	$\mu\text{g l}^{-1}$	2.51	1438	58.3	112	107
Rb	$\mu\text{g l}^{-1}$	1.45	31.6	5.0	6.38	107
Y	$\mu\text{g l}^{-1}$	<0.002	0.510	0.033	0.284	107
Mo	$\mu\text{g l}^{-1}$	2.72	991	61.5	107	107
Cd	$\mu\text{g l}^{-1}$	<0.02	2.70	0.11	0.28	107
Sb	$\mu\text{g l}^{-1}$	<0.05	0.92			107
Cs	$\mu\text{g l}^{-1}$	<0.01	0.22	0.02	0.10	107
Pb	$\mu\text{g l}^{-1}$	<0.45	13.8	0.39	0.82	107
U	$\mu\text{g l}^{-1}$	6.16	248	30.6	42.1	107

potentials. Groundwater pH values are neutral to alkaline (7.0–8.7). Figure 3.3 shows that the As(III)/As_T ratio in the groundwaters is usually very low, and particularly so where As_T concentrations are high. Since only As(III) and As(V) species are likely to be present, this indicates that most of the As present in solution is As(V).

Groundwater As correlates positively with pH, alkalinity (HCO₃) and with F and V (Figure 3.4). Weaker correlations are also observed between As and B, Mo, U and Be. The mobilisation of these elements is most likely achieved by desorption from iron, manganese and aluminium oxides in the sediments, particularly under the high-pH and high-alkalinity conditions. Mutual competition between these anions and oxyanions for sorption sites on oxide minerals may also have enhanced their mobilisation.

As described in Section 2, many of these element correlations are seen in other groundwaters where conditions are semi-arid and groundwaters are oxidising (e.g. western USA, Chile, Mexico).

Concentrations of As and other anions and oxyanions appear to be particularly high in groundwaters close to the low-lying depressions which act as localised groundwater-discharge zones. This is illustrated by the differences in concentrations of As in porewaters from the two cored boreholes. Concentrations up to 7490 $\mu\text{g l}^{-1}$ were found in porewaters from Tamagnoni borehole, sited adjacent to one such depression (Figure 3.5). The concentrations were an order of magnitude higher than those in porewaters from Talleres Norte borehole which was drilled in a flatter area with no nearby topographic depression. The high As concentrations in the Tamagnoni borehole are not related to evaporation because As does not correlate with indicators of salinity, such as chloride (Cl;

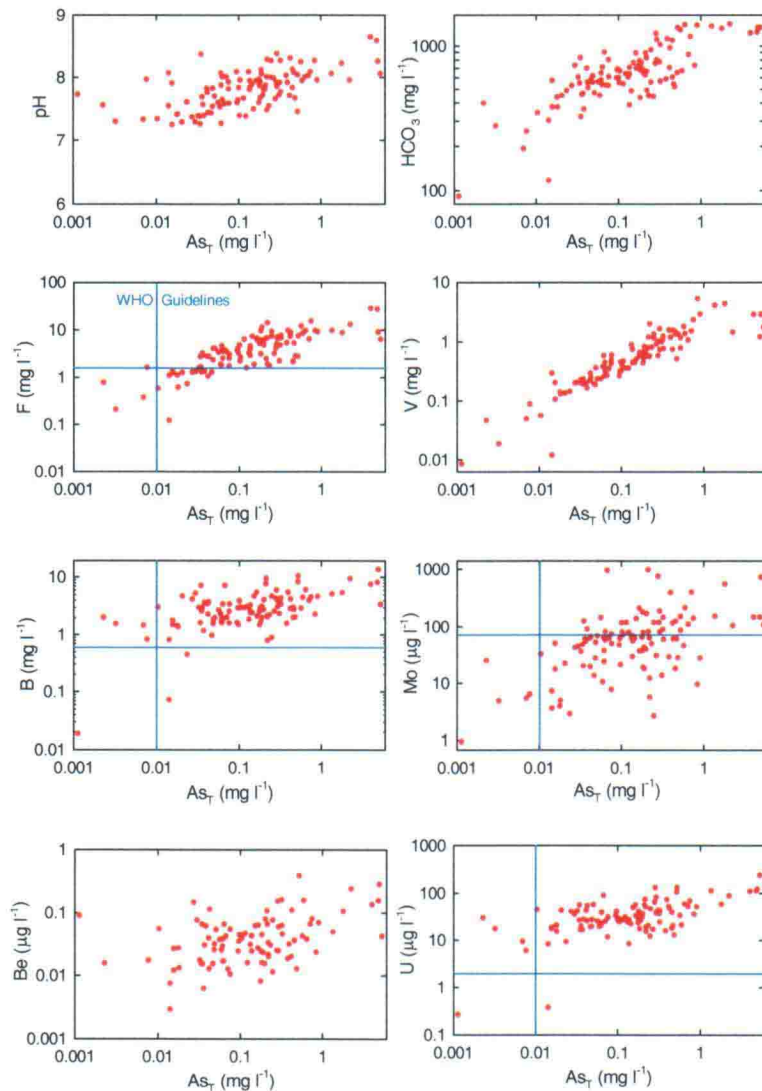


Figure 3.4. Relationship between As_T and other elements in groundwaters from La Pampa

Figure 3.5). In the Tamagnoni borehole, highest salinity was restricted to the top few metres of the profile where evaporation is expected to be strongest. Other anions and oxyanions (e.g. F, V) in the porewaters showed trends similar to As (Figure 3.5). However, upper limits are imposed on concentrations of F by saturation with, and hence likely precipitation of, the mineral fluorite (CaF_2).

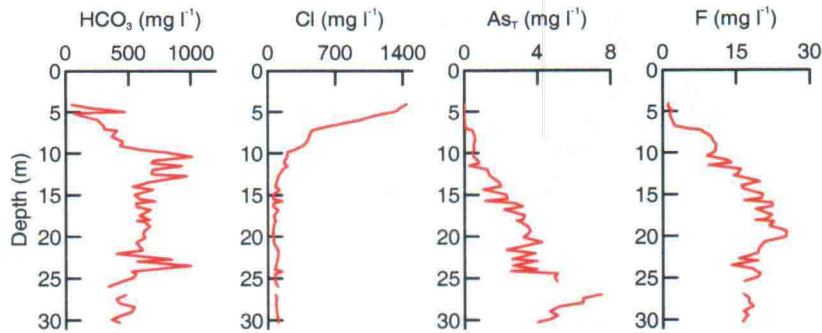
The regional groundwater survey also showed that As concentrations are often relatively high where groundwater is abstracted from close to the water table, perhaps because this zone is a location of more active weathering reactions (Smedley et al., 2000a, b).

The high pH values and alkalinity of many of the groundwaters are related to carbonate and silicate dissolution reactions (especially calcite and feldspar) in the aquifer under conditions which are closed to the atmosphere. The development of the chemical compositions of the groundwaters is facilitated by the semi-arid climatic conditions of the region.

3.4 Summary of sediment chemistry

Arsenic concentrations in the aquifer sediments are similar to average values for silty and sandy sediments, although high groundwater concentrations show some spatial relationship with high

TAMAGNONI POREWATERS



TALLERES NORTE POREWATERS

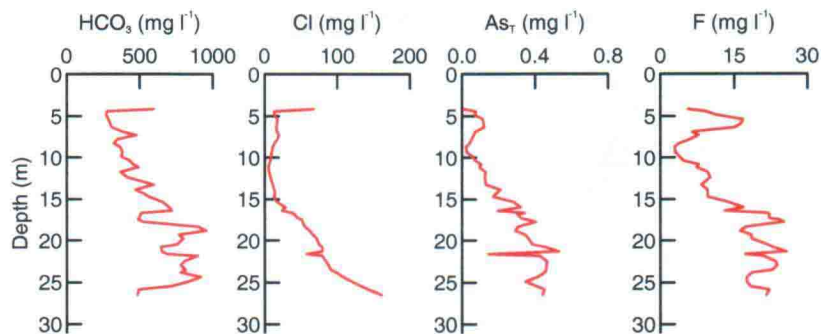


Figure 3.5. Profiles of HCO_3^- , Cl^- , As_T and F^- in porewaters from cored boreholes at Tamagnoni (adjacent to a small topographic depression) and Talleres Norte

sediment concentrations. The sediments contain no discrete As minerals. Total As concentrations lie in the range 3–18 mg kg^{-1} , the highest values being found in finer-grained sediments.

Selective extracts of sediments from the cored boreholes and road cuttings were prepared and analysed using acid ammonium oxalate solution (Tamm's Reagent) to estimate the amount of As associated with amorphous oxides (especially iron oxides) and hydroxylamine hydrochloride solution to estimate the amounts associated with manganese oxide. Oxalate-extractable As concentrations vary between 0.5–9.6 mg kg^{-1} (mean 2 mg kg^{-1}) and equate to up to half the total As present.

Hydroxylamine-extractable concentrations vary between 0.02–4.7 mg kg^{-1} (mean 1.0 mg kg^{-1}). A significant amount of As present in the sediments therefore appears to be associated with poorly-structured iron and manganese oxides. Much of the remaining As is thought to be associated with more structured iron oxides.

As much of the As is apparently associated with amorphous oxides, it may be leached relatively easily into solution given the appropriate geochemical conditions. Indeed, the proportion of oxalate-extractable As was found to be highest in sediments where corresponding porewater As concentrations were highest (Tamagnoni borehole; Figure 3.6). The As problem therefore appears to arise as a result of mobilisation under favourable conditions, rather being a function of a high-As mineral source in the aquifer.

It is concluded that the development of groundwaters with high pH and alkalinity, together with young age of the loess sediments and slow groundwater flow conditions, has enabled the

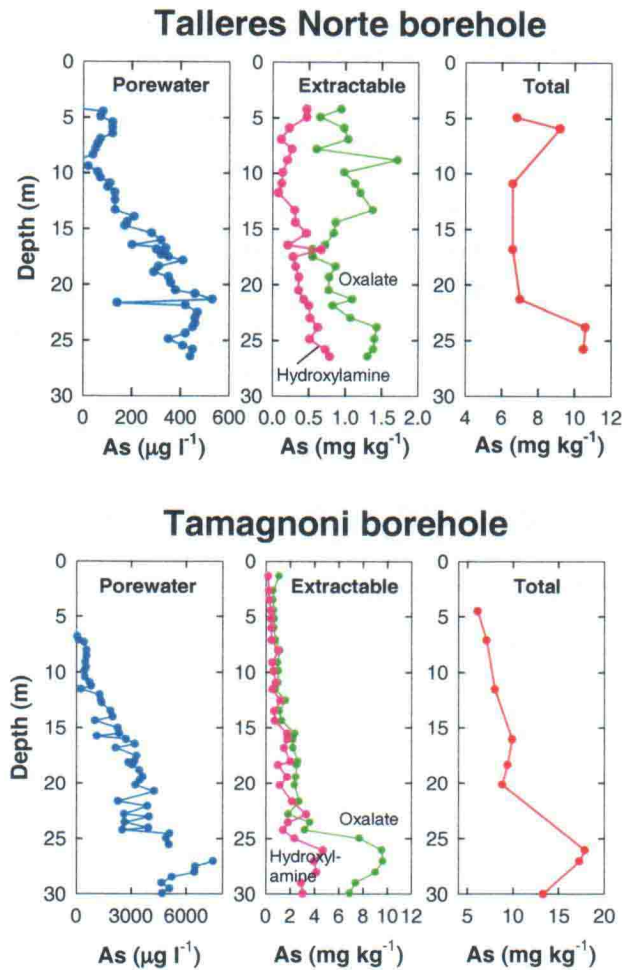


Figure 3.6. Concentrations of As in porewaters and sediments from cored boreholes at Talleres Norte and Tamagnoni. Profiles include selective sediment extracts and total concentrations

accumulation of high concentrations of As and other elements in solution without significant opportunity for flushing of the aquifer to enable their removal.

3.5 Implications for mitigation

3.5.1 Groundwater-quality situation

The groundwater clearly has many serious quality problems with potentially detrimental consequences for human and animal health. From the regional survey, very few samples had acceptable concentrations of As (27% less than $50 \mu\text{g l}^{-1}$ and only 5% less than $10 \mu\text{g l}^{-1}$). Additional problems due to high salinity, F, B, $\text{NO}_3\text{-N}$, Mo, U and a number of other constituents make the majority of groundwaters in the area unacceptable for potable supply. It is therefore critical that moves to mitigate the water-quality problems be implemented in order to safeguard public health. However, given the climatic and hydrogeological conditions in La Pampa, solutions to the problem are not easily found. Mitigation measures need to take adequate account of the many parameters which are potentially detrimental and/or undesirable.

3.5.2 Potential mitigation strategies

A logical mitigation step would be distinction of available water supplies according to their intended use. Better quality is required for potable supply than for agricultural, industrial and other domestic

Table 3.3. Summary of various mitigation options for La Pampa and their practical viability

Mitigation option	Viability
Surface water	No sustainable supplies available, not an option
Rainwater harvesting	Semi-arid climate means limited rainwater supply, and seasonal. Nonetheless, is likely to provide a suitable supply of water for some rural areas, at least for parts of the year
Groundwater treatment	<i>Urban scale:</i> Requires sophisticated and expensive treatment methods such as reverse osmosis or activated alumina. Reverse osmosis is the currently used method in most urban areas <i>Domestic/rural scale:</i> Treatment using coagulation/filtration (e.g. alum) will provide some improvement, but efficacy may be compromised by high salinity (and pH)
Borehole siting	Suitable for installation of new boreholes. Existing boreholes could be deepened to provide some improvement. This is likely to be limited as few groundwaters of acceptable quality are known to exist in the region, even given optimal siting

uses. However, irrigation using brackish water has potentially serious implications for crop production, and irrigation with water containing toxic elements including As, B, F and U has potentially detrimental consequences for plant uptake and accumulation in food. For potable supply, a number of options are discussed below.

Surface water

There are no sources of permanent surface water in the northern part of La Pampa. The nearest rivers are the Rio Salado, some 140 km west of the study area and the Rio Colorado over 300 km away, on the southern border of La Pampa. Use of surface water is therefore not a viable option for La Pampa.

Rainwater harvesting

Although the Pampean climate is semi-arid, storage of seasonal rainfall could be a potential option for provision of potable water supply, at least for part of the year. This option is practised in many parts of the world where either limited availability or poor quality of groundwater are a problem (e.g. Asia, Australia). In these areas, rainwater harvesting is able to supply potable water for at least parts of the year. Storage capacity in La Pampa would need to be sufficient to cater for the dry season of around 5 months. The potential benefits of rainwater harvesting in terms of water quality are obvious and the technology relatively simple. The method should therefore be worthy of investigation for La Pampa.

Groundwater treatment

Groundwater currently constitutes the only water source for potable and agricultural supply. Mitigation of water quality is complicated by the fact that As is only one of a number of chemical constituents that give rise to health or acceptability problems. One of the most serious problems for humans, livestock and crops is high salinity which can be extreme in many of the shallow groundwaters affected by evaporation. Water salinity cannot easily be reduced without expensive and centralised treatment methods.

As shown above, groundwaters with high concentrations of As also have high concentrations of many other undesirable elements. Even the samples with low As concentrations often have unacceptably high salinity. Treatment of groundwaters to remove other ions present (F, V, B, NO₃-N) also ideally requires sophisticated methods, although some low-technology methods can provide a degree of improvement at domestic level. In the urban areas of La Pampa, treatment is typically done by reverse osmosis. In the rural areas, groundwaters are usually used without prior treatment.

Treatment methods for removal of As from drinking water include co-precipitation (alum coagulation, iron coagulation, lime softening), adsorption methods (activated alumina, ion exchange) or membrane techniques (reverse osmosis, electrodialysis). In all these methods, removal is most efficiently carried out when As is present as As(V), as is the case in the Pampean groundwaters. In the case of treatment of urban water supplies, adsorption or membrane techniques are likely to be the most appropriate, although high salinity of many of the Pampean groundwaters leads to potential problems with water treatment. For rural groundwater supplies, treatment using coagulation/filtration is likely to be most appropriate, although again, treatment efficiency will be dependent on factors such as salinity, pH and initial As concentration. Use of ferric sulphate has been reported to be more effective coagulant than alum, although it is likely to be a more expensive option. The alum method suffers from the inherent problems of residual aluminium and sulphate in the treated water and from problems with disposal of contaminated sludge. All groundwater treatment methods have drawbacks in terms technical difficulty, cost, efficiency or disposal of waste materials. Nonetheless, these problems need to be balanced with the potential health risks from use of water in an untreated state. Given the widespread occurrence of poor-quality groundwater in La Pampa, groundwater treatment constitutes one of the most important remediation options available and requires further development, particularly in the rural areas, to ensure provision of safe drinking water.

Borehole siting

Large variations in chemical quality occur in the aquifers, both spatially and with depth. Although few parts of the aquifer appear to yield good-quality groundwater, there may be some benefit gained from siting of boreholes in optimal locations. The most saline groundwaters are mainly present in the shallow parts the aquifers, particularly in topographic depressions where the water table is close to or above ground level and where evaporation can take place. Ideally, such zones are best avoided when considering new sites for borehole drilling.

The correlations observed between As and many of the other elements of potential health concern (F, B, V, U, Be, Mo) indicate that the groundwaters having the lowest As concentrations are also likely to be of better quality with respect to these other problem elements. Highest concentrations of these have also been found in groundwaters in and close to low-lying depressions where groundwater flow is sluggish and has no easy exit from the catchment. Borehole siting should clearly aim to avoid such depressions. Spatial chemical variations also suggest that a degree of mitigation of water-quality problems can be achieved by completing boreholes in deeper parts of the Pampean aquifer.

It is likely that borehole-siting considerations can only provide limited amelioration of the water-quality problems because, even with optimal siting, the majority of groundwaters sampled are of unacceptable quality for potable use. Given the high degree of spatial variability in chemical compositions, it is also unlikely that water chemistry will ever be reliably predictable on a local scale.

3.5.3 Requirements for determination of the scale of the problem

It is clear that a very extensive area of the arid and semi-arid zones of Argentina is potentially affected by the water-quality problems demonstrated in La Pampa. Estimates are that similar groundwaters occupy aquifers of the Chaco-Pampean Plain over around 1 million km² and that up to 5 million people nationally may be drinking groundwater with >50 µg l⁻¹ (Nicolli et al., 1989; Nicolli and Merino, 2000). However, the distribution and scale of the problems are still poorly defined and need further investigation. Obtaining such data requires instigation of large-scale randomised groundwater surveys with testing of key elements, particularly measures of salinity, As and F and mapping of results. Laboratory measurements are clearly preferable, but rapid investigations may be facilitated by the use in particular of As field-test kits. Alongside further groundwater testing, public awareness campaigns would also help to disseminate the potential health concerns from drinking water and to highlight the need for mitigation measures.

4. BANGLADESH

4.1 Background

In terms of the numbers of people exposed, groundwaters from the aquifers of Bangladesh are now recognised as having the worst arsenic problems in the world. Recent years have seen a rapid proliferation of data and hypothesis about the scale and causes of the arsenic problem. Arsenic-related health problems were first recognised in neighbouring West Bengal in the early 1980s. Despite this, significant delays occurred in the recognition of the problem across the border and the occurrence of arsenic-related disease was not recognised in Bangladesh until 1993. Today, many Bangladeshi and international organisations are involved in the investigation of all aspects of the arsenic problem. It is estimated that around 28–35 million people are drinking water with more than $50 \mu\text{g l}^{-1}$ As and 46–57 millions are drinking water with more than $10 \mu\text{g l}^{-1}$ As (Kinniburgh and Smedley, 2000). The problem is indeed very serious.

Hydrogeological and geochemical investigations in this project began in Bangladesh in mid 1996, at a time when very little was known about the nature and scale of the arsenic problem in the country. Serious contamination was suspected because of the recognition of skin lesions in populations in parts of the western border area (Chapai Nawabganj) and because of the known severity of contamination in West Bengal. Nonetheless, the spatial distribution of arsenic problems in the aquifers was poorly defined and the western border area was at the time taken to be worst affected.

A reconnaissance field survey was carried out for the project in Chapai Nawabganj thana in early 1997. By this time, it was becoming clear that the scale of contamination was potentially much larger than previously recognised and that rapid large-scale testing of wells needed to be carried out as a priority to establish the true scale of the problem. As a result, investigations in Bangladesh under this project were halted. A larger Technical Assistance project with DFID support was initiated, in collaboration with the Government of Bangladesh. This larger Technical Assistance project has been carried out during the period 1998–2000. Results are given in detail in DPHE/BGS/MML (1999) and Kinniburgh and Smedley (2000).

Investigations carried out in Bangladesh under the project described here were therefore of a reconnaissance nature (29 samples collected) and the study area was on a small scale, with the majority of samples being collected in the Chapai Nawabganj municipal area. Nonetheless, the preliminary water-quality data served to establish two important principles: i) that the groundwaters with high arsenic concentrations are strongly reducing and show evidence of sulphate reduction; hence, arsenic release has occurred following *reduction* rather than as a result of *oxidation* of sulphide minerals caused by overabstraction of groundwaters; and ii) that the high arsenic concentrations of Chapai Nawabganj are a very localised feature (around 3 x 5 km in extent) and hence ‘hotspots’ of high-arsenic groundwaters can occur in parts of the aquifers which elsewhere have low concentrations. Such hotspots have since been recognised in other parts of Bangladesh.

4.2 Geology and hydrogeology

The contaminated groundwaters are from aquifers in Holocene alluvial and deltaic sediments associated with the Ganges, Brahmaputra and Meghna river systems. These occupy a substantial proportion of the Bangladesh land area. Groundwaters from older formations (Pleistocene and older) are generally not affected. The Holocene deposits form one of the most productive aquifer systems in the world and groundwater is the dominant source of water for the Bangladesh population, with around 95% using groundwater for potable supply. The country has an estimated 4.5 million handpump tubewells.

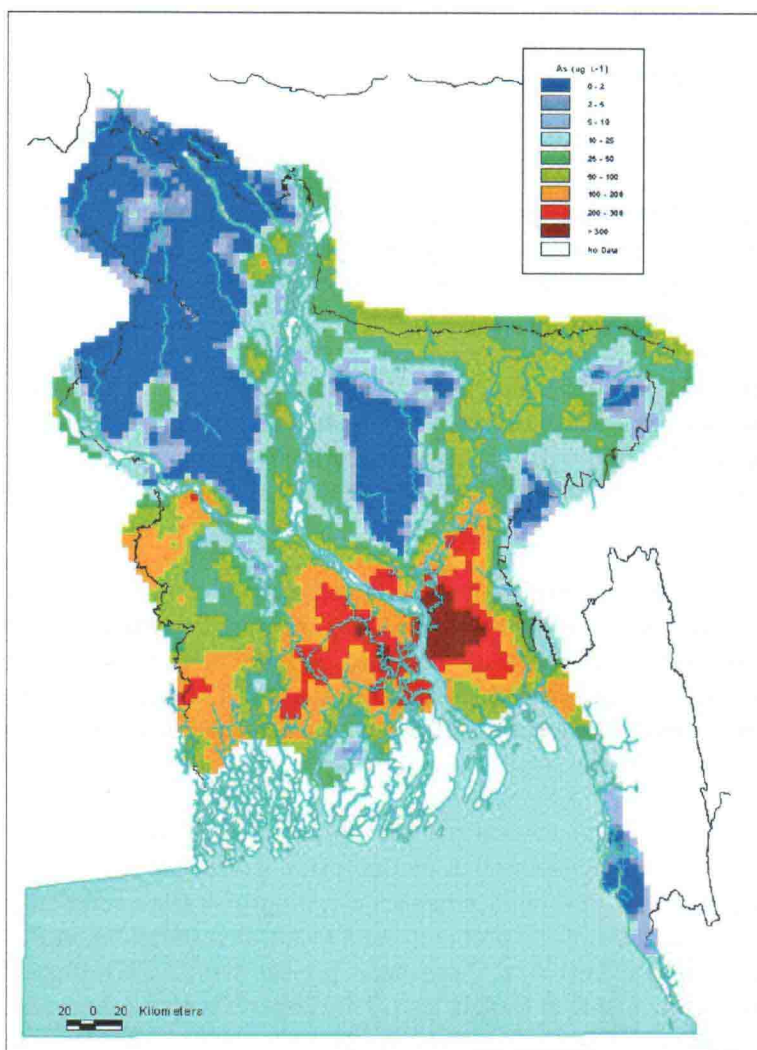
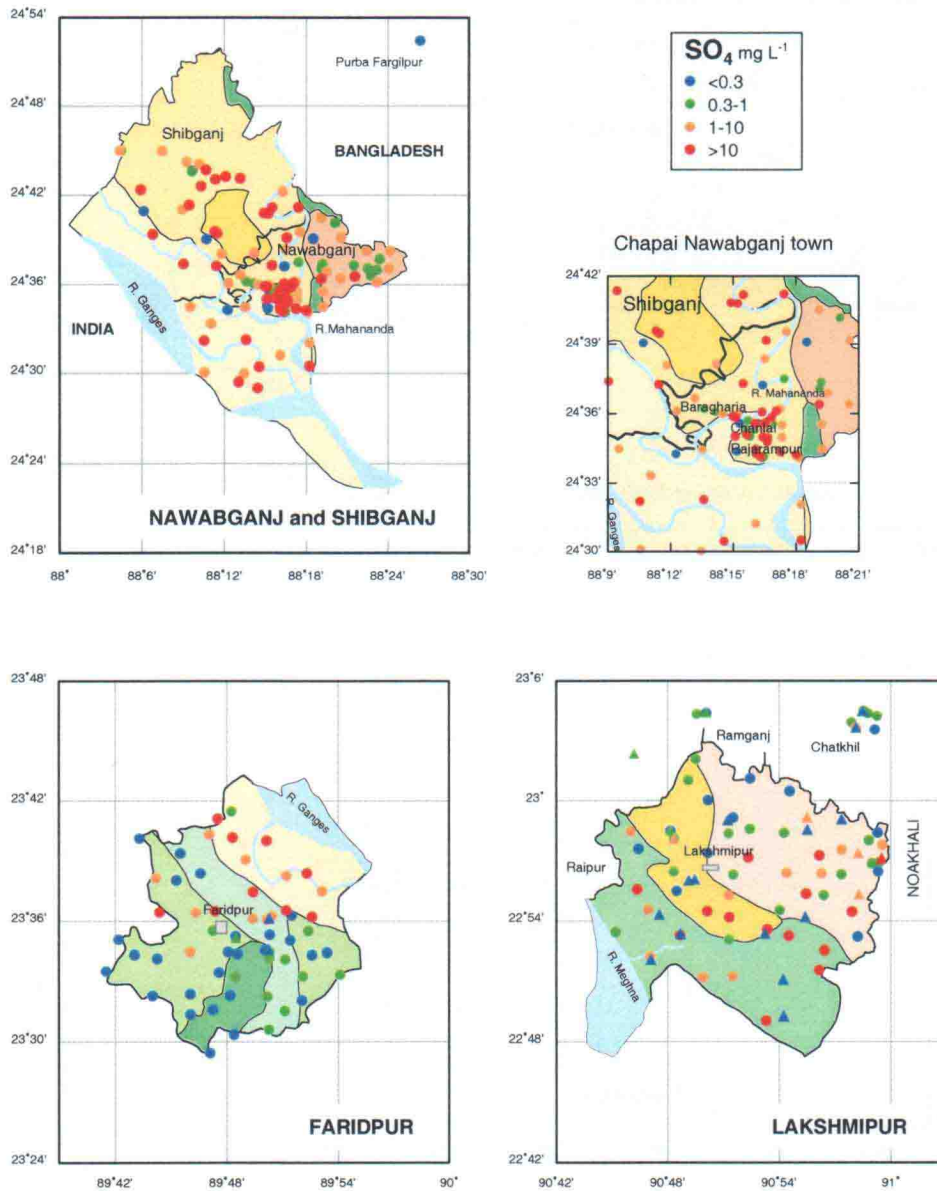


Figure 4.1. Smoothed map of arsenic concentrations in groundwater from Bangladesh (data from the DPHE/BGS national hydrochemical survey; Gaus et al., 2000)

Bangladesh has a tropical monsoon climate with an average annual rainfall of around 2000 mm. The aquifers are mostly fully recharged each year by the monsoon rains and floods. However, groundwater flow rates are slow, largely because of the extremely low hydraulic gradients across the aquifers. This is evidenced by observed low-tritium groundwaters at shallow depths in some areas, and ^{14}C dates for some deep groundwaters (>150 m) of several thousand years. Slow groundwater flow rates mean that there is likely to have been little flushing of the Holocene aquifers since deposition within the last few thousand years.

4.3 Summary of water chemistry

Summaries of BGS investigations of groundwater chemistry in Bangladesh, including a national groundwater survey (DPHE/BGS hydrochemical survey) are given in Kinniburgh and Smedley (2000). The majority of groundwaters from the Holocene alluvial and deltaic aquifers are reducing with very low or no detectable dissolved oxygen, low nitrate concentrations and high concentrations of Fe (median 1.1 mg l^{-1} ; maximum 61 mg l^{-1}), Mn (median 0.3 mg l^{-1} ; maximum 10 mg l^{-1}) and often $\text{NH}_4\text{-N}$ (17.6 mg l^{-1} ; Kinniburgh and Smedley, 2000). Both Mn and $\text{NH}_4\text{-N}$ concentrations frequently exceed WHO guideline values, though only the Mn guideline is a health-based value. Sulphate concentrations are also often low (median 1 mg l^{-1} ; minimum less than 0.4 mg l^{-1}).

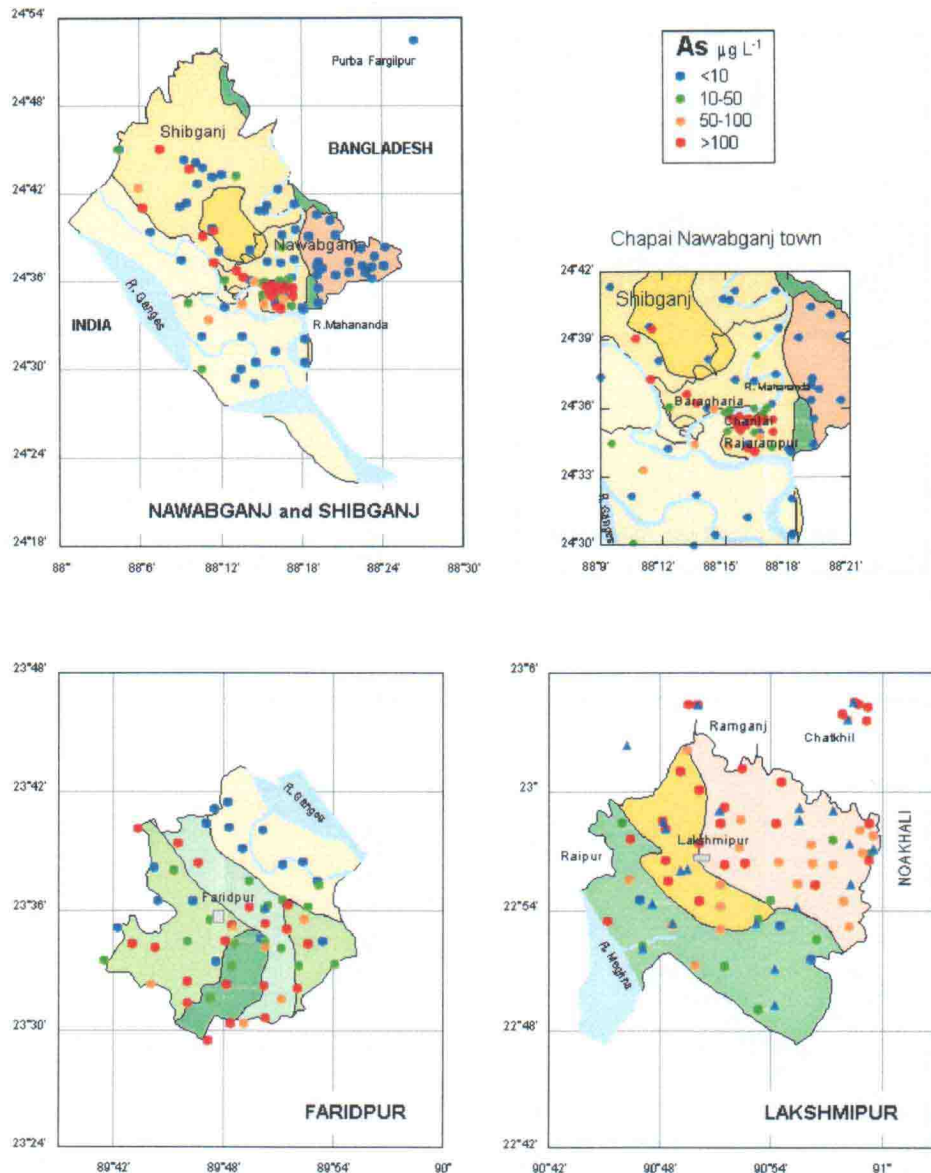


'Groundwater Studies of Arsenic Contamination in Bangladesh'
BGS/DPHE/DFID (2000)

Figure 4.3. Distributions of SO_4 in groundwaters from the selected study areas (from Smedley et al., 2000c). The distributions contrast strongly with those of As_T

More detailed surveys of groundwater chemistry in three selected study areas (parts of the thanas of Chapai Nawabganj, Lakshmipur and Faridpur) showed the high degree of spatial variability in arsenic concentrations, often within short distances of a few tens to hundreds of metres. Figure 4.2 (inset map, scale around 20 x 20 km) also highlights the localised arsenic hotspot centred around the town of Chapai Nawabganj. Here, the highest concentration observed was $2500 \mu\text{g l}^{-1}$. Despite the variability, there is apparently some spatial trend that can be related to surface geology (Figure 4.2).

Highest arsenic concentrations are generally found in groundwaters with the lowest SO_4 concentrations (compare Figures 4.2 and 4.3) and weak negative correlations are apparent between the two parameters in groundwaters from each of the study areas (Smedley et al., 2000c). This provides



'Groundwater Studies of Arsenic Contamination in Bangladesh'
BGS/DPHE/DFID (2000)

Figure 4.2. Regional distributions of arsenic in groundwaters from three study areas in Bangladesh. For details of locations and geology, see Smedley et al., 2000c

The DPHE/BGS national hydrochemical survey of some 3500 groundwater samples found arsenic concentrations in the range $<0.5\text{--}1660 \mu\text{g l}^{-1}$ (Kinniburgh and Smedley, 2000). The survey showed that 25% had As concentrations exceeding $50 \mu\text{g l}^{-1}$, 9% exceeded $200 \mu\text{g l}^{-1}$ and 0.1% exceeded $1000 \mu\text{g l}^{-1}$ (depths undifferentiated). Conversely, 24% of samples fell below the detection limit for arsenic ($0.25 \mu\text{g l}^{-1}$ or $0.5 \mu\text{g l}^{-1}$; Kinniburgh and Smedley, 2000). The spatial distribution was highly variable, but with the largest number of high-arsenic wells located in the south and south-east of the country (Figure 4.1). High arsenic concentrations were also largely restricted to the shallow ($<150 \text{ m}$) Holocene aquifers. Deep groundwaters ($>150 \text{ m}$) and those from older sedimentary formations (the Pleistocene Barind and Madhupur Tracts) had low concentrations, typically $1 \mu\text{g l}^{-1}$ or less. Low concentrations are also common in the less reducing groundwaters from northern Bangladesh (Figure 4.1). Dug wells have low arsenic concentrations as a result of comparatively oxidising conditions close to the water table.

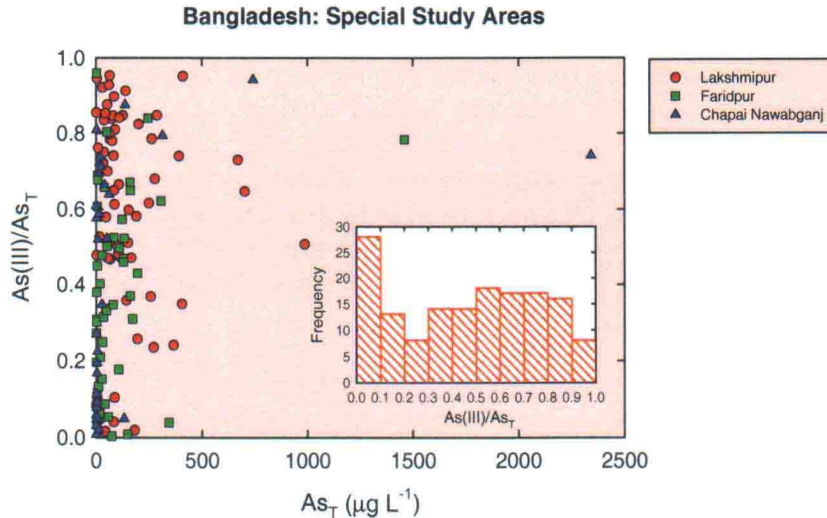


Figure 4.4. Variation of As(III)/As_T ratio with As_T concentration in groundwaters from the three study areas

strong evidence that initiation of strongly reducing conditions with sulphate reduction has been the key process controlling the release of As into the groundwater.

Under the reducing conditions, the proportion of As in the groundwaters present as As(III) is expected to be large. As(III)/As_T ratios are in fact very variable, ranging between <0.1 and >0.9 (Figure 4.4). However, where As_T concentrations are high, As(III)/As_T ratios are typically high, at around 0.5–0.6 (Figure 4.4). This again suggests that reduction of As to As(III) is important in the mobilisation of arsenic in water. However, since not all the arsenic is present in reduced form, simple reduction of As(V) to As(III) is probably not sufficient in itself to generate the high As concentrations found in the groundwaters. Other factors are also likely to be involved.

4.4 Summary of sediment chemistry

Preliminary studies of sediment chemistry began under this project in Chapai Nawabganj but were extended considerably under the subsequent main Bangladesh project. Analysed sediments had an average arsenic concentration of 4 mg kg⁻¹ with a range of 0.4–10 mg kg⁻¹. Concentrations were highest in the finer sediments and correlated well with sediment Fe concentrations (Kinniburgh and Smedley, 2000). Microscopic investigation identified various iron oxides in the sediments but no discrete arsenic minerals. The sediments appear to be typical alluvial and deltaic sediments and there is no indication that a unique arsenic-rich mineralised source somewhere upstream in the catchments is responsible for the groundwater arsenic problem.

Selective sediment extracts were carried out using acid ammonium oxalate to identify the amounts of amorphous oxide minerals (chiefly iron oxide) and associated arsenic in sediments from three cored boreholes in each of the special study areas. Average oxalate-extractable arsenic concentrations were 1.8 mg kg⁻¹ in Chapai Nawabganj, 0.8 mg kg⁻¹ in Faridpur and 2.1 mg kg⁻¹ in Lakshmipur. The highest concentrations in Lakshmipur corresponded with higher average dissolved As concentrations (Kinniburgh and Smedley, 2000). Concentrations of amorphous iron oxides are considered to be relatively high in the Bangladesh sediments, especially in the Lakshmipur area of south-east Bangladesh, and are believed to be an important source of arsenic. More structured iron oxides as well as other metal oxides (manganese and aluminium) may be additional sources of arsenic but are difficult to quantify. Evidence from the sediment chemistry suggests that desorption and dissolution of As from oxide minerals under the reducing conditions is an important control on arsenic mobilisation.

4.5 Options for mitigation

The scale of the arsenic problem in Bangladesh, together with infrastructural, economic and social factors, makes the task of mitigation extremely difficult. Options for the provision of safe drinking water include screening of affected groundwaters to locate safe sources, development of the deep aquifer, use of disinfected dug-well waters, treatment of arsenic-affected groundwaters (in situ or above ground at various scales), rainwater harvesting and development of piped surface-water schemes. Many of these are currently being assessed and tried. One clear outcome is that no single solution will be universally applicable to solve the problem and in practice, combinations of these approaches will eventually be set up to find solutions.

Regional spatial patterns in arsenic concentrations across the aquifers allow identification of the worst-affected parts of the country. These patterns should enable prioritisation of screening and mitigation programmes. The statistics indicate that an urgent priority should be given to the districts south and east of Bangladesh. However, the extremely high degree of local-scale spatial variability in arsenic concentrations in the aquifers means that all wells in the shallow aquifer used for drinking water should be tested. Periodic monitoring of selected wells is also required to assess temporal variability. The presence of arsenic hotspots within areas of low overall concentrations requires even the less contaminated areas in the shallow aquifer (e.g. northern Bangladesh) to be screened, probably at a lower density and in combination with other approaches such as public awareness campaigns and health checks.

Evidence to date suggests that the deep aquifer provides a potentially good source of low-arsenic drinking water. However, more investigations need to be made of the arsenic concentrations in the deep aquifer across Bangladesh. Data for deep tubewells in the DPHE/BGS national hydrochemical survey were mostly in the southern coastal area and the north-east. More surveys need to be carried out in other parts of the country where deep aquifers exist and a larger database of baseline data on arsenic and other trace elements needs to be produced. Investigations also need to focus on the consequences of increased development of the deep aquifer for the sustainability of the resource in the long term.

5. HUHHOT BASIN, INNER MONGOLIA

5.1 Background

Arsenic problems from groundwater used for drinking have been recognised recently in a number of areas of northern China, including Xinjiang and Shanxi Provinces and Inner Mongolia (Section 2; Figure 5.1). Many of these areas are poorly documented and the precise causes of the groundwater arsenic contamination are not well understood. However, available evidence suggests that many of the geological and geochemical features of the groundwaters of northern China have parallels with the situation in Bangladesh.

One area affected by arsenic contamination is the Huhhot Basin of Inner Mongolia. This is an enclosed basin, some 4800 km² in area, which incorporates Huhhot City, the capital city of the Inner Mongolia Autonomous Region. Symptoms of chronic arsenic poisoning were first noted in populations from villages in the central parts of the basin in 1990. Symptoms include skin keratosis, pigmentation disorders and skin cancers. Recognised internal cancers include lung, liver and bladder cancer. Since 1990, around 200 arsenic-affected patients have been identified in the area. Arsenic problems have also been identified to the west of the Huhhot Basin in the Ba Meng region of Inner Mongolia, as well as in neighbouring Xinjiang and Shanxi Provinces (Figure 5.1).

In addition to problems from arsenic in drinking water, significant problems are also encountered from high concentrations of fluoride, often in excess of the national standard for drinking water of 1.5 mg l⁻¹. The high concentrations have given rise to endemic dental fluorosis.

A survey of groundwater quality has been carried out in the Huhhot Basin. Around 70 groundwater samples and a small number of sediment samples were collected for chemical analysis, including arsenic.



Figure 5.1. Map of China showing areas of known and suspected natural arsenic problems in groundwater in Xinjiang Province and Inner Mongolia (after University of Texas map library)

5.2 Geology and hydrogeology

Huhhot City lies within an alluvial basin presently drained by the Black River and other minor rivers. The basin is fault-bounded to the north by the Da Qing Mountains (typical altitude 2200 m) and to the south-east by the Man Han Mountains (Figure 5.2). The alluvial plain has a gentle west-south-west slope (altitude 980 m at its lowest point) and is composed of a thick sequence (around 1500 m) of sands, silt and clay of Quaternary age. The sediments are the product of a former lake existing more than 8000 years ago, together with alluvial fan deposits along the mountain foothills. Sediments outcropping at surface are notably coarser-grained in the basin margins than in the low-lying parts. Drainage of the lake as a result of tectonic activity has left a large alluvial-lacustrine plain, around 4800 km² in area. The low slope of the basin and poor drainage to the Yellow River (Huang He) catchment has resulted in sluggish groundwater flow and the generation of an essentially closed basin.

The region lies on the edge of the Gobi Desert and hence the Basin receives a low average annual precipitation of around 440 mm (mainly July to September). Values are slightly higher, up to 500 mm, in the Da Qing Mountains to the north. Of this rainfall, some 15% (ca. 70 mm) is believed to be recharged to the aquifers. The region has an average monthly temperature ranging from -13 to +22°C.

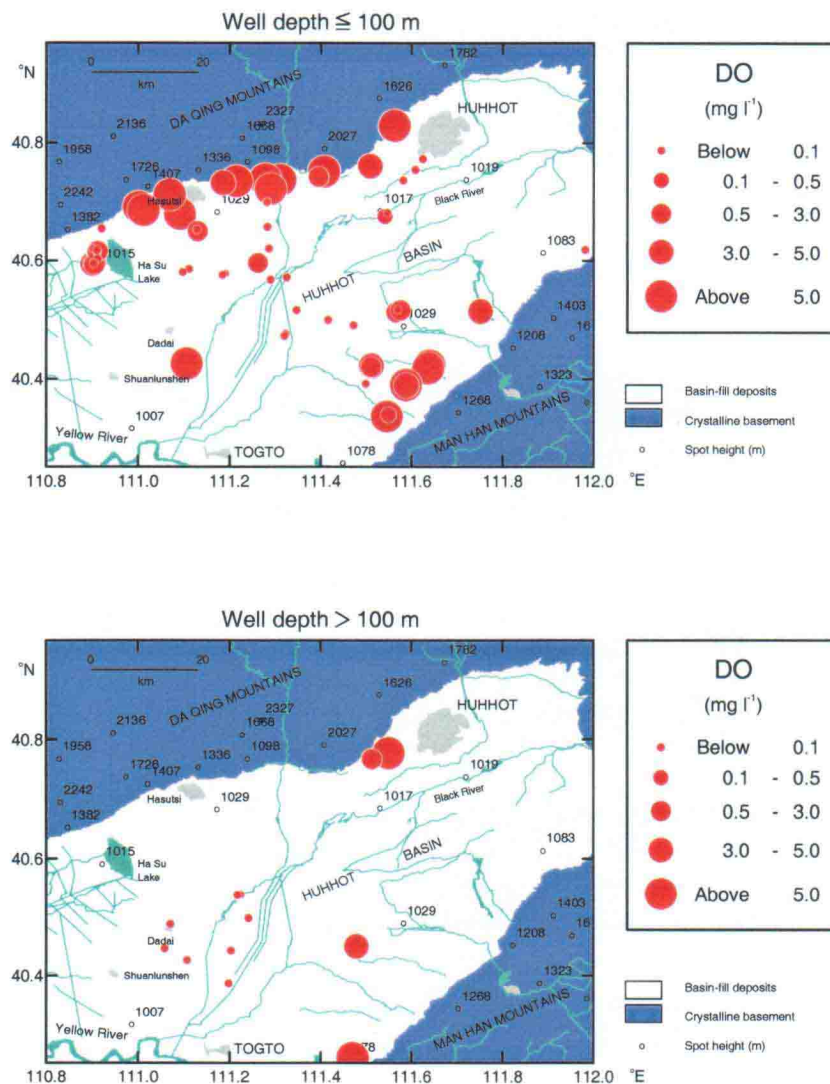


Figure 5.2. Dissolved-oxygen concentrations in groundwaters from the Huhhot Basin

The Black River (Figure 5.2) is currently an ephemeral river which in times of flood, flows into the Yellow River beyond the limit of the basin. Drainage to the Yellow River is restricted at other times due to high seasonal evaporation and irrigation losses.

Groundwater is an important resource for potable, agricultural and industrial use. Wells in the aquifers abstract from either shallow aquifers (mostly <30 m) or deep aquifers (>100 m). The water table in the aquifer is usually near surface (around 2–3 m below ground level), but the deep aquifer is artesian in places.

5.3 Summary of groundwater chemistry

Groundwaters were collected from handpump- or electrically-operated tubewells, shallow dug wells and deep artesian wells. Wells ranged in depth from <10 m to 400 m. Groundwaters from the shallow (100 m or less) and deep (>100 m) aquifers have been considered separately. Summaries of the data are given in Table 5.1 and selected regional chemical variations are shown in Figures 5.2–5.5.

Both shallow and deep groundwaters show a progression in groundwater chemistry down the flow gradient, from aerobic conditions along the basin margins to anaerobic conditions in the lowest parts

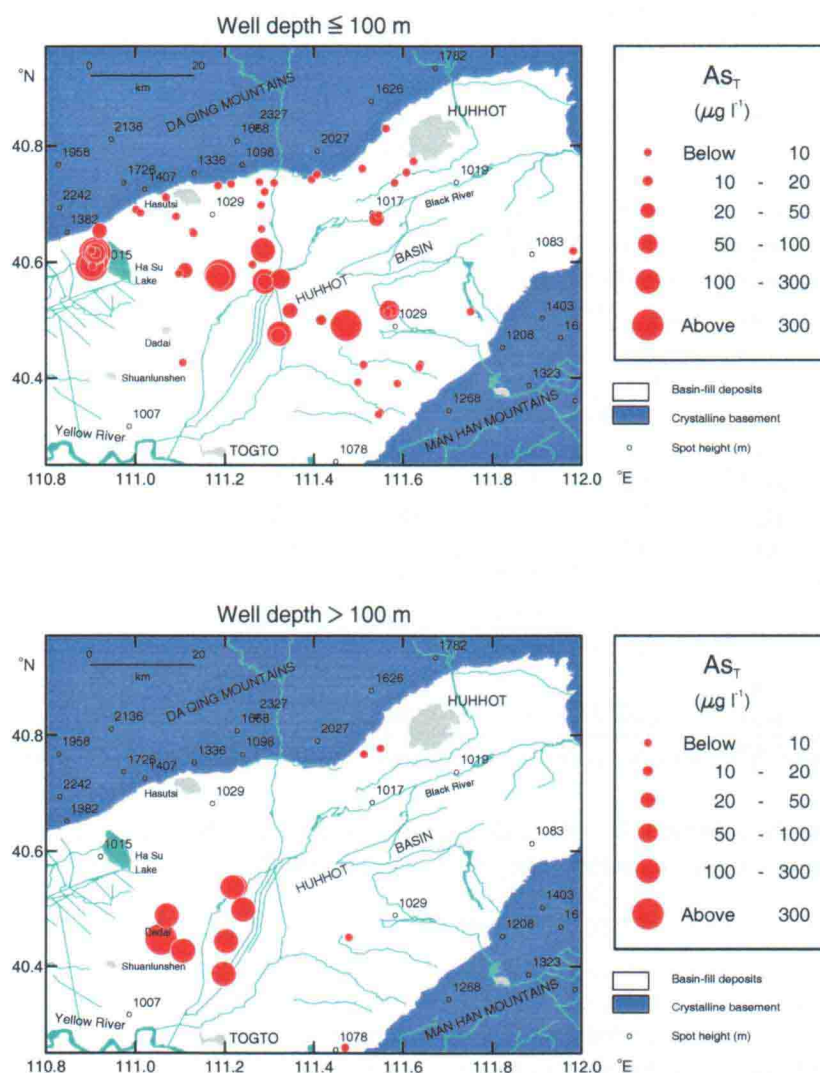


Figure 5.3. Concentrations of total As (As_T) in groundwaters from the Huhhot Basin

Table 5.1. Summary of groundwater chemistry in aquifers from the Huhhot Basin

Parameter	Units	Shallow aquifer (100 m or less)			Deep aquifer (>100 m)		
		Min	Median	Max	Min	Median	Max
Well depth	m	1	25	100	101	220	400
Temp	°C	5.2	9.4	13.0	10.6	13.8	16.0
DO	mg l ⁻¹	<0.1	0.7	9.8	<0.1	<0.1	8.6
Eh	mV	-45	178	386	-74	76	426
SEC	μS cm ⁻¹	463	830	4350	599	1039	1985
pH		7.00	7.73	8.56	7.56	7.90	8.46
Ca	mg l ⁻¹	5.6	57.1	190	4.2	21.3	59.6
Mg	mg l ⁻¹	10.3	39.7	192	3.5	25.5	40.3
Na	mg l ⁻¹	10.6	81.4	835	29.5	151	516
K	mg l ⁻¹	0.04	2.0	91	0.7	1.5	2.8
HCO ₃	mg l ⁻¹	194	389	944	182	409	1150
Cl	mg l ⁻¹	6.1	52.4	919	10.6	86.9	204
SO ₄	mg l ⁻¹	<0.2	36.5	1007	0.5	14.2	145
NO ₃ -N	mg l ⁻¹	<0.5	1.7	34.3	<0.5	0.05	6.1
NH ₄ -N	mg l ⁻¹	<0.01	<0.01	18.0	<0.01	0.81	5.9
DOC	mg l ⁻¹	0.3	3.5	14.9	1.3	5.0	30.6
P _T	mg l ⁻¹	<0.05	0.14	3.10	<0.05	0.53	2.86
B	mg l ⁻¹	<0.03	0.16	1.98	0.07	0.33	1.64
Mn	μg l ⁻¹	<1	34	1289	1	19	173
Fe _T	mg l ⁻¹	<0.006	0.068	4.51	<0.006	0.38	1.71
Se	μg l ⁻¹	<0.5	<0.5	5.4	<0.5	<0.5	1.3
As(III)	μg l ⁻¹	<0.9	2.7	1290	<0.9	100	199
As _T	μg l ⁻¹	<1.0	2.9	1484	<1.0	128	308
F	mg l ⁻¹	0.14	0.51	6.8	0.13	0.73	2.35
Br	μg l ⁻¹	<20	93	911	27	135	243
I	μg l ⁻¹	2	26	727	5	30	148
V	μg l ⁻¹	<0.5	0.8	10.3	<0.2	1.8	5.8
Cr	μg l ⁻¹	<1	1	12	<1	1	16
Co	μg l ⁻¹	0.08	0.21	1.06	0.07	0.16	0.59
Ni	μg l ⁻¹	<0.2	1.6	5.9	0.3	0.8	1.8
Cu	μg l ⁻¹	<1	<1	2	<1	<1	2
Zn	μg l ⁻¹	<2	2	40	1	2	5
Mo	μg l ⁻¹	<0.1	1.9	62.6	<0.1	1.6	14.4
Cd	μg l ⁻¹	<0.02	<0.02	0.27	<0.02	<0.02	0.03
Sb	μg l ⁻¹	<0.02	0.04	0.38	<0.02	0.00	0.21
Pb	μg l ⁻¹	<0.1	<0.1	1.6	<0.1	0.1	0.5
U	μg l ⁻¹	<0.01	1.88	52.8	<0.01	0.09	12.3
Hg	μg l ⁻¹	<0.010	0.018	0.128	<0.010	<0.010	0.032

DO: dissolved oxygen; SEC: specific electrical conductance. Shallow aquifer: n=59; deep aquifer n=14

of the basin. This is reflected in the regional distribution of dissolved oxygen concentrations (Figure 5.2). Those in the central parts of the basin are generally below detection limit.

The progression from aerobic to anaerobic conditions is reflected also in the distributions of dissolved arsenic (Figure 5.3). In both shallow and deep aquifers, concentrations are low in the aerobic groundwaters in the upper parts of the basin, but increase in the low-lying central parts. Concentrations of arsenic in analysed samples have a range of <1–1484 μg l⁻¹ in the shallow aquifer and between <1–308 μg l⁻¹ in the deep aquifer (Table 5.1).

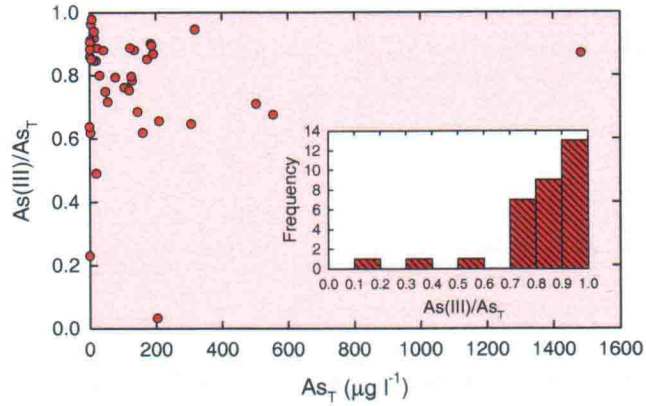


Figure 5.4. Variation in $As(III)/As_T$ with As_T in groundwaters from the Huhhot Basin

The dominant arsenic species present in the groundwaters is $As(III)$: $As(III)/As_T$ ratios are generally in the range 0.6–0.8 (Figure 5.4). As with Bangladesh groundwaters, this suggests that reduction of As to $As(III)$ is instrumental in the release of arsenic into solution.

Figure 5.5 shows that the spatial distribution of As in the groundwaters is different from that of SO_4 .

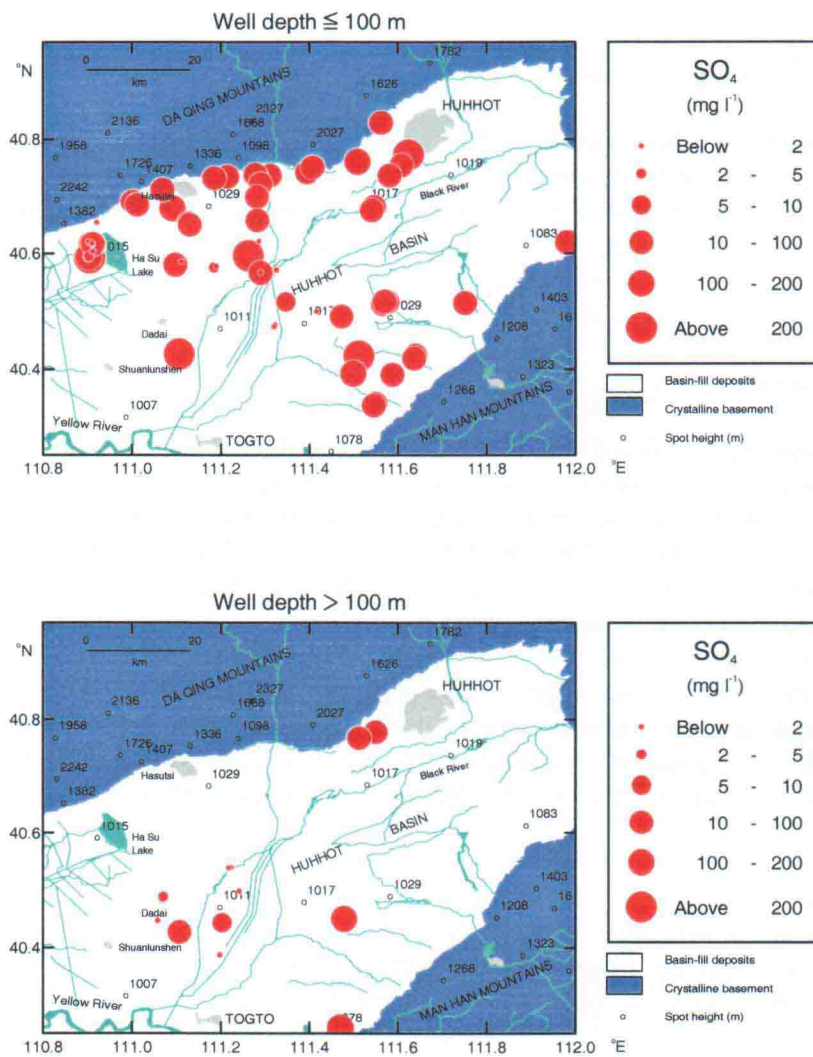


Figure 5.5. Dissolved SO_4 concentrations in groundwaters from the Huhhot Basin

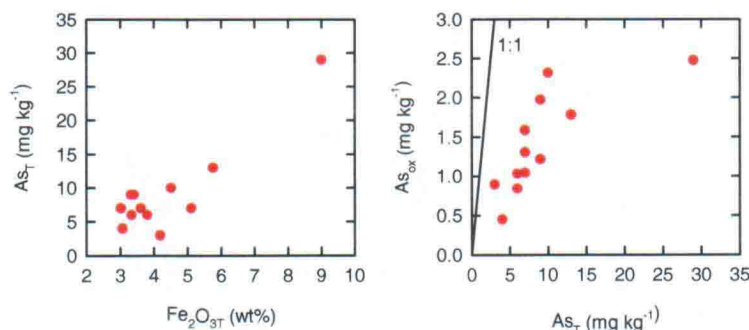


Figure 5.6. Total As against Fe₂O₃ concentration and total As against oxalate-extractable As (As_{ox}) in sediments from the Huhhot Basin

As with Bangladesh groundwaters, a weak negative correlation with SO₄ is apparent which suggests that the strongly reducing As-rich groundwaters have undergone some sulphate reduction.

Other features of the Huhhot groundwaters include high alkalinity values and high concentrations of Fe, Mn, P and dissolved organic carbon (DOC) in many of the anaerobic groundwaters (Table 5.1). Concentrations of fluoride are particularly high (up to 6.8 mg l⁻¹) in some of the shallow groundwaters. Concentrations of DOC are highest in the deep groundwaters. In many of the deep artesian groundwaters, humic acid is present at high concentrations (up to 64 mg l⁻¹).

5.4 Summary of sediment chemistry

Samples of Holocene sediments from the Huhhot Basin had arsenic concentrations of 3–29 mg kg⁻¹ (n=12). Arsenic is strongly correlated with Fe (Figure 5.6) and it is considered that iron oxides in the sediments provide an important source of the arsenic. Oxalate-extractable arsenic concentrations form a small proportion of the total arsenic in the few sediments analysed, suggesting that much of the arsenic is associated with the more structured iron oxides. However, whether this is more widely true of the aquifers is unknown and requires further study.

5.5 Options for mitigation

Reconnaissance sampling of groundwaters from the Huhhot Basin shows a large degree of spatial heterogeneity in arsenic concentrations as seen in other affected aquifers. However, highest arsenic concentrations are generally localised to the central parts of the basin as a result of the presence of more strongly reducing conditions. That part of the aquifer worst affected by arsenic contamination is therefore some 2400 km² in area. Clearly, this is an area for priority testing of every well used for potable supply. Groundwaters from other parts of the basin, as well as elsewhere within Inner Mongolia (especially along the Yellow River Plain) also require screening, though on a lower-density grid, at least in the first instance. The screening should be backed up with public-awareness campaigns. Presence of high concentrations of total dissolved solids (especially in the shallow groundwaters) and identification of F, Mn, B, U and Mo in concentrations close to or in excess of WHO guideline values indicate that testing for these constituents should also be carried out in groundwater surveys.

In the areas worst affected by arsenic contamination, alternative options for safe drinking water include use of surface water (the nearby Ha Su Lake (Figure 5.2) is a freshwater lake) or piped supplies of low-arsenic groundwater from the northern basin margins. Unlike Bangladesh, deep groundwaters are not likely to be a viable alternative because they too have high arsenic concentrations.

6. CONCLUSIONS AND IMPLICATIONS

6.1 Main findings

Many uncertainties remain over the causes of arsenic contamination in affected aquifers across the world and much research remains to be carried out on the precise mechanisms of arsenic release into solution and on mineral-water interactions. Differences exist in geochemical and hydrogeological conditions between aquifers in different regions. Arsenic can clearly be mobilised over a range of redox conditions for example. However, a number of common features are apparent from the recognised aquifers that allow some generalisations to be made about the key features involved in arsenic mobilisation and, significantly, the types of aquifers that are most at risk.

Combined data from arsenic-affected areas worldwide indicate that problems can occur under the following circumstances:

- i) strongly reducing groundwaters, often evidenced by high concentrations of iron, manganese, ammonium and sometimes humic acid, and low concentrations of nitrate and sulphate. High alkalinities and high concentrations of phosphate are also a key feature of many of these reducing groundwaters. Arsenic(III) is usually a major proportion of the total dissolved arsenic;
- ii) oxidising groundwaters with high pH values, often dominated by Na and HCO₃ ions. These are more common in arid and semi-arid areas where recharge is insufficient to counteract the high pH values generated by water-rock reactions, but can occur in Na-HCO₃ dominant groundwaters in other areas. In arid regions, evaporation of groundwater may also be responsible for some concentration of arsenic and other solutes;
- iii) groundwaters in sulphide mining or mineralised areas, where arsenic is released by oxidation of sulphide minerals. Conditions are oxidising or mildly reducing. These groundwaters typically have high concentrations of sulphate and many trace metals and are often acidic as a result of the oxidation reaction;
- iv) groundwaters in geothermal areas. These are recognisable by increased temperature and often have increased salinity (due to Na, Cl, Si, and possibly B, F); pH values are high (>7) in some.

Mining, mineralised and geothermal areas may have severe contamination with a number of inorganic constituents but tend to be relatively localised. Major affected aquifers are chiefly of the first two types.

A number of other features are common to the affected aquifers. Clearly, iron oxides (and possibly other metal oxides) are an important control on arsenic mobilisation and can act as sources or sinks under different conditions. Release of arsenic can occur by desorption reactions and, in reducing conditions, by reductive dissolution of the oxides themselves, although the precise mechanisms (changes in arsenic speciation, changes in iron-oxide structure, competition from other ions) remain in question. The areas studied (Table 6.1) share common features in that the aquifers are relatively young, of the order of thousands to tens of thousands of years old, and are characterised by thick sequences of rapidly accumulated sediments. These may be significant in respect of desorption of elements from oxide minerals. Unlike mineral dissolution reactions where constituent trace elements are likely to be released progressively until the mineral has dissolved completely, desorption of ions is likely to be a more rapid process, with much of the adsorbed element released to the first few flushes of porewater following sediment deposition. Large thicknesses of accumulated young sediment

Table 6.1. Summary of groundwater and aquifer characteristics in the three studied areas

Region/ Country	Aquifer	Groundwater chemistry	As source and mobilisation process	Groundwater flow
La Pampa, Argentina	Pleistocene & Holocene Aeolian (loess) silts, unconfined	Oxidising: Saline at shallow depths (evaporation) High pH, high alkalinity As present as As(V) Also high F, V, B, Be, Se, U, Mo, P	Fe, Mn oxides (and volcanic ash?) – desorption	Slow; regional flow gradients low. Local discharge zones (no outlet)
Huhhot Basin, Inner Mongolia	Holocene alluvial and lacustrine sands, silts, clays – Surface clay in centre of basin	Strongly reducing: Moderate Fe, Mn, high NH ₄ , alkalinity No DO, low SO ₄ , high humic acid As present mainly as As(III)	Fe oxides – desorption and dissolution	Slow in low- lying parts of the basin: 'closed basin'
Bangladesh	Holocene alluvial/deltaic sand, silt, clay Confined by surface clay	Strongly reducing: High Fe, Mn, NH ₄ , alkalinity No DO, NO ₃ , low SO ₄ – SO ₄ reduction As present as As(III) and As(V)	Fe oxides – desorption and dissolution	Very slow; regional flow gradients low

should involve more release of arsenic and other ions because of greater volumes of reactive oxide minerals.

Ageing of sediments also leads to development of more structured oxide minerals with time that may have more strongly bound, and lower concentrations of, trace elements. These may be reasons why older aquifers seem less prone to groundwater arsenic contamination. Slow groundwater flow is a key feature of all the studied aquifers (Table 6.1) and so little aquifer flushing with groundwater is thought to have taken place since sediment deposition. A summary of the key features of arsenic-vulnerable areas is given in Figure 6.1.

6.2 The need for arsenic screening

Young (Quaternary) aquifers with slow-moving groundwater are generally restricted to alluvial, deltaic and aeolian plains. Strongly reducing conditions can develop in low-lying areas, particularly large deltas (e.g. the Irrawaddy delta of Burma, the Nile delta of Egypt, the Indus valley of Pakistan and the Red River and Mekong deltas of Vietnam and Cambodia). Oxidising, high-pH groundwater conditions can develop in arid and semi-arid internal drainage basins such as the Yellow River Plain and other parts of northern China, as well as other areas of South America, including Uruguay and Paraguay. Chemical compositions of waters in vulnerable areas can be indicators of whether or not an arsenic problem is likely to exist (Figure 6.1).

Aquifers identified as 'at risk' require rapid randomised screening for arsenic to identify areas and scales of arsenic contamination and potential health risks. In identified problem areas, reconnaissance groundwater-quality surveys should be followed up by more detailed surveys, ideally to test every well used for potable supply. Consideration should also be given to other elements likely to be a risk factor in a given geological situation (e.g. fluoride in high-pH groundwaters; manganese in reducing groundwaters).

Methods of testing for arsenic depend on the scale of the area in question and the facilities available. Laboratory measurements are to be preferred, but where the scale of contamination is large, use of field-test kits, backed up with cross checks from reliable laboratory analysis, may be more

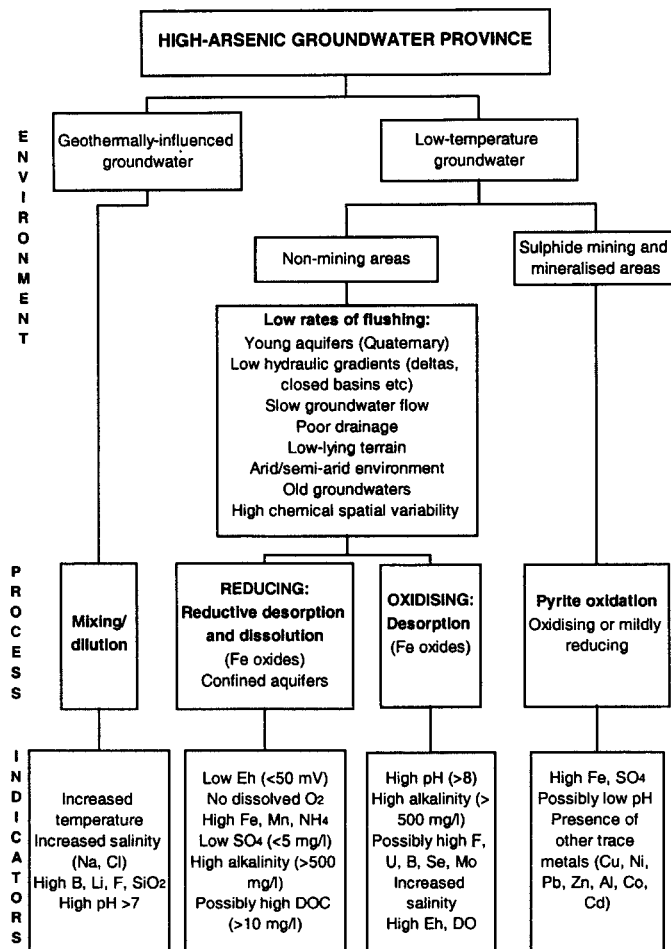


Figure 6.1. Classification of groundwater environments prone to arsenic problems from natural sources. This can be used as a tool to identify 'at risk' aquifers

appropriate. Many existing test kits for arsenic struggle to measure concentrations equivalent to national standard values (usually $50 \mu\text{g l}^{-1}$ at present) and usually are only reliable at concentrations of around $100 \mu\text{g l}^{-1}$ or higher. These will identify the very worst cases of contamination, but are not suitable for measurement at lower concentrations, particularly in the region of $50 \mu\text{g l}^{-1}$ or less. A number of new field-test kits are currently being developed which show considerably more promise, with more accurate detection down to $5 \mu\text{g l}^{-1}$ or so. The 'Arsenator' kit, under development at Karl-Franzens University of Graz, Austria, is one such instrument.

Often, new drilling programmes in developing countries place most emphasis on groundwater quantity rather than quality, especially in arid areas where groundwater resources are limited. The arsenic experience, especially from Bangladesh, has shown that groundwater quality is an important consideration and must be given due weight in determining groundwater development and groundwater-management strategies.

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