Chapter One

Introduction

1.1 Background

Arsenic, a notorious poison, is now recognised to be one of the world's greatest environmental hazards, threatening the lives of several hundred million people. Andrew Meharg (2005), in his book *Venomous Earth*, presents fascinating accounts of the use of arsenic for murder, medicine and wallpaper[1]. Sometimes known as the King of Poisons, arsenic has been known to humankind for thousands of years, being used to harden bronze in the Middle East around 3000 BC, and prized as a dye by the Egyptians, Greeks and Romans. In the fifth century BC, Hippocrates suggested using arsenic compounds as an ulcer treatment, while in the first and second centuries AD, the Roman Emperor Nero and Mithridates, King of Pontus, both used arsenic to murder their enemies. However, we will not describe the human use and abuse of arsenic further, because that is not the purpose of this book. Here, we are concerned with the insidious, creeping effects of naturally occurring arsenic in rocks and soils, which finds its way into underground water and streams, or is drawn into the roots of plants. This arsenic, withdrawn from the ground by wells and used for drinking, does not kill suddenly, but in the past 20 or 30 years has surely accounted for many more deaths than all the arsenical poisonings in history.

Long-term exposure to low levels of arsenic in food and water produces a broad array of effects on human health that are often described by the catch-all term arsenicosis. Early symptoms are non-specific effects such as muscular weakness, lassitude and mild psychological effects. These are followed by characteristic skin ailments such as changes in skin pigmentation and progressively painful skin lesions, known as keratosis. At the same time, arsenic causes a wide range of other effects on health, including diseases of the liver and kidney, cardio-vascular and peripheral vascular

diseases, neurological effects, diabetes and chronic and acute lung disease. Continued exposure to arsenic can lead to gangrene, cancers of the skin, lung, liver, kidney and bladder, and thereby to death.

Because the effects of arsenic depend on cumulative exposure, the symptoms are most commonly seen in adults and, because of lifestyle, in men more than in women. As symptoms develop, a person's ability to live a normal life is reduced. Sufferers may become unable to work, severely affecting the welfare of their families. Meanwhile, so long as exposure continues, the patient's condition will continue to deteriorate, while their ability to cope with the illness is reduced. The stigma of arsenic poisoning revealed in the symptoms of arsenicosis, and even of simply owning a polluted well, gives rise to social impacts such as ostracism and social and economic exclusion, with the burden falling disproportionately on women.

Naturally occurring arsenic in groundwater used for drinking and cooking is a catastrophe of global proportions. The World Health Organization (WHO) described the situation in Bangladesh as 'the largest poisoning of a population in history' (Smith et al., 2000). It is estimated that in 1998–99 around 27 million people were drinking water containing more than the national standard of 50 parts per billion (ppb) of arsenic. To this total should be added another 6 million people in the adjoining area of West Bengal in India. Worse, the WHO and many countries now consider 50 ppb unsafe, and recommend a limit of only 10 ppb. At this level, around 50 million people in Bangladesh, about 40% of the total population, and about 12 million people in West Bengal, are consuming dangerous concentrations of arsenic. If the statistics were not dire enough, these countries, striving to reduce the burden of poverty, are desperately ill-equipped to cope with the additional disease burden of arsenicosis. Moreover, suffering falls disproportionately on the poor, who are malnourished, drink more well-water, eat more arsenic in their diet and are less able to resist the toxic effects of arsenic than their better-off counterparts. Indeed, there is evidence that, within affected regions, the poor are more likely to show clinical symptoms of arsenicosis.

1.2   The Nature of Arsenic Pollution

Some of the features that made arsenic such an attractive poison – that it is colourless, tasteless and odourless – also contributed to its late discovery as an environmental contaminant. Further, when exposure is continuous over a period of years, arsenic is toxic at very low concentrations. In the past, it was no simple task to measure arsenic concentrations in water, and so, because it was not recognised as a problem, it was not routinely tested for. Unfortunately, in many parts of the world, arsenic is naturally present in

groundwater that is easily accessible and otherwise fit for drinking. Because it is in water used for drinking and cooking, and sometimes in staple foods as well, arsenic may be consumed in large quantities and for long periods. However, arsenic is almost never found in natural waters at concentrations that are acutely poisonous[2]. Chronic poisoning involves a long latent period before clinical symptoms develop. When water containing tens to a few hundreds of ppb is consumed continuously, symptoms of arsenicosis typically become apparent after periods of 2–10 years.

Natural arsenic pollution occurs in diverse geological and climatic conditions. It occurs most commonly in sands deposited by large rivers, and most of the worst cases are found in the tropical river basins of Asia. However, arsenic-contaminated groundwater is found in unconsolidated sediments and sedimentary, igneous and metamorphic rocks ranging in age from a few thousand to more than a billion years old. Arsenic pollution is found in climates ranging from the hot and humid tropics, to Arctic Alaska and hyperarid deserts. Despite this diversity, in any given location, contamination usually has a well-defined relationship to particular strata, or to particular depths of wells.

In many areas where groundwater contains high levels of arsenic, so too do the soils. Although the quantities vary greatly, most plants take up arsenic through their roots and into the edible parts. Where arsenic-rich groundwater is used for irrigation, the arsenic content of soils gradually builds up, and leads to more arsenic being taken up by plants. Thus, the effects of arsenic in food and water are both additive and cumulative. The worst conditions occur in the subsistence rice economies of Asia, where rice is irrigated with arsenic-contaminated water. The diet of the rural poor typically comprises locally grown rice with little fruit, vegetables or meat, and so a deficiency of vitamins, minerals and protein reduces their ability to resist the toxic effects of arsenic. If their food is cooked in, and washed down with, polluted well-water, the daily intake of arsenic can be ten times the recommended maximum. Thus, poverty and environmental hazards combine to exacerbate the suffering of poor, rural populations.

1.3 History of Natural Arsenic Contamination

1.3.1 Early discoveries

Although almost unknown 25 years ago, natural arsenic contamination affects more than 70 countries in the world (Figure 1.1). Unlike arsenic in minerals, such as orpiment and realgar, the occurrence of arsenic in natural waters has been known for barely a 100 years. The earliest measurement of arsenic in natural water was by the famous German chemist
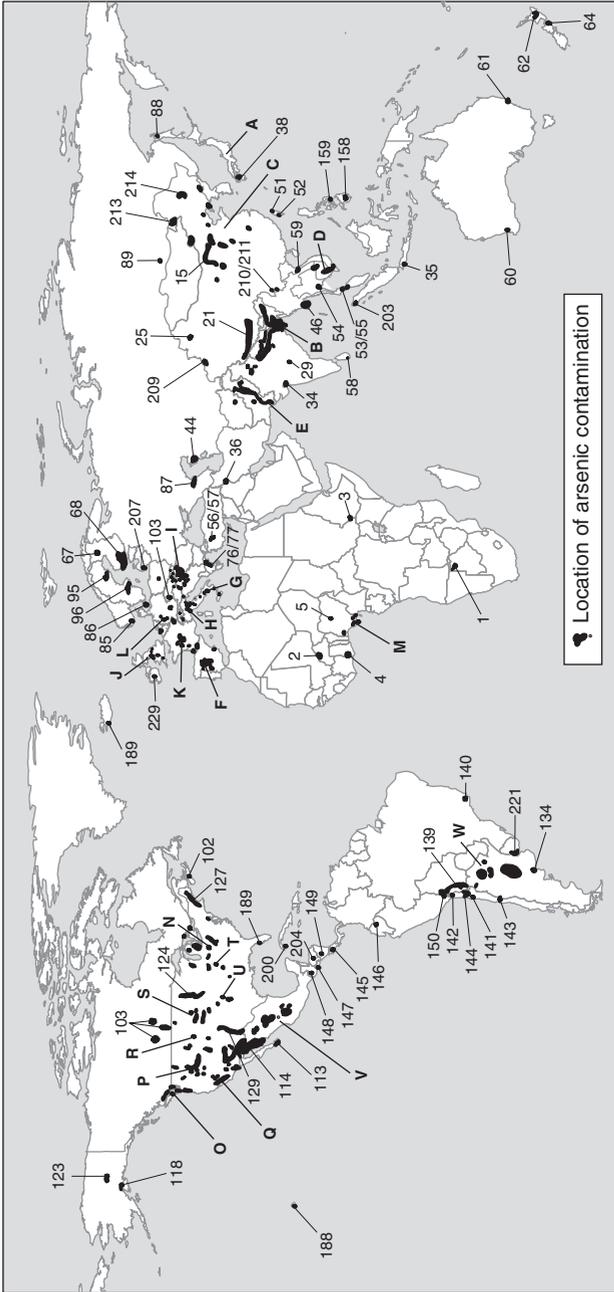
Figure 1.1 Global distribution of arsenic contamination. Note that the size of each affected area should not be confused with either the intensity and severity of pollution, or the numbers of people affected, which are elaborated in Chapters 8–10. The map numbers are detailed in Table 1.2. Where the numbered locations are too close to show on the map, groups of affected regions are identified by letter. Asia: A, 37, 39–41 & 43; B, 10, 11, 31–33, 154–157 and 205; C, 13, 14, 16–20, 22–24, 26; D, 12, 58, 201 and 202; E, 9, 28, 30, 47, 48 and 49 (see Fig. 8.1). Europe: F, 92, 93, 96 and 200; G, 80, 82, 83, 191 and 198; H, 79, 81, 166, 194, 195 and 215; I, 65, 78, 90, 91, 151, 161, 223; J, 97, 98, 216–220; K, 69–72, 152, 164; L, 73–75, 84, 165, 192 (see Fig. 9.17). Africa: M, 6–8, 190 (see Fig. 10.6). North America: N, 100, 101, 123, 133; O, 99, 104, 131, 132 and 187; P, 121, 170–174, 182; Q, 116, 117, 130, 175, 177, 188, 193; R, 126, 169, 176, 183, 186; S, 107, 119, 168, 184; T, 122, 178, 179, 181, 185; U, 128, 167; V, 106, 110–112, 115 (see Fig 10.1). South America: W, 135–138 (see Fig 10.1).

Fresenius at Wiesbaden Spa in 1885 (Schwenzer et al., 2001). Although historically interesting, this water was not consumed in sufficient quantities to cause illness. The earliest report of arsenic poisoning from well-water, which apparently caused skin cancer, was from Poland in 1898 (Mandal and Suzuki, 2002), although ironically there are no later reports from Poland. The first major case of endemic disease caused by arsenic in drinking water was reported in the 1920s in Cordoba Province of Argentina (Bado, 1939), where it is associated with a type of skin cancer known as Bel Ville disease. Although this affected thousands, perhaps tens of thousands, of people, it was little known outside Argentina until the end of the 20th century.

1.3.2   The mid-twentieth century

From the 1940s to the 1970s, there were few discoveries of natural arsenic contamination, although minor occurrences were noted in Canada (Wyllie, 1937) and New Zealand (Grimmett and McIntosh, 1939). In the 1960s, arsenic poisoning from well-water became well known in Taiwan, which has a special place in the history of epidemiological studies of arsenic. In Taiwan, arsenic caused a range of severe illnesses, including Blackfoot Disease, which is almost unique to southwest Taiwan. However, there were no international publications concerning the science of its occurrence, and the Taiwan case was largely unknown amongst water scientists[3]. Arsenic contamination is not only an issue in the developing world. The USA is, in fact, one of the most widely affected countries in the world, although the health impacts are quite small. The USA has been curiously slow to recognise and respond to the extent of contamination. A classic paper on the geochemistry of arsenic by Onishi and Sandell (1955) only recorded arsenic in hot springs and volcanic exhalations. A 1969 survey of 1000 water supplies reported that only 0.5% exceeded 10 ppb and 0.2% exceeded 50 ppb, and stated that arsenic represented 'no current threat to public health in the US' (Ferguson and Gavis, 1972). However, later surveys of water supplies reported that 1% exceeded 50 ppb and 8% exceeded 10 ppb (Ryker, 2003). In the 1970s, arsenic contamination was identified in Nova Scotia in Canada, where 25% of people drinking water with >50 ppb showed mild clinical symptoms (Grantham and Jones, 1977). Around the same time, almost the whole population of Antofagasta in northern Chile was exposed to 800 ppb As between 1958 and 1971, resulting in widespread and severe illness. However, the death toll attributed to arsenic-induced cancer, lung and heart disease in the decades following commissioning of a municipal treatment plant was about four times higher than during the period of peak exposure (Yuan et al., 2007).

1.3.3 The late twentieth century

Until the 1980s, the picture that emerges is one of isolated problems that did not attract international attention. The reasons are unclear, but there are probably three main explanations. First, arsenic was not routinely tested for in many countries, and second, there was a relatively poor knowledge of the health effects of low levels of arsenic. The third reason is cultural. The two major problems at the time (Argentina and Taiwan) were poorly known in Europe and North America and did not resonate with public health officials. Also, because arsenic was not perceived to be a problem in the home territories of the former colonial powers of Europe, they did not 'export' arsenic-testing protocols to their former colonies.

With hindsight, the 1980s may be seen as the period when the extent of pollution began to be recognised. Arsenic poisoning related to well-water was discovered in West Bengal (India) in 1983[4], although it took the rest of the decade for the size of the affected area to be appreciated. At about the same time, arsenic pollution was recognised in Hungary (Varsányi et al., 1991) and Xinjiang Province in China (Sun, 2004). However, in the political climate of the Cold War, there was apparently little awareness of the two latter problems in the west. Meanwhile, there was growing recognition of arsenic pollution in North America, with investigations of glacial aquifers in the mid-west by Matisoff et al. (1982), and a landmark publication by Welch et al. (1988) that documented 28 occurrences of groundwater arsenic in the southwest USA. While investigations in India and China had been triggered by medical diagnoses, the occurrences in the USA were not associated with clinical symptoms of arsenic poisoning.

In tropical Asia, drinking water was traditionally drawn from surface water or very shallow dug wells, and bacterial pollution of these water sources gave rise to epidemics of diarrhoeal diseases such as cholera and dysentery. Although the use of groundwater supplies began in the 1930s, it accelerated particularly after 1970 and into the 1990s, partly as a result of a deliberate policy promoted by UNICEF to reduce child mortality associated with enteric diseases. Tens of millions of cheap, shallow tubewells were drilled to obtain microbiologically safe drinking water. The major aim was to avoid polluted surface water sources that had caused widespread diarrhoeal disease. To this end, there was considerable success: in Bangladesh, between 1960 and 1996, child mortality dropped from 151 to 83 per thousand (Meharg, 2005). However, the switch from surface water did not occur without cost. For while the policy was largely successful in reducing enteric disease, and millions of deaths from this cause were prevented, in some areas the shallow tubewells that were substituted tapped arsenic-polluted groundwater, leading to chronic poisoning on a massive scale.

In the 1990s, arsenic pollution of groundwater burst from obscurity to receive the attention of the international press (e.g. Bearak, 1998), and radio and television networks such as CNN and the BBC. This transformation essentially took place in India and Bangladesh between 1994 and 1998, thanks particularly to the efforts of Dipankar Chakraborti and his colleagues at the School of Environmental Studies (SOES) at Jadavpur University in Kolkata, who described arsenic pollution in six districts of West Bengal as 'the biggest arsenic calamity in the world' (Das et al., 1994). For 10 years this was effectively unknown, even in neighbouring Bangladesh, except to a handful of individuals who chose to ignore or suppress the information. The tipping point was an international conference organised by Chakraborti in Kolkata in 1995. Almost overnight, the plight of millions of people in West Bengal was brought to the attention of the world's scientists, aid agencies and international media. The message was carried to Bangladesh, where geologists knew that the contamination must extend across the border, although none anticipated it would cover more than half of the country. Unlike its gradual revelation in West Bengal, Bangladesh progressed from discovery to comprehensive national mapping in two and a half years, and doctors soon began to recognise the symptoms of arsenic poisoning. From indifference in 1995, by the end of 1997, United Nations agencies, the World Bank and five bilateral donors were ready to commit millions of dollars to assist the Bangladesh Government implement a mitigation programme.

A second landmark conference took place in Dhaka in February 1998, organised by SOES and the Dhaka Community Hospital (DCH), which reiterated the magnitude of the problem in West Bengal, and revealed the even greater scale of contamination in Bangladesh. For the first time, the current scientific explanation of the pollution in Bengal was presented (Ahmed et al., 1998), showing that the cause was geological, and not anthropogenic, and acted as a stimulus for testing in surrounding countries. Over the next few years, extensive pollution was discovered in the river basins of Nepal, Myanmar, Cambodia, Vietnam and Pakistan (e.g. Jain and Ali, 2000; Nordstrom, 2002). Ironically, it was not until later that arsenic pollution was identified upstream from West Bengal in the Indian States of Bihar, Uttar Pradesh and Assam on the Ganges and Brahmaputra floodplains. Meanwhile, expanding studies in China discovered severe arsenic pollution in Inner Mongolia and Shanxi Provinces.

1.3.4   The twenty-first century

Since 2000, arsenic contamination has been found in other parts of the world, and new discoveries are regularly reported. In many parts of the world, especially Africa and South America, there is still a grave shortage of

information, and it seems inevitable that more cases will be found in the future. However, new discoveries have also been driven by the lowering of drinking water standards in many countries. From the middle of the 20th century, most countries specified a standard of 50 ppb, but in 1993, the WHO reduced its guideline value for drinking water to 10 ppb. Beginning with Germany in 1996, many countries have adopted the new guideline as a legal standard, leading to major testing programmes, so that countries that previously did not have an arsenic problem suddenly acquired one, and were obliged to retrofit arsenic treatment to many existing public supplies. However, the countries that face the most severe problems, mostly poor and in Asia, have retained 50 ppb as the standard for drinking water.

Where arsenic contamination has been discovered recently, one of the puzzles is to know how long the poisoning has been going on? Is it a new phenomenon, or has it always been present, and why was it not recognised before? In most cases, there are no clear answers to these questions, yet it is widely perceived that extensive arsenicosis is a recent phenomenon, and this has led many people to assume an anthropogenic cause. While this is generally incorrect, and arsenic has been present in groundwater for thousands of years, there is a human connection because of the deliberate shift towards groundwater supply in the 20th century.

1.3.5 The growth of knowledge

Knowledge of arsenic contamination has expanded enormously in the past two to three decades. Commenting on the first diagnosis of arsenic poisoning due to well-water in India, Datta and Kaul (1976) noted that the only equivalent reports of arsenical skin lesions were from Chile and Taiwan. While overlooking Argentina, they were correct in principle. Likewise, Fowler (1977), summarising the conclusions of an international conference intended to 'assess the current level of scientific knowledge about arsenic as an environmental toxicant and to identify areas of needed research', observed that the most important sources of arsenic exposure were non-ferrous smelting and burning of arsenic-rich coal. He 'suggested' that steel smelters, burning of impregnated wood, and abandoned mines should be studied. Finally, he noted that 'natural sources of environmental arsenic release such as volcanoes and hotsprings were also recognised as important.' The occurrence of non-geothermal arsenic in aquifers or soils received no mention.

The subsequent growth of knowledge is reflected in the literature consulted during the preparation of this book. Although far from comprehensive, a database of 1100 publications explicitly concerning arsenic was compiled, for the period up to the end of 2006. Classified by decade (Table 1.1), over 90% of all publications were produced after 1990. The database included 789 geographically related publications, of which the largest group, 444

Table 1.1   Publications concerning arsenic by decade (Source: Authors' database)

| *Period* | *Publications* | |
	Number	*%*
1931–40	3	0.3
1941–50	1	0.1
1951–60	1	0.1
1961–70	5	0.5
1971–80	26	2.4
1981–90	47	4.3
1991–2000	208	18.9
2001–2006	810	73.6

publications, concerned arsenic in Asia, of which 83% had been published since the year 2000.

Because of the history of arsenic as a poison, the occurrence of accidental industrial poisonings, and its use as a medicine, medical investigators were reasonably well prepared to anticipate the symptoms of chronic arsenic poisoning. Earth and environmental scientists, however, were ill-prepared to respond to the discoveries of the 1980s and 1990s. The causes of the few known natural cases of arsenic pollution in Argentina, Chile, India and Taiwan were not seriously investigated until at least the late 1980s. It is hardly surprising, therefore, that the initial discoveries in other countries were met with confusion and uncertainty and, in some cases, denial. Until recently (Hiscock, 2005), the general texts on groundwater chemistry (e.g. Appelo and Postma, 1996; Langmuir, 1997) and hydrogeology included negligible descriptions of natural arsenic contamination[5].

1.4   Arsenic Pollution

The environmental literature makes diverse use of the terms contamination and pollution. Some authors use the term pollution when the cause is anthropogenic, while others use it as a measure of severity. In discussing arsenic in groundwater, an anthropogenic distinction is not particularly helpful. In many cases, the background levels are harmful, and in others, naturally elevated concentrations of arsenic have been modified by human action. Here we follow Chapman (2007) in using contamination to refer to the presence of a substance where it would not normally occur, or at concentrations above the natural background, whereas pollution is contamination that results in actual or potential adverse biological effects.

However, arsenic in drinking water has no well-defined threshold for adverse health effects, so we apply this distinction loosely, preferring the term contamination where health effects are not apparent, or less likely.

1.4.1   Unnatural pollution by arsenic

Humans have often polluted their environment with arsenic, usually in the processing of geological materials such as coal and metaliferous ores (Han et al., 2003). In mining, pollution may occur from improper disposal of wastes from sulphide-rich ores (Abrahams and Thornton, 1987; Williams, 2001). Exposed to air and rainwater, sulphides are oxidised to produce sulphate-rich, acid mine drainage (AMD) that often contains high arsenic concentrations. Arsenic-rich spoil heaps, such as from the Cornish tin-mines, have left a legacy of contaminated soil that prevents their use for food crops more than a 100 years after the mines were abandoned. Arsenic pollutes the air through the smelting of sulphide ores. Airborne arsenic may be inhaled, but also accumulates as fallout on soils, from where it may be taken up by crops or enter streams in runoff. Globally, the burning of coal has been the major anthropogenic input of arsenic to the surface environment (Han et al., 2003). Some coals contain high concentrations of arsenic, the worst case being in Guizhou Province of China, where power stations cause extensive air pollution, and even worse health effects result from burning coal inside households (Ding et al., 2001). Although now largely abandoned, arsenical pesticides were widely applied to orchards and cotton and rice fields in the USA, resulting in serious soil contamination (Peryea, 2002; Renshaw et al., 2006). In addition, chromated copper arsenate compounds have been widely used as wood preservatives, although this practice is now being discouraged (Hingston et al., 2001). Arsenic is also mobilised by other polluting activities such as landfill (Hounslow, 1980) and oil spills (Burgess and Pinto, 2005).

Important sources of knowledge about chronic arsenic poisoning were tragic industrial accidents such as the Manchester Beer Incident (which provided part of the basis for the original 50 ppb standard for arsenic in water), and the contamination of milk powder and soy sauce in Japan (Pershagen, 1983; Dakeishi et al., 2006). Historically, arsenic has been used as a medicine, and is still used in some cancer treatments, where the side-effects may be tolerated. Arsenical medicines were particularly popular in the 19th century until their association with keratosis and skin cancer was recognised. Some were simply quack medicines, but others such as Fowler's Solution were still in use in the 1970s (Meharg, 2005). Fowler's *Liquor Arsenicalis* was a 1% solution of potassium arsenite, taken internally, and was promoted as a cure for ague, fever and headache. One of the more bizarre cases of arsenic poisoning is that of the Styrian arsenic eaters

in 19th century Austria (Meharg, 2005). The Styrian peasants believed that arsenic conferred plumpness to the figure and improved the complexion as well as aiding digestion and having aphrodisiac properties. These people consumed arsenic trioxide with food, at gradually increasing doses, eventually consuming doses that would normally be considered fatal. This latter observation suggests that the human body can develop a degree of tolerance to arsenic[6] (Przygoda et al., 2001).

1.4.2   Natural arsenic pollution

Arsenic in the natural environment

Arsenic is not a rare element in the Earth's crust, but it is unusual to find high concentrations in water. Although arsenic is found in some silicate minerals, such as biotite, the most important accumulations are found in two distinct mineral associations, sulphides and oxides, which themselves reflect how dissolved arsenic may be removed from groundwater. Arsenic can form sulphide minerals such as orpiment, realgar and arsenopyrite, and also substitutes for sulphur, to be trapped in more common minerals such as pyrite (iron sulphide), chalcopyrite (copper sulphide), galena (lead sulphide) and sphalerite (zinc sulphide). These minerals commonly form in areas of hydrothermal activity, and are often associated with metal ores. However, pyrite, the most abundant of these minerals, also forms in swamps, peat basins, beneath the beds of lakes and seas, and in some aquifers. The important point is that they are stable when there are no sources of oxygen, but they are easily broken down by oxidation. Oxide minerals do not take arsenic into their structure, but have a great capacity to adsorb arsenic onto their surface. Iron oxides are the most important minerals in controlling the occurrence of arsenic in groundwater. In contrast to sulphides, oxides are formed in environments where there are ready sources of oxygen, and conversely break down and dissolve in anaerobic environments. Thus, there are two competing means of trapping arsenic in minerals, under oxidising and reducing conditions, and so arsenic contamination occurs where, for reasons described later, neither sulphides nor oxides can remove arsenic from solution.

The causes of natural arsenic pollution of groundwater

In natural waters, arsenic is usually found in one of four chemical associations, which occur in more-or-less predictable geological and climatic settings, and each of these is associated with a characteristic cause, or mobilisation mechanism. These water types and mobilisation mechanisms are themes that recur throughout the book because they determine not only where arsenic is found, but also how it may be avoided, how it affects agriculture,

and how it may best be treated. The four mechanisms are described below in order of decreasing importance:

1 **Reductive dissolution** occurs when iron oxides, onto which arsenic is adsorbed, break down under the influence of decaying organic matter (which consumes oxygen sources) and dissolve, thereby releasing arsenic in the process. The groundwater produced by these processes is always strongly reducing, with high concentrations of iron and bicarbonate, while nitrate and sulphate are absent.
2 **Alkali desorption** occurs at high pH (≥ 8.0) and in the presence of dissolved oxygen, nitrate or sulphate, producing waters which can be termed 'alkali-oxic', and which have low concentrations of iron and manganese.
3 **Sulphide oxidation** occurs where sulphide minerals such as pyrite or arsenopyrite are exposed to oxygen, often at the water table, to produce waters that are typically both acid (pH 1–6) and sulphate-rich, but not necessarily high in iron.
4 **Geothermal** waters from deep, sometime volcanic, sources leach arsenic from the country rocks. The waters are distinguished primarily by elevated temperature, and usually also by a correlation of arsenic with chloride.

Soils, irrigation and agriculture

Combined exposure from food and water can significantly increase the disease burden from arsenic. In many affected areas, moderately high levels of arsenic are found in natural soils. Arsenic may be taken up through the roots of plants to accumulate in the edible parts. Where soil is the only source of arsenic, uptake by plants declines over time. However, greater problems may develop where arsenic in irrigation water accumulates in the soil and leads to increasing uptake by plants. In general, as a proportion of dry mass, leafy vegetables and some spices may take up the most arsenic, but when adjusted for dietary intake, grains such as rice make the largest contribution to human exposure. In some Asian countries this can be a larger source of exposure than drinking water. High concentrations of arsenic in soil can be toxic to rice, and can dramatically reduce yields. This worrying phenomenon has recently been recognised in South Asia (Duxbury and Panaullah, 2007), but as Reed and Sturgis (1936) noted 'Arsenic toxicity in soils is no new problem'.

Extent of natural arsenic contamination

Known sites of natural arsenic contamination of surface and groundwater are listed in Table 1.2 and their locations shown in Figure 1.1[7]. The reader should take care not to confuse geographical extent with significance. The quality of mapping varies between sources; contamination is not necessarily

Table 1.2 Locations of natural arsenic contamination of surface and groundwaters. See Chapters 8 to 10 for details of individual occurrences. Locations marked as 'Unspecified' are assigned a nominal location in the centre of the country, and Map ID refers to location numbers on Figure 1.1

Map ID	Name/location	Maximum As (ppb)	Map ID	Name/location	Maximum As (ppb)
Asia			25	Xinjiang Province	880
Afghanistan			209	W. Xinjiang – Tarim	
9	Logar and Ghazni		210	Yunnan (N)	200
Bangladesh			211	Yunnan (S)	200
10	Chittagong coastal plain		26	Zhongmou, Zhengzhou	186
11	Bengal Basin	4000	*India*		
Cambodia			27	Assam	657
12	Cambodia	1700	28	Chandigarh	545
China			29	Chattisgarh	1930
13	Datong Basin	1530	30	Himachal Pradesh	
14	Houshayu, near Beijing	91	31	Nagaland	278
15	Inner Mongolia, Huhhot	1480	32	Thoubal (Manipur)	986
212–2	Inner Mongolia		33	Tripura	444
16	Jilin Province	360	34	Vapi (Gujarat)	
17	Jinchuan, Sichuan	287	153	Chennai	146
18	Liaoning Province		157	Uttar Pradesh and Bihar	
19	Linbei, Wuhe, Anhui	500	205	Son River, Garwha District	1654
20	Ningxia Province		*Indonesia*		
21	Qinghai–Tibet Plateau	126,000	35	Citarum River	279
22	Shanxi	2783	203	Aceh	
23	Tongxiang, Zhejiang	70	*Iran*		
24	Weichang, Hebei	48	36	Kurdistan	104

(cont'd)

Table 1.2 (cont'd)

Map ID	Name/location	Maximum As (ppb)	Map ID	Name/location	Maximum As (ppb)
Japan			Vietnam		
37	Fukui	50	58	Mekong river	500
38	Fukuoka – Kumamoto	370	59	Red river	3050
39	Niigata Plain	10	Europe		
40	Osaka		Belgium		
41	Sendai		192	Neogene, Flanders	60
42	Shinji Plain	114	Croatia		
43	Takatsuki	60	65	Eastern Croatia	612
Kazakhstan			Czech Republic		
44	South Mangyshlak	1500	163	Celina – Mokrsko	1500
Lao PDR			Denmark		
201	Inchampasak and Sarava	54	66	Fensmark	30
202	Attapeu province	112	Finland		
Malaysia			67	Finnish Lapland	35
45	Kampong Sekolah		68	Southwest Finland	2230
Mongolia			France		
232	Dornod Steppe		69	Aquitaine	49
233	Gobi Altai – Hovd		70	Massif Central	100
234	Arkhangai		71	Pyrenees	
Myanmar			72	Vosges Mts	
46	Irrawaddy Delta		152	Centre	49
Nepal			164	W-C France	49
154	Terai (W)				

No.	Location	Value
155	Terai (E)	
156	Kathmandu Valley	
Pakistan		
47	Indus valley, Punjab	972
48	Kalalanwala, Punjab	1900
49	Indus valley, Sindh	906
Philippines		
158	Mount Apo	
159	Greater Tongonan	
Russia		
88	Sakhalin	10,000
Saudi Arabia		
231	Jubail	
Sri Lanka		
50	Near Colombo	
Taiwan		
51	N E Taiwan	3000
52	southwest Taiwan	1410
Thailand		
53	Hat Yai	1000
54	Nakorn Chaisi	100
55	Ron Phibun tin belt	5000
Turkey		
56	Afyon, Heybeli Spa	1240
57	Emet – Hisarcik	700

No.	Location	Value
Germany		
73	Bavaria	150
74	Paderborn	38
75	Wiesbaden	100
Greece		
76	E. Thessaly	125
77	Thessaloniki	
Hungary		
78	Tisza interfluve	4000
151	southwest Hungary	4000
160	Danube valley	
161–2	W. Hungary	
Ireland		
229	Unspecified*	32
Italy		
79	Anzasca Valley, Piedmont	
80	Etna	6390
81	Siena	14
82	Stromboli, Vulcano	130
83	Vesuvius	92
166	Po Basin	
191	Tiber valley	52
194	Emilia-Romagna	
195	Lombardia	
196	Veneto	
197	Toscana	
198	Lazio	

Table 1.2 (cont'd)

Map ID	Name/location	Maximum As (ppb)
Europe (cont'd)		
199	Ischia	460
Lithuania		
207	Unspecified*	33
Netherlands		
82	Gouda 15	
165	Brabant 44	
Norway		
85	Unspecified*	19
Poland		
230	Sudetes Mts	140
Romania		
86	Unspecified*	176
Russia		
87	East Caucasus Foothills	1500
89	Trans-Baikal	700
Slovakia		
90	W. Slovakia	39
221	E. Slovakia	
Slovenia		
91	Radovljica	559
Spain		
92	Castellon-Valencia	14

Map ID	Name/location	Maximum As (ppb)
111	Guanajuato – Salamanca	54
112	Rio Verde river basin	410
113	San Antonio, Baja California	305
114	Sonora	1100
115	Zimapán	
USA		
107	Grass Mt, S. Dakota	117
116	California	
117	Sierra Nevada	1000
118	Cook Inlet basin	110
119	Dakota	
120	Fairbanks, Alaska	1370
121	Idaho	
122	Illinois	266
123	Michigan	220
124	Minnesota, Iowa	145
125	N. Idaho	
126	Nebraska	
127	New England	408
128	Oklahoma	232
129	Rio Grande	264
130	southwest USA	1300
131	Washington State	33,000

No.	Location	Value
93	Duero Basin	290
94	Madrid Basin	91
206	Salamanca	52
Sweden		
95	S. Sweden	200
96	Uppsala300	
Switzerland		
215	Malcantone watershed	300
UK		
97	Bridgwater	
98	West Midlands	30
220	Carlisle Basin	233
219	Vale of York	39
218	Manchester-E. Cheshire	57
217	Liverpool-Rufford	355
216	North Humberside	63
North America		
Canada		
99	Bowen Island	580
100	Cobalt, Ontario	
101	Madoc, Ontario	3780
102	Nova Scotia	1050
103	Saskatchewan	117
104	Sunshine Coast/Powell Is.	
Mexico		
106	North central Mexico	624
110	Durango	
132	Willamette Basin, Oregon	2150
133	Wisconsin	12,000
167	Kansas	
168	Nebraska	
169	Colorado	
170	Washington	
171–2	Oregon	
173–4	Nevada	
175	Carson Desert, Nevada	1,000
176	Yellowstone	1000
177	Arizona	1000
178	Ohio	
179	Indiana	
180	Florida	
181	Arkansas	
182	Idaho	
183–4	Montana	
185	Kentucky	
186	Utah	
187	Washington	
188	San Joaquin valley	2600
193	Owens Lake	163,000
228	Newark Basin, Pennsylvania	70
South America		
Argentina		
134	Bahia Blanco	500
135	Tucuman	1000

(cont'd)

Table 1.2 (cont'd)

Map ID	Name/location	Maximum As (ppb)	Map ID	Name/location	Maximum As (ppb)
South America (cont'd)			Burkina Faso		
136	Cordoba	3810	2	Yatenga	1630
137	San Antonio de los Cobres	220	Cameroon		
138	Santiago del Estero	14,969	190	Ekondo Titi	2000
Bolivia			Ethiopia		
139	Altiplano	1000	3	Rift Valley	96
Brazil			Ghana		
140	Iron Quadrangle	250	4	Ashanti	557
Chile			Nigeria		
141	Antofagasta	870	7	Rivers State	
142	Rio Camarones	1252	5	Kaduna	9000
143	Rio Elqui	110	6	Ogunstate	220
144	Rio Loa	2000	8	Wari – Port Harcourt	780
Costa Rica					
145	Unspecified*		*Australasia*		
Cuba			Australia		
200	Isle of Youth		60	Perth 800	
Ecuador			61	Stuarts Point, Nsouthwest	337
146	Rio Tambo	5080	New Zealand		
El Salvador			62	Waikato River	1320
147	Lake Ilopango	770	63	Waiotapu valley	260
Guatemala			64	Wairu Plain	50
148	Unspecified*		237	N. Hawkes Bay	

Honduras			
204	Unspecified*	238	Bay of Plenty
Nicaragua		*Ocean Basins*	
149	Sebaco – Matagalpa	1320	Guam
Peru		208	Tumon Bay
150	Lake Aricota	500	Iceland
	Uruguay	189	1
221	S. W. Uruguay	58	USA
		188	Iceland
Africa			48
1	Okavango Delta	117	Hawaii
			70

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continuous within the map areas, and both arsenic concentrations and population densities vary enormously between and within areas. Arsenic contamination is very unevenly distributed between the continents. In terms of the exposed population, by far the worst pollution is found in Asia, especially in a band running from Pakistan, along the southern margins of the Himalayan and Indo-Burman ranges, to Taiwan, which we refer to as the South and Southeast Asian Arsenic Belt (SSAAB). In this area, groundwater in shallow alluvial aquifers is both the main source of drinking water and an important source of irrigation water. In India, Bangladesh and Taiwan, exposure has resulted in widespread clinical effects, ranging from skin lesions to cancer and death, yet in Nepal, Cambodia and Vietnam there have been few diagnoses of arsenicosis to date. Elsewhere, pollution of alluvial aquifers has resulted in severe arsenicosis in at least three provinces of China.

In North America, the USA is affected by extremely widespread and diverse cases of arsenic contamination, but the concentrations are typically lower than in Asia and diagnosed cases of arsenicosis are almost unknown. Europe has one severe case of arsenic pollution in Hungary, and many low-level occurrences that, as in the USA, were probably detected because of more intensive testing of water sources. South America contains two areas of severe arsenic pollution (the Pampean plains of Argentina and the Pacific Plains of Chile) that have both resulted in extensive arsenicosis and many deaths due to cancer, heart and lung disease. Elsewhere in South and Central America, arsenic contamination occurs along the volcanic mountains of the Pacific Rim.

In Africa, there are few reported occurrences of arsenic contamination. The only extensive, and reasonably well documented, case of arsenic pollution in Africa is in southwest Ghana, which is partly anthropogenic, and has been known for more than about 10 years. It appears that, in large areas of Africa, groundwater has simply not been tested. In Australasia, New Zealand is quite widely affected, but in Australia only two minor occurrences have been reported. There is very little information from the ocean basins, although arsenic has been reported from geothermal sources on Hawaii and Iceland.

1.5   Risk, Perception and Social Impacts

The promotion of shallow tubewells to reduce the incidence of enteric disease had the unintended consequence of creating a new risk of mass chronic poisoning. This is an example of the self-generated risks with unmanageable outcomes that characterise Ulrich Beck's 'risk society' (Beck, 1992). In the risk society, the social production of risk involves hazards that are produced by society itself, and that undermine the established safety systems of the state's existing risk assessments (Beck, 1996). Furthermore, responsibility for the risk is indeterminate because the chain of decision-making is so convoluted

and institutionalised that the attribution of blame is often impossible. Beck (1999) describes this as the 'travesty of the hazard technocracy', and it is exemplified by the unsuccessful outcome of the class action brought by 400 Bangladeshi villagers against the British Geological Survey (BGS) for failing to test for arsenic (Annexe 8.1). The BGS was deemed to be insufficiently 'proximate' to be directly responsible, although this lack of proximity reflects the complex structure of corporate, institutional and individual decision-making that typifies the risk society, and protects against legal liability even where it can be argued there was a failure to exercise a duty of care.

These issues must, however, also be judged in the light of the evolving understanding of the effects of exposure to arsenic contamination, which demonstrates the transition from ignorance of an environmental problem to a quantifiable risk (Wynne, 1980, 1994). To make the statements about risk (of health consequences of ingesting arsenic) that are quoted in Chapter 5 requires an ability to quantify the associated odds. However, these risks may have wide margins for error because, for example, of the very large sample sizes required to estimate probabilities at low doses. Uncertainty, however, is a lower-order problem than both ignorance and indeterminacy. In the case of uncertainty, the parameter is known, but its value is subject to error. Ignorance, on the other hand, implies a complete lack of knowledge about the existence of a parameter (the 'unknown unknowns' of Donald Rumsfeld, 12 February 2003). Equally, indeterminacy represents an open-ended state in which it may be known that a problem exists, but there are multiple, unknown and non-linear ways in which it can manifest itself. Quantifiable risk requires extensive data to remove the layers of ignorance, indeterminacy and uncertainty that surround environmental problems, and in some circumstances the sampling intensity required to achieve confidence in risk estimation is prohibitively expensive. This may indeed be true of arsenic mobilisation in alluvial sediments, where local variability in the stratigraphy is high, and closely separated wells may differ greatly in arsenic concentration.

A third set of issues arises in the estimation of the medical risks associated with arsenic ingestion, and how these are translated into regulatory standards for arsenic in water and food (section 5.4.3). It is evident that chronic poisoning depends on cumulative ingestion, which implies that a precautionary approach would specify a low standard. However, dose–response curves at low dose may be non-linear, and because it is difficult to extrapolate reliably to these concentrations, the future cancer burden is highly uncertain given the latency periods for such diseases. These estimates are further complicated when food is an important source of exposure. Epidemiological data also have to allow for subpopulations having distinctive susceptibilities, and failing to recognise this may underestimate the risks to the most vulnerable populations. The severe health impacts of drinking water with more than 100 ppb As are not disputed, but the consequences of drinking water containing arsenic in the range of 10–50 ppb (i.e. the difference

between the present and previous WHO guideline values) has received much discussion. Some have suggested that developing countries should delay adopting a lower standard in order to prioritise the worst affected groups, and optimise use of limited financial resources. However, an alternative, morally defensible position would be to adopt the lower standard, and implement it through a phased but time-limited programme.

1.6   Water-supply Mitigation

Historically, most water supplies were originally developed from local surface water sources and subsequently, due to the pressures of population growth and pollution, the source of supply has shifted to either groundwater or surface water transported from a remote source. There are three approaches to mitigating arsenic pollute water supplies: treat the contaminated water; resink the well at some distance away or at different depth; or develop a surface-water supply. There is no single best solution. Treating groundwater always involves significant cost and effort in operation and maintenance, and methods must be matched to the water quality, the size of installation, and the skills of the operators. Developing deeper groundwater is popular, but may involve risks of contamination over time. Surface water, drawn from ponds or streams, must be treated to remove microbial contamination, and requires a higher level of management, or else acute bacterial infections may be substituted for chronic arsenic poisoning.

Approaches to mitigating contaminated water supplies have varied greatly between countries, reflecting the extent and rate of discovery of the problem, and their economic condition. In the USA, where the extent of contamination emerged slowly, public authorities took responsibility, abandoning the most polluted sources, installing treatment at others, and occasionally importing surface water. In Taiwan, public authorities constructed a reservoir and piped water to the affected villages. In Chile, a municipal treatment plant was built to supply the whole city of Antofagasta. In Hungary, state utilities installed treatment plants at some wells, and piped in uncontaminated groundwater to replace others. In all these examples, arsenic exposure has been greatly reduced. In South Asia, there is still massive exposure of the rural population. To date, the main response has focused on surveying private wells and raising awareness to encourage arsenic avoidance. In West Bengal, government has played a leading role, initially installing thousands of small treatment plants, and later piping supplies from high-capacity deep tubewells and surface-water treatment plants to groups of villages. In Bangladesh, guided by donors, the government has promoted a demand-led approach, which has resulted in installing thousands of deep hand-pumped tubewells. In other states of India, Nepal, Cambodia and Vietnam, mitigation

is less advanced, although Vietnam and Nepal have promoted domestic and small community arsenic removal plants (ARPs).

Currently, tens of millions of people continue to depend on arsenic-polluted groundwater as a source of drinking water and for irrigation. Greatly increased mitigation efforts are needed to reduce, and eventually eliminate, exposure to arsenic, and thus to begin to reduce the current and growing burden of disease.

1.7   Structure and Scope of the Book

1.7.1   Objectives

The primary purpose of this book is to satisfy the need for an up-to-date, interdisciplinary and global perspective on arsenic pollution for researchers, both established and just entering the field, and for practitioners in arsenic mitigation, government officials, aid and development administrators and workers in non-government organisations. The recent recognition of the scale of natural arsenic pollution means that such a book could not have been written earlier. Further, as indicated above, anything written more than about five years ago will have overlooked three-quarters of the published material. Although there is a risk that this work could quickly become obsolete, we doubt that it will, because we believe that the past 10 years have been a special period in the history of arsenic research, and new ideas, as opposed to new data, will not be produced as quickly in the next 10 years. Most existing knowledge is scattered amongst hundreds of journal articles, conference proceedings and reports, which we attempt to synthesise. We anticipate that most readers will approach this book with knowledge of one or more of the technical areas covered, and hope that, after reading this book, they will feel comfortable to discuss and work with specialists in all subject areas. We also hope that the reader will gain a truly global perspective of arsenic pollution.

The book is divided into two main parts, each with a distinct focus. Chapters 2–7 approach arsenic pollution from the technical–disciplinary approaches of geochemistry, hydrology, health and water supply. In Chapters 8–10 we address arsenic pollution from a geographical perspective, seeking to present an integrated account of the characteristics, impacts and activities in each region. As far as practicable, the technical and geographical chapters are cross-referenced to minimise duplication, but the reader seeking more information on a specific subject should refer first to the corresponding technical or geographical chapter. Finally in Chapter 11, we summarise and synthesise the major findings and conclusions, and try to predict future trends of discovery, occurrence and impact.

1.7.2 Terminology

Inevitably, the literature uses different units. However, so far as it is sensible to do so, we have used consistent units and tried to help the reader by using forms that are specific to each medium. For concentrations of arsenic in water, we use parts per billion (ppb) as standard, which is equivalent to micrograms per litre (μg/L)[8]. Occasionally, we quote arsenic concentrations in water in units of parts per million (ppm), but only when referring to extreme concentrations. For other solutes in water, we use either ppb or ppm, equivalent to milligrams per litre (mg/L), as appropriate to make the concentrations easily comprehensible. For arsenic concentrations in soil, we use milligrams per kilogram (mg/kg) as standard, since it helps in differentiating solid and liquid concentrations in complex sections of text. Where referring to arsenic concentrations in plant materials and foodstuff, we express these in units of micrograms per kilogram (μg/kg), to differentiate the different media (i.e. water, soil and food) within the text; this also makes the quantities of arsenic in food numerically comparable to those in water (in ppb or μg/L).

The most severely affected area of the world is the delta of the Ganges, Brahmaputra and Meghna rivers, which form a large part of Bangladesh and the adjoining Indian state of West Bengal. Geologically, these areas form a continuum, known as the Bengal Basin, and have demographic and cultural similarities. The areas face very similar problems, and where we refer to matters of common concern, we use the trm Bengal Basin, or simply Bengal where there is no geological significance.

NOTES

1 It has been suggested that arsenical dyes in wallpaper were responsible for the accidental poisoning of Napoleon Bonaparte during his imprisonment on St Helena.
2 Acute poisoning follows from the ingestion of a few grams of arsenic over a short space of time, and results in life-threatening illness. Chronic poisoning results from months or years of low-level arsenic exposure, and causes no immediate suffering.
3 As judged by the absence of references in standards texts in water engineering, hydrogeology or geochemistry.
4 An earlier discovery in northern India by Datta and Kaul (1976) was largely ignored.
5 The reasons for this are not clear. Although the most affected areas were remote from the authors, contamination was widespread in the USA.
6 Apparently contradicting other evidence discussed in Chapter 5.
7 This includes rivers on the Pacific coast of South and Central America that are fed by geothermal groundwater from springs in the Andes. Almost all other locations in Figure 1.1 are groundwater bodies, including springs.
8 For all practical purposes, in dilute solutions μg/L and ppb (or mg/L and ppm) are identical. This is not true, however, for saline waters.