United Nations Synthesis Report on Arsenic in Drinking-Water

Water and Sanitation

Protection of the Human Environment

Chapter 1. Source and behaviour of arsenic in natural waters

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1.1 Importance of arsenic in drinking water

Arsenic (As) is a ubiquitous element found in the atmosphere, soils and rocks, natural waters and organisms. It is mobilised in the environment through a combination of natural processes such as weathering reactions, biological activity and volcanic emissions as well as through a range of anthropogenic activities. Most environmental arsenic problems are the result of mobilisation under natural conditions, but man has had an important impact through mining activity, combustion of fossil fuels, the use of arsenical pesticides, herbicides and crop desiccants and the use of arsenic as an additive to livestock feed, particularly for poultry. Although the use of arsenical products such as pesticides and herbicides has decreased significantly in the last few decades, their use for wood preservation is still common. The impact on the environment of the use of arsenical compounds, at least locally, will remain for some years.

Of the various sources of arsenic in the environment, drinking water probably poses the greatest threat to human health. Airborne arsenic, particularly through occupational exposure, has also given rise to known health problems in some areas.

Drinking water is derived from a variety of sources depending on local availability: surface water (rivers, lakes, reservoirs and ponds), groundwater (aquifers) and rain water. These sources are very variable in terms of arsenic risk. Alongside obvious point sources of arsenic contamination, high concentrations are mainly found in groundwaters. These are where the greatest number of, as yet unidentified, sources are likely to be found. This review therefore focuses on the factors controlling arsenic concentrations in groundwaters.

Following the accumulation of evidence for the chronic toxicological effects of As in drinking water, recommended and regulatory limits of many authorities are being reduced. The WHO guideline value for As in drinking water was provisionally reduced in 1993 from 50 $\mu g\ l^{-1}$ to 10 $\mu g\ l^{-1}$. The new recommended value is based largely on analytical capability. If the standard basis for risk assessment applied to industrial chemicals were applied to arsenic, the maximum permissible concentration would be lower still. The US-EPA limit was also reduced from 50 µg l^{-1} to 10 µg l^{-1} in January 2001 following prolonged debate over the most appropriate limit. The EC maximum admissible concentration (MAC) for As in drinking water is also to be reduced to 10 µg l^{-1}. The Japanese limit for drinking water is 10 µg l^{-1} and the interim maximum acceptable concentration for Canadian drinking water is 25 µg l^{-1}.

Whilst many national authorities are seeking to reduce their limits in line with the WHO guideline value, many countries and indeed all affected developing countries, still operate at present to the 50 µg l^{-1} standard, in part because of lack of adequate testing facilities for lower concentrations.

Until recently, arsenic was often not on the list of constituents in drinking water routinely analysed by national laboratories, water utilities and NGOs and so the body of information about the distribution of arsenic in drinking water is not as well known as for many other drinking-water constituents. In recent years, it has become apparent that both the WHO guideline value and current national standards are quite frequently exceeded in drinking-water sources, and often unexpectedly so. Indeed, arsenic and fluoride are now recognised as the most serious inorganic contaminants in drinking water on a worldwide basis. In areas of high arsenic concentrations, drinking water provides a potentially major source of arsenic in the diet and so its early detection is of great importance.

1.2 Arsenic in natural waters

1.2.1 Aqueous speciation

Arsenic is perhaps unique among the heavy metalloids and oxyanion-forming elements (e.g. arsenic, selenium, antimony, molybdenum, vanadium, chromium, uranium, rhenium) in its sensitivity to mobilisation at the pH values typically found in groundwaters (pH 6.5-8.5) and under both oxidising and reducing conditions. Arsenic can occur in the environment in several oxidation states (-3, 0, +3 and +5) but in natural waters is mostly found in inorganic form as oxyanions of trivalent arsenite (As(III)) or pentavalent arsenate (As(V)). Organic arsenic forms may be produced by biological activity, mostly in surface waters, but are rarely quantitatively important. Organic forms may however occur where waters are significantly impacted by industrial pollution.

Most toxic trace metals occur in solution as cations (e.g. Pb^{2+}, Cu^{2+}, Ni^{2+}, Cd^{2+}, Co^{2+}, Zn^{2+}) which generally become increasingly insoluble as the pH increases. At the near-neutral pH typical of most groundwaters, the solubility of most trace-metal cations is severely limited by precipitation as, or coprecipitation with, an oxide, hydroxide, carbonate or phosphate mineral, or more likely by their strong adsorption to hydrous metal oxides, clay or organic matter. In contrast, most oxyanions including arsenate tend to become less strongly sorbed as the pH increases (Dzombak and Morel, 1990). Under some conditions at least, these anions can persist in solution at relatively high concentrations (tens of µg l^{-1}) even at near-neutral pH values. Therefore the oxyanion-forming elements such as Cr, As, U and Se are some of the most common trace contaminants in groundwaters.

However, relative to the other oxyanion-forming elements, arsenic is among the most problematic in the environment because of its relative mobility over a wide range of redox conditions. Selenium is mobile as the selenate (SeO_4^{3-}) oxyanion under oxidising conditions but is immobilized under reducing conditions either due to the stronger adsorption of its reduced form, selenite (SeO_3^{3-}), or due to its reduction to the metal. Chromium can similarly be mobilized as stable Cr(VI) oxyanion species under oxidising conditions, but forms cationic Cr(III) species in reducing environments and hence behaves like other trace cations (i.e. is relatively immobile at near-neutral pH values). Other oxyanions such as molybdate, vanadate, uranyl and rhenate also appear to be less mobile under reducing conditions. In sulphur-rich, reducing environments, many of the trace metals also form insoluble sulphides. By contrast, arsenic is perhaps unique in being relatively mobile under reduced conditions. It can be found at concentrations in the mg l^{-1} range when all other oxyanion-forming metals are present in the µg l^{-1} range.

Redox potential (Eh) and pH are the most important factors controlling arsenic speciation. Under oxidising conditions, H_2AsO^{4-} is dominant at low pH (less than about pH 6.9), whilst at higher pH, $HAsO_4^{2-}$ becomes dominant ($H_3AsO_4^0$ and AsO_4^3 - may be present in extremely acidic and alkaline conditions respectively). Under reducing conditions at pH less than about pH 9.2, the uncharged arsenite species $H_3AsO_3^0$ will predominate (Figure 1.1; Brookins, 1988; Yan *et al.*, 2000). The distributions of the species as a function of pH are given in Figure 1.2. In practice, most studies in the literature report speciation data without consideration of the degree of protonation. In the presence of extremely high concentrations of reduced sulphur, dissolved arsenic-sulphide species can be significant. Reducing, acidic conditions favour precipitation of orpiment (As_2S_3), realgar (AsS) or other sulphide minerals containing coprecipitated arsenic. Therefore high arsenic waters are not expected where there is a high concentration of free sulphide (Moore *et al.*, 1988). Thioarsenite species will be more important at neutral and alkaline pH in the presence of very high sulphide concentrations.

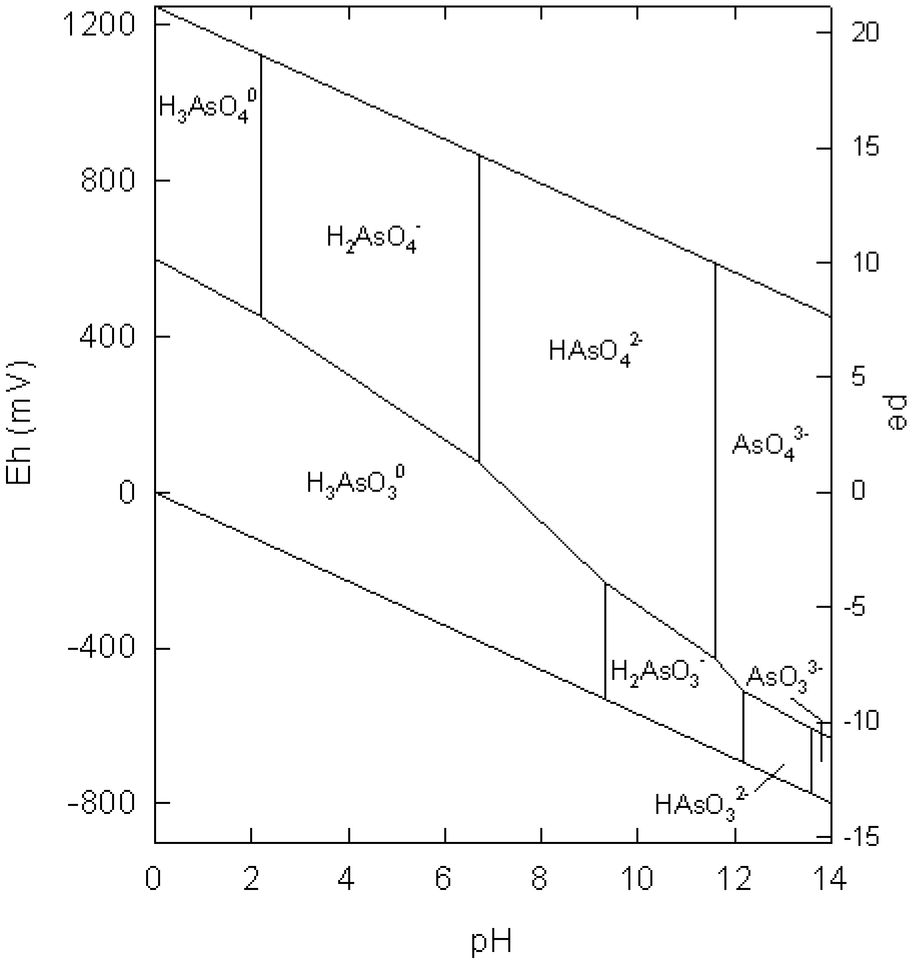

Figure 1.1 Eh-pH diagram of aqueous arsenic species in the system As-O_2-H_2O at 25°C and 1 bar total pressure

PENDING

Figure 1.2 Arsenic speciation (arsenite and arsenate) against pH

1.2.2 Abundance and distribution

Concentrations of arsenic in fresh water vary by more than four orders of magnitude (Table 1.1) depending on the source of arsenic, the amount available and the local geochemical environment. Under natural conditions, the greatest range and the highest concentrations of arsenic are found in groundwaters as a result of the strong influence of water-rock interactions and the greater tendency in aquifers for the physical and geochemical conditions to be favourable for arsenic mobilization and accumulation. The range of concentrations for many water bodies is large and hence ‘typical’ values are difficult to derive. Many studies of arsenic reported in the literature have also preferentially targeted known problem areas and hence reported ranges are often extreme and unrepresentative of natural waters as a whole. Nonetheless, the following compilation of data for ranges of arsenic concentrations found in various parts of the hydrosphere and lithosphere gives a broad indication of the expected concentration ranges and their variation in the environment.

Atmospheric precipitation

Arsenic enters the atmosphere through inputs from wind erosion, volcanic emissions, low-temperature volatilisation from soils, marine aerosols and pollution and is returned to the earth's surface by wet and dry deposition. The most important anthropogenic inputs are from smelter operations and fossil-fuel combustion. The arsenic appears to consist of mainly $As(III)_2O_3$ dust particles (Cullen and Reimer, 1989). Nriagu and Pacyna (1988) estimated that anthropogenic sources of atmospheric arsenic (around 18,800 tonnes yr^{-1}) amounted to around 30% of the global atmospheric arsenic flux. While it is accepted that these anthropogenic sources have an important impact on airborne arsenic compositions, their influence on the overall arsenic cycle is not well established.

Baseline concentrations of arsenic in rainfall and snow in rural areas are invariably low at typically less than 0.03 µg l^{-1} (Table 1.1). Concentrations in areas affected by smelter operations, coal burning and volcanic emissions are generally higher. Andreae (1980) found rainfall potentially affected by smelting and coal burning to have arsenic concentrations of around 0.5 µg l^{-1} (Table 1.1), although higher concentrations (average 16 µg l^{-1}) have been found in rainfall collected in Seattle some 35 km downwind of a copper smelter (Crecelius, 1975). Values given for Arizona snowpacks (Table 1.1; Barbaris and Betterton, 1996) are also probably slightly above baseline concentrations because of potential inputs of airborne As from smelters, power plants and soil dust. In general however, sources of airborne As in most industrialized nations are limited as a result of air-pollution control measures. Unless significantly contaminated with industrial sources of As, atmospheric precipitation contributes little As to surface and groundwater bodies.

River water

Baseline concentrations of arsenic in river waters are also low (in the region of 0.1-0.8 µg l^{-1} but up to ca. 2 µg l^{-1}; Table 1.1). They vary according to the composition of the surface recharge, the contribution from baseflow and the bedrock lithology. Concentrations at the low end of the range have been found in rivers draining As-poor bedrocks. Seyler and Martin (1991) found average river concentrations as low as 0.13 µg l^{-1} in the Krka region of Yugoslavia where the bedrock is As-poor karstic limestone (Table 1.1). Lenvik *et al.* (1978) also found low average concentrations of about 0.25 µg l^{-1} in rivers draining basement rocks in Norway, the lowest being in catchments on Precambrian rocks. Waslenchuk (1979) found concentrations in river waters from the south-eastern USA in the range 0.15-0.45 µg l^{-1} (Table 1.1).

Water body and location	**Arsenic concentration average or range (µg l^{-1})**	**Reference**
Rain water:		
Baseline:		
Maritime	0.02	Andreae (1980)
Terrestrial (w USA)	0.013-0.032	Andreae (1980)
Coastal (Mid-Atlantic, USA)	0.1 (<0.005-1.1)	Scudlark and Church (1988)

Snow (Arizona)	0.14 (0.02-0.42)	Barbaris and Betterton (1996)
Non-baseline:		
Terrestrial rain	0.46	Andreae (1980)
Seattle rain, impacted by copper smelter	16	Crecelius (1975)
River water:		
Baseline:		
Various	0.83 (0.13-2.1)	Andreae *et al.* (1983); Froelich *et al.* (1985); Seyler and Martin (1991)
Norway	0.25 (<0.02-1.1)	Lenvik *et al.* (1978)
South-east USA	0.15-0.45	Waslenchuk (1979)
USA	2.1	Sonderegger and Ohguchi (1988)
Dordogne, France	0.7	Seyler and Martin (1990)
Po River, Italy	1.3	Pettine *et al.* (1992)
Polluted European rivers	4.5-45	Seyler and Martin (1990)
River Danube, Bavaria	3 (1-8)	Quentin and Winkler (1974)
Schelde catchment, Belgium	0.75-3.8 (up to 30)	Andreae and Andreae (1989)
High-As groundwater influenced:		
Northern Chile	190-21800	Cáceres *et al.* (1992)
Northern Chile	400-450	Sancha (1999)
Córdoba, Argentina	7-114	Lerda and Prosperi (1996)
Geothermal influenced:		
Sierra Nevada, USA	0.20-264	Benson and Spencer (1983)
Waikato, New Zealand	32 (28-36)	McLaren and Kim (1995)
	44 (19-67)	Robinson *et al.* (1995)
Madison and Missouri Rivers, USA	10-370	Nimick et al. (1998)
Mining influenced:		
Ron Phibun, Thailand	218 (4.8-583)	Williams *et al.* (1996)
Ashanti, Ghana	284 (<2-7900)	Smedley *et al.* (1996)
British Columbia, Canada	17.5 (<0.2-556)	Azcue *et al.* (1994)
Lake water:		
Baseline		
British Columbia	0.28 (<0.2-0.42)	Azcue *et al.* (1994; 1995)
Ontario	0.7	Azcue and Nriagu (1995)
France	0.73-9.2 (high Fe)	Seyler and Martin (1989)

Japan	0.38-1.9	Baur and Onishi (1969)
Sweden	0.06-1.2	Reuther (1992)
Geothermal influenced:		
Western USA	0.38-1000	Benson and Spencer (1983)
Mining influenced:		
Northwest Territories, Canada	270 (64-530)	Bright *et al.* (1996)
Ontario, Canada	35-100	Azcue and Nriagu (1995)
Estuarine water:		
Baseline		
Oslofjord, Norway	0.7-2.0	Abdullah *et al.* (1995)
Saanich Inlet, British Columbia	1.2-2.5	Peterson and Carpenter (1983)
Rhône Estuary, France	2.2 (1.1-3.8)	Seyler and Martin (1990)
Krka Estuary, Yugoslavia	0.13-1.8	Seyler and Martin (1991)
Mining and industry influenced		
Loire Estuary, France	up to 16	Seyler and Martin (1990)
Tamar Estuary, UK	2.7-8.8	Howard *et al.* (1988)
Schelde Estuary, Belgium	1.8-4.9	Andreae and Andreae (1989)
Seawater:		
Deep Pacific and Atlantic	1.0-1.8	Cullen and Reimer (1989)
Coastal Malaysia	1.0 (0.7-1.8)	Yusof *et al.* (1994)
Coastal Spain	1.5 (0.5-3.7)	Navarro *et al.* (1993)
Coastal Australia	1.3 (1.1-1.6)	Maher (1985)
Groundwater:		
Baseline UK	<0.5-10	Edmunds *et al.* (1989)
As-rich provinces (e.g. Bengal Basin, Argentina, Mexico, northern China, Taiwan, Hungary)	10-5000	See section 1.5
Mining-contaminated groundwaters	50-5000	See section 1.5.6
Geothermal water	<10-50,000	Baur and Onishi (1969), White *et al*., (1963), Ellis and Mahon (1977)
Arsenical herbicide plant, Texas	408,000	Kuhlmeier (1997)
Mine drainage:		
Various, USA	<1-34,000	Plumlee *et al*. (1999)
Iron Mountain	up to 850,000	Nordstrom and Alpers (1999)

Ural Mountains	400,000	Gelova (1977)
Sediment pore water:		
Baseline, Swedish Estuary	1.3-166	Widerlund and Ingri (1995)
Baseline, clays, Saskatchewan, Canada	3.2-99	Yan *et al.* (2000)
Baseline, Amazon shelf sediments	up to 300	Sullivan and Aller (1996)
Mining-contam'd, British Columbia	50-360	Azcue *et al.* (1994)
Tailings impoundment, Ontario, Canada	300-100,000	McCreadie *et al*. (2000)
Oilfield and related brine:		
Ellis Pool, Alberta, Canada	230	White *et al*. (1963)
Searles Lake brine, California	up to 243,000	

Relatively high concentrations of naturally-occurring arsenic can occur in some areas as a result of inputs from geothermal sources or high-arsenic groundwaters. Arsenic concentrations in river waters from geothermal areas have been reported typically at around 10-70 µg l^{-1} (e.g. western USA and New Zealand; McLaren and Kim, 1995; Robinson *et al.*, 1995; Nimick et al., 1998; Table 1.1), although higher concentrations have been found. Nimick *et al*. (1998) for example found arsenic concentrations up to 370 µg l^{-1} in Madison River water (Wyoming and Montana) as a result of geothermal inputs from the Yellowstone geothermal system. Wilkie and Hering (1998) also found concentrations in the range 85-153 µg l^{-1} in Hot Creek (tributary of the Owens River, California). Some river waters affected by geothermal activity show distinct seasonal variations in arsenic concentration. Concentrations in the Madison River have been noted to be highest during low-flow conditions. This has been attributed to a greater contribution of geothermal water during times of low flow and dilution from spring runoff at times of high flow (Nimick et al., 1998). In the Waikato river system of New Zealand, As maxima were found in the summer months. These increases were linked to temperature-controlled microbial reduction of As(V) to As(III) with consequent increased mobility of As(III) (McLaren and Kim, 1995).

Increased concentrations are also reported in some river waters from arid areas where the surface water is dominated by river baseflow, i.e. by water flowing into the surface water from the surrounding rocks. The resulting surface waters often have a high pH and alkalinity. For example, in surface waters from the Loa River Basin of northern Chile (Antofagasta area, Atacama desert), Cáceres *et al.* (1992) found concentrations of naturally-occurring arsenic ranging between 190-21,800 µg l^{-1}. The high arsenic concentrations correlated well with salinity and were presumably related to evaporative concentration of baseflow-dominated river water. Increased arsenic concentrations (up to 114 µg l^{-1}) have also been reported in river waters from central Argentina where regional groundwater-arsenic concentrations (and pH, alkalinity) are high (Lerda and Prosperi, 1996).

Although bedrock inevitably has an influence on river-water arsenic concentrations, concentrations in rivers with more typical pH and alkalinity values (c. pH 5-7, alkalinity <100 mg l^{-1} as HCO_3) do not show the extremely high concentrations found in groundwaters because of oxidation and adsorption of arsenic species onto the river sediments as well as dilution by surface recharge and runoff. Arsenic concentrations in seven river water samples from Bangladesh have been reported in the range <0.5-2.7 µg l^{-1} but with one sample having a high concentration of 29 µg l^{-1} (BGS and DPHE, 2001). The highest value observed is significantly above world-average baseline concentrations (Table 1.1) but is much lower than some of the values found in the groundwaters (Section 1.5).

Significant increases in arsenic concentrations of river waters may also occur as a result of pollution from industrial or sewage effluents. Andreae and Andreae (1989) found concentrations of up to 30 µg l^{-1} in water from the River Zenne, Belgium which is affected by inputs from urban and industrial sources, particularly sewage. However, the concentration of arsenic in water from most of the catchment was in the range 0.75-3.8 µg l^{-1} and not significantly different from baseline concentrations. Durum *et al.* (1971) reported arsenic concentrations in 727 samples of surface waters from the United States. While 79% of the samples had As concentrations below the (rather high) detection limit of 10 µg l^{-1}, the highest observed concentration, 1,100 µg l^{-1}, was found in Sugar Creek, South Carolina, downstream of an industrial complex.

Arsenic can also be derived from mine wastes and mill tailings. Azcue and Nriagu (1995) found baseline concentrations in the Moira River, Ontario of 0.7 µg l^{-1} upstream of the influence of tailings from gold-mine workings. Downstream, concentrations increased to 23 µg l^{-1}. Azcue *et al.* (1994) found concentrations up to 556 µg l^{-1} (average 17.5 µg l^{-1}) in streams adjacent to tailings deposits in British Columbia. Williams *et al.* (1996) and Smedley *et al.* (1996) noted high arsenic concentrations (typically around 200-300 µg l^{-1}) in surface waters affected respectively by tin- and gold-mining activities. Though often involving notable increases above baseline concentrations, such anomalies tend to be relatively localised around the pollution source, principally because of the strong adsorption affinity of oxide minerals, especially iron oxide, for arsenic under oxidising, neutral to mildly acidic conditions.

Lake water

Concentrations of arsenic in lake waters are typically close to or lower than those found in river water. Baseline concentrations have been found at <1 µg l^{-1} in Canada (Azcue and Nriagu, 1995; Azcue *et al.*, 1995). As with river waters, increased concentrations are found in lake waters affected by geothermal water and by mining activity. Ranges of typically 100-500 µg l^{-1} have been reported in some mining areas and up to 1000 µg l^{-1} in geothermal areas (Table 1.1). Arsenic concentrations in mining-affected lake waters are not always high however, as removal from solution can be achieved effectively by adsorption onto iron oxides under neutral to mildly acidic conditions. Azcue *et al.* (1994), for example, found arsenic concentrations in Canadian lake waters affected by mining effluent similar to those not affected by mining effluent, in each case about 0.3 µg l^{-1}.

High arsenic concentrations are also found in some alkaline closed-basin lakes as a result of extreme evaporation and/or geothermal inputs. Mono Lake in the California, USA, for example, has concentrations of dissolved arsenic of 10-20 mg l^{-1}, with pH values in the range 9.5-10 as a result of inputs from geothermal springs and the weathering of volcanic rocks followed by evaporation (Maest *et al.*, 1992).

There is also much evidence for stratification of arsenic concentrations in some lake waters. Azcue and Nriagu (1995) found that concentrations increased with depth (up to 10 m) in lake waters from Ontario, probably because of an increasing ratio of As(III) to As(V) with depth and an influx of mining-contaminated sediment pore waters at the sediment-water interface. The concentrations were higher in summer when the proportion of As(III) was observed to be higher. Depleted oxygen levels in the bottom lake waters as a result of biological productivity during the summer months are a likely cause of the higher arsenic concentrations in the deeper lake waters.

Seawater and estuaries

Average arsenic concentrations in open seawater usually show little variation and are typically around 1.5 µg l^{-1} (Table 1.1).

Concentrations in estuarine water are more variable as a result of varying river inputs and salinity or redox gradients but are also usually low, at typically less than 4 µg l^{-1} under natural conditions. Peterson and Carpenter (1983) found concentrations between 1.2-2.5 µg l^{-1} in waters from Saanich Inlet, British Columbia. Values less than 2 µg l^{-1} were found in Oslofjord, Norway (Abdullah *et al.*, 1995; Table 1.1). Concentrations are commonly higher when riverine inputs are affected by industrial or mining effluent (e.g. Tamar, Schelde, Loire Estuaries; Table 1.1) or by geothermal water. Unlike some other trace elements such as boron, saline intrusion of seawater into an aquifer is unlikely to lead to a significant increase of arsenic in the affected groundwater.

Arsenate shares many chemical characteristics with phosphate and hence in oxic marine and estuarine waters, depletions in phosphate in biologically productive surface waters are mirrored by depletions in arsenate. Arsenate concentration minima often coincide with photosynthetic maxima evidenced by high concentrations of chlorophyll a (Cullen and Reimer, 1989).

Several studies have noted variations in the behaviour of arsenic during estuarine mixing. Some have reported conservative behaviour. In the unpolluted Krka Estuary of Yugoslavia, Seyler and Martin (1991) observed a linear increase in total As with increasing salinity ranging from 0.13 µg l^{-1} in fresh waters to 1.8 µg l^{-1} offshore (i.e. seawater value). However, other studies have observed non-conservative behaviour (departures from simple mixing) in estuaries due to processes such as diffusion from sediment pore waters, coprecipitation with iron oxides or anthropogenic inputs (e.g. Andreae *et al.*, 1983; Andreae and Andreae, 1989). The flocculation of iron oxides at the freshwater-saline interface is important as a result of increases in pH and salinity. This can lead to major decreases in the arsenic flux to the oceans (Cullen and Reimer, 1989).

Groundwater

Background concentrations of arsenic in groundwater are in most countries less than 10 µg l^{-1} (e.g. Edmunds *et al.*, 1989 for the UK; Welch *et al.*, 2000 for the USA) and sometimes substantially lower. However, values quoted in the literature show a very large range from <0.5-5000 µg l^{-1} (i.e. four orders of magnitude). This range occurs under natural conditions. High concentrations of arsenic are found in groundwater in a variety of environments. This includes both oxidising (under conditions of high pH) and reducing aquifers and in areas affected by geothermal, mining and industrial activity. Evaporative concentration can also increase concentrations substantially. Most high-arsenic groundwater provinces are the result of natural occurrences of arsenic. Cases of mining-induced arsenic pollution are numerous in the literature but tend to be localised. Cases of industrially-induced arsenic pollution (including that from agriculture) may be severe locally (Table 1.1) but occurrences are relatively rare. Groundwater provinces with naturally-occurring As problems are discussed in more detail in Section 1.5.

Mine drainage

Under the extremely acid conditions of some acid mine drainage (AMD), which can have negative pH values (Nordstrom *et al.*, 2000), high concentrations of a wide range of solutes are found, including iron and arsenic. The highest reported arsenic concentration of 850,000 µg l^{-1} is from an acid seep in the Richmond mine at Iron Mountain, California (Nordstrom and Alpers, 1999). In a compilation of some 180 samples of mine drainage from the USA, Plumlee *et al.* (1999) reported concentrations ranging from detection limits (<1 µg l^{-1} or more) to 340,000 µg l^{-1}, again the highest values being from the Richmond mine. Gelova (1977) also reported an arsenic concentration of 400,000 µg l^{-1} from the Ural Mountains. Dissolved arsenic in acid mine waters is rapidly removed as the iron is oxidised and precipitated and the arsenic scavenged through adsorption. At Iron Mountain, an efficient neutralization plant removes the arsenic and other metals for safe disposal.

Sediment pore waters

Some high concentrations of As have been found in pore waters extracted from unconsolidated sediments and often form sharp contrasts to the concentrations observed in overlying surface waters (e.g. Belzile and Tessier, 1990). Widerlund and Ingri (1995) found concentrations in the range 1.3-166 µg l^{-1} in pore waters from the Kalix River estuary of northern Sweden. Yan *et al*. (2000) found As concentrations in the range 3.2-99 µg l^{-1} in pore waters from clay sediments in Saskatchewan, Canada (Table 1.1). Even higher concentrations can be found in pore waters from sediments affected by mining contamination (tailings, mineral-rich deposits). McCreadie *et al*. (2000) reported As concentrations up to 100,000 µg l^{-1} in porewaters extracted from tailings in Ontario (Table 1.1). In such cases, high pore water arsenic concentrations are most likely to be linked to the strong redox gradients that occur below the sediment-water interface often over depth scales of centimeters. Burial of fresh organic matter and the slow diffusion of oxygen through the sediment leads to reducing conditions just below the sediment-water interface. This encourages the reduction of As(V) and desorption from Fe and Mn oxides, as well as reductive dissolution of these minerals. There is much evidence for cycling of As between shallow sediment pore waters and overlying surface waters in response to temporal variations in redox conditions.

Sullivan and Aller (1996) carried out an elegant study of the cycling of arsenic in shallow sediments from the offshore shelf of the Amazon situated far from population centres. They measured pore water As and Fe concentration profiles as well as sediment As and Fe(II) concentrations. There was frequently a well-correlated peak in dissolved As and Fe concentrations some 50 cm to 150 cm beneath the surface with As concentrations in the peak averaging about 135 µg l^{-1} and reaching a maximum of 300 µg l^{-1}, much greater than from marine coastal environments. The dissolved As/Fe molar ratio varied but was typically about 1:300. Dissolved As varied inversely with easily-leachable (6M HCl) As in the sediment and increased directly with solid-phase

Fe(II). In these sediments, Fe oxides were believed to be a much more important source of As than Mn oxides.

Oilfield and other brines

Only limited data are available for arsenic in oilfield and other brines, but some published accounts suggest that concentrations can be very high. White *et al*. (1963) reported a dissolved arsenic concentration of 230 µg l^{-1} in a sodium-bicarbonate groundwater from a 1000 m deep oilfield well from Ellis Pool, Alberta, Canada. They also reported a concentration of 5800 µg l^{-1} arsenic in a sodium-chloride-dominated brine from Tisakürt, Hungary. Composite brines from the interstices of salt deposits from Searles Lake, California, have arsenic concentrations up to 243 mg l^{-1} (Na 119 g l^{-1}; White *et al*., 1963; Table 1.1).

1.2.3 Distribution of arsenic species in water bodies

Most studies of arsenic speciation in natural waters attempt to separate the inorganic species into As(III) and As(V) usually by chromatographic separation or by making use of the relatively slow reduction of As(V) by sodium borohydride. Some studies also measure the organic arsenic species too. The sampling and analytical techniques required are far from trivial and not yet well-established (Edwards *et al.*, 1998). Separation of species may be carried out in the field to avoid the problem of preserving species for later laboratory analysis. Alternatively, preservation with HCl and ascorbic acid has been successful.

In rain water, oxidation states will vary according to the arsenic source. This is likely to be dominantly $As(III)_2O_3$ when derived from smelters, coal burning and volcanic sources, although organic species may be derived by volatilization from soils, arsine ($As(-III)H_3$) may derive from landfills and reducing soils such as peats and arsenate may be derived from marine aerosols. Reduced forms will undergo oxidation by O_2 in the atmosphere and reactions with atmospheric SO_2 or O_3 are likely (Cullen and Reimer, 1989).

In oxic seawater, the As is typically dominated by As(V), though some As(III) is invariably present and becomes of increasing importance in anoxic bottom waters. Ratios of As(V)/As(III) are typically in the range 10-100 in open seawater (Andreae, 1979; Peterson and Carpenter, 1983; Pettine *et al.*, 1992). Arsenic(V) should exist mainly as $HAsO_4^{2-}$ and $H_2AsO_4^-$ in the pH range of seawater (pH around 8.2; Figures 1.1. and 1.2) and As(III) will exist mainly as the neutral species H_3AsO_3. Relatively high proportions of H_3AsO_3 are found in surface waters. These coincide with zones of primary productivity. Increases in organic arsenic species have also been recorded in these zones as a result of methylation reactions by phytoplankton (Cullen and Reimer, 1989).

The relative proportions of arsenic species are more variable in estuarine waters because of variable redox and salinity, and terrestrial inputs (Howard *et al.*, 1988; Abdullah *et al.*, 1995). However, they are still dominated by As(V). Andreae and Andreae (1989) found As(V)/As(III) ratios varying between 5-50 in the Schelde Estuary of Belgium with the lowest ratios in anoxic zones where inputs of industrial effluent had an impact. Elevated proportions of As(III) also result from inputs of mine effluent (Klumpp and Peterson, 1979). Seasonal variations in As concentration and speciation have been noted in estuaries (Riedel, 1993). In seasonally anoxic estuarine waters, variations in the relative proportions of As(III) and As(V) can be large. Peterson and Carpenter (1983) found a distinct crossover in the proportions of the two species with increasing depth in response to the onset of anoxic conditions in the estuarine waters of Saanich Inlet of British Columbia. Arsenic(III) represented only 5% (0.10 µg l^{-1}) of the dissolved As above the redox front but 87% (1.58 µg l^{-1}) below it. In marine and estuarine waters, organic forms are usually less abundant but are nonetheless often detected (e.g. Riedel, 1993; Howard *et al.*, 1999). Concentrations of these will depend on abundance and species of biota present and on temperature.

In lake and river waters, As(V) is also generally the dominant species (e.g. Seyler and Martin, 1990; Pettine *et al.*, 1992), though significant seasonal variations in speciation as well as absolute concentration have been found. Concentrations and relative proportions of As(V) and As(III) vary according to changes in input sources, redox conditions and biological activity. The presence of As(III) may be maintained in oxic waters by biological reduction of As(V), particularly during summer months. Higher relative proportions of As(III) have been found in river stretches close to inputs of As(III)-dominated industrial effluent (Andreae and Andreae, 1989) and in waters with a component of geothermal water.

Proportions of As(III) and As(V) are particularly variable in stratified lakes where redox gradients can be large and seasonally variable (Kuhn and Sigg, 1993). As with estuarine waters, distinct changes in arsenic speciation occur in lake profiles as a result of redox changes. For example, in the stratified, hypersaline and hyperalkaline Mono Lake (California, USA), there is a predominance of As(V) in the upper oxic layer and of As(III) in the reducing part (Maest *et al.*, 1992; Oremland *et al.*, 2000). Rapid oxidation of As(III) occurs during the early stages of lake turnover as a result of microbial activity (Oremland *et al.*, 2000). This occurs before Fe(II) oxidation.

Unlike Mono Lake, speciation of As in lakes does not necessarily follow that expected from thermodynamic considerations. Recent studies have shown that arsenite predominates in the oxidised epilimnion of some stratified lakes whilst arsenate may persist in the anoxic hypolimnion (Kuhn and Sigg, 1993; Newman *et al.*, 1998). Proportions of arsenic species may also vary according to the availability of particulate Fe and Mn oxides (Pettine *et al.*, 1992; Kuhn and Sigg, 1993).

Organic forms of arsenic are usually minor in surface waters. In lake waters from Ontario, Azcue and Nriagu (1995) found As(III) concentrations of 7-75 µg l^{-1}, As(V) of 19-58 µg l^{-1} and only 0.01-1.5 µg l^{-1} of organic As. Nonetheless, proportions of organic forms of arsenic can increase as a result of methylation reactions catalysed by microbial activity (bacteria, yeasts, algae). The dominant organic forms found are dimethylarsinic acid (DMAA; $(CH_3)_2AsO(OH)$) and monomethylarsonic acid (MMAA; $CH_3AsO(OH)_2$), where As is present in both cases in the pentavalent oxidation state.

Proportions of these two species have been noted to increase in summer as a result of increased microbial activity (e.g. Hasegawa, 1997). The organic species may also be more prevalent close to the sediment-water interface (Hasegawa *et al.*, 1999).

In groundwaters, the ratio of As(III) to As(V) can vary enormously as a result of large variations in aquifer redox conditions, redox gradients and history. In strongly reducing aquifers (Fe(III)- and sulphate-reducing), As(III) typically dominates. Reducing arsenic-rich groundwaters from Bangladesh have As(III)/As_T ratios varying between 0.1-0.9 but are typically around 0.5-0.6 (DPHE/BGS/MML, 1999). Ratios in reducing groundwaters from Inner Mongolia are typically 0.7-0.9 (Smedley *et al.*, 2000b). Concentrations of organic forms are generally low or negligible in groundwaters (e.g. Chen *et al.*, 1995).

1.2.4 Redox and kinetics

Redox reactions are important for controlling the behaviour of many major and minor species in natural waters, including that of arsenic. However, in practice, redox equilibrium is often achieved only slowly. For example, Wersin *et al.* (1991) estimated that the complete reductive dissolution of Fe(III) oxides in an anoxic Swiss lake sediment would take more than 1000 years. Equilibrium thermodynamic calculations predict that As(V) should dominate over As(III) in all but strongly reducing conditions, i.e. at least sulphate-reducing conditions (Section 1.2.1). However, such theoretical behaviour is not necessarily followed quantitatively in natural waters where different redox couples can point to different implied redox potentials (Eh values) reflecting thermodynamic disequilibrium (Seyler and Martin, 1989; Eary and Schramke, 1990; Kuhn and Sigg, 1993). In Oslofjord, Norway, As(III) was found under oxidising conditions (Abdullah *et al.*, 1995). Also, in oxygenated seawater, the As(V)/As(III) ratios should be of the order of 10^{15}-10^{26} (Andreae, 1979) whereas measured ratios of 0.1-250 have been found largely supported by biological transformations (Johnson and Pilson, 1975; Cullen and Reimer, 1989). Oxidation of As(III) by dissolved oxygen, so-called oxygenation, is a particularly slow reaction. Johnson and Pilson (1975) gave half-lives for the oxygenation of As(III) in seawater ranging from several months to a year.

Other studies have demonstrated the stability of As(V)/As(III) ratios over periods of days or weeks during water sampling when no particular care was taken to prevent oxidation again suggesting relatively slow oxidation rates. Andreae (1979) found stable ratios in seawater for up to 10 days (4°C). Cherry *et al.* (1979) found from experimental studies that the As(V)/As(III) ratios were stable in anoxic solutions for up to 3 weeks but that gradual changes occurred over longer timescales. They also suggested that the measured As(V)/As(III) ratios in natural waters might be used as an indicator of the ambient redox (Eh) conditions, particularly in groundwater where equilibration times are long. Yan *et al.* (2000) have also concluded that the As(V)/As(III) ratio may be used as a reliable redox indicator for groundwater systems. However, this optimism may be unfounded since Welch *et al.* (1988) found that the Eh calculated from the As(V)-As(III) couple neither agreed with that from the Fe(II)-Fe(III) and other redox couples nor with the measured Eh. Therefore, the reliability of the arsenic redox couple as a redox indicator remains to be seen. It is clearly important that where such comparisons are made, reliable Eh measurements are carried out (Yan *et al.*, 2000). Perhaps the most that can be said at present is that the existence of As(III) implies reducing conditions somewhere in the system.

Laboratory studies show that the kinetics of oxygenation of As(III) are slowest in the slightly acid range, around pH 5 (Eary and Schramke, 1990) which is why water samples are often acidified to about this pH to preserve their *in situ* speciation. Eary and Schramke (1990) also gave an empirical rate equation for the reaction over the pH range 8-12.5. This was based on the concentration (activity) of the $H_2AsO_3^-$ species in solution. They suggested that the half-life for As(III) in natural waters is 1-3 years although the rate may be greater because of the presence of 'unknown aqueous species' or oxide particles, especially manganese oxides. Certainly there is considerable evidence that manganese oxides can increase the rate of As(III) oxidation with half-lives being reduced to as little as 10-20 min in the presence of manganese-oxide particles (Oscarson *et al.*, 1981; Scott and Morgan, 1995). This is used to advantage in the removal of As(III) from drinking water (Driehaus *et al.*, 1995). The rate of oxidation is independent of the concentration of dissolved oxygen (Scott and Morgan, 1995), the rate being controlled by the rate of a surface reaction. Less is known about the role of iron oxides in altering the oxygenation kinetics. Photochemical oxidation and reduction may be additional factors in surface waters. Ti-containing particles may aid the photo-oxidation (Foster *et al.*, 1998).

As with most redox reactions in the natural environment, both the oxidation of arsenite and the reduction of arsenate can be bacterially catalysed. Sterile water samples have been noted to be less susceptible to speciation changes than non-sterile samples (Cullen and Reimer, 1989). Wilkie and Hering (1998) found that As(III) in geothermal waters input to streams in south-west USA oxidised rapidly downstream (pseudo first-order half-life calculated at as little as 0.3 hours) and attributed the fast rate to bacterial mediation. The reduction of As(V) to As(III) in Mono Lake was also rapidly catalysed by bacteria with rate constants ranging from 0.02 to 0.3 day^{-1} (Oremland *et al.*, 2000). Methylated As species are also readily oxidised chemically and biologically (Abdullah *et al.*, 1995).

Less is known about the rate of solid-phase reduction of As(V) to As(III) but there have been some studies with soils and sediments. The evidence from soils is that under moderately reducing conditions (Eh < 100 mV) induced by flooding, As(V) is reduced to As(III) in a matter of days or several weeks and adsorbed As(V) is released as As(III) (Masscheleyn *et al.*, 1991; Reynolds *et al.*, 1999). Masscheleyn *et al.* (1991) found from laboratory experiments that some of the As was released before Fe, implying reductive desorption from iron oxides rather than reductive dissolution. Up to 10 per cent of the total As in the soil eventually became soluble. Smith and Jaffé (1998) modelled As(V) reduction in benthic sediments as a first order reaction with respect to arsenate with a rate coefficient of 125 yr^{-1}.

1.3 Sources of arsenic

1.3.1 Minerals

Major arsenic minerals

Arsenic occurs as a major constituent in more than 200 minerals, including elemental arsenic, arsenides, sulphides, oxides, arsenates and arsenites. A list of some of the most common As minerals is given in Table 1.2. Most are ore minerals or their alteration products. However, these minerals are relatively rare in the natural environment. The greatest concentrations of these minerals occur in mineralised areas and are found in close association with the transition metals as well as Cd, Pb, Ag, Au, Sb, P, W and Mo. The most abundant As ore mineral is arsenopyrite, FeAsS. It is generally accepted that arsenopyrite, together with the other dominant As-sulphide minerals realgar and orpiment, are only formed under high temperature conditions in the earth's crust. However, authigenic arsenopyrite has been reported in sediments by Rittle *et al.* (1995). Although often present in ore deposits, arsenopyrite is much less abundant than arsenian ('arsenic-rich') pyrite ($Fe(S,As)_2$) which is probably the most important source of As in ore zones (Nordstrom, 2000).

Table 1.2 Major arsenic minerals occurring in nature

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

Where arsenopyrite is present in sulphide ores associated with sediment-hosted gold deposits, it tends to be the earliest-formed mineral, derived from hydrothermal solutions and formed at temperatures typically of 100°C or more. This is followed by the formation of rarer native arsenic and thereafter arsenian pyrite. Realgar and orpiment generally form later still. This paragenetic sequence is often reflected by zonation within sulphide minerals, with arsenopyrite cores zoning out to arsenian pyrite and realgar-orpiment rims. Oxides and sulphates are formed at the latest stages of ore mineralisation (Arehart *et al.*, 1993).

Rock-forming minerals

Though not a major component, 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 is the most abundant. Concentrations in pyrite, chalcopyrite and galena can be very variable, even within a given grain, but in some cases reach up to 10 weight percent (Table 1.3). Arsenic is present in the crystal structure of many sulphide minerals as a substitute for sulphur.

Table 1.3. Typical arsenic concentrations in common rock-forming minerals

Mineral	As concentration range (mg kg^{-1})	References
Sulphide minerals:		
Pyrite	100-77,000	Baur and Onishi (1969); Arehart *et al.* (1993); Fleet and Mumin (1997)
Pyrrhotite	5-100	Boyle and Jonasson (1973);
Marcasite	20-126,000	Dudas (1984); Fleet and Mumin (1997)
Galena	5-10,000	
Sphalerite	5-17,000	
Chalcopyrite	10-5000	
Oxide minerals:		
Haematite	up to 160	
Fe oxide (undifferentiated)	up to 2000	
Fe(III) oxyhydroxide	up to 76,000	Pichler *et al.* (1999)
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	
Carbonates minerals:		
Calcite	1-8	
Dolomite	<3	
Siderite	<3	
Sulphate minerals:		
Gypsum/anhydrite	<1-6	
Barite	<1-12	
Jarosite	34-1000	
Other minerals:		
Apatite	<1-1000	
Halite	<3-30	Stewart (1963)
Fluorite	<2	

Besides being an important component of ore bodies, pyrite is also formed in low-temperature sedimentary environments under reducing conditions (authigenic pyrite). Authigenic pyrite plays a very important role in present-day geochemical cycles. It is present in the sediments of many rivers, lakes and the oceans as well as of many aquifers. Pyrite commonly forms preferentially in zones of intense reduction such as around buried plant roots or other nuclei of decomposing organic matter. It is sometimes present in a characteristic form as framboidal pyrite. During the formation of this pyrite, it is likely that some of the soluble arsenic will also be incorporated.

Pyrite is not stable in aerobic systems and oxidises to iron oxides with the release of large amounts of sulfate, acidity and associated trace constituents including arsenic. The presence of pyrite as a minor constituent in sulfide-rich coals is ultimately responsible for the production of 'acid rain' and acid mine drainage (AMD), and for the presence of arsenic problems around coal mines and areas of intensive coal burning.

High As concentrations are also found in many oxide minerals and hydrous metal oxides, either as part of the mineral structure or as sorbed species. Concentrations in Fe oxides can also reach weight percent values (Table 1.3), particularly where they form as the oxidation products of primary iron sulphide minerals which have an abundant supply of arsenic. Adsorption of arsenate to hydrous iron oxides is particularly strong and sorbed loadings can be appreciable even at very low arsenic concentrations in solution (Goldberg, 1986; Manning and Goldberg, 1996; Hiemstra and van Riemsdijk, 1996). Adsorption to hydrous Al and Mn oxides may also be important if these oxides are present in quantity (e.g. Peterson and Carpenter, 1983; Brannon and Patrick, 1987). Arsenic may also be sorbed to the edges of clays and on the surface of calcite (Goldberg and Glaubig, 1988), a common mineral in many sediments. However, these loadings are much smaller on a weight basis than for the iron oxides. Adsorption 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 (Table 1.3). However, phosphate minerals are much less abundant than oxide minerals and so make a correspondingly small contribution to the arsenic load of most sediments.

Arsenic can also substitute for Si^{4+}, Al^{3+}, Fe^{3+} and Ti^{4+} in many mineral structures and is therefore present in many other rock-forming minerals, albeit at much lower concentrations. Most common silicate minerals contain around 1 mg kg^{-1} or less. Carbonate minerals usually contain less than 10 mg kg^{-1} (Table 1.3).

1.3.2 Rocks, sediments and soils

Earth's crust

Few estimates exist for the concentration of arsenic in the earth's crust. However, the concentration is generally taken to be low. Onishi and Sandell (1955) gave the average arsenic concentration of the lithosphere as about 2 mg kg^{-1}.

Table 1.4. Typical arsenic concentrations in rocks, sediments, soils and other surficial deposits

Rock/sediment type	As concentration average and/or range (mg kg^{-1})	No of analyses	Reference
Igneous rocks:			
Ultrabasic rocks (peridotite, dunite, kimberlite etc)	1.5 (0.03-15.8)	40	

Basic rocks (basalt)	2.3 (0.18-113)	78	
Basic rocks (gabbro, dolerite)	1.5 (0.06-28)	112	
Intermediate (andesite, trachyte, latite)	2.7 (0.5-5.8)	30	
Intermediate (diorite, granodiorite, syenite)	1.0 (0.09-13.4)	39	Onishi and Sandell (1955); Baur and Onishi (1969); Boyle and Jonasson (1973); Ure and Berrow (1982); Riedel and Eikmann (1986)
Acidic rocks (rhyolite)	4.3 (3.2-5.4)	2	
Acidic rocks (granite, aplite)	1.3 (0.2-15)	116	
Acidic rocks (pitchstone)	1.7 (0.5-3.3)		
Volcanic glasses	5.9 (2.2-12.2)	12	
Metamorphic rocks:			
Quartzite	5.5 (2.2-7.6)	4	
Hornfels	5.5 (0.7-11)	2	
Phyllite/slate	18 (0.5-143)	75	Boyle and Jonasson (1973)
Schist/gneiss	1.1 (<0.1-18.5)	16	
Amphibolite and greenstone	6.3 (0.4-45)	45	
Sedimentary rocks:			
Marine shale/mudstone	3-15 (up to 490)		
Shale (Mid-Atlantic Ridge)	174 (48-361)		
Non-marine shale/mudstone	3.0-12		
Sandstone	4.1 (0.6-120)	15	
Limestone/dolomite	2.6 (0.1-20.1)	40	Onishi and Sandell (1955); Baur and Onishi (1969); Boyle and Jonasson (1973); Cronan (1972); Riedel and Eikmann (1986); Welch *et al.* (1988); Belkin *et al.* (2000)
Phosphorite	21 (0.4-188)	205	
Iron formations and Fe-rich sediment	1-2900	45	
Evaporites (gypsum/anhydrite)	3.5 (0.1-10)	5	
Coals	0.3-35,000		
Bituminous shale (Kupferschiefer, Germany)	100-900		

Unconsolidated sediments:			
Various	3 (0.6-50)		Azcue and Nriagu (1995)
Alluvial sand (Bangladesh)	2.9 (1.0-6.2)	13	BGS and DPHE (2001)
Alluvial mud/clay (Bangladesh)	6.5 (2.7-14.7)	23	BGS and DPHE (2001)
River bed sediments (Bangladesh)	1.2-5.9		Datta and Subramanian (1997)
Lake sediments, Lake Superior	2.0 (0.5-8.0)		Allan and Ball (1990)
Lake sediments, British Colombia	5.5 (0.9-44)	119	Cook *et al.* (1995)
Glacial till, British Colombia	9.2 (1.9-170)		Cook *et al.* (1995)
World average river sediments	5		Martin and Whitfield (1983)
Stream and lake silt (Canada)	6 (<1-72)	310	Boyle and Jonasson (1973)
Loess silts, Argentina	5.4-18		Arribére *et al.* (1997); Smedley *et al.* (2000a)
Continental margin sediments (argillaceous, some anoxic)	2.3-8.2		Legeleux *et al.* (1994)
Soils:			
Various	7.2 (0.1-55)	327	Boyle and Jonasson (1973)
Peaty and bog soils	13 (2-36)	14	
Acid sulphate soils (Vietnam)	6-41	25	Gustafsson and Tin (1994)
Acid sulphate soils (Canada)	1.5-45	18	Dudas (1984); Dudas *et al.* (1988)
Soils near sulphide deposits	126 (2-8000)	193	Boyle and Jonasson (1973)
Contaminated surficial deposits:			
Mining-contaminated lake sediment, British Colombia	342 (80-1104)		Azcue *et al.* (1994; 1995)
Mining-contaminated reservoir sediment, Montana	100-800		Moore *et al.* (1988)
Mine tailings, British Colombia	903 (396-2000)		Azcue *et al.* (1995)
Soils and tailings-contaminated soil, UK	120-52,600	86	Kavanagh *et al.* (1997)
Tailings-contaminated soil, Montana	up to 1100		Nagorski and Moore (1999)

Industrially polluted inter-tidal sediments, USA	0.38-1260	Davis *et al.* (1997)
Soils below chemicals factory, USA	1.3-4770	Hale *et al.* (1997)
Sewage sludge	9.8 (2.4-39.6)	Zhu and Tabatabai (1995)

Igneous rocks

Arsenic concentrations in igneous rocks are generally similar to those found in the crust. Ure and Berrow (1982) quoted an average value of 1.5 mg kg^{-1} for all rock types (undistinguished). Averages for different types distinguished by silica content (Table 1.4) are slightly higher than this value but generally less than 5 mg kg^{-1}. Volcanic glasses are only slightly higher with an average of around 5.9 mg kg^{-1} (Table 1.4). Overall, there is relatively little difference between the different igneous rock types. Despite not having exceptional concentrations of As, volcanic rocks, especially ashes, are often implicated in the generation of high-As waters. This may relate to the reactive nature of recent acidic volcanic material, especially fine-grained ash and its tendency to give rise to sodium-rich high-pH groundwaters (Section 1.5.3).

Metamorphic rocks

Arsenic concentrations in metamorphic rocks tend to reflect the concentrations in their igneous and sedimentary precursors. Most contain around 5 mg kg^{-1} or less. Pelitic rocks (slates, phyllites) typically have the highest concentrations with on average ca. 18 mg kg^{-1} (Table 1.4).

Sedimentary rocks

The concentration of As in sedimentary rocks is typically in the range 5-10 mg kg^{-1} (Webster, 1999), i.e. slightly above average terrestrial abundance. Average sediments are enriched in As relative to igneous rocks. Sands and sandstones tend to have the lowest concentrations, reflecting the low As concentrations of their dominant minerals, quartz and feldspars. Average sandstone As concentrations are around 4 mg kg^{-1} (Table 1.4) although Ure and Berrow (1982) gave a lower average figure of 1 mg kg^{-1}.

Argillaceous deposits have a broader range and higher average As concentrations than sandstones, typically an average of around 13 mg kg^{-1} (Table 1.4; Ure and Berrow, 1982). The higher values reflect the larger proportion of sulphide minerals, oxides, organic matter and clays. Black shales have As concentrations typically at the high end of the range principally because of their enhanced pyrite content. Data given in Table 1.4 suggest that marine argillaceous deposits have higher concentrations than non-marine deposits. This may also be a reflection of the grain-size distributions, with potential for a higher proportion of fine material in offshore pelagic sediments as well as systematic differences in sulphur and pyrite contents. Marine shales tend to contain higher sulphur concentrations. Sediment provenance is also a likely important factor. Particularly high As concentrations have been determined for shales from mid-ocean settings (Mid-Atlantic Ridge average 174 mg kg^{-1}; Table 1.4). Atlantic Ridge gases may in this case be a high-As source.

Concentrations in coals and bituminous deposits are variable but often high. Samples of organic-rich shale (Kupferschiefer) from Germany have As concentrations of 100-900 mg kg^{-1} (Table 1.4). Some coal samples have been found with extremely high concentrations up to 35,000 mg kg^{-1} (Belkin *et al*., 2000) although generally low concentrations of 2.5-17 mg kg^{-1} were reported by Palmer and Klizas (1997).

Carbonate rocks typically have low concentrations, reflecting the low concentrations of the constituent minerals (ca. 3 mg kg^{-1}; Table 1.4).

Some of the highest observed As concentrations, often several thousand mg kg^{-1}, are found in ironstones and Fe-rich rocks. Phosphorites are also relatively enriched in As (values up to ca. 400 mg kg^{-1} having been measured).

Unconsolidated sediments

Concentrations of As in unconsolidated sediments are not notably different from those in their indurated equivalents, muds and clays having typically higher concentrations than sands and carbonates. Values are typically 3-10 mg kg^{-1}, depending on texture and mineralogy (Table 1.4). Elevated concentrations tend to reflect the amounts of pyrite or Fe oxides present. Increases are also typically found in mineralised areas. Placer deposits in streams can have very high concentrations as a result of the abundance of sulphide minerals.

Average As concentrations for stream sediments in England and Wales are in the range 5-8 mg kg^{-1} (AGRG, 1978). Similar concentrations have also been found in river sediments where groundwater-arsenic concentrations are high: Datta and Subramanian (1997) found concentrations in sediments from the River Ganges averaging 2.0 mg kg^{-1} (range 1.2-2.6 mg kg^{-1}), from the Brahmaputra River averaging 2.8 mg kg^{-1} (range 1.4-5.9 mg kg^{-1}) and from the Meghna River averaging 3.5 mg kg^{-1} (range 1.3-5.6 mg kg^{-1}).

Cook *et al.* (1995) found concentrations in lake sediments ranging between 0.9-44 mg kg^{-1} (median 5.5 mg kg^{-1}) but noted that the highest concentrations were present up to a few kilometres down-slope of mineralised areas. The upper baseline concentration for these sediments is likely to be around 13 mg kg^{-1} (90th percentile). They also found concentrations in glacial till of 1.9-170 mg kg^{-1} (median 9.2 mg kg^{-1}; Table 1.4) and noted the highest concentrations down-ice of mineralised areas (upper baseline, 90th percentile, 22 mg kg^{-1}).

Relative arsenic enrichments have been observed in reducing sediments in both nearshore and continental-shelf deposits (Peterson and Carpenter, 1986; Legeleux *et al.*, 1994). Legeleux *et al.* (1994) noted concentrations increasing with depth (up to 30 cm) in continental shelf sediments as a result of the generation of increasingly reducing conditions. Concentrations varied between sites, but generally increased with depth in the range 2.3-8.2 mg kg^{-1} (Table 1.1).

Soils

Baseline concentrations of As in soils are generally of the order of 5-10 mg kg^{-1}. Boyle and Jonasson (1973) quoted an average baseline concentration in world soils of 7.2 mg kg^{-1} (Table 1.4) and Shacklette *et al.* (1974) quoted an average of 7.4 mg kg^{-1} (901 samples) for American soils. Ure and Berrow (1982) gave a higher average value of 11.3 mg kg^{-1}. Peats and bog soils can have higher concentrations (average 13 mg kg^{-1}; Table 1.4), principally because of increased prevalence of sulphide mineral phases under the reduced conditions. Acid sulphate soils which are generated by the oxidation of pyrite in sulphide-rich terrains such as pyrite-rich shales, mineral veins and dewatered mangrove swamps can also be relatively enriched in As. Dudas (1984) found As concentrations up to 45 mg kg^{-1} in the B horizons of acid sulphate soils derived from the weathering of pyrite-rich shales in Canada. Concentrations in the overlying leached (eluvial, E) horizons were low (1.5-8.0 mg kg^{-1}) as a result of volatilisation or leaching of As to lower levels. Gustafsson and Tin (1994) found similarly elevated concentrations (up to 41 mg kg^{-1}) in acid sulphate soils from the Mekong delta of Vietnam.

Although the dominant source of As in soils is geological, and hence dependent to some extent on the concentration in the parent rock material, additional inputs may be derived locally from industrial sources such as smelting and fossil-fuel combustion products and agricultural sources such as pesticides and phosphate fertilisers. Ure and Berrow (1982) quoted concentrations in the range 366-732 mg kg^{-1} in orchard soils as a result of the historical application of arsenical pesticides to fruit crops.

Contaminated surficial deposits

Arsenic concentrations much higher than baseline values have been found in sediments and soils contaminated by the products of mining activity, including mine tailings and effluent. Concentrations in tailings piles and tailings-contaminated soils can reach up to several thousand mg kg^{-1} (Table 1.4). The high concentrations reflect not only increased abundance of primary arsenic-rich sulphide minerals, but also secondary iron arsenates and iron oxides formed as reaction products of the original ore minerals. The primary sulphide minerals are susceptible to oxidation in the tailings pile and the secondary minerals have varying solubility in oxidising conditions in groundwaters and surface waters. Scorodite ($FeAsO_4.2H_2O$) is a common sulphide oxidation product and its solubility is considered to control arsenic concentrations in such oxidising sulphide environments. Scorodite is metastable under most groundwater conditions and tends to dissolve incongruently, forming iron oxides and releasing arsenic into solution (Robins, 1987; Kraus and Ettel, 1989). However, in practice, a wide range of Fe-As solubility relationships are found which in part relate to the mineral type (Kraus and Ettel, 1989). There is some confusion in the analysis of these solubility relationships between congruent dissolution, incongruent dissolution and sorption/desorption reactions. Secondary arsenolite (As_2O_3) is also relatively soluble. Arsenic bound to iron oxides is relatively immobile, particularly under oxidising conditions.

1.3.3 The atmosphere

The concentrations of arsenic in the atmosphere are usually low but as noted above, are increased by inputs from smelting and other industrial operations, fossil-fuel combustion and volcanic activity. Concentrations amounting to around 10^{-5}-10^{-3} µg m^{-3} have been recorded in unpolluted areas, increasing to 0.003-0.18 µg m^{-3} in urban areas and greater than 1 µg m^{-3} close to industrial plants (PCS/WHO, 2001). Much of the atmospheric arsenic is particulate. Total arsenic deposition rates have been calculated in the range <1-1000 µg m^{-2} yr^{-1} depending on the relative proportions of wet and dry deposition and proximity to contamination sources (Schroeder *et al.*, 1987). Values in the range 38-266 µg m^{-2} yr^{-1} (29-55% as dry deposition) were estimated for the mid-Atlantic coast (Scudlark and Church, 1988). Concentrations in atmospheric precipitation are given in Section 1.2.1.

Airborne arsenic is transferred to water bodies by wet or dry deposition and may therefore increase the aqueous concentration slightly. However, there is little evidence to suggest that atmospheric arsenic poses a real health threat for drinking-water sources. Atmospheric arsenic arising from coal burning has been invoked as a major cause of lung cancer in parts of China (Guizhou Province), but the threat is from direct inhalation of domestic coal-fire smoke and especially from consumption of foods dried over coal fires, rather than from drinking water affected by atmospheric inputs (Finkelman *et al.*, 1999).

1.4 Mineral-water interactions

1.4.1 Relevance to arsenic mobilisation

As with most trace metals, the concentration of arsenic in natural waters is probably normally controlled by some form of solid-solution interaction. This is most clearly the case for soil solutions, interstitial waters and groundwaters where the solid/solution ratio is large but it is also often true in open bodies of water (oceans, lakes and reservoirs) where the concentration of solid particles is small but still significant. In these open bodies, the particles can be of mineral and biological origin. It is likely that in most soils and aquifers, mineral-As interactions are likely to dominate over organic matter-As interactions, although organic matter may interact to some extent through its reactions with the surfaces of minerals.

Knowing the types of interaction involved is important because this will govern the response of As to changes in water chemistry. It will also determine the modelling approach required for making predictions about possible future changes and for understanding past changes in arsenic concentrations (see Box 1.1).

Box 1.1. Mineral-water interactions

Mineral-water interactions can be divided into two broad types from a geochemical point of view: *precipitation-dissolution* reactions and *adsorption-desorption* reactions. *Precipitation-dissolution* reactions involve the growth or erosion of a mineral structure and so only involve structural ions, i.e. those elements included in the chemical formula of the mineral. The solubility of minerals can in principle be described quite well by a solubility product, although this may vary with the particle size and crystallinity of the mineral. Also the rate of dissolution or precipitation can be very slow and so thermodynamic equilibrium is often not attained in practical time-scales.

Adsorption-desorption reactions involve the binding of chemicals to the surface of minerals (or other solids) and are described by adsorption (or desorption) isotherms. *Ion exchange* is a special type of surface reaction in which one ion (e.g. Ca^{2+}) replaces another ion or ions of equivalent charge (e.g. 2 Na^{+}). An *adsorption* or *exchange isotherm* relates the concentration of a chemical in *solution* to its concentration on a *surface*. Generally, the greater the concentration of a chemical in solution, the greater its concentration bound to the surface. The actual concentration on the surface depends on the chemical involved and with what else it is competing for space on the surface. There is always a preference for the binding of some ions over others but it is normal in nature for a wide variety of ions to be adsorbed at once. This competition for binding sites means that the amount of an ion adsorbed may be quite sensitive to the concentration of other ions present, i.e. the water quality. As a result, there are many complex formulae to describe adsorption-desorption and ion exchange reactions in the natural environment. Being surface reactions, these reactions tend to be rapid, certainly by geological time-scales.

Coprecipitation is also a common natural process whereby minor constituents are incorporated or scavenged into a mineral structure as it forms, e.g. arsenic can be coprecipitated during the formation of pyrite. Also, both phosphate and arsenic are coprecipitated during the formation of iron oxides. The term coprecipitation does not imply any particular mechanism and in practice both adsorption and precipitation may occur at the same time. The reverse process, which may be called *codissolution*, is also likely to be important for the release of trace metals in the natural environment. Coprecipitation often leads to *solid solutions* in which the mixing of components extends into the bulk mineral structure. Solid solutions are very common in nature since mineral precipitation tends to occur from highly 'impure' natural waters. Solid solutions occur most commonly between ions of similar size and character. If the composition of the solution from which the solid solution is forming changes during formation, then the resulting mineral may be 'zoned', i.e. its composition may vary from core to rim.

Adsorption reactions (e.g. on iron oxides) tend to apply to a broad range of ions since they are only based on the formation of a two-dimensional surface structure. Coprecipitation reactions are more selective and precipitation reactions even more so. The relatively unspecific nature of adsorption and coprecipitation reactions means that trace elements in nature are subject to a wide range of interactions that are often difficult to quantify, and therefore to model. This applies to the reactions that affect arsenic.

Precipitation-dissolution and adsorption-desorption reactions are not entirely unrelated processes and in practice, the distinction is not always that clear. For example, arsenic which forms highly insoluble arsenic-sulfide minerals will tend to adsorb strongly to other sulphide minerals such as pyrite (FeS_2).

The importance of oxides in controlling the concentration of arsenic in natural waters has been appreciated for a long time (Table 1.5) (Livesey and Huang, 1981; Matisoff *et al.*, 1982; Korte, 1991; Korte and Fernando, 1991). Clays can also adsorb As(III) and As(V) (Manning and Goldberg, 1997b). Frequently, one of the best correlations between the concentration of As in sediments and other elements is with iron. This is also the basis for the use of iron, aluminum and manganese salts in water treatment, including for arsenic removal (e.g. Edwards, 1994). The As content of residual sludges can be in the range 1,000-10,000 mg kg^{-1} (Forstner and Haase, 1998; Driehaus *et al.*, 1998).

Table 1.5 Studies of arsenic adsorption by metal oxides

Mineral	**Comment**	**Reference**
Aluminium oxides	As(V) and As(III) adsorption on activated alumina: pH dependence, kinetics, column breakthrough. Regeneration by desorbing with NaOH. Modelling with	Ghosh and Yuan (1987)

	pH-dependent Langmuir isotherm (for As) and surface complexation model (for protons).	
‘Amorphous’ aluminium hydroxide	As(V) on precipitated $Al(OH)_3$ (pH 3-10). ‘Adsorption’ exceeded 15 mol kg^{-1} at pH 5. Fitted data to pH dependent Langmuir isotherm.	Anderson *et al.* (1976)
Hfo	Kinetics and pH dependence of As(V) and As(III) adsorption on Hfo (202 m^2 g^{-1}). Found very high As(V) and As(III) loadings (up to 4-5 mol As kg^{-1}) at the highest concentrations, pH adsorption envelopes at various As_T loadings.	Raven *et al.* (1998)
Hfo	Adsorption isotherms for arsenite and arsenate over free concentration range from 10^{-7} M to 10^{-3} M (pH 4-10). Fitted to Langmuir isotherm at low concentrations and linear isotherm at higher concentrations. Dzombak and Morel (1990) fitted this data to their diffuse double layer model.	Pierce and Moore (1982)
Hfo	Sorption of As(V) and As(III) on Hfo at As concentrations of environmental significance (low micromolar range) and pH 4-9. Compared results with Dzombak and Morel (1990) model predictions-generally reasonable agreement. SO_4 decreased adsorption of As(V) and As(III), especially at low pH, while Ca increased As(V) adsorption at high pH. 1 mM bicarbonate did not affect either As(V) or As(III) adsorption greatly.	Wilkie and Hering (1996)
Hfo	A wide angle X-ray scattering (and EXAFS) study of 2-line ferrihydrite coprecipitated with varying amounts of As(V) suggested that the As reduced crystallite size because of the formation of strongly bound inner sphere complex between As(V) and edge sharing $Fe(O,OH)_6$ octahedra. Saturation at As/Fe mole ratio of 0.68.	Waychunas *et al.* (1996)
Hfo	As(III) and As(V) adsorption and OH^- release/uptake on synthetic two-line ferrihydrite. As(V) at pH 9.2 released up to 1 mol OH^- per mol As sorbed whereas As(III) released <0.25 mol As per mol Fe. At pH 4.6, OH^- release was much less for As(V) adsorption and under these conditions there was a net release of H^+ by arsenite. These differences reflect the mechanism of As adsorption and influence the pH dependence of adsorption.	Jain *et al.* (1999)
Granular ‘ferric hydroxide’ (akageneite)	As(V) isotherms given in the sub-µM concentration range; SO_4 competition significant at mM concentrations below pH 7 only; phosphate competition at ‘natural’ groundwater concentrations.	Driehaus *et al.* (1998)
Goethite	An EXAFS and XANES study of As(III) adsorption to a synthetic goethite suggested bidentate inner sphere binding. One plot of As(III) and As(V) pH adsorption envelopes. As(III) data fitted to Constant Capacitance SCM.	Manning *et al.* (1998)

Goethite	Batch adsorption of As(V) on synthetic goethite. Used Mo blue analysis for As. Shows pH edge at about pH 9. Data fitted Langmuir isotherm presumably at constant pH (up to 60 mg l^{-1} As).	Matis *et al.* (1997)
Goethite	Successfully applied the CD-MUSIC surface complexation model to literature data for anion adsorption to goethite including As(V)-P competition. The CD-MUSIC is the most promising of the SCMs for modelling complex natural systems.	Hiemstra and van Riemsdijk (1999)
Goethite	As(V) adsorption on synthetic goethite primarily for a study of impact on flocculation and electrokinetics. No isotherms. Final pH varied but not defined.	Matis *et al.* (1999)
Hematite		Fendorf *et al.* (1997)
Manganese oxides	As(III) & As(V) removal by MnO_2(s) is similar, up to say 5 mmol As mol^{-1} Mn at μM As equilibrium solution concentrations. Freundlich isotherm obeyed. As(III) oxidised to As(V). Rapid (minutes) oxidation and adsorption of As(III). Monitored Mn release and effect of pH, Ca, phosphate and sulphate.	Driehaus *et al.* (1995)
Birnessite, cryptomelane and pyrolusite	Studied adsorption of As(III) and As(V) and kinetics of As(III) oxidation in presence of various MnO_2. As(III) adsorption (per unit weight of oxide): cryptomelane>birnessite>pyrolusite whereas for As(V): Cryptomelane>pyrolusite>birnessite (not detectable). No isotherms given.	Oscarson *et al.* (1983)
Goethite, hematite and lepidocrocite	Batch adsorption of As(V), As(III), MMAA and DMAA on natural minerals (coarse-grained and very low He-Ar surface area). As adsorption: generally goethite > lepidocrocite >> hematite (pH 2-12, maximum often pH 5-8). At pH 7 on goethite, As(III) > MMAA > DMAA > As(V) (?). FA (up to 50 mg l^{-1}) tended to reduce As adsorption. Gives Kd values.	Bowell (1994)
Alumina, hematite, quartz and kaolin	As(V) adsorption on natural, low surface area alumina, hematite, quartz and kaolin (0.12-5 $m^2\ g^{-1}$) at pH 3-10. Adsorption decreases with pH; alumina = kaolin > hematite >> quartz. Gives Kd values and isotherms at low concentrations. Some SO_4^{2-} competition especially below pH 7. FA (>10 mg l^{-1}) generally reduced adsorption at pH 5-7 but not above pH 7 where FA is not adsorbed.	Xu *et al.* (1988)
Alumina	On natural alumina, adsorption was As(V) >As(III) >MMAA = DMAA (pH>6). Maximum adsorption at pH 5 for As(V) and pH 7 for As(III). As(V) but not As(III) adsorption decreased rapidly above pH 6. Log Kd ($l\ kg^{-1}$) at micromolar concentrations (pH 7) was 2.5-3.5 for As(V) and about 1.5 for As(III). FA decreased adsorption.	Xu *et al.* (1991)

Notes:

Hfo= Hydrous ferric oxide or ferrihydrite
SCM = Surface Complexation Model
EXAFS = Extended X-ray absorption fine structure
XANES = X-ray absorption near-edge structure
MMAA = monomethylarsonic acid, $CH_3AsO(OH)_2$
DMAA = dimethylarsinic acid, $(CH_3)_2AsO(OH)$
FA = fulvic acid
CD-MUSIC = Charge Distribution - Multisite Complexation model

It is difficult to study mineral-water interactions directly in aquifers. Most studies, including those with a bearing on arsenic in groundwater, have been undertaken either in soils, or in lake or ocean sediments and usually from quite shallow depths. There is much to be learnt from the studies with soils and sediments since the same general principles are expected to apply. One of the most important areas where cross-fertilization of ideas can occur is in understanding the behaviour of iron oxides in reducing soils and sediments and the influence of this on the release of arsenic. Matisoff *et al.* (1982) related reductive dissolution of iron oxides to the possible release of arsenic in groundwater from an alluvial aquifer in north-east Ohio. Korte (1991) also speculated that desorption of arsenic from iron oxides could occur in reducing, alluvial sediments and that this could lead to high-arsenic groundwaters.

1.4.2 Arsenic interactions in sediments

The major minerals binding arsenic (as both arsenate and arsenite) in sediments are the metal oxides, particularly those of iron, aluminum and manganese. About 50% of the iron in freshwater sediments is in the form of iron oxides and about 20% of the iron is 'reactive' iron. Clays also adsorb arsenic because of the oxide-like character of their edges, as do carbonates. Of these components, adsorption by iron oxides is probably most important in sandy aquifers because of their greater abundance and the strong binding affinity. Nevertheless, if studies of soil phosphate are a guide, then aluminium oxides can also be expected to play a significant role when present in quantity. Experience from water treatment (Edwards, 1994) suggests that below pH 7.5 aluminium hydroxides are about as effective as iron hydroxides (on a molar basis) for adsorbing As(V) but that iron salts are more efficient at higher pH and for adsorbing As(III). Arsenic(V), like phosphate, is expected to be strongly adsorbed by calcium carbonate minerals and this may limit As concentrations in groundwater from limestone aquifers.

The interactions of arsenic with iron oxides have been studied in considerable detail in the laboratory and therefore provide the best insight into the likely behavior of arsenic-mineral interactions in aquifers. However, most of these laboratory studies, particularly the older studies, have been undertaken at rather high arsenic concentrations and there is a paucity of reliable adsorption data at the low $\mu g\ l^{-1}$ level of relevance to natural waters. In addition, there is uncertainty over the extent to which the iron oxides most commonly studied in the laboratory reflect the iron oxides found in the field.

Field data for As(V) adsorption to natural 'diagenetic' Fe oxides (captured in a lake with vertically-installed Teflon sheets) closely paralleled the laboratory data of Pierce and Moore (1982) which was included in the Dzombak and Morel (1990) database (De Vitre *et al.*, 1991). However, it was considerably greater than that calculated using Hingston's (1971) data for As(V) adsorption on goethite highlighting the high affinity of freshly-formed ‘amorphous’ iron oxides for arsenic. Paige *et al.* (1997) measured the As/Fe ratios during the acid dissolution of a synthetic ferrihydrite containing sorbed As(V) and concluded that the dissolution was incongruent (i.e. iron and arsenic were not released in the same proportion as found in the bulk mineral) and that the initial As released was probably sorbed on the surface of the very small ferrihydrite particles. The same is likely to happen during reductive dissolution. The adsorbed As also slowed down the acid dissolution of the ferrihydrite.

1.4.3 Iron in reduced sediments and aquifers

The processes causing changes in iron redox chemistry need to be understood because they directly affect the mobility of arsenic. One of the principal causes of high arsenic concentrations in subsurface waters is the reductive dissolution of hydrous iron oxides and/or the release of adsorbed or combined arsenic. A sequence of reduction reactions occurs when lakes, fjords, soils, sediments and aquifers become anaerobic (Stumm and Morgan, 1995). This sequence begins with the consumption of oxygen and an increase in dissolved CO_2 from the decomposition of organic matter. Next, NO_3^- decreases by reduction to NO_2^- and the gases N_2O and N_2. Insoluble manganic oxides dissolve by reduction to soluble Mn^{2+} and hydrous ferric oxides are reduced to Fe^{2+}. These processes are followed by SO_4^{2-} reduction to S^{2-}, then CH_4 production from fermentation and methanogenesis, and finally reduction of N_2 to NH^{4+}. During sulphate reduction, the consequent sulphide reacts with any available iron to produce FeS and ultimately pyrite, FeS_2. Iron is often more abundant than sulphur so that there is ‘excess iron’ beyond that which can be converted to pyrite (Widerlund and Ingri, 1995). Arsenic(V) reduction would normally be expected to occur after Fe(III) reduction but before SO_4^{2-} reduction.

In sulphate-poor environments, iron from free iron oxides is solubilized as Fe^{2+} under reducing conditions. This gives rise to characteristically high-Fe waters, which in groundwaters tend to range from 0.1-30 mg l^{-1} Fe. The reaction is microbially mediated (Lovley and Chappelle, 1995). There is also evidence for solid-state transformations of the iron oxides under reducing conditions. This is most obviously reflected in a colour change from reddish/orange/brown/tan colours to grey/green/blue colours. Changes to the magnetic properties have also been documented (Sohlenius, 1996). Direct analysis of the Fe(II) and Fe(III) contents of iron oxides from reduced lake waters and sediments often indicates the presence of a mixed Fe(II)-Fe(III) oxide with an approximate average charge on the iron of 2.5 (Davison, 1993). The exact fate of iron during reduction is not well understood, in part because it is probably very fine-grained and difficult to observe directly. Mössbauer spectroscopy is a useful technique for identifying the form of iron oxides in sediments, including anoxic sediments (Boughriet *et al.*, 1997; Drodt *et al.*, 1997).

‘Green rusts’ are one possible product of the transformations. These have occasionally been identified or suspected in anoxic soils and sediments (Taylor, 1980; Boughriet *et al.*, 1997; Cummings *et al.*, 1999). They consist of a range of green-coloured Fe(II)-Fe(III) hydroxide minerals with a layered structure and a charge-balancing interlayer counterion, usually carbonate or sulphate. Green rusts were originally referred to as ‘hydrated magnetite’ and given a composition ‘$Fe_3(OH)_8$’. Boughriet *et al.* (1997) suspected the presence of either green-rust-like compounds, $Fe(III)-Fe(II)-(CO_3)(OH)$ or $Fe(II)_xCa_{1-x}CO_3$ solid solutions, in anoxic sediments from the Seine Estuary. They used ^{57}Fe Mössbauer spectroscopy to characterize the iron. Green rusts have also been identified in anaerobic soils and are thought to play an important role in controlling soil solution Fe concentrations (Genin *et al.*, 1998).

Authigenic magnetite (Fe_3O_4), is another possible product which has been identified in anaerobic sediments (Fredrickson *et al.*, 1998), often with extremely small particle sizes (Maher and Taylor, 1988; Canfield, 1989). Magnetite is frequently found in sediments as a residual detrital phase from rock weathering but very fine-grained magnetite is also formed by so-called ‘magnetotactic’ bacteria. Magnetite formation has been established under reducing conditions in the laboratory (Guerin and Blakemore, 1992). However, under strongly reducing conditions magnetite is unstable and in the presence of high concentrations of H_2S, it slowly converts to pyrite over a period of 100 years or more (Canfield and Berner, 1987). At the sediment/water interface in oceans, partial oxidation of primary magnetite (Fe_3O_4) can lead to a coating of maghemite,?-Fe_2O_3. Further burial and reduction leads to the dissolution of the primary magnetite (Torii, 1997).

These studies of Fe oxides in reducing environments indicate a lack of an as yet well-defined sequence of events taking place when Fe(III) oxides are subjected to strongly reducing conditions. The changes are evidently substantial and can result in the partial dissolution of the oxides and their transformation to completely new mineral phases. It is not yet clear what impact these transformations have on the adsorbed As load of the original Fe(III) oxides. Suffice it to say that even quite small changes in As binding could have a large impact on porewater As concentrations because of the large solid/solution ratio in sediments. Therefore, it is likely that understanding the changes to the nature of iron oxide minerals in sedimentary environments is an important aspect in understanding the processes leading to As mobilisation in sedimentary environments.

1.4.4 Arsenic release from soils and sediments following reduction

There is considerable evidence from laboratory studies that arsenic is released from soils following flooding and the development of anaerobic conditions (Deuel and Swoboda, 1972; Hess and Blanchar, 1977; McGeehan and Naylor, 1994; McGeehan, 1996; Reynolds *et al.*, 1999). Similar evidence is available from laboratory and field studies of marine and lake sediments. Numerous studies have demonstrated the release of both phosphorus (Mortimer, 1942; Farmer *et al.*, 1994; Slomp *et al.*, 1996) and arsenic below the redox boundary in sediments (Moore *et al.*, 1988; De Vitre *et al.*, 1991; Azcue and Nriagu, 1995; Widerlund and Ingri, 1995).

This release has long been associated with iron oxide dissolution. Deuel and Swoboda (1972) found that reducing an untreated black clay soil led to the release of As and that the amount released was related to the total arsenic content of the soil and the redox potential. They proposed that the release was primarily due to reduction (and dissolution) of ‘ferric arsenates’ rather than to changes in the As speciation. Arsenic release occurred in less than a week.

De Vitre *et al.* (1991) showed that there was a rapid increase in pore water As concentrations (up to about 30 $\mu g\ l^{-1}$) with depth in a lake sediment and that this was mirrored by an increase in dissolved Fe. Upwardly diffusing Fe^{2+} was oxidised near the sediment-water interface and precipitated as an iron oxide which then adsorbed the upwardly diffusing As. Guo *et al.* (1997) measured the rate of release of As (and other trace elements) as a spiked sediment was progressively reduced. Arsenic was rapidly released after the Fe and Mn had dissolved suggesting that dissolution rather than desorption was the dominant process, or at least that dissolution and adsorption occurred simultaneously. Selective extractions suggested that most of the As in the sediments was associated with Fe and Mn oxides. Riedel *et al.* (1997) monitored the release of metals when a column of estuarine sediment was subjected to reducing conditions for several months. Both As and Mn were released following reduction.

A few studies have attempted to differentiate between the oxidation states of arsenic sorbed by sediments. Masscheleyn *et al.* (1991) measured the release of As and other metals following the flooding and reduction of an arsenic-contaminated soil and found that the release of some As occurred before Fe dissolution but that the amount of As released rapidly increased as the amount of iron-oxide dissolution increased. Both As(V) and As(III) were released. Rochette *et al.* (1998) demonstrated with XANES spectroscopy that reducing conditions can lead to the conversion of As(V) to As(III) in the solid phase of arsenic minerals. Preliminary results based on XANES also indicate a change in solid-state speciation of the As in Bangladesh sediments in going from oxidising to reducing conditions (Foster *et al.*, 2000).

The As concentration in sediments is normally too low and/or the particles too small for direct investigation of solid phase arsenic speciation using techniques such as XAFS and PIXE and so selective dissolution has been most widely used. A number of extraction 'schemes' exist which attempt to allocate elements to particular solid phases.

Gómez-Ariza *et al.* (1998) developed a method to speciate solid phase arsenic based on selective extraction of sediments with hydroxylamine hydrochloride, an acidic and reducing extractant that is rather selective for extracting manganese oxides but that also extracts small amounts of iron oxides. Hydroxylamine hydrochloride did not reduce the As(V) during the extraction.

Brannon and Patrick (1987) studied the kinetics of As release and speciation (As(V), As(III), organic) from freshwater sediments when incubated under both oxidising and reducing conditions. This included sediments with and without added As(V). Most of the native and added As was found in the 'moderately reducible' (oxalate-extractable) fraction. During incubation, a steady release of As was observed over a three-month period, with As(V) occurring under oxidising conditions and As(III) under reducing conditions. There was no concomitant release of Fe (or Al or Mn) indicating that reductive dissolution of iron oxides was not responsible for the As release. Brannon and Patrick (1987) speculated that a change in the structure of the iron oxides may have been important. McGeehan (1996) was not sure whether the As(V) reduction that occurs in flooded soils occurs in the soil solution or on the soil particles.

Manning and Goldberg (1997a) measured As(V) and As(III) adsorption by three Californian soils and found that the soils with the highest citrate-dithionite-bicarbonate extractable Fe and percent clay had the greatest affinity for both As(III) and As(V). As(V) sorbed to a greater extent than As(III) at the micromolar As concentrations used, suggesting that As would be released under reducing conditions when As(V) is reduced to As(III).

Cummings *et al.* (1999) found that As(V) was released from hydrous ferric oxide (Hfo) under reducing conditions without any pre-reduction of As(V) to As(III). Scorodite, a ferric arsenate mineral (Table 1.2), was also in part transformed to various ferrous arsenates. Therefore, the reduction of As(V) to As(III) may follow the initial release of As into solution rather than initiate it.

All of these studies demonstrate the ability of soils and sediments to release As when subjected to reducing conditions but there is no clear consensus on the precise mechanisms involved particularly with respect to the roles played by reductive desorption, reductive dissolution and/or diagenetic changes to the mineral structure.

None of the extraction schemes is perfect or universally applicable and there is little consensus on the best techniques to use. The interpretation is particularly difficult for minor and trace constituents which may be released by both dissolution and desorption processes. Nonetheless, these extractants can probe the solid phase in a useful way that reflects to a varying extent the nature of an element in the solid phase, and therefore its potential behaviour or availability. In particular, such techniques are particularly useful for characterising the very fine-grained minerals or organic phases that are presently poorly characterised by direct examination but which nevertheless play an important role in the behaviour of many trace elements. The usefulness of the various extractants should increase as our quantitative understanding of the dissolution kinetics of typical minerals increases and as the various sorption/desorption reactions involved are quantified. In the meantime, they can serve as a useful guide to the forms of the elements present and to significant variations in such forms, but care has to be taken in interpreting their results in a quantitative and uncritical way.

1.4.5 Transport of arsenic

The transport of chemicals and adsorption are closely related in that adsorption slows down the transport of a chemical compared with the water flow (Appelo and Postma, 1992). In the simplest case of a linear adsorption isotherm, this relationship is straightforward and the partition coefficient, Kd, defines a constant retardation factor. With non-linear adsorption, which is most likely to be the case for arsenic adsorption, the value of Kd varies with concentration and is related to the slope of the isotherm. Normally, the Kd decreases with increasing concentration, leading to less retardation at high concentrations and ultimately to self-sharpening and diffuse fronts. For example, the greater the nonlinearity, the longer it will take to flush completely all of the arsenic from an aquifer - the last bit is removed reluctantly because the binding is so strong at low concentrations.

Since transport is so closely related to the adsorption isotherms, it follows that arsenate and arsenite should travel through an aquifer with different velocities leading to their increased separation along a flow path. This was demonstrated by Gulens *et al*. (1979) using breakthrough experiments with columns of sand (containing 0.6% Fe and 0.01% Mn) and various groundwaters pumped continuously from piezometers. They studied As(III) and As(V) mobility with groundwaters having a range of Eh and pH values using radioactive ^{74}As (t½=17.7 d) and ^{76}As (t½=26.4 hr) to monitor the breakthrough of As. They showed that: (i) As(III) moved 5-6 times faster than As(V) under oxidising conditions (pH 5.7); (ii) with a 'neutral' groundwater (pH 6.9), As(V) moved much faster than under (i) but was still slower than As(III); (iii) with reducing groundwater (pH 8.3), both As(III) and 'As(V)' moved rapidly through the column; (iv) when the amount of As injected was substantially reduced, the mobility of the As(III) and As(V) was greatly reduced.

This chromatographic effect may account in part for the highly variable As(III)/As(V) ratios found in many reducing aquifers. Such a separation is used to advantage in analytical chemistry to speciate arsenic with various columns. Chromatographic separation during transport will also tend to uncorrelate any correlations found at the source, for example in the As versus Fe relationship, thus complicating a simple interpretation of well water analyses.

There have been few studies of the transport of arsenic in aquifers derived from natural sources. Most studies of arsenic leaching have concerned industrially-contaminated sites. Kuhlmeier (1997a,b) studied the transport of arsenic in highly-contaminated clayey and sandy soils from around an old arsenic herbicide plant in Houston, Texas. He used column experiments to estimate 'apparent' Kd values. These were time- and implicitly concentration-dependent and for the sandy soils ranged from 0.26 l kg^{-1} after one void volume to 3.3 l kg^{-1} after 6 void volumes. They were not too different for the clayey materials. However, the overall As concentrations were very high: the groundwater was heavily contaminated with As (408-464 mg l^{-1}), mostly as MMAA. The sediment contained only a few mg kg^{-1} of inorganic As. Baes and Sharp (1983) gave Kd values of 1.0-8.3 l kg^{-1} (median 3.3) for As(III) binding by soils and 1.9-18.0 l kg^{-1} (median 6.7) for As(V).

1.5 Groundwater environments showing enhanced arsenic concentrations

1.5.1 World distribution of groundwater arsenic problems

A number of large aquifers in various parts of the world have been identified with problems from As occurring at concentrations above 50 µg l^{-1}, often significantly so. The most noteworthy occurrences are in parts of Argentina, Bangladesh, Chile, northern China, Hungary, India (West Bengal), Mexico, Romania, Taiwan (China) and many parts of the USA, particularly the south-west (Figure 1.3). Some of the better documented cases are summarised in Table 1.6. These include natural sources of contamination as well as mining-related sources. Arsenic associated with geothermal waters has also been reported in several areas, including hot springs from parts of Argentina, Japan, New Zealand, Chile, Kamchatka, Iceland, France, Dominica and the USA.

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Figure 1.3 Map of documented world arsenic problems

Localised groundwater arsenic problems are now being reported from an increasing number of countries and many new cases are likely to be discovered. Until recently, arsenic was not traditionally on the list of elements routinely tested by water quality testing laboratories and so many arsenic-rich sources undoubtedly remain to be identified. The intended revision of the drinking water standard for arsenic in a number of countries has prompted a reassessment of the situation in many countries. The recent discovery of arsenic contamination on a large scale in Bangladesh has highlighted the need for a rapid assessment of the situation in alluvial aquifers worldwide.

As described above, arsenic problems also occur in some areas where sulphide-mining activity is prevalent, the As being released from sulphide minerals as they are oxidised as a result of mining operations. In mining areas, As problems can be severe with concentrations in affected waters often being in the milligram-per-litre range. However, unlike As occurrences in major aquifers, the problems in these areas are typically localised, rather than of widespread occurrence. Mining-related As problems in water have been identified in many parts of the world, including Austria, Ghana, Greece, India (Madhya Pradesh), South Africa, Thailand and the USA (Fig. 1.3).

Table 1.6 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 (μg l^{-1})	Aquifer type	Groundwater conditions	Reference
Bangladesh	150,000	ca. 3x10^{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	6x10^{6}	<10 to 3200	As Bangladesh	As Bangladesh	CGWB (1999); POA (1999)
China:		5.6x10^{6}				Sun et al. (2000)
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), Zhai *et al.* (1998), Ma *et al.* (1999), Sun *et al.* (1999), Smedley *et al.* (2000b, 2001b)
Xinjiang (Tianshan Plain)	38,000	? (500 diagnosed)	40 to 750	Holocene alluvial plain	Reducing, deep wells (up to 660m) are artesian	Wang and Huang (1994)
Shanxi				Alluvial plain	? Reducing	Sun *et al.* (1999)
Hungary, Romania (Danube Basin)	110,000	29,000	<2 to 176	Quaternary alluvial plain	Reducing groundwater, some artesian. Some high in humic acid	Varsányi *et al.* (1991); Gurzau (2000)
Argentina (Chaco-Pampean Plain)	10^{6}	2x10^{6}	<1 to 5300 (7800 in some porewaters)	Holocene and earlier loess with rhyolitic volcanic ash	Oxidising, neutral to high pH, high alkalinity. Groundwaters often saline.	Nicolli *et al.*, 1989; Nicolli and Merino (2001); Smedley *et al.* (2001a); Sancha and Castro

					As(V), accompanied by high B, V, Mo, U. Also high As concentrations in some river waters	(2000)
Northern Chile (Antofagasta)	125,000	500,000	100 to 1000	?Quaternary volcanogenic sediment	Generally oxidising. Arid conditions, high salinity, high B. Also high-As river waters	Cáceres *et al.* (1992), Karcher *et al.* (1999); Sancha and Castro (2000) Smith *et al*. (1992)
South-west USA: Basin & Range, Arizona	200,000	3.5x10^{5} (tot)	up to 1300	Alluvial basins, some evaporites	Oxidising, high pH. As (mainly As(V)) correlates positively with Mo, Se, V, F	Robertson (1989)
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	4x10^{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)
Moira 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 Colombia	50		0.5-580	Sulphide mineral veins in volcanic country rocks	neutral to high-pH groundwaters (up to 8.9), As correlated with B, F	Boyle *et al.* (1998)

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

While natural high-arsenic groundwaters (with arsenic above drinking-water standards) are not uncommon, they are by no means typical of most aquifers and only exist under special circumstances. These relate to both the geochemical environment and to the past and present hydrogeology. Paradoxically, high-arsenic groundwaters are not necessarily related to areas of high arsenic concentrations in the source rocks.

Distinctive groundwater arsenic problems occur under both reducing and oxidising groundwater conditions; also in both 'wet' and 'dry' environments. Below we discuss the characteristics of the arsenic problems worldwide through a series of type examples. These examples have been ordered according to the type of environment under which they are developed.

1.5.2 Reducing environments

Bangladesh and India (West Bengal)

In terms of the population exposed, As problems in groundwater from the alluvial and deltaic aquifers of Bangladesh and West Bengal represent the most serious occurrences identified globally. Concentrations in groundwaters from the affected areas have a very large range from <0.5 µg l^{-1} to ca. 3200 µg l^{-1} (DPHE/BGS/MML, 1999; CGWB, 1999). Resultant health problems were first identified in West Bengal in the late 1980s but the first diagnosis in Bangladesh was not made until 1993. Between 30 and 36 million people in Bangladesh are estimated to be exposed to As in drinking water at concentrations above 50 µg l^{-1} (BGS and DPHE, 2001) and up to 6 million in West Bengal (Table 1.6). Skin disorders including hyper/hypopigmentation changes and keratosis are the most common external manifestations, although skin cancer has also been identified (see Chapter 4). Around 5000 patients have been identified with

As-related health problems in West Bengal (including skin pigmentation changes) although some estimates put the number of patients with arsenicosis at more than 200,000 (Smith *et al.*, 2000). The number in Bangladesh is not known but must be many times greater than in West Bengal. The instance of internal arsenic-related health problems is not known but could be appreciable.

Box 1.3. The Bangladesh groundwater arsenic problem

The map of Bangladesh shows quite clearly the regional pattern of arsenic contamination of the groundwater based on the analysis of water from 3500 wells. The blue and green areas are below the Bangladesh drinking-water standard (50 µg l^{-1}) while the blue areas are below the WHO guideline value (10 µg l^{-1}). The worst-affected area is in southern Bangladesh especially the south-east. Water from the southern-most coastal region has low arsenic concentrations because the water is drawn from wells greater than 200 m depth in order to avoid salinity problems in the shallower horizons. Most of the other wells are from a depth of 15-80 m. While many wells in northern Bangladesh have acceptably low arsenic concentrations, there are occasional, highly localised 'hot spots' as shown by the red dots. The concentration of arsenic in these hot spots can exceed 2000 µg l^{-1}.

MAP PENDING

West Bengal and Bangladesh rely heavily on groundwater for public drinking-water supply. Groundwater development has been actively encouraged in the region over the last few decades by government and other agencies as a means of providing an alternative to polluted surface water and thereby reducing the incidence of water-borne diseases. There has also been a rapid increase in the number of private tubewells and now the number of private tubewells exceeds the number of public tubewells. In this sense, the increase in use of groundwater has been very successful. The identification of chronic health problems related to As was unforeseen and has taken a number of years to become apparent.

The affected aquifers are generally shallow (less than 100-150 m deep), of Holocene age and comprise a mixed sequence of micaceous sands, silts and clays deposited by the Ganges, Brahmaputra and Meghna river systems and their precursors. The sediments are derived from the upland Himalayan catchments and from basement complexes of the northern and western parts of West Bengal. In most affected areas, the sediment sequence is capped by a layer of clay or silt (of variable thickness) which effectively restricts entry of air to the aquifers. This, together with an abundance of recent solid organic matter deposited with the sediments, has resulted in the development of highly reducing aquifer conditions which favour the mobilisation of As. The mobilisation has probably occurred by a complex combination of redox changes brought on by rapid burial of the alluvial and deltaic sediments, including reduction of the solid-phase As to As(III), desorption of As from iron oxides, reductive dissolution of the oxides themselves and likely changes in iron-oxide structure and surface properties following the onset of reducing conditions (BGS and DPHE, 2001). Deep wells, tapping depths greater than 150-200 m, almost invariably have low arsenic concentrations, less than 5 µg l^{-1} and usually less than 0.5 µg l^{-1} (BGS and DPHE, 2001). Also wells from the older Plio-Pleistocene sediments of the Barind and Madhupur Tracts have low arsenic concentrations. It is a fortunate fact that both Calcutta and Dhaka draw their water from older sediments and do not have an arsenic problem. Dhaka is sited at the southern tip of the Madhupur Tract (BGS and DPHE, 2001).

The characteristic chemical features of the high-arsenic groundwaters are high iron (>0.2 mg l^{-1}), manganese (>0.5 mg l^{-1}), bicarbonate (>500 mg l^{-1}) and often phosphorus (>0.5 mg l^{-1}) concentrations, and low chloride (<60 mg l^{-1}), sulphate (<1 mg l^{-1}), nitrate and fluoride (<1 mg l^{-1}) concentrations, with pH values close to or greater than 7. Measured redox potentials are typically less than 100 mV (AIP Steering Committee, 1991; CGWB, 1999; DPHE/BGS/MML, 1999; BGS and DPHE, 2001). However, the correlations between dissolved elements are usually far from perfect and where good correlations with arsenic are found, these are only applicable locally and are of limited value for quantitative prediction of arsenic concentrations, even at a village scale. For example, some workers have found a positive correlation between arsenic and iron in village studies (e.g. Nag *et al.*, 1996), but this is not true of Bangladesh and West Bengal as a whole. One commonly observed relationship in the groundwaters is a general negative correlation between As and SO_4 concentrations (BGS and DPHE, 2001). This association suggests that As mobilisation is effected under the most strongly reducing conditions, coincident with sulphate reduction. Some of the groundwaters of Bangladesh are sufficiently reducing for methane generation to have taken place.

The worst-affected areas of Bangladesh are to the south and east of Dhaka (Fig. 1.3) where in some villages, more than 90% of the wells have arsenic concentrations above 50 µg l^{-1}. The groundwaters are predominantly reducing, as evidenced by the major-element chemistry described above. Arsenic speciation studies have revealed a large range in the relative proportions of dissolved arsenate and arsenite (e.g. Das *et al.*, 1995; Acharyya, 1997). The modal proportion of arsenite appears to be between 50% and 60% of the total arsenic (BGS and DPHE, 2001). This may reflect lack of redox equilibrium in the aquifer or a mixed groundwater from a strongly stratified aquifer.

The regional distribution of the high-arsenic waters in West Bengal and Bangladesh is known to be extremely patchy (AIP Steering Committee, 1991; CSME, 1997; BGS and DHPE, 2001), presumably in part because of great variation in sedimentary characteristics and variations in abstraction depth. Estimates of the proportions of tubewells affected in West Bengal are not well-documented and difficult to assess. However, the indications are that the degree of contamination is not as severe in West Bengal as in the worst-affected districts of Bangladesh (e.g. Dhar *et al.* 1997), where in some instances more than 90% of tubewells investigated exceed the Bangladesh and Indian drinking-water standard for arsenic (50 µg l^{-1}; BGS and DPHE, 2001). Certainly, the overall areal extent of contamination in West Bengal is less than in Bangladesh.

The arsenic-affected groundwaters in the Bengal Basin are associated with sediments having total arsenic concentrations in the range <2-20 mg kg^{-1}, i.e. not exceptional by world-average values. This is not surprising given the scale of the problem. These sediments are derived from the drainage systems of three major rivers (Ganges, Brahmaputra and Meghna) which are themselves sourced from a wide area of the Himalaya. Therefore, while it could be argued that the source of much of the arsenic in the Bengal Basin sediments is derived from specific mineralised areas in the source region, these are likely to be so widespread as to be academic and of little practical relevance.

Isotopic evidence suggests that some groundwater from the Bengal Basin has had a long residence time in the aquifers. In Bangladesh, BGS and DPHE (2001) found that tritium, an indicator of modern groundwater, was usually detectable at a few TU in the shallowest groundwaters but deeper groundwaters usually had lower concentrations, typically <0.4 TU. Such low concentrations are indicative of older groundwater, with a large proportion having been recharged prior to the 1960s. Radiocarbon data also suggest the presence of old groundwater at some sites. Groundwater from 10-40 m depth in groundwaters from western Bangladesh was 'modern' (83 pmc or greater) indicating an age of the order of decades. Shallow groundwaters from south-central Bangladesh were also modern (78 pmc or greater), although groundwater from 150 m was notably older (51 pmc) with a model age of about 2000 years. Deep groundwaters analysed from southern Bangladesh were even older with ^{14}C activities of 28 pmc or less, suggesting the presence of palaeowaters with ages of 2,000-12,000 years.

The reasons for the distinction between groundwater As concentrations in the shallow and deep aquifers of the Bengal Basin are not yet well-understood. Differences between the sediments at depth may occur in terms of absolute As concentrations and in the oxidation states and binding properties of the As to the sediments. However, it is also possible that the history of groundwater movement and aquifer flushing in the Bengal Basin has been important in generating the differences in dissolved As concentrations between the shallow and deep aquifers. Older, deeper sediments have been subject to longer periods of groundwater flow, aided by greater hydraulic heads during the Pleistocene period when glacial sea levels around the Bangladesh landmass were up to 130 m lower than today (e.g. Umitsu, 1993). Flushing of the deeper older aquifers with groundwater is therefore likely to have been much more extensive than in the Holocene sediments deposited during the last 5000-10000 years. Hence, much of the As in the deep sediments may have previously been flushed away.

Salinity becomes a problem in the near-coastal parts of the aquifers in southern Bangladesh as a result of saline intrusion (BGS and DPHE, 2001). This affects the usability of the shallow aquifer in Bangladesh and means that deep wells, often more than 200 m deep, need to be constructed to obtain fresh water. As mentioned above, these almost always have low arsenic concentrations.

Taiwan (China)

The south-west coastal zone of Taiwan, China was perhaps the first area to be identified as a problem area for health effects arising from chronic arsenic exposure. Arsenic problems are also documented in north-eastern parts of the island (Hsu *et al.*, 1997). Awareness of the arsenic problem began during the 1960s (e.g. Tseng *et al.*, 1968) and arsenic-related health problems have been well-documented by several workers since then (e.g. Chen *et al.*, 1985). Taiwan is the classic area for the identification of black-foot disease but a number of other typical health problems, including internal cancers, have been described.

Kuo (1968) observed As concentrations in groundwater samples from south-west Taiwan ranging between 10 $\mu g\ l^{-1}$ and 1800 $\mu g\ l^{-1}$ (mean 500 $\mu g\ l^{-1}$, n=126) and found that half the samples analysed had concentrations between 400 $\mu g\ l^{-1}$ and 700 $\mu g\ l^{-1}$. A large study carried out by the Taiwan Provincial Institute of Environmental Sanitation established that 119 townships in the affected area had As concentrations in groundwater of >50 $\mu g\ l^{-1}$ and 58 townships had >350 $\mu g\ l^{-1}$ (Lo *et al.*, 1977). In north-eastern Taiwan, Hsu *et al.* (1997) found As concentrations in groundwaters in the range <10 to >600 $\mu g\ l^{-1}$ with an average of 135 $\mu g\ l^{-1}$ (377 samples).

In the south-west, the high As concentrations are found in groundwaters from deep artesian wells (mostly 100-280 m) abstracted from sediments which include fine sands, muds and black shale (Tseng *et al.*, 1968). Groundwaters abstracted from the north-east of Taiwan are also artesian, but of shallower depth (typically in the range 16-40 m; Hsu *et al.*, 1997). In each area, the groundwaters are likely to be strongly reducing and hence may be analogous to groundwaters in the affected areas of Bangladesh and India (West Bengal). This is supported by the observation that the As is present largely as As(III) (Chen *et al.*, 1994). However, both the geochemistry of the groundwaters and the mineral sources in Taiwan are poorly defined at present. Groundwater from shallow open dug wells in the area have low arsenic concentrations (Guo *et al.*, 1994).

Northern China

Arsenic has been found at high concentrations (in excess of the Chinese national standard of 50 µg l^{-1}) in groundwaters from Inner Mongolia as well as Xinjiang and Shanxi Provinces (Fig. 1.2; Wang, 1984; Wang and Huang, 1994; Niu *et al.*, 1997; Smedley *et al.*, 2001). The first cases of As poisoning were recognised in Xinjiang Province in the early 1980s. Wang (1984) found As concentrations in groundwaters from the province at up to 1200 µg l^{-1}. Wang and Huang (1994) reported As concentrations of between 40 µg l^{-1} and 750 µg l^{-1} in deep artesian groundwater from the Dzungaria Basin on the north side of the Tianshan Mountains (from Aibi Lake in the west to Mamas River in the east, a stretch of ca. 250 km). Arsenic concentrations in artesian groundwater from deep boreholes (up to 660 m) were found to increase with depth. Shallow (non-artesian) groundwaters had observed As concentrations between <10 µg l^{-1} and 68 µg l^{-1}. The concentration of As in the saline Aibi Lake was reported as 175 µg l^{-1}, while local rivers had concentrations of between 10 µg l^{-1} and 30 µg l^{-1}. Artesian groundwater has been used for drinking in the region since the 1960s and chronic health problems have been identified as a result (Wang and Huang, 1994).

Box 1.4: Arsenic in groundwater of the Huhhot Basin, Inner Mongolia, China

High arsenic concentrations in groundwaters and associated health problems have been identified in several parts of northern China, especially Inner Mongolia (e.g. Ba Meng, Tumet Plain, Huhhot Basin, Baiyingao), Xinjiang and Shanxi Provinces.

One of the worst-affected areas is the Huhhot Basin. Huhhot, the capital city of Inner Mongolia, lies within an alluvial basin bounded by mountains to the north, east and south. The alluvial sediments are of Holocene age and are composed of a mixed sequence of sands, silts and clays derived from a former lake and marginal alluvial fan deposits eroded from the surrounding mountains. Groundwater is important in the rural areas of the basin, both for irrigation and domestic supply and has been abstracted from dug wells since the 1930s. Today, groundwater is abstracted from tubewells using both motorised pumps and hand pumps.

The groundwater is derived from varying depths but mostly from a shallow (less than around 50 m) aquifer and a deeper aquifer (100-400 m). Both aquifers are in parts contaminated with arsenic. The observed range of total arsenic concentrations in groundwater varies from <1 µg l^{-1} to 1400 µg l^{-1}. The arsenic-rich groundwaters are highly reducing with low nitrate and high ammonium concentrations. Concentrations of arsenic are highest in the low-lying part of the basin where conditions are most reducing and groundwater flow is most sluggish. Like Bangladesh, the arsenic is present in both oxidised (arsenate) and reduced (arsenite) forms, although arsenite is dominant. The deep groundwaters often also have high concentrations of dissolved humic materials and can contain high concentrations of fluoride (up to 7 mg l^{-1}) though this is not correlated with arsenic. In a study by Smedley *et al.* (2001), about 40% of the wells sampled had arsenic concentrations exceeding the WHO guideline value of 10 µg l^{-1}. Many of the people in the region drinking high-arsenic groundwater have visible skin lesions. Currently, about 200 cases of arsenic-related disease have been identified in the basin including various cancers, lung cancer being the most common.

Figures: Map of Huhhot Basin with As concentrations; location map of China

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In Inner Mongolia, concentrations of As in excess of the Chinese national standard (50 µg l^{-1}) have been identified in groundwaters from aquifers in the Huhhot Basin, Ba Meng Region, and Tumet Plain (e.g. Luo *et al.*, 1997; Ma *et al.*, 1999). These areas include the cities of Boutou and Togto. In the Huhhot Basin, the problem is found in groundwaters from Holocene alluvial and lacustrine aquifers under highly reducing conditions and is worst in the lowest-lying parts of the basin (Smedley *et al.*, 2001b). Concentrations have been found in the groundwaters at up to 1500 µg l^{-1}, with a significant proportion of the As being present as As(III). Some shallow dug wells also have groundwater with relatively high As concentrations (up to 556 µg l^{-1}; Smedley *et al.*, 2001b). Shallow groundwaters in parts of the region are saline as a result of evaporative concentration exacerbated by irrigation and many have high fluoride concentrations, although the F does not generally correlate with As. In the affected region, As-related disease has been identified by Luo *et al.* (1997). Recognised health effects include lung, skin and bladder cancer as well as prevalent keratosis and skin-pigmentation problems.

Vietnam

The aquifers of the large deltas of the Mekong and Red Rivers are now widely exploited for drinking water. The total number of tubewells in Vietnam is unknown but could be on the order of one million, with perhaps 150,000 in the Red River delta region. The majority of these are private tubewells. The capital city, Hanoi, is now largely dependent on groundwater for its public water supply. The aquifers exploited are of both Holocene and Pleistocene age.

In the Red River delta region, the Holocene sediments form the shallowest aquifer but these may be only 10-15 m deep and in some cases are entirely absent. Older Pleistocene sediments are then exposed at the surface. Unlike Bangladesh, even when the Holocene sediments are present, there is not always a layer of fine silt-clay at the surface. Normally the Holocene sediments are separated from the underlying Pleistocene sediments by a clay layer several metres thick, although ‘windows’ in this clay layer exist where there is hydraulic continuity between the Holocene and Pleistocene aquifers. The total thickness of sediments is typically 100-200 m.

The groundwaters in the delta regions are usually strongly reducing with high concentrations of iron, manganese and ammonium. Much of the shallow aquifer in the

Vietnamese part of the Mekong delta region is affected by salinity and cannot be used for drinking water.

Little was known about the arsenic concentrations in groundwater in Vietnam until recently. UNICEF and EAWAG/CEC (Hanoi National University) are now carrying out extensive investigations to assess the scale of the problem. Preliminary results from Hanoi (Berg *et al.*, 2000; Wegelin *et al.*, 2000) indicate that there is a significant arsenic problem in shallow tubewells in the city, particularly in the south. There appears to be a seasonal pattern with significantly higher concentrations in the rainy season. This could be related to the local hydrology since there are significant interactions between the aquifer and the adjacent Red River.

Little is known about the arsenic concentrations in groundwater from the middle and upper parts of the Mekong delta (and into adjacent Cambodia and Laos) and other smaller alluvial aquifers in Vietnam but investigations are presently taking place.

Hungary

Concentrations of As above 50 µg l^{-1} have been identified in groundwaters from alluvial sediments associated with the River Danube in the southern part of the Great Hungarian Plain (Fig. 1.2). Concentrations up to 150 µg l^{-1} (average 32 µg l^{-1}, 85 samples) have been found by Varsányi *et al.* (1991). The Plain, some 110,000 km^2 in area, consists of a thick sequence of subsiding Quaternary sediments. Groundwaters vary from Ca-Mg-HCO_3-type in the recharge areas of the basin margins to Na-HCO_3-type in the low-lying discharge regions. Groundwaters in deep parts of the basin (80-560 m depth) with high As concentrations are reducing with high concentrations of Fe and NH_4 and many have reported high concentrations of humic acid (up to 20 mg l^{-1}; Varsányi *et al.*, 1991). The groundwaters have highest As concentrations in the lowest parts of the basin, where the sediment is fine-grained.

1.5.3 Arid oxidising environments

Mexico

The Lagunera Region of north central Mexico has a well-documented arsenic problem in groundwater with significant resulting chronic health problems. The region is arid and groundwater is an important resource for potable supply. Groundwaters from the region are predominantly oxidising with neutral to high pH. Del Razo *et al.* (1990) quoted pH values for groundwaters in the range 6.3 to 8.9. They found As concentrations in the range 8 µg l^{-1} to 624 µg l^{-1} (average 100 µg l^{-1}, n=128), with half the samples having concentrations greater than 50 µg l^{-1}. They also noted that most (>90%) of the groundwater samples investigated had As present predominantly as As(V). Del Razo *et al.* (1994) determined the average concentration of As in drinking water from Santa Ana town in the region as 404 µg l^{-1}. The estimated population exposed to As in drinking water with >50 µg l^{-1} is around 400,000 in Lagunera Region (Del Razo *et al.*, 1990). Groundwaters from the region also have high concentrations of 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 2-305 µg l^{-1} (76 samples) with highest concentrations in groundwaters from the towns of Hermosillo, Etchojoa, Magdalena and Caborca. The As concentrations were also positively correlated with fluoride. Highest observed F concentration in the area was 7.4 mg l^{-1}. It is also believed that high arsenic groundwaters have been found in other parts of northern Mexico.

Chile

Health problems related to As in drinking water were first recognised in northern Chile in 1962. Typical symptoms included skin-pigmentation changes, keratosis, squamous-cell carcinoma (skin cancer), cardiovascular problems and respiratory disease (Zaldivar, 1974). More recently, As ingestion has been linked to lung and bladder cancer. It has been estimated that around 7% of all deaths occurring in Antofagasta between 1989 and 1993 were due to past exposure to As in drinking water at concentrations of the order of 500 µg l^{-1} (Smith et al., 1998). Since exposure was chiefly in the period 1955-1970, this pointed to a long latency period of cancer mortality. Other reported symptoms include impaired resistance to viral infection and lip herpes (Karcher *et al.*, 1999).

High As concentrations have been 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 (Atacama Desert) and water resources are limited. High As concentrations are accompanied by high salinity (due to evaporation) and high B concentrations. Arsenic concentrations below 100 µg l^{-1} in surface waters and groundwaters are apparently quite rare, and concentrations up to 21,000 µg l^{-1} have been found. Karcher *et al.* (1999) quoted ranges of 100 µg l^{-1} to 1000 µg l^{-1} in raw waters (average 440 µg l^{-1}). The affected waters of Chile are taken to be predominantly oxidising (with dissolved oxygen present), largely because the As is reported to be present in the waters as arsenate (Thornton and Farago, 1997 and references cited therein). However, the geochemistry of the aquifers of Chile is as yet poorly understood. The aquifers are composed of volcanogenic sediments, but these have not been characterised in detail. In Antofagasta, concentrations of As in the sediments are ca. 3.2 mg kg^{-1} (Cáceres *et al.*, 1992). Additional As exposure from smelting of copper ore has also been noted in northern Chile (Cáceres *et al.*, 1992) and geothermal sources are also recognised (Section 1.5.5).

Arsenic treatment plants were installed in the towns of Antofagasta and Calama in 1969 to mitigate the problems. Today, the urban populations of the major towns are supplied with treated water from the Rivers Toconce and Loa (Karcher *et al.*, 1999) which is transported from the foot of the Andes mountains to the treatment works. However, rural communities still largely rely on untreated water supplies which contain As.

Argentina

The Chaco-Pampean Plain of central Argentina constitutes perhaps one of the largest regions of high-arsenic groundwaters known, covering around 1 million km^2. High concentrations of arsenic have been documented from Córdoba, La Pampa, Santa Fe and Buenos Aires Provinces in particular (Box 1.5). Symptoms typical of chronic arsenic poisoning, including skin lesions and some internal cancers, have been recorded in these areas (e.g. Hopenhayn-Rich *et al.*, 1996). The climate is temperate with increasing aridity towards the west. Groundwaters are derived from Quaternary deposits of loess (mainly silt) with intermixed rhyolitic or dacitic volcanic ash (Nicolli *et al.*, 1989; Nicolli and Merino, 1997; Smedley *et al.*, 1998). The sediments display abundant evidence of post-depositional diagenetic changes under semi-arid conditions, with common occurrences of calcrete in the form of cements, nodules and discrete layers, sometimes many centimetres thick.

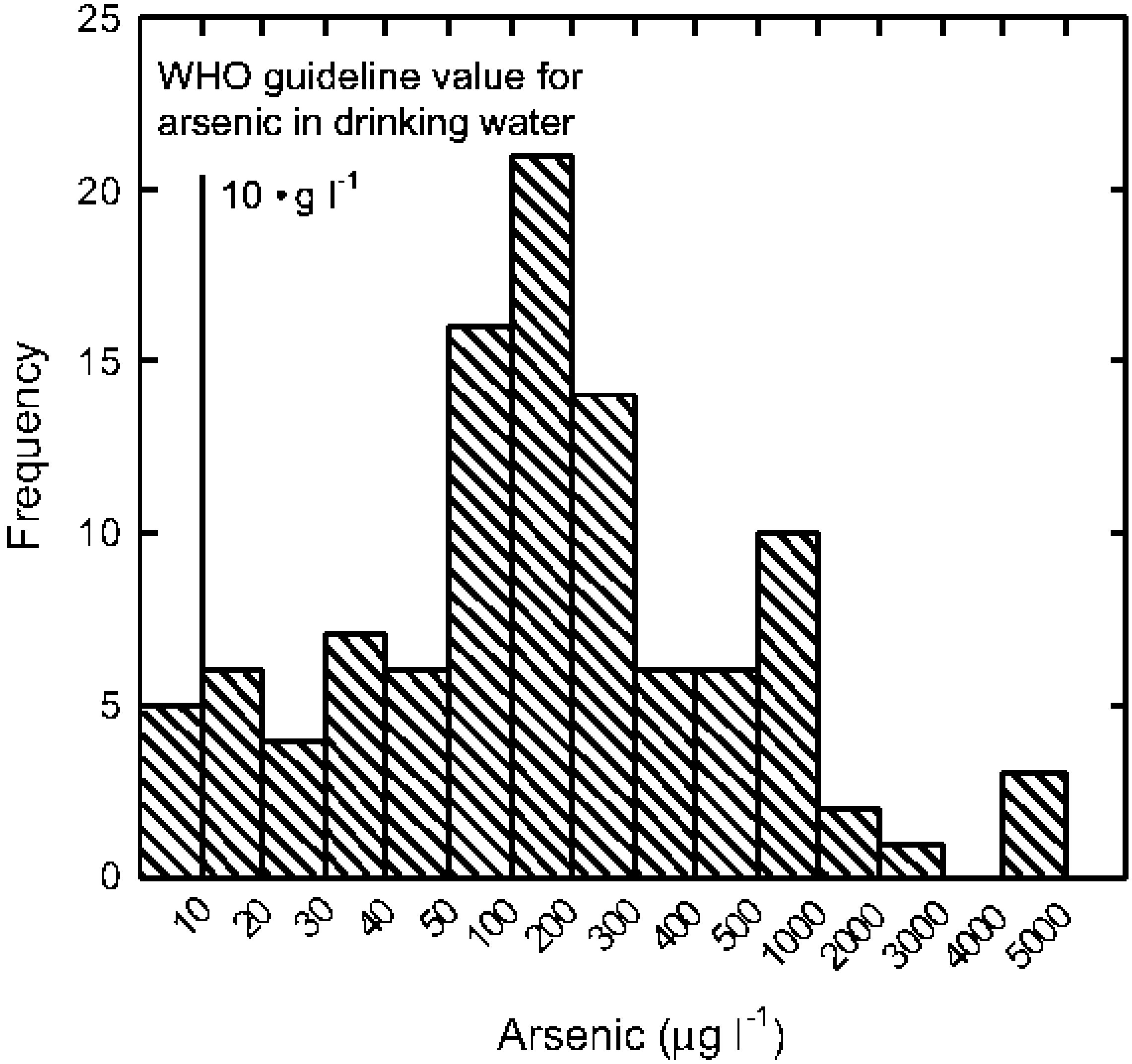
Box 1.5. Arsenic in La Pampa, Argentina

The population of La Pampa Province in central Argentina relies heavily upon groundwater for drinking and agricultural production. Water-quality problems from high arsenic concentrations are common. Concentrations in groundwater from wells and boreholes (having depths in the range 6-140 m) have been found by Smedley *et al.* (1998) ranging between <4 and 5300 µg l^{-1}. The concentrations are log-normally distributed, with a median of 145 µg l^{-1}. The spatial variability of arsenic concentrations is large and there is no distinct regional trend in the distribution of high-arsenic groundwaters. Of the groundwaters sampled, 95% were found to exceed the WHO guideline value for arsenic in drinking water. The high concentrations have been linked with development of skin lesions and internal cancers.

Arsenic is not the only element of health concern: high salinity, as well as fluoride (0.03-29 mg l^{-1}) and many other trace elements (uranium, boron, vanadium, molybdenum and nitrate) also occur in many of the groundwaters. Dental fluorosis from chronic exposure to fluoride is common but the health effects of other trace elements present in the drinking water are unknown.

Groundwaters from La Pampa are oxidising with typically high dissolved-oxygen concentrations and low concentrations of dissolved iron and manganese. Groundwater pHs are neutral to alkaline (up to 8.7). Groundwater arsenic is dominated by As(V), As(III) rarely exceeds 5% of the total present. Total arsenic correlates positively with pH, alkalinity (HCO_3) and with fluoride and vanadium and weaker positive correlations are also observed between arsenic and beryllium as well as boron. These occur in solution as anion (fluoride) and oxyanion (arsenate, vanadate, borate and molybdate) species. High salinity is caused by groundwater evaporation under arid conditions; high pH and alkalinity derive by extensive silicate and carbonate weathering reactions. These characteristics are particularly pronounced in low-lying depressions which act as local groundwater-discharge areas (ponding) during rainy periods and sites of evaporation during dry periods.

Concentrations of arsenic in the aquifer sediments are similar to average values for silty and sandy sediments. Measured total concentrations range between 3 mg kg^{-1} and 18 mg kg^{-1}, with finer-grained sediments being at the higher end of the range. Arsenic bound to amorphous oxides (iron, manganese, aluminum) ranges between 0.5 mg kg^{-1} and 9.6 mg kg^{-1} (mean 2 mg kg^{-1}) and represents around 10-50% of the total present. Of this fraction, roughly half (0.02 mg kg^{-1} to 4.7 mg kg^{-1}, mean 1.0 mg kg^{-1}) appears to be associated with the manganese oxides. This suggests that much of the arsenic present in the sediments is relatively labile. Much of the remaining arsenic appears to be bound to more crystalline iron-oxide minerals. Mobilisation of arsenic together with the other anionic and oxyanion species can be achieved readily by desorption from iron, manganese and possibly aluminium oxides in the sediments under the ambient conditions of high pH and alkalinity. The aquifer is also composed of young Quaternary loess sediments (silts and fine sands) with low regional hydraulic gradients and presumed slow groundwater-flow rates. Aquifer flushing rates, and rates of removal of problem elements, are therefore thought to be have been low.



Figures: map of La Pampa, location map of Argentina and histogram.

MAP PENDING

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

1.5.4 Mixed oxidising and reducing environments

South-western USA

Many areas have been identified in the USA with arsenic problems in groundwater. Most of the worst-affected and best-documented cases occur in the south-western states (Nevada, California, Arizona). However, within the last decade, aquifers in Maine, Michigan, Minnesota, South Dakota, Oklahoma and Wisconsin have been found with concentrations of arsenic exceeding 10 µg l^{-1} and smaller areas of high arsenic groundwaters have been found in many other States. Much water analysis and research has been carried out in the USA, particularly in view of the long-planned reduction in the US-EPA drinking-water limit and public concern over the possible long-term health effects. Occurrences in groundwater are therefore noted to be widespread, although of those reported, relatively few have significant numbers of sources with concentrations greater than 50 µg l^{-1}. A recent review of the analyses of some 17,000 water analyses from the USA suggested that around 40% exceeded 1 µg l^{-1} and about 5% exceeded 20 µg l^{-1} (percentage above 50 µg l^{-1} unknown; Welch *et al.*, 1999). The As is thought to be derived from various sources, including natural dissolution/desorption reactions, geothermal water and mining activity. The natural occurrences of arsenic in groundwater occur under both reducing and oxidising conditions in different areas. Concentration by evaporation is thought to be an important process in the more arid areas.

In Nevada, at least 1000 private wells have been found to contain As concentrations in excess of 50 µg l^{-1} (Fontaine, 1994). The city of Fallon, Nevada (population 8000) is served by a groundwater supply with an As concentration of 100 µg l^{-1} which for many years has been supplied without treatment other than chlorination. Welch and Lico (1998) reported high As concentrations, often exceeding 100 µg l^{-1} but with extremes up to 2600 µg l^{-1}, in shallow groundwaters from the southern Carson Desert. These are largely present under reducing conditions, having low dissolved-oxygen concentrations and high concentrations of dissolved organic C, Mn and Fe. The groundwaters also have associated high pH (>8) and high concentrations of P (locally >4 mg l^{-1}) and U (>100 µg l^{-1}; Welch and Lico, 1998). The high As and U concentrations were thought to be due to evaporative concentration of groundwater, combined with the influence of redox and desorption processes involving metal oxides.

In groundwaters from the Tulare Basin of the San Joaquin Valley, California, a large range of groundwater As concentrations from <1 µg l^{-1} to 2600 µg l^{-1} have been found (Fujii and Swain, 1995). Redox conditions in the aquifers appear to be highly variable and high As concentrations are found in both oxidising and reducing conditions. The proportion of As present as As(III) increases in the groundwaters with increasing well depth. The groundwaters from the Basin are often strongly affected by evaporative concentration with resulting high TDS values. Many also have high concentrations of Se (up to 1000 µg l^{-1}), U (up to 5400 µg l^{-1}), B (up to 73,000 µg l^{-1}) and Mo (up to 15,000 µg l^{-1}; Fujii and Swain, 1995).

Robertson (1989) also noted the occurrence of high As concentrations in groundwaters under oxidising conditions in alluvial aquifers in the Basin and Range Province in

Arizona. Dissolved oxygen values of the groundwaters were found to be in the range 3-7 mg l^{-1}. Arsenic in the groundwater was found from a limited number of samples to be present predominantly as As(V). The dissolved As correlated well with Mo, Se, V, F and pH, the latter being in the range 6.9-9.3. Of the 467 samples analysed, 7% had As concentrations greater than 50 µg l^{-1}. Arsenic concentrations in the sediments ranged between 2-88 mg kg^{-1}. Oxidising conditions (with dissolved oxygen present) were found to persist in the aquifers down to significant depths (600 m) despite significant groundwater age (up to 10,000 years old). The high arsenic (and other oxyanion) concentrations are a feature of the closed basins of the province.

1.5.5 Geothermal sources

Arsenic associated with geothermal waters has been reported in several areas, including hot springs from parts of the USA, Japan, New Zealand, Iceland, Kamchatka, France and Dominica (e.g. White *et al.*, 1963; Welch *et al.*, 1988; Criaud and Fouillac, 1989). Parts of Salta and Jujuy Provinces in north-west Argentina also have thermal springs with high As concentrations.

In the USA, occurrences of As linked to geothermal sources have been summarised by Welch *et al.* (1988). Reported occurrences include Honey Lake Basin, California (As up to 2600 µg l^{-1}), Coso Hot Springs, California (up to 7500 µg l^{-1}), Imperial Valley, California (up to 15,000 µg l^{-1}), Long Valley, California (up to 2500 µg l^{-1}) and Steamboat Springs, Nevada (up to 2700 µg l^{-1}). Geothermal waters in Yellowstone National Park also contain high concentrations of As (<1-7800 µg l^{-1} in geysers and hot springs; Thompson and Demonge, 1996; values up to 2830 µg l^{-1} reported by Ball *et al.*, 1998). As noted in Section 1.2.1, these have given rise to high concentrations (up to 370 µg l^{-1}) in waters of the Madison River (Nimick *et al.*, 1998). Geothermal waters at Lassen Park, California have arsenic concentrations ranging up to 27,000 µg l^{-1} (Thompson *et al.*, 1985). An arsenic concentration of 3800 µg l^{-1} has also been reported for Geyser Bight, Umnak Island, Alaska (White *et al.*, 1963). Geothermal inputs from Long Valley, California are believed to be responsible for relatively high concentrations (20 µg l^{-1}) of As in the Los Angeles Aqueduct which provides the water supply for the city of Los Angeles (Wilkie and Hering, 1998). Geothermal inputs also contribute significantly to the high dissolved As concentrations (up to 20 mg l^{-1}) in Mono Lake, California (Section 1.2.2; Maest *et al.*, 1992).

Welch *et al.* (1988) noted a general relationship between As and salinity in geothermal waters from the USA. Despite a lack of good positive correlation between As and Cl, geothermal waters with As greater than ca. 1000 µg l^{-1} generally had Cl concentrations of 800 mg l^{-1} or more. Wilkie and Hering (1998) noted the high alkalinity and pH values (average pH 8.3) as well as high Cl and B concentrations of As-rich geothermal waters in Long Valley.

Of 26 geothermal water samples analysed from five geothermal fields in Kyushu, Japan, As concentrations have been reported in the range 500-4600 µg l^{-1}. The waters are typically of Na-Cl type and the As is present in all but one sample overwhelmingly as As(III) (Yokoyama *et al.*, 1993).

Increased As concentrations have been documented in waters from the geothermal areas of New Zealand. Robinson *et al.* (1995) found an As concentration in groundwater from the Wairakei geothermal field of 3800 µg l^{-1} and found river and lake waters receiving inputs of geothermal water from the Wairakei, Broadlands, Orakei

Korako and Atiamuri geothermal fields to have concentrations up to 121 µg l^{-1}, although concentrations diminished significantly downstream away from the geothermal input areas.

High arsenic concentrations have also been found in geothermal waters from the El Tatio system in the Antofagasta region of Chile. The geothermal area lies in a basin (altitude 4250 m) between the volcanoes of the Andes and the Serrania de Tucle. The geothermal waters are highly saline (sodium-chloride solutions with sodium concentrations in the range 2000-5000 mg l^{-1}). Arsenic concentrations of the waters are reported to be in the range 45,000-50,000 µg l^{-1} (Ellis and Mahon, 1977).

White *et al*. (1963) also reported arsenic concentrations in the range 50-120 µg l^{-1} for thermal waters from Iceland and in the range 100-5900 µg l^{-1} for thermal waters from Kamchatka.

1.5.6 Sulphide mineralisation and mining-related arsenic problems

Thailand

Probably the worst recorded 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; Choprapawon and Rodcline, 1997). The affected area lies within the South-East Asian Tin Belt. Arsenic concentrations have been found at up to 5000 µg l^{-1} in shallow groundwaters from Quaternary alluvial sediment that has been extensively dredged during tin-mining operations. Deeper groundwaters from older limestone aquifers have been found to be less contaminated (Williams *et al.*, 1996) although a few high As concentrations occur, presumably also as a result of contamination from the mine workings. The mobilisation of As is believed to be caused by oxidation of arsenopyrite, exacerbated by the former tin-mining activities. The recent appearance in groundwater has occurred during post-mining groundwater rebound (Williams, 1997).

Ghana

Several workers have reported the effects of mining activity on the environment in Ghana. Ghana is an important gold-mining country and mining has been active since the late 19th century. Today, Ghana produces about one third of the world's gold. The most important mining area is the Ashanti Region of central Ghana. As with Ron Phibun District in Thailand, the gold is associated with sulphide mineralisation, particularly arsenopyrite. Arsenic mobilises in the local environment as a result of arsenopyrite oxidation, induced (or exacerbated) by the mining activity. Around the town of Obuasi, high As concentrations have been noted in soils close to the mines and treatment works (Amasa, 1975; Bowell, 1992; 1993). Some high concentrations have also been reported in river waters close to the mining activity (Smedley *et al.*, 1996).

Despite the presence of high As concentrations in the contaminated soils and in bedrocks close to the mines, Smedley *et al.* (1996) found that many of the groundwaters of the Obuasi area had low As concentrations, with a median concentration in tubewell waters of just 2 µg l^{-1}. Some high concentrations were observed (up to 64 µg l^{-1}) but these were not generally in the vicinity of the mines or related directly to mining activity. Rather, the higher concentrations were found to be present in relatively reducing groundwaters (Eh 220-250 mV). Oxidising groundwaters, especially from shallow hand-dug wells, had low As concentrations. This was taken to be due retardation of As by adsorption onto hydrous ferric oxides under the ambient low pH condition of the groundwaters (median pH 5.4 in dug wells; 5.8 in tubewells; Smedley *et al.*, 1996).

United States

Arsenic contamination from mining activities has been identified in numerous areas of the USA, many of which have been summarised by Welch *et al.* (1988; 1999). Groundwater from some areas has been reported to have very high As concentrations locally (up to 48,000 µg l^{-1}). Well-documented cases of As contamination include the Fairbanks gold-mining district of Alaska (Wilson and Hawkins, 1978; Welch *et al.*, 1988), the Coeur d'Alene Pb-Zn-Ag mining area of Idaho, (Mok and Wai, 1990), Leviathan Mine, California (Webster *et al*., 1994), Kelly Creek Valley, Nevada (Grimes *et al.*, 1995), Clark Fork river, Montana (Welch *et al.*, 2000) and Lake Oahe in South Dakota (Ficklin and Callender, 1989). Some mining areas of the USA have significant problems with acid mine drainage resulting from extensive oxidation of iron oxides. In these, pH values can be extremely low and iron oxides dissolve and release bound arsenic. Iron Mountain has some extremely acidic mine-drainage waters with negative pH values and As concentrations in the milligram-per-litre range (Nordstrom *et al.*, 2000; Section 1.2.1).

In Wisconsin, As and other trace-element problems in groundwater have arisen as a result of the oxidation of sulphide minerals (pyrite and marcasite) present as a discrete secondary cement horizon in the regional Ordovician sandstone aquifer. Concentrations of As up to 12,000 µg l^{-1} have been reported in the well waters (Schreiber *et al*., 2000). The oxidation appears to have been promoted by groundwater abstraction which has led to the lowering of the piezometric surface at a rate of around 0.6 m year^{-1} since the 1950s with partial dewatering of the aquifer. The high As concentrations are observed where the piezometric surface intersects, or lies close to, the sulphide cement horizon (Schreiber *et al.*, 2000).

Other areas

Many other areas have increased concentrations of As in soils, sediments and waters as a result of mining activity. Documented cases include the Lavrion region of Greece, associated with lead- and silver-mining activity (Komnitsas *et al.*, 1995), the Zimapán Valley of Mexico, parts of south-west England (Thornton and Farago, 1997), South Africa, Zimbabwe and Bowen Island, British Columbia (Boyle *et al.*, 1998). Although severe contamination of the environment has often been documented in these areas, the impact on groundwaters used for potable supply is usually minor.

1.6 Common features of groundwater arsenic problem areas

1.6.1 A hydrogeochemical perspective

Historically, as new sources of high arsenic groundwaters have been found, treatment plants have been built and the problem has receded from public attention. With the exception of a number of recent studies in the USA, there have been few detailed hydrogeochemical and hydrogeological studies of the arsenic-affected areas. Therefore much remains uncertain about the detailed mechanisms by which high-arsenic groundwaters have formed.

However, as described above, sufficient is already known that it is useful to attempt to bring together the common features and to speculate about the critical factors that could lead to high-As groundwaters. This will help to focus future scientific studies and should provide some guidance to those water undertakers who have to undertake a rapid assessment of their supplies for arsenic. It is helpful to consider the formation of high-arsenic groundwaters in terms of the three major factors involved, namely, the source of the arsenic, its mobilisation, and its subsequent transport (or lack of it).

1.6.2 The source of arsenic

In the cases where affected groundwaters are found close to obvious geological or industrial sources rich in arsenic (geothermal springs, drainage from mineralised and mining areas, specific contaminant sources), it is clear that the anomalously high arsenic concentrations in the source region are responsible. The extent of this contamination is usually highly localised because the geochemical conditions within most aquifers do not favour arsenic mobilisation on a regional scale. However, in areas strongly affected by geothermal activity, high-arsenic groundwaters may be more widespread as a result of the large source of arsenic and the fact that the source arsenic is already in solution.

Perhaps more puzzling is the way by which exceptionally high concentrations of arsenic - up to several mg l^{-1} - are found in groundwaters from areas with apparently near-average source rocks. In the extensive high groundwater arsenic areas, this appears to be the rule rather than the exception. Most of these cases arise in aquifers derived from relatively young aquifer materials, often consisting of alluvium or loess where the total As concentrations in the sediments are usually in the range 1-20 mg kg^{-1}. A recognition of this fact is a recent development and its late appreciation has delayed the discovery of many high-arsenic groundwater provinces.

A critical point is that the drinking-water limit for arsenic is very low in relation to the overall abundance of arsenic in the natural environment (Section 1.5.1 and Box 1.6). Fortunately, most of this arsenic is normally immobilized by various minerals, particularly iron oxides, and so is not available for abstraction. However, it only takes a small percentage of this ‘solid’ arsenic to dissolve or desorb to give rise to a serious groundwater problem. This can provide an explanation for both the oxidizing and reducing high-arsenic environments described in Section 1.5. An abundant source of iron oxides with its surface-bound and coprecipitated arsenic provides a ready source of arsenic that may be released given an appropriate change in geochemical conditions.

Box 1.6. Why is arsenic such a problem in some ‘natural’ groundwaters?

Importance of the very high solid/solution ratio in aquifers

One of the paradoxes of arsenic and groundwater is that extensive arsenic problems are found in areas in which the aquifer sediments themselves appear to have near-to-average arsenic concentrations, i.e. in the range 2-10 mg kg^{-1}. While the detailed mechanisms for the evolution of high-arsenic groundwaters are not yet well understood, sufficient is already known to provide some insight into the reasons for this. Firstly, because of the high solid/solution ratios found in soils and aquifers (3-6 kg l^{-1}) and the low absolute value of the drinking water limit for arsenic, even small changes in the distribution of arsenic between solid and solution are important. Secondly, in many soils and aquifers, much of the arsenic appears to be associated with secondary minerals such as iron, aluminium and manganese oxides, probably in large part as adsorbed arsenic species. This form is particularly sensitive to changes in the environment and it only takes a small change in the amount of arsenic adsorbed to change the concentration of arsenic in the groundwater significantly. For example, if it assumed that say 1 mg kg^{-1} of the sediment arsenic is present in a labile form, in the event of complete dissolution or desorption, this would produce up to 3000-6000 µg As l^{-1} in the groundwater, many times the WHO guideline value.

The triggers for change

There appear to be two main drivers leading to a change in the amount of arsenic adsorbed. Firstly, it is well known that an increase in pH leads to the release of many anions adsorbed onto iron, aluminium and manganese oxides, including that of arsenate but less so arsenite (see Box 1.2). For arsenate, a change from pH 7 to pH 8.5 or above can be critical. Such a change frequently occurs in arid and semi-arid areas as a result of evaporation in inland (closed) basins. These pH changes normally occur under oxidising conditions.

Secondly, a change from oxidising conditions to reducing conditions may promote the desorption of arsenic. This is likely to reflect changes in the oxidation state of arsenic in groundwater: changing from strongly sorbed arsenate under oxidising conditions to less strongly sorbed arsenite under reducing conditions. Changes in the oxide minerals themselves also appear to be important, including possible changes to their structure and surface properties as well as partial dissolution in the case of iron and manganese oxides. Again these changes occur under conditions that are not uncommon in aquifers, especially in young alluvial aquifers where a ready supply of organic carbon from the constituent sediments readily consumes any free oxygen.

However, these changes alone are not enough. An additional and critical factor is the extent to which the aquifer has been flushed. In closed basins, there is little flushing and a wide variety of chemicals accumulate, often including fluoride, phosphate, uranium, vanadium and selenium as well as arsenic. In aquifers with more active groundwater flow, any arsenic released by the above processes will eventually be flushed away and there is unlikely to be substantial further release since the sediments will have re-equilibrated with the new environment. Therefore present-day arsenic problem areas are most likely to be found in areas where the amount of flushing has been low either due to their young age or to very slow groundwater movement. The very low hydraulic gradients found in large delta regions, such as the Bengal Basin, are ideal for minimising the extent of flushing and hence preserving high arsenic concentrations in groundwater.

1.6.3 Mobilisation - the necessary geochemical trigger

There appear to be two key factors involved in the formation of high-As groundwaters on a regional scale: firstly, there must be some form of geochemical trigger which releases arsenic from the aquifer solid phase into the groundwater. Secondly, the released arsenic must remain in the groundwater and not be flushed away.

There are a number of possible geochemical triggers but the most important appears to be the desorption/dissolution of arsenic from oxide minerals, particularly iron oxides. An important feature of this process is that the initial adjustment is probably quite rapid since it involves a shift in the adsorption isotherm from one point on the isotherm to another point and adsorption reactions, being surface reactions, are usually rapid. The rate limiting factors are probably those controlling the major changes in pH, Eh and associated water quality parameters of the aquifer. These are in part related to physical factors such as the rate of diffusion of gases through the sediment and the rate of sedimentation, in part due to the extent of microbiological activity and in part related to the rates of chemical reactions. However, many of these factors can be seen as being rapid on a geological time scale (tens of thousands of years and longer). Dissolution reactions are slower but even oxide dissolution is rapid on a geological time scale and can be observed in a matter of weeks in paddy soils.

A qualification is that if diagenetic changes to the mineral structure are important (see below) or if burial to a certain depth is important, then there could be a slow release of arsenic over a much longer time scale. Details of the rate of release of arsenic and how this varies with time are not yet clear. It is likely that the rate will diminish with time with the greatest changes occurring early on. Natural groundwater flushing means that very slow releases of arsenic are likely to be of little consequence since the arsenic released will not tend to accumulate to a significant extent.

A corollary of this hypothesis is that once the diagenetic readjustment has taken place and the sediments have equilibrated with their new environment, there should be little further release of arsenic - this contrasts with some mineral-weathering reactions which occur in ‘open’ systems and can continue for millions of years until all of the mineral has dissolved. Seen in this context, the desorption/dissolution of arsenic in young aquifers is essentially a step change responding to a new set of conditions. As discussed above (Section 1.4), the type of reactions that may occur can be seen today most clearly where they occur at a small spatial scale and over a short time scale, for example, across a redox boundary in a lake sediment. The geochemical triggers involved could arise for a number of possible reasons. Below we speculate what these might be. Some model calculations of their possible impact are given in BGS and DPHE (2001).

Desorption at high pH under oxidising conditions

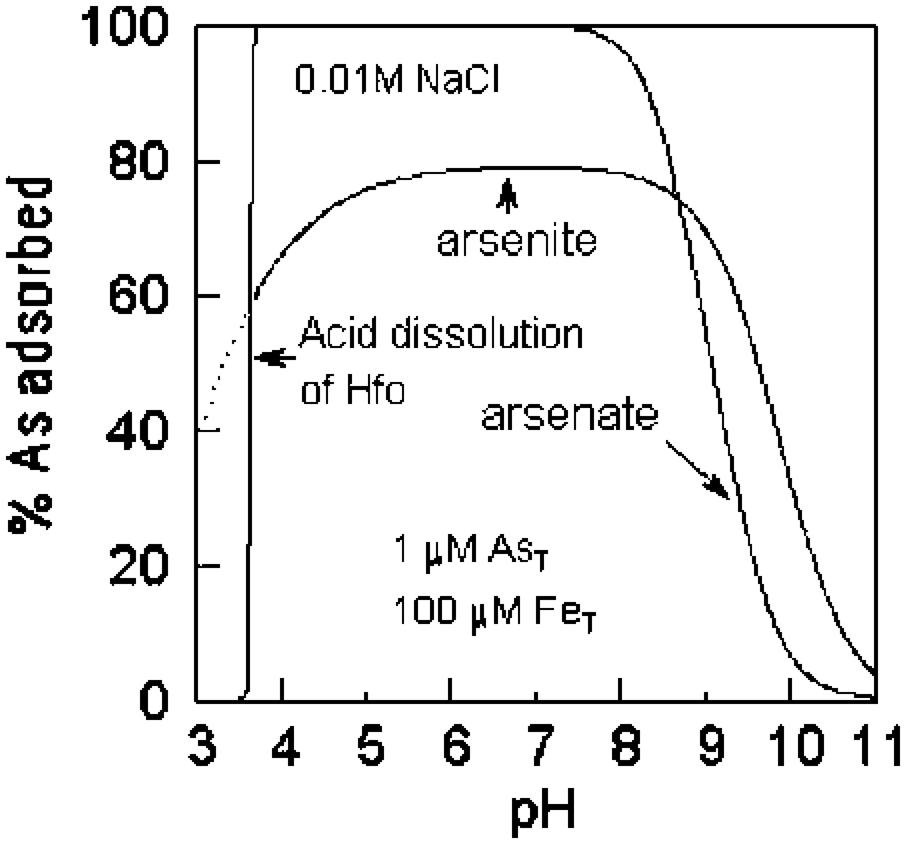
Under aerobic and acidic to near-neutral conditions, arsenic is very strongly adsorbed by oxide minerals as the arsenate ion (Box 1.2). The highly non-linear nature of the adsorption isotherm for arsenate ensures that the amount of arsenic adsorbed is relatively large, even at low solution concentrations. In a simple system with no competing anions, hydrous ferric oxide (Hfo) can have an As loading of nearly 15,000 mg kg^{-1} when in equilibrium with 1 µg As(V) l^{-1} at pH 7. This adsorption reaction protects many natural environments from widespread As toxicity problems. As the pH increases, especially above pH 8.5, arsenic desorbs from the oxide surfaces, thereby increasing the concentration of arsenic in solution. The impact of this is magnified by the high solid/solution ratios typical of aquifers (3-10 kg l^{-1}).

There are several reasons why the pH might increase but the most important in the present context is the uptake of protons by mineral weathering reactions combined with the effect of evaporation in arid and semi-arid regions. This pH increase is commonly associated with the development of salinity and the salinisation of soils. Inputs of high-pH geothermal waters may be important in maintaining high As concentrations in some alkaline lakes. Desorption at high pH is the most likely mechanism for the development of groundwater-arsenic problems under the oxidising conditions described in Section 1.5.3 and would account for the observed positive correlation of arsenic concentrations with increasing pH.

Box 1.2. Adsorption of arsenic by iron oxides

The adsorption of arsenic by iron oxides is a very important natural process that is to a large extent responsible for preventing widespread arsenic toxicity problems in nature. Arsenic is very strongly adsorbed by iron oxides, especially under oxidising and slightly acidic conditions. This is often the basis for the removal of arsenic during water treatment. The amount of adsorption is described by the *adsorption isotherm* which relates the concentration of arsenic adsorbed to its concentration in solution. Once this is known for a wide range of conditions then many properties can be calculated, including the percentage of arsenic adsorbed as a function of pH (see Figure), the likely efficiency of arsenic removal plants and the extent of retardation of arsenic during movement through soils and aquifers.

Adsorption isotherms are either *linear* or *non-linear*. A linear isotherm means that the amount of a species adsorbed is directly proportional to its concentration in solution. The isotherms for the two forms of arsenic, arsenate and arsenite, are very different including their pH dependence (see Figure). The arsenate isotherm is highly non-linear, the arsenite isotherm less so. An important consequence of the highly non-linear adsorption for arsenate is that even at the µg l^{-1} level of arsenic in solution, the arsenic loading on the oxide can be appreciable corresponding to thousands of mg As/kg in the case of hydrous ferric oxide (Hfo). The loading on more crystalline iron oxides such as goethite and hematite is somewhat lower because of their lower surface area, but is still appreciable.



Figure

Figure showing the pH dependence of arsenate and arsenite adsorption on hydrous ferric oxide (Hfo) calculated according to the Dzombak and Morel (1990) diffuse double-layer model. Arsenate is very strongly adsorbed below pH 8 while arsenite is more strongly bound than arsenate at pH values greater than about 9. Therefore desorption of arsenic can occur either from an increase in pH from say 8.0 to 9.0 or from a change in oxidation state from arsenate to arsenite. Unfortunately, applying these observations to the 'real world' is not so straightforward: the presence of other specifically adsorbed ions such as phosphate changes these relationships. Also natural iron oxides may differ significantly from Hfo.

While there have been many studies of arsenic adsorption important for understanding the groundwater arsenic problem remain unclear, including the best mathematical formulation of the isotherm and how adsorption changes with pH and redox status. The most popular basis at present for calculating the amount of arsenic adsorbed by iron oxides is the diffuse double-layer model of Dzombak and Morel (1990) and its associated database but this model cannot account for the competitive interactions found in nature very well and the database is based on a limited amount of experimental data. The CD-MUSIC model of Hiemstra and van Riemsdijk (1999) is more promising but is more complex and at present is not coded into the popular geochemical modelling packages.

As such a pH increase induces the desorption of a wide variety of oxyanions, other oxyanions such as phosphate, vanadate, uranyl and molybdate will also tend to accumulate. There is evidence that this is indeed the case (Box 1.5). These specifically-adsorbed anions all interact with the adsorption sites on the oxides in a competitive way and so influence, in a complex way, the extent of binding of each other. This is not well understood in a quantitative sense. Phosphate in particular may play an important role in arsenic binding since it is invariably more abundant than arsenic, often by a factor of 50 or more (in molar terms), and is also strongly bound to oxide surfaces. Phosphate is as strongly bound as arsenate. The role of bicarbonate, often the major anion in arsenic-affected groundwaters, in promoting the desorption of arsenate is unclear at present, as is the role of dissolved organic carbon (fulvic and humic acids). Some cations, because of their positive charge, may promote the adsorption of negatively charged arsenate (Wilkie and Hering, 1996). Calcium is likely to be the most important cation in this respect because of its abundance in most natural waters and its +2 charge. Divalent Fe may be important in reduced waters. Silica also exerts a control on the sorption of As (Swedlund and Webster, 1998).

The aridity described above enables the high pH values to be maintained and minimises the flushing of the arsenic. It also allows the build-up of high chloride and fluoride concentrations. Other high-pH environments (up to pH 8.3), particularly open-system calcareous environments, are likely to be too well flushed to allow any released arsenic to have accumulated. Arsenate may also be sorbed by carbonate minerals. The pH dependence of adsorption is critical but has not yet been measured in detail for any aquifer materials especially in the presence of typical groundwater compositions. The pH dependence is likely to depend to some extent on the heterogeneity of the aquifer material. Other specifically adsorbed anions, particularly phosphate and perhaps bicarbonate, may also significantly affect the pH dependence of As(V) and As(III) binding. High pH values cannot explain the development of high arsenic concentrations in reducing environments such as Bangladesh since groundwaters in reducing environments normally have a near-neutral pH.

Desorption and dissolution due to a change to reducing conditions

The onset of strongly reducing conditions - sufficient to enable iron(III) and probably sulphate reduction to take place - appears to be a second trigger for the release of arsenic. The most common cause of this is the rapid accumulation and burial of sediments. This occurs in river valleys, especially in broad valleys with wide meandering river channels carrying heavy sediment loads. Large, rapidly advancing deltas are an extreme case. Aeolian deposition of extensive deposits of loess can provide the necessary conditions. The organic carbon content of the buried sediment will largely determine the rate at which reducing conditions are created. Freshly-produced soil organic matter readily decomposes and it does not take much of this to use up all of the dissolved oxygen, nitrate and sulphate. Reducing conditions can only be maintained if the diffusion and convection of dissolved oxygen and other oxidants from the surface is less rapid than their consumption. This is helped if there is a confining layer of fine-grained material close to the surface. This often occurs in large deltas where fine-grained overbank deposits overly coarser-grained alluvial deposits.

Change in arsenic speciation

While the detailed reactions (in surface chemical terms) which occur when reduction takes place are not well understood, the change from normally strongly adsorbed As(V) to normally less strongly adsorbed As(III) may be one of the first reactions to take place, although not all the evidence supports this (e.g. De Vitre *et al.*, 1991). A change in the redox state of the adsorbed ions could have wider-ranging repercussions since it will also affect the extent to which other anions can compete for adsorption sites. Phosphate-arsenite competition, for example, is likely to be less important than phosphate-arsenate competition. There is also the potential for arsenite-arsenate competition. Model calculations suggest that adsorbed phosphate can reverse the relative affinity of As(III) and As(V) at near neutral pH values (BGS and DPHE, 2001). These complexities are poorly understood at present but are important if reliable quantitative predictions of arsenic concentrations under reducing conditions are to be made.

Reduction in surface area of oxide minerals

Freshly-precipitated metal oxides, particularly iron oxides, are often highly disordered and gradually transform to more ordered forms. Such disordered and fine-grained iron oxides, which may include Hfo, lepidocrocite, schwertmannite and magnetite, are commonly formed in the early stages of weathering. Furthermore, cycling between oxidized and reduced states of Fe in shallow sediments, with the aid of sulphide-sulphate cycling, may serve to keep the iron oxides in a 'reactive' state (Canfield, 1989). Once the oxides are more deeply buried and subject to groundwater flow, especially with oxidising water, they are likely to transform to the more stable forms of goethite and hematite.

There is ample evidence that this ageing reaction can take place rapidly in the laboratory but the rate of the reaction in nature is likely to be somewhat inhibited by the presence of other ions, particularly strongly adsorbed ions such as aluminium, phosphate, sulphate, arsenate and silicate (Cornell and Schwertmann, 1996).

All other things being equal, if the surface area of an oxide mineral is reduced, then adsorbed ions will be desorbed into solution. Some will be readsorbed, depending on the shape of the adsorption isotherm, the solid/solution ratio and the extent of inclusion within the evolving solid phase but the concentration in solution will tend to increase. Such reductions in surface area are well-established for Hfo which has a specific surface area of 100-600 m^2 g^{-1} compared with a much smaller specific surface area for its aged products, typically 150 m^2 g^{-1} or less for goethite and much less still for hematite (Cornell and Schwertmann, 1996).

Reduction in binding strength between arsenic and the mineral surfaces

It is perhaps not unreasonable to speculate that the diagenetic reactions that take place once a sediment is buried not only lead to a reduction in specific surface area but could also lead to a reduction in the binding strength of the adsorbed arsenic. This could arise from the mineral transformations described in section 1.4.3. However, it is also possible that the adsorption affinity (i.e. the intrinsic binding constant) could actually *increase* following crystallisation. This would tend to offset changes taking place due to a reduction in surface area. On balance, laboratory and field evidence suggests that at micromolar As concentrations freshly-formed Hfo does bind more arsenic than goethite on a mole of Fe basis (De Vitre *et al.*, 1991).

Under strongly reducing conditions, it appears that additional processes could operate which may lead to a reduction in the overall adsorption of arsenic. Specifically for iron oxides, some of the surface iron centers could be reduced from Fe^{3+} to Fe^{2+} to produce a mixed valence oxide perhaps akin to that of a magnetite or a green rust-type compound (section 1.3.4). This would tend to reduce the net positive charge of the surface (or increase its net negative charge) and would thereby reduce the electrostatic interaction between the surface and anions. This could result in the desorption of arsenic and a corresponding increase in the concentration of arsenic in solution.

The role of mineral dissolution

Mineral dissolution reactions would release both adsorbed As and irreversibly bound As located within the mineral structure. The most likely candidate for such a reaction is the reductive dissolution of iron oxides and this has been extensively discussed in the context of estuarine, lake and river sediments. Such a reaction accounts for the high ferrous iron content of anaerobic waters. While this undoubtedly accounts for some of the release of arsenic in reducing groundwaters, it does not appear to be sufficient to account for all of the arsenic released. In a few reducing groundwaters in Bangladesh, for example, the dissolved arsenic concentration is greater than that of iron (on a weight basis). If congruent dissolution alone were responsible for the arsenic release, this would require either the extensive precipitation of secondary iron phases (most likely carbonates or sulphides) or the chromatographic separation or iron and arsenic as a result groundwater movement. Congruent dissolution of a typical iron oxide without any precipitation of secondary iron phases would only release a few µg As l^{-1}. Reductive dissolution cannot of course explain the high-arsenic oxidising groundwaters.

The sequence of events that occur during the reductive dissolution of iron(III) oxides containing adsorbed and coprecipitated arsenic is complex and has not been studied in detail. Incongruent dissolution of arsenic from iron oxides probably occurs at the same time as desorption reactions. It is even more complex than for phosphate because of the added complication of the variable oxidation state of arsenic. The reduction of both the oxide and the arsenic are microbially catalyzed and the relative rates depend on the viability and nutrient supply of the specific microbial strains involved (Ehrlich, 1996).

Manganese oxides also undergo reductive desorption and dissolution and so could contribute to the arsenic load of groundwaters in the same way as iron. Certainly many of the reducing groundwaters of Bangladesh contain high concentrations of manganese (DPHE/BGS/MML, 1999). The Mn oxide surfaces also readily catalyse the oxidation of As(III) (Oscarson *et al.*, 1981). It is not known whether or not the dissolution of carbonate minerals (calcite, dolomite, siderite), which are common minerals in aquifers, contribute significantly to the release of arsenic to groundwater, or its uptake from groundwater.

Sulphide oxidation, particularly pyrite oxidation, can also be an important source of arsenic especially where these minerals are freshly exposed as a result of a lowering of the water table. This can occur locally in and around mines and on a more regional scale in aquifers. In extreme cases, this can lead to highly acidic groundwaters rich in sulphate, iron and trace metals. As the dissolved iron is neutralized, it tends to precipitate as a hydrous ferric oxide (sometimes schwertmannite) with a resultant adsorption and coprecipitation of dissolved As(V). In this sense, pyrite oxidation is not a very efficient mechanism for releasing As to surface and groundwaters.

1.6.4 Transport - the hydrogeological dimension

The geochemical triggers described above may release arsenic into groundwater but are not alone sufficient to account for the distribution of high-arsenic groundwaters observed. The additional factor is that the released arsenic must not have been flushed away or diluted by normal groundwater flow. This also places a time dimension on the problem since the rate of release must be set against the accumulated flushing of the aquifer that has taken place during the period of release. The rocks of most aquifers used for drinking water are several hundred million years old and yet contain groundwater that may be only a few thousand years old or younger. This implies that many pore volumes of fresh water have passed through the aquifer over its history.

The oldest fresh groundwaters are found in the Great Artesian Basin of Australia and are up to one million years old. The water moves slowly through this aquifer - at a rate of about 0.1 m yr^{-1} - and over its 2.5 billion year history, there have been many pore volumes of fresh water flushed through the system. Any desorbed arsenic will have long since disappeared. The same is true of most young aquifers with actively flowing groundwater. On the other hand, many deltaic and alluvial aquifers are characterised by relatively young sediments and often relatively old groundwater. The relative ages of the aquifer rocks and of the groundwater are important. It is only when the geochemical trigger to mobilise arsenic *and* the hydrogeological regime to preserve it are both operating that we see high groundwater arsenic concentrations on a regional scale.

It is also necessary to consider historical water flows which may have been very different from the present-day flows. One of the more significant 'recent' events is the global change in sea levels that has occurred over the last 130,000 years (Pirazzoli, 1996). Sea levels broadly respond to the amount of ice stored in glaciers and so reflect global climate patterns. Between about 120,000 years ago and 18,000 years ago, the sea-level steadily declined (with a few ups and downs) as glaciers expanded. The last glaciation was at a maximum some 21,000-13,500 years ago with sea levels being up to 130 m below present mean sea-level. This was a worldwide phenomenon and would have affected all then existing coastal aquifers. Continental and closed basin aquifers on the other hand would have been unaffected. The hydraulic gradient in coastal aquifers would therefore have been much greater than at present which would have resulted in correspondingly large groundwater flows and extensive flushing. The arsenic in these older aquifers would therefore tend to have been flushed away. The deep unsaturated zone would also have led to more extensive oxidation of the shallower horizons with possible increased sorption of As to Fe(III) oxides. Relics of these high flows are seen in the extensive fissure formation in some of the world's older carbonate aquifers.

Between some 13,500-7000 years ago, warming occurred and sea levels rapidly rose to their existing levels. Therefore aquifers that are younger than some 7,000 years old will not have been subjected to this increased flushing that occurred during the most recent glaciation.

The time taken to flush an aquifer depends on many factors (Appelo and Postma, 1994). A critical factor is the number of pore volumes of 'fresh' water that have passed through the aquifer since the initial release of arsenic has taken place. The other important factor is the partitioning of arsenic between the aquifer solid phase and the groundwater. This determines how easy it is to flush out the arsenic and is related to the slope of the adsorption isotherm (Appelo and Postma, 1994). In simple cases, this can be expressed by a partition coefficient or Kd. The greater the Kd, the greater the capacity of the sediment to withstand changes and the slower the arsenic will tend to be flushed from the aquifer. The Kd depends on many factors both relating to the aquifer material itself and to the chemistry of the groundwater, i.e. its pH, arsenic concentration and speciation, phosphate concentrations and so on. In practice, the adsorption isotherms are usually non-linear which means that the Kd varies with concentration which leads to more complex transport but the same general principles apply. The Kd will be less than under 'normal' oxidised conditions since a reduced Kd is precisely the reason for the arsenic problem in the first place. There have so far been no reliable studies of Kd values applicable to arsenic-affected aquifers. The greater the quantity of arsenic involved, the more strongly it is adsorbed and the slower the rate of groundwater movement, the longer that high-arsenic groundwaters will persist.

As described above, the number of pore volumes that have passed through the aquifer is itself a function of the groundwater flow velocity integrated over the time since sediment burial. In Bangladesh, the age of sediment - depth relationship is particularly important since this has a direct bearing on the extent of flushing. Many of the shallow sediments in southern Bangladesh are less than 13,000 years old, even less than 5,000 years old, and so will not have experienced the extensive flushing of the last glacial period. These are where the majority of the tubewells are situated. Certainly at present flushing is slow because of the extremely small hydraulic gradients especially in southern Bangladesh. However, deeper and older sediments, which may exceed 13,000 years old, will have been subjected to more extensive flushing. This may account for the 'arsenic-free' groundwaters found in the deep aquifers of Bangladesh. Geochemical factors may also play a role since the evidence is that while the deep groundwaters are currently reducing, they are less strongly reducing than the shallow aquifers. Certainly, the aquifers in the Pleistocene uplifted alluvial sediments of the Barind and Madhupur Tracts will have been well flushed since they are at least 25,000-125,000 years old. These sediments invariably yield low-As groundwaters, typically containing less than 0.5 µg l^{-1} arsenic. A complication is that the Bengal Basin is locally rapidly subsiding and filling in with sediments. This adds to the high degree of local and regional variation.

Not only are the regional flow patterns important. At a local scale, small variations in relief or in drainage patterns may dictate local flow patterns and hence the distribution of arsenic-rich groundwater. For example, there is evidence from Argentina that the highest groundwater arsenic concentrations are found in the slightly lower areas where seasonal discharge occurs. The same is true in Inner Mongolia and may also be true in Bangladesh. In any case, it is a characteristic of groundwater arsenic problem areas that there is a high degree of local-scale variation. This reflects the poor mixing and low flushing characteristic of the affected aquifers.

It is clear that flat low-lying areas, particularly large plains and delta regions, are particularly prone to potentially high arsenic groundwaters since they combine many of the risk factors identified above. The process of delta development also favours the separation of minerals based on particle size and produces the characteristic upwardly fining sequences of sand - silt - clay which leads to confining or semi-confining layers which aid the development of strongly reducing conditions. The youngest, distal part of the deltas will tend to contain the greatest concentration of fine-grained material and this provides an abundant source of arsenic in the form of colloidal-sized oxide materials. Flocculation of colloidal material, including iron oxides, at the freshwater-sea water interface will tend to lead to relatively large concentrations of these colloids in the lower parts of a delta. The larger the delta, and the more rapid the infilling, the lower the hydraulic gradient and the less flushing that is likely to have occurred.

However, some deltas - even large deltas - may be so old and well-flushed that even the existing low hydraulic gradients would have been sufficient to flush away any desorbed or dissolved arsenic.

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

1.7 Outstanding questions and further needs

1.7.1 Field analytical methods for arsenic determination

In view of the characteristic high degree of spatial variation of groundwater arsenic concentrations in arsenic-affected areas, the analysis of each water supply is the only certain way of determining its potability.

In countries such as Bangladesh which have a very large number of wells to be tested and in which the existing laboratory-testing infrastructure is not able to cope with the demand, a rapid field testing programme is necessary. Carrying out such a programme is a major organisational challenge and reliable field tests are critical to the success of such a programme. The less need for retesting in a laboratory the better since this involves difficult sample tracking and could result in confusion and could even discredit the field testing programme. If field testing is to be carried out, then ideally it should be capable of giving a reliable result first time. Of course, all analytical results have an uncertainty or error associated with them and this should be monitored through some form of quality control programme. It also means that there is inevitably some uncertainty in the classification of wells with concentrations close to the standard value.

Most of the current field test kits are based on the Gutzeit method which involves the reduction of As(III) and As(V) by zinc to give arsine gas which is then used to produce a stain on mercuric bromide paper. Hydrogen sulphide gas is removed with zinc acetate-treated glass wool. There have been many studies of the sensitivity and reliability of these kits, particularly in India and Bangladesh. The early kits were usually good at detecting high-As waters (say greater than 100 µg l^{-1}) but often were found to have rather poor reliability at lower concentrations. Ideally a field test kit for arsenic should be:

- sensitive and reliable - it should be quantitative at the 5-200 µg l^{-1} level and have a precision that is about the same as, or slightly better than, the short-term variability observed in the field, say ± 20 percent or ± 5 µg l^{-1} for low concentrations;

- robust - it should be able to maintain a good performance for long periods under actual field conditions assuming reasonable care is taken;

- simple to use - it should be designed to be as simple as possible to use by field workers with the minimum of technical training and supervision;

- affordable - it must not be so expensive as to preclude its use either in terms of capital or recurrent costs;

- safe to use - it must not pose a hazard to the user or environment even after heavy use.

A number of improvements have been made to the early kits and several promising kits are now either in production or in development. Perhaps the most promising is a field-test kit being developed by Professor Walter Kosmus of Karl-Franzens University of Graz, Austria. This is a logical development of the standard Gutzeit kit in that it: (i) replaces zinc with sodium borohydride and thus removes the problem of obtaining low-As zinc; (ii) uses solid tablets instead of liquid chemicals and thus avoids the need for carrying strong acids or sodium borohydride solution in the field; (iii) has a simple, robust and easy-to-make straight-through arsine generator; (iv) forces all of the arsine gas through a smaller portion of mercury bromide-treated filter paper to ensure maximum sensitivity and precision; (v) uses a separate, small calculator-style device to measure the stain developed photometrically; (vi) determines total arsenic, and (vii) is relatively stable and easily calibrated.

The challenge with all such devices is to reduce their costs sufficiently to enable them to be widely used where needed.

1.7.2 Surveys of groundwater quality

The first priority must be to carry out reconnaissance regional surveys of all possible high arsenic areas where there is currently little or suitable data. This should be done on as close to a stratified-random basis as possible with the stratification based on a knowledge of local geology and the desire to get a reasonably uniform coverage. Suspect areas should then be sampled in more detail.

Aside from its primary role as part of a public health programme, high density village-scale testing of wells for arsenic will also lead to a better understanding of the causes of the arsenic problem and ultimately will help to guide any future development of groundwater resources. Therefore an important task is the careful recording of well details and combining this with the test results into some form of database. Ideally the geographic coordinates of a well should be recorded to within 10 m or so that reliable large-scale maps can be made. Ordinary GPS devices can now usually give coordinates to better than about ± 10 m and can certainly aid this mapping.

In arsenic problem areas, detailed studies should be undertaken to provide a sounder basis for understanding the causes of the problem and its variation in space and time. These could include a more comprehensive range of water quality parameters including all of the major, and a range of minor, constituents. Age-related parameters such as ^{3}H and ^{14}C should also be measured. Studies should be made of the local geology and hydrogeology including water level monitoring, pumping tests, and studies of the mineralogy, sedimentology, chemical composition and adsorption behaviour of the aquifer materials. Either purpose-built piezometers or suitable production wells should be monitored for changes in arsenic and other water quality parameters with time. Such studies are expensive and are not warranted unless the scale of the problem is large. As experience is gained and the processes better understood, some of these studies may become unnecessary.

Perhaps one of the lessons from Bangladesh is that surprises can still happen and that in any new large-scale groundwater development, a broad-ranging 'water quality' survey should be carried out before full-scale development takes place. 'Water quality' here is taken to include a wide range of parameters not just those on the existing lists of statutory 'health-related' parameters. For the inorganic elements, recent advances in analytical methodology mean that this should now be possible in most well-equipped water quality laboratories. For the organics, particularly the anthropogenic persistent organic compounds, this is less straightforward but still possible albeit very expensive. The scope of such broad and open-ended surveys should be commensurate with the anticipated scale of the groundwater development.

1.7.3 Will the problem groundwaters get better or worse with time?

The answer to this question is probably 'better' but over a long time and on a timescale that is not relevant to the present exploitation. High arsenic groundwaters tend to be found in aquifers of Holocene age, i.e. aquifers in which the sediments have been deposited in the last ten thousand years. With time, the high concentrations of arsenic will be flushed away in the normal groundwater flow. The actual timescale depends on many factors that are poorly understood. The arsenic concentration in an individual well could increase before it decreases as arsenic is transported through the aquifer.

The influence of time is also connected to the relationship between the depth of well and the arsenic concentration since deeper sediments tend to be older. In Bangladesh, the deeper aquifer (below about 150-200 m depth) where studied appears to be essentially arsenic-free at present. Most of the problems are confined to the shallow aquifer, particularly over the depth interval 12-70 m beneath ground level. The past is not necessarily a good guide to the future - the extensive flushing of aquifers that took place during the last glaciation and the preceding period of globally low sea levels will have led to unusually high hydraulic gradients and relatively rapid flushing. At present sea levels are rising as a result of global warming further reducing hydraulic gradients. Of more importance in the Bengal Basin context is the extent to which present and future exploitation of both shallow and deep aquifers for domestic supply and for irrigation might impact on the present good quality of groundwater from the deep aquifer. There is the possibility that heavy pumping of the deep aquifer may draw contaminated shallow groundwater down to the deep aquifer especially in the absence of a confining layer of clay at intermediate depths. There is also the possibility that poor well construction may lead to the rapid movement of contaminated water to depth.

Significant changes in arsenic transport in groundwater may occur locally due to the influence of mining, groundwater pumping and irrigation. Mining in hardrock areas may in effect create a new aquifer with extensive fracturing, adits and other drainage channels. The water table is also often lowered by drainage or pumping and this can induce air entry and enhanced oxidation.

1.7.4 Transport under natural flow conditions

It is necessary to know how arsenic moves in an aquifer to predict how concentrations might change in the future. Arsenic, like any other solute, moves in response to the flow of groundwater and its interaction with the aquifer solid phase. Adsorption or precipitation reactions will tend to retard movement relative to that of the groundwater whereas the co-transport of chemicals, including phosphate from fertilisers, that enhance the release of arsenic could lead to its more rapid movement through the aquifer, albeit limited by the rate of flow of the groundwater. Establishing the basic groundwater flow patterns within an aquifer is a prerequisite to understanding the movement of arsenic. The concentration profile of a non-reactive solute such as chloride can help to establish this. Age-related tracers such as ^3H, ^{14}C and CFCs can also help as well as basic hydrogeological investigations of the aquifer.

Aside from the basic hydrogeology of the aquifer, it is also important to understand quantitatively the solid-solution interactions which take place. This refers principally to the nature of the adsorption-desorption isotherms and the mechanisms of reductive dissolution of iron and manganese oxides. It is likely that what is conveniently called ‘reductive dissolution’ is in fact a mixture of desorption, dissolution and structural rearrangement of the oxides themselves. A two-stranded approach is required: firstly, a detailed characterisation of sediments and associated pore waters is needed from a variety of aquifers, both affected and not affected, akin to that undertaken by limnologists and oceanographers when studying their sedimentary environments. In reduced aquifers, special care should be taken to avoid oxidation of the sediment. Secondly, these field studies need to be backed up by new theoretical advances in modelling the relevant surface chemical reactions of the oxides and sediments particularly in reducing environments. This will involve both modelling and laboratory work. There are probably some important scientific discoveries yet to be made!

1.7.5 Interaction of arsenic with sediments

Calculations of the rate of movement of arsenic through an aquifer depend on knowing the appropriate solid-solution partition coefficient (Kd), or more particularly, on knowing the nature of the adsorption isotherm and in being able to predict how the partitioning changes with changes in groundwater chemistry. Therefore there is a need for laboratory studies of the interaction of arsenate, and if appropriate of arsenite also, with the affected aquifer materials. These will need to be carried out under conditions as close as possible to those found in the field including reducing conditions if appropriate. This can be difficult.

These studies need to be backed up by laboratory studies of the interaction of arsenic with model oxide materials to establish better models for competitive adsorption of both arsenate and arsenite with other common anions and cations. It is likely that this will lead to the development of new models, or at least to a refinement of existing ones. Any new adsorption models need to be incorporated into a groundwater solute transport package.

Reductive dissolution of oxides with adsorbed As is poorly understood and needs careful experimental investigations to establish the sequence of events in terms of changes in arsenic and iron speciation, changes in mineral surface chemistry and the kinetics and stoichiometry of Fe and As release.

1.8 Strategy for locating arsenic problems in groundwater

The greatest challenge facing many water utilities and water providers in terms of the arsenic problem is the large number of wells that may not have been analysed for arsenic and that need to be tested. The challenge is to identify and mitigate any contaminated wells as soon as possible, and if there is going to be a substantial delay, the most seriously contaminated should be tackled first. Therefore a major task is to identify rapidly the most contaminated wells.

For many water providers, including NGOs in rural communities in developing countries, arsenic represents a new and poorly understood threat. There is almost certainly a general lack of understanding of the variation of arsenic concentrations in their area. In some cases, such as West Bengal (India) and Bangladesh, the scale of the testing programme required is unprecedented. In other cases, there is a lack of knowledge of the potential problem, or the lack of suitable facilities for testing. A rapid testing programme carried out in some randomised manner will establish if an extensive arsenic problem exists. It is far more difficult to identify every actual contaminated well in view of the high degree of spatial variability usually found in arsenic-contaminated areas. This is especially true where there is an extensive network of rural wells. Figure 1.4 helps to identify ‘at risk’ areas for priority testing. It can only be used to identify susceptible provinces, not individual wells.

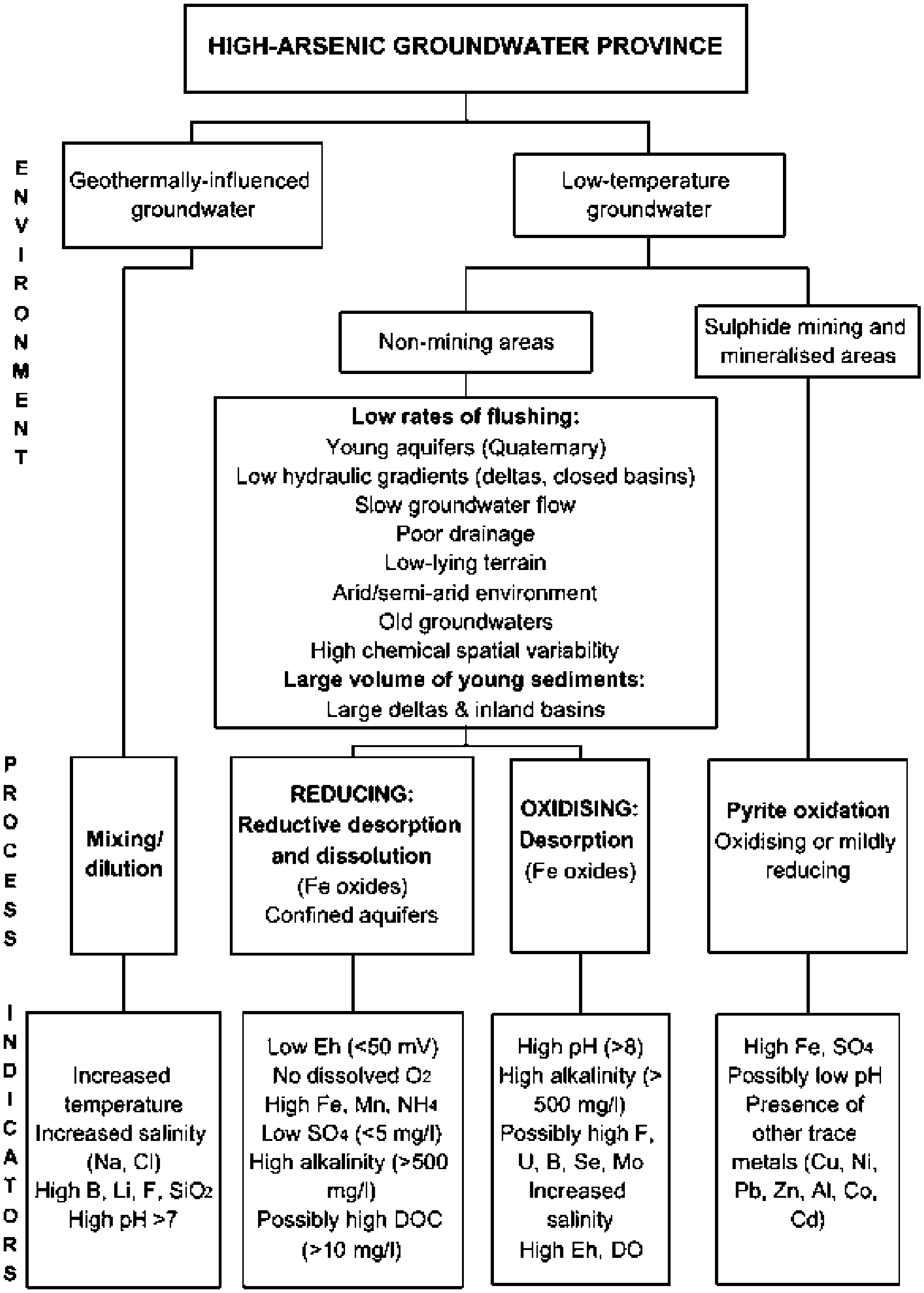


Figure 1.4 Flow diagram to aid locating possible high-arsenic groundwaters

1.9 Non-technical Summary

Arsenic in the environment

- Arsenic is a well-known poison. It has featured in history as a poison for killing people both in fact and in fiction. It was once a popular poison because it conveniently left no easily detectable trace. The analysis was difficult, and remains so.

- Arsenic is not that rare. Small amounts are found in all rocks, soils and sediments and arsenic can be detected at low concentrations in most natural waters - rain, rivers, lakes, groundwater and seawater. Occasionally it is present at much higher concentrations and this is of concern where the water is being used for drinking water or irrigation. Groundwater presents a particular risk since this is where most of the naturally high concentrations of arsenic have been found and groundwater is often used as a source of drinking water.

The scale of the problem

- Well-known cases of arsenic poisoning from natural arsenic in the drinking water have been found in Taiwan, Chile, Argentina, Mexico, China and more recently in West Bengal (India) and Bangladesh. The scale of the problem in terms of population exposed to high arsenic concentrations is greatest in the Bengal Basin with perhaps 40 million people drinking water containing ‘excessive’ arsenic. Many of the worst problems occur in poor countries without the necessary infrastructure to be able to respond rapidly.

- The problem in Bangladesh was undetected for many years because of the lack of suitable arsenic testing laboratories within the country. The problem is made worse by the very large number of wells present. An estimate of 6-11 million wells has been made. Most of these are operated by hand-pumps and obtain their water from depths of 10-70 metres.

National drinking-water standards

- Each country defines the maximum amount of arsenic that it permits in drinking water. This is usually done formally through a national drinking-water standard. The WHO has set its provisional guideline value at 10 $\mu g\ l^{-1}$ but many countries have yet to adopt this standard in their legislation.

- The standard currently adhered to in India, Bangladesh and most of the countries which have groundwater arsenic problems is 50 $\mu g\ l^{-1}$ although the US-EPA and EC limits have both recently been reduced to 10 $\mu g\ l^{-1}$. The chronic or long-term toxicity of arsenic is believed to be such that if the standard basis for risk assessment that is applied to industrial chemicals were applied to arsenic, the maximum permissible concentration would be lower still.

The nature and causes of the problem

- The range of arsenic concentrations found in natural waters is unusually large, ranging from less than 0.5 $\mu g\ l^{-1}$ to more than 5000 $\mu g\ l^{-1}$, i.e. a range of greater than ten thousand times. Typical concentrations in freshwater are less than 10 $\mu g\ l^{-1}$ and often less than 1 $\mu g\ l^{-1}$. Rarely, much higher concentrations are found and this gives rise to arsenic problem areas. In such areas, the percentage of ‘affected’ wells (defined as those exceeding 50 $\mu g\ l^{-1}$) may exceed 10 percent of all wells and even in the worst cases, may exceed 90 percent of wells.

- These large-scale ‘natural’ arsenic groundwater problem areas are found all over the world but they tend to be confined to two types of environment: firstly, inland or closed basins in arid or semi-arid areas, and secondly, strongly reducing aquifers often derived from alluvium. Both types of susceptible environments tend to contain very young sediments and to be in low-lying, flat areas where groundwater flow is sluggish. Historically, these are poorly flushed aquifers and any arsenic released from the sediments has therefore been able to accumulate in the groundwater. Arsenic-contaminated groundwaters are also found in geothermal areas and, on a more localised scale, in areas of mining activity or where sulphide oxidation has occurred. There are likely to be other known problems in mining areas related to acid mine drainage (AMD) and the generally metal-rich waters. In most cases, these mineralized sources do not pose a major threat to drinking water supplies.

- Similarly, sources of geothermal water are usually well known and suitably monitored.

- Although the way in which the high-arsenic groundwaters are formed is not well understood in detail, some general features are emerging. These are listed below:

- the arsenic content of the aquifer materials does not appear to be exceptionally high - it is normally in the range 2-10 mg kg^{-1};

- there appear to be two distinct ‘triggers’ that can lead to the release of arsenic from the aquifer material into the pore water. The first is the development of high pH (>8.5) conditions in semi-arid or arid environments usually as a result of the combined effects of mineral weathering and high evaporation rates. This pH change leads to the desorption of adsorbed arsenic (especially arsenate species) from natural mineral oxides, or prevents arsenic from being adsorbed in the first place. The second trigger is the development of strongly reducing conditions at near neutral pH values, leading to the reductive desorption of arsenic from natural mineral oxides and to the reductive dissolution of iron and manganese oxides also leading to arsenic release. These are both responses to a change in the geochemical environment;

- there is as yet little direct evidence to support these arsenic release mechanisms for aquifers but the circumstantial evidence is strong. Detailed observations from other related environments such as lake and ocean sediments and soils, and from laboratory experiments with pure minerals, also lends credence to them;

- high concentrations of phosphate, bicarbonate, silicate and possibly organic matter, either individually or in combination, can enhance the mobility of arsenic in water through competition for adsorption sites;

- there is also potential for release of arsenic into groundwaters through the oxidation of sulphide minerals, particularly pyrite, brought about by aeration of the aquifer, for example by ‘over-abstraction’ of groundwater. However, compared with the ‘iron-oxide reduction hypothesis’, the ‘pyrite oxidation hypothesis’ is not an efficient mechanism for releasing arsenic because of the readsorption of As by the iron(III) oxides that invariably precipitates further along the flow path.

The future

- Very little is known about how long it will take to flush out the arsenic released by the processes described above in specific aquifers. This is likely to depend on the past, present and future groundwater flows, and hence on the detailed palaeohydrogeology of the aquifer, and on the sediment chemistry. It is almost certainly longer than the timescales of relevance to the present groundwater As problems;

- the extent of flushing of an aquifer since the original deposition of the aquifer 'rocks' is clearly critical - the greater this is, the less likely it is that there will be an arsenic problem. This means that deeper, older aquifers will tend to suffer fewer problems (all other things being equal). Groundwater flows were greater than at present during the last glacial period (21,000-7,000 years ago) when sea levels were much lower and so aquifers laid down before this are less likely to be severely affected;

- while we suspect that the arsenic problem will gradually disappear under natural groundwater flow, this may take many thousands of years and in the meantime, some wells may increase in arsenic concentration and some may decrease. Some of the arsenic may return via baseflow to be readsorbed by iron(III) oxides in the river sediments. The quantities of arsenic involved in affected aquifers are very large and there is little possibility of completely flushing it out in the short-term by pumping;

- a characteristic feature of high groundwater arsenic areas is the large degree of spatial variability - the well-to-well variability is usually large which means that it may be difficult to predict what the concentration of arsenic is likely to be in a particular well from the results of neighbouring wells. This means that in affected areas there is little alternative but to analyse each well separately for arsenic. Affected aquifers are the exception rather than the rule. In most aquifers, the majority of wells are likely to be unaffected even when they contain high concentrations of dissolved iron.

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Revised/edited by
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Chapter 2

CHAPTER 2 IS STILL MISSING

Chapter 3. Exposure and health effects

3.1 Exposure Assessment

Given its ubiquitous nature in the environment, human exposure to arsenic is inevitable. Exposure can occur via all three principal routes, that is, through the inhalation of air, through the ingestion of food and water, and via dermal absorption. Worldwide, the degree of non-occupational exposure to arsenic varies greatly, being dependent on local geochemistry and the level and proximity of anthropogenic activity. Elevated environmental exposure to arsenic tends to be confined to relatively small, geologically arsenic-rich areas where levels of arsenic, particularly in drinking water, exceed those found elsewhere by an order of magnitude or more.

3.1.1 Environmental Levels

Arsenic is a natural component of the earth's crust where it is present at an average concentration of 2 mg/kg. Trace concentrations are found in all environmental media, including air, water, soils/sediments and biota. Available data on typical environmental levels are summarized in the following subsections.

3.1.1.1 Air and rainwater

Levels of arsenic in ambient air are generally low. In most remote and rural areas, concentrations average between 0.02 and 4 ng/m^3. Higher concentrations are evident in many urban areas, with levels ranging typically from 3 to about 200 ng/m^3. Concentrations in excess of 1000 ng/m^3 have, however, been measured in the vicinity of industrial sources, especially near non-ferrous metal smelters (WHO, 2001). In air, arsenic exists predominantly absorbed on particulate matter, and is usually present as a mixture of arsenite and arsenate, with the organic species being of negligible importance except in areas of arsenic pesticide application or biotic activity. (Beavington & Cawse, 1978; Brimblecombe, 1979; Davidson et al., 1985; Peirson et al., 1974).

A recent Europe-wide survey has found evidence of a gradual decline in ambient arsenic concentrations over the past few decades. This reduction in air arsenic is attributed to the progressive introduction of dust abatement equipment at industrial facilities. Typical arsenic levels for the European region are currently quoted as being between 0.2 - 1.5 ng/m^3 in rural areas, 0.5 - 3 ng/m^3 in urban areas and no more than 50 ng/m^3 in industrial areas (DG Environment, 2000).

Arsenic has been detected in rainwater. In non-polluted areas, mean concentrations range from 0.013 to 0.5 ug/L (Scudlark & Church, 1988; Andreae, 1980), whereas near a North Sea gas platform, mean arsenic concentrations up to 45 ug/L have been reported (Peirson et al., 1974).

3.1.1.2 Soils

Background concentrations of arsenic in soil range from 1 to 40 mg/kg, with a mean value of 5 mg/kg (Beyer & Cromartie, 1987; Bowen, 1979). Soils overlying naturally arsenic-rich geological deposits, such as sulphide ores, may have significantly higher concentrations, in some cases up to two orders of magnitude higher (NAS, 1977).

Whereas non-contaminated soils typically contain low levels of arsenic, human activity (for example, waste disposal and pesticide applications) can increase substantially the concentrations found in soils. Extremely high arsenic concentrations have been reported in soils contaminated with mine or smelter wastes (up to 27 000 mg/kg), and levels of 20 100 to 35 500 mg/kg have been found in soils around the effluent dumping point of an arsenical pesticide manufacturing plant (US EPA, 1982; Chatterjee & Mukherjee, 1999). In addition, mean total arsenic concentrations of 50 to 550 mg/kg have been recorded in agricultural soils applied with various arsenical pesticides (Sanok et al., 1995; Takamatsu et al., 1982; Walsh & Keeney, 1975; Stilwell & Gorny, 1997). Some peats and sewage sludges have been reported to contain considerable quantities of arsenic. Reported concentrations in peats vary from around 4 mg/kg up to 340 mg/kg (Minkkinen & Yliruokanen, 1978; Shotyk, 1996). Zhu & Tabatabai (1995) monitored total arsenic levels in sewage sludge from waste treatment plants in Iowa (USA) and found concentrations which ranged from 2.4 to 39.6 mg/kg, with a mean of 9.8 mg/kg.

Relatively little of the total arsenic measured in soils has been found to be present in bioavailable forms. In one study, which looked at garden soils near or at sites of past mining activity, the water-soluble extractable arsenic fraction was found to be less than 1% of the total (Xu & Thornton, 1985). In similar studies, the proportion of water-extractable arsenic in agricultural top soils ranged from 0.05% to 0.3%, and in mine wastes from 0.02% to 1.2% (Kavanagh et al., 1997). Ng et al. (1998) reported total arsenic concentrations of 32 to 1 597 mg/kg in soils that had been contaminated 30 years previously with arsenical pesticides. Based on a rat model, it was estimated that the absolute bioavailability of these contaminated soils relative to arsenite and arsenate ranged from 1.0 to 9.9% and 0.3 to 3.0%, respectively.

3.1.1.3 Surface water

Arsenic is widely distributed in surface water. Concentrations of arsenic in surface waters are usually low, although higher concentrations can occur near natural mineral deposits or near anthropogenic sources.

Measured levels of arsenic in surface freshwaters (rivers and lakes) are summarized in **Table 3.1**.

Surveys indicate that most values are below 10 ug/L, although some samples may exceed 1 mg/L (Page, 1981; Smith et al., 1987; Welch et al., 1988). A total arsenic concentration of 2 mg/L has been recorded near one pesticide plant (Faust et al., 1983; Faust et al., 1987). Crearley (1973) reported mean arsenic levels of 3200 and 7900 ug/L in two lakes near a manufacturing plant that had been producing arsenic-based cotton defoliants for 30 years. High levels of arsenic have been recorded in some thermal waters. For example, Tanaka (1990) found a mean concentration of 570 ug/L in Japan's geothermal waters, with a maximum level of 25.7 mg/L.

Table 3.1 Concentrations of arsenic in surface freshwaters (Source: WHO, 2001)

Location	Sampling period	Sampling details and/or arsenic source	Concentration (µg/litre)^{a}	Reference
Brazos River, Texas, U.S.A.	NS	0.2 µm filtered, arsenite	0.05	Chakraborti et al. (1986)
Madison River, Montana, U.S.A.	NS	Geothermal	51	Sonderegger & Ohguchi (1988)
Finfeather Lake, Texas, U.S.A.	1973	near manufacturing plant for arsenic-based	7900 (6000-8600)	Crearley (1973)

		cotton defoliants		
Municipal Lake, Texas, U.S.A.	1973	as above	3200 (1700-4400)	Crearley (1973)
Maurice river, NJ, U.S.A.	1982-1983	Upstream of pesticide plant	3.3 (1.05-4.4)	Faust et al. (1987a)
	1982-1983	0.6 km downstream	2222 (1320-4160)	Faust et al. (1987a)
	1982-1983	4.2 km downstream	266 (118-578)	Faust et al. (1987a)
Union Lake, NJ, U.S.A.	1982-1983	14-17 km downstream	86.1 (27.1-267)	Faust et al. (1987a)
Bowron Lake, British Columbia, Canada	1992	Reference lake; no mining activity	0.26 (<0.2-0.42)	Azcue et al. (1994a)
Lake water, British Columbia, Canada	1992	near abandoned gold mine	0.25 (<0.2-0.3)	Azcue et al. (1994a)
Lake Asososca, Nicaragua	1991-1992	Volcanic crater; includes surface, intermediate and bottom samples	5.9 (0.85-15.8)	Cruz et al. (1994)
Moira Lake, Ontario, Canada	1987-1988	past mining activity; 15% particle sorbed	43 (4-94)	Diamond (1995)
Lakes, Northwest Territories, Canada	1975	gold mining activity	700-5500 (range)	Wagemann et al. (1978)
Subarctic lakes, Northwest Territories, Canada	1991	gold mining activity	270 (64-530)	Bright et al. (1996)
Yangtze river (source area), China	NS	filtered water (<0.45 µm)	3.1 (0.1-28.3)	Zhang & Zhou (1992)
Antofagasta, Chile	1958-1970	Toconce River, Andes Mountains	<800	Borgono et al. (1977)
Mutare river, Zimbabwe	1993	Near gold/arsenic mine dumps	13-96 (range of means)	Jonnalagadda & Nenzou (1996b)
Odzi river, Zimbabwe	1993	2.2 km downstream from gold/arsenic mine dumps (after confluence with Mutare river)	1-3 (range of means)	Jonnalagadda & Nenzou (1996b)
Lake Xolotlan,	NS	Volcanic crater; range	10.2-30.1	Lacayo et al.

Nicaragua		of means	(range of means)	(1992)
Waikato river, New Zealand	1993-1994	Volcanic source	32.1 (28.4-35.8)	McLaren & Kim (1995)
Lake water, Lapland, Finland	1992	0.1 m below surface	0.17 (median)	Mannio et al. (1995)
Nakhon Si Thammarat Province, Thailand	1994	Mining activity	217.5 (4.8-583)	Williams et al. (1996)

NOTES: [a] - mean and ranges of total arsenic unless stated otherwise; NS - not stated

Sediments in aquatic systems often have higher arsenic concentrations than those of the overlying water. In most cases, concentrations are within the range 5-3000 mg/kg (WHO, 2001), with the higher levels occurring in areas of contamination, such as gold mining activity (Welch et al., 1988; Wagemann et al., 1978). Isolated reports of sediment concentrations in excess of 3000 mg/kg have been found in the literarature. Arsenic concentrations of up to 10 000 mg/kg (dry weight) were found in surface sediments near a copper smelter (Crecelius et al., 1975).

Arsenic levels in seawater are typically 1 to 2 ug/L. The dissolved forms of arsenic in seawater include arsenate, arsenite, methanearsonic acid (MMA) and dimethylarsinic acid (DMA) with adsorption onto particulate matter being the physical process most likely to limit dissolved arsenic concentrations (Maher & Butler, 1988). Reported concentrations in estuarine locations are generally a little higher (WHO, 2001). In one study conducted in the St Lawrence Estuary, Canada, it was noted that arsenic concentrations increased from 0.5 to 1.4 ug/L (or from 6.6 to 18.7 nM) with increasing salinity (from 0 to 31%) (Tremblay & Gobeil, 1990).

3.1.1.4 Groundwater

Arsenic levels in groundwater typically average around 1 to 2 ug/L (Table 3.2). However, in areas with volcanic rock and sulphide mineral deposits, arsenic levels in excess of 3000 ug/L have been measured (Page, 1981; Robertson, 1989; Welch et al., 1988).

Table 3.2: Concentrations of arsenic in groundwater (Source: WHO, 2001)

Location	Sampling period	Arsenic source	Concentration (µg/litre)[a]	Reference
Hungary	N.S.	deep groundwater	68 (1-174)	Varsanyi (1989)
South-west Finland	1993-1994	well waters; natural origin	17-980 (range)	Kurttio et al. (1998)
New Jersey, U.S.A.	1977-79	well waters	1 (median)	Page (1981)
			1160 (maximum)	Page (1981)
Western U.S.A.	N.S.	geochemical	48 000	Welch et al.

		environments	(maximum)	(1988)
South-west U.S.A.	1970-	alluvial aquifers	16-62 (range of means)	Robertson (1989)
Southern Iowa & western Missouri, U.S.A.	N.S.	natural origin	34-490 (range)	Korte & Fernando (1991)
Northeastern Ohio, U.S.A.	N.S.	natural origin	<1-100 (range)	Matisoff et al. (1982)
Lagunera region, northern Mexico	N.S.	well waters	8-624 (range)	Del Razo et al. (1990)
Cordoba, Argentina			>100	Astolfi et al. (1981)
Chile			470-770 (range)	De Sastre et al. (1992)
Pampa, Cordoba, Argentina	N.S.	2-15m, 61°45’-63 °W; 32 °20’-35 °00’S	100-3810 (range)	Nicolli et al. (1989)
Kuitun-Usum, Xinjiang, PR China	1980	well waters	850 (maximum)	Wang et al. (1993)
Hsinchu, Taiwan	N.S.	well waters	<0.7	Chen et al. (1994)
West Bengal, India	N.S.	arsenic-rich sediment	193-737 (range of means)	Chatterjee et al. (1995)
			3700 (maximum)	Chatterjee et al. (1995)
Calcutta, India	1990-1997	near pesticide production plant	<50-23080 (range)	Chakraborti et al. (1998)
Bangladesh	1996-1997	well waters	<10 - >1000 (range)	Dhar et al. (1997)
Nakhon Si Thammarat Province, Thailand	1994	shallow (alluvial) groundwater; mining activity	503.5 (1.25-5114)	Williams et al. (1996)
	1994	deep groundwater; mining activity	95.2 (1.25-1032)	Williams et al. (1996)

NOTES: [a] - mean and ranges of total arsenic unless stated otherwise; NS - not stated

According to the scientific literature, areas having elevated groundwater concentrations of arsenic, be they naturally occurring or due to human activity, can be found in all the major world regions. For example, in Iowa, Missouri and Ohio, arsenic, apparently of natural origin, was found in groundwaters at concentrations between 34 and 490 ug/L (Korte & Fernando, 1991; Matisoff et al., 1982). In Hungary, Varsanyi (1989) found that arsenic concentrations in deep groundwater ranged from 1 to 174 ug/L, with an average value of 68 ug/L. High arsenic levels originating from arsenic-rich bedrock were found in drilled wells in southwest Finland with concentrations ranging from 17 to 980 ug/L (Kurttio et al., 1998), while in parts of Mexico arsenic concentrations ranged from 8 to 624 ug/L with over 50% of samples in excess of 50 ug/L (Del Razo et al., 1990). Chen et al. (1994) reported mean arsenic levels in groundwaters of southwest Taiwan of 671 ug/L (as dissolved arsenic).

Arsenic contamination of groundwater from arsenic-rich sediment has been reported widely in both India and Bangladesh. Chatterjee et al. (1995) analysed groundwater from six districts of West Bengal, India. Mean total arsenic levels ranged from 193 to 737 ug/L with a maximum value of 3700 ug/L. Mandal et al. (1996) reported that 44% of groundwater samples collected in West Bengal up to January 1996 contained total arsenic levels greater than 50 ug/L. Dhar et al. (1997) found that 38% of groundwater samples collected from 27 districts of Bangladesh contained total arsenic levels greater than 50ug/L. During 1990 and 1991 Chatterjee et al. (1993) sampled groundwater in the vicinity of a chemical plant in Calcutta, India, which had produced the insecticide Paris-Green (acetocopper arsenite) for 20 years. Groundwater contained total arsenic levels ranging from <0.05 to 58 mg/L; the highest total arsenic level included 75% arsenite.

3.1.1.5 Biota

Levels of arsenic in marine organisms can range from < 1 mg/kg up to more than 100 mg/kg (Lunde, 1977; Maher & Butler, 1988; Phillips, 1990). Arsenic is present mainly in its organic forms, including for example as arsenosugars (in macroalgae) and arsenobetaine (in invertebrates and fish).

In freshwater organisms and terrestrial biota arsenic levels are normally less than 1 mg/kg (fresh weight). In the case of terrestrial biota, however, higher levels have been recorded in samples collected from areas with significant geothermal activity or from sites close to anthropogenic sources of arsenic. Mean concentrations of up to 3000 mg/kg have found at old arsenical mine sites (Porter & Peterson, 1975; Benson et al., 1981). Terrestrial plants accumulate arsenic by root uptake from the soil and by the adsorption of arsenic deposited on the leaves.

3.1.2 Exposure in the general population

As previously mentioned, exposure to environmental contaminants including arsenic can occur through one or more of three pathways, inhalation, ingestion and dermal absorption. In the case of arsenic, available evidence suggests that non-occupational exposure occurs primarily through the ingestion of food and water, with the inhalation pathway playing only a minor role. Food is more commonly the main contributor to total intake but in areas where drinking waters contain relatively high levels of arsenic, drinking water may be the most important source of arsenic intake. Intake via dermal absorption is believed to be negligible, and is not considered further here.

3.1.2.1 Air

Human exposure to arsenic in ambient air will be primarily to the inorganic forms of arsenic, organic species generally being negligible in airborne particulates, except in areas of substantial use of arsenic pesticides or in areas with high biotic activity (section 3.1.1.1). To some extent exposure will be governed by the size of the particulates, the smaller (submicron) particles being more significant. Based on the currently available measurements of arsenic in ambient air, it is estimated that inhalation of airborne particles would result in a pulmonary exposure of around 1 ug/day in a non-smoker. In areas of elevated atmospheric arsenic, i.e. in the vicinity of industrial operations, the contribution may well be higher than this.

3.1.2.2 Food and beverages

Food monitoring data indicate that trace concentrations of arsenic are present in all foodstuffs. Total arsenic concentrations in food from various countries vary widely, being dependent upon the food type, growing conditions (type of soil, water, geochemical activity, use of arsenical pesticides) and processing techniques. In general, however, the highest concentrations of total arsenic are found in seafood, followed by meats and grain; fruit, vegetables and diary products tend to have lower total concentrations (Gunderson, 1995; Yost et al., 1998; NRC, 1999; MAFF, 1997; Dabeka et al, 1993; ANZFA, 1994). Concentrations of total arsenic in found in various food groups in North America are given in Table 3.3. Analysis of various beverages from Denmark found low levels of arsenic (3-11 ug/L) (Pedersen et al., 1994).

Table 3.3 Total arsenic concentrations in various food groups from Canada(a)
(Source: WHO, 2001)

Food Category	**Sample Size**	**Mean (?g As/kg wet weight)**	**Range (?g As/kg wet weight)**
Milk and dairy products	89	3.8	<0.4-26
Meat and poultry	124	24.3	<1.3-536.0
Fish and shellfish	40	1662.4	77.0-4830.0
Soups	28	4.2	<0.2-11.0
Bakery goods and cereals	177	24.5	<0.1-365.0
Vegetables	262	7.0	<0.1-84.0
Fruit and fruit juices	176	4.5	<0.1-37.0
Fats and oils	21	19.0	<1.0-57.0
Sugar and candies	49	10.9	1.4-105
Beverages(b)	45	3.0	0.4-9.0
Miscellaneous(c)	33	12.5	<0.8-41.0

(a) Data from Dabeka *et al.*, (1993); (b) Includes: coffee, tea, soft drinks, wine and canned and bottled beer; (c) Includes: bran muffins, muffins with and without raisins, gelatin desserts, raisins, baked beans, weiners, and raw & canned beets

There are few data on the concentration of arsenic in human breast milk. What data are available suggest that levels are low; for example Grandjean et al. (1995) reported low concentrations of arsenic in breast milk from a population consuming large amounts of marine mammals. One study of ten lactating women by Concha et al. (1998a) found arsenic concentrations of between 0.83 and 7.6 ug/kg fresh weight (median 2.3 ug/kg) in breast milk from women consuming in excess of 200 ug/L in their drinking water. It was concluded that breast feeding provided 1-2 ug/day compared with 100-200 ug/day from formula milk made up with the arsenic-rich water.

Arsenic in foods occurs as a mixture of inorganic species and the less toxic organic arsenicals, including trimethyl species such as arsenobetaine. Preliminary findings suggest that inorganic arsenic accounts for 75% of the total arsenic burden in meats, 65% in poultry, 75% in dairy products and 65% in cereals (US EPA, 1988; Yost et al., 1998). In contrast, in fruits and vegetables, and fish/seafood, the organic species tend to predominate with inorganic arsenic contributing only 10%, 5%, and 0-10%, respectively.

A few studies have looked specifically at the relative proportions of organic and inorganic arsenic species in food. According to a report from the Netherlands (Vaessen and van Ooik, 1989), inorganic arsenic accounts for between 0.1 and 41% of the total arsenic burden in seafood.

Edmonds and Francesconi (1993), in their review of data on inorganic arsenic in seafood, concluded that inorganic arsenic represented less than 1% of the total amount of arsenic. Mohri et al. (1990) estimated that a typical Japanese diet contained 5.7% inorganic arsenic; the corresponding intake was estimated to be 27-376 ug total arsenic/day. In another study, Toa and Bolger (1998) estimated an intake of inorganic arsenic in US males and females, aged 60-65 years, of 12.5 and 9.7 ug/day, respectively. Other age groups had lower daily intakes, which varied from 1.3 ug/day for infants to 9.9 ug/day for young males (aged 25-30 years).

Collectively such studies indicate that inorganic arsenic levels in fish and shellfish are generally low (< 1%), but that other foodstuffs (meat, poultry, diary products and cereals) contain higher proportions of inorganic arsenic. Based on preliminary data it has been estimated that approximately 25% of the daily intake of dietary arsenic is as the inorganic forms; this is, however, highly dependent on the type and range of foods ingested (US EPA, 1988, Yost et al, 1998). More data are needed to obtain satisfactory information on the normal range of inorganic arsenic in food.

Representative mean daily intakes of total arsenic from food and beverages in several countries are summarized in Table 3.4. The variation in dietary intake of total arsenic in adults reflects in large part the variability in the consumption patterns worldwide of arsenic-rich food groups (fish/shellfish and meats) and confirms the need to consider such regional variations in arsenic intake when carrying out human health risk assessments for arsenic.

Table 3.4 Estimated average dietary intake of arsenic in various countries
(Source: WHO, 2001)

Country	**Method of Sampling(a)**		**Intake of Total Arsenic (?g/day)**	**Reference**
Australia	MB	(adult male)	73.3	ANZFA, 1994
		(adult female)	52.8	
		(2 year old)	17.3	
Brazil	DD(b)	(students)	18.7-19.5	Fávaro *et al.,* 1994
		(S. Catarina 1 region)	49.2-52.9	
		(Manaus region)	139.6-159.3	
			16.5-17.0	

Canada	TD	(5 cities-adult male)	59.2	Dabeka *et al.,* 1993
		(5 cities-1 to 4 yrs)	14.9	
Croatia	MB		11.7	Sapunar-Postruznik *et al.,* 1996
Japan	DD	(adult- male&female)	182	Mohri *et al.,* 1990
Spain	TD	(Basque Region-adult)	291	Urieta *et al.,* 1996
UK	TD	(adults)	63	MAFF, 1997
USA	MB	(adults)	52.6	Yost *et al.,* 1998
		(0.5-2 yrs)	27.6	

(a) MB-Market basket survey; TD - Total diet study; DD - Duplicate diet study;
(b) Mean values not reported.

3.1.2.3 Drinking-water

Concentrations of total arsenic in fresh surface and groundwaters, both potential sources of drinking-water, are given in Sections 3.1.1.3 and 3.1.1.4 (Tables 3.1 and 3.2). Although arsenic levels in natural waters are usually low (a few µg/L), drinking waters in some areas in the world contain concentrations of total arsenic well in excess of 100 of µg/L. These elevated arsenic concentrations are generally a result of natural geochemical activity. Arsenate is usually the predominant species; however, some groundwaters have been found to contain up to 50% arsenite. Concentrations of methylated species in natural waters are usually low, that is less than 0.3 µg/L (ATSDR, 1993). Unless stated otherwise, monitoring data for drinking water given in this section are reported as total arsenic.

A review of water quality monitoring data collected during the period 1976-1993 revealed that concentrations of arsenic in drinking waters in the USA lie between < 2.5 and 28 µg/L in surface waters, and between < 5 to 48 µg/L in groundwater sources. (Detection limits of 2 or 5 µg/L precluded more accurate estimates of the lower limit of these ranges). Based on these data, it was estimated that approximately 2% of the US population is exposed to drinking water containing more than 10 µg/L of arsenic (Borum & Abernathy, 1994). Areas of especially high arsenic concentrations have been identified by the US EPA in a detailed analysis of 1978 water quality monitoring data. These include parts of California and Neveda, were levels are arsenic in the bedrock are naturally high; mean arsenic concentrations of up to 80 µg/L and maximum levels of more than 1,400 µg/L have been reported. Arsenic was detected in 67% of 3,834 drinking water samples taken in this year (detection limit 0.1 µg/L); the mean concentration was reported to be 2.4 µg/L (US EPA, 1993).

Water quality monitoring data obtained from six Canadian Provinces over a four-year period (1985-1988) have also been compiled and analysed (NHW/DOE, 1993). It was found that the percentage of drinking water samples having total arsenic concentrations of > 5 µg/L varied from 0 to 32%. However, when 28 samples from 7 ground water sources in Nova Scotia were excluded from the analysis the range was reduced to 0-12%. In areas dominated by naturally occurring high arsenic-containing ores, or where gold mining had previously occurred, arsenic concentrations in drinking water supplies of between 150 and >500 µg/L were reported.

In the West Bengal Region of India, it has been estimated that over 1 million people are consuming drinking-water containing arsenic at concentrations above 50 µg/L. Levels as high as 3.7 mg/L have been recorded at some locations (Das et al, 1995; Choudry et al., 1997). Similarly, in areas of Bangladesh bordering India, 38% of ground water samples in 27 districts were found to contain arsenic at levels > 50ug/L (Dhar et al, 1997). In Southwest Taiwan, about 100,000 people are believed to have been exposed (i.e. prior to 1970) to high concentrations of arsenic in drinking-water (range 10 to 1800 µg/L, mean 500 µg/L) (Guo et al, 1994). Similar problems have been reported in Chile, where 100,000 people have consumed drinking water containing 800 ug/L of arsenic for up to 12 years (Borgono et al., 1977) and in North Central Mexico, where 200,000 people were exposed to >50 µg/L arsenic in drinking-water and to as much as 410 µg/L in at least one village (Cebrian et al., 1983). In the major Australian drinking water systems, levels of arsenic of up to 15 µg/L have been recorded; however, typical concentrations are usually below 5 µg/L (NHMRC, 1996).

3.1.2.4 Soil

Although ingestion of arsenic in soil and dust is unlikely to be a significant source of arsenic intake in adults, it may be so in the case of children, particularly in locations near industrial and hazardous waste sites. There is some evidence to suggest that children living near arsenic-contaminated sites do have elevated body burdens relative to children from uncontaminated sites (see section 3.2.1.5). The bioavailability of the arsenic in these soils is often low (see section 3.1.1.2); however, more data on the bioavailability of arsenic from such sources is necessary for a more accurate assessment of human risk from soil exposures.

3.1.2.5 Miscellaneous Exposures

Smokers are exposed to arsenic by the inhalation of mainstream cigarette smoke. It has been estimated that a person in the USA smoking 40 cigarettes per day would inhale about 10 µg of arsenic (ATSDR, 1993). Some dietary supplements, such as Chinese herbal medicines, may contain undesirable high arsenic concentrations (Chan, 1994).

3.1.3 Occupational exposures

There is the potential for significant occupational exposure to arsenic in several industries, in particular, non-ferrous smelting, electronics, wood preservation, wood joinery shops, arsenic production, glass manufacturing and, the production and application of arsenical pesticides. Exposure is primarily through the inhalation of arsenic-containing particulates; however, ingestion and dermal exposure may be significant in particular situations. It is extremely rare that workers are exposed to arsenic alone, but are usually exposed to arsenic in combination with other substances. At present a number of countries have established occupational regulations for arsenic which set limits on the permissible concentration of inorganic arsenic in the workplace. These range from 0.01 to 0.1 mg/m^3 (ILO, 1991; DFG, 1999; OSHA, 2000; MSZW, 2000).

The following examples are given to illustrate the range of arsenic levels and exposures that have been reported in specific industries in various locations world-wide. It is stressed that they should not be considered as representative of all similar industrial sites.

Exposure to arsenic in copper smelters has been assessed in a number of studies. For example, measurements of arsenic in air were made between 1943 and 1965 at one copper smelter in the USA.Very high airborne concentrations (>5 mg/m^3) were estimated in the following departments: arsenic roaster (20 mg/m^3), electrostatic precipitator (13 mg/m^3), arsenic refinery (7.5 mg/m^3) and main flue (6.9 mg/m^3). High concentrations (0.5-4.99 mg/m^3) were reported in four departments: masons shop (2.6 mg/m^3), ore roaster (1.4 mg/m^3), materials crushing (1.0 mg/m^3) and reverbatory furnaces (0.6 mg/m^3). The remaining 10 departments of the smelter had only medium (0.1-0.49 mg/m^3) to low (<0.1 mg/m^3) concentrations of arsenic (Welch et al., 1982).

Data on airborne arsenic concentrations inside a second US copper smelter have been reviewed by Enterline and Marsh (1982). As in Welch's study, reported levels varied by department, but in this case the arsenic concentrations were universally high. For example, between 1947 and 1953, a total of 25 samples from the arsenic plant found airborne arsenic concentrations ranging from 0.8 to 41.4 mg/m^3. As part of their study, Enterline and Marsh (1982) also measured the urinary excretion rates of workers; it was concluded, on the basis of measurements made during the period 1938-1957, that airborne arsenic concentrations in ug/m^3 are about one-third the urinary excretion concentrations in ug As/L of urine.

Arsenic exposures of workers in a copper mine and smelter complex in Chile have been assessed by Ferreccio et al. (1996). Using data obtained from 1952 to 1991, Ferreccio et al. (1996) reported that workers' exposure to airborne arsenic varied from 1.6 to 201.7 in ug As/m^3, with workers in the administration area experiencing the lowest arsenic levels and those in the smelter itself the highest. Similarly, Offergelt et al. (1992) reported levels of arsenic (as a time-weighted average or TWA) of between 6 and 502 ug/m^3 in a sulphuric acid plant. As part of an epidemiological investigation on lung cancer mortality of workers in non-ferrous mines, Liu and Chen (1996) measured airborne arsenic concentrations in 1978, 1981 and 1988. In chronological order, the concentrations of arsenic reported were: 0.23 mg/m^3 (range 0.004-0.577; 6 samples); 0.06 mg/m^3 (range 0.003-0.166; 14 samples), and 0.32 mg/m^3 (range 0.028-1.442; 8 samples).

Workers in selected glass manufacturing industries may be exposed to airborne arsenic through the use of arsenic trioxide (IARC, 1993). In Germany, for example, workers were found to have urinary arsenic concentrations ranging from 3 to 114 ug/g creatinine. In 1976, 36% of the cases were above the upper normal limit of 25 ug As/g creatinine; by 1981 this had dropped to 18% of cases (Schaller et al., 1982). The mean urinary arsenic excretion in 18 workers involved in weighing and mixing chemicals in a UK specialist glass manufacturing facility was 79.4 ug/g creatinine compared to 4.4 ug/g creatinine in controls (Farmer & Johnson, 1990). Similarly, in a Belgian glass factory, urinary excretion rates of arsenic in 10 workers ranged between 10 and 941 ug/g creatinine compared with a range of 7.6-59 ug/g creatinine in control workers (Roels et al., 1982). The authors concluded that the high urinary arsenic concentrations in the glass factory workers were more likely to be related to oral intake due to poor hygiene, rather than as a result of pulmonary uptake.

Exposure to arsenic in the air has been documented in 19 out of 27 workers using arsenic-containing materials in the following occupations and activities: taxidermy; workers producing garden fences, weekend cottages and new houses; workers impregnating wood with copper:chromium:arsenic (CCA) solutions, and workers impregnating electric pylons with arsenic solutions (Jensen & Olsen, 1995). Median arsenic exposures of indoor workers preparing fences and weekend cottages were 3.7 and 0.9 ug/m^3, respectively. Mean urine arsenic levels in taxidermists were 1.8 times the reference level of 14.5 nmoles As/mmole creatinine.

Airborne arsenic concentrations in a wood joinery shop handling treated wood were reported to be 0.043 - 0.36 mg/m^3 (WHO, 1981). In a more recent study involving wood joinery shops, airborne arsenic concentrations between 0.54 and 3.1 ug/m^3 were reported (Nygren et al, 1992). In two workshops machining CCA-treated wood, concentrations of arsenic in personal air samples ranged from 10 to 67 ug/m^3 (Subra et al., 1999).

Workers in coal-powered power plants may also be exposed to the arsenic found in the coal, or more likely to that found in fly ash during cleaning. Yager et al. (1997) have reported arsenic concentrations (8-hour TWA concentrations) of between 0.17 and 375.2 ug/m^3 (mean = 48.3 ug/m^3) in the breathing zone of maintenance workers from a coal-fired power plant in Slovakia. The urinary excretion of total urinary arsenic metabolites ranged between 2.6 and 50.8 ug As/g creatinine (with a mean of 16.9 ug As/g creatinine). The authors estimated a mean urinary excretion of 13.2 ug As/g creatinine in workers exposed to fly ash, from an 8-hr TWA exposure to 10 ug As/m^3, suggesting that the bioavailability of arsenic in coal fly ash is approximately one-third that seen in smelters.

It should be noted that some of the above studies refer to measurements made 20 to 40 years ago, and it is unlikely that present-day levels are as high as the earlier reports might indicate.

Nowadays, levels of arsenic in workplaces with up-to-date control equipment and good hygiene practices are generally below 10 ug/m^3 (expressed as a 8 hour TWA concentration) (WHO, 2001).

3.1.4 Total intake from all environmental pathways

On the basis of available data, it is estimated the daily intake of total arsenic from the consumption of food and beverages in the general population typically lies between 20 and 300 ug/day (WHO, 2001). This wide variation in intake reflects large differences in the composition of diets worldwide, particularly with regard to the proportion of fish/shellfish. It should also be noted that intake data refer to total arsenic and do not reflect the possible variation in intake of the less toxic organic derivatives versus the more toxic inorganic arsenic species. Limited data suggest that approximately 25% of the arsenic present in food is inorganic.

Although food is the main contributor to the daily intake of arsenic for much of the nonoccupationally exposed population, in areas where drinking water contains elevated levels of arsenic, drinking water will be a significant source of both total and inorganic arsenic. In some cases, i.e. where levels of arsenic exceed 50 ug/L, arsenic in drinking water may even be the major contributor. For example, consumption of 1.4 litres of drinking water containing >50 ug As/L could provide over 70 ug inorganic arsenic compared with an estimated intake of inorganic arsenic from food of between 12 and 14 ug, assuming a typical North American diet (Yost et al., 1998; NRC, 1999).

All other intakes of arsenic (inhalation and dermal) are usually small in comparison to the oral route (ATSDR, 1993). Inhalation would add about 1 ug As/day from airborne particulates in a non-smoker; this would rise to approximately 10 ug/day in a smoker on 40 cigarettes per day. Contaminated soils may be a significant source of arsenic intake in children in certain locations; however, the low bioavailability of soil arsenic would need to be taken into account in an exposure assessment (see section 3.1.2.5).

The most appropriate way to determine the internal (absorbed) dose of arsenic in individuals in specific populations is to measure the concentrations of arsenic species in urine. Concentrations of total urinary arsenic and metabolites of inorganic arsenic (i.e. inorganic arsenic + MMA + DMA) reflect the level of intake of total arsenic and inorganic arsenic, respectively.

Reported concentrations of metabolites of inorganic arsenic in urine of individuals with no known history of arsenic exposure are generally below 10 ug/L in European countries. Similar or slightly higher concentrations are reported in studies from the US and Japan. However, arsenic concentrations exceeding 1 mg/L have frequently been observed in the urine of individuals from in West Bengal and Bangladesh (WHO, 2001).

In general, the concentration of arsenic metabolites in urine correlate well with concentrations of arsenic in drinking water. Moreover, several studies conducted in the US have shown that the urinary arsenic concentration is approximately half that in drinking water (Harrington et al., 1978; Valentine et al., 1979). In other populations, for example in Argentina and Taiwan where a much greater proportion of the intake of fluids was from drinking water or drinks made from drinking water (as opposed to prepared beverages), the concentration of arsenic in urine was proportionately much higher (WHO, 2001).

3.2 Kinetics and metabolism

Humans are exposed to many different forms of inorganic and organic arsenic species (arsenicals) in food, water and other environmental media. Each of the forms of arsenic has different physicochemical properties and bioavailability and therefore the study of the kinetics and metabolism of arsenicals in animals and humans is a complex matter. Arsenic metabolism is also characterised by large interspecies differences compared with other metals and metalloids.

3.2.1 Inorganic arsenic

The fate of ingested or inhaled inorganic arsenic in the human body is largely dependent on its valence state. The two most common valence states to which humans might be environmentally exposed are the trivalent and pentavalent forms, arsenite (AsIII) and arsenate (AsV). Since arsenicals may change valence state depending on handling and preparation methodologies, studies cited in this review were evaluated with particular attention to the use of appropriate methods to ensure that the inorganic arsenic valence state was maintained.

3.2.1.1 Absorption

Respiratory deposition and absorption

Human inhalation exposure to inorganic arsenic can occur as a consequence of industrial activity (e.g., smelting of ores), production of energy (e.g., coal-fired power plants) and during cigarette smoking. The extent of arsenic deposition of inhaled arsenic will depend largely on the size of the inhaled particulates, while the absorption of deposited arsenic is highly dependent on the solubility of the arsenical.

Available human data are insufficient to estimate quantitatively regional arsenic deposition in the respiratory tract. However, occupational studies in which both the concentration of inorganic arsenic in the breathing zone and urinary excretion of inorganic arsenic and its metabolites were determined provide some information on arsenic absorption. Studies of this type demonstrate that the excretion of arsenic and methylated metabolites is significantly increased in exposed workers compared to unexposed workers (e.g. Vahter et al., 1986; Yamauchi et al., 1989; Offergelt et al., 1992; Hakala and Pyy, 1995; Yager et al., 1997). While this confirms that arsenic is absorbed from the respiratory tract, such studies do not provide enough information to estimate quantitatively arsenic absorption after inhalation because of the influence of confounding factors, such as the possible contribution of oral exposures.

Gastrointestinal absorption

Arsenic can be absorbed from the gastrointestinal tract following the ingestion of arsenic-containing food, water, beverages or medicines, or as a result of inhalation and subsequent mucociliary clearance. The bioavailability of ingested inorganic arsenic will vary depending on the matrix in which it is ingested (i.e. be it food, water, beverages or soil), the solubility of the arsenical compound itself and the presence of other food constituents and nutrients in the gastrointestinal tract.

In common with experimental animals, controlled ingestion studies in humans indicate that both tri- and pentavalent arsenic are readily absorbed from the gastrointestinal tract. For example, Pomroy et al. (1980) reported that healthy male human volunteers excreted 62.3 ± 4.0% of a 0.06 ng dose of ^{74}As-arsenic acid (AsV) in urine over a period of 7 days, whereas only 6.1 ± 2.8% of the dose was excreted in the faeces. Results obtained from similar studies show that between 45% and 75% of the trivalent forms of arsenic are excreted in the urine within a few days, indicating that gastrointestinal absorption is both relatively rapid and extensive (WHO, 2001).

Dermal absorption

Few investigations of dermal absorption rates for arsenicals have been undertaken. What data are available indicate that absorption rates are generally low (<10%); however, for certain forms of arsenic higher rates may be observed (WHO, 2001). Wester et al. (1993) studied the percutaneous absorption of arsenic acid (H_3AsO_4) from water and soil. In rhesus monkeys, arsenic uptake ranged from 6 to 2%. The same authors also reported that human cadaver skin absorbed approximately 1 to 2% of the administered dose over a 24-hr period.

Placental transfer

Both As(III) and As(V) have been found to cross the placenta of laboratory animals (WHO, 2001). Case reports of arsenic poisoning in pregnant women, in which the foetus died and was subsequently found to have toxic levels of arsenic in its organs and tissues, demonstrate that arsenite (arsenic trioxide) also readily passes through the placenta of humans (Lugo et al., 1969; Bollinger et al., 1992). This conclusion is substantiated by a more recent study conducted by Concha et al. (1998b) who observed that similar arsenic concentrations were found in cord blood and maternal blood (~9 ug/L) of maternal-infant pairs exposed to high arsenic-containing drinking water (~200 ug/L).

3.2.1.2 Distribution

Fate of inorganic arsenic in blood

Inorganic arsenic is rapidly cleared from the blood of most laboratory animals and humans; for this reason blood arsenic is considered to be a useful bioindicator of recent, relatively high-level exposures (see also section 3.2.3.2). Older studies (WHO, 1981) have indicated that the kinetics of arsenic clearance in the plasma and erythrocytes are similar, although levels in erythrocytes tended to be approximately 3-fold higher a few hours after exposure.

More recently, Zhang et al. (1996, 1997, 1998) have reported on the distribution of arsenical species in serum and arsenic-protein binding in serum of patients with renal disease. The predominant arsenic species present in serum were DMA (~15-30%) and arsenobetaine (~54-76%), with the remainder being protein-bound. Inorganic arsenic and MMA were undetectable (Zhang et al. 1996, 1997). Zhang et al. (1998) further reported that only inorganic arsenic was bound to serum proteins and that transferrin is the main carrier protein. It should be noted that since individuals with renal disease tend to accumulate arsenic in serum, these results may not be typical of the general population.

Tissue distribution

As in experimental animals, analysis of post mortem human tissues reveals that arsenic is widely distributed in the body following either long-term relatively low-level exposure or poisoning (Raie, 1996; Gerhardsson et al., 1988; Dang et al., 1983). Dang et al. (1983), using neutron activation analysis (NAA), found that arsenic concentrations were quite low in both the blood and brain of Bombay accident victims relative to other tissues, and that arsenic concentrations in any given tissue was quite variable.

Levels of total arsenic and major arsenic metabolites were measured by HGAAS in a variety of human tissues obtained from adult patients (aged between 36 and 79) suffering from cerebral haemorrhage, pneumonia or cancer in Kawasaki, Japan (Yamauchi & Yamamura, 1983). No sex-dependent differences in arsenical tissue levels were observed and inorganic arsenic was found to be the predominant form in tissues, followed by DMA. MMA levels were uniformly low and detected only in liver and kidney. It is interesting to note that total arsenic levels were higher than those reported in the Indian study of Dang et al. (1983) and that levels in the brain tended to be more comparable to arsenic levels in other tissues. Interindividual variation in total tissue arsenic was again quite high, as observed in the Dang study.

Raie (1996) compared tissue arsenic levels in infants (aged 1 day to 5 months) and adults from Glasgow, Scotland using NAA. Mean levels of arsenic (ppm or ug/g dry weight) in liver, lung and spleen in infants versus adults were 0.0099 vs. 0.048, 0.007 vs. 0.044, and 0.0049 vs. 0.015, respectively. These data suggest that arsenic accumulates in tissues with age, a finding that is wholly consistent with observations in laboratory animals (Marafante et al., 1982).

A number of studies have been conducted in humans with a view to determining whether there are differences in tissue arsenic accumulation in differing disease states. In the case of multiple sclerosis and non-multiple sclerosis patients, no significant differences were found (Warren et al., 1983). Narang & Datta (1983) have reported that concentrations of arsenic in both liver and brain of patients who died of fulminant hepatitis are high compared to patients who died of non-hepatic related causes. Collecchi et al. (1985) found that malignant laryngeal tissue had significantly higher levels of arsenic compared with normal tissue; plasma arsenic levels were also significantly higher in cancer patients compared with controls. Zhang et al. (1996, 1997) have reported that arsenic levels in serum are significantly elevated (~5 to 6-fold) in patients with chronic renal disease.

3.2.1.3 Metabolic transformation

Arsenic metabolism is characterized in many species by two main types of reactions: (1) oxidation/reduction reactions which interconvert arsenite and arsenate, and (2) methylation reactions in which trivalent forms of arsenic are sequentially methylated to form mono-, di- and trimethylated products using S-adenosyl methionine (SAM) as the methyl donor and GSH as an essential co-factor (see Figure 3.1). One striking feature of arsenic metabolism is that there are extreme qualitative and quantitative interspecies differences in methylation to the extent that some species do not appear to methylate arsenic at all (Styblo et al., 1995; Vahter, 1999).

Figure 3.1 Arsenic methylation in mammals

Source: WHO, 2001 (PENDING)

In common with that which is observed in most laboratory animal species, controlled ingestion studies indicate that both arsenate and arsenite are extensively methylated in humans, with DMA being the main methylated metabolite excreted in human urine. A noteworthy difference between humans and laboratory animals is that MMA is excreted in the urine of humans to a greater extent. The biological basis for this difference is unknown.

Several studies involving populations exposed to relatively high levels of arsenic in drinking water indicate that methylation patterns are not highly correlated with exposure level (Warner et al., 1994; Hopenhayn-Rich et al., 1996a). Hopenhayn-Rich et al. (1996b) compared methylation patterns in Chilean subjects (n=73) before and after changing from higher (600 ug/L) to lower (45 ug/L) arsenic-containing drinking water. There was a small but significant decrease in urinary inorganic arsenic (17.8% to 14.1%) and a decrease in the MMA to DMA ratio (0.23 to 0.18). The authors further noted that there was large interindividual variation in methylation profiles, and that factors such as smoking, gender, age, years of residence and ethnicity only accounted for ~20% of the variation observed. They speculated that much of the interindividual variation observed might be explained by genetic differences in the activity of methylating enzymes and related co-factors.

Vahter et al. (1995a) reported a unique pattern of urinary methylated metabolite excretion in a population of healthy native Andean women in north-western Argentina consuming an apparently protein-adequate diet. Reported arsenic concentrations in the drinking water of this population were ~200 ug/L. These women excreted mainly inorganic arsenic (median 25%, range 6.5 to 42%) and DMA (median 74%, range 54 to 93%) in their urine and very little MMA (median 2.1% with a range of 0.6 to 8.3%). The authors suggested that this finding indicates the existence of genetic polymorphism in the control of arsenic methyltransferases. They also suggested that the higher urinary DMA excretion in women in the village with the highest arsenic in drinking water (~200 ug/L) compared with women in the villages with lower arsenic in drinking water (2.5 to 31 ug/L) indicates induction of DMA excretion. It is interesting to note that differences in the activities of other methyltransferases have been explained by the existence of genetic polymorphisms (Weinshilboum, 1992).

In further studies of the same Andean population, Concha et al. (1998c) reported striking differences in urinary excretion patterns of arsenic metabolites in children compared to adult women. In one village, children (age 3-15 years) excreted a much higher median percentage of inorganic arsenic in urine (49% vs. 25%) and a much lower median percentage of DMA in urine (47% vs. 74%) compared to adult women (age 20-47 years). A low median % MMA excreted in urine was also observed in both the women (2.1%) and children (3.6%) which is consistent with previously reported results (Vahter et al., 1995a). Another significant finding in these children was that with increasing excretion of total arsenic metabolites in urine, the percentage of inorganic arsenic decreased and the percentage of DMA increased; the authors interpreted this as evidence for induction of arsenic methylation with increasing exposure (Concha et al., 1998c). In the few studies that have looked at methylation patterns in children, percentages of metabolites excreted in urine are similar to adults (Buchet et al., 1980; Kalman et al., 1990). However, in both these latter studies arsenic exposure was relatively low as indicated by total concentration of arsenic metabolites excreted in urine (i.e. < 20 ug/L).

Data suggestive of gender differences in arsenic metabolism have been reported in studies conducted in Chile and Taiwan (Hopenhayn-Rich et al., 1996a; Hsu et al., 1997). In both of these studies males were reported to have a significantly higher MMA:DMA ratio in urine, indicating that more DMA was being excreted by females compared to males. This has been interpreted to mean that females have greater methylation capacity compared to males (Hopenhayn-Rich et al., 1996a). Concha et al. (1998c) reported significant increases in the percentage DMA excreted in urine in Argentinean women during pregnancy, a possible reason for gender differences reported in some studies.

Inorganic arsenic metabolism is affected by liver disease. In patients with various forms of liver disease, the presence of disease had no effect on the total amount of arsenic excreted, but dramatically shifted the proportion of MMA and DMA excreted in the urine. The percentage of arsenic excreted as MMA was decreased in liver disease compared to controls (6.1±0.7 vs. 12.8±0.7), while DMA was increased (40.7±1.9 vs. 24.3±1.6) (Buchet et al., 1984). Geubel et al. (1988) reported similar findings in healthy subjects compared to subjects with cirrhotic liver disease; they further noted that in patients with other non-hepatic diseases arsenic methylation was unaffected.

3.2.1.4 Elimination and excretion

Inorganic arsenic and its metabolites are eliminated primarily via the kidney. Studies in adult human males voluntarily ingesting a known amount of either trivalent or pentavalent arsenic indicate that between 45% and 75% of the dose is excreted in the urine within a few days to a week. Although relatively few studies in volunteers have included measurement of arsenic in both faeces and urine, (Pomroy et al., 1980) reported that 6.1%±2.8% of a single oral dose of arsenic acid (pentavalent As) was excreted in the faeces over a period of 7 days compared to the 62.3%±4.0% in urine. No quantitative data was available that directly addressed the issue of biliary excretion of tri- or pentavalent arsenic in humans.

Although arsenic is excreted by other routes than via urine and faeces (e.g. in sweat), these routes of excretion are generally minor (WHO, 1981). Since arsenic can accumulate in keratin-containing tissues, skin, hair and nails could also be considered as potentially minor excretory routes. Both older (WHO, 1981) and recent studies indicate that arsenic can be excreted in human milk, although the levels are low (Dang et al., 1983; Grandjean et al., 1995; Concha et al., 1998a).

3.2.1.5 Retention and turnover

Pomroy et al. (1980) studied the whole body retention of radio labelled arsenic (^{74}As; 6.4 ci, 0.06 ng As) administered once orally as arsenic acid (AsV) in healthy male volunteers (aged 28 to 60 years) using whole body counting for periods of up to 103 days. While the averaged whole body clearance data for the six subjects in the study were best described by a triexponential model, the interindividual variation was quite high. It was reported that 65.9% of the dose was cleared with a half-life of 2.09 days, 30.4% with a half-life of 9.5 days and 3.7% with a half-life of 38.4 days. No comparable data for humans exist for trivalent inorganic arsenic.

Some studies have been conducted for the purpose of evaluating whether there is an increased body burden of arsenic in children living near arsenic contaminated sites relative to either children from low arsenic exposure areas or compared to adults. For example, Binder et al. (1987) reported that total urinary arsenic excretion was significantly increased in children living in a Montana (USA) community with high levels of arsenic in soil (average ~400 - 700 ppm) compared with a community with low levels (44 ppm) in soil. In urine samples taken in the high-arsenic soil community, mean total arsenic was 54 ug/L (53.8 ug/g creatinine) compared with 16.6 ug/L (17.1 ug/g creatinine) in the low-arsenic community.

Trepka et al. (1996) studied differences in arsenic burden among children in Germany. No striking age or gender-related differences were reported, although urinary arsenic excretion was slightly, but significantly increased in children from the most polluted area. However, the authors did not consider this increase to be toxicologically significant. In contrast, Diaz-Barriga et al. (1993) reported striking increases in body burden in children living closest to a copper smelter (median soil levels ~500 ppm arsenic) compared with children living 7 to 25 km away (median soil levels ~11 to 14 ppm arsenic). Urinary arsenic excretion (normalized to creatinine) was more than doubled and arsenic levels in hair were more than 10-fold higher.

3.2.1.6 Reaction with body components

Numerous mechanistic studies have documented basic differences in the interaction of pentavalent compared to trivalent inorganic arsenic with body components; this is an important determinant in observed differences in tissue distribution.

Pentavalent inorganic arsenic and phosphate are analogs; this means that arsenate (As(V)) can compete with phosphate for active transport processes. Consequently, the addition of phosphate can decrease the intestinal uptake and renal tubular reabsorption of arsenate (Gonzalez et al., 1995; Ginsburg & Lotspeich, 1963). Arsenate can also substitute for phosphate in the hydroxyapatite crystal of bone; this accounts for the higher concentrations of arsenic-derived radioactivity in bone after administration of arsenate compared to arsenite (Lindgren et al., 1982). At the biochemical level, arsenate can uncouple oxidative phosphorylation in mitochondria by substituting for inorganic phosphate in the synthesis of ATP (Gresser, 1981). It can also uncouple glycolysis by forming the dysfunctional compound, 1-arseno-3-phosphoglycerate, rather than 1:3-diphosphoglycerate (Mayes, 1983).

Arsenite (AsIII) reacts readily with vicinal sulfhydryl groups of a variety of enzymes and proteins. This affinity for sulfhydryl groups accounts for its accumulation in keratin-rich tissues such as skin, hair and nails. Arsenite also interacts with the ubiquitous sulfhydryl-containing cellular tripeptide, glutathione, at many different levels in the methylation process. Since arsenate can be reduced to arsenite in humans, administration of arsenate can cause inhibiton of enzymes and react with cellular enzymes and peptides. These may include the reduction of arsenic from pentavalency to trivalency following the addition of a methyl group and the formation of complexes with trivalent arsenicals which may be substrates for methylation (Styblo et al., 1996).

3.2.2 Organic arsenic compounds

The kinetics and metabolism of MMA, DMA, trimethylarsine (TMA) and trimethylarsine oxide (TMAO) as well as arsenobetaine and arsenocholine are discussed in this section. In general, relative to inorganic arsenic, organoarsenicals are less extensively metabolised and more rapidly eliminated.

3.2.2.1 Absorption

Respiratory deposition and absorption

No quantitative data concerning the respiratory deposition and absorption of organoarsenicals are available for humans or laboratory animals. However, the fact that increased urinary excretion of arsenic during the workweek with a return to baseline levels on weekends was observed in workers spraying the herbicide monosodium methanearsonate indicates that respiratory absorption of organoarsenicals can occur (Abdelghani et al., 1986).

Gastrointestinal absorption

Limited experimental studies in human volunteers suggest that both MMA and DMA are readily absorbed from the gastrointestinal tract. Buchet et al. (1981a) reported that on average 78.3% of an oral dose of 500 ug of MMA and 75.1% of an oral dose of 500 ug DMA were excreted in urine within 4 days.

Studies have been conducted on the metabolism of organoarsenicals ingested in seafood. In one such study, an adult Japanese male consumed prawns containing ~10 ug (As)/kg trimethyl arsenic (98.8% trimethylarsenic - presumably as arsenobetaine). About 90% of the ingested arsenic was excreted in urine within 72 hours (Yamauchi & Yamamura, 1984). In human volunteers consuming flounder (containing arsenic as arsenobetaine), an average of 60% of the ingested dose was excreted in the urine within two days (Freeman et al., 1979). These data suggest that arsenobetaine is extensively and rapidly absorbed from the gastrointestinal tract.

Dermal absorption

No data concerning the dermal absorption of organoarsenicals in humans have been located, but both *in vivo* and *in vitro* dermal absorption data have been reported for arsenical herbicides in laboratory animals. Using clipped dorsal skin of B6C3F1 mice, Rahman and Hughes (1994) found that a constant fraction of the applied dose of MMA sodium salts (~12.4%) in a water vehicle was absorbed during a 24-hr period over the entire dose range (10 to 500 ug). Absorption appeared to be unaffected by vehicle volume. Using the same experimental system with DMA, Hughes et al. (1995) again found no significant dose-dependency in absorption over a 24-hr period. However, vehicle volume exerted a significant effect on absorption (rates ranged from around 7% to 40%) and decreased with increasing volume of water. In both studies, skin absorption of the arsenical herbicides from soil was very low (<1%). Shah et al. (1987) studied the *in vivo* percutaneous absorption of MMA and DMA in young (33-day old) and adult (82-day old) Fischer 344 rats. On average, the old and young rats absorbed 15.1% and 3.0% of the recovered dose, respectively, indicating that the young animals absorbed significantly less via this route.

Placental transfer

Older studies have demonstrated that DMA is capable of crossing the placenta of rats (Stevens et al., 1977) and that the organoarsenical feed additive Roxarsone (3-nitro-4-hydroxyphenylarsonic acid) accumulates in eggs (Chiou et al., 1997). However, more recent human or animal data are not available to substantiate these findings.

3.2.2.2 Distribution

Fate of organic arsenic in blood

Studies concerning the fate of organoarsenicals in human blood are almost totally lacking. Following ingestion of 10 ug/kg of trimethyl arsenic (98.8% by analysis, presumably arsenobetaine) in prawns, trimethylarsenic levels were reported to be approximately 2.5 times higher in blood plasma compared with erythrocytes at two hours post ingestion in the single subject studied. Levels declined thereafter and were at background by 24 hours (Yamauchi & Yamamura, 1984). In rodents, dimethyl- and trimethylarsenic compounds are rapidly cleared from the blood stream (Yamauchi et al, 1988; 1990).

Tissue distribution

Tissue distribution data in humans are derived from limited studies in which human volunteers have ingested ^{74}As labelled organoarsenicals. Brown et al. (1990) reported that arsenobetaine is rapidly and widely distributed in soft tissues with no major concentration in any region or organ and that greater than 99% of tracer activity was eliminated from the body within 24 days. Similar studies were unavailable for other organoarsenicals.

3.2.2.3 Metabolic transformation

There are limited data on the metabolism of MMA and DMA in humans. Buchet et al. (1981a) have reported that after a single oral dose of 500 ug MMA (as As), 87.4% of the total metabolites excreted in urine after 4 days were in the form of MMA and 12.6% were in the form of DMA. In the same study, it was reported that all of the ingested DMA (500 ug as As) excreted in the urine was in the form of DMA. However in a later study, Marafante et al. (1987) reported that 3.5% of a single oral dose of DMA (0.1 mg As/kg) was eliminated in urine as TMAO within 3 days. No metabolism studies were identified in which humans specifically consumed TMA or TMAO alone rather than in seafood.

It appears that, in common with laboratory animals, humans eliminate arsenobetaine from seafood unchanged in their urine. This implies that arsenobetaine is not metabolized (Tam et al., 1982). Recently, Goessler et al. (1997) have suggested that humans can metabolise inhaled trimethylarsine to arsenobetaine; their conclusion is based on the fact that elevated levels of arsenobetaine appeared in the urine of a chemist synthesizing trimethylarsine.

3.2.2.4 Elimination and excretion

Humans eliminate orally administered MMA and DMA predominantly in urine. Buchet et al. (1981a) reported that an average of 78.3% and 75.1% of a single oral dose (500 ug as As) of MMA and DMA, respectively, were eliminated in urine of human volunteers within a four-day period. Arsenic ingested in seafood (where it is most likely to be present as arsenobetaine) is rapidly eliminated in urine. It is worthy of note that the percentage of the dose eliminated in urine following ingestion of arsenic in seafood is quite similar to that seen in laboratory animals dosed orally with arsenobetaine. No studies were identified that addressed the issue of biliary excretion or other routes of elimination for organoarsenicals in humans.

3.2.2.5 Retention and turnover

To date only animal studies have specifically measured retention and turnover rates of organoarsenicals. Vahter et al. (1984), for example, have compared the whole body retention of ^{74}As-DMA in mice and rats following a single oral dose of 0.4 mg (As)/kg. In mice, whole body clearance of DMA was triphasic, with 85% of the dose eliminated with a half-time of 2.5 hours, 14% with a half-time of 10 hours and the remainder (<0.5%) with a half-time of 20 days. In rats elimination was biphasic with 45% of the dose having a half-time of ~13 hours and the remaining 55% having a half-time of ~50 days. The longer retention of DMA in the rat was attributed to its greater tendency to accumulate arsenic in red blood cells.

Yamauchi et al. (1990) calculated the biological half-lives following oral administration of organoarsenicals to hamsters from multiple studies conducted in their laboratory. They reported half-lives of 7.4 hours for MMA, 5.6 hours for DMA, 5.3 hours for TMAO, 3.7 hours for TMA and 6.1 hours for arsenobetaine.

3.2.3 Biomarkers of arsenic exposure

The three most commonly employed biomarkers used to identify or quantify arsenic exposure are total arsenic in hair or nails, blood arsenic, and total or speciated metabolites of arsenic in urine.

3.2.3.1 Arsenic in hair and nails

Because arsenic (as the trivalent form) accumulates in keratin-rich tissues such as skin, hair and nails (see section 3.2.1.2), arsenic levels in hair and nails have been used as indicators of past arsenic exposure. Hair and nails have the advantage of being readily and non-invasively sampled, but can suffer from problems of external contamination. In the case of hair, sampling from less readily contaminated sites (e.g. the occipital area or the nape of neck) and closer to the scalp can minimize some of these problems.

Several studies have reported hair-As levels in subjects without known exposure to arsenic. In one such study, conducted by Zhuang et al. (1990), levels of 0.40 ± 0.22 ug/g were measured in the hair of adult male Chinese subjects who had died as a result of accidents. These authors also reported a significant positive correlation (r=0.75) of hair- arsenic with arsenic levels in kidney cortex, but not in lung or liver. Similar studies performed in other parts of the world (USA and Europe) have found lower levels of hair arsenic (Paschal et al., 1989; Wolfsperger et al., 1994)

Following acute poisoning, arsenic levels in both hair and nails are elevated within one to a few weeks and return to background levels within a few months (Choucair et al., 1988). Since the relative rate of hair growth is known (around 1 cm per month), the segmental distribution of arsenic along the hair shaft has been used to distinguish between acute and chronic poisoning, as well as to estimate length of time since a poisoning incident (Koons & Peters, 1994).

Arsenic levels in hair and nails can also be influenced by arsenic-induced disease state. Lin et al. (1998) have reported that both hair and fingernail arsenic are elevated in patients with black foot disease and Armienta et al. (1997) have reported that arsenic levels in hair are significantly elevated in patients displaying arsenic-induced hyperkeratosis compared to patients showing only hyper- or hypo-pigmentation. Hair samples from residents of Szolnok County, Hungary indicated that hair arsenic values were approximately 10-fold higher among those consuming drinking water containing increased arsenic concentrations (50-780 ug/L) compared with those whose drinking water contained only low levels of arsenic (1.02 +/- 0.08 mg/kg hair versus 0.14 +/- 0.04 mg/kg hair). There were also reports of skin effects (i.e. a higher prevalence for hyperkeratosis) in the Lokoshaza area among children exposed to increased arsenic concentrations.

The arsenic content of both fingernails and toenails has also been used as a bioindicator of past arsenic exposure. Fingernail arsenic has been reported to be significantly correlated with hair arsenic content (Lin et al., 1998). Agahian et al. (1990) reported that fingernail arsenic was elevated due to occupational arsenic exposure and correlated significantly (r=0.89) with mean arsenic air concentrations.

The use of toenails over fingernails has been recommended in some studies due to the larger amount of sample that can generally be provided. Toenails have the added advantages of slower growth (and so reflect exposures in the more distant past) and fewer external contamination problems (Karagas et al., 1996; Garland et al., 1993). Karagas et al. (1996) reported that mean toenail arsenic was significantly elevated in individuals using well water known to be high in arsenic (0.39±0.12) compared with individuals using water from low arsenic wells (0.14±0.02). Based on a regression analysis of these data, a 10-fold increase in arsenic concentration in water was associated with a two-fold increase in toenail arsenic levels.

3.2.3.2 Blood arsenic

As previously mentioned (section 3.2.1.2) inorganic arsenic is very quickly cleared from human blood. For this reason blood arsenic is only used only an indicator of very recent and/or relatively high level exposure, for example, in poisoning cases (Ellenhorn, 1997) or in cases of chronic stable exposure (i.e from drinking water).

Studies have shown that in general blood arsenic does not correlate well with arsenic exposure in drinking water, particularly at low levels. In five Californian communities having average concentrations of 6, 51, 98, 123 and 393 ug/L arsenic in their drinking water, blood arsenic concentrations (mean ± SD) were 0.49±0.12, 0.51±0.65, 0.29±0.18, 0.42±0.17 and 1.33±1.18 ug/dL, respectively. However, arsenic levels in drinking water were significantly correlated with increased total arsenic in both hair and urine (Valentine et al., 1979).

3.2.3.3 Arsenic and metabolites in urine

In common with other biomarkers of arsenic exposure, arsenic levels in urine may result from inhalation exposure as well as ingestion from food, water and soils (ATSDR, 1993) and as such provide a measure of the total absorbed dose. However, since arsenic is rapidly metabolised and excreted into the urine, levels in urine are best suited to indicate recent arsenic exposure. Total arsenic, inorganic arsenic and the sum of arsenic metabolites (inorganic arsenic + MMA + DMA) in urine have all been used as biomarkers of recent arsenic exposure.

In many older studies, total urinary arsenic was used as a biomarker of recent arsenic exposure. This approach has become increasingly uncommon because certain organoarsenicals (for example, the practically non-toxic compound arsenobetaine) present in substantial amounts in certain foodstuffs are excreted mainly unchanged in urine (Cullen & Reimer, 1989; Kaise & Fukui, 1992; Le et al., 1994a) (see also section 3.2.2.3.). Since consumption of seafood (e.g., marine fishes, crustaceans, bivalves, seaweeds) by human volunteers is associated with increased total urinary arsenic excretion (Arbouine & Wilson, 1992; Buchet et al., 1994, 1996), assessment of inorganic arsenic exposure using total urinary arsenic under these conditions would result in overestimation of inorganic arsenic exposure.

To avoid the potential for over-estimation of inorganic arsenic exposure inherent in using total urinary arsenic, most studies now measure speciated metabolites in urine, and use either inorganic arsenic or the sum of arsenic metabolites (inorganic arsenic + MMA + DMA) as an index of arsenic exposure. However, this can give misleading results unless a careful diet history is taken and/or seafood consumption is prohibited for two to three days prior to urine collection. There are two reasons for this. First, some seafoods contain the arsenic metabolites MMA and DMA, particularly DMA, in fairly high amounts. Secondly, arsenosugars present in seaweeds and some bivalves are extensively metabolised to DMA (either by the body itself or the gut microbiota), which is then excreted in urine (Le, et al., 1994b; Ma & Le, 1998; WHO, 2001).

3.3 Health effects

Arsenic has long been associated with toxic effects, producing marked impacts on health after both oral and inhalation exposure. Effects range from acute lethality to chronic effects, such as cancer and diseases of the vascular system. Studies in laboratory animals have demonstrated that the toxicity of arsenic is dependent on its form and its oxidation state. It is generally recognised that the soluble inorganic arsenicals are more toxic than the organic ones, and the trivalent forms (AsIII) are more toxic than the pentavalent ones (AsV). There are multiple end-points, with several different organ systems being affected, including the skin and the respiratory, cardiovascular, immune, genitourinary, reproductive, gastrointestinal and nervous systems.

Much of the information about the human health effects of arsenic, in particular in relation to its carcinogenicity, comes from evidence obtained through the study of exposed human populations. Unusually, it has been difficult to find any suitable animal model for the study of arsenic carcinogenicity. The human health effects of arsenic have been comprehensively reviewed by several leading national and international bodies including, WHO, IARC and the US NRC (IARC, 1973, 1980, 1987; ATSDR, 1993, 2000; NRC 1999; WHO, 1981, 2001).

3.3.1 Short-term effects

Ingestion of large doses of arsenic usually results in symptoms within 30 to 60 minutes, but may be delayed when taken with food. Acute arsenic poisoning usually starts with a metallic or garlic-like taste, burning lips and dysphagia. Violent vomiting may ensue and may eventually lead to hematemesis. These gastrointestinal symptoms are the result of intestinal injury caused by dilatation of splanchnic vessels leading to mucosal vesiculation. These vesicles rupture causing bleeding, diarrhoea, and protein wasting. Gastrointestinal symptoms often result in dehydration and electrolyte imbalance, and may lead to the development of hypotension and hypoxia (Brayer et al., 1997). After the initial gastrointestinal problems, multiorgan failures may occur, followed by death. Survivors of acute arsenic poisoning have been shown to develop hepatomegaly, melanosis, bone marrow suppression, hemolysis, and polyneuropathy resulting from damage to the peripheral nervous system.

Fatal arsenic poisonings have been reported after oral exposure to estimated single doses of 2 g (Levin-Scherz et al.,), 8 g (Benramdane et al., 1999) and 21 g (Civantos et al., 1995) Non-fatal outcomes (usually following treatment) have been documented after oral single doses of 1-4 g (Fincher & Koerker, 1987; Fesmire et al., 1988; Moore et al., 1994) and up to 8-16g (Mathieu et al., 1992; Bartolome et al, 1999). In children non-fatal but nevertheless serious acute effects have been observed after exposure to as little as 0.7 mg of As_2O_3 (Cullen et al., 1995). Incidents in which continuous or repeated exposure to high levels of arsenic over a short period of time have also been described. Following consumption of water containing 108 mg As/L for one week, two of nine persons died, four developed encephalopathy and eight showed gastrointestinal symptoms (Armstrong et al., 1984). In some cases, survivors of acute arsenic exposures are left with long-term or permanent health problems. Damage to the nervous system has been described in two cases involving subjects exposed to relatively high doses of arsenic (Murphy et al., 1981; Goebels et al., 1990). In both cases, despite some improvement in nervous system functions, neurological symptoms persisted for 2-3 years following exposure.

3.3.2 Chronic arsenic exposure

Chronic exposure to lower levels of arsenic has long since been linked to adverse health effects in human populations. The earliest reports date back to the latter part of the 19th century when the onset of skin effects (including pigmentation changes, hyperkerotosis and skin cancers) were linked to the consumption of arsenic in medicines and drinking water (WHO, 2001). In the early 1900s, numerous reports of skin disorders in Argentina, Chile, Mexico and Taiwan, which were attributed to arsenic exposure via drinking water, were published (Zaldivar, 1974). In the 1940s the discovery of a case of lung cancer, believed to be the result of exposure to arsenical dust in a British factory, sparked a series of more detailed investigations into the matter. These in turn revealed unexpectedly high lung cancer rates in a number of different occupational exposure situations (WHO, 2001).

Of the earliest reported cases of chronic arsenic poisoning, that of Blackfoot disease (BFD) or Wu Chiao Ping as it is locally known, is perhaps the most notorious. This peripheral vascular disease, which leads to progressive gangrenes of the legs, has been recognised in parts of Taiwan since the 1920s. During the 1950s its prevalence increased markedly, and since the late 1950s it has been the subject of intensive study.

3.3.2.1 Vascular diseases

Exposure to arsenic has been linked to various vascular diseases affecting both the large and small blood vessels. Much of the early work on arsenic and vascular disease focused on effects in small vessels (i.e. BFD and other peripheral vascular diseases), while later research has been directed primarily at effects in larger vessels (cardiovascular and cerebrovascular diseases). The findings of key studies in this area of research are summarised in Table 3.5 but for convenience the discussion which follows is divided into subsections on the peripheral vascular diseases and the cardio- and cerebrovascular diseases. Some work has also been done on the possible link between arsenic exposure and hypertension (a known vascular disease risk-factor); a brief sub-section on this topic is also included here.

Table 3.5 Effects of arsenic on vascular system (source: WHO, 2001)

Authors, study design	Study Population	Source and level of arsenic exposure	Health effects, metric of exposure and measure of association		Comments
Chen et al (1988b) case-referent	241 BFD patients and 759 age-sex-residence matched controls	Well water arsenic concentration = 1140 µg/L, with progressive decrease since 1956	Exp. time yrs	Peripheral vascular disease	OR adjusted for nutritional factors, family history of BFD, education, and evidence of skin lesions
				OR	
			<1	1.0	

			1-29		3.0		
			>30		3.4 p<0.001 for trend		
Chen et al (1988b) cohort	789 BFD patients	Well water arsenic concentration = 1140 µg/L, with progressive decrease since 1956	End point	$\text{SMR}_{\text{national}}$	$\text{SMR}_{\text{local}}$		No adjustment for potential confounders
			Periph. vasc. Disease	1243***	351***		
			Cardio-vasc. Disease	209***	160**		
			Cerebrovasc. Accid.	118 NS	107 NS		
			*** p < 0.001; ** p<0.01				
Wu et al(1989) ecological	Mortality and population data for 1973-1986 in 42 villages in Taiwan	Well water arsenic concentration = 1140 µg/L, with progressive decrease since 1956	Age adjusted mortality rates per 100,000 As exposure				No increase in cerebrovascular accidents in either males or females at any exposure dose. Used published Taiwan data from 1964 to 1966; The Natelson method was used (Tseng et al, 1968; Kuo, 1964).
				< 0.30	0.30-0.59	≥0.60ppm	
			All vascular diseases				
			Males	364	421	573	
			females	278	371	386	
			peripheral vascular diseases				
			males	23	58	60	
			females	18	48	35	
			cardiovascular diseases				
			males	126	154	260	
			females	1	153	145	
Chen et al (1995) cross-sectional	382 men and 516 women residing in villages in BFD-endemic area	Well water arsenic concentration = 1140 µg/L, with progressive decrease since 1956	Hypertension				Exposure determined from residential history and village median well water arsenic concentration, based on the analysis of Kuo (1968; 126 samples from 29 villages,

					Natelson method). ORs adjusted for age, sex, disease status of diabetes, proteinuria, body mass index, fasting serum triglyceride levels
			Cum expos.	OR	
			mg x L^{-1}yr		
			0	1.0	
			0.1-6.3	0.8 (0.2 - 3.2)	
			6.4-10.8	2.3 (0.8 - 6.8)	
			10.9-14.7	3.4 (1.2 - 9.2)	
			14.8-18.5	3.8 (1.4 - 10.3)	
			>18.5	2.9 (1.1 - 7.3)	
			unknown	1.5 (0.6 - 4.2)	
Tseng et al (1996) cross-sectional	582 residents of BFD-endemic area	Drinking water As range 1 to 1097 µg/L, 50% between 300 and 700 µg/L	Exposure category	Periph. vasc. dis.	142 water samples from 114 well analysed for AsUsed ratio of ankle and brachial systolic arterial pressure as indicator of PVD. Measurement by Doppler ultrasound. Those with ABI of >1.20 excluded due to possible misclassification of peripheral vascular disease. Adjusted for age, sex, body mass index, cigarette smoking, diabetes mellitus, hypertension, plasma lipids
			mg/l years	OR (CI 95%)	
			0	1	
			1 - 19	3.1 (0.9 - 10.4)	
			> 20	4.8 (1.4 - 16.7)	
Chen et al (1996) ecological	Residents of 60 villages in arsenic endemic area in Taiwan.	Well water arsenic concentration = 1140 µg/L,	Cumulative mortality from birth to age 79 from ischemic heart disease (1973-1986)		Exposure determined from village median well

	1,355,915 person years	with progressive decrease since 1956				water arsenic concentration, based on the analysis of Kuo (1968; 126 samples from 29 villages).
			Exposure category			
			As mg/L		cumulative mortality %	
			< 0.10		3.4	
			0.10-0.34		3.5	
			0.35-0.59		4.7	
			≥0.60		6.6	
Chen et al (1996) cohort	263 BFD patients and 2293 referents from the 60 villages above	Same as above	Expo category	Relative risk of isch. heart disease		Exposure determined from village median well water arsenic concentration, based on the analysis of Kuo (1968; 126 samples from 29 villages). Small number of deaths. Cox proportional hazard model adjusted for age, sex, smoking, body mass index, serum cholesterol, serum triglyceride level, hypertension, diabetes mellitus black foot disease. Relative risk of BFD patients vs non-BFD, 2.48 (1.1.4-5.4)
			$mg \cdot l^{-1} \cdot yrs$		(CI)	
			0	1.00		
			<10	2.2	(0.46-10.2)	
			10.0-19.9	3.3	(0.83-13.4)	
			20 +	4.9	(1.4-17.7)	
Hsueh et al., 1998 case-referent	74 cases of ISHD and 193 referents from the population of the Chen et al, 1995 study	Well water arsenic concentration = 1140 µg/L, with progressive decrease since 1956	Duration of drinking As containing water, yr	IHD	OR (CI)	Exposure determined from village median well water arsenic concentration, based on the analysis of Kuo (1968; 126 samples from 29 villages). OR

							Age- and sex adjusted No significant association with cumulative arsenic exposure
			>13		1.0		
			13-29		2.6	(1.0 - 6.4)	
			> 30		2.9	(1.0 - 8.3)	
Tsai et al (1999) Ecological	4 townships in BFD-endemic area, mortality in 1971-1994, compared to local and national rates	Well water arsenic concentration = 1140 µg/L, with progressive decrease since 1956	Mortality compared to local rates				National statistics were used to calculated expected deaths. 99% of causes of deaths based on diagnosis of a physician. Overlaps with earlier studies in the BFD-endemic area.
				SMR	CI		
			Hypertension	73	62 - 85		
			Isch. Heart dis.	175	159 - 192		
			Cerebrovasc. dis	114	108 - 121		
			Vasc. Dis.	356	291 - 430		
Chiou et al (1997) cross sectional	8102 males and females from the Lanyang Basin on the northeast coast of Taiwan	Arsenic in drinking water	Exposure category µg/L	Cerebrovascular disease	Cerebral infarction		OR adjusted for age, sex, smoking, alcohol intake, hypertension and diabetes. Exposure category determined by median arsenic concentratoin of well water.
				OR (CV)	OR (CV)		
			<0.1	1.0			
			0.1-50	2.5 (1.5-4.5)	3.4 (1.6-7.3)		
			50-299.9	2.8 (1.6-5.0)	4.5 (2.0-9.9)		
			≥300	3.6 (1.8-7.1)	6.9 (2.9-16.4)		
Engel & Smith (1994) Ecological	Mortality study from 30 US counties 1968-84	Arsenic in drinking water	Diseases of arteries, arterioles and capillaries				No effects were observed for all circulatory diseases, ischaemic heart disease or cerebral vascular disease. Expected numbers of

						deaths generated using US mortality rates. Arsenic concentrations were from public water supply records.
			Expos. category	SMRs (CI)		
			μg/L	Males	Females	
			5-10	110 (110-120)	110 (110-120)	
			10-20	110 (100-110)	110 (100-120)	
			>20	160 (150-180)	190 (170-210)	
Lewis et al (1999) cohort	4058 members of The Church of Jesus Christ of Latter Day Saints in Millard Co., Utah	Range of exposure from 3.5 μg/L to 620 μg/L; median exposures range from 14 to 166 μg/L depending on location.		Males	Females	for 2073 cohort members, “most” had at least 20 years history of exposure in their respective towns. The balance of the cohort (n = 1985) were included if they had spent any lenght of time in the arsenic-affected community. Existing and historic arsenic concentrations used. Death rates for the state of Utah for the years 1960 to 1992 were used to generate the expected deaths. No indication of exposure-response relationship for any of the vascular health effects. Exposure for the highest exposure group likely to be overestimated because of introduction of low-arsenic water into one community, which was not considered in the analysis
				SMR (CI)	SMR (CI)	

			Cerebrovasc. Dis.	79	(62-99)	87	(71-106)	
			All heart dis.	80	(73-88)	81	(72-91)	
			Isch. heart dis.	76	(67-85)	64	(53-76)	
			Dis. of arter. & capill.	93	(61-135)	86	(52-132)	
			Arteriosclerosis	124	(69-204)	118	(68-188)	
			Aortic aneurysm	76	(35-144)	48	(6-173)	
			Hypert. heart dis.	220	(136-336)	173	(111-258)	
			Other heart dis.	94	(71-122)	143	(111-180)	
Rahman et al (1999a) cross-sectional	1595 people from 4 villages in Bangladesh.1481 exposed to arsenic and 114 non exposed controls	Arsenic in drinking water. For 39, 36, 18, and 7%, the exposure was <0.5, 0.5 - 1, and >1 mg/L, and unknown, resp.	Expo category	mg/L yrs		PR* for hypertension (CI)		Used existing arsenic water measurements (measured by flow-injection hydride generation AAS). Hypertension defined as >140 mmHg systolic BP together with >90 mmHg diastolic BPStudy limited to the 1595 individuals out of 1794 eligible, who were at home at the time of the interview. 114 persons were considered unexposed and were used as the reference group.*PR = Mantel-Haenszel prevalence ratio adjusted for age, sex and BMI
			0			0.8 (0.3 - 1.7)		
			< 5			1.5 (0.7 - 2.9)		
			5 - 10			2.2 (1.1 - 4.4)		
			>10			3.0 (1.5 - 5.8)		
Cuzick et al, 1992 cohort	478 patients treated with Fowler's solution for 2 weeks - 12 years in 1946-60 and followed until 1990	Cumulative dose <500 mg, 500-999 mg, 1000-1999 mg; ≥2000 mg	Mortality from vascular diseases					The SMR's for the whole group. No dose-response relationship observed, but the numbers

						were small.
				SMR	CI	
			Cardiovascular disease	91	74-110	
			Ischemic disease	85	60-110	
			Cerebrovascular disease	72	40-110	
Enterline et al (1995) cohort	2802 men who worked in the smelter for ≥ 1 yr during 1940-64, vital status followed 1941-1986	Ambient air in a smelter	Cum. exp.	Isch. Heart dis	Cases	Exposure assessed from industrial hygiene data (available from 1938) and extrapolation from urinary arsenic concentrations
			$mg \cdot m^{-3} \cdot yr$	SMR		
			< 0.75	108	55	
			0.75 -	103	67	
			2.0	107	74	
			4.0	122	87	
			8.0	128	91	
			20	132	46	
			≥ 45	90	8	
Hertz-Picciotto et al, 2000 Cohort	2802 men who worked in the smelter for ≥ 1 yr during 1940-64, vital status followed 1940-1976 (same cohort as in Enterline et al., 1995, but a shorter follow-up time)	Ambient air in a smelter	Cum. exp.	Isch.	Heart dis	20-year lag and work status imcluded in the modelNo effects found for cerebrovascular disease.
			$mg \cdot m^{-3} \cdot yr$	RR	CI	
			< 0.75	1.0		
			0.75 - 1.999	0.9	0.64-1.3	
			2.0-3.999	1.1	0.78-1.6	
			4.0-7.999	1.4	0.98-2.0	
			8.0-19.999	1.7	1.2-2.5	
			>20	1.5	0.95-2.5	
Lubin et al (2000) cohort	8104 white males employed for ≥ 1 yr before 1957. Vital status followed 1938 - 1987.	Ambient air in a smelter	Arteriosclerosis and coronary heart disease SMR 105 (CI 99-110); Cerebrovascular disease SMR 103 CI (93-115)			
Järup et al, 1989 cohort	3916 men who worked ≥ 3 mo in the smelter in 1928-1967. Vital status followed until 1981	Ambient air in a smelter. Categories for cumulative exposure < 0.25, 0.25 - 15, 15-100 and ≥ 100	Ischaemic heart disease SMR 107 (CI 97-117); Cerebrovascular disease SMR 106 (CI 88-126)			In an earlier report (Axelson et al, 1978), a two-fold increase in mortality from cardiovascular disease

		mg m^3 yr			
Tokudome & Kuratsune (1976); cohort	839 copper smelter workers	Ambient air in a smelter	7 Deaths from heart diseases vs 14.9 expected		
Armstrong et al (1979); cohort	1974 gold miners	Air-borne exposure to arsenic, radon, silica	Ischaemic heart disease SMR 103 (173 expected cases)		
Simonato et al (1994); cohort	1330 gold mine and refinery workers	Air-borne exposure to arsenic, radon and silica	SMR for “diseases of the circulatory system” 54 (CI 39-73)		
Sobel et al (1988); cohort	611 workers of a pesticide plant	Inhalation exposure to arsenic	SMR for all circulatory diseases 80 (CI 65-98)		
Jensen & Hansen (1998) cross-sectional	32 arsenic exposed workers and 26 non-exposed referents	Average urinary As 35.9 for the exposed and 14.5 µmol/mol creatinine for the referents	Average systolic blood pressure 128 among the exposed, and 120 among the referents, p = 0.023		The exposed group included taxidermists, garden fence makers, week-end cottage constructors, wood impregnators, electric pole impregnators, new house constructors

Peripheral vascular diseases

As mentioned above, arsenic has been linked to development of the peripheral artery disease, Blackfoot disease (BFD) that is endemic in parts of Taiwan. The condition is characterized by an insidious onset of coldness and numbness in the feet, followed by ulceration, black discoloration and subsequently dry gangrene of the affected parts.

Studies from Taiwan have clearly demonstrated that exposure to arsenic via drinking water is associated with BFD, with significant exposure-response relationships relating both the duration and level of exposure to observed effects (WHO, 2001). For example, in a cohort of 789 BFD-patients followed for 15 years, Chen et al. (1988) have reported that there was a significant increase in the number of deaths from peripheral vascular diseases (and from cardiovascular diseases) relative to death rates in both the general Taiwanese population and among residents of the BFD-endemic area. The same authors have also demonstrated that in case-control study of 241 BFD-patients, there was a significant exposure-response relationship between the risk of BFD mortality and length of duration of residence in the area of arsenic-contaminated artesian well water.

An increased risk of peripheral vascular disease (PVD) was also found in a study of subjects residing in 42 villages located in the BFD-endemic area of south western Taiwan (Wu et al., 1989). Age-adjusted mortality rates for peripheral vascular diseases increased with increasing median concentrations of arsenic well water of < 0.30 mg/L, 0.30-0.59 mg/L and > 60 mg/L in a dose-response relationship. More recently, Tseng et al. (1996) have attempted to establish a link between long-term arsenic exposure and PVD morbidity using Doppler ultrasound techniques to detect the presence of disease. Again, the risk of PVD was found to increase with increasing cumulative exposure to arsenic; the effect was evident also among people whose exposure to arsenic had significantly decreased.

The extreme form and high prevalence of BFD found in Taiwan has not been observed in other regions. It is probable therefore, that other factors, such as malnutrition or concurrent exposures, are playing a role in the pathopyhysiology of the disease (WHO, 2001). There is, however, good evidence from several studies performed in other countries that exposure to arsenic causes other forms of PVD. For example, Swedish copper smelter workers (n=47) who had been exposed to arsenic (for a mean of 23 years), had a high prevalence of “white fingers” or Raynaud’s phenomenon compared with 48 controls (Lagerkvist et al., 1988). As the condition did not disappear during the summer, when workers took their long holiday, it was considered to be related to arsenic exposure.

Cardio- and cerebrovascular diseases

Studies linking exposure to arsenic and mortality from cardiovascular diseases are also summarized in Table 3.5. Whereas studies in Taiwan involving BDF-patients have shown significant associations, including exposure-response relationships between arsenic concentrations in well waters and death rates from cardiovascular disease (Chen et al., 1988; Wu et al., 1989; Chen et al., 1996; Tsai et al., 1999), drinking water studies conducted in other world regions, albeit at lower exposure levels, have been less conclusive (WHO, 2001). For instance, Engel and Smith (1994) carried out an ecologic mortality study in which mortality due to cardiovascular diseases in 30 US counties was compared to the expected numbers of deaths generated by US mortality rates. The results indicated excess mortality rates for diseases of the arteries and anomalies of the circulatory system. The standard mortality ratios (SMRs) for these diseases were elevated for areas with an arsenic concentration of greater than 20 ug/L, but wereclose to 1.0 in the two lower concentration categories (5-10 ug/L and 10-20 ug/L) for both sexes. SMRs for aneurysms and arteriosclerosis were also elevated for arsenic concentrations greater than 20 ug/L. The SMRs for congenital anomalies of the heart and for congenital anomalies of the circulatory system were elevated in females at arsenic concentrations of greater than 20 ug/L only (Engel & Smith, 1994).

A subsequent mortality study by Lewis et al. (1999) examined several mortality outcomes among a cohort of individuals from Millard County, Utah, USA. The cohort was assembled using historic membership records dating from the early 1900s through to the mid-1940s from the Church of Jesus Christ of Latter-Day Saints (Lewis et al., 1998b). SMRs were calculated separately for males and females using death rates from the State of Utah to generate the expected numbers for selected causes of death coded from the death certificates. Results indicate a significant excess of deaths for cardiovascular diseases (including hypertensive heart disease) among males (SMR=2.20) and among females (SMR=1.73), and all other heart disease among females (SMR=1.43) (Lewis et al., 1998a; 1999). When SMRs were analysed according to low (<1000 ppb-ug/L), medium (1000-4999 pbb-ug/L), and high arsenic exposure index values (5000 to >5000 ppb-ug/L), the increases of hypertensive heart diseases were not sequential (i.e. there wasno dose-response relationship) from low to high exposed groups (SMRs=2.37, 1.91, 2.29 respectively, for low, medium, and high groups). A non-significant excess of deaths from arteriosclerosis was also noted (Lewis et al., 1999).

In contrast, there is only limited evidence for an association between arsenic exposure and cerebrovascular diseases. A few Taiwanese studies have shown an elevated risk of death from cerebrovascular disease with increasing arsenic exposure, most notably that of Chiou et al. (1997). Other studies in this region have, however, not produced similar findings (Wu et al., 1989); elevations in mortality rates due to cerebrovascular diseases, if present at all, are only small compared with those for cardiovascular disease (Tasi et al., 1999). Furthermore, studies from other countries provide only very limited support for the Taiwanese findings (WHO, 2001).

Studies involving occupationally-exposed subjects have also been used to explore the relationship between arsenic exposure and vascular diseases. Again, the weight of evidence points to a fairly strong association between arsenic exposure and cardiovascular diseases, but only a weak link with cerebrovascular diseases. Most of the studies of this type are concerned with miners and metal smelter workers where the inhalation of arsenic-polluted air is the main route of exposure (see Table 3.5). In the Tacoma cohort Enterline et al. (1995) reported a significant excess of ischaemic heart disease (428 deaths, $p<0.01$), with a weak dose-response relationship. In an updated analysis of the same cohort, evidence of an association was stronger and a clear-cut dose-response relationship observed (Hertz-Picciotto et al., 2000). This is in marked contrast to an earlier study, when no excess in heart disease was found (Enterline and Marsh, 1982).

Mortality during 1939-1977 from diseases of the heart was elevated among the members of the Montana cohort (SMR 1.30 based on 1366 observed and 1051.5 expected cases, $p<0.01$) (Lee-Feldstein, 1983). In a subsequent study among workers at the same smelter, no significant increase in mortality from arteriosclerosis/coronary heart disease or from cerebrovascular disease was observed (Lubin et al., 2000). Although the first report on the Rönnskär cohort reported a two-fold increase in the mortality from cardiovascular disease (Axelson et al., 1978), a later update found no relationship (Järup et al., 1989). In the Japanese smelter cohort (Tokudome & Kuratsune, 1976), there was a deficit in the mortality from heart diseases. No elevated mortality from cardiovascular disease mortality was observed among French or Australian gold miners, or US pesticide production workers (Simonato et al., 1994; Sobel et al., 1988; Armstrong et al., 1979).

Hypertension

Evidence for an association between long-term exposure to arsenic and the prevalence of hypertension is limited to only a few studies, two environmental and one occupational.

Nevertheless, all three studies found elevations in blood pressure with arsenic exposure. Chen et al. (1995) studied a total of 382 men and 516 women residing in villages in the BFD-endemic regions of Taiwan. Arsenic-exposed residents had a 1.5-fold increase in age- and sex-adjusted prevalence of hypertension compared with residents in non-endemic areas. This study concluded that long-term arsenic exposure may induce hypertension in humans (Chen et al., 1995).

The prevalence of hypertension among residents in Bangladesh, with and without arsenic exposure, has been evaluated recently by Rahman et al. (1999). A total of 1,481 subjects exposed to arsenic contaminated drinking water and 114 unexposed subjects were analysed for their time-weighted mean arsenic levels. There was a significant dose-response relationship between arsenic exposure and increased blood pressure ($p<0.01$). Potential limitations of the study include lack of information on other trace elements in the water, not all eligible participants were identified and that direct measurement of exposure rather than recall of exposure is preferred.

In a group of 40 Danish workers exposed to arsenic in different trades (average urinary arsenic level 22.3 umol/mol creatinine; twice that of the referents), blood pressure was slightly elevated among the exposed group, reaching statistical significance for the systolic but not for the diastolic value (Jensen & Hansen, 1998).

3.3.2.2 Cancer

The earliest indications that exposure to arsenic and cancer were related date back to the late 1930s and early 1940s. In the seminal investigation of 1948, a remarkably elevated relative cancer mortality rate from lung and skin cancer was observed amongst workers at a sheep-dip factory that manufactured sodium arsenite (Hill & Faning, 1948). Subsequently, Roth (1958) reported that autopsies of 47 winegrowers, who had showed signs of arsenic intoxication, revealed that 13 of the subjects had altogether 40 skin cancers and 19 had lung cancer. Case series indicated that the lung cancer mortality was unexpectedly high among Rhodesian gold miners; exposure to arsenic was considered an etiological factor (Osburn, 1957, 1969). Original suspicions that ingested arsenic could cause lung cancer were provided by a study in the Argentine province of Cordoba, where mortality records for all deaths occurring between 1949 and 1959 in areas with high arsenic level in drinking water (weighted average approximately 600 ug/L) were compared with cause-specific mortality rates from the entire province. Thirty five percent of all cancer deaths were related to respiratory organs (Bergoglio, 1964).

Detailed investigations into elevated cancer risks amongst copper smelter workers exposed to arsenic in the air were initiated in the 1960s; these studies were primarily concerned with the development of respiratory cancers, in particular lung cancers. Over the past 20-30 years, research effort has also focused on the likely relationship between various types of cancers and exposure to arsenic through the consumption of drinking water. Much of this type of work has centred on populations in the BFD-endemic parts of Taiwan, but there are reports of elevated cancer risks at multiple sites (notably lung, skin, bladder, kidney and liver) from other parts of the world including Japan, Chile and Argentina where subsets of the population are exposed to arsenic-contaminated drinking water. A considerable body of scientific research work has accumulated on the subject and several comprehensive reviews have been published in recent years (WHO, 1981, 2001; IARC, 1973, 1980, 1987).

Cancers of the lung, bladder and kidney

Exposures via drinking water

As mentioned above, the link between cancers of the lung, bladder and kidney and arsenic exposure in drinking water has been most thoroughly studied in Taiwan. Here, studies of differing design have consistently shown high mortality risks from lung, bladder and kidney cancers among populations exposed to arsenic via drinking water. Moreover, where exposure-response relationships have been investigated, the risk of cancer for these sites increases with increasing exposure.

The findings of selected epidemiological studies based on the Taiwanese populations are briefly outlined below; additional details are provided in **Table 3.6.** Chen and co-workers (Chen et al. 1985) published one of the first mortality studies; they investigated cancer mortalities in 84 communities in four townships located in the south-western coastal region of Taiwan (a known BFD-endemic area) and found a statistically significant excess of bladder, kidney, skin, lung and liver cancer deaths for both males and females, compared to the Taiwanese population as a whole. Areas with a greater Blackfoot disease generally had more of an excess of cancer mortality than did areas with lower Blackfoot disease prevalence (Chen et al., 1985).

Table 3.6 Studies on cancer following oral exposure to arsenic (via drinking water, unless otherwise stated; excludes skin cancers)

Source: WHO, 2001

Table 3.6 Studies on cancer following oral exposure (via drinking water, unless otherwise stated). For cancer of the skin, see Table 3.7

Authors, study design	**Study Population**	**Source and level of arsenic exposure**	**Health effects, metric of exposure and measure of association**			**Comments**
Chen et al (1985) Ecological	BFD-endemic area of Taiwan; mortality 1968-1982	Drinking water up to 1.14 mg/L, decreasing with take into use of reservoir water starting in 1956		SMR (CI), Males	Females	Small intestine, oesophagus, rectum, stomach, naso-pharynx, leukaemia, thyroid were not significantly elevated in males or females. Population of Taiwan as the reference
			Bladder:	1100 (933-1267)	2009 (1702-2316)	
			Kidney:	772 (537-1007)	1119 (938-1400)	
			Liver:	170 (151-189)	229 (192-266)	
			Colon:	160 (117-203)	168 (126-210)	
			Lung:	320 (286-354)	413 (360-466)	
Chen et al (1986) case-referent	69 bladder, 76 lung, 65 liver cancer decedents in Taiwan in 1980-1982. 65 live controls	<40 years of use of artesian water in black foot disease endemic area up to 1.14 mg/L	OR for years of use of arsenic contaminated water:			Deceased cancer cases.OR's adjusted for age, sex, cigarette smoking, tea drinking, vegetarian habit, vegetable

	matched by age and sex.							consumption frequency and fermented bean consuption frequency, when the factor was significant at $p<0.1$.Referents from the same area
			Site	none	1-20	21-40	>40	
			Bladder	1.0	1.3	1.7	4.1 ($p<0.01$)	
			lung	1.0	1.1	1.5	3.0 ($p<0.01$)	
			liver	1.0	0.9	1.1	2.0 ($p<0.1$)	
Chen et al (1988b) Cohort	Cohort of 789 Blackfoot disease patients (15 years and 7278 person years of follow-up).	Drinking water concentrations 350-1140 μg/L	SMR	National ref rate		local ref rate		10.6% lost to follow-up
			Bladder	3880	($p<0.001$)	255	($p<0.01$)	
			Kidney	1953	(NS)	160	(NS)	
			Prostate	1729	(NS)	268	(NS)	
			Lung	1049	($p<0.001$)	284	($p<0.01$)	
			Liver	466	($p<0.001$)	248	($p<0.01$)	
			Colon	381	($p<0.05$)	230	(NS)	
			Esophagus	305	(NS)	222	(NS)	
			Stomach	194	(NS)	202	(NS)	
Wu et al (1989)	Mortality and population	Used data from the 1964-1966	Age-adjusted mortality rates per 10^5 in males by well As conc.					Observed numbers of

Ecological	data from 1973-1986 in 42 villages in Taiwan.	survey of 155 wells in 42 villages and used village medians in the analysis						deaths smaller than in the Chen et al 1992 study, although the person-years are identical.No significant association for leukemia or cancer of nasopharynx, oesophagus, stomach, colon or uterine cervix
			Males	< 300	300 - 599	³600 µg/L	p	
			Bladder	22.6	61.0	92.7	< 0.001	
			Kidney	8.4	18.9	25.3	< 0.05	
			Lung	49.2	100.7	104.8	< 0.001	
			Liver	47.8	67.6	86.7	< 0.05	
			Prostate	1.0	9.0	9.2	< 0.05	
			Females					
			Bladder	25.6	57.0	111.3	< 0.001	
			Kidney	3.4	19.4	58.0	< 0.001	
			Lung	36.7	60.8	122.2	< 0.001	
			Liver	21.4	24.2	31.8	NS	
Chen & Wang (1990) Ecological	Mortality from malignant neoplasms in 1972-83 in 314 precincts and townships in Taiwan	74% or precincts had <5% wells with ≥50µg/L As, 15% has 5-14% and 12% had ≥15% such wells. Village mean used in analysis.	Statistically significant association between arsenic level in well water and mortality from the cancer of the lung, liver, kidney, bladder, skin, prostate, and nasopharynx after adjustment for indices of urbanisation and industrialisation					Nearly all cancer deaths among the arsenic exposed included in the Chen et al (1985) study No numerical risk estimates given.
Chiang et al	Incident	Arsenic-	Average annual age-adjusted incidence of bladder cancer per					Tumour registry

(1993), ecological	bladder cancer cases 1981-5 identified from tumour registry in 4 BFD-endemic and 2 neighbouring counties vs whole Taiwan	contaminated water in the BFD-endemic area in Taiwan	100 000 in the 4 counties 23.5, in the neighbouring counties, 4.45 and 2.29 in the whole of Taiwan			not validated
Chiou et al (1995) Cohort	263 blackfoot disease patients and 2293 residents in Taiwan. Follow-up of 7 years.	Cumulative As exposure for drinking water from village median well As concentration as determined in the 1964-6 survey	Cum expos	SMR (CI)		Adjusted for age, sex, smoking, black foot diseaseDeaths not overlapping with older studies in Taiwan. Cases of BFD and referents largely from different villages
			mg/L-yr	Bladder Cancer	Lung cancer:	
			0	100	100	
			0.1-19.9	160 (44 - 560)	274 (69 - 1100)	
			20+	360* (110 - 1220)	401 (100 - 1612)	
Guo et al (1997) Ecological	243 Taiwanese townships - approximately 11.4 million residents. Incident cases of urothelial and kidney cancer 1980-87	Arsenic measured in over 80,000 wells from 1974-1976 in 78% of townships average As content was nondetectable, in 91, below 50 and in 99.5%, below 640 µg/L	Estimated rate difference per 10^5 for 1% increase in the proportion of wells in the highest exposure category (640 µg/L):			Used mercuric bromide method to analyse arsenic. Smoking not included in the models as not good predictor for any cancer in this study. Tumor registry not validated
				Males	Females	
			Transitional cancer/bladder	0.57	0.33	
			Transitional cell/kidney	0.03	0.14	
			Transitional cell/ureter	0.11	0.10	
			All urethral cancer	0.056	0.027	
Tsai et al (1999) Ecological	4 townships in BFD-endemic area in Taiwan, mortality in 1971-1994, compared to local and national rates	Drinking water up to 1.14 mg/L, decreasing with take into use of reservoir water starting in 1956	Cancer SMRs for females and males combined, compared to local rates			Age- and sex-specific mortality rates based on population data from Miniistry of Interior, deaths from computer data base on deaths. 99% of causes of deaths based on diagnosis of a physician. All cancers

									confirmed by pathological examination. Overlaps with earlier Taiwan studies.
				SMR	CI	SMR	CI		
			All malignant	219	211-228				
			Oesophagus	167	130-212	Lung	310	288-334	
			Stomach	136	117-146	Bone	246	177-334	
			Small intestine	210	120-354	Prostate	252	186-334	
			Colon	149	120-183	Bladder	892	796-996	
			Liver	183	169-198	Kidney	676	546-827	
			Nasal	300	214-409	Lymphoma	163	123-211	
			Laryngeal	178	120-255	Leucaemia	134	104-170	
Morales et al, 2000 Ecological	Mortality and population data from 1973-1986 in 42 villages in Taiwan.	Drinking water concentrations 350-1140 µg/L	SMRs men and women,						Used data from the 1964-1966 survey of 155 wells in 42 villages and used village medians in the analysis
			Well water As (µg/l)	Bladder cancer		Lung cancer			
			<50	1002		156			
			50-100	415		143			
			100-200	1047		243			
			200-300	766		308			
			300-400	744		197			
			400-500	2968		365			
			500-600	1490		332			
			600+	3270		514			
Hopenhayn-	Residents in	In the high	SMRs (95% CI) by exposure group:						No smoking

Rich et al (1996a, 1998) Ecological	Cordoba vs rest of Argentina	exposure group, in two selected towns, 42/61 and 49/57 measurements ≥40 µg/L. Highest measured concentration 533 µg/L					data, but no difference in COPD, used as surrogate, between exposure groupsCancer of liver, stomach or skin not significantly related to arsenic exposure
					<u>Males</u>		
				low	intermed.	high	
			Bladder	80 (66-096)	128 (105-153)	214 (178-253)	
			Lung	92 (85-098)	154 (144-164)	177 (163-190)	
			Kidney	87 (66-110)	133 (102-168)	157 (117-205)	
					<u>Females</u>		
			Bladder	122 (86-167)	139 (93-199)	182 (119 - 264)	
			Lung	124 (106-142)	134 (112-158)	216 (183 - 252)	
			Kidney	100 (71-137)	136 (94-189)	181 (119 - 264)	
Rivara et al (1997) Ecological	Region 2 (high exposure) Northern Chile compared to Region 8 (low exposure). Region 2 is arsenic endemic area Mortality 1952-1990	Drinking water arsenic concentration in 1950 - 1992 ND to 860 µg/L in different locations in Region 2. Average concentration < 200 before 1958, >500 1959-1977, < 100 thereafter	Cancer mortality	rate ratio	CI		Air levels of arsenic were measured in some locations and concentration s up to 2.7 µg/m^3 were observed at Chuquichamata, a copper smelter area in Region 2.
			All cancer:	1.2	1.17 - 1.21		
			Lung	5.6	5.3 - 6.3		
			Bladder	6.7	5.9 - 7.7		
			Kidney	2.7	2.4 - 3.1		
			Larynx	3.2	2.7 - 4.0		
			Liver	1.1	1.0 - 1.2		
Smith et al (1998) Ecological	Region 2 Chile (1989-1993) compared to the rest of Chile.	Drinking water Avg. 43-568 µg/L (1950-1994) Exposure decreased over time: 569 µg/L (1955-69) to 43	SMR (CI)	Males	Females		Routinely collected arsenic concentration measurements. Population is partially overlapping

		µg/L (1990-94)				Rivara (1997)
			Bladder cancer:	600 (480-740)	820 (630-1050)	
			Lung cancer:	380 (350-410)	301 (270-370)	
			Kidney cancer:	160 (110-210)	270 (190-380)	
			Liver cancer:	110 (80-150)	110 (80-150)	
Ferreccio et al (1998, 2000) Case-control	Three Regions in Northern Chile. 151 lung cancer cases in 1994-6, histologically confirmed. 2 referents per case	Drinking water levels measured in 1950-1996 by water companies	Mean lifetime exposure mg/L	OR (CI)		Some gaps in exposure measures in some yearsPatients with skin lesions had higher risk of lung cancer.Adjusted for age, sex and smoking status, occupational history.
			0-0.01	1		
			0.01-0.029	1.7 (0.5-5.1)		
			0.03-0.049	3.9 (1.2-13.4)		
			0.05-0.199	5.5 (2.2-13.5)		
			0.2-0.40	9.0 (3.6-22)		
Tsuda et al (1989, 1995) Cohort	Residents of Niigata, Japan (n = 467).	Drinking water contaminated with As from a factory in 1955-9. Water analysed for arsenic in 1959	SMR for ≥ 1 mg/L compared to 0 mg/L.			97.2% of residents in 1959 followed for vital status 1959-1992. RR controlled for smoking and age: Gender was correlated with smoking.
			All causes of death	174	110 - 274	
			All cancer	482	209 - 1114	
			Lung cancer	1972	434 - 895000	
			Mortality from “urinary” cancer significanlty elevated, SMR 627 (CI 171 - 1839).			
Bates et al (1995) Case-control	117 newly diagnosed histologically confirmed cases of bladder cancer in Utah, US and 266 population referents	Drinking water; Cumulative dose categories: <19 mg; 19-<33 mg; 33-<53 mg; ≥53 mg	OR for bladder cancer, adj. for sex, age, smoking, exposure to chlorinated water, history of bladder infection, high risk occupation, education level, urbanisation, in different cumulative exposure groups: 1.00; 1.6 (0.8 - 3.2); 1.0 (0.4 - 2.0); 1.4 (0.7 - 2.9)			Among ever smokers with As expousre 10-19 years earlier, an association between OR of quartiles of total proportion or arsenic contining drinking water of total daily fluid intake.
Buchet & Lison (1998) Ecological	Belgium, residents in areas with various exposures to arsenic.	Exposure from air (0.3 $\mu g/m^3$ annual mean); and water (20-50 µg.As/L). Daily geometric mean U-As 35 µg in the most exposed group (smelter area), 7-12 µg/d	Cancer of lung, kidney, bladder and leukemia studied. Increased RR, 1.3 (1.14 - 1.43) observed for lung cancer in males in smelter area compared to a lesser-exposed group.			Directly standardized rate ratios (SRRs) were used. The authors explained the increase lung cancer risk by occupational exposure. Other

		in the less exposed				“arsenic-linked” diagnosis was analyzed showing no elevated risks.
Hinwood et al (1999) ecological	Cancer incidence in 22 areas in Victoria, Australia, in 1982-91. Population size in 1986, 152 246	Soil/water arsenic elevated in some parts, medians for low water As areas 1 - 2 µg/L, and between 13 and 1077 for high water-As areas (median of medians, 80 µg/L)	SIR were below 120, and the confidence interval included unity for cancers of nasal cavity, lung, bladder, stomach, colon, rectum, Hodgkin’s lymphoma, non-Hodgkin’s lymphoma, multiple myeloma, acute and chronic lymphatic leukaemia, and acute myeloid leukaemia. The SIR for prostate cancer was 114 (CI 105-123), melanoma 136 (124-148), breast 110 (103-148), and for chronic myeloid leukaemia 154 (113-210). For liver cancer, the SIR was 53 (CI 34-82).			No information on coverage or frequency of water arsenic sampling. Postal codes that were used for calculating expected cases, represent large geographic areas and may lead to random misclassification. Rain water reservoirs at least at present are an important alternative source of drinking water again leading to exposure misclassification
Lewis et al (1999) Cohort	Mormons in Millard County, Utah, USAs	Median range: 14 µg/L - 166µg/L	SMR (CI)	Males	Females	Historic arsenic concentrations in drinking water used.Death rates for the state of Utah for the years 1960 to 1992 were used to generate the expected deaths.Decreased SMR for lung and bladder cancer and all cancers may be due to lower prevalence of smoking among cohort members than in the reference population of the State of Utah.Exposure for the highest exposure group likely to be overestimated because of introduction of low-arsenic water into one community, which was not considered in the analysis

			All causes	91 (86-96)	96 (92-104)	
			Non-malign. resp.	68 (54-85)	93 (70-120)	
			All cancer	82 (70-95)	73 (61-87)	
			Large intestine	50 (28-99)	74 (40-124)	
			Biliary tract &liver	85 (18-248)	142 (57-293)	
			Respiratory System	57 (38-82)	44 (16-95)	
			Prostate	145 (107-191)		
			Kidney	175 (80-332)	160 (44-411)	
			Bladder & other urinary organs	42 (8-122)	81 (10-293)	
Kurttio et al (1999) Case-referent	61 bladder and 49 kidney cancer cases and 275 referents not serviced by municipal drinking water supply, Finland	5% of reference group had arsenic in drinking water >5 µg/L and 1% (11/275) had consumed > 10 µg/L. Arsenic in drinking water <0.05 to maximum 64 µg/L. Detection limit 0.05 µg/L	Age-, sex- and smoking-adjusted risk ratios for bladder cancer when exposure 3-9 years prior to diagnosis			No association between cumulative arsenic exposure and bladder cancer.No association between well water arsenic and kidney cancer
			As in water	RR	CI	
			µg/L			
			< 0.1	1.0		
			0.1-0.5	1.5	0.8 - 3.1	
			³ 0.5	2.4	1.1 - 5.4	
Cuzick, et al (1992) cohort	478 patients treated with Fowler's solution for 2 weeks - 12 years in 1946-60 and followed until 1990	Exposure from treatment with Fowler's solution. Cumulative dose <500 mg, 500-999 mg, 1000-1999 mg; ≥ 2000 mg	Mortality from cancer in the entire cohort			No dose response observed
				SMR	CI	
			All cancer	95	17 - 130	
			Bladder	307	101 - 730	
			Liver	123	40 - 470	
			Hematopoietic system	38	1 - 200	
			Digestive organs	119	70 - 190	
			Stomach	99	30 - 170)	
			Respiratory System	100	50 - 170	
			Skin	244	8 - 1400	

Chen and co-workers also performed a case-referent study on malignant neoplasms in the same population (Chen et al., 1986). The cases comprised persons who had died of bladder, lung or liver cancer, the diagnosis having been confirmed by biopsy or other techniques. The results demonstrated an increasing risk of cancers of the lung, bladder and liver with increasing duration of exposure. The trend remained significant for cancers of the lung and bladder after adjustments for age, sex, cigarette smoking, tea drinking, vegetarian habits and vegetable consumption, and fermented bean consumption (all potential confounders) had been made (Chen et al., 1986).

Cancer mortality statistics of residents from 42 villages in five townships in the BFD-endemic part of Taiwan (i.e. a smaller, but partly overlapping population sample relative to that considered by Chen et al. (1985, 1986)) have been analysed by Wu et al. (1989). The mortality data spanned the period 1973-1986; well water arsenic concentrations had been monitored in the early 1960s and were used to classify the villages into three categories based on median well water concentrations, < 300 ug/L, 300-590 ug/L and > 600 ug/L. Again, the age-adjusted mortality rates for lung, liver, kidney, bladder (and skin) cancer showed a significant dose-response increase in relation to drinking water arsenic concentration in both men and women (Wu et al., 1989).

An island-wide ecologic study of cancer mortality was conducted by Chen & Wang (1990) using data on deaths from cancer in 1972-83 and on arsenic concentrations in well water from 1974-76. The average township well water arsenic concentration was taken as the indicator of arsenic exposure. The relationship between arsenic exposure and mortality from cancer at 21 different sites was analysed by multiple linear regression, the results of which (after adjusting for levels of industrialisation and urbanisation) indicated that the magnitude of the increase in risk associated with arsenic concentration in well water was similar for both males and females for nasal cavity, lung, skin, bladder, and kidney cancers. Mortality from liver cancer was three times higher for men than for women. In addition, a positive association between well water arsenic and mortality from prostate cancer was observed (Chen et al., 1990).

The incidence of bladder cancer has been investigated by (Chiang et al., 1993) who found a higher annual incidence of bladder cancer (23.53 per 100,000 persons) in the BFD-endemic area compared with the average incidence in Taiwan as a whole (2.29 per 100,000 persons). The ratio of male to female bladder cancer in the BFD-endemic area and the neighbouring area was 1.24 and 1.09, which was lower than that in all of Taiwan (2.75) and compared with elsewhere around the world. The lack of disparity of bladder cancer rates between males and females supports the view that a common environmental factor shared by both sexes in the endemic area is responsible (Chiang et al., 1993). Another study found increased incidence rates for bladder cancers and transitional kidney cell cancers when incidence rates at high and low exposures to arsenic were compared (Guo et al., 1997).

Deaths from cancer occurring between 1986-1993 in a study population of 263 BFD-patients and 2,293 healthy subjects, not previously included in the Taiwanese studies, were analysed as part of a cohort study by Chiou et al. (1995). A statistically significant positive association between arsenic exposure (i.e estimated cumulative arsenic exposure from drinking artesian well water in $mg/yr/L^{-1}$) and cancer of the lung and bladder was found to exist even after adjustment for age, sex, cigarette smoking and Blackfoot disease status.

The work of Tsai and colleagues (Tsai et al., 1998) indicates that reductions in drinking water arsenic concentrations may have contributed to a decrease in the incidence rates of various cancers. Analysis of age-adjusted mortality rates for cancers of the lung, liver, bladder and skin combined in 4 townships in Taiwan, where there had been a fall in arsenic concentrations in drinking water since the 1970s, showed a gradual decrease in the risk of cancer in males aged > 40 years. In women the lowest risk was found to be in the most recent time periods studied (i.e. since 1988) irrespective of age, while for men < 40 years of age little change was observed.

Reports of increased cancer risk from exposure to exposure to arsenic in drinking water are not confined to Taiwan; studies from Argentina, Chile Japan and Finland have also demonstrated positive associations. For example, a small historical cohort study carried out between 1959-1992 in the Niiagata Prefecture, Japan, followed 454 subjects exposed to arsenic-contaminated well water; the contamination arose as a result the discharge of wastewater effluents from a factory producing arsenic trisulfide (King's yellow). This study found that subjects exposed to arsenic in well water of greater than 1 mg/L had a significant number of excess deaths from lung cancer (SMR=15.69, number observed = 8) and urinary tract cancer (SMR=31.18, number observed = 3) while subjects exposed to moderate or low concentrations of arsenic of 0.05-0.99 mg/L and less than 0.05 mg/L respectively showed a nonsignificant excess for lung cancer at the 0.05-0.99 mg/L level. Significantly elevated SMRs were also found for liver and uterine cancers with SMRs of 7.17, and 13.47 for exposures >1 mg/L (2 deaths were observed for each of these causes). A strong association was also observed between arsenic-induced lesions identified in 1959 and subsequent mortality from lung cancer (Tsuda et al., 1995).

A similar study was carried out in Northern Chile; cancer mortality data for Region II (an area where arsenic concentrations in drinking water had been high; range <100 ug/L to 570 ug/L) covering the period between 1989 and 1993 region were compared with age-adjusted mortality rates for the rest of Chile. Mortality rates for both lung and bladder cancers were elevated in Region II; SMRs for bladder cancer were 6.0 (95% CI= 4.8-7.4) for men and 8.2 (95% CI=6.3-10.5) for women. The SMRs for lung cancer were 3.8 (95% CI = 3.50-4.10) for men and SMR=3.1 (CI = 2.70-3.70) for women in this region, and smoking did not appear to be a major confounding factor (Smith et al., 1998). In a more recent Chilean study, based on a set of 151 lung cancer patients (and 417 referents), lung cancer risk was found to increase in a dose-response relationship over five exposure categories. The increased risk was statistically significant at concentrations of 30-50 ug/L and above (Ferreccio et al., 1998, 2000).

Increased mortality from lung and bladder cancers was also found to be linked to increased drinking water arsenic concentrations in the eastern region of the Cordoba province in Argentina (Hopenhayn-Rich et al., 1996). Mortality data from 26 counties in the Cordoba province for the period 1986-1991 were compared with estimated mortality data for the whole of Argentina. The counties were divided into three exposure groups - low, medium and high - depending on their drinking water arsenic concentration (limited number of available measurements) and on the number of reports of arsenical skin diseases. The mortality from lung, kidney and bladder cancer was lowest in the counties with the presumed lowest drinking water concentration, intermediate in the medium exposure counties and greatest in the high-exposure counties (average concentration in the high-exposure group=178 ug/L in drinking water). Despite the different genetic composition and the high protein diet of the study population, the findings generally support results from studies in Taiwan (Hopenhayn-Rich et al., 1996; 1998).

A study of the risk of bladder and kidney cancer in a cohort of people from Finland that had been using drilled well water as drinking water over a period of 13 years (1967-1980) has recently been published (Kurttio et al. 1999). The study population comprised a group of 61 bladder cancer cases, 49 kidney cancer cases and 275 control subjects; exposure history was reconstructed from questionnaire data on residence and from measurements of arsenic in the well water made in 1996 (range < 0.05 - 64 ug/L; median 0.14 ug/L). No association was made for kidney cancer.

However, in the case of bladder cancer, there was an increased risk associated with an increased arsenic intake during the third to ninth year prior to the cancer diagnosis, which reached statistical significance in the high-dose group (i.e. well arsenic > 0.5 - 64ug/L). Bladder cancer risk ratios for longer latency periods of 10 years or more were not elevated.

Not all studies of populations exposed to arsenic via drinking water have conclusively shown positive findings for increased, lung, bladder and kidney cancer (see **Table 3.6**). Several mortality studies from the USA, for example, have not shown positive associations between ingested arsenic and lung cancer. An ecological study based on records of average drinking water arsenic concentration at the county level found no significant excess county lung cancer mortality (Engel & Smith, 1994). The case-referent study conducted by Bates et al. (1995) as part of the US National Bladder Cancer Study involving communities in Utah showed no significant increase in bladder cancer risk with increasing exposure to arsenic in drinking water in non-smokers.

However, among smokers, there is some evidence to suggest that bladder cancer risk may be associated with arsenic intake (two indices of arsenic exposure were used, but only one of the two gave a positive result). The drinking water arsenic concentrations were relatively low, 0.5 - 160 ug/L with an average of 5.0 ug/L.

A recent analysis by Lewis et al. (1998b, 1999) of cancer incidence among Mormons in Utah found no evidence of excess deaths for lung or bladder cancer among males or females. However, the study indicated a slightly elevated, but not statistically significant mortality from kidney cancer in both males and females (SMR = 1.75 and 1.60, respectively). Significant excess mortality from nephritis and nephrosis, a noncancerous condition of the kidneys, for males (SMR=1.72) and females (SMR=1.21, non-significant) leaves the possibility that the kidney is a target organ of arsenic for noncancerous conditions (Lewis et al., 1998b).

Studies in Belgium and Australia have also failed to find conclusive evidence of a link between arsenic exposure in drinking water and cancers of the lung, bladder and kidney. Buchet & Lison (1998) reported that mortality ratios did not support an association of cancer with drinking water exposures in a population living in the vicinity of a conglomeration of non-ferrous smelters. Arsenic concentrations were again relatively low, the area of highest exposure having measured concentrations in the range 20-50 ug/L. Similarly in Victoria, Australia Hinwood et al. (1999) SIRs were below 120 (with the confidence interval including unity) for most cancers, including lung and bladder.

In addition to drinking water, the ingestion of Fowler’s solution (potassium arsenite) by individuals has also been associated with elevated cancer mortality. An excess of skin cancer and a significant excess of bladder cancer mortality have been observed in a cohort of patients exposed to Fowler’s solution (Cuzick et al., 1992).

Exposures via inhalation

Studies on populations occupationally exposed to arsenic, such as non-ferrous metal smelter workers, pesticide manufacturers and miners, have consistently demonstrated an excess lung cancer risk among those exposed. Dose-response relationships have been investigated in those populations were there is sufficient information on the levels of exposure. The most important studies of this type are based on data obtained from three copper smelters, in Tacoma (Washington, USA), Anaconda (Montana, USA) and Rönnskär (Sweden). In all three cohorts, a statistically significant increase in lung cancer risk with increasing exposure has been demonstrated.

Results of studies from the Tacoma copper smelter have been published in a series of papers (Pinto & Bennett, 1963; Pinto et al., 1977, 1978; Enterline & Marsh, 1980, 1982; Enterline et al., 1987a, 1995). The most recent considers mortality rates among 2,802 men, all of whom had worked at the smelter for at least one year during the period 1940-1964 (Enterline et al., 1995). An increase in lung cancer risk with increasing cumulative arsenic exposure was observed (SMR of 316 in the highest exposure category). When the SMR is plotted against cumulative arsenic exposure on an arithmetic exposure scale, relatively larger increments in respiratory cancer risk are observed at low exposure levels, i.e., the dose-response curve is concave downward (Figure 3.2).

Figure 3.2 Respiratory cancer risk in three copper smelter cohorts

Source: Enterline et al., 1995 (PENDING)

Elevated lung cancer risks among workers in the Anaconda copper smelter have also been well documented in the literature (Lee and Fraumeni, 1969; Lee-Feldstein, 1983, 1986, 1989; Lubin et al., 1981; Welch et al., 1982; Brown and Chu, 1983a,b). The study population of the most recent cohort study (Lubin et al., 2000) consists of 8,014 white males, who were alive on 1 January 1938 and who had been employed at the smelter at least 12 months prior to 1957. Vital status was followed from 1938 to 1987. In the “heavy” arsenic exposure work areas the estimated mean airborne arsenic concentration was 11.3 mg/m^3, and for the “medium” and “light” exposure areas it was 0.6 and 0.3 mg/m^3, respectively. For each worker, the cumulative exposure was estimated from his time of working in different work areas. Of the total 4,930 known deaths amongst the study population, 446 were due to lung cancer (SMR = 155). A trend of increasing risk with increasing estimated exposure was seen; the risk increased linearly with length of employment in each exposure category.

The elevated lung cancer incidence among workers of the Rönnskär smelter in northern Sweden was originally reported in a population-based case-referent study in St Örjan parish in 1978 (Axelson et al., 1978). Thereafter, studies using both cohort and case-referent approaches have been published (Wall, 1980; Pershagen et al., 1981, 1987; Järup et al., 1989; Sandström et al., 1989; Järup & Pershagen, 1991; Sandström & Wall, 1993). The study population comprises 3916 male smelter workers, who had worked for at least 3 months in the smelter between 1928 and 1967. Using air concentrations estimated by the factory industrial hygienists, each work site has been characterised by an exposure level during three consecutive time periods, and the workers’ cumulative exposure derived from his working history in these different work sites. Information on mortality was compiled from death certificates, and mortality rates due to lung cancer compared with local rates. A dose-dependent increase in lung cancer mortality was observed, and a statistically significantly increased risk was observed even in the lowest exposure category, that is < 0.25 mg/m^3/yr. However, in a nested case-referent study on the interaction between smoking and arsenic exposure little increased risk of lung cancer due to arsenic exposure was observed among smokers or non-smokers in exposure categories below 15 mg/m^3/yr (Järup & Pershagen, 1991). In most subcohorts, and in the total cohort, the mortality increased with increasing average intensity of exposure, but no clear-cut trend was observed for the duration of exposure. Exposure to sulphur dioxide was also assessed. The lung cancer risk was elevated in all sulphur dioxide-exposed groups, but there was no dose-response relationship between cancer risk and the estimated cumulative sulphur dioxide exposure.

Collectively, these three studies demonstrate a statistically significant excess risk of lung cancer at arsenic exposure levels of approximately > 75 mg/m^3/yr. The risk seems to increase more rapidly with dose at low cumulative dose levels than at higher exposures. It is interesting to note that the general form of the dose-response is rather similar in the three studies; however, the relative risks differ substantially between the Swedish study on one hand, and the American studies on the other (Figure 3.2). Although these groups of workers will have been exposed to other chemicals in addition to arsenic, it is considered unlikely that some other common factor could explain the findings. The role of tobacco smoking has been considered in several studies and was not generally found to be the cause of the increased lung cancer. It was, however, found to be interactive with arsenic in increasing the risk of lung cancer (WHO, 2001).

Increased lung cancer risks have also been observed in workers employed at pesticide manufacturing plants (Ott et al., 1974; Sobel et al., 1988; Mabuchi et al., 1979, 1980) and amongst tin miners in the UK and China (Hodgson & Jones, 1990; Qiao et al., 1997) and gold miners in France (Simonato et al., 1994), Canada (Kusiak et al., 1991, 1993) and Australia (Armstrong et al., 1979). Furthermore, several studies have reported an increased mortality from lung cancer in populations residing in areas close to arsenic-emitting industries, including for example, nonferrous metal smelter complexes (Blot & Fraumeni, 1975; Brown, et al., 1984; Pershagen, 1985) and factories producing arsenical pesticides (Matanoski et al., 1981).

In contrast to the situation for lung cancers, kidney or bladder cancer risks are not consistently elevated in studies among people occupationally exposed to arsenic. Although early autopsy series (Roth, 1955, 1957a; b) on wine growers have linked exposure to arsenic to hepatic angiosarcoma, later studies have failed to provide conclusive evidence for such a link. Among 168 persons diagnosed with hepatic angiosarcoma in the USA, occupational exposure to arsenic could be demonstrated in only four cases and exposure to Fowler's solution in only six (Falk et al., 1981a,b). There was no significant association of arsenic exposure with kidney cancer in the Tacoma smelter cohort (Enterline et al., 1995) or in the 1938-1977 follow-up of the Anaconda cohort (Lubin et al., 1981). In addition, no increase in kidney cancer was observed in the French gold miner cohort (Simonato et al., 1994), in the US pesticide producer cohort (Sobel et al., 1988) or "urogenital organs" in the Swedish cohort (Sandström et al., 1989). This difference between the occupational and environmental studies may reflect lower systemic concentrations of arsenic after inhalation exposure (WHO, 2001).

Skin cancer and precancerous lesions of the skin

Several early case reports have suggested that arsenic from medicinal use, drinking water and occupational exposure may be related to skin diseases, including cancer (Hill & Fanning, 1948; Zaldivar, 1974). Exposure to arsenic via drinking water has since been shown to be associated with an increased risk of skin cancer and other skin diseases.

Skin cancer often arises from a keratotic change, the developed forms of which are classified as Bowen's disease; keratosis in turn may be preceded by disturbances in the skin pigmentation (hyper- and/or hypopigmentation). Arsenical skin cancers are usually squamous or basal in histologic type and arise primarily on unexposed areas of the body, including the palms and feet (Scotto et al., 1996). It has been hypothesized that arsenic combines with sulphydryl groups in body tissues and interferes with pyruvate-oxidase activity (see section 3.2.1.6), both mechanisms that are associated with cancers of the skin (Leonard & Lauwerys, 1980).

The cutaneous effects of ingested arsenic have been most intensively studied in environmentally exposed populations in Taiwan, South America, India, Mexico and the USA; a representative selection of these studies are summarized below and in **Table 3.7**.

Table 3.7 Effects of arsenic exposure on the skin (Source: WHO, 2001)

Authors study design	Study Population	Source and level of arsenic exposure	Health effects, metric of exposure and and measure of association	Comments
Tseng et al (1968), Tseng (1977) cross-sectional	40,421 males and females in 37 villages in arsenic southwest Taiwan high exposure area and 7500 in low exposure area	142 water samples from 114 well analysed for As.Variation 1 to 1097 µg/L, 50% between 300 and 700 µg/L	Prevalence (10^{-3}) of hyperpigmentation 183.5, of keratosis 71.0 in high exposure area, 0 for both in low exposure (1-17µg/L) area	Reference cited for arsenic analysis. The exposure-response effect was seen across age and gender
			As conc. µg/L Prevalence of skin cancer (10^{-3})	
			<300 4 (M) 1.3 (F)	
			300-600 14.4 (M) 6.3 (F)	
			>600 31.0 (M) 12.1 (F)	
			unknown 16.3(M) 4.7 (F)	
Chen et al (1985) ecological	Arsenic exposed areas of Taiwan	Drinking water up to 1.14 mg/L decreasing with take into use of reservoir water starting in 1956	SMR values from 1973-1986 mortality in arsenic exposed area of SW Taiwan: Skin: 534 (379-689) (M) 652 (469-835) (F)	Population of Taiwan as the reference
Chen et al (1988b) cohort	Cohort of 789 Blackfoot disease patients (7278 person years of observation)	Drinking water concentrations 350-1140 µg/L	SMR 2846 ($p<0.01$) Taiwan Reference pop. SMR 451 ($p<0.05$) Local Reference pop.	10.6% lost on follow-p
Chen & Wang (1990) ecological	Mortality from malignant neoplasms in 1972-83 in 314 precincts and townships	74% or precincts had <5% wells with ≥50µg/L As, 15% has 5-14% and	statistically significant association between arsenic level in well water and mortality from skin cancer after adjustment for indices of urbanisation and industrialisation	

	in Taiwan	12% had ≥15% such wells. Village mean used in analysis.		
Wu et al, (1989) ecological	Mortality and population data from 1973-1986 in 42 villages in Taiwan.	Used published Taiwan data from 1964-1966 and village medians in the analysis	Age-adjusted mortality rates per 10^5 by well As concentration.	Observed numbers of deaths smaller than in the Chen et al 1992 study, although the person-years are identical
			Well As < 300 300 - 599 ^{3}600 µg/L p	
			Males 2.03 14.01 32.41 < 0.001	
			Females 1.73 14.75 18.66 < 0.05	
Hsueh et al (1995) cross-sectional	1571 residents >30 years of age from high arsenic exposure areas of Taiwan	Median As in well water 0.70 - 0.93 mg/L in early 1960's	Cum expos. Prevalence OR	Drinking water arsenic concentration estimates based on the study done in 1960's (Kuo 1964), using the Natelson metod. 68.8% perticipation rate, for approx 25% cumulative exposure history not known. Exposure-response between duration of consumption of sweet potato and prevalence of skin cancer. OR's adjusted for age and sex, duration of consumption of sweet potato, working in rice fields and hepatitis B - surface antigen.
			< 4 mg/L-yrs 1.0	
			5-24 mg/L-yrs 6.7 (1.1 - 59)	
			> 25 mg/L-yrs 13.8 (1.1 - 77)	
Guo et al (1998) Ecological	243 Taiwanese townships - approximately 11.4 million residents. Incident cases of urothelial and kidney cancer 1980-	Arsenic measured in over 80,000 wells from 1974-1976 in 78% of townships average As content was nondetectable,	No relationship between skin cancer incidence and the mean township well water arsenic concentration. A positive association between skin cancer and percentage of wells in the highest concentration category (> 640 µg/L) and a negative association between skin cancer and percentage of wells in the lowest concentratin category.	Used data from the 1970's survey on arsenic in well water, using mercuric bromide method to analyse arsenic. Smoking not included in the models as not good predictor for

	87	in 91, below 50 and in 99.5%, below 640 µg/L				any cancer in this study. Potential bias from source of case ascertainment, ie tumor registry not validated
Tsai et al (1999) Ecological	4 townships in BFD-endemic area in Taiwan, mortality in 1971-1994, compared to local and national rates	Drinking water up to 1.14 mg/L, decreasing with take into use of reservoir water starting in 1956	Skin cancer SMR for females and males combined, compared to local rates			Age- and sex-specific mortality rates based on population data from Miniistry of Interior, deaths from computer data base on deaths. 99% of causes of deaths based on diagnosis of a physician. All cancers confimred by pathological examination. Overlaps with earlier Taiwan studies.
			SMR	CI		
			483	374 - 615 (Local rates)		
			597	462 - 760 (National rates)		
Hopenhayn-Rich et al (1998) ecological	Residents in Cordoba vs rest of Argentina	In the high exposure group, in two selected towns, 42/61 and 49/57 measurements ≥40 µg/L. Highest measured concentration 533 µg/L	Exposure SMR (CI)			
				males	females	
			low	204 (138-289)	85 (42-151)	
			medium	149 (83-245)	82 (32-168)	
			high	149 (71-273)	278 (161-444)	
Rivara et al (1997) ecological	Region 2 (higher exposure) Northern Chile compared to Region 8 (low exposure). Region 2 is arsenic endemic area	Drinking water Arsenic concentration varied during 1950 - 1992 ranging from ND to 860 µg/L through the time period in different locations in Region 2.	Mortality Rate Ratio (CI) Region II vs Region VIII 4.3 (2.3 - 5.1)			Air levels of arsenic were measured in some locations ad were considerably elevated at Chuquicamata copper smelter in Region 2.
Smith et al (1998) ecological	Region II Chile (1989-1993) compared to the rest of	Drinking water Avg. 43-568 µg/L(1950-1994) Exposure		SMR (CI)		Measurements taken by water company. Population is partially

	Chile.	decreased over time: 569 µg/L (1955-69) to 43 µg/L (1990-94)		overlapping Rivara (1997)

Males	770 (470 - 1190)
Females	320 (130 - 660)

Cebrian et al (1983) cross sectional	One third of households in two towns in North Mexico, one with arsenic contaminated drinking water, and the other without	Average water As 400 (SD 114) µg/L for the exposed, based on 20 samples in 1975-8. For the referents, mean (SD), 5 (7) µg/L	Prevalence of hypopigmentation, hyperpigmentation, palmoplantar keratosis, papular keratosis and cancer 17.6, 12.2, 11.2, 5.1 and 1.4% among the exposed, and 2.2, 1.9, 0.3, 0.0, 0.0% among the referents	Prevalence rates not age-standardized, but among the referents, the proportion of >60 year-olds greater than among the exposed.
Mazumder et al (1998) cross-sectional	7683 inhabitants in 25 villages in West-Bengal in 1995-6.Exposure to arsenic started most likely in the late 1960s	For 45%, drinking water As was <50 µg/L, for 69% <200 µg/L, for 88% < 500 µg/L and for 99.8% <800 µg/L	Prevalence of keratosis and hyperpigmentation	Keratosis but not hyperpigmentation more prevalent among individuals with body weight in the lowest quintile. Drinking water source of each recruited household analysed for arsenic using hydride generation AAS

As-conc	Keratosis		Hyperpigmentation	
µg/L	Males	Females	Males	Females
< 50	0.2	0	0.4	0.3
50 - 99	1.5	0.4	3.2	0.8
100-149	1.6	1.2	11.0	5.7
150-199	4.7	2.3	7.8	5.1
200-349	4.9	2.0	13.1	6.5
350-499	9.0	2.7	15.7	9.5
500-799	8.9	3.1	13.8	5.3
³ 800	10.7	8.3	22.7	11.5

Tondel et al (1999) cross sectional	1481 subjects in 4 villages in Bangladesh	Well water As concentration at the time of the study, 10 - 2040 µg/L	Well water As concentration-dependent increase in the prevalence of skin lesions (hyper- or hypopigmentation, or keratosis)	Data on individual skin lesion types not given. As concentration from previous studies, analyses by hydride generation AAS. Number or representativity of analyses not discussed

As-conc	Skin lesion prevalence, %	
µg/L	Males	Females
< 150	18.6	17.9
151 - 350	21.9	20.5
351-550	32.9	32.1
551-1000	36.8	34.0

³ 1000	37.0	24.9

A series of studies from BFD-endemic parts of Taiwan have clearly demonstrated the existence of an exposure-response relationship between the magnitude of arsenic exposure and incidence of skin cancer and other manifestations including keratosis and hyperpigmentation. Tseng et al. (1968) found that ascending rates for skin cancer, keratosis and hyperpigmentation corresponded with increasing arsenic content of well water in a study population comprising 40,000 "exposed" and 7,500 "comparison" individuals; a dose-response relationship for arsenic concentration and black foot disease prevalence was also reported. The studies of Chen et al. (1985; 1988), Chen & Wang (1990), Wu et al. (1989) and Tasi et al (1999), which found evidence of links between mortality from cancers of the lung and bladder and arsenic exposure (see previous section), all report similar associations for cancers of the skin. Given that the fatality rates of non-melanoma skin cancers are low relative to other cancers, it is likely that mortality studies of this type markedly underestimate the incidence of the disease.

Hsueh et al. (1995) conducted a detailed investigation of the relationship between skin cancer and arsenic exposure in three Taiwanese villages. Out of a study population of 1,081 inhabitants, who were interviewed about their drinking water consumption patterns and personal histories in 1988-89, 66 were diagnosed as having skin cancer. The age- and sex-adjusted prevalence odds ratio of skin cancer was related to all the chosen indicators of arsenic exposure, i.e. village well-water mean concentration (based on analyses made in the early 1960s), duration of living in the BFD-endemic area, duration of drinking artesian well water and cumulative arsenic exposure.

Evidence for the link between skin cancers and arsenic is further supported by the results of studies conducted in other world regions. The work of Hopenhayn-Rich et al. (1998) in Argentina and Smith et al (1998) in Chile, mentioned previously in the context of lung and bladder cancers, both demonstrated positive associations between mortality from skin cancer and arsenic exposure (although in Argentina the positive association was confined to women). In a more recent analysis, Smith et al. (2000) documented skin changes in 6 out of 44 well-nourished subjects from a village in northern Chile supplied by water containing up to 800 ug/L of arsenic. Arsenic exposure in this village is reported to have been present for thousands of years, suggesting that there has been no adaptation to arsenic exposure by the population.

The prevalence of skin lesions was reported to be significantly elevated in two towns in Mexico (where the average concentration of arsenic in water samples was 0.41 mg/L) relative to a "control" town (average concentration 0.005 mg/L) (Cebrian et al., 1983). In the "exposed" town there were 52 cases (or 17.6%) of hypopigmentation, 36 (12.2%) cases of hyperpigmentation, 33 cases (11.2%) of palmoplantar keratosis, 15 cases (5.1%) of papular keratosis and 4 cases (1.4%) of ulcerative zones (cancers). In the "control" town the prevalence rates were significantly lower: 7 cases of hypopigmentaion, 6 cases of hyperpigmentation, 1 case of palmoplantar keratosis, no cases of papular keratosis and no cases of ulcerative zones (cancers). The prevalence of all skin lesions was found to increase with age. Non-specific symptoms such as nausea, epigastric pain, abdominal pain, diarrhoea, headache and oedema were found to be more prevalent in the exposed town and more common in those with lesions.

Recent studies from West Bengal, India and Bangladesh in populations with a history of exposure to arsenic-contaminated drinking water, have documented similar findings.

In West Bengal, a survey of 7,683 participants from "high" and "low" exposure areas, found that the age-adjusted prevalence of keratosis rose from zero in the lowest exposure level (< 50 ug/L) to 8.3 per 100 women drinking water containing > 800 ug/L. For men, the age-adjusted prevalence rates rose from 0.2 per 100 in the lowest exposure category to 10.7 per 100 in the high exposure group. Similar results were reported for hyperpigmentation prevalence. Comparison by dose per body weight revealed that men had roughly 2-3 times the prevalence of both keratosis and hyperpigmentation compared to women for the same apparent ingested dose. Subjects below 80% of their body weight for their age and sex had a 1.6-fold increase in the prevalence of keratoses, suggesting that malnutrition may play a role in increasing susceptibility. However, no such difference was observed for hyperpigmentation (Mazumder et al., 1998).

In Bangladesh, Tondel et al. (1999) examined a total of 1,481 subjects (aged 30 or over) residing in four villages were arsenic concentrations in drinking water ranged from 10 to 2,040 ug/L. Almost one third (430) were found to have skin lesions (i.e. pigmentation changes or keratois). A statistically significant exposure-response relationship was also demonstrated; the age-adjusted prevalence rate of skin lesions increased from 18.6 per 100 in the lowest exposure group (< 150 ug/L), to 37.0 per 100 in the highest exposure category (> 1000 ug/L) for males and from 17.9 to 24.9 per 100 in females. Again, when the exposure was considered by dose (in ug/L per kg body weight) there was an increase in the age-adjusted prevalence rates of skin lesions for males and females across dose groups.

In contrast, studies carried out in the USA have not shown any excess of skin disorders. For example, Morton and colleagues (1976) examined the incidence rates of skin cancer in Lane County, Oregon and found that neither basal cell or squamous cell carcinoma were positively associated with the arsenic levels ranging from 0 to 2,150 ug/L (average = 8.6 µg/L).

A recent analysis by Valberg et al. (1998) reviewed data obtained from a series of studies of skin cancer in US populations. Populations included were from Fallon, Nevada (105 individuals at 100 ug/L, 0.091 predicted arsenic skin cancers), Fairbanks, Alaska (49 individuals at 401 ug/L, 0.072 predicted arsenic skin cancers; and 30 individuals at 76 ug/L, 0.012 predicted arsenic skin cancers) and Millard County, Utah (145 individuals at 208 ug/L, 0.630 predicted arsenic skin cancers). Using the US EPA (1988) cancer slope factor for ingested arsenic to predict the incidence of skin cancer in these populations, the total number of predicted arsenic skin cancers from all four areas is not quite one case. The data from Millard County, Utah alone also indicated that the risk of no additional skin cancer was more likely by a factor of nearly two. The relatively small sample sizes and the low arsenic exposures mean that these US results do not necessarily contradict previous reports of positive correlations from other countries.

Exposure to arsenic via other exposure routes have also been linked to dermal effects. Although an early study linked excess skin cancer mortalities to occupational arsenic exposure (Fierz, 1965), more recent occupational studies involving arsenic exposure do not support this finding (WHO, 2001). Isolated reports of other dermal effects have, however, been found in the literature. For example, Goncalo et al. (1980), concluded that arsenite (As_2O_3) can induce an irritative contact dermatitis following occupational exposure. Three glass workers suffered cutaneous lesions, including pruritic maculopapules, pustules and folliculitis, that were localized primarily in exposed and moist areas. Patch tests of the powders the workers were exposed to were positive, and there was a weak positive response to a 5% concentration of As_2O_3 in petrolatum. A change in work practices by the workers alleviated the skin conditions. Barbaud et al. (1995) reported on a case of contact hypersensitivity to arsenic in a crystal factory employee, who had no previous history of skin disorders. A patch test was done with various diluted compounds and sodium arsenate was the only chemical that tested positive. The skin disorder healed after treatment and reassignment to another position.

Cancer at other sites

Several studies in Taiwan have suggested that arsenic may be related to cancers of the oesophagus, stomach, small intestine, colon, nose, larynx, bone and prostate, as well as lymphoma and leukaemia. In several studies, an elevated mortality from liver cancer was associated with high exposures to arsenic via drinking water (Chen et al., 1986; Chen & Wang, 1990). Increased rates of prostate cancer with increasing exposure to arsenic have been noted (Chen et al.1985).

Links between arsenic exposure and cancer at sites other than skin, lung, bladder and kidney have not been investigated in any great detail in countries outside of Taiwan. Of the studies available, results are generally mixed. In one of two studies in Chile (Smith et al., 1998), mortality from liver cancer was positively associated with drinking water arsenic exposure. The study by Hopenhayn-Rich et al. (1996) in Argentina, however, found no such relationship. One study in the USA (Lewis et al. 1999) and another in Australia, neither of which showed a clear cut increase in the risk of lung, bladder or kidney cancer, found evidence of a moderately elevated mortality of cancer of the prostate.

Similarly, occupational studies of arsenic exposure have not revealed any consistent relationship between cancer incidence at sites other than the lung. A significant relationship was observed between arsenic exposure and the incidence of cancers of a large category of “digestive organs” in a Swedish cohort (Sandström et al., 1989). In the Montana cohort, a small, non-exposure related excess of digestive tract cancers was observed (Lee-Feldstein, 1983).

There was a statistically significant association between arsenic exposure and cancer of the buccal cavity and pharynx in the Tacoma cohort (Enterline et al., 1995), but not in the Anaconda cohort in 1964-1977 (Lubin et al., 1981) or in the US pesticide producer cohort (Sobel et al., 1988). Similarly, no excess of stomach cancer was observed in the Japanese smelter cohort (Tokudome & Kuratsune, 1976). However, in UK tin miners, two deaths from stomach cancer were observed (0.2 expected, SMR 890, $p<0.05$; Hodgson & Jones, 1990). In the Tacoma cohort, there was an increase in the cancer of large intestine ($p < 0.01$) but not a significant excess of rectal or bone cancer (Enterline et al., 1995). An excess of rectal cancer was observed in the French gold miner cohort (Simonato et al., 1994) and of cancer of the large intestine (except rectum) in the Japanese smelter cohort (Tokudome & Kuratsune, 1976).

Supporting evidence from experimental studies in animals

A number of animal carcinogenicity studies on arsenic have been carried out, the results of which are reviewed by IARC (1973, 1980, 1987) and most recently by WHO (2001). Results are inconclusive owing to the fact that the majority of such studies are considered to suffer from limitations of one sort or another, either high dose levels, relatively short exposure times and small sample sizes. Furthermore, some studies have been conducted using strains of animals that are believed to have a high background number of tumours.

These comments notwithstanding, a recent study involving mice exposed to arsenic in drinking water at a relevant level of exposure (i.e. at concentrations similar to those commonly found in BFD-endemic parts of Taiwan) has provided what some researchers consider to be the first clear evidence of a treatment-related increase in the number of tumours (Ng et al., 1998, 1999). Sodium arsenate in drinking water was given to 90 female C57BL/6J mice, 140 metallothionein knock-out transgenic mice and 120 control mice (60 in each group) over a period of up to 26 months.

C57BL/6J mice have a very low incidence of spontaneous tumours, whereas metallothionein knock-out transgenic mice are expected to be more susceptible to arsenic toxicity on account of absence of the metallothionein protein which has an affinity for metals.

The average arsenic intake by the mice was 2-2.5 ug per day and mice that survived for 2 years consumed approximately 1.5 - 1.8 mg As. 81% of the C57BL/6J and 74% of the knock-out mice survived the arsenic treatment, compared with 98% in the controls groups. One or more tumours were detected in 41% of the C57BL/6J mice and 26% in the knock-out mice; tumours were found in the gastrointestinal tract, lung, liver, spleen, skin and reproductive organs. Pathological and histopathological examination confirmed the ovary, lung and skin tumour findings (Ng, 1999). No macroscopic tumours were observed in the control groups.

Other animal experimental studies have shown that inorganic arsenic can produce chromosomal aberrations in vitro, affect methylation and repair of DNA, induce cell proliferation, transform cells and promote tumours. However, inorganic arsenic was not seen to induce genetic point mutations in either bacteria or mammalian cells (WHO, 2001).

3.3.2.3 Genotoxicity and related end points

Genotoxicity studies in relation to arsenic exposure have included exposed and unexposed individuals from several populations, and have based their analyses on various tissues, including blood, buccal and bladder cells as well as sections from tumour sections or Bowen's disease. Studies of this type usually take the form on one of three distinct groupings according to the focus of investigation:

a) p53 mutations in tumour samples,

b) SCE, chromosome aberrations (CA) and RI in cultured lymphocytes, and

c) MN in exfoliated bladder and buccal cells (possible target tissues from direct exposure to arsenic from drinking water).

A brief description, plus a summary of the key findings, of all three types of study can be found in **Table 3.8**.

Table 3.8 Genotoxicity of arsenic in exposed humans (Source: WHO, 2001)

Author, study design	Study Population, end-points measured	Source and level of arsenic exposure	Health effects, metric of exposure and measure of association							Com
Warner et al (1994), cross sectional	18 exposed and 18 referents in Nevada MN in bladder and buccal cells	High exposure: well water As concentration >500 (average 1312) µg/L. Referents, average 16 µg/L	Bladder cells							Refere and sn match
			MN/100 cells (SE)		Freq. ratio (CI)					
				Males						
			Exposed	Referents						
			5.00 (1.50)	2.14 (0.46)	2.34 (1.27, 4.29)					
				Females						
			1.82 (0.53)	1.28 (0.31)	1.43 (0.76, 2.65)					
			Both acentric and whole chromosomes increased. No effect on MN in buccal cells.							
Moore et al (1996); cross-sectional	Same as Warner et al (1994) Absence/presence of centromeres by FISH in bladder cells	High exposure: well water As concentration >500 (average 1312) µg/L. Referents, average 16 µg/L		MN+ (%)			MN-(%)			
				Expos.	Ref	P	Exp.	Ref	p	
			Males	0.190	0.102	0.08	0.167	0.081	0.07	
			Females	0.078	0.072	0.31	0.057	0.041	0.48	
			MN+/- = aberrations with/without centromere							
Moore et al (1997a) cross sectional	70 Chilean males with high water arsenic exposure and 50 referents Bladder cell MN using FISH for centromeres	High exposure: 600 µg/L As, referents 15 µg/L. Average U-As levels 616	U-As µg/L	MN+ *	CI		MN-*	CI		Expos stratifi quintil

		and 66 µg/L, respectively						
			<54	1.0		1.0		
			54 - 137	2.3	1.0-5.0	4.7	1.7-13.2	
			137 - 415	2.0	0.9-4.5	7.5	2.8-20.3	
			415 - 729	3.1	1.4-6.6	5.2	1.9-14.6	
			>729	0.9	0.4-2.2	1.0	0.3-3.3	
			* prevalence ratio					
Moore et al (1997b) intervention	34 men from the exposed group in the previous (Moore et al 1997a) study Bladder cell MN	Water with 45 µg/L As supplied to participants for 8 weeks. U-As decreased from 742 to 225 µg/L	MN frequency decreased from 2.6 to 1.8/1000 (prevalence ratio 0.7, p<0.05). For those whose U-As was <700 µg/L at the beginning of the intervention, the decrease was from 3.5 to 1.5 (prevalence ratio 0.4, p=0.002).					
Ostrosky-Wegman et al (1991) cross-sectional	13 exposed and 15 less exposed habitants in North Mexico; CA, SCE, HPRT mutations in lymphocytes	Average drinking water As concentration for the exposed 390 µg/L, 19-60 µg/L for the referents		CA% (SD)	SCE (SD)	Vf (SD)*		Compl chrom aberra (dicen rings, translo increas among more h expose (0.73% 0.16%
			High esp.	2.55 (1.73)	9.10 (2.7)	2.42 (2.26)		
			Low exp.	3.00 (2.82)	8.80 (1.6)	5.03 (2.99)		
			All nonsignificant; *: HPRT mutations					
Gonsebatt et al (1994) cross-sectional	33 exposed and 30 referents in Lagunera region, Mexico Labeling index, mitotic index, replication index in lymphocytes	Water arsenic in average 412 µg/L for the exposed and 37 µg/L for the referents	Labeling index controls 3.37 (SE 0.61), exposed without skin lesions: 3.95 (0.56), exposed with skin lesions 2.42 (0.49; p<0.05). Mitotic index at 72 h for controls 3.78 (SE 0.34), for exposed 6.34 (0.45; p < 0.01); no difference at 48 or 72 hReplication index lower in exposed females at 48, 60 and 72h; no difference among males.					
Gonsebatt et al (1997) cross sectional	35 exposed volunteers and 35 referents in Lagunera region, Mexico CA in lymphocytes, MN in buccal and	Water arsenic in average 410 µg/L for the exposed and 30 µg/L for the referents		CA (SE)	MN_{buccal} (SE)	$MN_{bladder}$ (SE)		Statist compa include variabl such a smokir and ge

	bladder cells						
			Refer	2.96 (0.54)	0.56 (0.13)	0.48 (0.10)	
			Exposed	7.12 (1.00)*	2.21 (0.47)*	2.22 (0.99)*	
			Skin les.	7.38 (1.46)	3.28 (0.96)*	4.64 (2.59)*	
			§ buccal; §§ bladder cells. * $p<0.05$				
Lerda et al (1994) cross sectional	282 nonsmoking exposed inhabitants and 155 referents from neighbouring province in Argentina. Lmphocyte SCE	Water arsenic for the exposed province ≥130 µg/L, for the reference area, = 20 µg/L. Duration of exposure ≥ 20 years	Lymphocyte SCE/cell among exposed 10.46 (SD 1.02) and among referents (7.49 SD 0.97, $p< 0.001$). Correlation between urinary arsenic and SCE: R^2 0.64 for females and 0.33 for males				The ex conside younge referer (mean 38.9 v. years) sex no conside the an
Dulout et al (1996) cross sectional	12 exposed women and 10 exposed children & 10 referent women and 12 referent children in Argentina MN & SCE in lymphocytes; FISH for aberration type	Drinking water As 0.2 - 0.5 mg/l for the exposed. U-As median 260 µg/L for exposed women and 310 for exposed children, and 8 and 13 µg/L for the nonexposed		MN/1000 (SE)	SCE/cell (SD)		MN fre unusua among referer Arseni metab patterr differe that re earlier Caucas popula
			Exp. children	35 (46)	4.4 (1.1)		
			Exp. women	41 (4.9)	5.7 (1.3)		
			Ref. children	5.6 (1.6)	4.6 (1.2)		
			Ref. women	8.5 (3.4)	5.5 (1.3)		
			No differences in chromosomal translocations; aneuploidy more frequent (0.21 vs 0%) among the exposed				
Mäki-Paakkanen et al (1998) cross sectional	32 current and 10 ex-users of arsenic-containing well water plus 8 referents in Finland; lymphocyte CA	Median well water arsenic concentration 410 µg/l for the exposed (all > 1 µg/L) and < 1µg/L for the		CA incl gaps (SD);p	CA excl gaps (SD);p		

		referents				
			current users	6.9 (3.4)	3.5 (2.5)	
			Ex-users	4.2 (1.9)	1.9 (1.3)	
			Referents	8.6 (3.6); 0.02	3.6 (1.7); 0.1	
			Cum dose mg/lifetime*			
			< 1.894	6.0 (2.9)	2.8 (4.3)	
			> 1.894	8.6 (4.3); 0.02	4.5 (3.0); 0.02	
			As in urine µg/L*			
			< 206	6.1 (3.0)	2.8 (1.8)	
			>206	8.9 (4.4); 0.02	4.8 (3.0); 0.008	
			*Cut-off point 75th percentile. P-values from analysis of variance			
Kuo et al (1997) cross-sectional	26 individuals with Bowen's disease with known drinking water arsenic exposure and 22 non-exposed BfD patients from the BFD endemic area. p53 overexpression and proliferation in the tumour	Well water arsenic concentration = 1140 µg/L, with progressive decrease since 1956	>10% immunohistochemical staining for p53 protein in tumours from 11/26 exposed and 2/22 non-exposed (p=0.01). No difference in cell proliferative activity			
Hsu et al (1997) cross-sectional	15 cases of Bowen disease and 34 referents from the BFD endemic area	Well water arsenic concentration = 1140 µg/L, with progressive decrease since 1956		SCE/cell (SE); p	HFC % (SE); p	Refere match age, s reside
			Patients	8.42 (51)	17.89 (2.83)	
			Referents	6.94 (0.37); <0.05	8.59 (1.66) < 0.05	
Liou et al (1996) cross sectional	22 patients with cancer, 10 with BFD, 8 with cancer and BFD, 26 healthy individuals from the BFD endemic area, and 23 healthy non-exposed referents.	Well water arsenic concentration = 1140 µg/L, with progressive decrease since 1956	SCE frequencies not different among different groups. Mitomycin-induced SCE frequencies higher among individuals from the BFD area than among referents not exposed ot arsenic.			
Liou et al	686 residents of	Well water		Cases	Referents p	For 9

(1999) prospective	the Taiwan BFD endemic area, out of whom 31 developed cancer during a 4-year-follow up period;SCE and CA in lymphocytes	arsenic concentration = 1140 µg/L, with progressive decrease since 1956					31 CA not be analys final a done o cases referen
			SCE/cell (SD)	6.73 (1.53)	6.22 (1.11)	0.36	
			CA (chromosome-type)	2.6 (1.7)	0.9 (1.0)	0.01	
			CA (chromatid-type)	3.3 (1.8)	3.4 (2.0)	NS	
			CA Total	6.1 (2.4)	4.4 (2.6)	0.018	
Shibata et al (1994) cross sectional	13 Cases (age, 37-74 years) of urothelial cancer from BFD-endemic area in Taiwan	Well water arsenic concentration = 1140 µg/L, with progressive decrease since 1956	8/13 cases had a mutation in exxons 5-8 of the P-53 gene. 9/10 point mutations were transitions.				The au conclu the mu patter observ not dif from t observ transit cell tu patien withou arseni exposu
Hsieh et al (1994) cross sectional	26 skin biopsies from 16 Bowen's disease patients from the BFD endemic arear as and p53 mutations	Well water arsenic concentration = 1140 µg/L, with progressive decrease since 1956	No mutations observed in exons 5-8 in p53, or in codons 12, 13 or 61 H-, K- or N-ras oncogenes				No inform person exposu or dur the stu subjec any pe charac such a sex or smoki
Hsu et al (1999) cross sectional	23 patients with Bowen's disease, 7 with basal cell carcinoma, and 9 with squamous cell carcinoma from the BFD endemic area	Well water arsenic concentration = 1140 µg/L, with progressive decrease since 1956	9/23 (39%) of Bowen's disease patients, 23/7 (29%) of BCC cases, and 5/9 (56%) of SCC cases had mutations in the p53 gene.				The au conclu the p5 mutati rates, and ty arseni related cancer

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Despite some negative findings, the weight of evidence indicates that arsenic can cause clastogenic damage in a variety of cell types, with differing end points, in exposed individuals. Clastogenic effects have also been observed in cells from cancer patients (WHO, 2001). In the case of point mutations the results are largely negative. No HPRT gene mutation was seen in the single available study in lymphocytes (Ostrosky-Wegman et al., 1991). Mutations of ras genes and p53 mutations were rarely found in the cells taken from patients with cancer or Bowen's disease from the BFD-endemic parts of Taiwan. One study did, however, report increased p53 expression in Bowen's disease patients (Kuo et al., 1997).

3.3.2.4 Diabetes mellitus

Diabetes mellitus has also been linked with drinking water arsenic exposure. Lai et al. (1994) assessed the relationship between ingested inorganic arsenic and prevalence of diabetes mellitus in 891 adults residing in southern Taiwan. Their study found that residents in the BFD-endemic areas had a two-fold increase in the prevalence of diabetes mellitus (after adjustment for age and sex) when compared to residents in Taipei and the entire Taiwan population. The authors also described a dose-response relationship between the level of arsenic in water and the prevalence of diabetes after adjusting for age, sex, body mass index and activity level. Positive associations were also demonstrated in two further studies from Taiwan. An excess mortality from diabetes among the arsenic exposed population in four townships, relative to local and national rates, has been reported by Tsai et al. (1999). The incidence of diabetes mellitus in a cohort of inhabitants of the Taiwan BFD area was related to the cumulative exposure to arsenic in drinking water (Tseng et al., 2000).

A positive association with diabetes has also been found in Bangladesh. Rahman et al. (1998) used the presence of keratosis as an indicator of arsenic exposure and showed elevated risks for diabetes in those exposed to arsenic in their drinking water (prevalence ratio= 5.9). On the other hand, in the Utah mortality study, Lewis et al. (1999) failed to find a significant excess in the number of deaths from diabetes in males and females exposed to elevated levels of arsenic in drinking water. However, in the US diabetes is a condition with a low-case fatality rate, so an association with diabetes mellitus may not be observed. More work is needed prior to deciding whether there is an association in the US between diabetes and drinking water arsenic.

Two occupational studies have found an association between arsenic exposure and diabetes mellitus. In both cases, however, the results were of borderline significance. Based on a case-referent analysis involving glass workers, Rahman et al. (1996) found a slightly elevated risk for diabetes among those glasswork employees considered to be exposed to inhaled forms of arsenic. In a smaller (12 exposed cases) case-referent study (Rahman & Axelson, 1995) in the Rönnskär cohort (Axelson et al., 1978), a slightly elevated risk of diabetes mellitus associated with arsenic exposure was also observed.

3.3.2.5 Neurological effects

It is generally accepted that acute arsenic poisoning causes neurological effects in humans, especially in the peripheral nervous system (see section on acute effects).To date, however, little work has been done on the possibility that lower-level, long-term exposure to arsenic may also lead to neurological effects. Of the limited number of available studies on this topic, several have described the onset of various neurological symptoms in subjects exposed to arsenic. Hindmarsh et al. (1977), for example, reported a positive association between electromyography (EMG) abnormalities and arsenic levels in drinking water and hair samples in residents of Waverley, Nova Scotia, Canada. Among those using water with more than 1 mg/L arsenic, the frequency of ENG abnormalities was 50%.

Workers at a copper smelting plant exposed to arsenic trioxide were examined for peripheral neuropathy (Feldman et al., 1979). A total of 70 factory workers and 41 non-arsenic workers were evaluated. The data suggested an association between exposure to arsenic and a higher number of peripheral neuropathological disorders (sensory and motor neuropathy) and electrophysiological abnormalities (reduced nerve conduction velocity and amplitude measurements) among the exposed workers. Not all studies have found evidence of positive associations; in a cross-sectional study of 211 residents of Fairbanks, Alaska Harrington et al. (1978) could find no evidence of neurotoxicity amongst the exposed population.

On balance therefore, the evidence for a link between exposure to arsenic and neurological effects remains weak. Although a handful of studies have suggested that changes in nerve function may occur following exposure to arsenic, such studies are typically limited by their small sample populations, differing end-points and methods of measurement and probable coexposure to other known neurotoxins (WHO, 2001).

3.3.2.6 Reproductive effects

In addition to the health effects already mentioned, arsenic has also been linked to adverse reproductive outcomes. A number of studies have attempted to investigate this possible connection, the results of which suggest increased foetal, neonatal and postnatal mortalities, and elevations in low birth weights, spontaneous abortions, stillbirths, pre-eclampsia and congenital malformations.

A series of ecological studies involving workers and their families living in the vicinity of the Ronnskar copper smelter in Sweden, for example, have reported an increase in the prevalence of low birthweight infants (Nordstrom et al., 1978a; 1979a), higher rates of spontaneous abortions (Nordstrom et al., 1978b; 1979b) and elevations in congenital malformations (Nordstrom et al., 1979b) among female employees and in women living close to the smelter relative to women living further afield. According to Tabocova & Hunter (1994) the frequency of pregnancy complications, mortality rates at birth and low birth weights were significantly higher in 49 maternal-infant pairs living near a Bulgarian copper smelter, relative to country-wide rates. Placental arsenic levels were also found to be higher for the smelter area than for the non-smelter area. In both cases, however, a lack of rigorous treatment of the potential role of confounding risk factors, such as coexposures (lead, copper, cadmium), maternal age, lifestyle/socioeconomic status and smoking habits, have cast doubts over the validity of these findings (WHO, 2001).

Other studies involving arsenic exposure via drinking water have produced conflicting results. Zierler et al. (1988) found no evidence of an increased frequency of congenital heart disease in infants born to women consuming drinking water containing arsenic levels between 0.8-22 ug/L. A 1.4-fold increase in spontaneous abortions and a 2.8-fold increase in still births were, however, observed in a group of “exposed” individuals (arsenic concentrations in water samples > 100 ug/L, N = 25,648) compared with a “low” exposure group (unspecified low arsenic concentration in water samples, N = 20,836) from the south eastern part of Hungary (Borzsonyi et al., 1992).

In sum, there does not appear to be consistent evidence linking any one particular reproductive outcome to arsenic exposure, and at the present time it is generally accepted that there is insufficient evidence to support the notion that arsenic causes reproductive effects in humans.

3.4 Evaluation of human health risks

3.4.1 Environmental levels and human exposures

Arsenic concentrations in all environmental media are reasonably well documented.

Concentrations in air range from a few ng/m^3 in remote and rural areas, up to 1,000 ng/m^3 and above in the vicinity of industrial sources. Concentrations in rivers and lakes are generally below 10 ug/L, but can reach 5 mg/L near industrial sources. Similarily, ground water concentrations are typically 1-2 ug/L, but can exceed 3 mg/L in geologically-rich arsenic areas. Levels in soils average around 5 mg/kg, with a range of 1 to 40 mg/kg. Background concentrations in freshwater and terrestrial biota rarely exceed 1 mg/kg, but in areas near anthropogenic sources or in areas of geothermal activity markedly higher levels have been observed, in some cases up to 3000 mg/kg.

Whereas the majority of measurements of arsenic concentrations are for total arsenic, accurate estimates of human health risks require the determination of the relative proportions of organic and inorganic arsenicals in air, soil, food and drinking water. It has been established that the arsenic present in water, soil and absorbed on air particulates is predominantly inorganic. In contrast, there is a significant amount of organic arsenic in foodstuffs especially in fish and shellfish. Preliminary data indicate that the proportion of inorganic species in foods varies between 75% in meat, poultry and dairy products and < 1% in fish/shellfish. More work on the speciation of various arsenicals in foods is needed.

For most non-occupationally exposed adults, ingestion of arsenic in food is the main route of arsenic exposure. In areas where concentrations of arsenic in drinking water exceed 100 ug/L, this source is significant and, in some cases, may even be the principle contributor to the daily intake of arsenic. Depending upon the bioavailability, soil may be a potentially significant source of arsenic intake in children, particularly in areas near industrial and hazardous waste sites.

Daily intake of total arsenic by adults varies widely across the globe, primarily because of differences in the amount of fish and shellfish consumed in the diet. Best estimates indicate that daily intake of total arsenic due to the ingestion of food and beverages generally lies in the range 20-300 µg/day. According to a limited data set, about 25% of the arsenic found in food is present in inorganic forms (assuming a typical “western-style diet”); however, this proportion is significantly reduced (< 10%) in diets having a high fish/shell fish component. In non-polluted areas, inhalation of airborne particulates contributes a further 1 ug As/day to the total intake of non-smokers, and up to 10ug As/day in a heavy smoker. Total daily intakes may be significantly higher in all age groups living in the vicinity of industrial point sources, hazardous waste facilities, or in regions with high inorganic arsenic concentrations in groundwater. It is believed that there are millions of people potentially at risk due to the consumption of arsenic-contaminated drinking water in several world regions including West Bengal, Bangladesh, Inner Mongolia and the Xinjiang province in China.

In addition to exposure to arsenic in ambient air, water and food, some workers may be exposed to airborne arsenic and arsenic-containing dusts within the workplace. Actual levels of exposure depend on the specific tasks performed, the type of arsenical compound encountered, and the adequacy of workplace hygiene practices. In workplaces with up-to-date occupational hygiene practices and well-maintained pollution control equipment, levels of arsenic are likely to be below 10 ug/m^3. In some cases, however, workroom atmospheric arsenic concentrations could be as high as several mg/m^3.

3.4.2 Critical issues relating exposure to dose

The assessment of toxic effects of arsenic is complicated by the fact that arsenic can exist in more than one valence state and as both inorganic and organic compounds. For acute and sub-acute toxicity of arsenic, it has been established that the inorganic forms of arsenic are more toxic than the organic, and that the trivalent arsenicals (arsenite) are more toxic than the pentavalent forms (arsenate). Accurate determination of the chemical speciation of arsenic is thus an important concern in studies involving assessment of arsenic toxicity.

Arsenic is relatively unusual amongst metals and metalloids in that it exhibits large interspecies differences in its metabolism. As a result of this, there is no obvious “best”animal model which can be used to assist in the study of the kinetics and metabolism of arsenic in humans. Fortunately, there is a considerable amount of available information from human studies, and thus human arsenic metabolism is reasonably well understood.

For most people exposure to arsenic occurs via the ingestion pathway. Subsequent absorption will depend upon the bioavailability of the ingested arsenic, which in turn will vary according to the form of arsenic and on the matrix (i.e. food, water, soil) in which it is ingested. In drinking water, arsenic occurs mainly as inorganic, bioavailable forms. Arsenic in food occurs as both inorganic and organic forms, most of which appears to be bioavailable. The bioavailability of arsenic from mine tailings and soils on the other hand varies widely from a few percent to about 70%. Such differences indicate that risk assessment of arsenic at contaminated sites should be site specific.

Respiratory absorption of arsenic is a two-stage process involving first, the deposition of inhaled particles onto airway and lung surfaces, followed by the absorption of arsenic from deposited particles. The rate of absorption of inhaled arsenic is thus not only highly dependent on the solubility of the arsenicals, but also on the size of the inhaled particles.

A combination of human and animal studies confirms that both the pentavalent and trivalent soluble inorganic arsenic compounds are readily absorbed from the respiratory and gastrointestinal tracts of humans. Absorption of the organic forms is also thought to occur readily, although there are few studies which substantiate this.

During the metabolic process of arsenic, reduction of pentavalent arsenic species to trivalent arsenic takes places prior to the sequential methylation to the MMA and DMA metabolites. Methylation facilitates the excretion of inorganic arsenic from the body as the end-products, MMA and DMA, are readily excreted in the urine. In “healthy” humans, the urinary excretion of unchanged inorganic arsenic (Asi) concentrations are usually less than 20% of the total metabolites concentrations (i.e. Asi +MMA + DMA). Ingested organoarsenicals (MMA, DMA and arsenobetaine) are much less extensively metabolised and more rapidly eliminated in the urine.

There are major qualitative and quantitative interspecies differences in the extent of methylation to the extent that some species do not appear to methylate arsenic at all. In human urine, the percentage of MMA is higher than that of any other animal species, while the percentage of DMA is similar to that excreted by the rat. In contrast, the highest concentrations of DMA are found in the mouse and rabbit. Large interindividual variation in arsenic methylation is also a feature of arsenic metabolism. Factors such as dose, age, gender and smoking habits account for only part of the variation seen between individuals. It is speculated that much of the observed variation might be explained by genetic differences in the activity of methylating enzymes and related co-factors; furthermore, the existence of polymorphism has been hypothesised. There are some indications that arsenic methylation may be inhibited at high acute exposures.

Levels of arsenic in blood, hair nails and urine are used as biomarkers of arsenic exposure. Blood arsenic is useful only as an indicator of acute poisoning or stable chronic high-level exposure. Arsenic in hair and nails can be good indicators of past exposure, provided care is taken to avoid external contamination. Speciated arsenic in urine, expressed as either inorganic arsenic or inorganic arsenic + MMA + DMA, provides the best estimate of a recently absorbed dose of arsenic. In order to reflect exposure to inorganic arsenic, however, consumption of fish and shellfish should be avoided for 2-3 days prior to urine sampling.

3.4.3 Risk evaluation

Acute and chronic arsenic exposure can result in a wide variety of adverse health outcomes. Acute arsenic poisoning occurs usually as an acute gastrointestinal syndrome. Indirect effects caused by arsenic include renal failure, bone marrow suppression, hemolysis, respiratory failure and polyneuropathy. Deaths have been reported from ingestion of arsenic doses of approximately 1 g. Ingestion by a child of 1 mg arsenic trioxide has resulted in non-fatal but nevertheless severe adverse effects.

Arsenic is unusual in that sufficient human epidemiological data of acceptable scientific quality are available for the assessment of health risks associated with the long-term exposure to arsenic. Long-term exposure to arsenic in drinking water is causally related to increased risks of cancer in the skin, lungs, bladder and kidney, as well as other skin changes such as hyperkeratosis and pigmentation changes. These effects have been clearly demonstrated in a number of epidemiological studies of differing design. High risks and exposure-dose relationships have been observed for each of these end-points.

Determining the lowest arsenic concentration in drinking water at which an increased risk of cancers of the skin, lung, kidney and bladder is likely to occur is not easy. This is partly due to the fact that the exposure categories used in the majority of epidemiological studies have historically been rather broad (e.g. < 300ug/L, 300-600 ug/L and >600 ug/L).

According to a recent report, based on data from the BFD-endemic part of Taiwan, there is an increased risk of lung and bladder cancer mortality in persons consuming drinking water containing arsenic concentrations at < 50 ug/L. Evidence from Chile suggests an increased risk of lung cancer at concentrations in the range 30-50 ug/L and above. A case-control from Finland indicates that there is an elevated risk of bladder cancer at drinking water concentrations of > 0.5 to 64 ug/L (but only when exposure occurred 3-9 years prior to diagnosis). Based on an analysis of data from Argentina, elevated risks from cancers of the lung, bladder and kidney were observed in a group of “highly” exposed individuals exposed to concentrations of arsenic in drinking water which averaged 178 ug/L. However, bladder, kidney and lung were significantly elevated in the “intermediate” exposure group for which concentrations were not available. It is probable therefore that the lowest exposure at which elevated cancer risks could be observed would have been considerably lower than 178 ug/L. In the case of skin cancer, the lowest arsenic drinking water concentration at which an increased risk of skin cancer was observed is 300 ug/L; this is based on the results of a Taiwanese study which used very broad exposure categories. It is likely that the concentration associated with increased skin cancer risk is lower than this. According to a study from West Bengal, elevated risks of arsenic-associated skin lesions (hyperpigmentation and/or keratosis) are associated with drinking water concentrations of < 50 ug/L.

On the basis of the above, it is concluded that increased risks of lung and bladder cancers, and of arsenic-induced skin lesions, are likely to occur following the ingestion of drinking water containing arsenic at concentration of < 50 ug/L (WHO, 2001).

Studies involving occupationally-exposed populations have also demonstrated a causal link between arsenic exposure and lung cancer. Exposure-response relationships and high risks have again been observed. Increased risks have been observed at cumulative exposure levels in excess of 0.75 $mg/^3$.year (e.g. 15 years of exposure to a workroom air concentrations of 50 ug/m^3). It has been shown that tobacco smoking is interactive with arsenic in increasing arsenic risk.

In the past, arsenic has been classified as a carcinogen on the strength of evidence from human epidemiological studies. Although several animal carcinogenicity studies have been conducted, they have been inconclusive. In a recent study, however, in which female mice were exposed to arsenic in drinking water at concentrations commonly found in BFD-endemic areas, a high incidence of tumours were found in lungs (17.5%) and the intestinal tract (14.4%). Supporting evidence for the carcinogenicity of arsenic has been obtained from other laboratory studies.

Inorganic arsenic has not been seen to induce point mutations in bacteria or in mammalian cells, but it can produce chromosomal aberrations in vitro, transform cells and promote tumours. Arsenic has caused clastogenic damage in different types of cells from exposed humans and in human-derived *in vitro* test systems.

In addition to cancer of the lung, skin, bladder and kidney, long-term exposure to arsenic has also been linked to a number of other health effects. Chronic exposure via drinking water has been shown to cause peripheral vascular diseases. Whether arsenic alone is sufficient to cause the severe form of this disease, Blackfoot disease, is not known. Genotoxic effects are also evident.

Cancer at sites other than the lung, bladder kidney and skin, hypertension, ischemic heart disease, cerebrovascular disease and diabetes-mellitus have all been associated with long-term exposure to arsenic. Neurological effects and reproductive effects have also been reported in exposed populations. However, conclusions regarding the causality of the relationship between arsenic exposure and these other effects are less clear-cut. The evidence is strongest for hypertension and cardiovascular diseases, suggestive for diabetes and reproductive diseases and weakest for cerebrovascular diseases, long-term neurological effects and cancer at sites other than the skin, lung, bladder and kidney.

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Chapter 4. Diagnosis and treatment of chronic arsenic poisoning

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Humans are exposed to arsenic (As) primarily from air, food and water. However, elevated inorganic As in drinking water is the major cause of As toxicity. Most of the reports of chronic As toxicity in man focus attention on skin manifestations because of its diagnostic specificity, but As often affects most systems of the body. The clinical manifestations of chronic As intoxication are dependent on host susceptibility, the dose and the time course of exposure. The symptoms are often insidious in onset and varied in nature. However in a few epidemiological studies no significant clinical features of toxicity were attributed to chronic intake of As contaminated water.

4.1 Diagnosis

Although chronic As toxicity produces varied non malignant manifestations as well as cancer of skin and different internal organs, dermal manifestations such as hyperpigmentation and hyperkeratosis are diagnostic of chronic arsenicosis. The pigmentation of chronic As poisoning commonly appears in a finely freckled, “raindrop” pattern of pigmentation or depigmentation that is particularly pronounced on the trunk and extremities and has a bilateral symmetrical distribution (Fig. 4.1.1 - Mild pigmentation (a) Diffuse melanosis (with mild keratosis), (b) Mild spotty pigmentations, (c) Mild spotty depigmentations. (Guha Mazumder DN & Ghosh AK, personal collection) and Fig. 4.1.2 - (a) Moderate pigmentation, (b) Severe pigmentation. (Guha Mazumder DN & Ghosh AK, personal collection) (PENDING)) Pigmentation may sometimes be blotchy and involve mucous membranes such as the undersurface of the tongue or buccal mucosa (Black 1967; Yeh 1973; Tay 1974; Saha 1984, 1995, Guha Mazumder 1988, 1998a). The raindrop appearance results from the presence of numerous rounded hyperpigmented or hypopigmented macules (typically 2-4 mm in diameter) widely dispersed against a tan-to-brown hyperpigmented background (Tay 1974). Although less common, other patterns include diffuse hyperpigmentation (melanosis) (Tay 1974; Saha 1984), and localized or patchy pigmentation, particularly affecting skin folds (Tay 1974; Szuler et al. 1979; Luchtrath 1983). So-called leukodermia or leukomelanosis, (Saha 1984, 1995) in which the hypopigmented macules take a spotty, white appearance usually occur in the early stages of intoxication.

Arsenical hyperkeratosis appears predominantly on the palms and the plantar aspect of the feet, although involvement of the dorsum of the extremities and the trunk have also been described. In the early stages, the involved skin might have an indurated, gritlike character that can be best appreciated by palpation; however, the lesions usually advance to form raised, punctated, 2-4 mm wartlike keratosis that are readily visible (Tay 1974). Occasional lesions might be larger (0.5 to 1 cm) and have a nodular or horny appearance occurring in the palm or dorsum of the feet. In severe cases, the hands and soles present with diffuse verrucous lesions (Fig. 4.1.3 (a) Mild keratosis, (b) moderate keratosis (i) moderate diffuse thickening of the palm, (ii) a few nodules over thickened palm (associated lesions: Bowen’s disease of the abdomen and squamous cell carcinoma on the finger). (Guha Mazumder DN & Ghosh AK, personal collection) and Fig. 4.1.4 Severe keratosis (a) Verrucous lesion of the palm with keratotic horn, (b) Big nodules over the dorsum of feet (associated lesion: Squamous cell carcinoma). (Guha Mauzmder et al, 1997) (PENDING)). Cracks and fissures may be severe in the soles (Saha 1984, Guha Mazumder et al 1997). Histological examination of the lesions typically reveals hyperkeratosis with or without parakeratosis, acanthosis, and enlargement of the rete ridges. In some cases, there might be evidence of cellular atypia, mitotic figures, in large vacuolated epidermal cells (Black 1967; Tay 1974; Ratnam et al. 1992; Alain et al. 1993, Guha Mazumder et al., 1998c). Yeh (1973) classified arsenical keratosis into two types: a benign type A, further subgrouped into those with no cell atypia and those with mild cellular atypia; and a malignant type B, consisting of lesions of Bowen’s disease (intraepithelial carcinoma, or carcinoma in situ), basal-cell carcinoma, or squamous-cell carcinoma. The later might arise in the hyperkeratotic areas or might appear on nonkeratotic areas of the trunk, extremities, or head (Sommers and McManus 1953; Yeh 1973).

A history of As exposure through inhalation or ingestion is helpful in corroborating a diagnosis of arsenicosis since skin manifestations such as diffuse melanosis can not be differentiated from normal dark complexioned farmers in the tropics who work in the field bare bodied under direct sunlight. However, spotty rain drop pigmentation of the skin distributed bilaterally and symmetrically over trunks and limbs is the best diagnostic feature of arsenical hyperpigmentation. Though spotty depigmented spots, similarly distributed are also diagnostic for this condition, sometimes blotchy depigmented spots are seen and these need to be differentiated from other depigmented skin lesions like tinea versicolor, seborrheic dermatitis. Diffuse hyperkeratitic lesions of the palms and soles are distinctive lesions of chronic arsenicosis. However, manual labourers, who work with bare hands, might have thickening of the palms. The thickening of palms in manual labourers are usually localised in the pressure points. Bare footed farmers who work in the fields might have diffuse thickening of the soles. However, when the lesions become nodular the diagnosis becomes obvious.

The duration of the patient's As exposure with the date of onset of symptoms does not follow a particular time frame. Arsenical skin lesions have been reported to occur in West Bengal after drinking As contaminated water for one year or even less (Garai et al, 1984, Guha Mazumder et al., 1997). In Taiwan, the youngest patient drinking As contaminated water who developed hyperpigmentation was 3 years old (USEPA 1988). Among the population exposed to As in drinking water in the Antofagasta region of Chile, cases of cutaneous arsenicosis, including both hyperpigmentation and hyperkeratosis, have been described in children as young as 2 years of age (Rosenberg 1974; Zaldivar and Guillier 1977). The mean As dose in Antofagasta was estimated to be approximately 0.06 mg/kg per day for subgroups of children aged 3.13±3.33 years but was approximately 0.02 mg/kg per day for subgroups in their teens and twenties and 0.006 mg/kg per day for a subgroup in their sixties, indicating an inverse relationship between daily As dose rate/kg body weight and age (Zaldivar and Ghai 1980). In a retrospective study of 262 adults treated with Fowler's solution, Fierz (1965) reported the minimal latency period for hyperkeratosis to be 2.5 years, following ingestion of approximately 2.2 g of arsenite. Rattner and Dorne (1943) reported the development of hyperpigmentation within 6-12 months of the start of treatment with As at a dose of 4.75 mg/day. Hyperkeratosis appeared after approximately 3 years. Hence a history of chronic As exposure for more than 6 months is essential for diagnosis of As related skin manifestation.

With history of chronic As exposure and arsenical skin lesions, other indicators of chronic arsenicosis are weakness, anaemia, peripheral neuropathy, hepatomegaly with portal zone fibrosis (with/without portal hypertension), chronic lung disease and peripheral vascular disease (Espinosa 1963, Zaldivar 1974, Zaldivar & Ghai 1980, Datta 1976, Tseng 1977, Guha Mazumder et al. 1988, 1992, 1997, 1998a, Chen et al. 1988a, Engel and Smith 1994, Lagerkvist and Zitterlund 1994, Nins 1997, Kilburn 1997, Guo et al 1998). These features are manifested variably in different exposed populations and may also be caused by As unrelated conditions. Infrequent manifestations, which have been reported to occur by some investigators in people giving a history of chronic As exposure and which may be As unrelated are: conjunctivitis, keratitis, rhinitis, cardiovascular disease, gastrointestinal disease, hematological abnormalities, cerebrovascular disease, dysosmia, perceptive hearing loss, cataract, nephropathy, solid edema of the limbs, and diabetes mellitus (Tay and Seah 1975, Hotta 1989, Lai et al 1994, Gorby 1994, Morton and Dunnette 1994, Chen et al 1997, Guha Mazumder e t al 1998a, Rahman et al 1998).

These have least diagnostic value of chronic As toxicity inspite of their reported occurrence amongst people with a history of chronic As exposure.

Proper investigations need to be carried out to define the various clinical manifestations of chronic arsenicosis. Routine investigations should include haematology (Hb, total and differential count, RBC morphology), urine and stool examination, chest X-ray, electrocardiogram, determination of blood sugar, urea and creatinine. Patients with hepatomegaly need further investigation such as tests for hepatitis B and hepatitis C, liver function, ultrasonography and liver biopsy. Those having history of chronic cough and/or dyspnoea should be investigated by lung function tests. People having features of restrictive lung disease need further investigation by high resolution CT scan for the diagnosis of interstitial lung disease or bronchiectasis. Testing of nerve conduction velocity and electromyogram would help in the diagnosis of peripheral neuropathy. Upper GI endoscopy need to be done in people presenting with features of dyspepsia and portal hypertension. Doppler study of peripheral vessels may help in the diagnosis of peripheral vascular disease.

That chronic arsenicosis produces protean manifestations is evident from the report of the clinical features in 156 cases who had been drinking As contaminated water in West Bengal (Guha Mazumder et al 1998a) (Table 4.1.1).

Table 4.1.1: Clinical features of chronic toxicity; study of 156 cases in West Bengal.

Symptoms	No. of cases	(%)	Signs	No of cases	(%)
Weakness	110	(70.5)	Pigmentation	156	(100.0)
Headache	32	(20.5)	Keratosis	96	(61.5)
Burning of the eyes	69	(44.2)	Anaemia	74	(47.4)
Nausea	17	(10.9)	Hepatomegaly	120	(76.9)
Pain abdomen	60	(38.4)	Splenomegaly	49	(31.4)
* epigastric	39	(25.0)	Ascites	5	(3.0)
* paraumbilical	21	(13.4)	Pedal oedema	18	(11.5)
Diarrhoea	51	(32.6)	Sign of lung disease	45	(28.8)
Cough	89	(57.0)			
* with expectoration	53	(33.9)	Sign of polyneuropathy	21	(13.4)
* without expectoration	36	(23.1)			
Heamoptysis	8	(5.1)			
Dyspnoea	37	(23.7)			
Paresthesia	74	(47.4)			

Guha Mazumder et al. 1997.

Though pigmentation was seen in all cases, keratosis was found in 96 patients (61.5%), and skin cancer was detected in two (13%) cases. Weakness was a predominant symptom (70%) while anemia was present in 47% of cases. Nausea, anorexia, abdominal pain and diarrhoea were present in 91 patients (58.3%). Symptoms of respiratory disease were found in 89 (57.1%) cases. Lung function tests carried out on 17 patients showed features of restrictive lung disease in 9 and combined obstructive and restrictive lung disease in 7. Evidence of polyneuropathy was found in 79 (50.6%) cases. Objective evaluation of neuronal involvement could be done on 29 patients. Of these abnormal EMG was found in 10 (30.8%) and altered nerve conduction velocity and EMG in 11 (38%) cases. Perceptive hearing loss was found in two cases. Liver enlargement was found in 120 (76.9%) cases and was palpable 2-6 cm below the costal arch. Spleen was palpable 1.5-8 cm below the costal arch in 41 (31.4%) cases while ascites was present in 5 (3%) cases. Liver function tests could be done in 76 patients. Abnormal serum globulin (>3.5 gm/dl) level and alkaline phosphatase (>200 IU/dl) values were found in 12 (15.8%) and 39 (51.3%) cases respectively. Significant elevation of serum alanine aminotransferase (ALT) and aspartate aminotransferase (AST) activities were found in 9 (11.8%) and 21 (27.6%) cases respectively. Biopsy reports were available from 45 patients. Non-cirrhotic portal fibrosis was found on histology in 41 cases and cirrhosis in 2 cases while normal histology was observed in 2 patients. The liver histology of noncirrhotic portal fibrosis (NCPF) was characterized by expansion of the portal zone of varying degrees (Figure 4.1.5 - Liver histology of a case of chronic arsenicosis showing fibrous expansion of portal zone with extension in the liver lobule (H & E). (Guha Mazumder DN & Ghosh AK, personal collection) (PENDING)). Fine to thick stellate scars were found to spread out of the portal tracts which frequently contained leash of vessels. There was paucity of inflammatory cells in the portal zone and absence of gross hepatocellular damage. The fibrosis in the liver was mostly found to be mild (Grade-I 53.6%, Grade-II 29.6%) while moderate to severe fibrosis was found in a smaller number of cases (Grade-III 9.75% and Grade - IV 7.31%) (Fig. 4.1.6 - Various grades of noncirrhotic portal fibrosis of liver in chronic arsenicosis. Grade I and II (upper panel) Grade III and IV (lower panel) (Reticulin Stain) (Guha Mazumder DN & Ghosh AK, personal collection) (PENDING)). Portal hypertension was found in 52 cases (33.3%) as evidenced by splenomegaly and/or esophageal varices. However only three of these patients had hematemesis and melena. Except for lowered blood hemoglobin, no other hematological alnormality was detected in any of the cases. Urine reports and blood sugar, urea and creatinine values were found to be within normal limits. Peripheral vascular disease was detected in 3 cases when 64 more patients from severely affected area have been further investigated.

As exposure is a major risk factor for blackfoot disease, a unique peripheral arterial disease characterized by the severe systemic arteriosclerosis as well as dry gangrene and spontaneous amputations of affected extremities at end stages (Tseng, 1977; Chen et al., 1988a). Diagnostic criteria for blackfoot disease include objective signs of ischemia, i.e., absence or diminution of arterial pulsation, pallor on elevation or rubor on dependency of ischemic extermities, and various degrees of ischemic changes in the skin, as well as subjective symptoms of ischemia, i.e., intermittent claudication, pain at rest, and ischemic neuropathy. Not all patients are affected with black, mummified dry gangrene (Tseng et al., 1961). Extensive pathological study showed that 30% of blackfoot disease patients had histological lesions compatible with thromboangiitis obliterans, and 70% showed changes of arteriosclerosis obliterans. Marked generalized atherosclerosis was observed in all autopsied cases of blackfoot disease. Any of the fundamental vascular changes of the disease represent an unduly developed severe arteriosclerosis (Yeh and How, 1963). A recent study has shown a dose-response relationship between cumulative As exposure and subclinical peripheral vascular disorder detected by Doppler ultrasonography among seemingly normal subjects after cessation of drinking artesian well water in the endemic area of blackfoot disease in Taiwan (Tseng et al., 1995a).

Skin cancer of chronic arsenicosis is quite distinctive. The lesions are frequently multiple and involve covered areas of the body, contrary to non arsenical skin cancer which usually presents as a single lesion and which occur in exposed parts of the body (Tseng, 1977; Zaldivar et al 1981). Though other types of cancers, e.g. lung cancer, bladder cancer, kidney cancer, prostate cancer, angiosarcoma of the liver are observed in significantly higher number among cases of chronic arsenicosis (NRC 1999), these have no characteristic feature suggestive of arsenic etiology.

The As content of water consumed by patients with involvement of major organ system, as studied by Guha Mazumder et al 1997 is shown in Fig. 4.1.7 Various levels of arsenic in drinking water and its relation with initial presentation. (Guha Mauzmder, et al, 1997).(PENDING) Most of the patients had keratosis and hepatomegaly when As concentrations levels in drinking water were more than 0.5 mg/L. On the other hand a number of people did not have any lung or neurological manifestation even when they were drinking water containing more than 1 mg/L As. Thus keratosis and hepatomegaly have more diagnostic specificity than neurological or respiratory manifestations of chronic As toxicity. Since hepatomegaly may be caused by many other factors, it is not a specific indicator of As exposure. Because few conditions cause keratotic lesions in the skin these are most diagnostic for chronic arsenicosis. Other biomarkers for chronic As toxicity such as micronuclei, sister chromatid exchange and hprt mutant frequency have been described but are not specific for As. Given the relationship of skin cancer and hyperkeratosis observed in Taiwan, a dose-response analysis of hyperkeratosis in a US population exposed to As was found to be consistent with the EPA (US) skin cancer dose response estimate made from the Taiwan data (Chen and Chen 1991). Hyperkeratotic lesions occur much earlier following As exposure than does skin cancer and are much more prevalent. In the Tseng study (Tseng et al. 1968) of an As endemic area in Taiwan, the youngest person with hyperkeratosis was 4 year old; the youngest skin cancer case was 23 years of age. Hyperkeratosis was almost 20 times more prevalent in the As exposed population than skin cancer. Further, according to some, skin cancer arises from hyperkeratotic lesion (Yeh, 1973). This hyperkeratosis occurs more commonly and earlier in an As exposed population than does skin cancer. A dose response analysis of hyperkeratotic lesions may therefore allow one to observe potential carcinogenic response at lower exposures than has been done with skin cancer. Necessary information for the risk assessor to estimate dose-response would be the length and intensity of exposure and the prevalence (or incidence if possible) of hyperkeratosis by exposure and age (H. Gibbs in North et al 1997).

It becomes evident that with the exception of cutaneons manifestations other symptoms and signs of chronic arsenicosis are non specific and can occur with other unrelated medical conditions. Hence, history of As exposure by drinking As contaminated water and high level of As in urine and/or in hair and nails in association with those symptoms may help in the diagnosis of chronic arsenicosis. But its normal value in those materials do not exclude such diagnosis. Diagnostic criteria, grading of severity of dermatological manifestations and case definition of chronic As toxicity are summarised in the Tables 4.1.2, 4.1.3 and 4.1.4.

Table 4.1.2. Diagnostic criteria of Chronic arsenicosis.

1. At least 6 months exposure to arsenic levels of greater than 50 μg/L or exposure of high arsenic level from food and air.

2. Dermatological features characteristic of chronic arsenicosis.

3. Non carcinomatous manifestations: Weakness, chronic lung disease, non cirrhotic portal fibrosis of liver with/without portal hypertension, peripheral neuropathy, peripheral vascular disease, non pitting edema of feet/hand.

4. Cancers: Bowens disease, Squamous cell carcinoma, Basal cell carcinoma at multiple sites, occurring in unexposed parts of the body.

5. Arsenic level in hair and nail above 1 mg/kg and 1.08 mg/kg respectively and/or arsenic level in urine, above 50 µg/L (without any history of taking seafood).

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Table 4.1.3. Dermatological criteria and grading of severity of chronic arsenic toxicity.

Grade I	Mild	a) Diffuse melanosis.
		b) Suspicious spotty depigmentation/pigmentation over trunk/limbs.
		c) Mild diffuse thickening of soles and palms.
Grade II	Moderate	a) Definite spotty pigmentation/depigmentation on the trunk and limbs, bilaterally distributed.
		b) Severe diffuse thickening (with/without wart like nodules of the palms and soles).
Grade III.	Severe	a) Definite spotty pigmentation/depigmentation as above with few blotchy pigmented/depigmented macular patches over trunks or limbs.
		b) Pigmentation involving the undersurface of tongue and/or buccal mucosa.
		c) Larger nodules over thickened palms and soles occasionally over dorsal aspect of hands and feet. Diffuse verrucous lesions of the soles with cracks and fissures and keratotic horns over palms/soles.

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Table 4.1.4. Case definition of chronic arsenic toxicity.

Definite

1. Criteria 1 + Criteria 2 ± Criteria 3 ± Criteria 4 + Criteria 5
2. Criteria 1 + Criteria 2 (Grade II/III) ± Criteria 3 ± Criteria 4
3. Criteria 2 (Grade II/III) ± Criteria 3 ± Criteria 4 + Criteria 5

Probable.

1. Criteria 1 + Criteria 2 (Grade I) ± Criteria 3 ± Criteria 4
2. Criteria 2 (Grade I) ± Criteria 3 ± Criteria 4 + Criteria 5
3. Criteria 2 (Grade II/III) ± Criteria 3 ± Criteria 4

4. Criteria 3 + Criteria 5
5. Criteria 4+ Criteria 5

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A few epidemiological studies have highlighted that none of the exposed population to environmental As show any clinical manifestation of chronic As toxicity. (Goldsmith 1980. Harrington et al 1978. Valentine et al 1985). Further, there is a wide variation in the incidence of chronic arsenicosis in an affected population. Even not all members of an affected family show clinical effect. The reasons for such variation of disease expression is an enigma. However, as the As exposed people are at risk for developing As related cancer, they should be subjected to prolonged surveillance.

4.2 Biomarkers with special focus exclusively on diagnosis.

On the basis of As metabolism data, important biomarkers of internal exposure are: the urinary excretion of the element and its concentration in hair and nail (blood concentrations are generally too low and transient). Despite some encouraging reports, the use of As measurements in hair and nail as indices of absorbed dose appears limited. Efforts are needed to develop a standardized procedure to solve the problem of external contamination of samples. The relationship between As air concentration and urinary excretion of inorganic arsenic, and of mono and dimethyl arsonic acid, appears better. As urinary excretion (seafood As excluded) as a function of As oral intake via drinking water in steady state conditions, has been reported by several authors from different countries. Despite possible ethnic and environmental differences, reported results display a quite satisfactory consistency. Most strikingly, an increased excretion rate is observed when the water As concentration reaches 100 - 200 µg/L (Buchet and Hoet, 1998).

4.2.1 Urine

The concentration of total As in urine has often been used as an indicator of recent As exposure because urine is the main route of excretion of most As species (Buchet et al. 1981, Vahter 1994).

The half-time of inorganic As in humans is about 4 days. Average background concentrations of As in urine are generally below 10 µg/L in Europe (Apel and Stoeppler 1983; Valkonen et al. 1983; Foa et al. 1984; Vahter et al 1986; Andren et al. 1988; Jensen et al. 1991; Buchet et al. 1996; Trepka et al. 1996; Kristiansen et al. 1997; Kavanagh et al. 1998), somewhat higher in some parts of the US in people living near point source emissions, especially copper smelters (Smith et al. 1977; Morse et al. 1979; Binder et al. 1987), and around 50 µg/L in Japan (Yamauchi and Yamamura 1979; Yamauchi et al. 1992). In certain areas in the US, an average concentration of As of 10 µg/L or less has been reported for children (Kalman et al. 1990; Pollisar et al. 1990; Gottlieb et al. 1993).

Urinary As concentrations have also been shown to correlate with As intake in drinking-water. A survey was conducted by Harrington, et al. (1978) among a population in an area with elevated As concentrations in well water. Drinking well water with an As content exceeding 100 µg/L (mean 401 µg/L and an estimated total daily intake of 324 mg/L of As) gave an average urinary total As concentration of 178 µg/L (atomic absorption spectrophotometry). Drinkers of well water containing an average As concentration of 31 µg/L (estimated daily intake of 46 µg of As) had a mean urinary As concentration of 41 µg/L.

Seafood in the diet may influence urinary As measurements. Certain seafoods (particularly cold water fin fish, crustaceans, and molluscs) may contain large amounts of organo arsenic compounds, that have no known mammalian toxicity. In addition, certain edible marine foods, such as seaweed or kelp, may contain arsenosugars that are without recognized toxicity. These compounds are well absorbed from the gastrointestinal tract, and in the case of arsenobetaine, are largely excreted unchanged in the urine. When a clinical laboratory measures and reports the total As content in urine, the value may be markedly elevated (up to hundreds or thousands of µg/L) if they have ingested seafood within the past 1-2 days. In an effort to avoid the contribution of complex organo arsenicals in seafood, some clinical laboratories use a speciation method that only measures inorganic As, or its metabolites, monomethylarsnoic acid (MMA) and dimethylarsonic acid (DMA). However, certain marine organisms, particularly bivalves such as clams, may contain over one hundred micrograms of dimethylarsonic acid in a typical serving, and may thus elevate urine As values even when the more restrictive speciation methods of analysis are used. Consequently, a urine As measurement may not be a valid reflection of As ingestion from drinking water if there has been any consumption of seafood (including seaweed products) within the past three days.

The pattern of As species in urine from individuals chronically exposed to high concentrations of As via drinking water in Region Lagunera, Mexico was studied by Del Razo et al (1994). The urinary concentrations of As species and consequently of total As, were significantly higher in the exposed group. The sum of As species accounted for at least 95% of total As in urine. No significant differences in the proportion of inorganic and total organic As compounds in urine were observed (Table 4.2.1.1).

Table 4.2.1.1: Arsenic species excreted in urine from humans chronically exposed to arsenic (geometric mean (range)).

		CONTROL	**EXPOSED**
Total As	(µg g^{-1} creat.)	39.3	1,156[1]
		(12-104)	(456-1,981)
Inorganic As	(µg g^{-1} creat.) %	5.6	187.9[1]
		(0.5-22)	(34-503)
		10.9	16.7
		(1.4-29.5)	(9.3-25.5)
Organic As	(µg g^{-1} creat.) %	35.1	834.8[1]
		(8.4-103.4)	(234.2-1,832)
		84.8	82
		(70.4-98.6)	(74.5-96.8)
MMA	(µg g^{-1} creat.) %	3.24	189.4[1]
		(0.7-16.6)	(44-645)
		7.12	18.42[1]
		(1.8-2.5)	(6.2-29.5)

DMA	(μg g^{-1} creat.) %	30.56	680.21[2]
		(5.7-93.4)	(187-1,264)
		74.8	61.73[2]
		(46.8-94.6)	(47.9-81.8)
		22	23

Del Razo LM et al. 1997.
[1] p = 0.00002. Mann - Whitney's U test
[2] p = 0.002. Mann-Whitney's U test.

However, detailed study of the organic species showed that the exposed group had a significant increase in the proportion of MMA excreted in urine, accompanied by a significant decrease in the proportion of DMA excreted Figure 4.2.1.1.- Proportions of arsenic species in urine of individuals chronically exposed to arsenic via drinking water. Region Lagunera, Mexico. (Del Razo, et al, 1994). (PENDING). Nonetheless, DMA was the major single As species excreted by both groups. The mean percentages of urinary inorganic As were within the ranges described for two other populations chronically exposed to relatively large amounts of As in drinking water, one in Nevada, USA (Warner et al 1994) and the other in San Pedro, Chile (Hopenhayn-Rich et al., 1996).

Because of the variations in the proportions of different As metabolites in urine, sum of the metabolites is a better indicator of exposure than the concentration of inorganic As or DMA in urine. The exact reasons for the variations are largely unknown, but probable influences are age, sex, health status, genetic factors, and analytical variability. Genetic polymorphism of the still uncharacterized As methylation enzymes may help explain the inter individual variation. Similar genetic differences may exist in arsenic-specific binding proteins, which are thought to decrease the toxicity of inorganic As by decreasing its tissue availability until it can be methylated (Bogdan GM et al 1994). In a population, group-average concentrations of As metabolites in the urine correlate with the average concentrations of As in drinking water. However, the relationship can vary considerably depending on the amount of water consumed and the amount of water used for cooking.

For measuring concentrations of exposure markers in the urine, an important question is whether to collect 24-hr urine samples, spot urine samples, or early morning urine samples. Ideally, the amount of As excreted over a certain period of time should be assessed. Usually this is done by measuring As excretion in a 24 hr collection. However, obtaining complete 24-hr urine collections may be difficult (Bingham and Cummings 1983; Johansson et al. 1998) and requires supervision and validation. Because of these difficulties and other problems (e.g. the risk of contamination of the urine during sampling), the first-morning urine or spot urine samples are generally collected for measurement of the urinary concentration of inorganic As or As metabolites. There are several reasons why a single spot urine measurement, despite, its limitations could reflect the 'usual' dose in the study population. Under chronic exposure conditions, one can assume that the participants were exposed to As in a fairly constant manner. To evaluate the concentration properly, especially in the case of spot urine samples, the dilution of the urine has to be considered. The urine flow is highly variable, being dependent on numerous factors, such as body size, body water content, solute intake, physical activity, and diurnal variation (Diamond 1988). A short time after the consumption of large amounts of fluid, the urine is very diluted and has a low solute content. To compensate for the dilution, the concentration of As species can be related to the concentration of creatinine or the specific gravity. A disadvantage of using the creatinine-adjusted urinary As measurement is that it is dependent on the muscle mass and thus is often quite different for men and women. Protein intake might also influence urinary creatinine concentration.

Though high AS excretion in urine is indicative of continued As exposure, this is not always diagnostic of chronic As toxicity. In West Bengal, India, a significant number of people who were drinking As contaminated water and had high urinary As excretion did not show cutaneous manifestations of chronic As toxicity (9 out of 17). On the other hand many of the chronically As exposed people showing arsenical skin lesions did not have high urinary As excretion (33 out of 40). (Chowdhury TR et al. 1997). These results might be explained by the fact that all those who are drinking As contaminated water at a point of time may not be showing clinical features of chronic As toxicity, while others who might have taken As contaminated water for a long time in the past but have then stopped drinking contaminated water might still have clinical expression of As toxicity.

4.2.2 Hair and Nail

Arsenic is normally found in higher concentrations in human hair and nails than in other parts of the body. This has been explained by the high content of keratin in these tissues (Shapiro, 1967). Hair As levels can provide useful information in chronic As poisoning but undue weight should not be given to the results. Several problems confront the toxicologist when using this test: there is only a very approximate relationship between hair As concentration and As toxicity. Thus, patients with chronic As poisoning may have hair concentrations varying, from 10 ppm (10 mg/kg hair) to 100 ppm whereas levels of around 45 ppm have been reported in Aa-related fatalities. Results derived from the analysis of a single hair or of one site along the shaft of a single hair are much less reliable than mean levels from larger hair samples because the inter and intra-hair variations in As content can be very large. Thus, samples should consist of at least one gram of hair cut close to the scalp and derived from several sites on the head and the whole sample should be analysed. External contamination of the hair by As must be excluded in order to use hair As concentrations to assess toxicity. Ingested As and As derived from external contamination are both avidly bound to the outer surface of the hair and these two sources cannot be differentiated by any known technique. External contamination can produce As concentrations of several thousand ppm and therefore can mislead investigators attempting to diagnose chronic As poisoning. Despite these pitfalls, the test can give useful information if carefully interpreted (Hindmash JT, 1998).

In people with no known exposure to As the concentration of As in hair is generally 0.02-0.2 mg/kg (Valentine et al. 1979; Olguin et al. 1983; Narang et al. 1987; Takagi et al. 1988; Koons and Peters 1994; Wang et al. 1994; Wolfsperger et al. 1994; Vienna et al. 1995; Raie 1996; Paulsen et al.1996; Rogers et al. 1997; Kurttio et al. 1998). The concentrations of As in hair are clearly increased in people drinking water with high As concentration. For example, concentrations ranging from 3 to 10 mg/kg are reportedly common in people in areas in West Bengal that have high As concentrations in drinking water (Das et al. 1995).

On a group basis, a few reports indicate that the correlation between the concentration of As in drinking water and the concentration in hair is fairly good, although it is not known how much of the As in hair originates from As in blood and how much is bound due to external contact with the water, as discussed above. In studies carried out in

California and Nevada, a concentration of 400 µg/L in drinking water corresponded to about 1.2 mg/kg in hair and 100 µg/L in water corresponded to about 0.5 mg/kg in hair (Valentine et al. 1979). In Alaska, an average of 400 µg/L in drinking water corresponded to 3.3 mg/kg in hair (Harrington et al. 1978). In Hungary, people with drinking-water concentrations ranging from 50 to 100 µg/L had an average hair concentration of 3 mg/kg (Borzsonyi et al. 1992). The highest hair As concentrations were found in children (Grantham and Jones 1977).

Normal As values in nails appear to range from 0.02 to 0.5 mg/kg (Narang et al. 1987; Takagi et al. 1988). Several tens of mg per kg have been reported in cases of chronic poisoning (Pounds et al. 1979; Das et al. 1995). A single dose of As can be detected at the distal tip of the nails about 100 days after exposure (Pounds et al. 1979; Pirl et al. 1983). Presumably, As is deposited in the nail roots from the blood and then migrates distally as the nails grow (at about 0.12 mm a day).

In one case of repeated ingestion of As over a period of one year, the value of sectional nail analysis was investigated by Henke et al. (1982). The As determinations were performed by instrumental neutron activation analysis. After subdividing the nail transversely into segments of 0.5 mm length, several maxima and minima of As concentrations were found. Taking the nail growth into consideration, the results corresponded to the known dates of treatment and discharge from hospital. The results excluded external contamination of the nail.

Although hair/nail As has been found to be elevated in people drinking As contaminated water there is no correlation between As concentration in hair and nail and the degree of exposure (Guha Mazumder et al. 1997). Similarly there is no correlation between hair and nails As and clinical features of chronic As toxicity. In a village of West Bengal all 17 people drinking As contaminated water had raised hair and nail As, but only 8 had cutaneous lesions. Further, out of 40 people with arsenical skin lesions in another village of West Bengal with a history of drinking As contaminated water, normal hair and nail As was found in 31 and 26 cases respectively (Chowdhury et al. 1997).

4.2.3 Blood

Most inorganic and organic As in blood is cleared fairly rapidly in man. Blood As will therefore reflect exposure for only a short period following absorption and will be very time dependent. Only if exposure is continuous and steady, as is sometimes the case with exposure through drinking-water, will As reach steady-state in the blood and thus make it possible to discern a relationship between blood As and exposure. Even so, there are no data that indicate a quantitative relationship in man between As exposure and blood As concentrations. The short half-life of As in the blood compared with the half-life in the body makes it difficult to discern a relationship between blood As concentration and total body As burden or As concentrations in different organs.

Partial speciation of As in blood has been reported in few cases (Zhang et al. 1996; Concha et al. 1998b). When using total As in blood as an indicator of exposure to inorganic As, the interference from organic As compounds originating from seafood has to be considered. Furthermore, because of the low concentrations, the analytical error might be significant, unless relatively sensitive methods are used. Data on concentrations of As in blood in people with no known exposure to As are in the range

0.3 - 2 µg/L (Bencko and Symon 1977; Heydorn 1970; Kagey et al. 1977; Olguin et al. 1983; Hamilton et al. 1994; Vahter et al. 1995; Concha et al. 1998a,b).

In people exposed to As in drinking water (200 µg/L) in northern Argentina, the mean blood As concentration was about 10 µg/L (Vahter et al. 1995; Concha et al. 1998a.b). In studies carried out in California and Nevada, an As concentration of 400 µg/L in water corresponded to about 13 µg/L in blood, and 100 µg/L in water corresponded to 3-4 µg/L in blood (Valentine et al. 1979). Obviously, compared with urine, blood is a much less sensitive biomarker of exposure to As via drinking water (NRC 1999).

4.2.4 Other Tissues

The concentrations of As in various human tissues determined by neutron activation analysis and reported by Liebscher & Smith (1968), Larsen et al. (1972), and Brune et al. (1980) are shown in Table 4.2.4.1.

Table 4.2.4.1.: Arsenic concentration in human organs and tissues.

	Arsenic concentration (mg/kg)		
Tissue or organ	**Dry weight[a] (geometric mean values)**	**Wet weight[b] (mean values)**	**Wet weight[c] (median values)**
adrenal	0.03		
aorta	0.04		
whole blood	0.04		
brain	0.01		
hair	0.46		
heart	0.02		
kidney	0.03	0.007	0.004
liver	0.03	0.011	0.003
lung	0.08	0.010	0.008
muscle	0.06 (pectoral)	0.004	
nail	0.28		
ovary	0.05		
pancreas	0.05	0.005	
prostate	0.04		
skin	0.08		
spleen	0.02	0.003	
stomach	0.02		
teeth	0.05		
thymus	0.02		
thyroid	0.04		
uterus	0.04		

WHO, 1981.
[a] Compiled from Liebscher & Smith (1968).
[b] Complied from Larsen et al. (1972).
[c] Complied from Brune et al. (1980).

Several autopsy studies have linked exposure to inhaled As in smelter workers with persistence of As in lung (Brune et al 1980, Gerhardsson et al, 1988). In one study, exposed workers had lung As concentrations six times higher than in controls (47 μg/kg tissue versus 8 μg/kg). These increases were not seen consistently in the kidney or in the liver, and the elevation in the lung did not decline significantly even as the time from retirement to death increased, suggesting a long halflife (Brune et al, 1980). Other evidence also indicates that ingested As reaches the lungs. A fatal poisoning following As ingestion by a 3 year old boy resulted in an As concentration in the lungs of 7550 μg/kg (Saddy et al 1989). In another fatal case the As lung concentration was 2750 μg/kg (Quatrehommc et al. 1992).

Maximum As content of the liver in people with hepatomegaly drinking As contaminated water in West Bengal, India, was 6 mg/kg (neutron activation analysis) although As was undetectable in 6 out of 21 case samples tested (mean 1.39 ± 0.3 mg/kg, control 0.016 ± 0.04 mg/kg). There was no correlation between the As content in biological tissues (liver, hair and nails) and the As dose taken by the patients (Fig. 4.2.4.1 - Correlation of arsenic content in biological tissue (Liver, Hair & Nail) with quantum of arsenic exposure.(Guha Mazumder et al, 1997) (PENDING)).

4.3 Treatment of chronic Arsenic toxicity.

Chronic arsenicosis leads to irreversible damage in several vital organs and As and is an established carcinogen. Despite the magnitude of this potentially fatal toxicity, there is no effective therapy for this disease; patients once affected may not recover even after remediation of the As contaminated water. The need for an effective therapy for chronic arsenicosis is obvious.

Chelation therapy for chronic As toxicity is thought to be the specific therapy for relief of systemic clinical manifestations and reduction of As stores in the body, reducing subsequent cancer risk. Chelation therapy is presumed to be more effective with early features of the toxicity, as severe manifestation of polyneuropathy, chronic lung and liver disease, swelling of hand and legs, defect of hearing and vision are less likely to respond to this therapy. Chelating agents like, DMSA (Dimercaptosuccinic Acid), DMPS (Dimercaptopropane succinate) d-penicillamine have frequently been considered for treatment of chronic As toxicity. However, their usefulness are yet to be established.

4.3.1 Chelators

A chelating agent forms ring structure with a metal or metalloid. When used for treating heavy metal poisoning, the administration of the chelating agent results in the formation of a chelate structure which has a water solubility greater than that of the offending metal and thus increases its excretion by the kidney. The chelating agent usually has a greater affinity for the metal ion than do endogenous legends to which the offending metal is bound. A number of chelating agents are considered for use against As poisoning.

4.3.1.1 DMSA (meso - 2,3-dimercaptosuccinc acid, Succimer, Chemet) and DMPS (sodium 2,3 - dimercapto-1-propane sulfonic acid, Dimaval)

(Fig. 4.3.1.1.1 - Chemical formula for chelating agents used for treating heavy metal poisoning in humans - PENDING)

DMSA and DMPS are water soluble analogues of dimercaprol developed as heavy metal chelators in the 1950s (Liang et al 1957, Petrunkin 1956). Evaluations of poisoning by lewisite in rabbits (Inns et al 1990, Inns and Rice 1993) and As trioxide in mice (Kreppel et al 1990, 1993) and in guinea pigs (Reichle et al 1991) showed better results by treatment with DMSA and DMPS over BAL (British anti Lewsite). Reichl et al (1992) reported that the biliary excretion of As from perfused guinea pig liver increased from 0.1% with BAL to 12.3% with DMPS. The significantly lower toxicity, the ease of oral administration, and the enhanced biliary clearance of As, all contribute to the clinical consensus that DMSA and DMPS and not BAL are the first choice for As poisoning (Kelafant et al 1993, Kew et al 1993, Marcovigi et al 1993). DMPS appears to be biotransformed in humans to acyclic and cyclic disulfides. Whereas DMSA in humans is biotransformed almost completely to a DMSA: CySH (1:2) mixed disulfide (Maiorino et al 1989), a DMPS-Cysteine mixed disulfide has been found only in minute amounts after administration of DMPS. Another difference between DMSA and DMPS is that the later is distributed both in an extracellular and to a small extent an intracellular nanner while the former is distributed only extracellularly (Zheng et al 1990, Wildenaner et al 1982, Reuther et al, 1982). Both renal and biliary excretion of DMPS occur (Zheng et al, 1990).

Controlled animal experiments have demonstrated that dimercaprol, DMSA, and DMPS increase survival when administered within minutes to hours after acute poisoning with lethal doses of organic or inorganic arsenicals (Stocken and Thompson, 1946; Tadlock and Aposhian, 1980). However, the efficacy of these agents declined in proportion to the length of time after acute As exposure before that treatment was begun. In studies of the effect of dimercaprol on experimental organoarsenical poisoning in rabbits, Eagle et al (1946) noted that all animals survived when a signle injection of dimercaprol was administered 5 minutes after the exposure of arsenical, compared to no survival if treatment was delayed for 6 hours. Data obtained by Tadlock and Aposhian (1980) on the efficacy of single dose of DMSA (0.25 mmol/kg, i.p.) against a lethal dose of sodium arsenite (0.14 mg/kg, s.c.) in mice suggests that beneficial effects on survival may begin to diminish when treatment is delayed for 2 or more hours.

The first prospective randomised controlled trial to evaluate the efficacy and safety of dimercaptosuccinic acid (DMSA) to chronic arsenicosis patients was carried out by Guha Mazumder et al. (1998c). Twenty-one consecutive patients with chronic arsenicosis were randomized into 2 groups. Eleven patients (10 males, ages 25.5 ± 8.0 years) received DMSA 1400 mg/d (1000 mg/m^2) in 4 divided doses in the first week and then 1050 mg/d (750 mg/m^2) in 3 divided doses during the next 2 weeks. The same was repeated after 3 weeks during which no drug was administered. The other 10 patients (all males, ages 32.2 ± 9.7 years) were given placebo capsules (resembling DMSA) in the same schedule. The patients were blinded about the nature of treatment being given. The patients included in the study were selected from the As clinic on the basis of history of drinking As contaminated water (≥ 0.05 mg/L) for 2 years or more and clinical symptoms and signs of chronic arsenicosis. The symptoms and signs of patients were evaluated by a scoring system before and after treatment (c.f. Table 4.3.1.1.1)

Table 4.3.1.1.1.: System of Clinical Scoring of the Symptoms and Signs Before and After Therapy with DMSA and Placebo.

Symptoms and Signs	None	Mild	Present Moderate	Severe
Weakness	0	1		
Cough	0	1		
Dyspnea	0	1	2	3
Rales, rhonchi	0	1		
Hepatomegaly	0	1 (14 cm span)	2 (16 cm)	3 (> 16 cm)
Splenomegaly	0	1 (2 cm)	2 (4 cm)	3 (> 4cm)
Pigmentation	0	1 (Diffuse)	2 (Spotty)	3 (Blotchy)
Keratosis	0	1 (Thickening)	2 (Few nodules)	3 (Multiple nodules)
Flushing of face	0	1		
Conjunctivitis nonpitting	0	1		
Edema leg/hand	0	1		
Abdominal pain	0	1		
Anorexia	0	1		
Nausea	0	1		
Diarrhea	0	1		
Hearing defect	0	1		
Claudication	0	1		
Hand/leg ulcers	0	1		
Paresthesia	0	1 (Only legs)	2 (Leg + hands)	
Pallor	0	1		
Ascites	0	1		
Loss of ankle jerk	0	1		

Guha Mazumder et al., 1998c Maximum score 33.

Any possible therapy-related side effect was monitored in every patient. All the patients were kept hospitalized during the study period. Skin was biopsied from unexposed areas by punch biopsy technique for histologic evaluation before and after treatment. Urine samples were collected for 2 consecutive days before, and then at 48 and 72 hours after starting the drug or placebo. Urine As was determined by graphite furnace atomic absorption with Zeeman-background correction.

There were no differences in age, sex, duration of exposure to the As contaminated water, As concentration in the drinking water, duration of drinking As free water before inclusion into the study, and clinical score of symptoms and signs between patients on the drug and in controls. Therapy with DMSA did not cause any significant clinical improvement as compared to patients treated with placebo. The clinical score improved after therapy with DMSA, but similar improvement was observed in patients treated with placebo (Table 4.3.1.1.2).

Table 4.3.1.1.2: Clinical scores of patients before and after therapy.

	Before	After	p value
DMSA	9.33±3.33	6.2±2.11	0.017
n = 11			
Control	10.6±3.20	6.7±1.70	0.003
n=10			

(Guha Mazumder et al. 1988)

(Fig. - 4.3.1.1.2 - Clinical score of DMSA and placebo treated cases before and after therapy. (Guha Mauzmder et al. 1998c) (PENDING)) There was no difference in the results of the urinary excretion of As, liver function tests and As concentration in hair and nails before and after treatment. No patient developed any therapy related side effects. The histologic abnormalities in skin biopsy did not show any difference in patients treated with DMSA and placebo before and after therapy. In this study the authors did not find DMSA for 2 courses at 3 week intervals to have any clinical or biochemical benefit in patients with chronic arsenicosis.

Shum and Whitehead (Shum S et al. 1995) reported that treatment of an adult who had ingested 80 g methane arsenate with DMSA 30 mg.kg/d x 5d over 1 month reduced serum As from 2871 μg/L to 6 μg/L. Lenz et al (Lenz K et al, 1981) also found DMSA to be effective in man. However, Kew et al (1993) found no improvement in peripheral neuropathy of 4 months duration after DMPS 300 g/d x 3 weeks and DMSA 1.2 g/d x 2 weeks.

In a recent study (Aposhian et al. 1997), the administration of DMPS to subjects with very recent, long-term ingestion of As in drinking water was found to be associated with a prompt increase in the excretion of As in the urine that was several fold above pre-chelation levels. In 13 subjects consuming As in drinking water (528 μg/L) until one day prior to the administration of a single oral 300 mg dose of DMPS, total urine As increased from a baseline of 605±81 μg/g creatinine (Cr) to a peak of 2325±258 μg/g Cr in the first two hours post chelator. In 11 control subjects chronically consuming water containing As at a concentration of 21 μg/L, DMPS resulted in the baseline urine As concentration of 91±17 μg/g Cr transiently increasing to 305±79 μg/g Cr. The data are consistent with chelation accelerating the decorporation of As in chronically exposed humans. However, animal experiments suggest that compared to cessation of exposure alone, DMPS chelation may predominantly effect the rate of As excretion, rather than longterm net excretion (Maiorino and Aposhian, 1985).

Recently Guha Mazumder et al. (1998d) presented their preliminary data on the efficacy of treatment of DMPS in a single blind placebo controlled trial in patients suffering from chronic As toxicity in West Bengal. The trial design was similar to that carried out in DMSA trial (vide supra). DMPS was given in a dose of 100 mg capsules 4 time a day for a course of 7 days for four courses with one week drug free period between each course. Nine patients received the drugs, while 6 patients received palcebo capsules. Baseline data and clinical scores before and after the treatment are given in table 4.3.1.1.3.

Table 4.3.1.1.3. Clinical score of patients pre and post therapy with DMPS and placebo.

	DMPS Treated group	Placebo group	P value
	(n = 9)	(n = 6)	
Age (year)	31.11±12.18	31.00±7.24	
Sex (M:F)	7:2	4:2	
As level in drinking water mg/l	0.60±0.40	1.38±1.07	ns
Duration (in years)	20.1±11.24	18.3±3.35	ns
Clinical score:			
Pre treatment	14.8±8	13.2±3.1	ns
Post treatment	4.3±1.8[a]	9.6±0.96[b]	$p < 0.01$

(Guha Mazumder et al.1998d.

[a] $p < 0.01$ pre and post treatment DMPS

[b] $p < 0.05$ pre and post treatment placebo.

Though there was significant decrease of clinical score from pretreatment to post treatment values amongst both DMPS and placebo groups, there was significant difference in decrement of clinical score among DMPS treatment patents compared to placebo group (Fig. 4.3.1.1.3 - Clinical score of patients pre- and post therapy with DMPS and placebo. (Guha Mazumder et al, unpublished data) (PENDING)). However, there was no change of skin histology score of pre and post treatment skin biopsy carried out on 4 DMPS and 3 placebo treated cases. There was also no significant difference in the hematological and liver function test parameters amongst both the groups of patients before and after therapy with either DMPS or placebo. No side effects were noticed among the patients treated with DMPS. From the preliminary analysis of the data it appears that DMPS is more effective than placebo in improving clinical features of chronic As toxicity. However, follow up study of the cases treated need to be carried out to assess the efficacy of this initial improvement of clinical symptoms in altering the natural history of chronic As toxicity. At the present time, there is no follow-up data available to determine whether a short term increase in urinary As excretion associated with chelation will result in a lower risk of long term adverse outcomes, such as cancer (Kosnett MJ in press).

4.3.1.2 D-Penicillamine

Penicillamine was first isolated in 1953 from the urine of patients with liver disease who were receiving penicillin. It is an effective chelator of copper, mercury, zinc and lead and promotes the excretion of these metals in the urine. The usual dose is 1 to 1.5 gm per day. The drug has been suggested for the treatment of long term exposure to arsenic either alone or in combination with dimercaprol. However with long term use, penicillamine induces several cutaneous lesions including urticaria, macular or papular lesion, pemphigoid lesion, lupus erythematosus. Hematological system also may be affected severely causing leukopeina, aplastic anemia and agranulocytosis. Affection of other systems e.g. renal, pulmonary and gastrointestinal system may also show evidence of toxic manifestation (Goodman and Gilman, 1996). D-Penicillamine is a costly drug with associated toxic side effects in 20% to 30% of patients.

Therapy with d-penicillamin in a dose of 250 mg thrice daily for 15 days in a group of 5 patients suffering from chronic arsenicosis in West Bengal when followed up for 2-5 years, did not show any difference with control patients (Guha Mazumder et al, 1998d). In contrast, Bansal et al (1991) reported significant improvement in neuropathy of 6 weeks duration after 2 to 4 weeks of D-penicillamine, 750 mg/day even though it was experimentally found to be ineffective in relieving the systemic symptoms of acute As poisoning (Kreppel et al. 1989). Study on the effect of long term treatment with this agent need to be carried out to ascertain whether such therapy could alter the natural course of chronic As toxicity.

4.3.2 Retinoids

More than 50 years ago, Hall (1946) and colleagues described a beneficial effect of oral supplementation with Vitamin A (retinol) in the treatment of cutaneous arsenicosis. In that report, oral Vitamin A, 150, 000 USP units per day for 3 months resulted in a partial regression of hyperpigmentation and hyperkeratosis of palms in a 39 year old male who had taken Fowler's solution (potassium arsenite) for treatment of childhood chorea. More recently, Thiaprasit (1984) presented a case series of 9 patients with cutaneous aresenicosis who were treated for 2 to 7 months with oral etretinate, a synthetic aromatic retinoid. Clinical and histopathological improvement was noted in arsenical hyperkeratosis, but not in hyperpigmentation. Other case reports of regression of arsenical keratosis with etretinate treatment have been published (Biczo et al, 1986; Sass et al, 1993). It is noteworthy that etretinate and other retinoids have been reported to have antikeratinizing effects in other disorders of keratinization, such as hereditary palmo plantar keratoderma, Pityriasis rubra pilaris, and certain ichthyoses (Fritsch, 1992).

In addition to causing regression in arsenical keratosis, retinoids may offer significant promise in the chemoprevention of As-related cancers. The interaction of endogenous and exogenous retinoids with nuclear receptors influences the expression of genes that effect cell differentiation, proliferation, and induction of apoptosis (Miller, 1998). Some clinical trials, recently reviewed by Lotan (1996) and Hong and Sporn (1997) suggest a beneficial role for retinoids in chemoprevention of cancer in multiple organs. For example, Bouwes Bavinck et al (1995) reported a prospective, double-blind, placebo controlled trial of acitretin in renal transplant patients that resulted in decreased occurrence of cutaneous squamous cell carcinoma and keratotic skin lesions. A prospective randomized, controlled trial of retinoids in patients with chronic cutaneous arsenicosis is clearly indicated at this point of time. However, the therapeutic challenge will lie in selecting the right drug, at the proper dosage, at the correct stage of carcinogenesis. In addition, because retinoids and high dose retinol may have adverse effects, including teratogenesis, such trials will require careful attention to patient selection and surveillance. (Kosnett MJ in press).

4.3.3 Supportive and symptomatic treatment

Though efficacy of specific chelation therapy for patients suffering from chronic As toxicity has not yet been fully substantiated, supportive treatment could help in reducing many symptoms of the patients. Treatment in hospital with good nutritious diet has been found to reduce symptom score in a subset of placebo treated patients in West Bengal during the course of DMSA trial (Guha Mazumder et al 1998c). High protein containing diet, possibly helps in clearance of inorganic As (more toxic) by increased methylation. Thus people should be urged to take food containing proteins in good quantity either from animal source or if unable, from vegetable sources like pulses, soybeans, wheat etc. People should be advised to stop drinking As contaminated water or exposure to As from any other source. Follow up study carried out in West Bengal showed that drinking of As free water did cause improvement of skin manifestations, weakness, anaemia and neuropathy in a significant number of cases (Guha Mazumder et al 1998d). Whether this could decrease the incidence of cancer in the As exposed population is not know.

The various clinical manifestations should be treated symptomatically. Chronic bornchitis with or without obstruction are the common cause of mortality in many cases of chronic As toxicity. It is extremely important that bronchial irritation should be reduced to a minimum. The patient who smokes should be urged to stop completely and permanently. Dusty and smoke laden atomospheres should be avoided. Respiratory infection should be treated promptly because it aggravates breathlessness. Purulent sputum may be treated with oral oxytetracycline or ampicillin in a dose of 250-500 mg 4 times a day or Co-trimoxazole 960 mg twice daily. A 5-10 day course of treatment is usually effective and sputum becomes mucoid. Bronchodilators are much less effective in chronic bronchitis than in bronchial asthma, but should be given to all patients with reversible airflow obstruction. Regular treatment with an inhaled beta$_2$-adrenoreceptor agoinst (Salbutamal 200 mcg or terbutatine 500 mcg, 4-6 hourly) may be sufficient in patients with mild to moderate disease. The anticholinergic bronchodilator drug ipratropium bromide in a dose of 36-72 mcg 6 hourly may be added in patients with more severe air flow obstruction. Theophyllin therapy often has little measurable effect on the airway obstruction associated with chronic bronchitis, but it will improve quality of life in some patients. Treatment option for interstitial lung disease is limited. Dyspeptic symptoms associated with chronic arsenicosis could be easily managed by use of H_2 receptor blockers with/without prokinetic drugs. Though non cirrhotic portal fibrosis occur frequently in these patients, the incidence of portal hypertension is quite low.

When varices are detected by endoscopy prophylactic therapy by betablockers may be of help. Sclerotherapy or banding may be needed for the management of variceal haemohage. Peripheral vascular disease associated with gangrene are difficult to treat because of severe pain. Pharmacological agents like pentoxyphyllin or calcium channel blockers are found to have limited effect. Most of these patients need surgical amputation. Symptoms of peripheral neuropathy improve in some on stoppage of drinking As contaminated water. Tricyclic antidepressents such as amitryptiline may have utility in relieving painful dysthesias of arsenical peripheral neuropathy (Wilner and Low 1993). Skin thickening of the sole and palm can be treated by local application of keratolytic ointment (Containing 3% salicylic acid) (Saha KC, 1995, Guha Mazumder DN, 1996).

Excision of early skin cancer and bladder cancer due to chronic arsenicosis can be curative. However in advanced cases of those cancers and in cases of internal cancers the treatment options are meager.

4.4 Natural history

Not much information is available in the literature regarding the long-term effect of chronic As toxicity after stoppage of drinking As containing water. Arguello et al (1938) reported that keratodermia appeared insidiously between 2nd and 3rd year of intoxication and didn't disappear after cessation of exposure. Some individuals were followed up for more than 30 years after termination of exposure.

To know the effect of providing safe water to the affected people, a cohort of 24 patients of chronic arsenicosis were re examined after drinking As free water (As < 10 µg/L) for a period varying from 2-10 years (13 patients 10 years, 11 patients 2-5 years). These people were drinking As contaminated water (130 to 2000 µg/L) earlier for 4 to 15 years. Weakness and anaemia were present in 91.6% and 58.3% of cases initially and was persistent in 60.8% and 33% of cases respectively on repeat examination. Partial improvement of pigmentation and keratosis were observed in 45% and 46% of patients respectively. But liver enlargement was persistent in 86% of cases. However, most distressing observation was new appearance of signs of chronic lung disease (cough, shortness of breath and chest signs) in 41.6% of cases. There was slight reduction of clinical symptoms of neuropathy. It was present in 11 cases (45.8%) at the time of initial examination while in 8 cases (33.8%) during the subsequent period (P<0.5). No new case of neuropathy was detected in any of the follow-up patients. However, diminished hearing was observed in 5 cases during follow-up examination though it was present in 2 cases initially. Similarly 3 patients complained of dimness of vision during follow-up examination though none had such symptom earlier. None of these three patients had cataract or any other abnormality on fundoscopy. From the above it becomes apparent that not only many of the clinical manifestations of chronic arsenicosis persist for long duration inspite of stoppage of taking As containing water, but new symptoms may appear in some of them. (Guha Mazumder et al. 1998d).

4.5 Outstanding questions and future research needs

Pigmentation and keratosis are considered diagnostic of chronic As toxicity. However, varied clinical manifestations have been reported to occur in As exposed population. Proper epidemiological study comparing their incidence in As exposed and control population with similar age, sex and socioeconomic status need to be carried out. This will help in identifying specific clinical feature which could be considered diagnostic of chronic As toxicity. It need to be emphasised that many people remain asymptomatic in spite of drinking As contaminated water for many years. Not only there is much variation in the incidence of As related symptoms in an exposed population but only some of an affected family show such features. Goldsmith et al (1980) evaluated the effects of well water As (0.1 to 1.4 mg/l) on health status of residents of Lassen county, California. No particular illness was found to have greater prevalence in groups exposed to elevated As level. Harrington et al (1978) studied exposure level and possible health effect of As in drinking water among residents of a 150 square miles area near Faireblanks, Alaska. The mean concentration of As in water was 0.22 mg/l with some values as high as 2.45 mg/l. No differences were found in signs, symptoms and physical examination findings in the various exposure categories. Valentine et al (1985) surveyed groups of 20 to 57 residents in six United States cities where drinking water concentrations of As ranged from 0.5 to 395 µg/l. No significant difference in the prevalence of gastrointestinal, dermal or neurological symptoms were detected between any of the groups studied. The reasons for non expression of clinical manifestation of chronic As toxicity in many people exposed to prolonged intake of As contaminated water need further study.

Skin lesions are often used as useful precursors to more severe effects like cancer of skin or other internal organs. Cuzick and Co-workers (1984, 1992) observed that palmer keratosis occur early before people develop As related cancers. However, according to the Technical Panel of the EPA Risk Assessment Forum (USEPA 1988) appearance of such lesions could not be interpreted as a precursor to skin cancer as some malignant skin lesions arise *de novo*. Thus surveillance study of large population exposed to As need to be carried out to ascertain whether As related skin lesions could be used as precursor for cancer of skin or other internal organs.

Chen et al, (1988b) reported that after adjusting for artesian well water consumption, As poisoning (evidence of hyperkeratosis and skin cancer) and undernourishment that a family tendency of Black foot disease persisted and suggested a genetic susceptibility was a sound explanation. Epidemiological study in West Bengal, India, showed that male sex and malnutrition were associated with increased prevalence of skin manifestation in As exposed population. That study further showed that skin lesions occurred in some people with As levels less than 100 μg/L (pigmentation 3.2% & 0.8% and keratosis 1.5% & 0.4% among 274 males and 313 females, respectively, Guha Mazumder et al 1998b). As people in tropical countries like West Bengal, drink water varying from 2 litre to 5 litres per day, significant amount of As exposure occur in these people even with lower level of As in water. Hence for developing a biologically based dose-response model, more studies on individual susceptibility to As need to be carried out after taking into consideration factors like quantity of water taken by people, nutritional status, associated infection, genetic factor etc. Further epidemiological studies with non cancer and cancer end points with low dose of As exposure (0.01-0.05) are also essential to establish safe limit in the population who drink large quantity of water.

Estimation of As level in urine, hair and nail could only give us a corroborative evidence of As exposure either currently or in the recent past. However, high value in these biomarkers can not be solely utilized for the diagnosis of arsenicosis. A better biomarker diagnostic of As related toxicity and carcinognesis need to be developed.

Genetic bio-marker studies have not only been useful in establishing the link between ingested As and genetic damage, but they are currently being used to provide information into the mechanistic and susceptibility issues of As carcinogenesis as well. Several studies have used one particular genetic biomarker, the micronucleus (MN) assay, to establish the association between drinking water As and genetic damage in the bladder. This assay measures the frequency with which chromosomes and chromosomal fragments are lost to the nucleus during cell division. Studies done on As exposed and unexposed populations in Nevada, Chile, and Mexico have all shown higher prevalence of MN cells in the urine of exposed subjects compared to unexposed subjects (Warner et al, 1994, Moore et al 1997a, Gonsebatt et al 1997). In one study, an increase in MN cells was seen at urinary As levels of 54 μg/L, a level similar to that attained from drinking water containing 50 μg/L, the permissible upper safe limit of many countries. To further investigate the relationship between As ingestion and MN cells, an intervention study was performed in which the prevalence of these cells in a group of highly exposed Chilean men were measured before and after these men were supplied with water low in As (Moore et al 1997b). After eight weeks of drinking low As containing water, the prevalence of MN cells fell from 2.63 to 1.79 per 1000 cells adding further evidence that ingested As caused genetic injury to the bladder. Despite these findings, it should be emphasized that the relevance of the MN cell biomarker to cancer, as with many genetic biomarkers, remains further to be elucidated.

To develop insight into the actual mechanisms by which As exerts its effects, as well as factors that may determine individual susceptibility to As, other genetic biomarkers are currently being investigated. For example, Steinmaus et al (in press) are currently conducting a bladder cancer case control study in Argentina in which they are collecting oral epithelial cells from cases and controls as a source of DNA for genotype analysis. Two metabolism enzymes, glutathione S-transferase μ (GSTM1) and glutathione S-transferase θ (GSTT1) are important in cancer susceptibility because they may regulate an individual's ability to methylate arsenic (Oya-Ohta et al 1996, Huang et al 1993, Chiou et al, 1997). Carriers of homozygous deletions in these genes (null genotypes) have an absence of enzyme activity and may be more susceptible to potential carcinogens. Hence, the results of this genetic susceptibility analysis can be used to determine if GST genotype influences methylation capabilities and susceptibility to the genotoxic effects of arsenic.

Using lymphocytes from individuals exposed to As, Menzel et al (1997) have searched for a biomarker and mechanism of action of As compounds. AsIII treatment induces a number of proteins as shown by polyacrylamide gel electrophoresis (PAGE). One of the AsIII-induced proteins is heme oxygenase 1 (HO1), an early response enzyme. They have found HO1 was induced in 6 individuals to about the same extent for the same AsIII concentration. A Single dose-response relationship seemed to exist for lymphocyte HO1 content and AsIII dose. Determining HO1 content of circulating lymphocyte for persons exposed to As could provide a biomarker of biological activity. By observing rapid upregulation of proteins like HOI by AsIII treatment they further conjectured that a nuclear transcription factor might be involved in the signalling mechanism. Using fresh lymphocytes and lymphoblastoid cells they found that the nuclear transcription factor nuclear factor-kB (NF-kB), but not activator protein 1 (AP-1) was activated by AsIII in a dose-response manner. They propose using the dose-response relationship for activation of lymphocyte NF-kB as a biomarker of the toxic effects of arsenic. Similar dose-response data for Sister Chromatid exchanges/cell (SCEs/cell) can also be used as a biomarker. However, molecular epidemiological studies using various genetic bio-markers need to be carried out to find out whether any of these markers could be used to predict clinical or carginogenic end point of chronic As exposure in a dose related fashion.

A few reports are available regarding the natural history of chronic As toxicity after the people stop taking As contaminated water. It has been highlighted earlier that though some of the cutaneous and neurological manifestations improve, feature of chronic lung disease appear afresh in new cases. Many of the reports from Taiwan suggest increased incidence of neurological, cardiovascular, cerobrovascular and metabolic (Diabetes mellitus) disease in the previously As exposed population (Chen et al 1997). However individual As exposure data and duration of previous exposure are not available in those reports. Thus to understand the natural history, a well controlled follow up study need to be carried out in an As exposed population having knowledge of individual data regarding dose and duration of As exposure after stoppage of intake of As contaminated water. Any modifying influence of interventions like administration of high protein containing nutritious diet and vitamins need also be studied to find out their efficacy in preventing the occurrence of various non carcinomatous manifestations and development of cancer.

Animal models have demonstrated that various chelating agents like BAL, DMSA and DMPS are efficacious in averting morbidity and mortality if administered within minutes to hours of acute As exposure. In one placebo controlled trial DMSA has not been found to be superior to placebo in altering the clinical score. In a preliminary report

DMPS has been shown to have some effect in reducing the symptoms of the treated patients (vide supra). However further study with this agent with a long period of follow up data are still needed before this agent can be advocated for therapeutic use. Limited case series supported by recent insights into the potential mechanisms of As induced carcrinogenesis suggest that oral treatment with retinoids (Vitamin A analogues) may have promise in the treatment of chronic cutaneous manifestation of arsneicosis, and may also have impact on the development of neoplasia. Selenium, an antioxidant nutrient that antagonizes many of the effects of As in biological systems, also merits attention as a potential therapeutic agent for patients with history of chronic As exposure (Kosnett MJ in press). Further studies with retinoids and selenium need to be carried out on As exposed people to ascertain their therapeutic efficacy in modifying the natural history of chronic As toxicity.

4.6 Executive Summary

Chronic arsenic toxicity in man produces a range of clinical manifestations. However, skin manifestations are the most diagnostic. These are characterized by pigmentation of the body and limbs and keratosis of the palms and soles. Rain-drop like spotty pigmentation or depigmentation or diffuse melanosis affecting the whole body are the features of pigmentation. Diffuse thickening of palms and soles with or without nodular elevations are diagnostic of keratosis. Other important clinical features are weakness, anaemia, peripheral neuropathy, liver enlargement, chronic lung disease, and peripheral vascular disease. These features are manifested variably in different exposed populations, and may also be caused by As unrelated conditions. Infrequent manifestations which have also been reported to occur by some investigators in people having history of As exposure and which may also be As unrelated are conjunctivitis, keratitis, rhinitrs, cardiovascular disease, nephropathy, and diabetes mellitus. However, many people do not show any such feature despite of drinking arsenic contaminated water for a long time.

Though the various noncarcinomatous manifestations as described above occur in association with chronic arsenicosis, with the exception of skin manifestation others are nonspecific. Hence evidence of chronic As exposure and detection of high levels of As in urine and/or in hair and nails in association with those symptoms need to be considered for the diagnosis of chronic As toxicity. However, normal values in those materials do not exclude the diagnosis of chronic arsenicosis. Presence of specific raindrop pigmentation/depigmentation and keratosis with the history of intake As contaminated water need to be considered as diagnostic hall mark of chronic As toxicity.

Many of the clinical manifestations of chronic As toxicity are irreversible. Epidemiological studies have established As as an important agent which produces cancer of the skin, bladder and lung. Though it produces significant morbidity and occasional fatality, no specific therapy has yet been available. Treatment for chronic As intoxication need to be directed towards a) stoppage of As exposure by providing As free safe water to the exposed population, b) providing specific drug for helping recovery and/or averting disease progression and c) general measures and symptomatic treatment. Stoppage of intake of As contaminated water and intake of nutritious diets can reduce some of the symptoms of chronic arsenicosis. Whether this could prevent the development of cancer is not known. No specific drug for altering the natural history of the disease has yet been available. However, supportive and symptomatic treatment could help a lot to reduce the suffering of patients.

Arsenic induced skin cancer and bladder cancer could be cured if detected early. Hence a good cancer surveillance programme in chronic As exposed population is essential for preventing cancer related deaths. Mass communication measures should be undertaken highlighting the source of As contamination of drinking water and methodology for obtaining As free safe water in the affected area. People must be desisted from getting panicky. Communication material should aim to debunk myths around As. A belief that arsenicosis is contagious, or similar to leprosy has serious social consequences especially for women and children. The campaign should promote that people sick from arsenic are not a threat to others and need care and attention.

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Chapter 5. Drinking water guidelines and standards

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Chapter Summary

The primary aim of the WHO Guidelines for Drinking-water Quality (GDWQ) is the protection of public health. The Guidelines are intended to be used as a basis for the development of national standards that, if properly implemented, will ensure the safety of drinking water supplies through the elimination, or reduction to a minimum concentration, of constituents in drinking water that are known to be hazardous to health. The guideline values recommended are not mandatory limits. They are intended to be used in the development of risk management strategies which may include national or regional standards in the context of local or national environmental, social, economic and cultural conditions.

The main reason for not promoting the adoption of international standards for drinking water quality is the advantage provided by the use of a risk-benefit approach (qualitative or quantitative) to the establishment of national standards or regulations. This approach should lead to standards and regulations that can be readily implemented and enforced and which ensure the use of available national financial, technical and institutional resources for maximum public health benefit.

WHO has had a public position on arsenic in drinking water since 1958. The last edition of WHO GDWQ (1993) established 0.01 mg/L as a provisional guideline value for arsenic in drinking water with a view to reducing the concentration of arsenic in drinking-water, because lower levels preferred for health protection are not reliably measurable.

In a number of countries, the WHO provisional guidelines of 0.01 mg/L has been adopted as the standard. However, many countries have kept 0.05 mg/L, established in an earlier edition of the guidelines, as the national standard or as an interim target before tackling populations exposed to lower but still significant concentrations in the 0.01-0.05 range.

In developing national drinking water standards based on the guideline values, it will be necessary to take account of a variety of geographical, socio-economic, dietary and other conditions affecting potential exposure.

5.1 Introduction

The primary aim of the Guidelines for Drinking Water Quality is the protection of public health. In 1984 and 1985, WHO published the first edition in three volumes. The development of these Guidelines was organized and carried out jointly by WHO HQ and WHO EURO. In 1988, WHO (HQ & EURO) decided to initiate the revision of the

Guidelines. The revised Guidelines have again been published in three volumes. They have been widely used as a basis for setting national standards to ensure the safety of public water supplies.

The guideline values recommended are not mandatory limits. Such limits should be set by national authorities, using a risk-benefit approach and taking into consideration local environmental, social, economic and cultural conditions.

Volume 1 Recommendations (published in 1993)
This volume sets out guideline values for a large number of water contaminants relevant to the quality of drinking-water. The book also provides an explanation of how the guideline values should be applied, the criteria used in selecting the various chemical, physical, microbiological, and radiological contaminants considered, a description of the approaches used to derive the guideline values, and brief summary statements supporting the values recommended or explaining why no health-based guideline value is necessary at present.

Addendum to Volume 1 (published in 1998): **Recommendations**
The addendum is part of WHO's ongoing effort to ensure that recommendations about the safety of chemical substances found in drinking-water are in line with the latest scientific data. This addendum to volume one of *Guidelines for Drinking-water Quality* summarizes new findings that have become available since the second edition was published in 1993, and that call for a reconsideration of selected guideline values issued at that time. For some of the substances under review, previously established guideline values have been revised in the light of new evidence. For others, new findings confirm the continuing validity of previous recommendations. Evaluations of chemical substances published in this addendum supersede evaluations of the same substances previously published in the second edition of Guidelines for Drinking-water Quality. Updated or new evaluations are provided for seven inorganic substances (aluminium, boron, copper, nickel, nitrate, nitrite, and uranium), four organic substances (edetic acid, microcystin-LR, benzo[a]pyrene, and fluoranthene), ten pesticides (bentazone, carbofuran, cyanazine, 1,2-dibromoethane, 2,4-dichlorophenoxyacetic acid, 1,2-dichloropropane, diquat, glyphosate, pentachlorophenol, and terbuthylazine), and a disinfectant by-product (chloroform).

Addendum to Volume 2 (published in 1998**): Health Criteria and Other Supporting Information**
This companion volume reviews and interprets the extensive toxicological, epidemiological, and clinical evidence that formed the basis for the new or updated evaluations issued in the addendum to Volume 1 of the Guidelines. Covering the same 22 chemical substances, the volume communicates the scientific rationale for each individual recommendation. Well over 1,000 references to the recent literature are included. Evaluations of chemical substances published in this addendum supersede evaluations of the same substances previously published in the second edition of Guidelines for Drinking-water Quality.

Volume 2 - Health criteria and other supporting information (published in 1996), reviews and interprets the extensive toxicological, epidemiological, and clinical evidence that shaped the determination of guideline values for drinking-water quality. Organized to parallel and extend the coverage of volume 1, which presented the recommended guideline values and brief summary statements supporting these values, this second work communicates the scientific rationale for individual recommendations based on a critical review of data linking health hazards to specific exposure levels. In so doing, it aims to establish an authoritative basis for national water-quality standards that are consistent with the goal of providing wholesome, safe drinking-water in a sufficient quantity. Well over 3000 references to the literature are included.

The book has 17 chapters presented in three parts. The first, on microbiological aspects, addresses the common and widespread health risks associated with the direct or indirect contamination of drinking-water with human or animal excreta, particularly faeces. The second and most extensive part, which contains almost 800 pages, provides evaluations, supported by toxicological monographs, for each of 36 inorganic constituents and physical parameters, 27 industrial chemicals, 36 pesticides, four disinfectants, and some 23 disinfectant by-products. The final part explains application of the reference level of dose for radiological contaminants in drinking-water. The volume concludes with a list of the hundreds of experts who collaborated in the evaluations, a convenient tabular presentation of the guideline values, and a comprehensive index.

Volume 3 - Surveillance and control of community supplies (published in 1997), is a comprehensive guide to all practical procedures and technical measures required to ensure the safety of drinking-water supplies in small communities and periurban areas of developing countries. Now in its second edition, the book has been vastly expanded in line with broadened appreciation for the many factors that influence water quality and determine its impact on health. Revisions and additions also reflect considerable new knowledge about the specific technical and social interventions that have the greatest chance of success in situations where resources are scarce and logistic problems are formidable.

Since quality controls may be especially difficult to implement in small communities, the book concentrates on the most essential requirements, emphasizing the crucial need to ensure microbiological safety. Details range from advice on how to design simple pictorial reporting forms for sanitary inspections, to guidance on setting priorities for remedial action, from a comparison of different methods for the analysis of coliform bacteria, to drawings of measures for protecting water sources. Throughout, numerous checklists, charts, diagrams, and model forms are used to enhance the volume’s practical value.

The book has eight chapter organized to reflect the key stages in the development of surveillance. Chapter one explains how the basic principles of surveillance and control apply to small-community supplies and alerts readers to several unique problems that need to be overcome. Planning and implementation are discussed in the second chapter, which gives particular attention to the distinct yet complementary responsibilities of the water supply agency and the public health protection agency. Subsequent chapters offer advice on the nature, scope, and timing of sanitary inspections, describe the most appropriate methods for sampling water and assessing its hygienic quality, and explain how the resulting data can be used to improve the quality, coverage, quantity, cost, and continuity of the water supply.

The most extensive chapter describes and illustrates numerous technical interventions for preventing or correcting hazards associated with water from different sources, procedures for water treatment, and methods used to treat and store water in households. Additional strategies for improvement are covered in the remaining chapters, which outline methods of hygiene education in communities and discuss the important role of legislation and regulation.

Further practical guidance is provided in a series of annexes, which give examples of sanitary inspection and hazard scoring forms for 11 different types of water supply, list responsibilities for different categories of surveillance staff, and provide illustrated step-by-step instructions for several sampling methods and analytical tests for use in laboratories and the field.

5.2 History of drinking water quality standards/guidelines

The origin of WHO Guidelines for Drinking-Water Quality (GDWQ) goes back to the 1950s. At that time the requirements for safe and potable water supplies became particularly pertinent with the great increase in travel, especially global air travel. It became apparent that the traveler must be provided with potable drinking-water. In 1953, WHO distributed a questionnaire to all member states to assess the status of water treatment plants and their production of acceptable water quality. The replies to the questionnaire clearly indicated the magnitude of the problem and the need for WHO to establish drinking water standards. (WHO 1958)

Following a series of expert consultations culminating in a meeting in 1956 in Geneva the **International Standards for Drinking-Water** were published in 1958. In this instance the term “standards” was used to be applied to the suggested criteria of water quality (WHO 1958).

In addition to being cited in the International Sanitary Regulations for deciding what constitutes pure and acceptable water supply at ports and airports, the 1958 International Standards became to be widely used as a reference in the development of local national standards and as a basis for improved water treatment practices.

Some countries adopted the International Standards as the official and legal standards of water quality while other countries developed national standards based in part or in whole on the International Standards. Increasing knowledge of the nature and effect of various contaminants, and improved techniques for identifying and determining their concentrations, have led to a demand for further revision of the recommendations. Accordingly the International Standards for Drinking-Water were revised in 1963 and 1971. (WHO 1958, 1963, 1971)

The International Standards had been in existence for over a decade until they were superseded by the **WHO Guidelines for Drinking-Water Quality (GDWQ)** in 1984. While it was recognized that it might not be possible by a number of member states to attain all of the recommended guideline levels, it was anticipated that member states would develop water quality standards as close as possible to these guidelines in the endeavour to protect public health.

The change from Standards to Guidelines meant that the guidelines were intended for use by member states as a basis for the development of national standards which, if properly implemented, would ensure the safety of drinking-water supplies both in the urban and rural settings. The philosophy and content of the WHO Guidelines constituted a drastic departure from the previous International Standards. The revised guidelines were published in three volumes including criteria monographs prepared for each substance or contaminant listed in the guidelines. (WHO 1984, 1985).

The second edition of the GDWQ Volume 1 was published in 1993 followed by Volume 2 in 1996 and Volume 3 in 1997. The work involved numerous institutions, over 200 experts from nearly 40 different developing and developed countries and 18 meetings of the various coordination and review groups. The International Programme on Chemical Safety (IPCS) provided major input to the health risk assessments of chemicals in drinking-water.

In establishing WHO guideline values for chemicals in drinking-water, guideline values were calculated using a tolerable daily intake (TDI) for chemicals showing a threshold for toxic effects. For carcinogens, for which there is convincing evidence to suggest a non-genotoxic mechanism, guideline values were calculated using a TDI approach. In the case of compounds considered to be genotoxic and carcinogenic, the International Agency for Research on Cancer (IARC) classification for carcinogenic compounds was taken into consideration and guideline values were established using a mathematical model, usually the linearized multistage extrapolation model. The guideline values are presented as the concentration in drinking-water associated with an estimated excess lifetime cancer risk of 10-5 (one additional cancer case per 100 000 of the population ingesting drinking-water containing the substance at the guideline value for 70 years). In cases in which the concentration associated with a 10-5 excess lifetime cancer risk was not practical, because of inadequate analytical methodology, a provisional guideline value was set at a practicable level and the estimated associated cancer risk was presented (WHO 1993).

A continuing process of updating guideline values was established with a number of chemical substances and microbiological agents subject to periodic evaluation. Addenda containing these evaluations were issued in 1998 for Volumes 1 and 2 and will be issued as necessary until the third edition of the GDWQ is published approximately 10 years after the second edition (WHO 1998).

5.3 Purpose of the GDWQ

In GDWQ, it is often emphasized that the guideline values recommended are not mandatory limits. In order to define such limits, it is necessary to consider the guideline values in the context of local or national environmental, social, economic, and cultural conditions. The main reason for not promoting the adoption of international standards for drinking-water quality is the advantage provided by the use of a risk-benefit approach (qualitative and quantitative) to the establishment of national standards and regulations.

This approach should lead to standards and regulations that can be readily implemented and enforced. For example, the adoption of drinking-water standards that are too stringent could limit the availability of water supplies that meet those standards a significant consideration in regions of water shortage. However, considerations of policy and convenience must never be allowed to endanger public health. The judgement of safety or what is an acceptable level of risk in particular circumstances B is a matter in which society as a whole has a role to play. The final judgement as to whether the benefit resulting from the adoption of any of the guideline values given here as standards justifies the cost is for each country to decide (WHO 1993).

5.4 Drinking Water Quality Guideline on Arsenic

WHO has had a public position on arsenic in drinking water since 1958. The first version of International Standards for Drinking-Water in 1958 included arsenic in the category of toxic substances which, if present in drinking-water supplies at concentrations above certain levels, may give rise to actual danger to health. It established 0.20 mg/L as an allowable concentration (WHO 1958). The updated standards in 1963 kept arsenic in the same category and established a stricter concentration of 0.05 mg/L, although no specific reason for this reduction was disclosed (WHO 1963).

An update in 1971, kept arsenic in the toxic substances category and reaffirmed the value of 0.05 mg/L. Its explanatory notes referred to the fact that figures higher than that quoted are found in a number of Latin American countries and levels up to 0.2 mg/L were not known to have caused difficulties in drinking water. It also referred to some epidemiological studies which have suggested that arsenic is carcinogenic but mentioned that no real proof of its carcinogenicity to man had been established. It concluded that it would seem wise to keep the level of arsenic in drinking-water as low as possible (WHO 1971).

The WHO Guidelines for Drinking-water Quality in 1984 were intended as a basis for the development of national standards in the context of national environmental, social, economic and cultural conditions. It introduced new categories in the drinking-water guidelines. The categories of toxic and specific substances in the preceding publications were abolished and arsenic was categorized among the inorganic constituents of significance to health. It recommended 0.05 mg/L as a guideline value with the explanation that, based on available human health data, a concentration of 0.05 mg of arsenic per litre in drinking water is not associated with any adverse health effects. Supporting evidence in the relevant criteria monograph included the case in Chile and China (Province of Taiwan). (WHO 1984)

The last edition of WHO GDWQ (1993) established 0.01 mg/L as a provisional guideline value for arsenic in drinking water. The fact that inorganic arsenic compounds are classified by IARC in Group 1 (carcinogenic to humans) on the basis of sufficient evidence for carcinogenicity in humans and limited evidence for carcinogenicity in animals was taken into consideration. Based on the increased incidence of skin cancer observed in the population in China (Province of Taiwan), the lifetime risk of skin cancer was estimated using a multistage model.

There are at least two reasons why 0.01 mg/L was selected as a provisional guideline value. These are: (1) On the basis of observations in a population ingesting arsenic-contaminated drinking-water, the concentration associated with an excess life-time skin cancer risk of 10-5 was calculated to be 0.00017mg/L. However, this value may overestimate the actual risk of skin cancer owing to the possible dose-dependent variations in metabolism could not be taken into consideration. (2) This value is below the practical quantification limit of 0.01mg/L. The estimated excess lifetime skin cancer risk associated with exposure to this concentration is 6×10^{-4} (WHO 1993).

IPCS Environmental Health Criteria on Arsenic was published in 1981 and provided first consensus on international health risk assessments regarding arsenic in drinking water. The updated version is now under preparation and is to be completed in 2000.

Box 5-1: Provisional guideline value

Inorganic arsenic compounds are classified by IARC in Group 1 (carcinogenic to humans) on the basis of sufficient evidence for carcinogenicity in humans and limited evidence for carcinogenicity in animals (IARC 1987). No adequate data on the carcinogenicity of organic arsenicals were available. The guideline value has been derived on the basis of estimated lifetime cancer risk.

Data on the association between internal cancers and ingestion of arsenic in drinking-water are limited and insufficient for quantitative assessment of an exposure-response relationship (USEPA 1988). However, based on the increased incidence of skin observed in the population in China (Province of Taiwan), the US Environmental Protection Agency has used a multistage model that is both linear and quadratic dose to estimate the lifetime skin cancer risk associated with the ingestion of arsenic drinking-water. With this model and data on males (USEPA 1988), the concentrations of arsenic in drinking-water associated with estimated excess lifetime skin cancer of 10^{-4}, 10^{-5}, and 10^{-6} are 0.0017, 0.00017 and 0.000017 mg/L, respectively.

It should be noted, however, that these values may overestimate the actual risk of cancer because of possible simultaneous exposure to other compounds in the water and possible dose-dependent variations in metabolism that could not be taken into consideration. In addition, the concentration of arsenic in drinking-water at an estimated skin cancer risk of 10^{-5} is below the practical quantification limit of 0.01mg/L.

A value of 0.013mg/litre may be derived (assuming a 20% allocation to drinking-on the basis of the provisional maximum tolerable daily intake (PMTDI) of inorganic arsenic of 0.002 mg/kg of body weight set by the joint FAO/WHO Expert Committee on Food Additives (JECFA) in 1983 and confirmed as a provisional tolerable weekly intake (PTWI) of 0.015mg/kg of body weight in 1988 (FAO/WHO 1989). JECFA noted, however, that the margin between the PTWI and intakes reported to have effects in epidemiological studies was narrow.

With a view to reducing the concentration of arsenic in drinking-water, a provisional guideline value of 0.01 mg/litre is recommended. The estimated excess lifetime skin cancer associated with exposure to this concentration is 6 x 10^{-4}.

WHO Guidelines for drinking-water quality, volume 2, 1996

Box 5-2: Arsenic health effects data in China (Province of Taiwan)

In a large study conducted in China (Province of Taiwan), a population of 40 421 was divided into three groups based on the arsenic content of their well-water (high, >0.60 mg/litre; medium, 0.30-0.59 mg/litre; and low, <0.29 mg/litre) (Tseng 1977). There was a clear dose-response relationship between exposure to arsenic and the frequency of dermal legions,? blackfoot disease? (a peripheral vascular disorder), and skin cancer.

However, several methodological weaknesses (e.g. investigators were not? blinded?) complicate the interpretation of the results. In addition, the possibility that other compounds present in the water supply might have been responsible for blackfoot disease was not considered. It has been suggested, for example, that humic acid in artesian well-water is the cause of the disease, not arsenic (Lu 1990).

In a study in which cancer mortality was examined in relation to the arsenic content of contaminated drinking-water in the same villages of China (Province of Taiwan) and at the same three levels, there were significant dose-response relationships for age-adjusted rates for cancers of the bladder, kidney, skin, and lung in both sexes and cancers of the prostate and liver in males (Wu 1989).

A study in which the ecological correlations between the arsenic level of well-water and mortality from various malignant neoplasms in China (Province of Taiwan) were examined demonstrated a significant association with the arsenic level in well-water for cancers of the liver, nasal cavity, lung, skin, bladder, and kidney in both males and females and for prostate cancer in males (Chen 1990).

In an investigation of the association between cancer incidence and the ingestion of arsenic-contaminated water in a limited area of China (Province of Taiwan), standardized mortality ratios (SMRs) for cancers of the bladder, kidney, skin, lung, liver, and colon were significantly elevated in the area of arsenic contamination. The SMRs for all but colon cancer also correlated well with the prevalence rate for blackfoot disease (Chen 1985).

In a case-control study of 204 subjects who died of cancer (69 of bladder, 76 of lung, and 59 of liver cancer) and 368 community controls matched for age and sex, the odds ratios of developing these cancers for those who had used artesian well-water for 40 or more years were 3.90, 3.39, and 2.67, respectively. Dose-response relationships were observed for all three cancer types by duration of exposure, and the odds ratios were not changed significantly when several other risk factors were taken into consideration in logistic regression analysis (Chen 1986). A technical Panel on Arsenic established by the US Environmental Protection Agency concluded that, although these studies demonstrated a qualitative relationship between the ingestion of arsenic-contaminated water and internal cancers, the data were not sufficient to enable the dose-response relationship to be assessed (USEPA 1988).

WHO Guidelines for drinking-water quality, volume 2, 1996

Box 5-3: Risk assessment by Multistage model

Clear evidence of health effects are usually available at high level of exposure. Extrapolation from high to lower levels of exposure becomes critical for regulatory setting. Numerous mathematical models have been developed for estimating the effects of exposure levels well below levels for which cancer data are available. This is based on two fundamental assumptions: (a) There is no threshold dose for the caicinogenic effect; and (b) carcinogenic effects of chemicals are directly proportional to dose at low-dose levels, i.e., the dose response is linear at low doses.

Multistage model is one of the mathematical models, which is most frequently used in the regulatory process. It was also applied in the 1988 risk assessment for arsenic in drinking water done by USEPA using the data of an epidemiological study by Tseng et al. in 1968. This model is based on the concept that a tumour develops from a single cell in an organ as a result of a number of biological events or stages (e.g. mutation) that occur in a prescribed order. According to this model, the probability of developing tumours, $P(d)$, is

$$P(d) = 1- \exp[-(a + q_1 d + q_2 d^2 + ?.+ q_m d^m)]$$

Where the parameter m is the number of stages, a is the background tumour rate and the q? s are the values that maximize the likelihood of observing the experimental results. In practice the a, the q? s and the m are estimated from the data. Some of the q? s may be zero but none can be negative. When the unknown values of the multistage model parameters are replaced by their maximum likelihood estimates (MLEs), the resulting model estimates what the risk is most likely to be in the experimental situation. At low doses the dose-response relationship is thus approximately linear. This model will fit almost any observed data set as long as the dose-response curve is not markedly concave downward at low responses.

Although the mathematical models are useful as one tool in the regulatory process, they are oversimplifications of complex systems. It is important to note that quantitative risk estimates may give an impression of accuracy which in fact they do not have. In general, the risk assessment values for carcinogens are at best, “order of magnitude” estimates.

It should be emphasized that the guideline values for carcinogenic substances have been computed from hypothetical mathematical models that cannot be verified experimentally and that the values should be interpreted differently than TDI-based values because of the lack of precision of the models. At best, these values must be regarded as rough estimates of cancer risk. However, the models used are conservative and probably err on the side of caution. Moderate short-term exposure to levels exceeding the guideline value for carcinogens does not significantly affect the risk.

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WHO, 1993

5.5 National standards on Arsenic

In a number of countries, the WHO provisional guidelines of 0.01 mg/L has been adopted as the standard. However, many countries have retained the earlier WHO guideline of 0.05 mg/L as the national standard or as an interim target.

A number of European countries have adopted the WHO provisional guideline of 0.01 mg/L as their standard. In the United States of America, the Safe Drinking Water Act (SDWA) directs the U.S. Environmental Protection Agency (EPA) to establish national standards for public drinking-water supplies. EPA’s interim maximum contaminant level (MCL) for arsenic in drinking water is 0.05 mg/L. Under the 1996 SDWA amendments, EPA has proposed a new standard (an MCL) for arsenic in drinking water in June 2000 and will finalize it by January 2001. New standard value currently proposed is 0.005 mg/L (see BOX 5-4).

Countries where the national standard for arsenic in drinking water remains at 0.05 mg/L include Bangladesh, China and India. The Table 5-1 shows the currently accepted national standards for arsenic in drinking water in some selected countries.

Table 5-1 The currently accepted national standards for arsenic in drinking water

Standard	Countries
Countries whose standard is lower than 0.01 mg/L	Australia (0.007 mg/L, 1996)
Countries whose standard is 0.01 mg/L	European Union (1998), Japan (1993), Jordan (1991), Laos (1999), Laos, Mongolia (1998), Namibia, Syria (1994)
Countries whose standard is lower than 0.05 mg/l but higher than 0.01 mg/l	Canada (1999) 0.025 mg/l
Countries considering to lower the standard from 0.05 mg/L	United States (1986*), Mexico(1994)
Countries whose standard is 0.05 mg/l	Bahrain, Bangladesh (unknown), Bolivia (1997), China (unknown), Egypt (1995), India (unknown), Indonesia (1990), Oman, Philippines (1978), Saudi Arabia, Sri Lanka (1983), Viet Nam (1989), Zimbabwe

() shows the year standard was established
* new standard value 0.005 mg/L is being proposed

In developing national drinking water standards based on the guideline values, it will be necessary to take account of a variety of geographical, socio-economic, dietary and other conditions affecting potential exposure. This may lead to national standards that differ appreciably from the guideline values.

Box 5-4: USEPA Proposed Revision to Arsenic Drinking Water Standard

The current standard of 50 ppb (0.05 mg/L) was set by EPA in 1975, based on a Public Health Service standard originally established in 1942. A March 1999, report by the National Academy of Sciences concluded that the current standard does not achieve EPA? s goal of protecting public health and should be lowered as soon as possible. Under the Safe Drinking Water Act Amendments of 1996, EPA is required to promulgate a final rule by January 1, 2001.

EPA is proposing to change the arsenic standard in drinking water to 5 ppb (0.005 mg/L) to more adequately protect public health. The proposed arsenic standard is intended to protect consumers against the effects of long-term, chronic exposure to arsenic in drinking water. The new standard will apply to all 54,000 community water systems, serving approximately 254 million people.

EPA is taking comment on other proposed levels for arsenic [namely, 0.003 mg/L, 0.010 mg/L, and 0.020 mg/L]. EPA is for the first time proposing a drinking water standard (5 ppb) that is higher than the technically feasible level (3 ppb). The Safe Drinking Water Act (SDWA) requires EPA to determine the health goal, then to set the standard as close to the goal as technically feasible.

EPA is also proposing a public health goal of zero for arsenic. The health goal is the level below which no known or anticipated health effects would occur. EPA sets public health goals at zero for all known carcinogens for which there is no dose considered safe.

While many systems may not have detected arsenic in their drinking water above 5 ppb, there may be ?hot spots? with systems higher than the predicted occurrence for an area. More water systems in western states that depend on underground sources of drinking water have naturally-occurring levels of arsenic at levels greater than 10 ppb (0.01 mg/L) than in other parts of the U.S.. Parts of the Midwest and New England have some systems whose current arsenic levels range from 2-10 ppb.

For systems that require corrective action to meet a standard of 5 ppb, annual household costs will average $28 for Americans served by large systems and $85 for those served by small systems (those serving fewer than 10,000 people). Over 98 percent of the cost to water systems comes from adding treatment equipment, chemicals, and oversight of the new treatment.

USEPA, 2000

Box 5-5: Application of national arsenic drinking water guidelines/standards in Hungary

Hungary has made a great effort to decrease the arsenic (As) in drinking water concentrations in 80 waterworks systems (supplying about 400,000 people) to below the 50 µg/L guideline. WHO and the EU however, decreased this guideline (1993 and 1998, respectively) to 10 µg/L. To comply with this new guideline or standard will be a very costly proposition.

Hungarian authorities have examined this issue very carefully and have suggested that the data for the development of this new guideline/standard be reviewed. For example, based on Hungarian experience which is supported by many referenced publications, no significantly elevated frequency of skin cancer was detected below a threshold value of 200µg/capita of daily exposure.

According to another toxicological approach (JECFA, cited by WHO), the daily exposure from food and drinking water together must not exceed 140 µg/capita or, if it is possible, 100 µg/capita. If the food contains less arsenic (e.g. in Hungary 20 µg/day capita), drinking water can contain more arsenic without increasing the risk. Based on these considerations, the proposed limit of arsenic in drinking water was set by Hungarian authorities at 30 µg/L. From the toxicological approach this would appear to be acceptable, but not from legal point of view, in terms of the new EU regulations.

In Hungary, more than 1.2 million people consume drinking water with an arsenic concentration in the range 10-30 µg/L. To decrease this concentration below 10 µg/L within the foreseeable future appears to be very difficult without the development of appropriate and economically viable water treatment technologies which can be utilised at the municipal level.

5.6 Surveillance

WHO Guidelines Vol. 3 focuses on the surveillance of drinking-water quality in small-community supplies keeping in mind the special needs of developing countries. In such countries a stepwise approach to initiating a sustainable water quality surveillance programme may be called for. It is anticipated that this approach will ultimately lead to the implementation of a programme that will be a step towards the achievement of guideline values.

Surveillance is an investigative activity undertaken to identify and evaluate factors associated with drinking-water which could pose a risk to health. Surveillance contributes to the protection of public health by promoting improvement of the quality, quantity, coverage, cost, and continuity of water supplies. Its principal objective is to identify public health risks so that action may be taken promptly to prevent public health problems. Surveillance requires a systematic programme of surveys that combine analysis, sanitary inspection, and institutional and community aspects.

In most countries the agency responsible for the surveillance of drinking-water supply supplies (urban and rural) is the ministry of health. In some countries, the ministry of environment or the ministry of local government may have that responsibility. The surveillance agency should preferably be an established national institution designated by appropriate legislation and should be able to operate at central, provincial and local levels.

Water-quality surveillance requires an appropriate institutional framework and adequate resources (financial, infrastructure & human) to function effectively. Surveillance activities need to be adapted to local conditions and to the availability of local financial resources, personnel, infrastructure and political commitment.

The objective of water quality surveillance is not simply to collect and collate information, but also to contribute to the protection of public health by promoting the improvement of water supply with respect to quality, coverage, cost and continuity.

5.7 Basic management aspects

The Guidelines for drinking-water quality cover a large number of possible contaminants in order to meet the varied needs of countries. However, it is very unlikely that all of the contaminants mentioned will occur in a water supply. Care should therefore be taken in selecting substances for which national standards will be developed. Scare resources should not be wasted on developing standards for, and monitoring, substances of minor importance.

In countries where economic and human resources are limited, short - and medium-term targets should be set in establishing national drinking-water standards, water-quality surveillance, and quality-control programmes so that the most significant risks to human health are controlled first.

The most common and widespread health risk associated with drinking-water is microbial contamination, the consequences of which are so serious that its control must always be of paramount importance. It is therefore necessary to ensure that priority is given to water supplies presenting the greatest public health risk.

When a guideline values is exceeded, this should be a signal: (1) to investigate the cause with a view to taking remedial action; and (2) to consult with, and seek advice from, the authority responsible for public health.

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WHO Guidelines for Drinking Water Quality Training Pack, March 2000
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Acronyms used in this chapter

EU: European Union
GDWQ: WHO guidelines for Drinking-water Quality
IARC: International Agency for research on Cancer
IPCS: International Programme on Chemical safety
JECFA: Joint FAO/WHO Expert Committee on Food Additives
MCL: maximum contaminant level
MLE: maximum likelihood estimates
PMTDI: provisional maximum tolerable daily intake
PTWI: provisional tolerable weekly intake
SDWA: Safe Drinking Water Act
SMR: standardized mortality ratios
TDI: tolerable daily intake
USEPA: United States of America, Environmental Protection Agency
WHO EURO: The World Health Organization Regional Office for Europe
WHO HQ: WHO Head Quarters (in Geneva)
WHO: World Health Organization

Chapter 6. Safe Water Technology

Richard Johnston, Han Heijnen and Peter Wurzel

Previous chapters have documented the serious health effects that are posed by ingestion of arsenic through drinking water. While some palliative treatment of arsenicosis patients is possible, it is clear that the first step in treating patients, and preventing others from falling sick, is to identify safe sources of water for drinking and cooking in arsenic-affected areas. This chapter will present a brief overview of safe drinking water supply technologies that can provide arsenic-free[1] drinking water, either through identifying an arsenic-free source or by removing arsenic from contaminated water. The main focus of this chapter is on rural and peri-urban settings, though many of the technologies discussed are applied in central water supply systems as well, and a few examples of centralized arsenic removal are given.

[1] No water is ever completely free of arsenic - trace levels will always be present, even if they cannot be measured. In this chapter the term 'arsenic-free' is taken to mean free from unsafe levels of arsenic.

Conventional water supplies are briefly discussed, but as these systems are extensively described elsewhere, the reader is referred to authoritative documents for more detailed information. Arsenic removal technologies are less well documented in standard water supply texts, though a large and growing literature exists in technical journals. In addition, many other valuable papers are found in seminar and conference proceedings, particularly in Latin America and Asia. Since many of these resources are less accessible for some readers, this chapter presents a detailed review of arsenic removal technologies. Many of these technologies are under development, and a sample protocol is presented for evaluation of new technologies for arsenic removal, as well as a more general framework for selection of an appropriate approach in a given socioeconomic and environmental context. A series of case studies are presented of technological responses to arsenic contamination at municipal, community, and household levels. The final section presents some general conclusions and identifies areas where more knowledge or research is required.

Acronyms and abbreviations

Units of measurement

m	meters
M	moles, molar
meq/mL	milliequivalents per milliliter
mg/L	milligrams per liter, equivalent to parts per million (ppm)
mM	millimolar
MW	molecular weight
µg/L	micrograms per liter, equivalent to parts per billion (ppb)
ppm	parts per million
ppb	parts per billion
psi	pounds per square inch

Technical terms

BOD	Biochemical oxygen demand
EBCT	Empty bed contact time
HAO	Hydrous aluminum oxide
HFO	Hydrous ferric oxide

MCL	Maximum contaminant level
NF	Nanofiltration
NTU	Nephelometric turbidity units
POU	Point of use
PZC	Point of zero charge
RO	Reverse osmosis
SODIS	Solar disinfection
SORAS	Solar removal of arsenic
TC	Total coliforms
TCLP	Toxicity characteristic leaching procedure
TDS	Total dissolved solids
THM	Trihalomethanes
TOC	Total organic carbon

Organizations

AWWA	American Water Works Association
BGS	British Geological Survey
BRAC	Bangladesh Rural Advancement Committee
DPHE	Department of Public Health Engineering
ENSIC	Environmental Sanitation Information Center
IRC	International Reference Centre for Water Supply and Sanitation
ITP	Intermediate Technology Publications
MML	Mott MacDonald, Ltd.
NGO	Non-governmental organization
UNEP	United Nations Environment Programme
UNICEF	United Nations Children's Fund
USEPA	United States Environmental Protection Agency
WHO	World Health Organization

Executive Summary

In areas where the drinking water supply contains unsafe levels of arsenic, the immediate concern is finding a safe source of drinking water. There are two main options: finding a new safe source, and removing arsenic from the contaminated source. In either case, the drinking water supplied must be free from harmful levels of arsenic, but also from bacteriological contamination, and other chemical contaminants. This chapter reviews available technologies for source substitution and arsenic removal. The main focus is on rural and peri-urban areas, though centralized systems are briefly discussed.

Source Substitution

Three main sources of water can be considered as substitutes for contaminated water: groundwater, rainwater, and surface water. Much has been written about these sources, so this chapter offers only a brief review, with key references.

- **Groundwater** is largely free from harmful bacteria and fecal contamination, though a poorly designed or constructed well can become contaminated from surface water. To prevent this, wells should be grouted around the borehole, and finished at the surface with a concrete platform, with good drainage away from the well.

Most commonly, groundwater is reached through boreholes, drilled either by hand or machine. When drilling in arsenic-affected areas, precautions should be taken to make sure that safe aquifers do not become contaminated. If a borehole must penetrate a contaminated aquifer to reach safe water below, the borehole should be grouted after drilling is completed.

In some areas, groundwater can have naturally occurring water quality problems aside from arsenic, such as high levels of iron, manganese, nitrate, chloride, or fluoride. Before promoting new sources of groundwater, the chemical quality should be tested in laboratories.

- **Rainwater** is free from arsenic, and if properly collected, can provide a safe drinking water source. Bacterial contamination is a concern, but this can be minimized by collecting rain from a roof (galvanized metal makes a good collection surface). Tree branches should not overhang the roof, and the roof should periodically be cleaned. Water can be collected through gutters, and piped into a storage tank. Tanks can be built of many materials, but ferrocement (cement with wire reinforcement) is strong and inexpensive, and also can keep the water pH near neutral. When rain first begins to fall, especially at the end of a dry season, roof water should be allowed to run off for 10-15 minutes before collection, to clean the roof.

Close to urban areas, and when metal roofs are used, collected rainwater can contain unsafe levels of lead and zinc, and possibly other metals. Typically, collected rainwater contains low levels of bacteria (fecal and total coliform counts average 5-15 and 25-75 per 100 ml, respectively). Water quality testing should be done to ensure that collected water meets relevant standards. In some cases, rainwater may be the safest source of drinking water available, even if low levels of bacteria are present.

Often, rainfall is seasonal, and large storage tanks would be required to bridge the dry season. While water can be safely stored for long periods, the large tanks may be too expensive. In such cases, small storage tanks provide an inexpensive and convenient water source during the rainy season, and other sources should be found for the dry season.

- **Surface water** requires more treatment than groundwater or rainwater, since it usually has very high bacterial contamination. In order to ensure that treatment is always effective, it is important to include multiple barriers to contamination. The most effective treatment appropriate at the rural, community level, is slow sand filtration, followed by a safety dose of chlorine. In slow sand filtration, surface water passes through prefilters, and is then filtered through 80-100 cm of sand. A bio-layer develops near the surface of the sand, which can effectively destroy most pathogens. Operation of the slow sand filter may be improved through pretreatment with bank infiltration, sedimentation or roughing filtration. The use of roughing filters, in particular, permits effective treatment of water containing higher levels of turbidity, color, and pathogens. This ‘multi-stage filtration’ is a robust and reliable treatment method in rural communities, and for small and medium size municipalities.

Slow sand filtration will not efficiently remove arsenic or agricultural chemicals such as pesticides. It is important to test the water quality of the unfiltered water to make sure that arsenic and pesticides are not present. Likewise, for bacteria, the cleaner the source water, the cleaner the treated water will be. Ponds and other surface water sources used for slow sand filtration should be protected: latrines should not be located near the water, and people and animals should not bathe nearby. Slow sand filters must be regularly cleaned, and the top few centimeters of sand in the filter should be scraped off. After cleaning, the filter will need several days to ‘ripen’, and treat water effectively. During this ripening period, filtered water should be disinfected before drinking.

Solar disinfection, or *SODI*S, is a promising new technology that uses clear plastic bottles to purify water. Bottles are filled with clear water and left in the sun for several hours. The combination of ultraviolet radiation and high temperature is able to destroy most pathogens. *SODIS* will not improve the chemical quality of water, but it can provide an inexpensive, easy way to improve microbiological quality.

Surface water may also be purified by drawing the water from shallow wells located close to the surface water body. This ‘bank infiltration’ can improve the chemical as well as microbiological quality of water, and is becoming more popular in Europe.

Arsenic Removal

In some areas source substitution may be impossible during part or all of the year, or may be very expensive. Arsenic removal may be more appropriate in these situations. Since arsenic removal is not covered in many standard texts, this chapter examines removal technologies in more detail.

- **Coagulation and filtration** is the most common arsenic removal technology. By adding a coagulant such as alum, ferric chloride, or ferric sulfate to contaminated water, much of the arsenic can be removed. If arsenic is present as arsenite, the water should be oxidized first, using chlorine, permanganate, ozone, or other oxidants. After adding the coagulant, the water should be stirred, allowed to settle, and filtered for best results. Coagulation improves parameters such as turbidity and color, and can reduce levels of organic matter, bacteria, iron, manganese, and fluoride, depending on operating conditions.

Coagulation with ferric salts works best at pH below 8. Alum has a narrower effective range, from pH 6-7. If pH is above 7, removal may be improved by adding acid to lower pH. In general, the higher the coagulant dose, the better the arsenic removal. Typical doses are 5 to 30 mg/L ferric salts or 10 to 50 mg/L alum. If the source water has high levels of phosphate or silicate, coagulation may be less effective. However, sulfate, carbonate, and chloride have little effect on removal rates.

- **Ion exchange resins** are commercially produced, synthetic materials that can remove some compounds from water. Most commonly they are used in water softening, but some resins are very good at removing arsenic. These resins only remove arsenate, so if the raw water contains arsenite, it should be oxidized first.

Other compounds, including sulfate, nitrate, nitrite, and chromate, are also removed to some degree by most arsenic removal resins.

Ion exchange resins usually come as sand-like grains, and are used in packed beds or columns, most often with an Empty Bed Contact Time (EBCT) of 1.5 to 3 minutes. A bed can typically treat several hundred to a thousand bed volumes before the resin must be regenerated. The amount of water a bed can treat is largely independent of arsenic concentration and pH. Instead, run lengths are largely determined by sulfate levels, since sulfate can quickly saturate the resin. For this reason, ion exchange resins are only appropriate in waters with under 120 mg/L sulfate, and work best with waters with under 25 mg/L sulfate. High levels of dissolved solids (TDS > 500 mg/L) will also shorten run times.

Resins will not adsorb iron, but if the raw water contains high levels of dissolved iron, the iron can precipitate out and clog the filter. When the resin is saturated, it can easily be regenerated with a simple brine solution. Regenerated resin can be used over and over again.

- **Activated alumin**a, like ion exchange resins, is commercially available in coarse grains. Activated alumina is used in packed beds, with longer EBCTs (about 5 to 8 minutes) than ion exchange resins. Activated alumina beds usually have much longer run times than ion exchange resins, typically several tens of thousands of beds can be treated before arsenic breakthrough. Activated alumina works best in slightly acidic waters (pH 5.5 to 6) - above pH 7 removal efficiency drops sharply. The main factors controlling bed run length are pH and arsenic concentration. Concentrations of other solutes have a relatively small effect.

For best results, raw water containing arsenite should be oxidized before treatment. Phosphate, sulfate, chromate and fluoride are also removed by activated alumina, but nitrate is not. Saturated activated alumina can be regenerated with flushing with strong base followed by strong acid. Regenerated media loses some volume and eventually must be replaced. Like ion-exchange resins, activated alumina beds can be clogged by precipitation of iron.

- **Membrane methods** for arsenic removal include reverse osmosis and nanofiltration. These make use of synthetic membranes, which allow water through but reject larger molecules, including arsenic, chloride, sulfate, nitrate, and heavy metals. The membranes must be operated at high pressures, and usually require pretreatment of the raw water. Household level membrane units usually only treat about 10% of the water, resulting in a large waste stream. Municipal membrane units can achieve higher total recovery rates by using membranes in series. Currently available membranes are more expensive than other arsenic removal options, and are more appropriate in municipal settings, where very low arsenic levels are required. However, membrane technology is advancing rapidly, and it is conceivable that future generations of membranes could be used effectively in rural settings.

- **Other techniques** exist for arsenic removal, but are less well documented. When arsenic-rich water also contains high levels of dissolved iron, iron removal will also remove much of the arsenic. Many new materials are being tested for arsenic removal, including low-tech iron-coated sand and greensand, novel iron-based sorbents, and specially engineered synthetic resins. Some of this research is promising, but these technologies are still under development.

All arsenic removal technologies generate some kind of arsenic-rich waste. These wastes are generally not hazardous to handle, but special care must be taken in disposing of them, especially at centralized plants. At the community or household level, the volume of waste generated is usually not enough to have a major environmental impact, and stabilized wastes can be disposed of with other solid wastes, solidified in concrete, buried, or discarded in sanitary latrines.

Selection of an appropriate technology

With so many options available for source substitution, and so many different types of arsenic removal technology, it is not always clear which alternate water source is best for a given setting. In all cases, technologies should meet several basic **technical criteria**. Water supply options must first of all be able to produce water of the required **quality**, both chemical and bacteriological. Systems should also be able to supply water in adequate **quantity**, throughout different seasons.

Technologies should be reliable and **robust**, with little opportunity for errors to occur through systemic weaknesses or through user error. As community systems will be operated by non-technical community members, it is important that **operational safety** be ensured. Finally, technologies should not have an undue adverse effect on the **environment**.

Technologies meeting these technical criteria can be evaluated under several **socioeconomic criteria**. First, the systems must be **economically feasible** for members of affected communities. Users can be expected to contribute to costs, but most new water supply systems will require some level of subsidy. Introduction of new technologies requires **institutional capability**, for aspects such as production and delivery of materials, training, quality control, and monitoring. **Gender** impacts should be considered, so that the workload of women and girls is not increased. New options must be **convenient**, or people will not use them. New technologies require behavioral change on the part of the user for optimal use, health and hygiene impact, so **communication** interventions should be considered. Finally, technologies must be **socially acceptable** to community members in order to be successful as a long-term safe water supply option.

Ideally, after considering the above technical and socioeconomic criteria, one technology would clearly emerge as a superior option. In reality, this is unlikely - each option will have benefits and disadvantages. In some cases one option alone will not suffice, and a combination of systems will need to be used - e.g. rainwater collection during the wet season and arsenic removal during the dry.

The key to selecting an appropriate technology (or technologies) is to involve community members in all stages of the process, from technology selection to operation and maintenance. In this way, a sense of ownership can be generated, and an appropriate, sustainable technology can be selected. To allow water users to make their own informed choice, they need information about a wide range of options. Until water users understand the problem of arsenic contamination and its impact on their health, and have reliable information about safe alternatives, they will be unwilling and unable to make an informed choice to change their water use patterns. The biggest challenges ahead lie in applying the technologies described in this chapter in poor, rural settings, and in enabling those communities to choose safe sources of water for drinking and cooking.

6.1 Safe drinking water supply

In most industrialized countries, access to safe drinking water is nearly universal, and is often taken for granted. This access has come as the result of massive public expenditures, though now more and more water supply agencies are being privatized.

In contrast, access is typically lower in developing countries, where economies are weaker, and infrastructure is not as developed. The situation is the worst for the poorest people in developing countries, who often have no access to piped water supply. It has been estimated that 20-30% of urban residents in the developing world rely on water vendors, who sell water at prices much higher than piped water would cost. These families typically spend one fifth of their income on water, though the poorer segments pay a larger proportion (Cairncross and Kinnear, 1991). In rural areas, piped distribution systems are generally not available, and women and children must spend many hours each day collecting water from rivers, ponds, and wells. One analysis calculated that in Africa alone, women and children spend over 40 billion hours annually collecting water for household use (de Rooy and Doyle, 1992).

The economic impact of convenient access to a safe drinking water source, along with the prospect of reducing the drudgery associated with water collection, provide sufficient justification for safe drinking water supply initiatives. Yet the main reason for water supply interventions is associated with public health.

The largest public health impact of unsafe drinking water is diarrhoeal disease, which contributes to the deaths of some 1.9 million children every year. In addition, about a third of the population of the developing world is infected with intestinal worms. These and several other diseases can be reduced through better sanitation, hygiene and water supply (UNICEF, 1999a). Safe water initiatives, notably the International Drinking Water Supply and Sanitation Decade, from 1981 to 1990, have focused on improving both the quantity and quality of drinking water supplies, and on increasing use of sanitary means of excreta disposal.

Because of such interventions, access to safe drinking water has improved dramatically, especially in rural areas, over the last twenty years, as shown in **Table 6.1.** This has contributed, along with advances in sanitation and treatment of diarrhea, to a significant reduction in diarrhoeal disease and general improvements to children’s health. The infant mortality rate in developing countries has dropped dramatically - from 137 per thousand in 1960 to 66 per thousand in 1996. Over the same time period, the under-five mortality rate also dropped by over half, from 216 per thousand to 97 per thousand (UNICEF, 1998). Even in the last ten years, child deaths from diarrhoeal diseases in developing countries have declined by more than a third, mainly due to increased use of oral rehydration therapy, improvements in sanitation and access to safe water, and subsequent behavioral change (UNICEF, 1999a).

Table 6.1: Drinking water and sanitation access in developing countries

	Water supply service coverage (%)			**Sanitation service coverage (%)**		
	Rural	**Urban**	**Total**	**Rural**	**Urban**	**Total**
1980	29	75	43	13	53	25
1990	63	93	73	28	73	44

2000	69	92	79	34	81	53

Source: **(WHO/UNICEF, 2000)**

Notes:

1) Figures should be regarded as rough approximations.

2) 1980 data exclude People's Republic of China, for which statistics are unavailable.

3) After 1980, many countries adopted a more stringent definition of sanitation, and therefore only a rough comparison of 1980 and later data can be made.

One main strategy in the quest for safe drinking water has been the shift away from surface water. Surface water can be heavily contaminated with fecal pathogens, especially in areas where sanitary disposal of excreta is not practiced. In contrast, groundwater is typically free of microbiological contamination. Rather than attempt to disinfect surface water, it is often more economical to abstract groundwater, which requires little or no treatment for pathogen removal. Even so, proper storage and handling of water is essential to prevent contamination of safe water by users.

Reflecting the goal of reduction of diarrhoeal disease, water quality testing has focused heavily on microbiological tests. Water was tested for inorganic parameters only when a taste or color problem was apparent (e.g. high iron or chloride) in the area. It is now clear that both groundwater and surface water can contain harmful levels of other hazardous compounds, many of which cannot be detected by sight or taste alone. WHO has set Guideline Values for 17 inorganic compounds which have adverse health effects, 27 organic constituents, 33 pesticides, and 17 disinfectants or disinfectant byproducts (WHO, 1993). Obviously it is not feasible, or necessary, to test every water source for all 94 of these constituents, particularly for small systems. Fortunately, few of these compounds commonly occur naturally, and testing can therefore be limited to compounds that are known or suspected to have been applied by humans, or to exist naturally in the local environment.

Since the discovery of widespread occurrence of fluoride and arsenic in groundwater in various parts of the world, and in view of the increasing contamination of groundwater from agricultural chemicals, public regulatory and surveillance organizations have begun more widespread monitoring of drinking water quality parameters. It remains unfeasible to test all water sources for all parameters, but water producers should consider carefully their drinking water sources, and consider whether more comprehensive water quality testing is warranted. In many developing countries only limited water quality testing is done routinely. Large water providers should at least initially test source waters for compounds of health concern that are known to sometimes contaminate drinking water supplies, such as fluoride, arsenic, manganese, nitrate, nitrite, and trace elements such as heavy metals. A useful overview of inorganic compounds of health significance sometimes found in groundwater and conditions leading to their mobilization is given by Edmunds and Smedley (Edmunds and Smedley, 1996). Other compounds of health concern listed by the WHO, including chlorinated solvents, aromatic hydrocarbons, pesticides, and disinfectants, do not occur naturally in groundwater. Drinking water supplies should be tested for these compounds when there is reason to suspect that human application of such chemicals in agriculture or industry may have contaminated the drinking water source.

When arsenic contamination is identified, the immediate priority must be to find a safe alternate source of drinking and cooking water for affected communities. Alternate sources must be not only arsenic-free, but also microbiologically safe - it would be a serious mistake to revert back to unsafe use of surface water sources. In some cases, there may be no one technology that can provide communities with a sustainable, continuous, affordable, safe water supply. If a year-round safe water source is not currently available, it may be necessary as a short-term solution to use one source during wet seasons (e.g. groundwater, rainwater) and another during dry seasons (e.g. removing arsenic from contaminated water). If a completely satisfactory, arsenic-free water source cannot be established, the short-term goal should be to reduce arsenic levels in drinking water as much as possible, as quickly as possible, even if regulatory standards cannot be immediately met. It should be recalled that health effects of arsenic are dose-dependent, and a partial solution is better than no solution. However the long-term goal should be affordable and convenient sources of safe drinking water meeting all regulatory standards for every community. The implementation of a temporary solution should not be used as a reason to delay design and implementation of a long-term plan.

6.2 Sources of arsenic-free drinking water

When a drinking water source is found to contain unsafe levels of arsenic, one mitigation option is to install another water supply point, drawing from arsenic-free sources. This source should be sufficient for drinking and cooking needs, though with centralized water supply systems it is usually necessary to provide water of high quality for all needs.

In municipal plants with multiple production wells or surface sources, it may be possible to blend low-arsenic and high-arsenic waters to meet a regulatory standard. However, wherever possible, full source substitution would be preferable to blending. In the short term, or in emergency situations, safe water for cooking and drinking needs can even be transported into affected areas, either as bottled water or in tanks[2]. It will nearly always be more cost effective, however, to find a local source of water that is either arsenic-free or can be treated.

[2] Bottled water is not necessarily free from unsafe levels of inorganic contaminants: a recent water quality survey of 56 bottled European mineral waters found that only 15 would meet drinking water standards for all parameters where action levels are defined. Nine percent of the mineral waters tested contained arsenic ranging from 10 to 20 µg/L (Misund et al., 1999).

There are three main sources of water to be considered for substitution for contaminated water: groundwater, rainwater, and surface water.

6.2.1 Groundwater

Groundwater quality

Where available and of good quality, groundwater is usually the most acceptable source for drinking water supply. Due to the natural filtering of aquifer materials, and long underground retention times, groundwater typically has very little pathogenic contamination, and requires little or no disinfection. In contrast, surface water is often heavily polluted with fecal material as a result of poor sanitation and hygiene practices.

Surface water is also more susceptible to chemical contamination from industrial or agricultural runoff, such as heavy metals, pesticides, or nitrate.

However, groundwater quality should not be taken for granted. In very shallow aquifers, bacterial contamination is possible, and even likely if the wellhead is poorly protected. In addition to arsenic, other inorganic constituents in groundwater can cause health or aesthetic problems, notably iron, manganese, nitrate, chloride, and fluoride. Other contaminants listed in the WHO Guideline Values should be tested for if their presence is suspected, either from human activity or from naturally occurring sources (WHO, 1993).

If some existing groundwater supplies are found to be arsenic-free, these will usually be the most preferred water source, at least in the short term. The simple act of testing all of a community's wells for arsenic is valuable in that it will identify safe, as well as unsafe, wells. People can be encouraged to share safe water resources, though if safe wells are scarce or absent, this may not be feasible. If safe wells are privately owned, the owners may be reluctant to allow others access to the wells, out of concern for privacy or a fear that increased use will result in increased maintenance and replacement costs. In some cultures, women are the main water collectors, but also have limited social mobility, and privacy concerns can make sharing of a household well uncomfortable or unacceptable. The complicated issue of women's role in water collection is discussed more fully in a series of IRC reports (van Wijk-Sijbesma, 1985; van Wijk-Sijbesma, 1998).

Based on an understanding of the geological origins of contamination, it may be possible to identify areas or strata that are at relatively low risk of arsenic contamination. In some areas arsenic contamination is confined to highly localized sedimentary deposits. If these hot spots are identified through widespread arsenic testing, new wells can be preferentially installed in relatively safe areas. In areas where some geological units are arseniferous and others are not, it is important to avoid cross-contamination, which can occur in several ways. In some cases, the arsenic-rich zones may be naturally in hydraulic connection with arsenic-free zones. By pumping water from arsenic-free zones, arsenic-rich water may be induced to flow into previously uncontaminated strata, and eventually may reach the well. In other cases, the arsenic-rich and arsenic-free zones may be separated by low-permeability materials such as clays. Drilling can disturb this natural barrier, and the borehole itself (specifically, the annular space around the well pipe) may provide a high-permeability conduit from one zone to another. When wells are drilled with mechanical rotary rigs, it is possible to inject impermeable material such as grouting or clay into this annular space at the level of the impermeable layer, to prevent this kind of contamination. However, in many developing countries, grouting is not used, either to save money or because the drilling technologies are not compatible with grouting.

Arsenic-free wells might become contaminated over time through a third mechanism: arsenic could initially be present in a stable, solid form in aquifer sediments. If the geochemistry of the pore water, especially the pH and redox potential, should change, arsenic could become mobilized, and make its way into the abstracted groundwater.

Box 6.1: Deep aquifer in Bangladesh

In Bangladesh, the most serious arsenic contamination is seen in shallow tubewells, while only a few deep tubewells have been shown to contain high levels of arsenic. A major hydrogeological survey found that in surveyed areas, while over 40% of wells less than 100 m deep (n=1662) exceeded the Bangladesh drinking water standard of 50 µg/L, less than 1% of the wells deeper than 150 m (n=317) exceeded the limit. The deeper wells are less prone to arsenic contamination because they are screened in a pre-Pleistocene aquifer. These aquifer sediments are millions of years old, and any arsenic present has probably been flushed out, or is present in a stable solid form. The shallow wells, in contrast, are screened in Holocene aquifers that are only thousands of years old, and have not been completely flushed since deposition. These shallow sediments are rich in organic matter, which creates the reducing conditions that encourage mobilization of arsenic, as well as elevated iron levels (DPHE/BGS/MML, 1999).

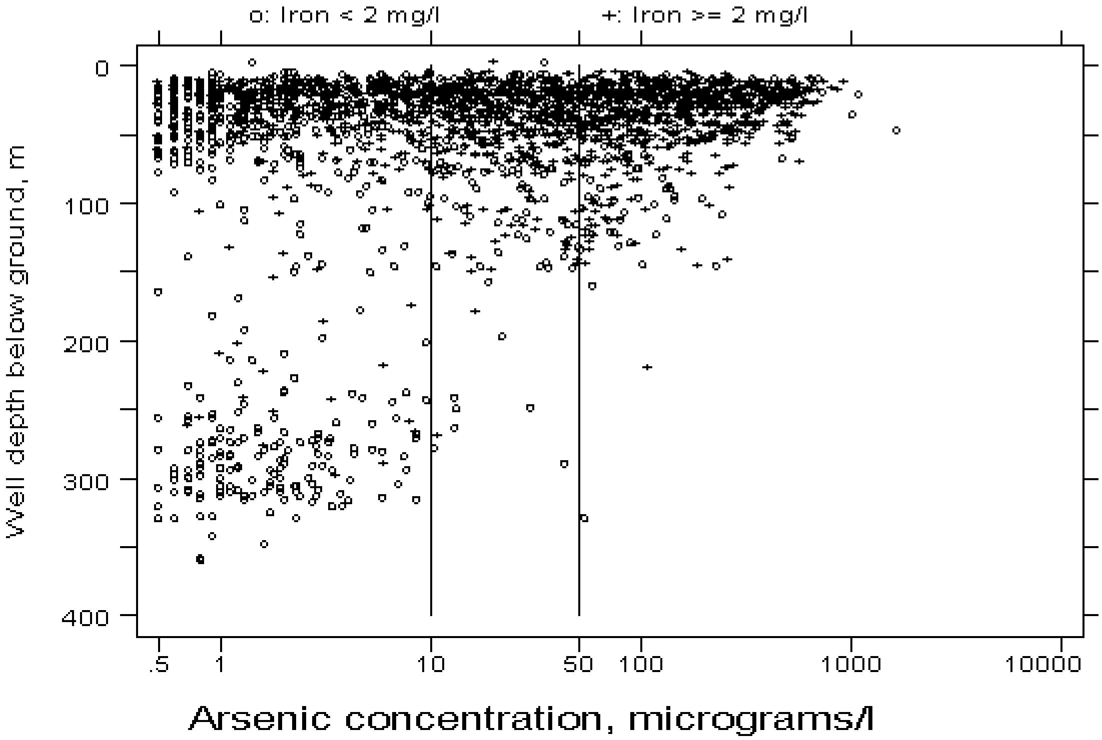

Figure 6.1: Arsenic and well depth in Bangladesh (DPHE/BGS/MML, 2000)

Note: vertical lines at 10 and 50 µg/l represent the WHO Guideline Value and Bangladesh Standard, respectively. (Editors: you may wish to redraw or copy the similar figure from the GSACB Phase I report - Volume S2, Figure 5.7 - to get a prettier image, but it doesn't have the iron breakdown. I assume you will redraft the figure to make it prettier, - especially the legend and text - please contact me if you need the data.)

Accordingly, there have been many calls for interventions to prioritize installation of new deep tubewells in arsenic affected areas. However, experience from neighboring West Bengal suggests that deep tubewells may not always remain arsenic-free. In one village eight new tubewells with depths of 140 m were installed that initially showed safe levels of arsenic, but within a year of installation, all had reportedly become unsafe. This is not inconsistent with **Figure 6.1**, which shows significant arsenic contamination between 100 and 150 m in Bangladesh. In West Bengal, one deeper well (260 m) also showed arsenic contamination (Mandal et al., 1996).

At present, not enough is known about the deep aquifer in these areas to say with certainty whether or not its groundwater will remain arsenic-free. It must be remembered that the absence of arsenic in deep wells indicates the controlling influence of geology and geochemistry, not of depth. Two equally deep tubewells in different parts of Bangladesh might draw water from different aquifers with radically different chemical composition. In the coastal belt, deep tubewells have operated for decades without becoming contaminated with salt from the overlying brackish aquifer, which suggests that cross-contamination is not likely. However, since deep tubewells in Bangladesh have almost exclusively been installed in a relatively small coastal zone where the shallow aquifer is saline, the extent and properties of the deep aquifer further inland are not well known. It is to be expected, however, that the thick impermeable clay layer that separates the two aquifers in coastal areas will thin towards the inland, which may increase the possibility of cross-contamination. More hydrogeological work will need to be conducted before the long-term viability of the pre-Pleistocene aquifer as a source of arsenic-free water can be determined.

Systems for groundwater exploitation

Groundwater resources can be accessed in five main ways: sub-surface dams, protected springs, hand-dug wells, hand-drilled borewells, and machine drilled borewells. These are described in detail in the UNICEF Water Handbook (UNICEF, 1999b). Machine and hand-drilled borewells are the most common systems, though in hilly areas spring protection may be more economical. An extensive literature exists on water pumping technology, the interested reader is referred to (IRC, 1981), (Arlosoroff et al., 1987), and (IRC, 1988).

6.2.2 Rainwater

Rainwater collection can provide a safe, arsenic-free source of drinking water if weather conditions are appropriate. When properly collected and stored, rainwater can keep a fairly constant water quality for months.

Collection

In areas with low population density and hard rocks surfaces (rock outcrops or cement), rainwater can be collected from the ground surface by constructing microdams to channel surface runoff into underground storage tanks. In more densely populated areas, rooftop collection is more common. Corrugated iron roofs are ideally suited for this purpose, though terra cotta or wood tiles, or concrete roofs are also acceptable. Thatched roofs are not appropriate for rainwater collection, as the collected water is high in organic matter. These roofs, however, can be made suitable with the simple use of inexpensive plastic sheeting. Roofs should be cleaned thoroughly at the beginning of every rainy season, regular maintenance is also crucial.

Water is collected from the roof surface in gutters, which are connected to a storage tank with a downpipe. In order to minimize the amount of contamination and organic matter in collected water, a fine mesh netting or coarse sand filter should be placed between the downpipe and the storage tank. This will also help to keep insects and small animals out of the tank, and has been shown to improve water quality, and reduce the risk of mosquito breeding.

When rain falls after a dry period, water should not be collected for the first ten to fifteen minutes, in order to clean the collection surface. This ‘first flush’ can be achieved through use of a bypass valve, or through a variety of simple designs.

Storage

A rainwater storage tank should be completely covered, and have a tap or pump for withdrawing water, to prevent contamination from users. If water is stored in open containers, or users dip cups or pitchers in a tank to retrieve water, the stored water can easily become contaminated with fecal pathogens.

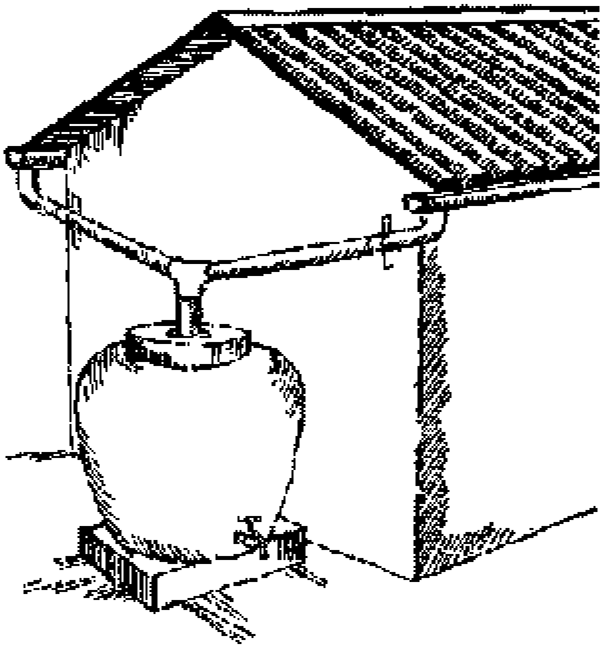

Figure 6.2: Rooftop catchment with tank (after UNICEF, 1999b, p. 40)

The amount of storage required will depend on local rainfall patterns, especially on the extent of dry seasons. If rainfall is scarce or absent for several months, large tanks will be required, or alternate sources of drinking water used during the dry season. In rainy periods, small, inexpensive tanks are able to provide adequate storage for most household needs.

Aboveground tanks can be made of locally available materials such as brick or cement. Ferrocement (cement reinforced with iron mesh or wires) is much stronger than cement, so ferrocement tanks can be thinner and less expensive than simple cement or brick tanks. Prefabricated plastic tanks can also be used, though these are not as easy for rural users to repair, and may impart a taste to the stored water. Tanks should be cleaned at least annually, and if possible, disinfected.

Underground storage tanks can be quite large, and have smaller unit capital costs. However, underground tanks are more vulnerable to contamination from surface waters, flooding, and animal invasion, more difficult to clean, and require the use of a pump to draw water to the surface.

Water Quality

The bacteriological quality of rainwater will depend on the collection and storage methods. In a well-designed system, pathogenic bacteria counts are low in collected rainwater, and the conditions (lack of light or food source) do not promote their growth. Under these conditions pathogen levels will actually decrease with storage, rather than increase. Typically, some coliform bacteria can be found in collected rainwater, but usually the bacteria are not fecal in origin (Pacey and Cullis, 1986).

Several reviews of bacteriological quality of rainwater have been made: in some cases, fecal and total coliform counts are extremely low (e.g. Dillaha and Zolan, 1985), but more commonly low levels of coliform bacteria are found. Typical fecal and total coliform counts in water collected from rooftops average 5-15 and 25-75 per 100 ml, respectively (e.g. Pinfold et al., 1993; Appan, 1997; Simmons et al., 1999a). By examining the ratio of fecal coliforms to fecal streptococci, Appan showed that approximately 80% of the fecal contamination was of non-human origin, presumably from animal droppings on the rooftop (Appan, 1997). Simmons and others found similar coliform counts in rural New Zealand, though occasionally counts were significantly higher (maximum total and fecal coliforms were 19,000 and 840 per 100 ml). Two samples showed *Cryptosporidiu*m, but none showed *Giardi*a, *Campylobacte*r, or *Legionella pneumophila* (Simmons et al., 1999a).

Yaziz and others found moderate levels of coliform bacteria in rainwater collected from rooftops, and showed that the highest counts were in the first samples collected during a rainfall. When samples were collected after a ‘first flush’ equivalent to 35 liters per 100 square meters of roof catchment area, no fecal coliforms could be detected, and total coliforms were reduced by over 50% (Yaziz et al., 1989).

If bacterial quality of stored water is unacceptable, disinfection may be required (see **Section 6.2.4**).

The chemical composition of collected rainwater is very different from that of surface or groundwater. Rainwater is very low in dissolved minerals, and as such is relatively corrosive. This lack of minerals may also cause mineral deficiency in the diets of poorly-nourished consumers.

Due to atmospheric carbon dioxide, rainwater is naturally slightly acidic. Industrial activity, especially production of sulfurous aerosols, can result in the well-known phenomenon of acid rain, which can extend well beyond zones of industrial activity. Acid rain has been documented in rainwater collection systems: drinking water collected from rooftops in Singapore was found to have pH as low as 4.2 (Appan, 1997). The pH of collected rainwater can be raised slightly through storage in ferrocement tanks.

Natural arsenic levels in rainwater are low, generally less than 1 µg/L (Andreae, 1980), though industrial sources, notably smelters and coal plants, can emit arsenic compounds and potentially contaminate rainwater. Likewise, in urban settings, rainwater may have elevated concentrations of human-caused pollutants such as hydrocarbons and heavy metals. Several water quality studies have documented elevated lead levels in rainwater collected from rooftops (e.g. Yaziz et al., 1989; Chang and Crowley, 1993; Thomas and Greene, 1993; Appan, 1997), often at several times the WHO Guideline value of 50 µg/L. In some cases this is most likely due to atmospheric contamination, rather than leaching from roof materials, since similar levels have been found in rainwater collected directly, and in waters collected from metal and concrete roofs (Yaziz et al., 1989). However, others report elevated lead levels in rural New Zealand, where atmospheric lead should be low. Lead levels were highest in houses using lead or galvanised iron flashing (Simmons et al., 1999b).

Especially when rainwater is acidic, other contaminants can be leached from roof catchment or tank materials. Terra cotta and concrete materials can result in highly alkaline waters (Chang and Crowley, 1993). When rainwater is collected from corrugated sheet metal roofs, elevated zinc levels are commonly reported, typically ranging from 2-6 mg/L (Yaziz et al., 1989; Appan, 1997), sometimes exceeding the WHO Guideline value[3] of 3.0 mg/L.

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[3] The guideline value for zinc is based on aesthetic grounds, relating to taste and appearance. WHO has not set a health-based guidance value for zinc in drinking water.

In addition to being microbiologically and chemically safe, it is important that collected rainwater have a taste that is acceptable to users. Rainwater is much less mineralized than surface water and groundwater, which can give the water a flat taste which some may find objectionable. In parts of South America, ground tree bark is added to rainwater to improve taste; elsewhere crushed seeds, curd from sour milk, or tree leaves are used in the same way (Pacey and Cullis, 1986).

Although collected rainwater commonly contains low levels of coliform bacteria, in many cases it is of much better microbiological quality than other available water sources. Chemical parameters, especially pH and lead and zinc levels, should be monitored regularly to ensure that appropriate water quality standards are met. In most cases, however, the relative purity of rainwater makes it an attractive option in areas with uniformly high arsenic levels in other water sources. A large literature on the collection, storage, treatment, and distribution of rainwater exists, drawing on experiences from around the world. For more detailed information, the reader should consult the excellent reports produced by ENSIC (Gould, 1991), IRC (IRC, 1981; IRC, 1990), ITDG (Pacey and Cullis, 1986; Cullis and Pacey, 1991; Gould and Nissen-Petersen, 1999), and UNEP (UNEP, 1983). In recent years, several valuable websites have been set up with ready reference material on the application of rainwater collection and storage. Many such sites exist, two good introductory sites containing many links are (IRCSA, 2001) and (EU, 2001).

6.2.3 Surface Water

Surface water presents more of a challenge than groundwater or rainwater in that it is usually heavily contaminated with fecal bacteria. Other contaminants may be contributed from agricultural sources, such as nitrates, phosphates, and pesticides. Finally, surface water is more vulnerable to industrial contamination. In urban and peri-urban areas, surface water often receives untreated wastes from industrial factories, untreated solid wastes, and urban runoff. As a result surface waters can have very high biochemical oxygen demands (BOD), and be seriously contaminated with organic compounds and trace metals.

Surface water can also have naturally high levels of inorganic compounds, eroded from source rocks upstream, that can cause human health problems. The well-documented case of arsenic contamination of drinking water in Chile arose from the use of rivers which drain arsenic-rich rocks in the Andes. Unsafe levels of arsenic have also been reported in surface waters of Argentina, Ghana, and Bangladesh (see **Chapter 1**). If surface water resources are to be turned to in areas showing elevated arsenic levels in groundwater, it is imperative that surface water sources also be tested.

In spite of the higher risk of contamination, in many cases surface water is the only feasible water source, and various low-cost, low-tech options for water treatment are available. Surface water treatment in municipal treatment plants is a highly engineered process, and such plants must be operated by trained professionals. In smaller, community level treatment plants, simpler equipment is usually used, systems are operated by non-technical community members, and the risk of system failure is higher. The only proven method for treating contaminated surface water in this type of setting is by means of a multiple-barrier system, in which several processes are used in series, which progressively remove bacterial and other contaminants. This design protects against the transmission of pathogens in the event that one barrier should fail. Two typical multiple-barrier series for community water supply are shown in **Figure 6.3** (WHO, 1997b).

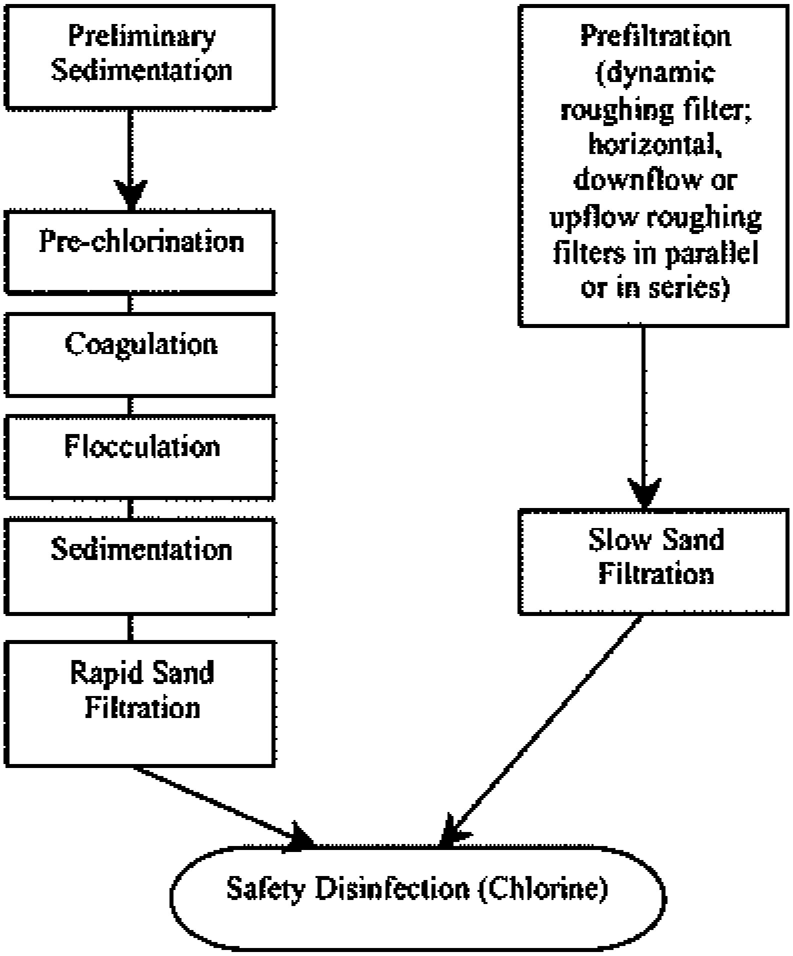


Figure 6.3: Multiple barriers to microbiological contamination in surface water treatment

The first treatment system shown above makes use of three main stages: pre-treatment, addition of coagulant and subsequent removal of solids, and a safety chlorination of the filtered water. The second system depicted above makes use of prefiltration and slow sand filtration in place of chemical addition. This system would require fewer operator inputs.

Preliminary Sedimentation

The first stage of surface water treatment is typically storage and preliminary sedimentation to remove coarse suspended solids that could clog filters or reduce disinfection efficiency. This is especially needed in tropical areas where rivers often have high silt loads. Preliminary sedimentation tanks can remove at least 50%, and up to 90% of turbidity and suspended solids. If the tanks are open to the atmosphere, sunlight may promote algae growth. Preliminary sedimentation is usually followed by a primary disinfectant dose, as shown above, to improve subsequent coagulation and to prevent the growth of algae and slime in treatment tanks.

Coagulation and Filtration

The majority of pathogen removal takes place during coagulation and filtration. Coagulants such as alum or ferric salts are added to the water, and form small solid particles (flocs) which aggregate (flocculate) and settle out of suspension. This settling, or sedimentation, most commonly takes place in horizontal-flow tanks, where water slowly moves from one end to the other, though in more advanced systems other designs such as upward-flow or spiral-flow tanks are sometimes used. Sedimentation can be improved by use of plate and tube settlers, though these devices may cause problems with clogging and odors (Metcalf & Eddy, 1991). Following sedimentation, the remaining suspended solids are removed by passing the water through filter beds of sand or anthracite (rapid sand filtration).

Coagulation and filtration can effectively reduce turbidity and suspended solids. When coagulation and filtration systems are managed properly, removal of 90 to 99% of bacteria and viruses, and over 90% of protozoa can be expected (Salvato, 1992, p. 346). However, a safety dose of chlorine should be given following filtration, to destroy any remaining pathogens, and impart a residual disinfectant to the water. Chlorination at any stage of treatment can produce harmful disinfection by-products, depending upon the dose and composition of the treated water. The health risks posed by these by-products are smaller than the risks posed by pathogens, so disinfection should not be neglected simply to avoid by-product formation. For a full review of the issue of disinfection by-products of chlorination, see (Singer, 2000). Coagulation and filtration can also remove dissolved constituents such as phosphorus, metal ions, and natural organic matter, under correct operating conditions.

Slow sand filtration

An inexpensive alternate to coagulation and filtration is slow sand filtration, one of the oldest technologies for surface water treatment. The first stage in slow sand filtration is some sort of coarse prefiltration (often through gravel or coconut husk) to remove gross particulate matter. The prefilter feeds into the main tank, which contains a thick bed of sand. The water level in the tank is always kept well above the sand bed, providing a driving pressure and preventing the filter from drying out. Water moves through the sand beds at about 0.2 m/h, and passes into a storage tank, fitted with taps for users to draw water from.

Slow sand filtration can effectively remove suspended solids larger than about 2 microns. A detailed description of particulate removal in slow sand filtration is given in (Weber-Shirk and Dick, 1997). Pathogens are removed through a combination of physical, chemical, and biological processes, the last of which is the most important. After the filter has been in operation for some time, a layer of microbes develops near the top of the sand bed. In this zone, called the *schmutzdecke*, predatory microbes attack and consume pathogens in the influent water, such as viruses, bacteria, protozoal cysts (including *Giardia*, and *Cryptosporidium,* which is resistant to chlorination), and helminth eggs (Bellamy et al., 1985a; Cairncross and Feacham, 1993). In a well-operated slow sand filter pathogen removal may exceed 99% (WHO, 1997b). Nonetheless, slow sand filtration is typically followed by a safety disinfection with chlorine (IRC, 1978; IRC, 1982b).

After one to three months of operation, slow sand filters can become clogged, and the driving pressure must be restored by scraping off the top few centimeters of sand, including the *schmutzdecke.* After this scraping, the filter will require several days to 'ripen', and become effective again, depending on the water quality and temperature. After ripening the filter can be commissioned again. After many scrapings, when the sand bed reaches some minimum depth (usually about 45 cm) then new sand or the scraped and washed sand is added to the bottom of the sand bed. This necessarily involves a complete removal of the remaining sand bed. The replacement sand is not simply put on top of the remaining sand bed, because the older sand is already 'inoculated' with micro-organisms.

Table 6.2: Typical removal efficiencies in slow sand filtration

Source: (Bellamy et al., 1985b; Ellis, 1985; Huck, 1987; Rachwal et al., 1988; Hrubec, 1991; and Fox et al., 1994), as cited in (Galvis et al., 1998)

Water quality parameter	***Effluent or removal efficiency***	***Comments***
Turbidity	**<** 1 NTU	The level of turbidity and the nature and distribution of particles affect the treatment efficiency
Enterobacteria	90 to 99.9%	Affected by temperature, filtration rate, size, uniformity and depth of sand bed, cleaning operation
Enteroviruses and *Giardia* cysts	99 to 99.99%	High removal efficiencies, even directly after cleaning (removal of the *schmutzdecke*)
Cercaria	100%	In good operation and maintenance conditions virtual complete removal is obtained
True color	25 to 30%	Color associated with organic material and humic acids
TOC	**<** 15 - 25%	TOC, total organic carbon

THM precursors	**<** 25%	Precursors of trihalomethanes
Iron, manganese	30 to 90%	Iron levels above 1 mg/l reduce filter run length

Several detailed overviews of slow sand filtration are given by the WHO and IRC: (Huisman, 1974; IRC, 1982b; Raman et al., 1987). The American Water Works Association has published a useful manual for the design and construction of slow sand filters (Hendricks, 1991). Recently, a regular international conference on slow sand filtration and biological filtration has been established: the proceedings from these conferences contain many valuable papers about recent research (Graham and Collins, 1994; Graham and Collins, 1996).

Slow sand filtration works best with relatively clear source waters. An influent turbidity of under 10 NTU is recommended, though somewhat higher levels can be tolerated for short periods (IRC, 1982b). Recent work in Colombia has shown that the use of more rigorous pre-filtration steps can allow treatment of surface water with higher turbidity and pathogen loads. This system is called multi-stage filtration, and uses various types of upflow and/or downflow coarse gravel prefilters in combination with conventional slow sand filtration to provide much better treatment than slow sand filtration alone. Multi-stage filtration is discussed in detail in an IRC technical paper (Galvis et al., 1998).

An innovation in multi-stage filtration that has improved operation, particularly by increasing the intervals between cleaning of slow sand filters has been the ‘dynamic roughing filter’. This is essentially a coarse downflow roughing filter of gravel, with an overflow mechanism. When the gravel bed becomes clogged, water flows to waste instead of into subsequent filters, protecting them from excessive suspended loads. If the source water is relatively clean, a dynamic roughing filter, followed by slow sand filtration and disinfection may be adequate to consistently provide safe water. If the raw water is less pure, additional roughing filters may be required between the dynamic roughing filter and the slow sand filter. **Figure 6.4** shows a multiple-stage filtration system consisting of a dynamic roughing filter, one or more upflow roughing filters, a slow sand filter, and a disinfection step. This system illustrates the concept of multiple barriers to ensure that finished water will remain safe, even if one component should fail.

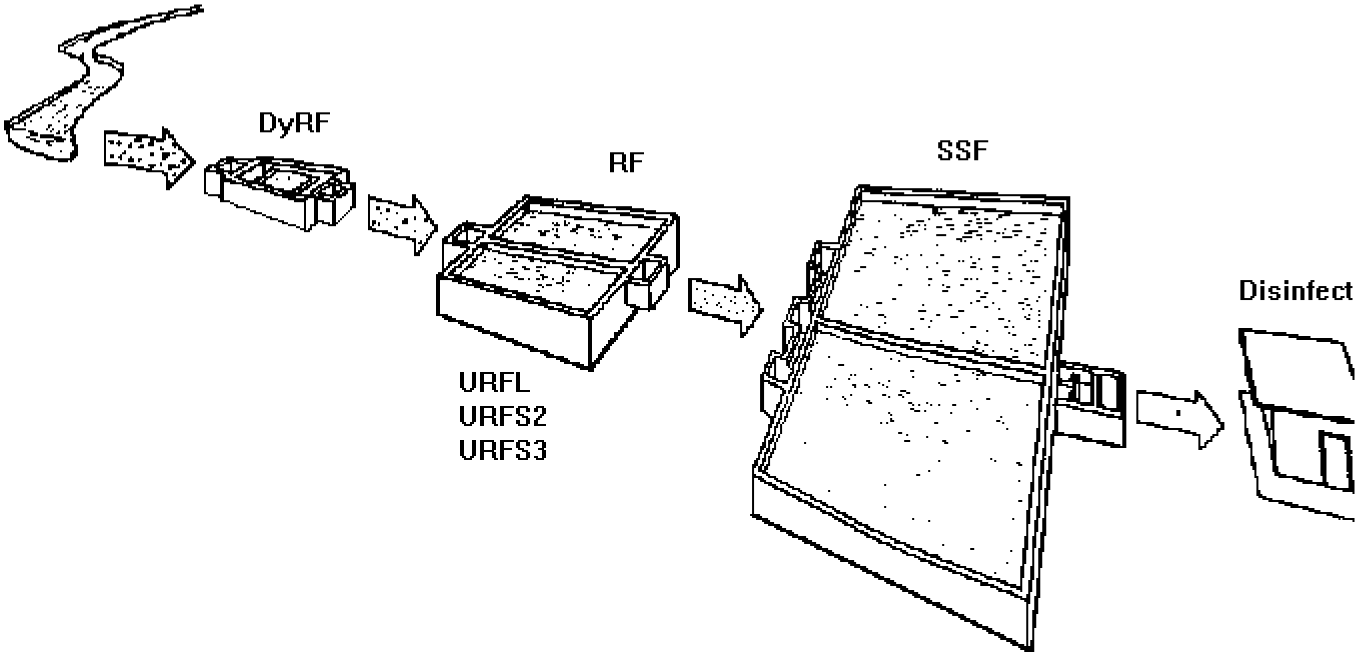


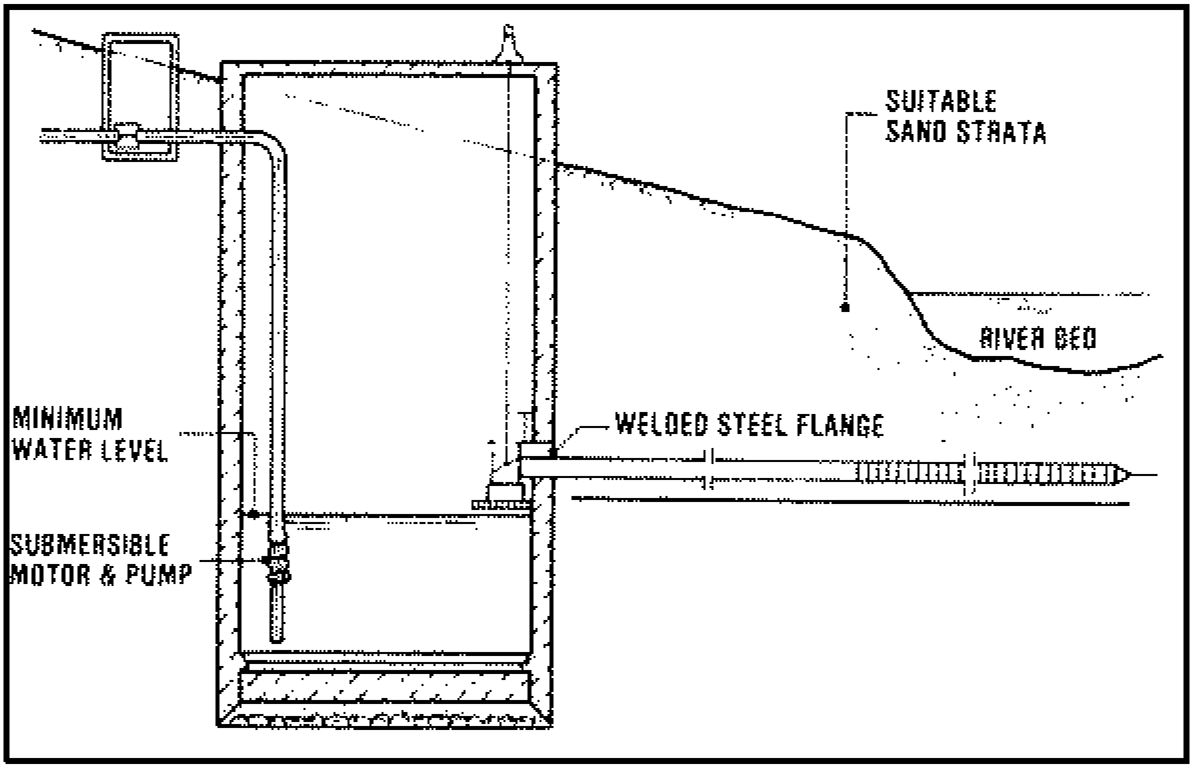
Figure 6.4: Multi-stage filtration (Galvis et al., 1998)

Simple filtration can also be applied at the household level to reduce suspended solids. Household sand filters, candle filters, and cloth filtration can all improve the physical quality of water. Such simple filtration will reduce fecal contamination to some extent, but should always be followed by disinfection (WHO, 1997b).

Bank infiltration

An alternative to constructing engineered sand filters to remove suspended solids and pathogens from surface water is to make use of naturally occurring sediments in the subsurface. In bank filtration (also called induced recharge), a shallow well or series of wells are installed in the vicinity of a river or lake. When water is pumped from the well(s), the local groundwater flow patterns are changed. If the water table is lowered below the level of the river or lake, surface water will be induced to enter the aquifer and flow towards the well. If the shallow groundwater is contaminated with arsenic, it may be possible to induce arsenic-free recharge from surface water bodies, and develop a safe drinking water source. The introduction of oxygenated water might also reduce the mobility of the dissolved arsenic present in the groundwater. However, to date there are no documented examples of bank infiltration in arsenic-affected areas.

In order to allow sufficient filtration and bacterial purification to take place, wells should be installed at least 20 m, and preferably 50 m or more away from the surface water source. Underground travel times should be at least three weeks, and preferably more than two months. One benefit of bank infiltration is that water can be abstracted from the well even during the dry season, when the surface water source may dry up, if the well screen is located below the dry season water table (IRC, 1981). Bank infiltration can improve the chemical as well as microbiological quality of surface water. Phosphate and trace metals, in particular, are likely to be removed by adsorption onto sediments during infiltration (Stute et al., 1997). A bank infiltration system is shown in **Figure 6.5**.



Bank river intake using infiltration drains

Figure 6.5: Bank Infiltration (IRC, 1981)

Box 6.2: Bank infiltration in Hungary

Hungary has developed what is probably the largest bank infiltration system in Europe. The municipal water works in the capital, Budapest, has installed a network of shallow wells (typically 6-10 meters deep) on two large islands in the Danube river. Supply wells are most often sited 100-300 m from the shore, but in some cases are as close as 30 meters. Isotopic tests have shown that the abstracted water is very young, and almost entirely derived from the river. However, bacteriological quality is good, and the water requires little treatment - only iron and manganese removal from some wells, and safety chlorination in all cases to provide a residual for distribution. Underground tunnels deliver the water to the capital and surrounding areas, meeting the needs of some 4.5 million inhabitants, or about 45% of the country’s population. Similar bank infiltration systems supply water to most major settlements on the Danube. Source: (Csanady, 1999)

6.2.4 Disinfection

Delivered water can contain pathogens which were either present in the raw water source, or were introduced during water production, storage and delivery. Pathogens can occur in water derived from groundwater, rainwater, or surface water, though the risks are greatest with surface water, because of the raw water quality. Physical or chemical disinfection is the most effective and reliable way to reduce the number of microorganisms in drinking water to acceptable levels. Disinfection can be practiced at either community or household levels. A comprehensive manual reviewing the needs for and limitations of disinfection in small communities is given by the Water Research Centre (WRC, 1989).

Physical Disinfection

Boiling can effectively kill ova, cysts, bacteria, and viruses present in water. Water should be brought to a full rolling boil, and maintained for one minute. Water boils at lower temperatures at higher altitudes, so for every 1000 meters of elevation an additional minute of boiling should be required. Boiling is generally not recommended for several reasons: it requires a large amount of fuel; it may give the water a flat, unpleasant taste; there is a risk that people may heat the water without boiling, and consider the water purified. Boiling in closed kettles can concentrate some volatile organic compounds. Large-scale boiling is not a feasible option for drinking water in most cases because fuel costs would be prohibitive (WHO, 1997b).

Ultraviolet radiation can effectively kill pathogens. Electrical ultraviolet lamps have been used to irradiate water, and several schemes have been developed to utilize solar energy for disinfection (Acra et al., 1989; EAWAG, 1999).

The Swiss research center EAWAG has shown that by storing water in clear bottles and exposing them to at least 4 hours of sunlight, over 99% pathogen removal can be achieved. The sunlight both heats and irradiates the water, and these two processes have a synergistic effect on pathogen removal. Raw water must have low turbidity (<30 NTU), for radiation to penetrate sufficiently. Bacteria, viruses, *Giardia* and *Cryptosporidium* cysts, and parasite eggs can all be effectively inactivated through the combination of ultraviolet radiation and elevated water temperature. **Figure 6.6** shows that in one study, pathogen inactivation was initially low, but as water temperature rose above about 50°C, the effects of radiation and elevated temperature acted synergistically, resulting in increased inactivation efficiency. This technique, called SODIS (Solar Disinfection) involves very minimal capital and operational costs, and is promising, both for use in arsenic-affected areas, and for rural water supply in general. Large field tests of SODIS are currently being conducted in a number of countries in South America, Africa, and Asia (EAWAG, 1999).

Whether solar or artificial radiation is used, disinfection will be less effective in turbid waters, since suspended particles will scatter the radiation. Dissolved iron and manganese can also interfere with the efficacy of ultraviolet disinfection.

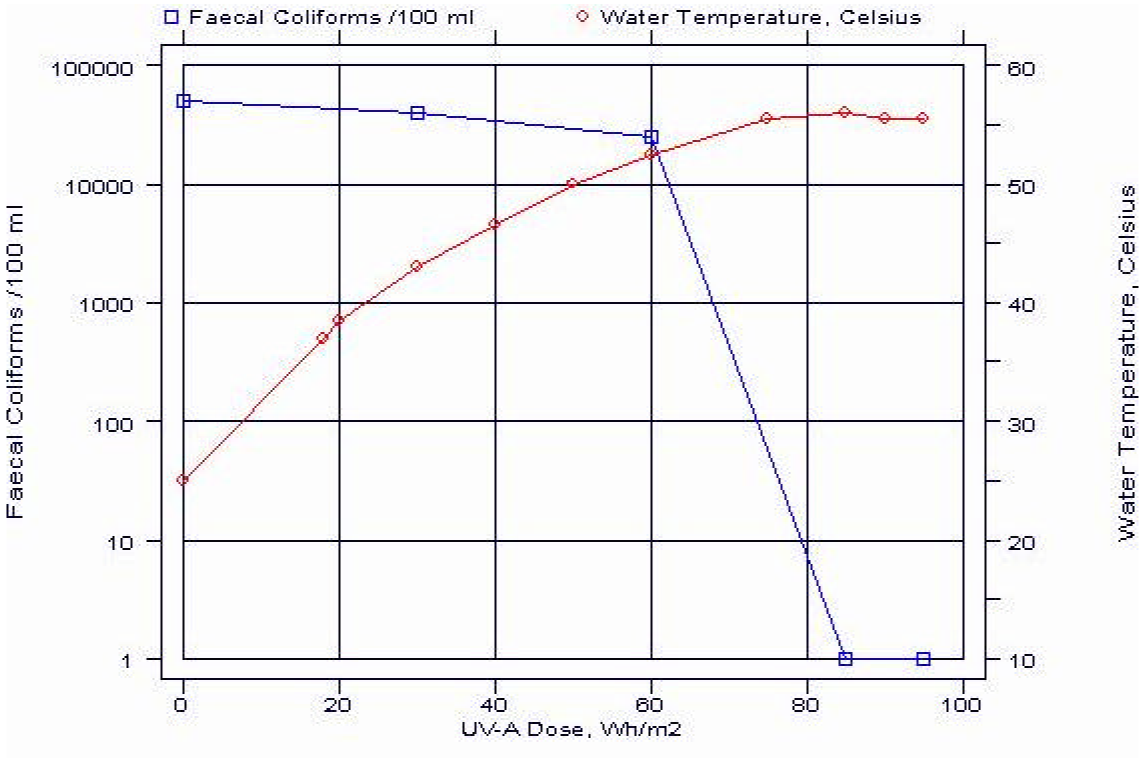


Figure 6.6: Temperature and pathogen removal in SODIS treatment (after EAWAG, 1999, Technical Note #1)

Chemical Disinfection

Chemical disinfectants include ozone and several chlorine compounds. In rural areas, the most common forms of chlorine are liquid bleach (sodium hypochlorite, about 1% available chlorine); bleaching powder (calcium hypochlorite, up to 30% available chlorine); and high-test hypochlorite (50-70% available chlorine). Chlorine compounds are very reactive and if improperly stored, available chlorine levels can be much lower than expected. The appropriate chlorine dose will depend on the chemical and physical composition of the water, and should be sufficient to satisfy both the chlorine demand and to produce a free residual of 0.5 mg/L. A minimum contact time of 30 minutes is recommended.

Various systems have been developed for chlorination at community and household levels (WRC, 1989; WHO, 1997b). Chlorine disinfection has several obvious advantages: it is very effective at pathogen reduction, and the free residual provides some protection against contamination during storage or transportation. However, if too little or too much chlorine is added, serious problems can arise: in the former case, users may incorrectly believe that the water is pathogen-free, while in the latter case the water may be unpalatable because of a strong chlorine taste[4]. Especially at community and household levels, it can be very difficult to ensure that the correct dose of chlorine is delivered. Even when the optimal dose of chlorine is achieved, water users unaccustomed to chlorinated water may find the taste unpleasant, and may choose to abandon chlorination. In both industrialized and developing countries, experience has shown that users have chosen unsafe sources over safe waters with too strong a chlorine taste.

[4] For health reasons, WHO recommends that chlorine in drinking water not exceed 5.0 mg/L. In practice water becomes unpalatable at much lower chlorine levels (WHO, 1993).

6.3 Technologies for arsenic removal

In some areas, arsenic-contaminated water will be abundant, and arsenic-free sources scarce or polluted with other compounds. In these areas it may be most efficient to remove arsenic from the contaminated water, at least as a short term measure. Many technologies have been developed for the removal of arsenic. Most of the documented experience has been with large municipal treatment plants, but some of the same technologies can be applied at community or household levels.

All of the technologies for arsenic removal rely on a few basic chemical processes, which are summarized below:

- Oxidation/reduction: reactions that reduce (add electrons to) or oxidize (remove electrons from) chemicals, altering their chemical form. These reactions do not remove arsenic from solution, but are often used to optimize other processes.

- Precipitation: Causing dissolved arsenic to form a low-solubility solid mineral, such as calcium arsenate. This solid can then be removed through sedimentation and filtration. When coagulants are added and form flocs, other dissolved compounds such as arsenic can become insoluble and form solids, this is known as coprecipitation. The solids formed may remain suspended, and require removal through solid/liquid separation processes, typically coagulation and filtration.

- Adsorption and ion exchange: various solid materials, including iron and aluminum hydroxide flocs, have a strong affinity for dissolved arsenic. Arsenic is strongly attracted to sorption sites on the surfaces of these solids, and is effectively removed from solution. Ion exchange can be considered as a special form of adsorption, though it is often considered separately. Ion exchange involves the reversible displacement of an ion adsorbed onto a solid surface by a dissolved ion. Other forms of adsorption involve stronger bonds, and are less easily reversed.

- Solid/liquid separation: precipitation, co-precipitation, adsorption, and ion exchange all transfer the contaminant from the dissolved to a solid phase. In some cases the solid is large and fixed (e.g. grains of ion exchange resin), and no solid/liquid separation is required. If the solids are formed *in situ* (through precipitation or coagulation) they must be separated from the water. Gravity settling (also called sedimentation) can accomplish some of this, but filtration is more effective. Most commonly, sand filters are used for this purpose.

- Physical exclusion: some synthetic membranes are permeable to certain dissolved compounds but exclude others. These membranes can act as a molecular filter to remove dissolved arsenic, along with many other dissolved and particulate compounds.

- Biological removal processes: bacteria can play an important role in catalyzing many of the above processes. Relatively little is known about the potential for biological removal of arsenic from water.

Boiling does not remove arsenic from water; in fact it will concentrate arsenic, as some water will be lost as steam. In many developing countries, though, boiling is known to 'purify water' because it effectively kills pathogens. Education campaigns may need to specifically dispel the myth that boiling water can reduce the risk of arsenic poisoning. Boiling of water could be used to remove arsenic as part of a distillation process, in which the steam is collected and condensed. However, this is unlikely to be a practical option.

Most of the established technologies for arsenic removal make use of several of these processes, either at the same time or in sequence. All of the removal technologies have the added benefit of removing other undesirable compounds along with arsenic - depending on the technology, bacteria, turbidity, color, odor, hardness, phosphate, fluoride, nitrate, iron, manganese, and other metals can be removed.

Historically, the most common technologies for arsenic removal have been coagulation with metal salts, lime softening, and iron/manganese removal. Since the WHO Guideline Value for arsenic in drinking water was lowered from 50 to 10 µg/L in 1993, several countries have lowered their drinking water standards, in some cases to below 10 µg/L. In 2001, the USEPA lowered the U.S. drinking water standard from 50 to 10 µg/L. Coagulation processes are sometimes unable to efficiently remove arsenic to these low levels. As a result, various alternate technologies have been developed or adapted that are capable of removing arsenic to trace levels. These advanced treatment options include ion exchange, activated alumina, and membrane methods such as reverse osmosis and nanofiltration. While these technologies have all been shown to be effective in lab or pilot studies, there is still relatively little experience with full-scale treatment. In addition, a number of novel removal technologies are under development, some of which show great promise.

The main arsenic removal technologies are presented below, along with a brief description of how removal efficiency is affected by arsenic concentration and speciation, pH, and the presence of other dissolved constituents. The interested reader is referred to key references for each technology. A more detailed review of arsenic removal technologies is presented in (Sorg and Logsdon, 1978). Though dated, this paper gives a good overview of the mechanisms involved in arsenic removal. In a more recent review, Jekel has documented several advances in arsenic removal technologies (Jekel, 1994). A review was made considering economic factors in implementing an anticipated new, lower drinking water standard to be set by the USEPA (Chen et al., 1999). Many of the technologies are discussed in detail in an AWWA reference book, though the focus is not on arsenic removal (Letterman, 1999). Recently a compilation has been made identifying companies and organizations that are involved in arsenic removal technologies, a listing on the Internet includes contact details (Murcott, 2000).

6.3.1 Oxidation

Most arsenic removal technologies are most effective at removing the pentavalent form of arsenic (arsenate), since the trivalent form (arsenite) is predominantly non-charged below pH 9.2 (See **Figure 1.X** (Editor: refer to pH-Eh chart from Chapter 1)). Therefore, many treatment systems include an oxidation step to convert arsenite to arsenate. Oxidation alone does not remove arsenic from solution, and must be coupled with a removal process such as coagulation, adsorption or ion exchange.

Air oxidation

Atmospheric oxygen is a readily available oxidizing agent, however the kinetics of air oxidation of arsenic are very slow, taking weeks (Pierce and Moore, 1982). Cherry and others showed that even when distilled water spiked with arsenite (pH 7) is saturated with oxygen, arsenic speciation stays relatively unchanged for days (Cherry et al., 1979). When water is saturated with air instead of pure oxygen, dissolved oxygen levels are much lower, so oxidation rates are even slower. Kim and Nriagu have reported half-lives of arsenite in water saturated with oxygen and air as 2-5 and 4-9 days, respectively (Kim and Nriagu, 2000). Air oxidation of arsenite can be catalyzed by bacteria, strong acidic or alkali solutions, copper, powdered activated carbon, and higher temperature (Edwards, 1994).

Reduction of arsenate in the absence of oxygen is also quite slow, though thermodynamically favorable (Ferguson and Gavis, 1972; Edwards, 1994).

Chemical oxidation

Arsenite can also be directly oxidized by a number of other chemicals, including gaseous chlorine, hypochlorite, ozone, permanganate, hydrogen peroxide, and Fenton's reagent (H_2O_2/Fe^{2+}). Some solids such as manganese oxides can also oxidize arsenic. Ultraviolet radiation can catalyze the oxidization of arsenite in the presence of other oxidants, such as oxygen. Direct UV oxidation of arsenite is slow, but may be catalyzed by the presence of sulfite (Ghurye and Clifford, 2000), ferric iron (Emett and Khoe, 2001) or citrate (EAWAG, 1999).

Chlorine is a rapid and effective oxidant, but may lead to reactions with organic matter, producing toxic trihalomethanes as a by-product. Also, locally available chlorine in developing countries can be of uncertain quality. The amount of chlorine added will depend on the composition of the water. Doses generally range from 0.8 to 2.0 mg/L, with the goal of at least 0.2 mg/L residual chlorine, to provide protection against microbial contamination after treatment. Chlorine is widely available globally, though if improperly stored it can lose its potency rapidly.

In Europe, and increasingly in the USA, ozone is being used as an oxidant. In developing countries, ozone has not been widely used. An ozone dose of 2 mg/L, contacted with the water for 1 minute prior to filtration, has been shown to be effective in oxidizing iron and manganese, at the same time removing arsenic and other metals to below detection limits (Nieminski and Evans, 1995). At a similar ozone dose, arsenite was shown to have a half-life of approximately 4 minutes (Kim and Nriagu, 2000). Ozone is also a potent disinfectant, but unlike chlorine, does not impart a lasting residual to treated water.

Permanganate effectively oxidizes arsenite, along with Fe(II) and Mn(II). It is a poor disinfectant, though it can produce a bacteriostatic effect. Potassium permanganate ($KMnO_4$) is widely available in developing countries, where it is used as a topical antibiotic for minor cuts. It is relatively stable with a long shelf life. Residual manganese in treated water should not exceed the WHO guideline of 0.5 mg/L (WHO, 1993).

Hydrogen peroxide may be an effective oxidant if the raw water contains high levels of dissolved iron, which often occur in conjunction with arsenic contamination. The ferric ions formed will precipitate the oxidized arsenic directly (Jekel, 1994).

Solid manganese oxides have long been known to oxidize arsenite (Oscarson and al, 1981). Recently, this knowledge has been used to advantage in arsenic removal systems, where beds containing manganese oxide convert arsenite to arsenate, eliminating the need for dosing with a liquid or gas oxidant. Oxidation is effective over a wide pH range and does not release excessive manganese to solution. (Driehaus et al., 1998). Recently, other research has shown that the rate of oxidation is rapid (Chiu and Hering, 2000; Daus et al., 2000).

6.3.2 Coagulation and filtration

The most heavily documented treatment methods for arsenic removal involve coagulation and filtration, either using metal salts or lime softening. This treatment can effectively remove many suspended and dissolved constituents from water besides arsenic, notably turbidity, iron, manganese, phosphate and fluoride. Significant reductions are also possible in odor, color, and potential for trihalomethane formation. Thus coagulation and filtration to remove arsenic will improve other water quality parameters, resulting in ancillary health and esthetic benefits. However, the optimal conditions vary for removal of different constituents, and coagulation to remove arsenic may not be optimal for removal of other compounds, notably phosphate and fluoride.

Arsenic removal with metal salts has been shown since at least 1934 (Buswell, 1943). The most commonly used metal salts are aluminum salts such as alum, and ferric salts such as ferric chloride or ferric sulfate. Ferrous sulfate has also been used, but is less effective (Jekel, 1994; Hering et al., 1996; Hering et al., 1997). Excellent arsenic removal is possible with either ferric or aluminum salts, with laboratories reporting over 99% removal under optimal conditions, and residual arsenic concentrations of less than 1 µg/L (Cheng et al., 1994). Full-scale plants typically report a somewhat lower efficiency, from 50% to over 90% removal.

Alum and ferric salts dissolve upon addition to water, forming amorphous hydrous aluminum and ferric oxides[5] (HAO and HFO, respectively), which are relatively insoluble in circumneutral pH ranges. These metal hydroxides form gelatinous flocs that bind to other flocs and settle out of solution, scavenging many dissolved and particulate materials in the process. Vigorous stirring is usually required to ensure uniform mixing for optimal coagulation. If water is soft and of low alkalinity it may be necessary to add alkalinity to ensure floc formation. Sometimes polymers or colloidal substances such as clays are added to improve flocculation and sedimentation (Gulledge and O'Connor, 1973). Cheng and others have shown that addition of 2-4 mg/L of cationic polymer allows coagulant dose to be reduced by two-thirds while maintaining good arsenic removal (Cheng et al., 1994). Thus polymers or clays can be used to improve arsenic removal efficiency, and to reduce the volume of sludge generated. Sludges are usually not regenerated, but disposed of directly.

[5] When ferric salts dissolve, the ferric ion forms an amorphous solid with oxygen and hydroxyl groups. This is variously called amorphous iron oxyhydroxide, iron (oxy)hydroxide, hydrous ferric oxide (HFO), and ferrihydrite. As this solid ages, the atoms arrange themselves into more ordered groupings, and form minerals such as the coarsely crystalline goethite, and eventually the highly structured hematite (Fe_2O_3).

Mechanisms of Removal

During coagulation and filtration, arsenic is removed through three main mechanisms (Edwards, 1994):

- precipitation: the formation of the insoluble compounds $Al(AsO_4)$ or $Fe(AsO_4)$

- coprecipitation: the incorporation of soluble arsenic species into a growing metal hydroxide phase

- adsorption: the electrostatic binding of soluble arsenic to the external surfaces of the insoluble metal hydroxide.

All three of these mechanisms can independently contribute towards contaminant removal. In the case of arsenic removal, direct precipitation has not been shown to play an important role. However, coprecipitation and adsorption are both active arsenic removal mechanisms. Some studies suggest that coprecipitation is the more important removal mechanism, by showing that HFO formed *in situ* can remove approximately five times as much arsenic from contaminated water as preformed HFO (Edwards, 1994). Others, however, hold that adsorption is the dominant mechanism for arsenic removal, at least at high coagulant doses (Hering et al., 1996). For a detailed analysis of operative mechanisms in arsenic removal, the interested reader is referred to the papers of Edwards and Hering cited above.

Numerous studies have shown that filtration is an important step to ensure efficient arsenic removal. After coagulation and simple sedimentation, HAO and HFO - along with their sorbed arsenic load - can remain suspended in colloidal form. Hering and others showed that coagulation and sedimentation without filtration achieved arsenate removal efficiencies of 30%; after filtration through a 1.0 micron filter, efficiency was improved to over 96%. Only marginal improvements were made by reducing the filter size to 0.1 micron (Hering et al., 1996). In field applications, some plants improve arsenic removal with two-stage filtration (Sancha, 1999b).

Box 6.3: Sorbent capacity

It is convenient to consider sorbents in terms of their maximum adsorption density. Adsorption density is simply the amount of sorbate (arsenic, in this case), that is adsorbed onto the sorbent (HFO or HAO). At some point, called the maximum adsorption density, or adsorption capacity, the sorbent becomes saturated, and can retain no more sorbate. Adsorption capacities are reported either on a molar (moles arsenic sorbed per mole sorbent) or on a weight basis (typically g arsenic per kg sorbent).

Table 6.3: Molecular weights of compounds used in arsenic removal

Compound	Chemical Formula	Molecular weight (grams/mole)
Aluminum	Al	27.0
Iron	Fe	55.8
Arsenic	As	74.9
Arsenate	AsO_4^{3-}	139
Arsenite	AsO_3^{3-}	123
Alum (reagent)*	$Al_2(SO_4)_3 \cdot 18(H_2O)$	666 (333 g/mole Al)

Alum (commercial)*	$Al_2(SO_4)_3 \bullet 14(H_2O)$	602 (301 g/mole Al)
Ferric chloride	$FeCl_3$	162
Ferric sulfate	$Fe_2(SO_4)_3$	400 (200 g/mole Fe)
* Note: reagent-grade alum is more hydrated than commercial grade, so doses reported in the academic literature do not exactly match doses used in most applications. Doses should be calculated based on actual aluminum content, either using molar or mass units.		
If the arsenic adsorption capacity for a hypothetical sorbent were reported as one mole of arsenic per mole aluminum (complete coverage), this would be equivalent to 75 grams of arsenic sorbed per 27 grams of aluminum added, or 75 g As/333 g alum (since one mole of alum contains two moles of aluminum). The capacity would most likely be given as 225 mg As/g alum. In reality, sorbents usually have lower molar capacities. When reading capacities given on a weight basis, it is important to note whether the reported capacity is for arsenic (MW 75) or for arsenate (MW 139). Likewise, coagulant doses are sometimes given in terms of the coagulant and sometimes in terms of the metal ion (e.g. 16.2 mg/L $FeCl_3$ is equivalent to 5.6 mg/L Fe).		

Removal of arsenate

Arsenate is relatively easy to remove from water, since it bears a negative charge in natural waters above pH 2.2, and is electrostatically attracted to the positive charge on metal hydroxide surfaces. Fresh, preformed HFO and HAO have reported maximum arsenic adsorption capacities in the range of 0.1 M As(V)/M Fe or Al. When the sorbents are formed *in situ*, capacities are much higher, in the vicinity of 0.5 to 0.6 M As(V)/M Fe or Al. This difference reflects the effects of coprecipitation: preformed hydroxides only remove arsenic through adsorption, while *in situ* formation leads to coprecipitation as well (Edwards, 1994).

The percentage of arsenate removed by coagulation is chiefly controlled by pH and coagulant dose, and is largely independent of initial arsenic concentration. Adsorption is theoretically favored at a pH below a sorbent's point of zero charge, since the positively charged surface can attract the arsenate anion. Laboratory tests have shown that arsenate adsorption onto HFO is optimal below pH 8, and below pH 7 for HAO. Adjustment of pH will often result in greater improvements in efficiency than increasing coagulant dose (Sorg and Logsdon, 1978; Edwards, 1994; Hering et al., 1996).

HFO remains stable and relatively insoluble at pH levels as low as 4-5, but HAO becomes much more soluble below pH 6, and above pH 8. Consequently effective arsenic removal with alum is restricted to a relatively narrow pH range around pH 6-7 (Hering et al., 1997).

Figure 6.7: Arsenate removal by coagulation (after Hering et al., 1997, Figure 1)

(PENDING)

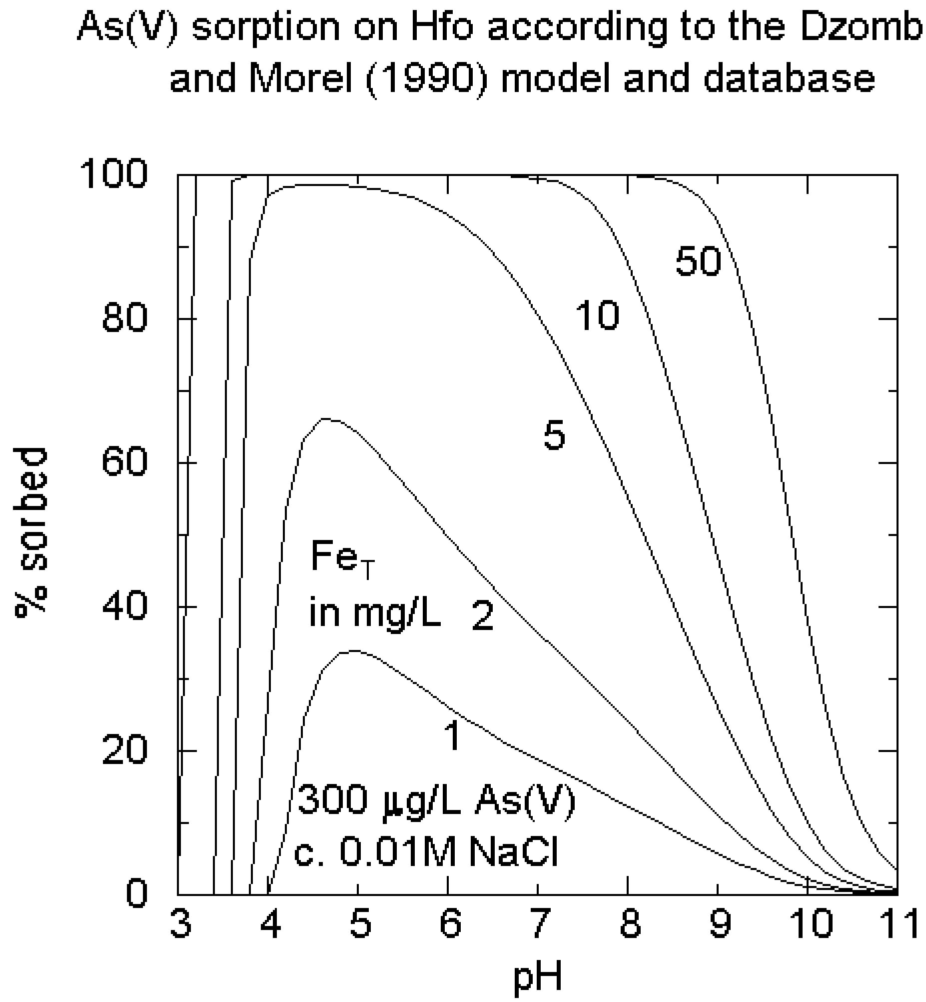


Figure 6.8: Arsenate adsorption onto preformed HFO (DPHE/BGS/MML, 1999, Volume S4)

Figure 6.8 shows the theoretical adsorption capacity of HFO over a wide range of pH and iron doses. Below pH 4-5 HFO will dissolve when in chemical equilibrium, though equilibrium may not be reached during the relatively short coagulation and filtration treatment.

Optimal dosing will depend on the specific water chemistry and required removal efficiency, but typical doses range from 5 to 30 mg/L $FeCl_3$. A similar graph for HAO would show a similar drop in removal efficiency at high pH, though the drop would occur at slightly lower pH since HAO has a lower point of zero charge than HFO. However, the graph would show a sharp decrease in removal efficiency below pH 6, due to the increased solubility of HAO. Alum doses are generally higher, typically ranging from 10 to 50 mg/L.

The laboratory data plotted in **Figure 6.7** show much better arsenic removal for a coagulant dose of approximately 2 mg/L Fe than in **Figure 6.8**, because the HFO was formed *in situ*, allowing coprecipitation to occur along with adsorption. In general, smaller amounts of sorbent will be needed if coagulation and flocculation take place *in situ*.

Over the pH range where both HFO and HAO are insoluble (roughly pH 6-7) ferric salts and alum are equally efficient at arsenate removal, on a molar basis. However, on a weight basis, ferric salts are significantly superior. This difference is due to the higher molecular weight of alum, which consists of aluminum and sulfate bound to eighteen water molecules, compared to the unhydrated ferric chloride (see **Box 6.3**) (Hering et al., 1996). One mole of aluminum as alum weighs approximately twice as much as one mole of iron as ferric chloride. Therefore, it takes about twice as much alum as ferric chloride (by weight) in order to produce a comparable amount of sorbent. Field research in Chile in the 1980s showed that HFO was superior to HAO because it led to larger flocs with better sedimentation, and is efficient over a wider pH range (Sancha, 1999a). The highly hydrated state of alum does confer one benefit over ferric chloride - the solid is stable under humid conditions, whereas ferric chloride can absorb water from air and lose its consistency.

Removal of arsenite

Arsenite is uncharged in most natural waters (below pH 9.2) and as such is more difficult to remove, since there is no electrostatic attraction to charged solids. Alum is very ineffective at removal of arsenite, with maximum surface densities of approximately 0.04 M As/M Al for preformed HAO, about one third the density reported for arsenate (Edwards, 1994). Ferric salts are much more efficient, with reported maximum surface densities on preformed HFO ranging up to 0.4 M As/M Fe, which is significantly higher than the comparable density for arsenate! Edwards offers several explanations for this anomalous reporting, the most convincing of which is that ferric solids oxidize the arsenite, forming arsenate and ferrous ions, which are subsequently reoxidized to ferric iron by oxygen, causing co-precipitation of arsenate (Edwards, 1994). Most researchers, however, have reported arsenite removal with HFO to be somewhat less effective than arsenate removal.

Adsorption of arsenite onto HFO is relatively insensitive to pH within most natural waters, and is theoretically favored from about pH 5 to 8 (Sorg and Logsdon, 1978). However, one laboratory study that examined arsenite removal through coagulation, rather than adsorption onto preformed HFO, found arsenite removal to be best at extreme pH values (4 and 9), and lowest at pH 6. The authors propose that this unexpected result is due to the formation of smaller flocs at extreme pH values, which would have a larger surface area for adsorption. A second possible explanation is that even over the short period between formation and application, the surface of the HFO may undergo significant structural evolution, altering its sorption capacity (Hering et al., 1996). The unexpected findings reported by both Edwards and Hering indicate that arsenite removal with HFO is still not completely understood.

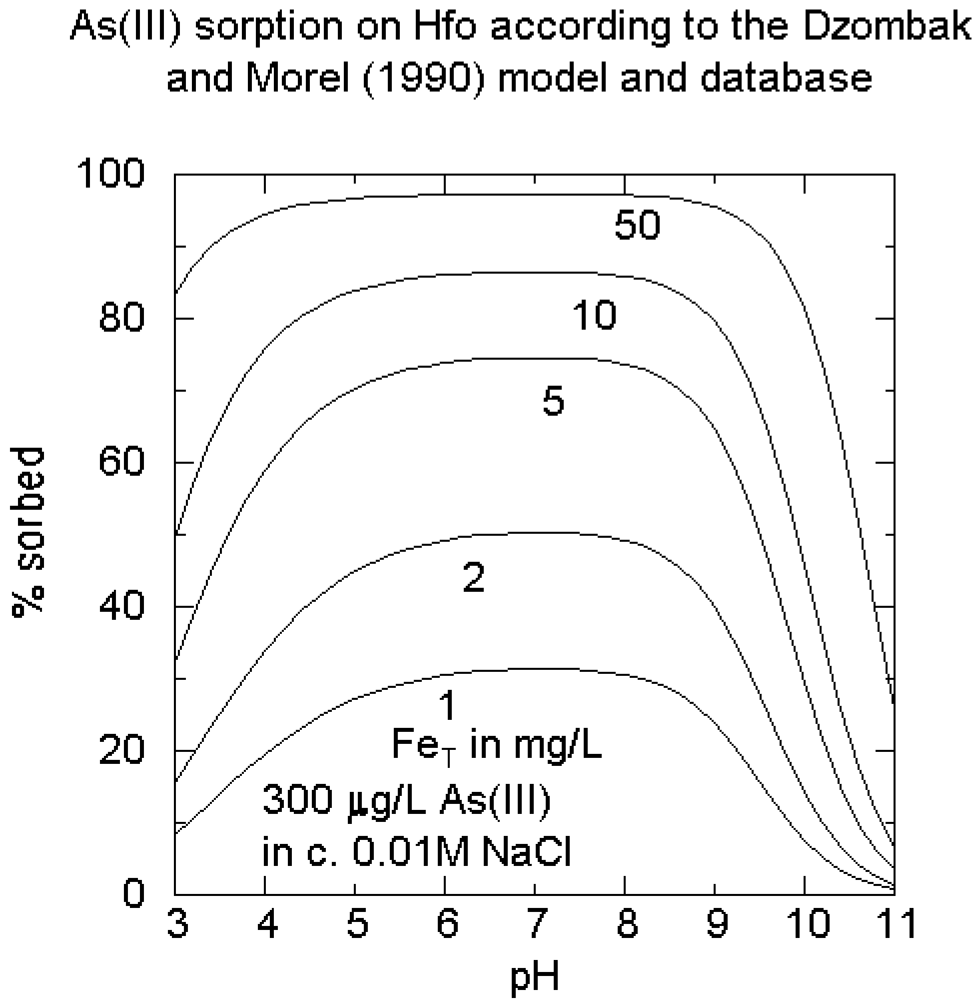


Figure 6.9: Arsenite adsorption onto HFO (DPHE/BGS/MML, 1999, Volume S4)

Effects of competing ions

Arsenic removal through coagulation will be affected by the presence of other anions and cations. Some anions will lower removal rates, by competing with arsenic for sorption sites and lowering the surface charge. Cations, in contrast, can increase the positive surface charge, and enhance arsenic adsorption. Relatively few studies have examined these types of effects. Those that have, however, agree on certain fundamental principles:

- effects of co-occurring solutes will be most pronounced when adsorption density is nearing saturation;

- arsenite makes a weaker bond than arsenate with metal oxides, and is thus more likely to be displaced by competing anions; and

- surface complexation chemistry is complex, particularly when multiple anions are present.

At near-neutral pH, Manning and Goldberg give the theoretical affinity for anion sorption on metal oxides as (Manning and Goldberg, 1996):

$PO_4 > SeO_3 > AsO_4 > AsO_3 >> SiO_4 > SO_2 > F > B(OH)_3$.

Phosphate is the anion considered most likely to compete with arsenic for adsorption sites, because of its strong affinity for metal oxides, and its similarity to the arsenate ion. Phosphate has been shown to mobilize arsenic in soils contaminated with lead pesticides (Davenport and Peryea, 1991; Peryea, 1991; Peryea and Creger, 1994; Peryea and Kammereck, 1997). Recently Meng and others showed that phosphate can reduce arsenite removal in coagulation with ferric salts (see **Table 6.4**) (Meng et al., 2000).

Dissolved silicate is usually found in much higher concentrations than phosphate, and can interfere with removal of both arsenate and arsenite. Ghurye and others report that in slightly basic waters (pH > 7) silicate levels above 15-30 mg Si/L can reduce arsenate removal efficiency (Ghurye et al., 1999). Meng and others report that arsenite removal rates declined from 95% to under 50% with the addition of 18 mg/L Si. Arsenate removal decreased by 13%. The authors argue that silicate reduces arsenic removal efficiency in two ways: by competing directly for adsorption sites, and by changing the electrostatic properties of the HFO surface (Meng et al., 1999; Meng et al., 2000).

Elevated levels of sulfate and carbonate can slightly reduce arsenite removal rates, but have little effect on arsenate removal (Wilkie and Hering, 1996; Meng et al., 1999; Meng et al., 2000).

Ammonium can interfere with floc formation, and thus indirectly reduce arsenic removal rates (Csanady, 1999). Natural organic matter also somewhat reduces the efficiency of arsenite removal at pH 4 through 9. In contrast, the presence of calcium and magnesium can enhance arsenic removal, by increasing the positive charge on the HFO surface. (Hering et al., 1996; Wilkie and Hering, 1996; Hering et al., 1997).

Meng and others have also shown that competing anions can have a synergistic effect. The following table shows that the addition of either silicate or phosphate has only a minor effect on removal of arsenate. When both anions are added, however, removal drops by some 40%.

Table 6.4: Effects of anions on removal of arsenite and arsenate in coagulation (Meng et al., 2000)

	Arsenite removal %	**Arsenate removal %**
310 mg/L Cl	95	99
133 mg/L HCO_3	74	99
18 mg/L Si	48	86
1.9 mg/L P	38	96
18 mg/L Si + 133 mg/L HCO_3	45	96
1.9 mg/L P + 133 mg/L HCO_3	33	63

1.9 mg/L P + 18 mg/L Si	31	61
1.9 mg/L P + 18 mg/L Si + 133 mg/L HCO_3	26	59

Note: initial arsenic = 300 µg/L; total Fe(III) = 6.7 mg/L; equilibrium pH = 6.9 ± 0.1; matrix is simulated Bangladesh groundwater (2.5 mM $CaCl_2$, 0.82 mM $MgCl_2$, 2.2 mM NaCl); settled water was filtered with a 0.45 µm filter.

Most of the competitive effects noted above were seen in laboratory studies using relatively low coagulant doses. The competitive effects can be overcome by using higher coagulant doses. If competing anions (particularly phosphate and silicate) are present, the amount of coagulant required may be higher than standard values reported in the literature. For this reason, and because of the synergistic effects noted above, it is important to conduct bench-scale testing using the actual water to be treated when designing field-scale arsenic removal systems.

Lime Softening

Lime softening is a similar process to coagulation with metal salts. Lime ($Ca(OH)_2$) hydrolyzes and combines with carbonic acid to form calcium carbonate, which acts as the sorbing agent for arsenic removal. This process is typically used only with very hard waters, and shifts the pH of treated water markedly higher, in the range of 10-12.

Early jar-test studies found that at pH 10.5 and higher, nearly 100% removal of arsenate is possible; the maximum arsenite removal was found to be about 80% at pH 11.1 (Logsdon et al., 1974). More recently, McNeill and Edwards examined arsenic removal during softening in detail, and found the main removal mechanism to be sorption of arsenic onto magnesium hydroxide solids that form during softening. Like Logsdon and others, they found arsenate removal to be excellent above pH 11, and much poorer at pH 10. Arsenic removal at lower pH can be greatly improved by the addition of low levels of iron, but when carbonate is present this effect is less pronounced. Trace levels of phosphate were found to slightly reduce arsenic removal, especially below pH 12 (McNeill and Edwards, 1997).

McNeill and Edwards found arsenite removal to be very poor, with arsenite sorption densities about an order of magnitude less than for arsenate. However, Dutta and Chaudhuri showed that arsenite levels could be reduced by over 90% using lime softening supplemented with a powdered coal additive (Dutta and Chaudhuri, 1991). The authors theorize that arsenite is directly adsorbed, but others suggest that the carbon could catalyze arsenic oxidation (Jekel, 1994).

Disadvantages of lime softening for arsenic removal are that large coagulant doses are required, on the order of 800-1200 mg/L, and consequently a large volume of sludge is produced. Also the operating pH is rather extreme, and strong acids would probably be needed to adjust the pH after treatment.

Variations on conventional coagulation and filtration

While conventional coagulation with iron salts, alum, and lime are the most common applications of coagulation and filtration, many variations are possible.

Researchers from the Australian Nuclear Science and Technology Organization have developed an arsenic removal system based on coagulation and filtration with ferric sulfate. Instead of using a chemical oxidant, the ANSTO system uses the ultraviolet radiation in natural sunlight to catalyze both the oxidation of arsenite and the formation of HFO (Khoe and Emett, 1999).

As mentioned above, settling can be improved by addition of synthetic polymers or clays during coagulation. Brewster has further shown that standard coagulation and filtration can be improved by addition of a polymer and by pumping the contaminated water through an electrochemical cell during treatment (Brewster, 1992).

In some cultures plant products are used as natural coagulants. The crushed seeds of moringa trees *(Moringa oleifera lam* and *Moringa peregrina fior*i) are particularly effective coagulants, comparing favorably with alum in terms of removal of turbidity. A dosing rate of 200 mg crushed seeds per liter of water is suggested as optimal (IRC, 1982a).

Seeds of red sorrela *(Hibiscus sabdariff*a) can be dried, crushed, and mixed with sodium carbonate in a 9:1 ratio, then mixed with water and heated to produce a milky coagulant solution. Neither red sorrela nor moringa has been evaluated for arsenic removal (IRC, 1982a).

6.3.3 Ion-Exchange Resins

Synthetic ion exchange resins are widely used in water treatment to remove many undesirable dissolved solids, most commonly hardness, from water. These resins are based on a cross-linked polymer skeleton, called the 'matrix'. Most commonly, this matrix is composed of polystyrene cross-linked with divinylbenzene. Charged functional groups are attached to the matrix through covalent bonding, and fall into four groups (Clifford, 1999):

- Strongly acidic (e.g. sulfonate, $-SO_3^-$)
- Weakly acidic (e.g. carboxylate, $-COO^-$)
- Strongly basic [e.g. quaternary amine, $-N + (CH_3)_3$]
- Weakly basic [e.g. tertiary amine, $-N(CH_3)_2$]

The acidic resins are negatively charged, and can be loaded with cations (e.g. Na^+), which are easily displaced by other cations during water treatment. This type of cation exchange is most commonly applied to soften hard waters.

Conversely, strongly basic resins can be pretreated with anions, such as Cl^-, and used to remove a wide range of negatively charged species. Clifford gives the following relative affinities of some common anions for a type 1 strong-base anion resins (Clifford, 1999):

$CrO_4^{2-} >> SeO_4^{2-} >> SO_4^{2-} >> HSO_4^- > NO_3^- > Br^- > HAsO_4^{2-} > SeO_3^{2-} > HSO_3^{3-} > NO_2^- > Cl^-$

Different resins will have differing selectivity sequences, and resins have been developed specifically to optimize removal of sulfate, nitrate, and organic matter. Various strong-base anion exchange resins are commercially available which can effectively remove arsenate from solution, producing effluent with less than 1 µg/L arsenic. Arsenite, being uncharged, is not removed. Analysts have taken advantage of this specificity to develop procedures for analytical differentiation of arsenite and arsenate (e.g. Ficklin, 1983; Edwards et al., 1998). Therefore, unless arsenic is present exclusively as arsenate, an oxidation step will be a necessary precursor to arsenic removal.

Conventional sulfate-selective resins are particularly suited for arsenate removal. Nitrate-selective resins also remove arsenic, but arsenic breakthrough occurs earlier. Most commonly, resins are pretreated with hydrochloric acid, to establish chloride ions at the surface, which are easily displaced by arsenic (Ghurye et al., 1999), though the resin can be primed with other anions such as bromide or acetate (Edwards et al., 1998). Packed beds are commonly designed to have an Empty Bed Contact Time (EBCT) of 1.5 to 3 minutes.

Arsenate removal is relatively independent of pH and influent concentration. On the other hand, competing anions, especially sulfate, have a strong effect. The number of bed volumes that can be treated before arsenic breakthrough (defined as 10% of the influent concentration) can be roughly estimated with two simple formulas: (Clifford and Majano, 1993; cited in Chen et al., 1999).

For $[SO_4^{2-}] < 120$ mg/L: Bed Volumes = $-606 * \ln[SO_4^{2-}] + 3{,}150$

For $[SO_4^{2-}] > 120$ mg/L: Bed Volumes = $-200 * \ln[SO_4^{2-}] + 1{,}250$

where $[SO_4^{2-}]$ is the initial sulfate concentration in mg/L. In low-sulfate waters, ion exchange resin can easily remove over 95% of arsenate, and treat from several hundreds to over a thousand bed volumes before arsenic breakthrough occurs. Accordingly, the USEPA recommends that ion exchange resins not be used in waters with >120 mg/L sulfate or >500 mg/L TDS, and will be most effective in waters with even lower sulfate levels (<25 mg/L) (USEPA, 2000).

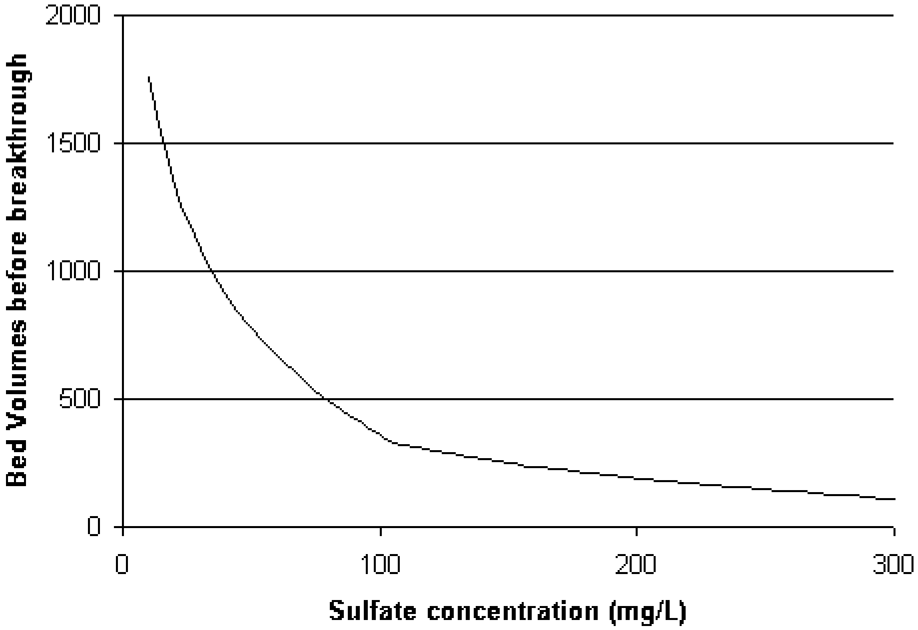


Figure 6.10: Bed volumes treated with ion exchange resin

Ion exchange capacity, analogous to the adsorption capacity discussed in the previous section, is a measure of the number of exchange sites, and is usually measured in milliequivalents (meq) per mL (wet volume, including pore spaces). The dry-weight capacity (meq/g) can be more precise, and is sometimes used in scientific research. The operating capacity measures actual performance of resins under environmental conditions, and is always less than the advertised exchange capacity, due to incomplete regeneration and contaminant leakage. For a particular sorbate, capacity can be converted from meq/mL to mg/mL by multiplying by the molecular weight (75 in the case of arsenic). Typical theoretical exchange capacities of strong base anion exchange resins range from 1 to 1.4 meq/mL, (Clifford, 1999) or 3.0 to 4.2 meq/g dry weight This would imply a maximum sorption capacity of approximately 315 mg As/g. However, actual reported capacities are typically much lower. One study using laboratory reagents found the maximum operational capacity for arsenate removal of a strong-base anion exchange resin to be about 64 mg As/g (Baes et al., 1997). Under field conditions, capacity will be lower, especially in waters with high TDS or sulfate levels.

Ion exchange resins are easily regenerated by flushing with concentrated salt solutions (1.0 M NaCl is commonly used). Clifford has demonstrated that this brine can be reused 20-30 times, in spite of increasingly concentrated arsenic levels in the regenerant. Recovery of arsenic is nearly complete (85 to 100%). Regenerated media generally have slightly lower arsenic capacities than virgin media, but after three to four regenerations no further loss in capacity occurs. Some systems take advantage of this by regenerating resin beds daily or even more frequently. Regeneration could easily be done by water users with a moderate amount of training.

One drawback of ion exchange is that exhausted resins, unlike activated alumina, have chromatographic properties such that exhausted resin can release nearly all previously removed arsenic over a few bed volumes, resulting in ‘arsenic peaking’ with concentrations several times higher than the influent (Edwards et al., 1998; Ghurye et al., 1999). A second drawback is that resins can be fouled by precipitation of iron or manganese oxides: these metal coatings can reduce flow rates, and prevent contact between arsenic and the resin (Fox, 1989). These coatings themselves may adsorb arsenic, but this does not make use of the ion-exchange properties of the resin. Furthermore, colloidal iron may pass through the resin bed, and could transport adsorbed arsenic, causing significant leakage through the bed (Ghurye et al., 1999). Advantages of ion exchange resins, however, include easy regeneration, applicability over a wide pH range, and overall improvements in water quality, through the removal of chromate, selenate, nitrate, and nitrite.

6.3.4 Activated Alumina

Activated alumina is a granulated form of aluminum oxide (Al_2O_3) with very high internal surface area, in the range of 200-300 m^2/g. This high surface area gives the material a very large number of sites where sorption can occur, and activated alumina has been widely used for removal of fluoride. In the early 1970s Bellack accidentally discovered that activated alumina could remove arsenic from water (Bellack, 1971; Sorg and Logsdon, 1978).

The mechanisms of arsenic removal are similar to those of a weak base ion exchange resin, and are often collectively referred to as 'adsorption', though ligand exchange and chemisorption are technically more appropriate terms (Clifford, 1999). The kinetics of arsenic removal onto the alumina surface are slower than those of ion exchange resins, and some arsenic leakage is often noted in activated alumina systems.

Arsenic removal efficiency is excellent (typically > 95%), for both arsenate and arsenate, but arsenic capacity varies significantly, and is controlled primarily by pH and influent arsenic concentration and speciation. Arsenate removal capacity is best in the narrow range from pH 5.5 to 6.0, where the alumina surfaces are protonated, but acid anions are not yet concentrated enough to compete with arsenic for sorption sites (Trussell et al., 1980; Rosenblum and Clifford, 1984; Clifford, 1999). Typically, activated alumina has a point of zero charge (PZC), below which the surface is positively charged, and above which the surface bears a negative charge, at pH 8.2. Arsenic removal capacity drops sharply as the PZC is approached, and above pH 8.5, is reduced to only 2-5% of capacity at optimal pH (Clifford, 1999). For neutral and basic waters, therefore, pH adjustment may be necessary for effective arsenic removal.

Figure 6.11: Effect of pH on arsenate adsorption onto activated alumina (after Clifford, 1999)

[Editors, I have sent a photocopy of this figure to WHO Geneva, contact me if you need another - RJ]

Fine (28-48 mesh) particles of activated alumina are typically used for arsenic removal, with an Empty Bed Contact Time of five to eight minutes (Rubel and Woosely, 1979). When operated in the optimal pH range, activated alumina beds have much longer run times than ion exchange resins. The number of bed volumes that can be treated at optimal pH before arsenate breaks through is mainly controlled by the influent arsenic concentration, and can be estimated with the following equation: (Ghurye et al., 1999)

$$\text{Bed Volumes} = 210{,}000 * [\text{As}]^{-0.57}$$

where [As] is the initial arsenate concentration in micrograms per liter.

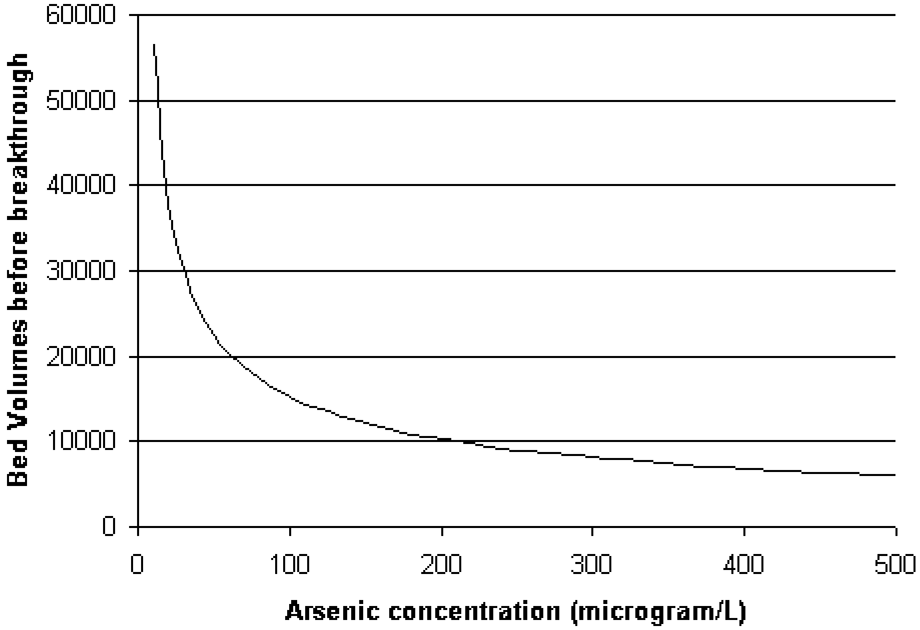


Figure 6.12: Bed volumes treated with activated alumina

Frank and Clifford reported an arsenate capacity (at pH 6) of about 1.6 g/L of activated alumina, consistent with an earlier reported capacity of 4 mg/g, assuming a bulk density of 0.5 kg/L (Gupta and Chen, 1978). Fox reported a somewhat lower capacity of 1 mg/g, but this is likely due to the elevated pH (7.4-8.0) of the influent water (Fox, 1989).

Effects of arsenic speciation

The Frank and Clifford study showed that under optimal conditions, activated alumina could treat an influent containing 100 µg/L arsenate for 10,000 to 20,000 bed volumes before gradual breakthrough was observed, consistent with **Figure 6.12**. Arsenite, in contrast, broke through completely after only a few hundred bed volumes (Frank and Clifford, 1986).

Other researchers, however, have found that activated alumina can remove arsenite for longer run lengths. Datta and others showed that after pretreatment with caustic soda, activated alumina can remove over 1000 bed volumes of arsenite in lab water, and several thousands of bed volumes of groundwater containing a mixture of arsenite and arsenate (Datta et al., 1997). Likewise, Clifford and Lin found that activated alumina performed better than expected in removing arsenite from natural waters. At pH 6, approximately 9000 bed volumes of groundwater containing 31 µg/L arsenite and 57 µg/L arsenate were treated before effluent exceeded the MCL of 50 µg/L. At pH 7.2, however, only 1900 bed volumes could be treated, highlighting the strong dependency on pH (Clifford and Lin, 1991). These findings suggest that the aluminum oxide surface may catalyze oxidation of arsenite to arsenate, as manganese oxides are known to do.

Effects of co-occurring solutes

The sorption sites on the activated alumina surface are also attractive to a number of anions other than arsenate: Clifford reports the selectivity sequence of activated alumina in the pH range of 5.5 to 8.5 as (Clifford, 1999):

$OH^- > H_2AsO_4^- > Si(OH)_3O^- > HSeO_3^- > F^- > SO_4^{2-} > CrO_4^{2-} >> HCO_3^- > Cl^- > NO_3^- >$
$Br^- > I^-$

Trussell and others reported a similar selectivity sequence, but included phosphate as the second most preferred anion, after hydroxyl, and placed fluoride above arsenate in the sequence (Trussell et al., 1980).

Because of activated alumina's strong selectivity for arsenate, competing anions pose less of a problem than with ion exchange resins. Sulfate, and to a lesser extent, chloride, have been shown to reduce capacity, but the competition effect is not as dramatic as with ion exchange resins (Rosenblum and Clifford, 1984). Phosphate and fluoride are also sorbed onto activated alumina, producing improvements in drinking water quality, but at the same time reducing arsenic removal potential.

Activated alumina can be regenerated by flushing with a solution of 4% sodium hydroxide, which displaces arsenic from the alumina surface, followed by flushing with acid, to re-establish a positive charge on the grain surfaces. Regeneration is more difficult, and less complete (generally 50-80%) than with ion exchange resins (Clifford, 1986). Some of the arsenic remains irreversibly bound to the alumina, and the caustic and acid treatment dissolves some of the alumina, reducing the bed volume. Therefore, after a certain number of regeneration cycles, fresh activated alumina must be added to make up the lost media. Relatively little is known about the effectiveness of activated alumina after multiple regenerations, though limited experience suggests that run lengths will be approximately 25% shorter (Ghurye et al., 1999).

The advantages of activated alumina are that simple removal systems can be developed at community or household levels that require no chemical addition. Since activated alumina can treat thousands of bed volumes before breakthrough, filters could be operated for months before the media need to be changed or regenerated. Activated alumina will also remove selenite, fluoride, sulfate, and chromate. Disadvantages include the possibility that the media will be fouled or clogged by precipitated iron, the relatively narrow pH range for optimal operation, and the relative difficulty of regeneration. Also, compared with ion exchange resins, a significantly longer EBCT is required.

Box 6.4: Residual aluminum in treated waters

Both activated alumina and alum are composed of aluminum. There has been a good deal of controversy about health risks associated with aluminum levels in drinking water, particularly about a possible link with Alzheimer's disease. Several studies have shown that the brain tissues of patients with Alzheimer's disease have elevated aluminum levels (Harrington et al., 1994; Walton et al., 1995). A few studies have found a significant link between aluminum in drinking water and incidence of Alzheimer's disease and other forms of dementia (e.g. Martyn et al., 1989; Crapper-McLachlan et al., 1991; Martyn et al., 1997). Investigations are complicated by the large numbers of forms or species of dissolved aluminum, and because of the tendency of aluminum to form natural colloids with organic carbon, fluoride, and sulfate (Smith et al., 1996). The link between neurological effects and aluminum in drinking water is particularly elusive because the average adult intake of aluminum from food is 5 mg/day (WHO, 1998), which tends to be much higher than any intake from drinking water.

The 1993 WHO Guidelines for Drinking Water Quality did not set a health-based guideline for aluminum. However, aluminum in drinking water can cause several practical problems, such as discoloration of treated water and formation of floc in piped distribution systems. WHO remarked that “although further studies were needed, the balance of epidemiological and physiological evidence did not support a causal role for aluminum in Alzheimer disease. An aluminum concentration of 0.2 mg/L in drinking water provided a compromise between the practical use of aluminum salts in water treatment and discoloration of distributed water” (WHO, 1993).

WHO subsequently conducted a detailed review of health effects of aluminum through various exposure routes. Twenty available epidemiological studies were evaluated, and half of the high quality studies found a relationship between aluminum in drinking water and Alzheimer’s disease or dementia, but the other half did not. Even in those studies that found links, relative risks were mall (<2), and confidence intervals broad.

“Hazards to neurological development and brain function from exposure to aluminum have been identified through animal studies. However, aluminum has not been demonstrated to pose a health risk to healthy, non-occupationally exposed humans. There is no evidence to support a primary causative role of aluminum in Alzheimer’s disease (AD), and aluminum does not induce AD pathology *in vivo* in any species, including humans... There is insufficient health-related evidence to justify revisions to existing WHO Guidelines for aluminum exposure in healthy, non-occupationally exposed humans. As an example, there is an inadequate scientific basis for setting a health-based standard for aluminum in drinking water.” (WHO, 1997a, p. 11)

In an addendum to the GDWQ, WHO noted that under good operating conditions, large water treatment plants should be able to use alum while ensuring residual aluminum levels of less than 0.1 mg/L. For smaller facilities, 0.2 mg/L is a practicable level for aluminum in finished waters (WHO, 1998).

Surveys of aluminum in waters treated with alum show that residual levels sometimes exceed these levels, but generally average around 0.01 - 0.1 mg/L (WHO, 1997a). A review of rural defluoridation units composed of activated alumina found residual aluminum to be less than 0.01 mg/L in 75% of cases, but above 0.2 mg/L in 17% of cases (Iyengar, 1999).

6.3.5 Membrane methods

Synthetic membranes are available which are selectively permeable: the structure of the membrane is such that some molecules can pass through, while others are excluded, or rejected. Membrane filtration has the advantage of removing many contaminants from water, including bacteria, salts, and various heavy metals.

Two classes of membrane filtration can be considered: low-pressure membranes, such as microfiltration and ultrafiltration; and high-pressure membranes such as nanofiltration and reverse osmosis. Low-pressure membranes have larger nominal pore sizes, and are operated at pressures of 10-30 psi. The tighter high-pressure membranes are typically operated at pressures from 75 to 250 psi, or even higher (Letterman, 1999).

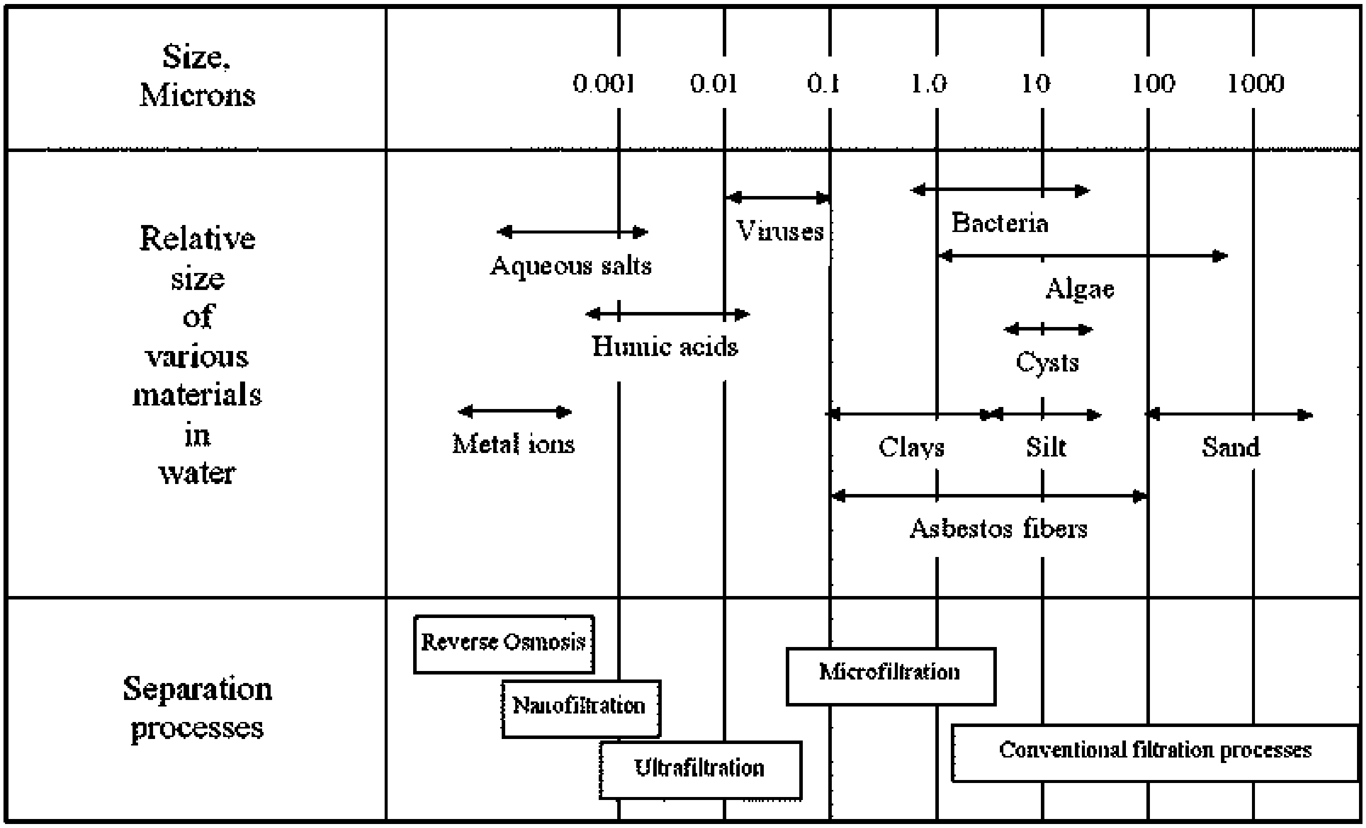


Figure 6.13: Pore size of various membranes, and size of materials subject to filtration (redrawn after Letterman, 1999)

From the above figure it is clear that reverse osmosis (RO) and nanofiltration (NF) membranes have pore sizes appropriate for removal of dissolved arsenic, which is in the ‘metal ion’ size range.

When membranes were first evaluated for arsenic removal in the 1980s, cellulose-acetate RO membranes were operated at high pressures (typically 400 psi), and good arsenate rejection was reported (>90%) (Schneiter and Middlebrooks, 1983; Clifford, 1986). However, arsenite rejection was less efficient (<70%), and oxidation was difficult because residual oxidants could damage the membranes (e.g. Fox, 1989). In the mid-90s NF membranes, which are more permeable and can be operated at pressures less than 100 psi, were also found effective for arsenic removal (Legault et al., 1993; Waypa et al., 1997). Both RO and NF membranes are most often operated in lateral configurations, in which only a small amount of the raw water (10-15%) passes through the membrane as permeate. In household systems, where only a small amount of treated water is required for cooking and drinking, this low recovery rate may be acceptable. Municipal systems achieve higher recovery rates (80 to over 90%) by using multiple membrane units in series.

In recent years, a new generation of RO and NF membranes have been developed that are less expensive and operate at lower pressures, yet allow improved flux and are capable of efficient rejection of both arsenate and arsenite. Waypa and others have showed that some of the new membranes, operated at pressures ranging from 40-400 psi, were able to reject from 96-99% of both arsenate and arsenite in spiked natural waters. The authors attribute this rejection of arsenite to the relatively large molecular weight of both arsenate and arsenic, rather than charge repulsion. At these high arsenic rejection rates, membrane filtration can result in extremely low arsenic levels in treated water.

Arsenic removal was found to be independent of pH and the presence of co-occurring solutes, but was somewhat improved at lower temperatures. Interestingly, the NF membrane tested performed comparably to the RO membranes, even though the operating pressure was much lower (40-120 psi, compared to 200-400 psi) (Waypa et al., 1997).

Membrane filtration requires a relatively high-quality influent water. Membranes can be fouled by colloidal matter in the raw water, particularly organic matter. Iron and manganese can also lead to scaling and membrane fouling. To prevent fouling, reverse osmosis filters are almost always preceded by a filtration step.

Membrane filtration has the advantage of lowering the concentrations of many other components in addition to arsenic. Even ultrafiltration (UF) membranes are able to remove over 99.9% of bacteria, *Giardia* and viruses. Also, the membrane itself does not accumulate arsenic, so disposal of used membranes would be simple. Operation and maintenance requirements are minimal: no chemicals need be added, and maintenance would consist of ensuring a reasonably constant pressure, and periodically wiping the membrane clean. The main disadvantages are low water recovery rates (typically only 10-20% of the raw water passes through the membrane), the need to operate at high pressures, relatively high capital and operating costs, and the risk of membrane fouling. Also, particularly with RO, the treated water has very low levels of dissolved solids, and can be very corrosive, and deficient in minerals which can be important micronutrients for humans. A comprehensive discussion of the many issues involved in membrane technology is found in (Mallevialle et al., 1996).

High-pressure membrane methods are currently more expensive than other arsenic removal methods (household units in the United States cost upwards of $1000), and are only used when very low arsenic levels are required in the treated water, generally in conjunction with some other primary treatment process such as coagulation. However, recent advances made in membrane technology are promising. If improvements continue to be made, particularly in operating low-pressure systems at high recovery rates, membrane removal could become a feasible and cost-effective technology for arsenic removal in developing settings.

6.3.6 Emerging technologies

The four technologies described above (coagulation and filtration, ion exchange resin, activated alumina, and membrane removal) are fairly well documented, even though some of the systems have only come into prominence in recent decades. In recent years, a tremendous amount of research has been conducted to identify novel technologies for arsenic removal, particularly low-cost, low-tech systems that can be applied in rural areas. Most of these technologies rely on oxidation of arsenite, followed by filtration through some sort of porous material, where arsenic is removed through adsorption and coprecipitation. Many of these systems make use of iron compounds, which have a very strong affinity for arsenic. A brief, though not exhaustive, review of some of the most documented technologies is given below.

Fe-Mn Oxidation

Conventional iron and manganese removal can result in significant arsenic removal, through coprecipitation and sorption onto ferric or manganic hydroxides. The mechanisms involved are the same as in coagulation and filtration, as discussed above. Much time and effort has been expended on developing reliable, low-cost technologies for iron removal. Most low-cost technologies for arsenic and manganese removal rely on aeration and filtration through porous media such as sand and gravel. Several systems that have been applied in developing countries are described in (IRC, 1982a) and (Cairncross and Feacham, 1993). Any technology that effectively removes iron and manganese could be evaluated to see if arsenic is also removed effectively. In this respect arsenic removal is more convenient than that of fluoride, which does not undergo oxidation, and is not removed by coprecipitation with iron.

Edwards has commented that the contribution of manganese oxidation to arsenic removal is likely to be minimal compared to iron oxidation, unless manganese concentrations are extreme (>3 mg/L). In contrast, even removal of 1 mg/L Fe(II) is theoretically able to sorb 83% of a 22 µg/L arsenate solution (Edwards, 1994).

In Taiwan, Shen and others attempted to remove arsenic from groundwater through simple aeration and sedimentation. Iron and manganese levels were elevated at 0.8 and 0.12 mg/L, respectively. After one full day of settling, arsenic concentration was reduced from 800 µg/L by only 9%; even after 15 days, removal was only 50%. Iron concentrations in the sedimented water were not reported; poor arsenic removal may be related to poor iron oxidation (Shen, 1973). It seems likely, though, that the influent iron concentration was too low to effectively remove arsenic. In contrast, Clifford and Lin showed that 60% of a 188 µg/L arsenate influent could be removed by oxidative precipitation of 2 mg/L Fe(II) (Clifford and Lin, 1991).

In Bangladesh and West Bengal, elevated arsenic concentrations are often associated with high iron and manganese levels. One survey in Bangladesh found that over 80% of arsenic-affected tubewells (>50 µg/L) also contained iron levels of 2 mg/L or more. However, iron alone is not a good indicator of arsenic: 30% of the wells with safe levels of arsenic also had 2 mg/L iron or more (DPHE/BGS/MML, 1999). Because of the link between arsenic and iron levels, and the affinity of arsenic for iron hydroxides, there have been calls for a simple solution to arsenic contamination: simple storage of pumped water to allow iron to settle out, scavenging arsenic in the process. While this is an appealing idea, successful application of this type of 'passive Fe-Mn oxidation' is not simple, for several reasons:

- iron removal is not always easily accomplished. Some waters contain iron in a form that is slow to oxidize, or may be complexed with organic material that impedes oxidation and filtration. Precipitation may not occur if alkalinity is low;

- without a filtration step, much of the iron can remain suspended as colloidal matter, even after oxidation;

- arsenite is not as strongly bound to iron as arsenate, if the waters contain mostly arsenite arsenic removal will be less efficient; and

- when water is stored in household containers, there is a high risk of bacterial contamination.

The Swiss research agency, EAWAG, is exploring the possibility of catalyzing iron and arsenic oxidation with lemon juice and sunlight in order to remove arsenic from iron-rich waters. A major advantage of this approach is that the treatment also disinfects the treated water, like the solar disinfection (SODIS) discussed in **Section 6.2**. This solar removal of arsenic (SORAS) project is in the early stages of testing in Bangladesh, early results suggest that arsenic removal is limited to 50-75%. This technology would be best applied at the household level, using locally available plastic bottles.

When considering passive Fe-Mn oxidation, particularly at the household level, careful pilot studies should be made using the local waters and local storage conditions, in order to assess the effectiveness of this technique, and the possibility of pathogenic contamination. It should be noted that chlorine addition would improve oxidation of both iron and arsenic, and would provide protection against bacterial growth. However, as discussed above, chlorination at the household level involves difficulties in ensuring the correct dose, and the potency of the chlorine agent.

Box 6.5: 18-DTP Arsenic Removal Plants in Bangladesh

With support from the Dutch Government, the Bangladesh government has constructed three arsenic removal plants in small municipalities. These plants are basically iron removal plants, and add no chemicals, but pump groundwater over a series of cascades to aerate the water. Filtration then removes the resulting iron and arsenic precipitate, and the water is chlorinated and stored in an elevated tank for distribution. Water stored in the tank is periodically used to backwash the filters. The waste water is stored in sludge ponds, and sludge is removed once or twice annually.

Arsenic removal efficiency varies considerably, and seems to improve with higher iron levels:

Table 6.5: Arsenic removal in three 18-DTP plants

Municipality	Influent iron (mg/L)	Iron removal efficiency (%)	Influent arsenic (μg/L)	Arsenic removal efficiency (%)
Satkira Razzak	3.4	95	57.0	51
Satkira Polash	5.8	95	67.5	67
Manikganj	7.6	99	84.8	72

Source: (18-DTP, 1999)

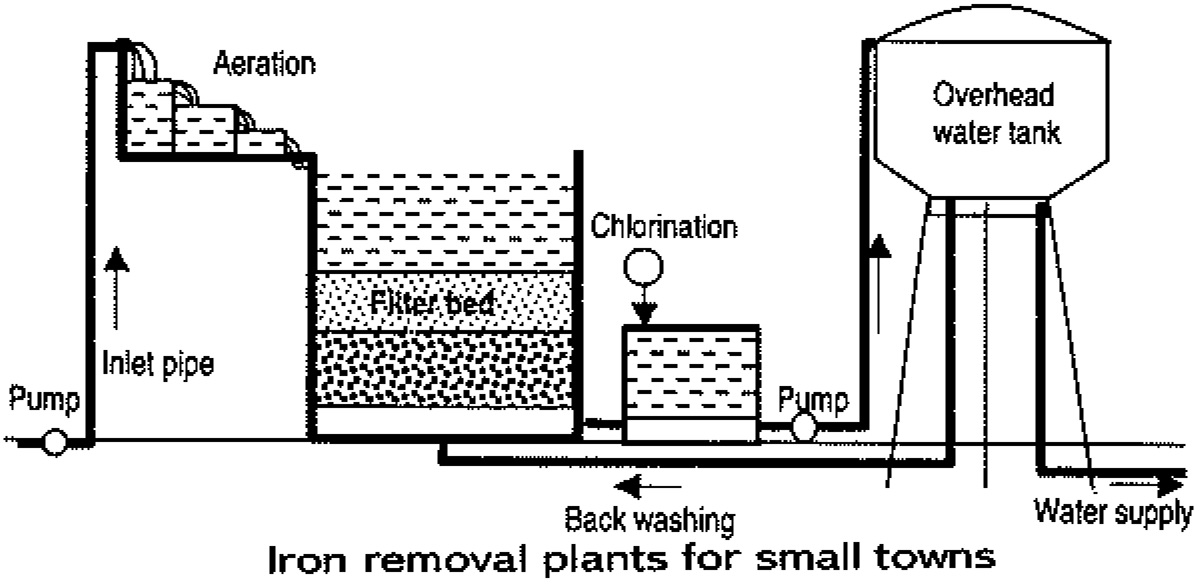


Figure 6.14: 18-DTP Arsenic removal plant design

Source: (Ahmed and Rahman, 2000)

Although removal rates are not very high, in all cases it is effective enough to bring waters into compliance with the Bangladesh drinking water standard of 50 µg/L. Plant managers experimented with addition of coagulants (4 mg/L $FeCl_3$) and oxidants (0.9 mg/L bleaching powder), but found that arsenic removal efficiency was not significantly improved.

Box 6.6: WaterAid in Bangladesh

In Bangladesh, the British NGO WaterAid, collaborating with their local partner VERC, investigated the possibility of storing groundwater to allow iron to oxidize and settle out as a means of arsenic removal. In the experimental site, a village in southeastern Bangladesh, water supply consisted of approximately 200 private shallow tubewells, some three quarters of which produced water with arsenic levels over 50 µg/L. Iron levels were also high in many, though not all wells. Water was collected from the contaminated wells, ad stored in covered pitchers for 12-24 hours. The effects of enhanced aeration, achieved by pouring water repeatedly from one pitcher to another, were also evaluated.

The NGO workers found that in some cases, good arsenic removal was effected by passive sedimentation of iron-rich waters. Influent concentrations were reduced from over 500 µg/L to below 50 µg/L in some cases. However, in some cases, little or no change in arsenic level was produced. Contrary to expectations, the best arsenic removal did not occur in waters with the highest iron levels - in fact some of the waters that showed no arsenic reduction contained over 5 mg/L iron. Arsenic removal was not significantly improved by attempts to enhance aeration. Other chemical parameters such as pH, alkalinity, and hardness were also measured, but the only significant correlation noted was a tendency for better arsenic removal in waters with lower electroconductivity.

One clear trend, however, was noted. Freshly collected water was of very high microbiological quality, but after being stored in pitchers for twelve hours, very high fecal coliform counts were found. Apparently the pitchers, in spite of regular hand scrubbings, harbor reserves of fecal bacteria which are effectively incubated during home storage.

Sorption onto other metal oxides

Besides activated alumina, other metal oxides have strong affinities for arsenic, and can serve as effective sorbents, and in some cases as oxidants. Quartz is very poor at removing arsenic under most environmental conditions, because the mineral surface is negatively charged above a pH of 2. However, quartz sand, or indeed any other granular media, can be made highly sorptive by coating the grains with metal oxides. In recent years many researchers have used this principle to develop low-cost arsenic removal methods using locally available materials.

Vaishya showed that sand from the Ganges river, which presumably is rich in iron coatings, could remove arsenite from solution, with a reported capacity of 0.024 mg/g. Removal was found to be pH-dependent, and best from pH 7-9 (Vaishya and Agarwal, 1993).

Joshi and Chaudhuri showed that iron oxide coated sand (IOCS) is able to remove both arsenite and arsenate. A simple fixed bed unit was able to treat about 160-190 bed volumes of water containing 1000 µg/L arsenite and 150-165 bed volumes of water with 1000 µg/L arsenate. Flushing with 0.2 N sodium hydroxide regenerates the media. The authors propose that this media would be very useful for domestic arsenic removal units (Joshi and Chaudhuri, 1996). This technique may be most appropriate for arsenate removal: Viraraghavan and others found that quartz sand coated with iron oxides was initially able to remove arsenite, but that breakthrough occurred relatively quickly (Viraraghavan et al., 1999). Khaodhiar and others showed that IOCS could effectively remove copper and chromium, as well as arsenate (Khaodhiar et al., 2000). Lombi and others investigated the kinetics of arsenite and arsenate adsorption onto IOCS, and found that adsorption was relatively slow: about half of the arsenic was adsorbed within ten hours, and after five days removal exceeded 97% (Lombi et al., 1999).

A similar coated sand material can be prepared using manganese dioxide instead of iron. Since MnO_2 is a good oxidant, this material can remove arsenite as well as arsenate. In fact, the treated sand was able to remove 80% of a 1 mg/L solution of arsenite within two hours, but slightly less than 70% of an equivalent solution of arsenate. A prototype household unit was developed, which could treat about 150 bed volumes of 1 mg/L arsenic (half arsenite and half arsenate) before breakthrough (Bajpai and Chaudhuri, 1999).

Greensand is a granular material composed of the mineral glauconite, which has been coated with manganese oxide. It is a natural zeolite, and has strong ion exchange properties, and will remove iron, manganese, arsenic, sulfide, and many other anions. Like manganese dioxide coated sand, greensand surface is strongly oxidizing, and is thus able to remove both arsenite and arsenate. The media is typically recharged by application of potassium permanganate, which not only reestablishes the oxidizing environment, but deposits a fresh layer of manganese oxide on grain surfaces (Ficek, 1996). Viraraghavan and others showed that greensand could reduce arsenite levels from 200 µg/L by about 40% in the absence of iron. When ferrous iron was also present, arsenite removal improved to above 80% (Subramanian et al., 1997; Viraraghavan et al., 1999). Little information is available about the capacity of greensand for arsenic removal, or the effects of pH or competing anions on arsenic removal.

Several proprietary iron-based adsorption materials have been developed recently. Granular ferric hydroxides are being used in full scale systems in Germany (Driehaus et al., 1998), and similar materials have been developed in Canada and the United States. These materials generally have high removal efficiency and capacity. For a review of proprietary arsenic removal technologies, the reader is directed to (Murcott, 2000).

Metal oxides need not be supported in a granular matrix. Lin and Gan showed that 20 mL of a sorbent consisting of ferric hydroxides supported on paper pulp could be used to treat 30 liters of water, reducing arsenic levels from 67 µg/L to below the drinking water standard (Lin and Gan, 1991). Low and Lee investigated the potential of chrome sludge for arsenic removal. They found that the sludge rapidly removed arsenate from solution, and had commendable sorption capacity of 21 mg/g (Low and Lee, 1995).

Sorption onto reduced metals

Most of the above processes rely on arsenate adsorption onto surfaces of metal oxides. However, arsenic also has a strong affinity to reduced metal surfaces, such as sulfides. A few researchers have taken advantage of this property to remove arsenic through reduction and sorption.

Lackovic and others have demonstrated that zero-valent iron filings can be used either in situ or ex situ to reduce arsenate, and produce ferrous iron. The ferrous ions precipitate out with sulfide, which is also added to the system. Arsenite is removed either through coprecipitation or adsorption onto pyrite. This system is promising for use in rural areas, because of the low cost of materials, and the simple operation. However, treated water is very high in ferrous iron, and must undergo iron removal treatment before distribution or consumption (Lackovic et al., 2000). A similar system using zero-valent iron to treat water stored in individual homes was tested in Bangladesh and West Bengal. Arsenic removal was approximately 95% for highly contaminated waters, containing 2000 µg/L arsenic in the presence of sulfate at pH 7. Removal is rapid, but if batches are left for too long, dissolved iron concentrations become unacceptably high (Ramaswami et al., 2000). Similarly, Kuhlmeier has shown that packed columns containing pyrite can remove inorganic and organic arsenic compounds (Kuhlmeier and Sherwood, 1996).

Box 6.7: Three Kolshi Filter in Bangladesh

A simple arsenic removal system has been developed in Bangladesh, based on a traditional sand filtration water purification system. Three 18-L clay pitchers (called *kolshi*) are stacked vertically in a metal rack. The top pitcher contains coarse sand and metal iron filings, the second pitcher wood charcoal and fine sand, and the third serves as storage. Arsenic-rich groundwater is poured into the top pitcher, and trickles through small holes into the second and third pitchers. One unit costs about $5, and flow rates average 2.6 to 2.9 liters per hour.

Laboratory tests show that the three *kolshi* filter can remove arsenic from groundwater containing a wide range of arsenic concentrations (80 to over 1000 µg/L). Arsenite proportions in the groundwater ranged from 40% to near total, and were typically greater than 70%. Filtered water generally contained from 5-30 µg/L arsenic, all as arsenate. In some cases arsenic removal exceeded 99%.

Field testing of two hundred units confirms this impressive finding: after one week of operation, 90% of the filters produced water in which no arsenic could be detected using field kits, and 7% produced water with significantly reduced but detectable arsenic levels. Iron levels were also dramatically reduced, in some cases from over 1 mg/L to below 0.1 mg/L. After four months of operation, the filters were still operating efficiently.

This system shows great promise in that it is highly effective, inexpensive, easy to operate, and is similar a traditional water treatment method. A significant drawback of the three *kolshi* filter is that treated water can easily become contaminated with faecal bacteria, either during transport of the water from the well, or storage in the household. Bacteria may also be present in the media, if it is not sterilized. Field tests showed that some slight contamination occurred before filtration (15% of samples showed some contamination, with a maximum of 130 TC/100 ml), but that bacteria counts increased dramatically during filtration and storage: nearly two thirds of treated samples showed counts higher than 100 TC/100 ml, and a fifth had levels above 10,000 TC/100 ml. It may be possible to reduce the risk of bacterial contamination by sterilizing the media before filter construction.

Source: (Rasul et al., 1999; DPHE/UNICEF/BRAC, 2000)

Ion exchange and adsorption

Ion exchange resins developed for removal of anions such as sulfate and nitrate have proven to be reasonably effective at removing arsenic, as discussed above. As materials engineering becomes more advanced, researchers are increasingly able to design novel ion-exchange materials with surficial properties that are particularly specific to arsenate. In particular, several researchers have found that copper-doped materials have a strong, specific affinity for arsenate (e.g. Rajakovic and Mitrovicm, 1992; Ramana and Sengupta, 1992; Lorenzen et al., 1995). Fryxell and others have developed a novel mesoporous silica sorbent which makes use of Cu(II)-based functional groups. This material has a higher ion exchange capacity (75 mg As/g) than conventional resins, and shows a stronger affinity for arsenate and chromate than for sulfate or nitrate. Therefore, unlike the conventional resins, these materials will not release chromatographic peaks of arsenic when exposed to high levels of sulfate (Fryxell et al., 1999).

While conventional synthetic ion exchange resins are the most commonly used media in ion exchange, costs are relatively high ($USD 2-5 per liter of wet resin). A variety of naturally occurring materials also have high ion exchange capacities, sometimes after chemical pretreatment. Many of these materials are not pure ion exchangers: some arsenic removal is through less reversible chemisorption. Especially in developing countries, researchers have been evaluating the potential of these materials for use as low-cost arsenic removal systems.

Zeolites are naturally occurring minerals with a crystalline structure characterized by large internal pore spaces. Accordingly, they have very large surface areas, and ion exchange capacities: zeolites were used extensively for water softening, before the development of synthetic resins with faster exchange rates, higher capacity, and longer life. A few arsenic removal studies have been conducted with zeolites.

Natural zeolite minerals such as clinoptilolite and chabazite have a strong affinity for both arsenite and arsenate. A chabazite filter was able to remove 1000 µg/L arsenate from over 235 bed volumes before arsenic was detected in the effluent (Bonnin, 1997). Adsorption of arsenate onto natural zeolites can be improved by organically modifying the zeolite structure (Misaelides et al., 1998).

Chitosan and chitin are natural polyaminosaccharides occurring in crustacean shells, that have good ion exchange properties. Shellfish wastes containing chitosan have been used to remove arsenic from water contaminated by mining wastes (Luong and Brown, 1984). Elson and others investigated a mixture of chitosan and chitin, and found a relatively low arsenic removal capacity of about 0.01 mg As/g (Elson et al., 1980).

The ion exchange properties of modified coconut coir dust have been investigated for a variety of anions, including nitrate, chromate, selenate, and arsenate. Coconut coir dust, composed chiefly of cellulose and lignin, is chemically modified to have secondary and tertiary amine functional groups, similar to a weakly basic ion exchange resin. Chromate, nitrate, and selenate were efficiently removed by the resulting media, but arsenate removal was less good, with a maximum capacity of about 6.5 mg As/g, about one tenth of the capacity of a synthetic anion exchange resin also evaluated. However, the material is inexpensive and could be produced at low expense in many tropical countries. No attempts were made to regenerate the media (Baes et al., 1997).

A similar material has been produced out of ground rice husks, which are modified with an ammonium treatment to produce 'quaternized rice husk'. Arsenate removal from highly concentrated solutions (100,000-600,000 µg/L) was good, but dependent on pH, with maximum removal of about 80% from pH 6 through 10. The estimated maximum sorption capacity was over 19 mg As/g. Chromate, sulfate, and to a lesser extent, nitrate, all diminished arsenic removal rates (Lee et al., 1999).

Fly ash, a by-product of coal combustion in power stations, has a very strong affinity for arsenate. Diamadopoulos and others found that a lignite-based fly ash was able to remove 80% of arsenate from solution, with an optimal pH of 4. The arsenic capacity was nearly 28 mg As/g. Desorption studies showed that very little arsenic could be removed from the fly ash, indicating that chemisorption rather than ion exchange is the likely removal mechanism (Diamadopoulos et al., 1993). One drawback of the use of fly ash is that when arsenic-rich coal is combusted, the resulting fly ash can have very high concentrations of arsenic, up to 47% by weight (Dutre and Vandecasteele, 1998).

Activated carbon has a high surface area, which attracts many dissolved compounds, and allows the removal of organic compounds, including compounds that can give water an undesirable taste or color. Activated carbon may remove arsenic for a short time, but as the surface is not very selective for arsenic, overall capacity for arsenic removal is low (Sorg and Logsdon, 1978).

In Situ arsenic immobilization

When arsenic is mobilized in groundwater under reducing conditions, it is possible to immobilize the arsenic by creating oxidized conditions in the subsurface. In Germany, in order to remediate an aquifer containing high-arsenite, high ferrous iron, low-pH groundwater, Matthess injected 29 tons of potassium permanganate directly into 17 contaminated wells, oxidizing arsenite, which coprecipitated out with ferric oxides. Mean arsenic concentrations were reduced by over 99%, from 13,600 to 60 µg/L (Matthess, 1981). More recently, atmospheric oxygen was used to reduce arsenic concentrations *in situ* from approximately 20 to 5 µg/L, while iron and manganese levels were also lowered (Rott and Friedle, 1999).

Under reducing conditions, and in the presence of sulfur, arsenic can precipitate out of solution and form relatively insoluble arsenic sulfides. In theory, reductants and/or sulfide could be injected into contaminated groundwater to promote formation of sulfide minerals, and consequent sequestration of arsenic (Ahmed and Rahman, 2000).

In situ immobilization has the great advantage of not producing any wastes that must be disposed of. However, experience is limited, and the technique should be considered with caution. Oxidants are by definition reactive compounds, and may have unforeseen effects on subsurface ecological systems, as well as on the water chemistry. Care must also be taken to avoid contaminating the subsurface by introducing microbes from the surface. Also, at some point pore spaces can become clogged with precipitates, particularly if dissolved iron and manganese levels are high in the untreated water.

6.3.7 Waste disposal

All of the arsenic removal methods at some point produce an arsenic-rich waste stream, which must be disposed of in a safe manner. Typically municipal water plants are accustomed to handling chemicals and disposing of wastes. At community and household levels, operators will need to be given special training in responsible handling of wastes. In addition, some of the techniques described above require additional chemicals, either during routine operation or for media regeneration; the disposal of all these potentially hazardous waste materials must be considered when designing any arsenic removal system.

Liquid Wastes

The regeneration of activated alumina and ion exchange resins results in various liquid waste streams that may be too acidic, caustic, saline, or arsenic-rich for simple disposal. Arsenic can be isolated from these liquid wastes through coagulation and filtration as described above. The resulting liquid waste will have low arsenic levels, but may require additional pH correction for safe disposal. Ion exchange regenerant brines may be too saline for safe surface disposal, but once arsenic is removed through coagulation, the regenerant can be reused.

Solid Wastes

A variety of arsenic-rich solids can be generated in arsenic removal. The most common include saturated filters and sludges such as hydrous ferric or aluminum oxides (HFO and HAO). Arsenic levels in wastes will depend on influent concentrations, but may reach several hundred mg/kg dry weight. Depending on costs, it may be economical to dispose of saturated filters rather than regenerating them. The stability of these solids needs to be evaluated when considering disposal options. If arsenic is likely to leach out of the solids after disposal, the wastes may require a specially constructed hazardous waste disposal facility, or additional treatment to immobilize arsenic. If the arsenic is so tightly bound to the solid wastes that it will not leach out, the wastes can be disposed of along with other municipal solid wastes.

Landfill disposal and the TCLP

The United States Environmental Protection Agency has developed a lab procedure called the toxicity characteristic leaching procedure (TCLP) to identify wastes likely to leach dangerous concentrations of certain known toxic chemicals into groundwater. The TCLP duplicates the conditions that solid waste would be exposed to in a typical sanitary landfill.

The TCLP involves crushing the solid waste to a certain size, soaking the solids in a weakly acidic solution for 18 hours, and measuring the resulting liquid (leachate) for toxic chemicals. EPA has produced a list of 39 regulated contaminants and set permissible levels for TCLP leachate, generally at one hundred times the drinking water MCL.

If the leachate exceeds the permissible level for any of the specified chemicals (or if the waste is ignitable, corrosive, or reactive) the waste is considered hazardous, and must be disposed of in a special hazardous waste landfill.

Several researchers have conducted TCLP tests on sludges resulting from arsenic removal by coagulation with Al and Fe salts, and produced leachates with arsenic levels of 0.009-1.5 mg/L (Brewster, 1992; Chen et al., 1999). These levels are all well below the current level required for classification as hazardous waste. These studies suggest that where HAO and HFO are used for arsenic removal, the resulting sludges will not require any special disposal.

One TCLP test made on arsenic-rich zeolites found no detectable arsenic in the leachate (Bonnin, 1997). No information is currently available on TCLP tests of arsenic-rich sludges from lime softening, or of exhausted activated alumina or ion-exchange resins.

Note that if the solid waste is not deposited in a landfill, but subjected to some other solid waste disposal, such as incineration or disposal under reducing conditions, the TCLP may not be an appropriate tool to assess the stability of the solid waste. Studies have shown that arsenic adsorbed onto iron hydroxides in aquifer materials can be mobilized under high pH conditions (Mariner et al., 1996) or reducing conditions generated by solid waste (Puls et al., 1992) or industrial effluents (Lieberman, 1996).

Other disposal options

Arsenic removal systems could be designed so that the removal media (metal hydroxide, ion exchange resin, activated alumina, etc., perhaps encased in a cartridge or sack) would be provided by a central distributor, who would be responsible for collecting and processing the spent media. This approach has many advantages, especially in rural settings. A trained specialist is more likely to be able to consistently perform chemical regeneration or stabilization procedures, and certain economies of scale might be realized. The main challenge in implementing such a system would to ensure that the distribution network was strong enough to reliably pick up the spent material as needed, and supply new sorbent. Most of the sorbents give no obvious indication when they are exhausted, they simply cease to work.

Hazardous wastes are often made less hazardous by blending the wastes into stable solid materials such as glass, brick, or cement. Extremely arsenic-rich wastes such as coal fly ash have been successfully stabilized through solidification in brick or cement. When solidifying with brick, there is the risk that some of the arsenic will volatilize during brick firing, and possibly contaminate air and water downwind of the kiln smokestack. In Hungary, experiments showed that some 30% of arsenic in the coagulant sludge was lost to the atmosphere in this way.

Solidification with cement is better documented. Dutre mixed fly ash with lime and cement, and subjected the resulting solid (approx. 10% arsenic by weight) to a leaching test similar to the TCLP. Arsenic concentrations in the resulting leachate averaged 5 mg/L, which would constitute borderline hazardous waste under the EPA definition (Dutre and Vandecasteele, 1998). Similarly, the Bengal Engineering College in India has immobilized arsenic-rich HFO sludge in cement (30% sludge by weight), conducted TCLP testing on the cement, and found the leachate to have negligible arsenic levels (Gupta et al., 2000).

A recent study of arsenic chemistry in sewage sludge concluded that redox potential and pH were the most important controls on speciation and solubility of arsenic after disposal. Arsenic solubility was highest under mildly reducing conditions, due to the dissolution of iron hydroxide compounds. Under very reducing conditions, arsenic solubility is limited by the formation of insoluble sulfides. At near neutral pH values, biomethylation was found to be an important process, converting inorganic arsenic into organic compounds, particularly dimethylarsinic acid (Carbonell-Barrachina et al., 2000). Some researchers in West Bengal and Bangladesh have advocated mixing arsenic-rich sludges with animal manure, so that bacteria can methylate the inorganic arsenic, transforming it into less toxic and volatile compounds. At Jadavpur University, over 90% of arsenic bound in sludge was found to be removed in this way (Chakraborti, 1999), but further documentation is required.

Box 6.8: Disposal of arsenic-rich sludge generated at the household level

Only a small percentage of water collected, perhaps 10-30%, is used for drinking and cooking, the rest is typically used for washing, bathing, and household chores. Furthermore, domestic water consumption typically accounts for only a fraction (5-15%) of the water used by humans. Irrigation is by far a larger drain on water resources. Ideally, no arsenic-contaminated water would be used for any purpose, but in areas where arsenic is endemic, the first priority should be to provide safe water for drinking and cooking. The use of contaminated water for other purposes, while not desirable in the long term, does not pose the same direct threat to human health that contaminated drinking water does.

In Bangladesh, a family of six drinking highly contaminated water (say, 500 µg/L arsenic) will need approximately thirty liters per day for drinking and cooking. If a household arsenic removal system is used, some 15 milligrams of arsenic will need to be removed from water daily. This translates to about 5 grams, or 1/6 of an ounce, of arsenic per year, assuming that the family has no other sources of water for drinking and cooking.

Obviously, it would not be safe to ingest this amount of arsenic, either day-by-day or at one dose. This amount of arsenic might be fatal - the fatal dose of arsenic trioxide in humans is reported to range from 70 to 180 mg (WHO, 1980a, p. 88). However, the toxicity of arsenic varies considerably according to the solubility of the ingested form, and arsenic bound onto sludges or other solid wastes will be much less soluble than arsenic trioxide. In any case, the amount of arsenic 'generated' by a single household can be considered environmentally insignificant, when compared to the amounts of contaminated water that is collected for household chores, or especially for irrigation.

Irrigated crops can require from less than 0.5 to over 2 m of irrigation water annually, depending on crop type, soil type, and precipitation. A typical requirement to produce a crop in an arid environment is 1.2 m/year (Chang et al., 1995). The FAO recommends a limit of 100 µg/L arsenic for irrigation waters, but permits levels of up to 2000 µg/L "for use up to 20 years on fine textured soils of pH 6.0 to 8.5" (Ayers and Westcot, 1976). The US and Canada also have standards of 100 µg/L for irrigation waters (Chang et al., 1995). At this concentration, 1.2 kg of arsenic could be applied annually per hectare.

With this perspective, the household annual production of 5 grams of arsenic is insignificant. Waste should still be handled responsibly - it is not recommended to simply discard arsenic-rich sludges on the ground, since children are known to consume significant amounts of dust and dirt. However, the sludge could be deposited along with other solid wastes, mixed with animal manure, or simply flushed down toilets or sanitary latrines. Even if the small amount of arsenic bound to the sludge were to dissolve in a properly constructed latrine or septic tank, latrines and septic tanks are generally well isolated from drinking water sources, and the arsenic would not easily make its way into drinking water.

Concerns about the possible health threats posed by handling and disposing of arsenic-rich wastes should be weighed against the much greater, and definitely known risks of continuing to drink contaminated water. At least at the household level, wastes from arsenic removal can be handled responsibly and safely without causing a significant health risk.

6.3.8 Summary

The following table summarizes some of the key technologies for arsenic removal, with special reference to experiences gained from field level application. Research needs are also identified. Arsenic removal efficiency will vary according to many site-specific chemical, geographic, and economic conditions, so actual applications may vary from the generalizations listed below. Because of the many factors that can affect arsenic removal efficiency (including arsenic concentration, speciation, pH and co-occurring solutes), any technology should be tested using the actual water to be treated, before implementation of arsenic removal systems at the field scale.

Table 6.6: Summary of technologies for arsenic removal

Technology	Removal Efficiency		Institutional experience and issues
	As (III)	As (V)	
Coagulation with iron salts	++	+++	Well proven at central level, piloted at community and household levels. Phosphate and silicate may reduce arsenic removal rates. Generates arsenic-rich sludge. Relatively inexpensive.
Coagulation with alum	-	+++	Proven at central level, piloted at household levels. Phosphate and silicate may reduce arsenic removal rates. Optimal over a relatively narrow pH range. Generates arsenic-rich sludge. Relatively inexpensive
Lime softening	+	+++	Proven effective in laboratories and at pilot scale. Efficiency of this chemical process should be largely independent of scale. Chiefly seen in central systems in conjunction with water softening. Disadvantages include extreme pH and large volume of waste generated. Relatively inexpensive, but more expensive than coagulation with iron salts or alum because of larger doses required, and waste handling.
Ion exchange resins	-	+++	Pilot scale in central and household systems, mostly in industrialized countries. Interference from sulfate and TDS. High adsorption capacity, but long-term performance of regenerated media needs documentation. Waters rich in iron and manganese may require pre-treatment to prevent media clogging. Moderately expensive. Regeneration produces arsenic-rich brine.
Activated alumina	+/ ++	+++	Pilot scale in community and household systems, in industrialized and developing countries. Arsenite removal is poorly understood, but capacity is much less than for arsenate. Regeneration requires strong acid and base, and produces arsenic-rich waste. Long-term performance of regenerated media needs documentation. Waters rich in iron and manganese may require pre-treatment to prevent media clogging. Moderately expensive.
Membrane methods	- /+++	+++	Shown effective in laboratory studies in industrialized countries. Research needed on removal of arsenite, and efficiency at high recovery rates, especially with low-pressure membranes. Pretreatment usually required. Relatively expensive, especially if operated at high pressures.
Fe-Mn oxidation	?	+/ ++/ +++	Small-scale application in central systems, limited studies in community and household levels. More research needed on which hydrochemical conditions are

			conducive for good arsenic removal. Inexpensive.
Porous media sorbents (iron oxide coated sand, greensand, etc.)	+/++	++/ +++	Shown effective in laboratory studies in industrialized and developing countries. Need to be evaluated under different environmental conditions, and in field settings. Simple media are inexpensive, advanced media can be relatively expensive.
In situ immobilization	++	+++	Very limited experience. Long-term sustainability and other effects of chemical injection not well documented. Major advantage is no arsenic-rich wastes are generated at the surface, major disadvantage is the possibility of aquifer clogging. Should be relatively inexpensive.

Key:		
	+++	Consistently > 90% removal
	++	Generally 60 - 90% removal
	+	Generally 30 - 60% removal
	-	< 30% removal
	?	Insufficient information

6.4 Evaluation and selection of arsenic-free water supply technologies

When considering sources and water supply technologies for arsenic mitigation, selection should be on the basis of avoidance or of a substantial and consistent reduction of the ingestion of arsenic. Each source has specific characteristics relating to quality, quantity, reliability, user acceptability and costs that will determine its applicability in different contexts.

In most instances choice is not straightforward and no one source or technology is likely superior in a given situation. Rather it will be necessary to undertake a risk assessment considering the range of parameters pertinent to the locality and situation, before one can list solutions that are adequate, suitable and appropriate. Previous sections and documents referred to therein describe in more detail the functioning and effectiveness of the various technologies now available.

The purpose of this section is to describe a protocol for the selection of an arsenic-free water supply technology or hybrid set of arsenic mitigation technologies. The protocol will need to lead to the consideration and selection of suitable technologies that meet the conditions of producing water that is safe bacteriologically and from the perspective of arsenic. The criteria to be met are found in the WHO Guidelines for Drinking Water Quality (WHO, 1993) and national guidelines or standards. The protocol developed in the following pages has a bias to the requirements and capacities of the household or a small community. The latter is an important consideration as it is implicitly assumed that no higher skill based capacity is available for operation and maintenance or water quality monitoring. Technologies applied should be able to function consistently in the absence of such skills.

The protocol involves a set of five technical criteria that should be met for any technology to be considered as technically appropriate. Technically appropriate systems are then examined with respect to six socioeconomic criteria to evaluate the practicability of the system.

6.4.1 Technical criteria

Five main criteria are proposed. Water supply options must first of all be able to produce water of the required **quality**. The system should also be able to supply water in adequate **quantity**, through out different seasons. Technologies should be reliable and **robust**, in that there is little opportunity for errors to occur, either through inherent systemic weaknesses, or through user error. As these systems will be operated by non-technical community members, it is important that **operational safety** be ensured. Finally, technologies should not have an undue adverse effect on the **environment**.

Water quality

For a technology to be suitable, the resultant water should be microbiologically safe and have a concentration of arsenic (and other relevant chemicals) that meets WHO guidelines or nationally determined standards. Another aspect of water quality to be considered is feed water quality: some treatment systems will require pre-treatment of the feed water (e.g. pH correction, sedimentation) for efficient operation.

An assessment has to be made how a proposed mitigation solution compares with the situation before intervention. If an option removes the arsenic risk but substitutes for it another threat, the net result may be just as poor for the health of the family. Not only bacterial water quality, but also other contaminants that may be present in the alternate source water or introduced through the treatment (e.g. pesticides or heavy metals) should be considered.

Household arsenic removal technologies should be subjected to rigorous testing at laboratory and pilot scale before being tested and monitored in a larger field sample. These technologies should consistently perform as anticipated, not only in the laboratory or in supervised field conditions, but also in the households of community members. They should be able to produce good water even when the technology is subject to a certain degree of “abuse” such as may be caused by improper mixing, use beyond indicated safe removal capacity of a filter, shortcuts, etc. Removal technologies should be such that their presentation (sachet, pill or adsorbent layer), operation and functioning (mixing, settling), storage and abstraction, favor correct operation at the household and community level. They should be designed to minimize the likelihood that local users will modify the dose or application method.

The concept of the multiple barrier series discussed earlier in the context of enhanced protection against the transmission of pathogens in surface water systems should be applied when designing or scrutinizing technologies.

Technologies that do not conform to these technical criteria are suspect and should only be applied when alternative options carry even higher health risks or risks of failing to meet critical performance indicators.

Water quantity

Preference is given to water supply solutions that are able to provide safe water throughout the year. In many parts of the world, water resources, land and capital for impounding water, and declining ground water reserves do not allow for the establishment of comprehensive year round solutions anymore. Especially in developing countries, population pressure, limitations in funds and professional capacity, and competing economic needs make it ever more difficult to secure a good quantity of good water for domestic purposes all year round.

Domestic water needs are manifold. Water is needed for drinking, cooking, food preparation, dishwashing, bathing, laundry, cattle, sanitation and other cleaning activities around the house. The first three water needs demand bacteriologically and chemically safe water, generally about 7-10 liters per capita per day.

If all water needs can not be met from one perennial safe water supply system, it is necessary to assist the community to make an inventory of the sources of water that are used by households and clusters of houses in the community. Sources for drinking should be classified as safe, acceptable or bad, based on bacterial and arsenic quality. Periods of safe or convenient usage during the year should be established. The risk of contamination or deterioration should be recorded, as well as a historical record of reliability and ownership or control of the source. The information can be gathered and ranked by community members. The resulting information is an essential decision making tool for the household, the community and public health field staff in designing or deciding on feasible water supply solutions. The risk of the solution failing, whether known or unknown to the user, should be considered, especially if failure means a return to the pre-intervention solution.

The ultimate solution or set of solutions should provide sufficient water for drinking and cooking for everyone in the household or the community, throughout the year and inclusive of locations members of the household frequent daily, such as the school, fields, factory, mosque, etc.

Robustness

Safe water supply technologies should be reliable and robust, able to provide water of the required quantity and quality, even under suboptimal conditions. All systems have some potential for breakdown, but this likelihood should be minimized, and local operators should ideally have the skills, materials and motivation needed to correct most problems.

Some technologies involve microbiological or chemical treatment of water resources; many of these systems have limited run times before replacement, and cleaning or regeneration is required. Users may not be able to tell easily whether or not a treatment process is working. People will assume the treated water is safe to drink: if system failure occurs, and is not readily identified, users can unknowingly consume unsafe water. Technologies would ideally have an indicator telling users when to perform maintenance or replacement. A well falling dry is an obvious indicator, as can be the color or taste of water produced by a poorly run treatment plant.

Indicators are more difficult in the case of arsenic removal technologies. Indicators might be developed based on the volume of water treated, by use of a water meter. Some sorbents reportedly make changes to water chemistry while operational (e.g. change in pH) that could be used as monitoring indicators. Finally, if reliable arsenic field kits are available, users could directly monitor treated water quality themselves.

As novel arsenic mitigation technologies are introduced, it is necessary to ensure that adequate water quality and performance surveillance systems are set up to monitor and evaluate the effectiveness of the technology and its application. For domestic systems it will often not be feasible to do this monitoring continuously, but it may still be advisable to contract out field work on a regular basis to ensure correct functioning of the technology. This task may be coordinated by public health institutes. Shortcomings identified can subsequently be corrected and become part of public information programmes. Community based arsenic mitigation technologies will need to be monitored for compliance on a continuous basis.

The **reliability** of any arsenic-free solution is dependent on the risk of poor operation. Wells can provide safe water, but poor hygiene in storing drinking water in the household can reintroduce bacterial contamination. Similarly, discipline (and habit) is required to manually mix a pre-measured quantity of reagents in a bucket of water so as to produce arsenic-free water. Putting in a sufficient quantity of mixture, stirring it as indicated, allowing water to settle, etc. can all be critical to the effectiveness of a removal process. Technical applications and innovations should ensure that the reliability of the process is guaranteed to a large degree even when it is not operated under optimal conditions. For instance, in traditional water treatment systems using surface water sources, the application of the multi-barrier concept will lead to greater reliability in producing water of the required quality.

Operational Safety

Users should not have to expose themselves to undue health risks during standard operation or maintenance of the technology. For technologies that require chemical addition, a key safety criterion should be that the chemicals used are safe in handling and can be stored safely. For community level systems, the safety of caretakers and operators should be considered; for household level systems, chemicals should be stored in a place safe from curious children.

Environmental soundness

The technology to be employed should in its production and application not cause any undue environmental risks. This applies to the ecological effects that may be caused by abstraction, transport and disposal of water and wastewater, as well as to disposal of chemical waste during production or generated when using chemical mixtures. Developed protocols for environmental impact assessment and technical tests such as the TCLP (see **Section 6.3.7**) can be useful in evaluating the environmental safety of a process. It should be recalled that the TCLP is meant to assess stability within a sanitary landfill, and may not be an appropriate measure for assessing environmental impacts in other conditions. The magnitude of the negative environmental impact of technologies such as arsenic removal should be kept in perspective, relative to environmental contamination from other sources such as irrigation and non-drinking water uses.

6.4.2 Socioeconomic criteria

In the previous paragraphs a set of more or less absolute technical criteria have been discussed that any technology or a water supply option will have to meet. To make a technology sustainable and successful, various other non-technical criteria need to be considered as well. These may not directly influence the capability of the technology to function but could hamper effectiveness and widespread application.

In this section six main categories of socioeconomic criteria are proposed against which technologies, hybrids or combinations of technologies should be evaluated. These categories are: economic considerations; institutional considerations; gender considerations; convenience; communication considerations; and social acceptability. Many of these parameters are discussed extensively in programme development and appraisal manuals (e.g. Narayan, 1993; DFID, 1998; European Economic Commission, 1998). Readers are invited to consult these publications for more detail on these important development issues.

Economic Considerations

Public subsidies are extensively used to meet both the capital and running cost of water and sanitation schemes. This is normally done from an economic or income redistribution perspective.

In the case of arsenic however, the consequences of limited or no sustained access to safe, arsenic-free water by the poorer section of society, and thus continued exposure, will be an increase in social and health costs. While accepting that the application of subsidy is always difficult, it is clear that tailored solutions are appropriate to ensure that all those who need, can indeed drink arsenic-free water. Safe drinking water is a basic human right and national governments and society at large should ensure that all members of society have equitable access to meet basic needs for safe drinking water.

BOX 6.9: The right to safe drinking water

Several international statements express a basic human right to safe drinking water. For example, the Convention of the Rights of the Child states in article 24.2(c) that

“States Parties shall pursue full implementation of this right (of access to quality health care services) and, in particular, shall take appropriate measures: ... to combat disease and malnutrition.... through, *inter ali*a, the application of readily available technology and through the provision of adequate nutritious food and clean drinking water, taking into consideration the dangers and risks of environmental pollution...”

The Convention of the Rights of the Child was adopted and opened for signature, ratification and accession by General Assembly resolution 44/25 (November 20, 1989). It entered into force on September 2, 1990. It has been signed by all countries of the world, except for the United States and Somalia.

Different safe water options offer different degrees of water security and convenience, and come with different price tags for capital investment and operation and maintenance. Ideally, every household should have the ability to obtain sufficient drinking water safe from arsenic and pathogens, either in the individual home or through a community level arrangement. To meet this goal, government policy, social marketing and the public/private sector continuum should ensure that a range of proven technical solutions are available and known to the consumer. To meet the needs of different socioeconomic groups in society, differently priced solutions and packages must be available in the market. The range of options on offer might include (but is not limited to): cheap and expensive arsenic removal systems; piped and bottled water; water collected from a central distribution point; water delivered to the home regularly; community level treated surface water systems; and household based rain water collection and storage.

Which of the available options will be affordable for a given group of users will depend on local socioeconomic conditions and on government policies with respect to initial subsidies to offset the cost of investment to the consumer. However, to allow communities and individual water users to make their own informed choice a wide range of options should be available.

Institutional Considerations

The successful introduction and application of any water supply system will require change and adaptation to the new situation. Various actors, legal provisions, incentives and disincentives determine the way in which this change is going to be managed. Clearly, the institutional set-up and responsibilities of the various seen and unseen stakeholders is critical to the implementation and management of the process of introduction and application. Awareness raising, technology identification and verification, application and monitoring of arsenic mitigation will require coordination and understanding by various public and private representatives.

Lack of appreciation of the institutional conditions and pre-requirements at various levels, can easily scuttle the whole project. Ways to engender institutional change are nowadays at the forefront of many development processes and many useful books have been written about it. The following paragraphs are therefore limited to some aspects of institutional development as one may find in a less-developed country.

Establishment of the water supply solution in a community or household will require institutional mechanisms and safeguards relating to:

- Production and delivery through private sector and NGOs (including local dealers, contractors and artisans)

- Product quality control and monitoring by independent third party (government agency, NGO) or the principal/consumer

- financing options through banks and credit/grant providers

- development/upgrading of local technical know-how for operation and maintenance, including repair, and for the availability of spares; preferably among small-scale local private sector and NGOs

- training and capacity building to ensure proper handling and operation of the technology or the water supply option in the community or household

- the potential for promoting the options locally, for acquisition of or participation in (participatory or commercial development of) the option, as well as for its sustained use

- (for hybrid systems) ease of management of different sources/systems (including control over sources/operations)

- surveillance of water quality and consumer behavior by independent third party (government or NGO) to avoid health risks and promote continued improvement and cost efficiency

- incremental upgrading of the water supply service, e.g. by increased storage in case of rainwater harvesting, by moving from a deep tube well to a DTW with motorized pump and overhead tank and (yield permitting) a small reticulation system.

The relative importance of the considerations listed above will differ greatly between technologies and options. The importance will also be viewed differently by different actors depending on their role and on the risk they are taking in establishing or marketing the option. In this respect it may be worthwhile to put forward that venture capital (sometimes in the form of development (aid) grants) and subsidy can play an important role in creating a marketable situation. At the same time these economic interventions can obscure sustainable marketability and application of a technology in the absence of favorable financial conditions.

Box 6.10: Hypothetical example of effects of initial subsidization

As an example, let us say that a safe water treatment system is introduced into a hypothetical, arsenic-affected area, with a supportive financing environment. Fifty systems are installed as part of an agreement with an initial donor. The systems work and are evaluated positively, but the manufacturer is not prepared to continue sales in the absence of conducive financial conditions as these have been cut from the second phase of the project. Due to the limited number of systems established no O&M system or effective dealership is set up. Within a year or two the systems start breaking down, and what looked promising after two years is a failure after four due to inadequate consideration of the overall establishment cycle.

Stakeholders at every level will have to critically appraise the importance of institutional elements on sustainability, O&M and recurrent costs before deciding to embark on the adoption of the water supply option.

Gender considerations

Water is most often the concern of women and girls, though at times sons and husbands join the chore of collecting water. Surely the concern for safe drinking water is to be shared by women and men. Reality dictates that designers have to assume that the main burden will still be on the womenfolk, even though through awareness raising and proper design a more balanced division of labor is encouraged. The technologies or solutions that are put forward should preferably offer an opportunity for more sharing in water collection and treatment among the members of the household. They should certainly <u>not add to the burden</u> already carried by the women. It means that ergonomically, culturally and time wise the technology should at least be gender-neutral if not favoring part of the burden to be taken up by men.

Water security, i.e. the sustained availability of sufficient water for human consumption and for other domestic chores, will remain the concern of the women in the household. In the process of information gathering and consultation the suggestions and concerns of women should be reflected in the options shortlisted by and available to the community and individual households. The cost and effort of using the water supply option eventually selected should be acceptable and sustainable for women and men, the young and the elderly. For further reading on this subject, the reader is referred to (van Wijk-Sijbesma, 1985; van Wijk-Sijbesma, 1988; van Wijk-Sijbesma, 1998).

Convenience

Even if a technology meets all of the above technical criteria and is cost-effective, the time and effort required to collect water from the system must be reasonable. The convenience criterion should to take into account the effort required to go to the safe communal source and wait in a queue for one's turn to collect water, or the time needed to collect contaminated water, bring it to the household, and treat it with arsenic removal methods. If consumers find waiting time at communal sources inordinately long, or treatment technologies too slow, they may choose to return to the old, unsafe sources. Poor understanding by users of the risk of exposure to arsenic or the effect of slackening of discipline, may lead to continued or regular use of contaminated sources by some or all water collectors in the household. Relaxation of safe water discipline can not be underestimated and should be countered by peer-support groups at community level, primary health care staff and public information campaigns.

Similarly, planners should appreciate the various social aspects of access to a water source. Physical access may be granted, at times or always, initially and not anymore after neighbors fell out with each other over an unrelated matter. Even if access is unrestricted, the social pressure on its use that may be building up over time may create (perceived) dependencies that will lead users to look for more convenient alternatives, which may be less safe. A sensitivity to these issues will help planners adjust choices available to users.

Communication considerations

Any option needs to be explained and promoted to the user. The strongest advocacy is usually achieved by inviting current and satisfied users of the same background as the target group to share information. Options that are already common in the country can thus easily be promoted through person-to community contacts or through different communication media.

New options need more time to get accepted as communities and households want to have reasonable proof that this new option is good for them in their circumstances. Whatever is the case, all options need to be clearly understood by the users and they need to be able to ascertain in detail what benefits and limitations the options bring them. Incomplete understanding of new water supply options with respect to arsenic avoidance or removal may prevent users from reducing their arsenic intake, thus leaving the population at risk. Likewise, users must be aware of the continued need for good hygiene practices and personal cleanliness in order to prevent the transmission of disease. It is critical that government or NGO workers monitor the behavior of water users following communication interventions, in order to ensure full understanding and compliance.

This concern can not be underestimated in the introduction of any behavioral change intervention and needs careful appraisal before approving or promoting wide-scale application of the technology or option. Effective methods for communication for behavioral change are covered in detail in **Chapter 7**.

Social acceptability

Finally, any solution must be socially acceptable to community members in order for it to be successful as a long-term safe water supply option. This issue has already been addressed implicitly in previous sections: any technology fulfilling all of the previously mentioned criteria will almost inevitably be socially acceptable. However, a few points are worth making.

Any option should preferably blend into the existing water supply background. It should be suitable and sustainable in terms of the local topography, hydrology, socio-cultural conditions, settlement pattern and population density, etc. It should also be effective in local condition, and the options put forward for community or household selection should certainly have a substantially higher effectiveness than other options that were evaluated.

The technologies that will be most readily adopted by communities are those that are familiar to them, or are at least new applications based on familiar materials and supplies.

6.4.3 Feasibility

Several critical aspects of the introduction of a technology or an application have been discussed in the preceding sections. Depending on socio-economic status and infrastructure development in a location it may or may not be feasible to introduce a particular technology at a given time. Poverty or other priorities in the face of serious challenges to the household or the community may not allow some solutions to be proposed confidently. Non-availability of electricity, frequent and lengthy black-outs, or other power related problems may prevent proper use of equipment, while difficulties in obtaining or importing spare parts and treatment media may cause health risks due to breakdown, use beyond indicated life time, or even bypassing of the treatment system.

The planner and/or manufacturer will have to consider all critical location-specific aspects and decide how feasible it is to propose a particular treatment option in light of the feasibility of the technology performing as intended.

6.4.4 Environmental Technology Verification

In recent years the process of environmental technology verification (ETV) has been developed to ascertain whether corrective processes introduced to reduce or avoid problems that threaten human health or the environment, actually perform as claimed. In the case of water supply technology, ETV can be applied to specific commercial-ready products based on the principles reviewed in **Section 6.3.** Both the USEPA and the Ontario Centre for Environmental Technology Advancement (OCETA) have developed ETV protocols for evaluation of commercially available arsenic removal systems. The difference between an the protocol described in this section and an ETV protocol is that the former applies to technical processes in general, and the latter involves specific market-ready products applying these processes. ETV programs generally require collection of performance data under a range of operating conditions, and sophisticated quality assurance and control measures.

Clearly, the principles underlying ETV need to be applied to all water supply options proposed to avoid or reduce arsenic, and should in fact be applied in a broader sense to all water supply options.

BOX 6.11: Verifying arsenic mitigation technologies in Bangladesh

In the period since the detection of arsenic in Bangladesh, it has become quite clear that technologies may work abroad, but give very erratic results in Bangladesh, or may work in one part of Bangladesh but not another. The varied chemical matrix of groundwaters in Bangladesh has shown that local testing of arsenic removal technologies is essential to ensure adequate performance.

The Government of Bangladesh has decided to allow introduction of an arsenic mitigation technology when three steps have been satisfactorily completed:

- the proponent or manufacturer should make available for scrutiny certified test results from the country of origin of the technology;

- the technology should be re-tested and its technological performance verified by a competent scientific institute in Bangladesh. Evaluation will be limited to technical issues (e.g. removal of arsenic, effects of water quality, power requirements, etc....);

- Field testing should be conducted through the dissemination of 10-20 plants or 100-200 domestic solutions in 3-4 locations in Bangladesh, and performance should be tested and monitored for 1-6 months. Evaluation includes both technical and non-technical issues (e.g. socio-economic, cultural considerations).

In order to apply these principles, and to regulate the introduction of arsenic removal and reduction technologies, the Government of Bangladesh recently started a process of Environmental Technology Verification for Arsenic Mitigation (ETV-AM). The Canadian International Development Agency and the UK Department for International Development are assisting the Government through OCETA and WS Atkins/WaterAid respectively in a fast track preliminary verification of nine traditional and commercially developed technologies, based on coagulation and filtration, activated alumina, and ion exchange resins.

The fast track approach involves a first phase, in which the dozens of potential candidates for evaluation are screened using a protocol similar to that developed in these pages. The most promising technologies move on to a second phase, and undergo a rigorous evaluation similar to the ETV programmes being used in Canada and the US. Technologies that pass this evaluation will be awarded a Verification Certificate by the government. CIDA is also financing a longer term (three year) programme that will allow for the development of a full indigenous ETV testing programme including the testing of further technologies as they become available. Results are expected throughout 2001.

6.5 Case study: application of evaluation protocol in Bangladesh

The protocol developed in the previous section makes use of a number of technical and non-technical parameters for use in evaluation of various safe water supply options in a given socioeconomic and cultural setting. As an example, this section will document the application of this protocol to a number of water supply options that are available in the seriously arsenic-affected areas of Bangladesh.

Six safe water technologies that hold promise for application in Bangladesh are described in comparative detail, and evaluated as far as possible in terms of the parameters described in the previous section. Each technology is rated for each parameter with a score ranging from 1 to 5, with the higher marks indicating greater acceptability. Scoring is necessarily somewhat subjective, but does allow the various strengths and weaknesses of a particular technology to be clearly seen and weighed.

6.5.1 Water supply and treatment options for consideration

As described in **Chapter 1**, the shallow aquifer in parts of Bangladesh is heavily contaminated with arsenic. Arsenic contaminated tubewells are found in almost all parts of the country, but are strongly concentrated in the south-west and south-east regions and the north-west Sylhet basin. While there is high spatial variability, in the south-east in particular there are extensive areas where more than 90% of the wells are contaminated (DPHE/BGS/MML, 1999).

In some arsenic affected areas, only a small number of wells are contaminated, and users of these wells can relatively easily find safe water by sharing water from a well that has been tested and found safe, or installing another well at a different depth. In areas of more intense contamination, however, alternative water supplies are required; either in the form of an arsenic-free, bacteriologically safe water source, or of an arsenic removal system. In most communities at least some tubewell water will be arsenic-free, and community members can be encouraged to share this valuable resource (See **Chapter 7**).

The traditional sources of drinking water in Bangladesh have been surface water and shallow dug wells. Because of the heavy fecal contamination of both of these sources, groundwater was heavily promoted, and readily accepted by the private sector. It is estimated that some 70-80% of the country's 4-6 million shallow tubewells are privately owned. In certain areas of the country, the shallow aquifer is either saline or unproductive, and alternate sources of drinking water have been promoted, such as deep tubewells, protected shallow dug wells, slow sand filtration, and rainwater collection. This section will apply the evaluation protocol presented in **Section 6.4** to these four technologies, as well as to two novel alternatives being tested in Bangladesh: SODIS and arsenic removal through coagulation and filtration. These should not be considered as the only options available for safe water supply in Bangladesh, but they represent the most promising technologies at the time of preparation of this document, for which at least preliminary results are available.

Disinfection of surface water is not commonly practiced in Bangladesh, except in larger townships. Use of decentralized small-scale hypochlorite production units has been considered but not implemented. Reverse osmosis and ion-exchange or adsorption media also hold promise for arsenic removal, but very little field experience exists at this time.

Deep tubewells

Below a depth of 150-200 m groundwater in Bangladesh is generally arsenic-free. The drilling technology used for deep tubewell (DTW) installation in Bangladesh is unique, and reflects the special geological setting. In much of the country, the first several hundred meters of subsurface consists of loose, unconsolidated sands, silts, and clays, with occasional gravel but rare rocky layers. Accordingly, drilling can be done without the use of a rig, using instead a rotary jetting method with a pump operated by a donkey, or a team of men. This method is efficient, cost effective and suited to local geology. Depths of 300-400 m are routinely drilled, rapidly and at low cost. At the ground level a concrete apron around the borehole with a drainage outlet prevents surface water from seeping down the sides of the well and contaminating the water supply.

In arsenic-affected areas, it is critical to ensure that the drilling process itself does not introduce arsenic into the deep aquifer by providing a hydraulic connection with contaminated shallow sediments. Deep tubewells should therefore have a seal between the upper and lower aquifers. This can be done by injecting clay or grouting into the annular space between the borehole and aquifer sediments. However, this is reportedly difficult to accomplish with the donkey drilling method. Drillers and water supply engineers in Bangladesh claim that after completion of a deep borehole, the annular space around the borehole collapses onto the rising main, forming a natural seal. More data is required to determine to what extent this takes place and hence the efficacy of such a naturally formed seal as opposed to grouting. One indication that cross-contamination is not occurring is the continued ability of deep tubewells in the coastal zone to produce fresh water, even after decades of pumping in areas where the shallow aquifer is saline. The use of deep groundwater has been the subject of debate for some time in Bangladesh. An international workshop held in August 2000 by DPHE concluded that water abstracted below the deep confining unit (at 150-250 m) would remain safe from arsenic. No quantitative or qualitative problems were anticipated in exploiting this resource for drinking water purposes.

Since the piezometric surface of the deep aquifer is generally close to the ground, water can usually be abstracted with simple handpumps. The most common DTW configuration in Bangladesh is a 4-inch diameter well, mounted with a suction-mode handpump (No. 6). In areas where the piezometric surface is naturally lower, or where seasonal abstraction for irrigation lowers the piezometric surface below the range of a suction pump, force-mode pumps such as the Tara are sometimes used.

In areas of particularly high population density, such as peri-urban communities and urban areas not reached by municipal water systems, it may be more effective to install one deep tubewell and deliver water to several standposts through a small reticulation system. In this case a motorized pump is required, and the well should be larger in diameter (6 to 8 inches), with a 4-inch diameter screen and a submersible pump. The well can feed water into an overhead storage tank, which provides the pressure to distribute the water to households or public standposts through a small pipe network. Public standposts don’t require users to pump, and can be designed with multiple taps and good flow rates. Thus, more people can be served at a time than would be possible at a handpump. An additional advantage is that if any water treatment is required (e.g. to remove iron), it can be done at one central location.

It is further assumed here that the water taken is used for drinking and cooking. An appropriate management system needs to be put in place to ensure that the costs of water production are covered by sales and other income. A lease contract and a system of (subsidized) tokens for water collection at the standpost can be considered. If sufficient water can be produced at a reasonable cost, a distribution network can offer different levels of service: those willing to pay higher prices can have household connections, while those with less money can make use of communal standposts. Disadvantages of reticulated systems include higher capital costs, and the need for more attention to sustainable operation and maintenance.

Protected shallow dug wells

Hand dug wells are an old technology, which has been largely replaced in Bangladesh by handpump-mounted shallow tubewells. Shallow tubewells can be cheaply and rapidly constructed using manual drilling methods, and most importantly, are less susceptible to surface water bacteriological contamination. Nonetheless, in some areas of the country where the shallow aquifer is rocky or unproductive, hand dug wells, or ringwells, continue to be an important source of drinking water. The dug wells in use in Bangladesh generally provide water with arsenic concentrations within the Bangladesh limit.

Dug wells are typically less than 10 meters deep, and from 1 to 3 meters in diameter. During construction, dug wells are lined with concrete rings, bricks, or porous masonry, to prevent the collapse of the walls. Most commonly in Bangladesh, concrete rings are used, and the dugwells known as ringwells.

Traditional ringwells are open at the surface, and water is drawn by hand with buckets. This system is inexpensive but very prone to bacterial contamination. This risk can be minimized by extending the well lining at least 0.5 m above the ground, forming a ‘head wall’. A concrete apron can be constructed on the ground surface around the head wall. Ideally, the top of the head wall will also be sealed with a watertight lid, and mounted with a handpump for raising water.

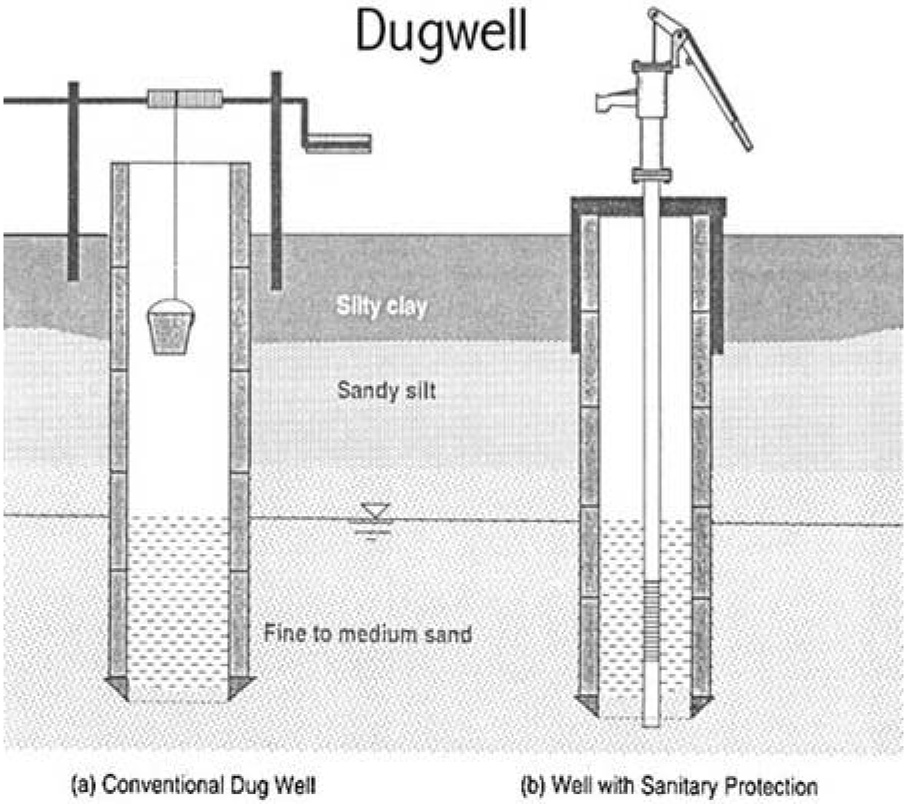


Figure 6.15: Dug wells

Slow sand filtration - the Pond Sand Filter

Ponds of various sizes (most commonly one to two hundred square meters) are ubiquitous in Bangladesh. These ponds formerly served as the major source of drinking water, but since the advent of shallow tubewells both rural and urban families have switched drinking water sources. Over the past three decades a massive drilling program, initially supported by foreign aid agencies, but then taken up by private enterprise, has resulted in the installation of 4-8 million shallow tubewells fitted with inexpensive handpumps.

Today, pond water remains the most frequent source of water for cooking and bathing in rural areas. In coastal areas of the country, where the shallow aquifer is saline, slow sand filtration of pond water has been promoted as a safe drinking water source. The Bangladesh Department of Public Health Engineering has standardized a design for a ‘Pond Sand Filter’, which can serve approximately 100-300 users.

Following widespread concern about arsenic in groundwater, there have been numerous calls for a return to surface water as a drinking source, and there is strong political will to promote pond water, treated through Pond Sand Filters, as an alternate source of safe drinking water.

Rainwater Collection

Bangladesh receives an immense amount of rainfall every year, but very few Bangladeshis collect rainwater as a primary source of drinking water, perhaps because of the ubiquitous surface and groundwater resources. Many families informally practice rainwater collection from rooftops, using a variety of different size containers. In the 1970s rooftop rainwater collection became a formally recognized rural water supply technique, and designs for large ferrocement storage jars, based on Thai designs, were standardized. These jars range from 1 to 3.2 cubic meters, and serve individual households or small clusters of homes. The jars have a sealed lid, and a tap near the base for water collection, to minimize the possibility of bacterial contamination.

Recently, as part of a joint DPHE/UNICEF/BRAC arsenic project, smaller storage tanks have been built using the widely available concrete rings used for pit latrines. Five hundred-liter tanks can be constructed easily at significantly lower cost, and can store enough water to provide a good level of service during the rainy season and drinking water for a few weeks into the dry period.

Corrugated iron roofs are present in about 50% of households in Bangladesh, and are clearly the most suitable collection surface, although tiled and asbestos-sheet roofs can also be used. Roof run-off is fed through gutters into aboveground ferrocement storage containers. Some private users have used other materials such as brick, and have constructed tanks of various sizes both above and below ground.

Solar Disinfection

The solar disinfection system promoted as SODIS, described in **Section 6.2**, has recently been introduced into Bangladesh as a large field-scale project. This technology is unfamiliar to Bangladeshis, and one of the biggest difficulties has been convincing water users, community leaders, and local government officials of the safety of treated water. Nonetheless, initial results are encouraging, and show both that conditions in Bangladesh are favorable for SODIS, and that with proper education and motivation, water users can become enthusiastic converts. SODIS can be used effectively in conjunction with rainwater harvesting. When stored rainwater runs out, the household can secure safe drinking water from nearby ponds by applying SODIS for the remainder of the dry season.

Arsenic Removal

Arsenic elimination techniques are described in detail in **Section 6.3**, and in recent years many systems have been tried out in Bangladesh, mostly as small pilot studies. The most commonly used technology has been coagulation and filtration, most likely because these processes are relatively well documented, have been applied successfully in other arsenic-affected areas, and the materials required are available locally. This section will consider a generic system in which an oxidant (chlorine or permanganate) is added to contaminated water, followed by a coagulant, either ferric chloride or alum.

6.5.2 Technical Criteria

Water Quality

Drinking water sources must be free from unsafe levels of arsenic, but also from undue microbiological contamination, and other chemical contaminants. Since the arsenic problem in Bangladesh has been largely restricted to shallow tubewells, it has been suggested to abandon the contaminated wells - and even seal them - and return to surface water. Cholera and typhoid once devastated millions in Bangladesh because of lack of safe water. In the last two decades diarrhoeal diseases have been brought under control through bacteriologically safe drinking water, better hygiene and household based case management through oral rehydration therapy. Diarrhea-linked illness and death have been reduced to a large extent. Now, as it turns out that groundwater is contaminated another change of direction is necessary, but one that should build on earlier achievements in water, health and hygiene, rather than forcing households back in time. It is critical that any alternate source of drinking water should be free from microbiological contamination, as well as arsenic.

Deep tubewells probably offer the highest water quality of the various options under consideration. Deep groundwater is not only low in arsenic, but also free from the high levels of iron and manganese that make much of the shallow groundwater unpalatable. A properly constructed deep tube well provides excellent protection against anthropogenic microbiological contamination.

In contrast, the shallow aquifer is highly contaminated with arsenic in some areas. Nonetheless, researchers from Jadavpur University (West Bengal) have tested over 100 dug wells in arsenic-affected areas of West Bengal and Bangladesh, and in all cases arsenic levels were below 50 µg/L. This is thought to be due to the fact that during storage in the dug well, water is exposed to oxygen, and dissolved iron in the groundwater is able to precipitate as ferric hydroxide, removing any arsenic from solution in the process (Chakraborti, 1999). Dug well water may also contain a higher proportion of recent rainwater than other groundwater sources. Dug wells are, however, very susceptible to microbiological contamination, unless they are protected with head walls and rope or hand pumps for raising water.

Ponds in Bangladesh generally contain safe levels of arsenic, though arsenic levels of over 150 µg/L have been found in some areas (Islam et al., 2000). Therefore, pond water should be tested for arsenic before installation of pond sand filters. Many large ponds in rural areas are privately owned, and used for raising of fish. Owners dose the ponds with pesticides to kill predator fish before they introduce fingerlings. Large amounts of fertilizers are applied as well. The use of these ponds for fish-rearing has made it difficult to find suitable ponds for construction of community pond sand filter systems. Agricultural runoff can also contaminate ponds, though most ponds are surrounded by berms that normally keep out the bulk of external surface water.

Ponds are also used for washing of clothing, dishes and livestock, and for bathing. In too many cases, hanging latrines drain directly into ponds. Recent studies by the NGO BRAC indicate that the initial high bacterial pollution load is difficult, but not impossible, to eliminate. Once a Pond Sand Filter has been constructed by the side of a pond, there is some evidence that communities may become more disciplined in protecting the pond from various types of contamination.

Collected rainwater in Bangladesh has been examined and found to have low to negligible levels of coliform bacteria, and no detectable arsenic. Further research on other parameters, especially pH, zinc, and lead, has yet to be conducted. Storage tanks should be designed with screens to prevent the entry of small animals and the breeding of mosquitoes.

Field studies have demonstrated that SODIS can effectively eliminate microbiological contamination from surface waters in Bangladesh. However, any chemical contaminants in the source (typically pond water) will not be removed by solar disinfection. Water users often like the taste of the water, and if bottles are stored on a rooftop through an afternoon and overnight, cool, safe water is available the following morning.

Arsenic removal systems applied in Bangladesh have been able to reduce even highly contaminated levels of arsenic down to 10-30 µg/L, well below the national standard. Iron and manganese are also effectively removed. Potential water quality problems include lowered pH, residual aluminum if alum is used as the coagulant, and microbiological quality of stored water. Limited data suggest that none of these water quality parameters pose a problem in waters treated in well-designed systems. In fact, drinking water collected from traditional sources, including tubewells, often becomes highly contaminated with fecal pathogens during household storage, and a well-designed household arsenic removal system significantly reduces this risk.

Water Supply Option	Score	Water Quality
Deep tubewell	5	Excellent inorganic and biological water quality.
Dug well	3	Arsenic-free, but relatively high risk of chemical or biological contamination from surface water.
Pond sand filter	3	Can provide excellent pathogen removal, but users will not be aware if system fails and pathogens break through. Potential for contamination from agricultural chemicals.
Rainwater collection	4	Excellent inorganic quality, low levels of coliform contamination. More information needed on pH and trace metals.
SODIS	4	Excellent microbiological quality, some risk of contamination from agricultural chemicals.
Arsenic removal	5	Adequate, though incomplete arsenic removal. Appropriate design can minimize pathogen contamination during household storage.

Water Quantity

Since one person needs from seven to ten liters of water per day, a family of six will need about 1200-1800 liters of water monthly for drinking and cooking purposes. Safe water technologies should be able to meet this need throughout the year, either on their own or in combination with other safe sources.

The piezometric surface of the deep aquifer in Bangladesh undergoes some seasonal fluctuation, but on a much smaller scale than the shallow aquifer, and in most areas suction-mode handpumps are able to abstract water throughout the year. Recharge mechanisms and rates are not well understood, and a sudden change to large-scale abstraction might stress deep aquifer resources. While the amount of water needed for drinking water alone would not likely have much of an impact, water abstracted for large-scale irrigation might. Handpump-mounted DTWs can serve from fifty to over three hundred users, whereas a reticulated system with a half-kilometer radius and five standposts could serve a population of two to three thousand in built-up areas such as peri-urban fringes, small towns and sub-district headquarters.

Dug wells and Pond Sand Filters both rely on near-surface water resources, which are prone to running dry during the dry season, especially in the west of the country. For both systems, local climatic conditions, along with the size and depth of the pond or well, will determine the effective season for water supply. In coastal areas and in the northeast, these systems are often able to provide water through most of the year. If ponds are adequately full, one Pond Sand Filter can produce water for two to three hundred users, whereas a dug well is adequate for about fifty users.

SODIS and arsenic removal can produce drinking water in whatever quantity is required, as long as the water source (surface water or contaminated shallow groundwater) remains available. SODIS users generally only treat water needed for drinking purposes, since cooking destroys pathogens effectively.

Rainfall in Bangladesh is highly seasonal, with over 80 percent of rain falling between May and September. The quantity of rainfall varies significantly throughout the country, with the rainiest area (Sylhet) receiving nearly three times as much precipitation as the driest area (Rajshahi). However, the seasonal nature of precipitation is fairly consistent, with a dry season ranging from December through March.

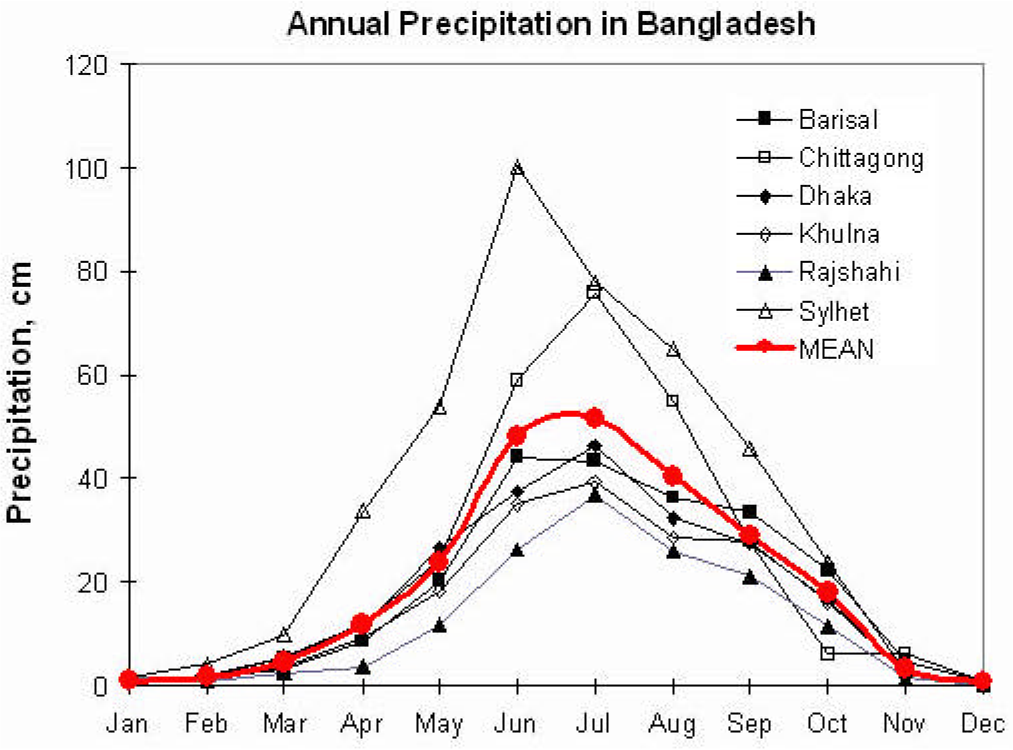


Figure 6.16: Annual precipitation in Bangladesh (Rashid, 1991)

A small dwelling with a corrugated iron roof measuring five by eight meters will be able to collect approximately 32 liters per millimeter of precipitation, assuming an 80% collection efficiency to account for evaporation, lost water, and the first flush. On average, then, such a rooftop collection system in Bangladesh could collect nearly 75 cubic meters of water annually, enough to meet the needs of over 35 people. However, because of the extreme seasonality of precipitation, water availability is not constant. With the above five by eight meter rooftop, and a very small (200-500 L) storage tank, rainwater collection could meet the drinking water needs of six family members for about nine months. If larger storage tanks, or larger catchment areas were used, rainfall could meet needs for longer periods. With the above catchment, a tank of about two cubic meters could provide enough storage to get completely through the dry season. In Rajshahi, however, at least three cubic meters of storage would be required, because of the later onset of the rainy season.

Water Supply Option	Score	Water Quantity
Deep tubewell	5	Should be able to provide sufficient water. Handpump-mounted systems can serve up to 300, reticulated systems from 2000-3000.
Dug well	3	Vulnerable to drying up during dry season, slow to refill. 50 users served.
Pond sand filter	3-4	Depending on size and local climate, may dry up or become unusable during dry season. 200-300 users served.
Rainwater collection	4	With storage, the dry season can be partly or completely bridged.
SODIS	3-4	Depends on access to source waters during dry season.
Arsenic removal	3-4	Depends on access to source waters during dry season.

Reliability and robustness

Handpump-mounted deep tubewells are fairly reliable, but do break down on occasion. Sometimes newly installed wells become clogged with fine sediments and must be purged or abandoned. Deep tubewells with motorized pumps attached to storage tanks and reticulation networks must be installed professionally, and require more frequent maintenance. Due to the large number of people such systems serve, system breakdowns can have quite serious impacts in the absence of spares and a capable maintenance crew.

One drawback of Pond Sand Filters is that pathogens can break through without any visible change in water quality, so users do not know when the filter has failed. Chlorination after filtration as a safety measure could guard against this danger, but ensuring a correct and continuous dose can be difficult and the PSF designs used in Bangladesh have omitted this step.

Dug wells and rainwater collection are unlikely to break down and regular maintenance and repair generally lies within the ability of the users. Arsenic removal efficiency, however, relies heavily on user inputs, and if chemicals are added wrongly or the system is operated incorrectly, arsenic might break through into the treated water. The reliability of SODIS in Bangladesh is under evaluation, but in other countries has proved robust even during periods of cloudy weather and relatively low temperatures.

Water Supply Option	Score	Robustness
Deep tubewell	4	Possible breakdown, clogging, risk of failure in reticulated

		system.
Dug well	5	Low maintenance
Pond sand filter	3	Frequent maintenance, possibility of failure without warning
Rainwater collection	4	Minor maintenance and repairs required periodically.
SODIS	?	Testing in Bangladesh underway.
Arsenic removal	3	Significant opportunity for user error to prevent effective removal.

Operational Safety

Among the technologies considered, only arsenic removal involves the addition of chemicals. Both of the oxidants commonly used in Bangladesh, permanganate and bleaching powder, are corrosive, caustic skin irritants that are toxic if ingested directly. Special care is required during application and storage of these chemicals to prevent exposure to household members, particularly children.

Water Supply Option	**Score**	**Operational safety**
Deep tubewell	5	No operational risks to users.
Dug well	5	No operational risks to users.
Pond sand filter	5	No operational risks to users.
Rainwater collection	5	No operational risks to users, except for falling off roof during cleaning.
SODIS	5	No operational risks to users.
Arsenic removal	4	Possible exposure of users to hazardous chemicals.

Environment

Deep tubewell abstraction for drinking water alone likely would have no significant impact on the environment. The amount of water needed for drinking and cooking purposes is relatively small, and should not put undue pressure on deep groundwater resources, except possibly in large municipal settings.

Dug wells and rainwater collection have no significant environmental impacts. When Pond Sand Filters are installed, communities typically take steps to improve the environmental conditions around the pond, producing improved environmental conditions. Likewise, SODIS actually has a slight positive impact, in that it converts ubiquitous plastic bottles from annoying rubbish into useful tools.

Arsenic removal can have a slight negative impact on the environment, especially when applied at the household level, because arsenic-rich sludge will need to be disposed of safely. However, this impact is minor since arsenic adsorbed onto sludge is fairly stable (see **Section 6.3.6**). Furthermore, only that water required for drinking and cooking need be treated, so the amount of arsenic sequestered into the sludge will be small compared to the amount in water pumped for non-drinking purposes, especially irrigation.

Water Supply Option	Score	Environment
Deep tubewell	4	No impact, unless irrigation led to unsustainable withdrawal
Dug well	4	No impact
Pond sand filter	5	Slight positive impact through pond protection
Rainwater collection	4	No impact
SODIS	5	Slight positive impact through conversion of plastic bottles to valued commodity
Arsenic removal	3	Slight negative impact from arsenic-rich wastes.

6.5.3 Socioeconomic criteria

Economic considerations

The economic costs will often determine which technically viable technologies can be implemented. These costs include not only the start-up costs, but also the costs of operation and periodic maintenance and repair.

In Bangladesh it is generally accepted that users contribute to the investment and operational cost of water supply. Presently 97% of the population has access to pathogen-safe drinking water, and it is estimated that at least 75% of water supply points have been constructed by the private sector, without direct government support. This achievement bears out the willingness and ability of the population to invest in water supply, and shows the capacity of the private sector and the social banks to support development.

Bangladesh is a poor country and many households are economically overstretched. The Government of Bangladesh and many NGOs assist the poor in obtaining access to good water, mainly through water points equipped with a handpump. Government subsidization rates vary according to the technology, with users contributing about 10% of the capital costs of shallow tubewells, dug wells, and pond sand filters. The more expensive deep tubewells are slightly more heavily subsidized, with cost recovery rates of 6-9%. All cost recovery rates are somewhat dependent on local economic conditions. Users are trained to operate and maintain these sources, and are responsible for recurring economic costs such as replacement of parts. Government tubewell mechanics are available for more serious repairs.

Typically, a deep tubewell (250 m) fitted with a handpump will cost from $800 to $1000[6], but in rocky areas costs could be much higher. When a submersible pump, diesel generator, storage tank and reticulation network are added, capital costs rise considerably, but the population served also increases significantly. The major factor determining costs is the walking distance from household to supply point, which in turn dictates the length of the reticulation network. With a network of five standposts and a radius of 500 meters, a reticulated deep tubewell system could cost approximately $12,000. Operation and maintenance costs would also be significantly higher.

[6] All price calculations in this section are based on the simplifying assumptions of an average household size of six and an exchange rate of USD$1 = Taka50. The actual

exchange rate as of January 2001 was 53.81, and in recent years has been slowly increasing.

The cost of a protected dug well, lined to a depth of ten meters with concrete rings and including a properly constructed apron and all fittings for a handpump, is approximately US$160. Operating and maintenance costs are low, and consist of periodic cleanings and minor repairs to the handpump.

Pond sand filters are slightly less expensive than handpump-fitted deep tubewells, with startup costs of approximately $800. Maintenance costs are relatively high, since the filter must be cleaned monthly, and new sand periodically added to replace lost volume.

The costs of rainwater collection depend largely on the storage tank size. Large 3.2 m 3 ferrocement tanks can be built for about $110, but smaller 500-liter tanks can be easily constructed from the ubiquitous concrete rings used for pit latrine construction for under $25. Existing rooftops are usually used, but guttering and downpipes are required, adding approximately $10 per unit. While the use of larger tanks permits some bridging of the dry season, increasing the catchment area can have the same effect, often at lower costs.

SODIS costs are very low, since appropriate plastic drinking water bottles are ubiquitous in Bangladesh. A small amount of money must be spent in painting one side of the bottles black, and in occasional replacement of bottles. A family of six will require at least twelve bottles, to meet drinking water needs alone, which would cost approximately $6.

The cost of arsenic removal systems will vary somewhat, most systems in Bangladesh require two or three water containers, some type of filter, and a water tap. All of the required materials are locally available, and should cost from five to ten dollars. Chemicals must regularly be procured, but the costs are relatively low.

Water Supply Option (households served)	**Score**	**Economic Considerations**	
		Startup costs per household	**Annual costs per household**
Deep tubewell w/handpump (15-50)	2-3	$20-$65	$1 to $2
Reticulated deep tubewell (350-500)	3-4	$25-$35	$5 to $8
Dug well (10)	4	$15	$1 to $2
Pond sand filter (40-50)	4	$15-$20	$2 to $3
Rainwater collection w/3200 L tank (2)	3	$55	< $1
Rainwater collection w/500 L tank (1)	4	$25	< $1
SODIS (1)	5	$5	< $1
Arsenic removal (1)	5	$5 to $10	$2 to $4

Scoring system: 5 = < $10; 4 = $10-$30; 3 = $30-$60; 2 = $60-$100; 1 = > $100

Institutional Considerations

Deep tubewells, either with or without reticulation systems, are admirably suited for private sector involvement. A vibrant economy exists in the installation of shallow tubewells, and this trained workforce could easily adapt to the installation of deep tubewells. With motorized systems, there is a danger of power loss, either if the local grid goes down, the diesel generator should become broken, or generator operators are unable (or unwilling) to procure fuel. A relatively skilled team of operators and monitors is required to ensure success.

Dug wells, pond sand filters and rainwater collection systems can also be easily installed by local masons, once they are given some training from enabling institutions such as government or NGOs. There is opportunity for the use of community labor to reduce costs and to assume responsibility for most operation and maintenance tasks.

SODIS and arsenic removal systems are more alien to water users, and to the network of civil servants involved in public health and water supply. Considerable training will be required to ensure that these technologies are applied correctly, especially for arsenic removal. Continued monitoring of water quality will be essential, and will require sophisticated management. However, all of the operations and maintenance can eventually be done by the water users themselves. Arsenic removal systems also require an established mechanism for supply of reagents.

Water Supply Option	Score	Institutional Considerations
Deep tubewell	4	Private sector already heavily involved in tubewell installation. High startup costs mean that credit will probably be required.
Dug well	5	Private sector familiar with technology, all materials locally available
Pond sand filter	4	Private sector has skills required for this technology, but will require some training
Rainwater collection	4	Private sector has skills required for this technology, but will require some training. All materials locally available
SODIS	4	Main institutional needs are for promotion, training, and some water quality monitoring. Material needs are minimal.
Arsenic removal	3	Training required, as well as supply network and regular water quality monitoring

Gender considerations

The most direct impact of water technology on women will be the amount of time and effort required for water collection and/or treatment. The further the water source is from the house, the more physically burdensome the new technology will be. In Bangladesh, women's social mobility is more limited than that of men, and it may be socially unacceptable for women to travel outside of their neighborhood, or *bari*, to collect water. Therefore, the gender criteria ranking closely parallels that discussed under 'convenience'. It is important, however, to recognize that the inconvenience of water collection falls mainly on the shoulders of women, who already have heavy work burdens in the household. An optimal system would impose no greater additional burden on women than on men, and would favor sharing of the water workload between women and men. However, as practiced currently in Bangladesh all of the technologies under consideration rely almost exclusively on women's labor. Therefore, in the following table, none of the technologies are given high marks.

Water Supply Option	**Score**	**Gender consideration**
Deep tubewell	2-3	Handpump-mounted DTW, depending on distance and population served.
	4	DTW with reticulation network, source is close and no pumping required.
Dug well	3	Nearby, some pumping involved.
Pond sand filter	3	Medium distance, pumping required.
Rainwater collection	4	In-house access, no pumping or queues involved.
SODIS	3	Water must be collected, each bottle filled individually.
Arsenic removal	3	Water must be collected from nearby source, and is then treated within the household.

Convenience

Deep tubewells mounted with handpumps can be relatively inconvenient, as collectors (women and children) must walk to the site, which may be several hundreds of meters away. If large populations are served, long queues may form at the wellhead. Reticulated systems could greatly improve the convenience of this option, by bringing water to standposts much closer to users, or even directly into households. These systems require a motorized pump, which would further reduce the work burden of water collectors.

Deep tubewells fitted with handpumps require periodic maintenance and repair from professional mechanics and/or trained tubewell caretakers within the community. When motorized pumps are used, much more regular maintenance is required. Annually, the pump should be overhauled, the inlet screen cleaned and the valves inspected. Occasional maintenance and repair of the pump house, storage tanks, reticulation system and standposts will also be required.

Since dug wells serve a relatively small population, they are usually located fairly conveniently, close to water users. Maintenance needs are minimal. At the end of the dry season the well can be cleaned, checked, if yield is low well can be deepened and lining extended. Occasionally there may be a need to disinfect the well with chlorine.

Pond Sand Filters serve larger communities, and sometimes queues form during hours of peak use. Some community members must regularly clean the sand filter, which requires several hours of manual labor.

During the raining seasons rainwater harvesting provides a very good level of service, while in the period after the end of the rainy season water security remains high. Household rainwater collection is extremely convenient - water is readily available from on-site storage containers. This system is also more convenient than many other options in that no pumping is required, unless underground storage tanks are used.

Maintenance is important, but consists mostly of keeping the catchment, gutters and tank clean.

SODIS requires more active work on the part of household water managers: water must be collected from a reasonably clean source, and poured into plastic bottles, which must be placed in a dedicated spot, typically on corrugated roofing. Water is not instantly available, so water managers must plan their water needs at least a day in advance. However, once households are accustomed to a SODIS routine, the added work burden would not be terribly onerous.

Household arsenic removal using oxidation and coagulation requires systematic, sustained input from water users. Water can be collected from nearby tubewells, but for each batch of water treated, chemicals must be added in the correct dose, stirred for the appropriate amount of time (ten to fifteen minutes is recommended for optimal floc formation), and allowed to settle for a fixed period of time. As with SODIS, water is not immediately available for consumption, so water planning is required. Once a routine is established, however, water users have the convenience of safe water on tap, within the household. It should be noted that other arsenic removal systems require less intensive user input, but have not yet been as extensively tested in Bangladesh, and are not considered in this section.

Water Supply Option	**Score**	**Convenience**
Deep tubewell	3-4	Handpump-mounted DTW, depending on distance and population served.
	5	DTW with reticulation network, source is close and no pumping required.
Dug well	4	Nearby, some pumping involved.
Pond sand filter	3-4	Medium distance, pumping required. Regular cleaning required.
Rainwater collection	5	In house access, no pumping or queues involved. Water on tap.
SODIS	3	Water must be collected, each bottle filled individually.
Arsenic removal	2	Users must treat each batch of water, stir for several minutes, and allow floc to settle before use.

Communication

Communities in arsenic-affected areas need information about arsenic contamination in their homes, and about safe options available to them. Familiar, accepted technologies will always be easier to promote than unfamiliar systems. It is more difficult to promote options that contradict or conflict with community beliefs regarding safe water.

For the past three decades, water supply communication activities have tried to convince people that pond water is unclean and unsafe, and that groundwater represents the only appropriate drinking water source. Dug wells have been seen as something of a ‘next-best’ alternate in areas where tubewells are not feasible. It will be a major challenge to encourage behavioral change towards sources that were recently discouraged (e.g. ponds) or towards sources that are unfamiliar to people.

Regarding arsenic removal, users are sometimes understandably reluctant to add 'chemicals' to drinking water. Some of the reagents suitable for arsenic removal, notably potassium permanganate and alum, are locally available and accepted as safe. Alum, in particular, is already used to remove suspended solids from pond water for cooking and household uses (though not for drinking purposes).

Water Supply Option	Score	Communication
Deep tubewell	5	Familiar and popular technology.
Dug well	4	Familiar technology, seen as older and less safe than groundwater.
Pond sand filter	3	Pond water is a familiar source, though filters are novel. Users understand the concept that the filter is required for water purification.
Rainwater collection	3	Not widely practiced, public concerns remain.
SODIS	2	Completely novel, runs against previous messages that surface water must be boiled before drinking.
Arsenic removal	2	Completely novel, requires detailed training

Social acceptability

The most socially acceptable options will be those that have scored well in previous categories: that provide what is perceived as sufficient water of high quality, that are convenient and familiar. Affordability often does not enter into user's consideration of acceptability, since users expect government to provide the source for free or at very low cost.

In Bangladesh, by far the most socially acceptable source of drinking water is the tubewell. Older technologies such as pond water treatment and dug wells are seen as inferior alternates, only to be resorted to when tubewells are impossible. The new technologies being tested in Bangladesh, SODIS and various types of arsenic removal systems, have been very popular among communities, but it remains to be seen whether such enthusiasm will outlast the pilot trials.

Water Supply Option	Score	Social acceptability
Deep tubewell	5	Tubewell water is the most widely accepted form of drinking water, and is considered interchangeable with 'safe water'. Users like the prospect of having piped water.

Dug well	3	A traditional technology, but users are aware of some hazards.
Pond sand filter	3	Users are reluctant to return to surface water, pond water is visibly impure, and ponds can no longer be used for fish culture.
Rainwater collection	3	Users are not convinced that water quality is high, especially for stored water.
SODIS	4	Users appreciate the low cost and ease of this system.
Arsenic removal	4	Water on tap in the home, which often tastes better than local groundwater, makes this technology appealing to users.

6.5.4 Conclusions

The following table summarizes scores given to each technology in the preceding discussion:

Table 6.7: Summary of protocol scores

	Deep tubewell	**Dug Well**	**Pond Sand Filter**	**Rainwater Collection**	**SODIS**	**Arsenic Removal**
Technical Criteria						
Water quality	5	3	3	4	4	5
Water quantity	5	3	3-4	4	3-4	3-4
Reliability/robustness	4	5	3	4	?	3
Operational safety	5	5	5	5	5	4
Environment	4	4	5	4	5	3
Socio-cultural considerations						
Economic	2-3	3-4	4	3-4	5	5
Institutional	4	5	4	4	4	3
Gender	2-4	3	3	4	3	3
Convenience	3-5	4	3-4	5	3	2
Communication	5	4	3	3	2	2
Social acceptability	5	3	3	3	4	4

The various criteria summarized above are not all of equal importance, and an overall score should not be calculated simply by summing all of the scores. For example, shallow tubewells in intensely arsenic-affected areas would score very highly in all categories except for water quality, but obviously would not be the appropriate mitigation choice.

In an ideal hydrological and hydrogeological setting, one of the above technologies should be the method of choice. But as is to be expected, there is no single universal technology solution for a specific area. Local geography, geology, climate, soil characteristics, population density, community willingness to pay for a particular technology, and community acceptance, all play important roles in technology selection. The question of household versus community level technology is a function of community acceptance, cost and technical parameters.

It is perhaps not surprising that the most acceptable technologies in terms of many of the technical criteria are also the more expensive options. Further work is needed to make these options more affordable, the development of small, inexpensive rainwater storage tanks using pit latrine rings is a good example.

Of the more established water supply options considered in this section, rainwater harvesting and the deep tubewell emerge as superior to the dug well and the pond sand filter. The chief difference between these two options is essentially scale of application: the deep tubewell is optimally suitable for small to medium-sized communities, and is most cost-effective when large numbers of users are served, whereas rainwater harvesting is presently best suited to the individual household.

There are many aspects of the deep tubewell option that call for caution and further research: key questions exist regarding over-pumping and saline intrusion near the coastal areas; the availability and productivity of the deep aquifer outside of coastal zones; how to deal with major breakdowns in rural settings; the absolute need for meticulous operation and maintenance and relatively highly trained mechanics (for reticulated systems); and most importantly a significant community revenue contribution.

The novel technologies of SODIS and arsenic removal achieve comparable scores to deep tubewells and rainwater collection, and are economically much more feasible. These technologies should be considered as viable alternatives. Because of their novelty, both will require more extensive promotion and communication efforts. Both of these technologies might best be used as complements to other systems that are only viable seasonally, especially rainwater collection.

6.6 Application of safe drinking water supply technologies in arsenic-affected areas

Previous sections have shown that there are technically viable technologies for removal of arsenic from drinking water, at least to the 50 µg/L level. Some of the technical processes may be more difficult to operate in developing countries, or may be prohibitively expensive. However, in many cases, technical challenges may be small compared to logistical and institutional difficulties. Different institutional structures and approaches will be required for arsenic removal at municipal, community, and household levels.

6.6.1 Municipal level

Most large-scale experience with arsenic removal to date has been conducted in urban settings, where governments have been able to install arsenic removal systems. These experiences have shown that publicly operated, centralized treatment can effectively provide arsenic-free water to urban populations.

Plants generally involve large engineered production/treatment facilities, which are often custom-designed, and a large piped distribution network. This type of system requires trained professional operators, and rigorous quality assurance and quality control. The design parameters of such plants are well beyond the scope of this review, but all arsenic removal plants will make use of the physical and chemical processes discussed in **Section 6.3**. For more information on design and operation of municipal water treatment plants the reader is referred to standard texts (e.g. Twort et al., 1985; Viessman and Hammer, 1985; ASCE/AWWA, 1990; Salvato, 1992).

Not all of the water supply technologies used in industrialized nations are appropriate for conditions in developing countries. Some of the technology is too difficult to operate, maintain and repair, due to a lack of spare parts, supplier support, and trained staff. Some technologies will also be prohibitively expensive in poorer countries. It is important, therefore to choose an appropriate technology that can be understood by local operators, and can be readily maintained and repaired.

Water supply utilities are responsible for ensuring the quality of water produced and delivered. Water quality should be monitored periodically, according to national drinking water regulations. Parameters to be sampled and sampling frequency are usually determined by the regulatory agency in order to ensure compliance, though plant operators may need to monitor certain parameters more closely in order to better control plant operation and quality of produced water.

Most experience with municipal arsenic mitigation has been in relatively industrialized countries and regions such as Chile, Taiwan, and Hungary, where a mix of source substitution and arsenic removal has been practiced. In all of these places, and in the US and Europe, coagulation with iron salts has been chosen as the most appropriate technology for arsenic removal in large centralized water supply plants. Alternate and emerging technologies for arsenic removal have not yet been applied in large-scale plants, though some of the advanced technologies will likely become necessary where drinking water standards are well below 50 µg/L.

Centralized treatment for arsenic removal offers certain economies of scale, and in areas of high population density, capital costs can be distributed over a large number of consumers, so per capita costs need not be high. One disadvantage of centralized arsenic removal systems is that all of the water produced must be treated, even though only a small fraction will eventually be consumed through drinking or cooking. It is also possible to design a centralized system with two distribution networks, one for highly treated water for consumption and one with less treated water for other uses. Distribution costs would necessarily be higher, but treatment costs would decrease, and in some instances this dual distribution networks might be appropriate.

Another disadvantage of central plants is that they generate significant amounts of arsenic-rich wastes. Proper plant operation and handling of chemical supplies and wastes is crucial in any country, but water utilities in industrialized nations typically have more experience in compliance with environmental regulations. In developing countries, special consideration should be given to monitoring of plant operations, to quality control assurance, and to ensuring that arsenic-rich wastes are disposed of appropriately, in accordance with national regulations.

There is typically little or no community involvement in design and operation of central arsenic removal plants, though beneficiaries may contribute to the costs of arsenic removal through taxes or water fees.

Box 6.12: Source substitution and arsenic removal in Hungary

In the early 1980s, arsenic was found in deep groundwater of five counties of southern

Hungary, with concentrations ranging up to 220 µg/L in municipal water works. Some 400,000 people were exposed to drinking water over the national standard of 50 µg/L. The first steps taken were to close the most affected municipal production wells, and to modify mixing ratios with the remaining wells, to reduce arsenic levels by about 50%. However, most of the water supplies still remained above the national standard. For a short period bottled water was supplied for children under 14 (two liters per day), but this proved expensive and ineffective. Hydrogeological investigations were conducted to find arsenic-free aquifers, and in some parts of the country new, deeper wells were installed. In one area a safe aquifer was identified 20-30 km from the affected region, and a new regional water works was established to transport water to the affected settlements.

In some affected areas, no safe aquifer could be found, and the government commissioned several arsenic removal plants, using the standard technology of oxidation, coagulation with ferric chloride, and filtration. These plants were able to reduce arsenic levels by 80-90%, to 20-40 µg/L, bringing communities into compliance. Experiments were also made with various adsorption and ion exchange technologies, but coagulation proved more practical.

By 1998, due to the combination of source substitution and arsenic removal, only about 10,000 people were drinking water slightly over the national limit. However, as Hungary joins the European Union, it is compelled to adopt the lower EU standard of 10 µg/L for arsenic in drinking water. Since source substitution and standard coagulation have already been used, Hungary faces a serious challenge in lowering arsenic levels even further, by an additional 50-80%. Water quality engineers are examining new strategies, including modification of the coagulation process; adsorption or ion exchange; membrane technologies; and *in situ* immobilization. It seems likely that the costs of compliance with the new standard will be significantly higher than the initial costs of reducing arsenic levels to under 50 µg/L.

Box 6.13: Arsenic removal plants in Taiwan and Chile

In both Taiwan and Chile, drinking water was found to be contaminated with arsenic in the 1960s. Although the water sources were very different (groundwater in Taiwan, surface water in Chile), in both cases the majority of the exposed populations was concentrated in urban areas served by a piped water supply. Accordingly, after laboratory experiments and pilot testing, full-scale arsenic removal at a central location was chosen in both cases. Both the Taiwan and Chile plants used chlorine to oxidize arsenite (1.0 mg/L in Chile, 12 mg/L in Taiwan), then added ferric chloride (30 mg/L in Chile, 32 mg/L in Taiwan), and removed the resulting HFO through sedimentation and filtration. In Taiwan, arsenic levels were reduced from 600-800 µg/L to below 50 µg/L, while in Chile concentrations were reduced from 350-500 µg/L to 40-50 µg/L.

Sources: (Shen, 1973; Sancha and Ruiz, 1984; Sancha et al., 1998; Sancha, 1999).

6.6.2 Community level

In most small towns and rural communities, water supply conditions are very different from in urban settings. The population served is smaller, often infrastructure such as reticulation systems are missing, and there is a shortage of trained personnel to operate plants. Rural populations tend to be poorer than urban ones, and less accustomed to considering water as an economic good.

Small piped water supply systems tend to have relatively high startup costs, particularly regarding the establishment of a reticulation network. Piped systems also require trained operators, who have the technical skills not only to keep the system in operation, but to make repairs in the case of system failure. For these reasons, piped water supply systems are the norm in urban water supply, but are less common in rural, developing contexts. In certain socioeconomic and geographical contexts, however, small reticulated systems can be an economically feasible option. An excellent manual for technical planning and implementation of community piped water supply systems is given by (Okun and Ernst, 1987). In some piped water systems, rather than establishing connections at individual households, communal collection points, sometimes with a storage tank, are established. These 'standposts' are described in detail in (IRC, 1979).

In some cases, rather than distribute water through a piped system, a 'point source' of drinking water is established, where community members come to the water source to collect safe water as needed. Most commonly, wells are used in this way, though surface water treatment (e.g. slow sand filtration) or rainwater collection can also serve as community water supply points. Two good resources on the use of tubewells in community water supply systems developed during the International Drinking Water Supply and Sanitation Decade are (Arlosoroff et al., 1987) and (IRC, 1988).

In arsenic-affected areas, any of the technologies for source substitution or arsenic removal discussed in **Sections 6.2 and 6.3** could be applied, in theory. In practice, some of these technologies will not be appropriate in a rural setting, because of high capital costs, the need for highly trained operators and repair technicians, and other infrastructure needs that may be absent. Technologies best suited for application at the community level will be those that are robust, operate well under a range of environmental conditions, and can be effectively operated and maintained by people without extensive technical training (See **Section 6.4**). A useful collection of articles covering community level sources of water, abstraction, pumping and distribution, and training and maintenance is given in (Kerr, 1989). UNICEF, WHO and the IRC have all produced important documents describing water supply in small communities (IRC, 1981; WHO, 1997b; UNICEF, 1999b).

The past twenty years have seen the gradual evolution of consensus that greater participation of community members in supply, construction, financing, and operation of water supply systems is crucial for sustainable rural water supply. In theory, increased community participation can generate a greater sense of involvement and ownership among the beneficiaries, and lead to a more sustainable water supply system. Communities acquire new management and organization skills, and develop into self-reliant, informed consumers, rather than passive beneficiaries of government largesse.

Increased community participation has fundamental implications for the role of central governments - decision-making power, and financial responsibility, must be decentralized to locally composed bodies, either in the form of local government institutions or community groups. This paradigm shift was endorsed at the 1990 New Delhi meeting that marked the end of the International Drinking Water Supply and Sanitation Decade. Participants agreed on a resolution that "a changing role of government is envisaged, from that of provider to that of promoter and facilitator, enabling local public, private and community institutions to deliver services."

Much has been written about the challenges of truly involving community members, including sections of the community which are typically excluded from decision-making such as women and the poor, in planning and implementing water and sanitation supply projects. Some particularly valuable documents for those interested in enabling community participation have been produced by various UN agencies (Whyte, 1986; Srinivasan, 1990; WHO, 1997b; UNICEF, 1999b); the IRC (IRC, 1981); and the German agency for overseas aid (GTZ, 1989). Two IRC papers focus particularly on the participation of women in water supply: (van Wijk-Sijbesma, 1985; van Wijk-Sijbesma, 1988)

One of the most important issues in community participation is the role of community members in operation and maintenance of water supply systems. In most developing countries, an estimated one quarter of rural water supply systems are out of order (Cairncross and Feacham, 1993). Often the problem is simple, but goes unattended due to a lack of an effective structure for maintenance and repair. Many governments, unable to mobilize civil servants to maintain decentralized community water supplies, have sought greater community involvement in operation and repair of rural water supply systems.

In practice, this type of self-help has proved difficult to implement, and there are at least as many examples of failure as of success. In numerous cases, governments have promised to provide technical support and matching funds, if communities were able to raise money (typically 50% of capital costs) and contribute labor. Often, communities have risen to the challenge, but governments have found themselves unable to make good on promises of support. Even when water supply systems are constructed with community participation, communities are often less involved with operation and maintenance. Consistent maintenance can be much more difficult than construction, and poor maintenance cannot always be blamed on insufficient motivation and skills among community members (Cairncross and Feacham, 1993).

Several IRC documents directly address community management of water and sanitation systems (Appelton and Evans, 1993; IRC, 1993; Kurup, 1996). Good reviews are also provided by the UNDP/World Bank Water and Sanitation Program (McCommon et al., 1990) and the USAID-funded WASH project (Yacoob and Rosensweig, 1992).

Only a few examples of arsenic removal at the community level have been documented. Most of these are preliminary or pilot level experiments, in Bangladesh, India, China and Argentina, where large rural populations are exposed to arsenic in drinking water.

Maintenance of most arsenic removal systems involves periodic tasks that can easily be done by unskilled laborers, such as backwashing and cleaning of porous media beds and scrubbing of tanks. Community members can also be responsible for collection and disposal of arsenic-rich wastes, though external support may be necessary, depending on the type of waste. Tasks that involve hazardous chemicals, such as chlorine dosing or regeneration of spent media, will require detailed training, but it may be possible to designate a responsible community member for these tasks, particularly if they are given some financial compensation.

When making community-level interventions, consideration must be given to logistic concerns such as supply of fresh chemicals and disposal of wastes. Appropriate institutions will need to be identified that can procure and distribute chemicals, and collect arsenic-rich wastes, if necessary (see **Section 6.3.7**, above). This role could be played by government agencies, NGOs, or the private sector. Any of these groups might require external support during the design and start-up phases.

Box 6.14: Community level arsenic removal with ferric chloride in Argentina

A well containing 270 µg/L arsenic was selected for a pilot wellhead filter in Rufino, Argentina. The filter consists of a cylindrical tank nearly 4 m high. Sulfuric acid is added to lower the pH from 8.5 to 6.5, followed by sodium hypochlorite to oxidize arsenite, and the coagulant, ferric chloride (30 mg/L). Treated water is then filtered through a bed of anthracite (1 m, 1.3 mm diameter) and sand (50 cm, 0.5 mm diameter). HFO forms in the tank and in the anthracite bed, and is removed in the anthracite and sand beds. The anthracite and sand beds are periodically cleaned with air blowing and caudal rinsing, using raw water from the well. Arsenic levels in the treated water are low, ranging from 20 to 40 µg/L. Iron levels were also dramatically reduced, though after 8 hours of operation, iron levels rose in the treated water. Source: (Madeic et al., 1999)

Box 6.15: Community level arsenic removal with activated alumina in India

The Bengal Engineering College (Deemed University) of Howrah, West Bengal (India), has developed a rural, community-level arsenic removal unit using domestically produced activated alumina. Contaminated groundwater is manually pumped directly into a column containing about 100 liters of activated alumina. The unit treats about 2500-4000 liters of water per day, and removes influent arsenic (a mix of arsenite and arsenate in nearly equal proportion) from about 500 µg/L to less than 50 µg/L. Several pilot units, each serving 800-1000 people, have been installed with support from the US NGO, *Water For People*, and one has been in operation since 1998, and has treated 12,000 bed volumes without regeneration as of January 2000. The influent water is high in iron (8-10 mg/L), which precipitates out and slows flow rates. However, periodic backwashing clears the filter and restores adequate flow rates. A village water use committee is responsible for maintaining the system, and charges users a small fee for access. These funds are kept in a bank account, and used for the regeneration and eventual replacement of exhausted media. Local contractors are trained to regenerate saturated activated alumina and to immobilize the resulting arsenic wastes in cement blocks. Source: (Gupta et al., 2000)

Box 6.16: Small private arsenic removal plants in the United States

Activated alumina and ion exchange resins have been the methods of choice for arsenic removal in small systems in the United States. A review of two activated alumina and two ion exchange small treatment plants, serving two schools, a medical facility and an industrial facility, showed that arsenic levels can be reduced from 50-80 µg/L to under 5 µg/L. All of the plants included an oxidation step, either with chlorine or a solid manganese-based oxidant. The activated alumina plants both backwashed tanks every 4-6 months. Both of these plants use activated alumina on a throw-away basis, replacing half of the media every 1.5 years. The ion exchange resin plants regenerate media automatically, including backwashing and rinse steps. One system regenerated every six days and had excellent effluent quality. The other system regenerated every three months, and effluent water showed periodic spikes of arsenic, sometimes at higher levels than the influent. It was recommended that this system regenerate more frequently to prevent arsenic peaking. Source: (Sorg and Wang, 2000)

6.6.3 Household level arsenic removal

Arsenic removal at central or community levels is generally cost-efficient, because of economies of scale. Large capital costs are made bearable when shared by a large number of users. In contrast, household systems have a small number of beneficiaries, and can be relatively expensive.

However, household systems have several advantages over larger systems. Small systems will have smaller capital costs (even if per capita costs are higher). There is no ambiguity about who is responsible for operating and maintenance, and there is less chance of ‘freeloaders’ who enjoy the benefits of arsenic-free water but do not contribute to the costs of obtaining it. Experience from decades of water supply and sanitation projects has shown that families are better at maintaining household systems correctly than community members are at managing larger systems. Another key advantage is that in household systems, only the water that is required for drinking and cooking need be treated. In the case of a system breakdown, only a small number of users are affected.

In industrialized countries, household treatment, often called Point-Of-Use (POU) treatment is sometimes the most cost-effective option, especially in rural settings. POU systems are typically installed and monitored with support from local government agencies. In developing countries, governments may not have the capacity to provide support to household level arsenic removal systems, especially if a large number of households are affected. Private sector and NGO groups are more likely to have the grass-roots networks necessary to disseminate information and supply materials at the local level, though government and multinational agencies can play an important role in providing technical assistance to these groups.

Box 6.17: Point-of-use arsenic removal in the Southwestern US

San Ysidro is a small rural community of 200 people in central New Mexico. The local water supply draws on groundwater which contains leachate from geothermal waters, and exceeds maximum contaminant levels (MCLs) for arsenic, fluoride, iron, manganese, chloride, and total dissolved solids. When the water quality problem was discovered, source substitution was attempted, but deeper tubewells were also contaminated. Central treatment of water was not considered feasible for many reasons. After reviewing available treatment technologies, water supply engineers determined that reverse osmosis would be the most appropriate for the community. Accordingly, the village passed an ordinance which made the use of village water contingent upon installation of the reverse osmosis unit in the home, and 70 units were installed. Arsenic removal has been good, and other advantages have included easy installation, overall improvements in water quality, and relatively low cost. Disadvantages have included high sampling costs, training for new members of the community, and do-it-yourself plumbers.

Source: (Rogers, 1988)

POU technologies in industrialized countries have focused on technologies that require little or no operator input for extended periods of time: activated alumina, ion exchange resin, and membrane filtration. Coagulation and filtration have not traditionally been considered for household use, because the procedures require handling of hazardous chemicals. However, in developing countries advanced technologies may not be available, while materials required for coagulation (e.g. chlorine, permanganate, alum, ferric salts) are often locally available and inexpensive. Alum, particularly, is very inexpensive and is widely used in rural communities for water clarification. This last point is important, because people are often reluctant to add chemicals to drinking water - if the coagulant is locally known and accepted, this problem can be avoided. Because of these concerns, most household arsenic removal systems in developing countries have been based on coagulation and filtration. If coagulation and filtration are to be practiced at the household level for arsenic removal, system operators must be given solid training in chemical dosing and maintenance. Where alum is the coagulant of choice, an oxidation step will be necessary if arsenic is present in the form of arsenite. One major difficulty is ensuring the correct dosage: for small volumes of water, only trace amounts of the oxidant will be needed, and over-or under-dosing will have serious effects. It may be possible to minimize this risk by pre-packaging reagents.

Box 6.18: Household arsenic removal in Bangladesh (1)

A simple household removal system has been developed by the Bangladesh government with Danish support that relies on high doses (200 mg/L) of locally available alum as a coagulant. Potassium permanganate, also locally available, is used as an oxidant (1.5 mg/L). The two chemicals are mixed in powder form, and supplied to users, who add a fixed amount of the mixture to a 20-L plastic bucket full of water. The user stirs the mixture vigorously, and allows the water to settle for at least 4 hours. Water is then decanted into a second bucket, which is fitted with a coarse sand filter and tap. This system has been tested in affected households for over two years, and consistently reduces arsenic to less than 20 µg/L, even from influents of over 1000 µg/L. Over 400 households in the pilot area now use this system regularly. This system has the added benefit of removing iron and manganese from the groundwater, making the treated water aesthetically appealing to users. One challenge identified has been that users don’t always stir the coagulants as briskly or as long as recommended, resulting in relatively poor floc formation.

Box 6.19: Household arsenic removal in Argentina

The Pan American Center for Sanitary Engineering and Environmental Sciences (CEPIS) has developed a system for arsenic removal at the household level. CEPIS engineers have evaluated the efficiency of mixtures based on alum (called Alufloc) and ferric chloride (Ferrifloc). The mixtures also contain chlorine, to oxidize arsenite, and activated clays, which increase the surface area of the floc, allowing more area for sorption and coprecipitation of arsenic. The mixture is added to arsenic-rich water, stirred rapidly for one minute and slowly for fifteen minutes, and then allowed to settle for one hour. In laboratories, both materials have achieved from 95-98% removal of arsenic. Field testing of both mixtures was done in Salta, Argentina, on groundwater containing 300 µg/L arsenic. One important finding has been that when alum is used as the coagulant, filtration greatly improves arsenic removal.

Table 6.8: Field testing of Alufloc and Ferrifloc in Salta, Argentina

	Composition (mg/L)			% Arsenic removal	
	Activated	**Coagulant**	**Oxidant**	**Without**	**After**

	Clay		**($Ca(OCl)_2$)**	**filtration**	**filtration**
Alufloc	500	50	5	70	97
Ferrifloc	1000	60	5	94	94

CEPIS engineers found that when arsenic levels are below 1000 µg/L, Alufloc and Ferrifloc perform equally well. For more contaminated waters, Ferrifloc is more efficient. At lower concentrations, Alufloc is slightly preferable, since the mixture is less expensive, and more stable (Ferrifloc absorbs water from the atmosphere). Residual aluminum levels in waters treated with Alufloc were below the WHO guideline value (based on aesthetic concerns) of 0.2 mg/L.

Both mixtures come in double-compartment sachets, since it was found that when stored in single compartments, chlorine would react with clay and lose its strength rapidly. The double-compartment sachets remain stable for at least a year and a half. Each set of sachets can treat 20 liters of water, and costs US$0.22, though unit costs could decline to US$0.15 if produced in quantity. Alufloc is currently being pilot tested in three communities in rural Argentina.

Source: (Castro de Esparza and Wong de Medina, 1998)

Box 6.20: Household arsenic removal in Bangladesh (2)

In Bangladesh, researchers at Rajshahi University have taken advantage of the fact that HFO can adsorb both arsenite and arsenate. They have fitted a simple 100-L plastic tank with a tap a few inches from the bottom, and added pre-formed HFO (200 mg/L as $FeCl_3$). The tank is filled with contaminated water (~800 µg/L, mostly as arsenite) in the evening, settled overnight, and filtered through a coarse sand filter. The HFO can treat over a dozen batches before residual arsenic exceeds the drinking water standard of 50 µg/L. University workers visit the filters every two weeks to provide fresh HFO, and regenerate the spent HFO in laboratories.

6.7 Conclusions and continuing needs

In both developing and industrialized countries that have faced arsenic contamination of drinking water resources, source substitution, where possible, has been the preferred alternative. However, in some areas, arsenic removal may be a more practical, economically feasible strategy, at least for short-term supply of safe drinking water. Contaminated sources can still be safely used for purposes other than drinking and cooking, and should not be sealed unless safe water is conveniently available in the quantities required for all purposes.

Conventional systems for drinking water supply are well-documented, and those striving to develop safe sources of drinking water in areas affected by arsenic can turn to a rich library of manuals, texts, and journal articles, a selection of which are referenced above. Locally, research may be needed to determine what water resources are available, but once inventoried, conventional systems for water supply are relatively well understood.

The situation is slightly different regarding arsenic removal technologies. Some systems are fairly well documented. Conventional coagulation, notably, has been extensively reviewed in the literature in recent years. Arsenic removal under varying geochemical conditions has been investigated, and the effects of coagulant dose, influent arsenic concentration, pH, and the presence of competing co-solutes have been described in some detail. While some details, such as the mechanisms of arsenite adsorption onto HFO and effects of competition from phosphate, are not yet quantitatively documented, enough is known about the mechanisms of arsenic removal through coagulation to design effective removal systems, at least to reduce arsenic levels below 50 µg/L.

For the newly emerging technologies, such as semi-permeable membranes and various sorptive media, less is known about the effects of dose and pH, and even less about the effects of competing solutes. Global interest in improved methods of arsenic removal has led to a rich period of experimentation, in which novel sorbents have been essayed, and existing technologies for arsenic removal modified and/or combined to yield substantially different systems. These novel systems have typically been evaluated only by a handful of researchers, under a narrow range of environmental conditions, for short periods of time. In many cases advances in removal of arsenic, particularly of arsenite, has been demonstrated, but mechanisms are still poorly understood. Much more research needs to be conducted to identify those technologies that can effectively remove arsenic under real-world conditions, and consistently do so for extended periods of time.

Especially with regard to arsenic removal in rural settings, more research needs to be done on the safe handling and disposal of arsenic-rich wastes. Experiments in the US have shown that coagulant sludge is generally safe for disposal in municipal landfills. However, in developing countries sanitary landfills are usually nonexistent, and solid waste often ends up simply dumped into rubbish heaps. The stability of arsenic waste streams under such environmental conditions has not been investigated. Simple burial, biomethylation, and stabilization of wastes into cement or brick have all been proposed, but not thoroughly researched.

Numerous technical questions remain unanswered. Nonetheless, based on the technology available, it is certainly possible to design arsenic removal systems that can reduce even highly contaminated influents to below 50 µg/L. Centralized arsenic removal plants in various countries have proven that such plants can be effective under a wide range of environmental and economic conditions. However, the great majority of people exposed to arsenic in drinking water globally live in rural, generally poor areas, where centralized arsenic removal is not practicable. Arsenic mitigation interventions in these areas must make use of source substitution, decentralized arsenic removal, or a combination of both.

Experiences with decentralized arsenic mitigation remain scarce, and are generally limited to a handful of pilot studies that are heavily donor-dependent. Accordingly, there is a great need for operations research, to determine how the technologies (both conventional water supply and arsenic removal) described above can be effectively applied as arsenic mitigation interventions in rural settings. The limited experiences available indicate that effecting change in water use practices in arsenic-affected areas requires much more than telling users not to use a specific source. Affected communities are often ignorant both of the threat posed by arsenic in their water supply, and of potential sources of arsenic-free water. Until water users understand the problem of arsenic contamination and its impact on their health, and have reliable information about safe alternatives, they will be unwilling and unable to make an informed choice to change their water use patterns. The biggest challenges ahead lie in adapting the technologies described in this chapter for application in poor, rural settings, and in enabling those communities to choose safe sources of water for drinking and cooking.

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Chapter 7. Communication for Development

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Summary

There is limited information about attempts to communicate with families and communities about arsenic in drinking water supplies. Despite the global nature of the problem, little documentation exists about efforts in different countries to communicate with people about the risk to their health from arsenic. This chapter fills that void by providing a synthesis of the global experience to date.

The single largest communication initiative on arsenic comes from Bangladesh. A multi-media, multi-level communication strategy was launched by the national government, with UNICEF assistance, in four rural areas in late 1999. An initial evaluation indicates that the strategy is raising awareness and villagers are switching to safe sources of water. Until more results are available, the Bangladesh example offers communicators with some 'best practices' for designing and implementing a large-scale communication strategy.

Limited experiences from other countries, such as India, Argentina, Australia and the United States, also provide insights into ways of communicating effectively about the arsenic problem.

In addition to these examples, there is a rich and varied body of literature that documents the global experiences of public health communications. The chapter reviews case studies from Asia, Latin America and Africa on how communicators are addressing issues critical to people's health, such as sanitation and hygiene, reproductive health and HIV/AIDS. These experiences reflect a significant evolution in theory and approaches to changing people's behaviour that are relevant to communicators working on arsenic.

Principles for communicating about arsenic

Notions of how to communicate with families and communities about their health are changing in significant ways. The concept of communicating *to* someone is giving way to more democratic and egalitarian ideas of communicating *with* a person whose health is at risk.

Top-down health education models are being replaced with more participatory approaches. Communicators are using more rigorous methodologies to develop strategies. Some of the best practices from private sector advertising are being adopted for effective 'social marketing'. More fundamentally, there is a growing recognition that communication generally needs to address underlying conditions - socio-economic, cultural, legal and policy environments - that influence why people act the way they do.

A number of key principles (Jackson, 1997) derived from the global experience of public health communication can guide efforts to address the arsenic problem in various countries.

- ***Levels of knowledge can be raised, but may have little or no effect on behaviour****.*
In Bangladesh, a one-year project with Dutch funding to raise awareness about arsenic in six district towns did not achieve its hoped-for breakthrough in behavioural change. Fifty per cent of families who knew their tubewells were contaminated by arsenic continued to drink the water, despite access to new or safe sources (Hanchett *et al.*, 1999).

- ***Beliefs and values influence how people behave.*** The roots of people's beliefs and values are complex and multi-faceted. In Bangladesh, a belief that "I will/will not get sick from drinking arsenic affected water" could have several underlying beliefs. "It's the devil's water" or "Allah will decide whether I get sick" (Asiatic, 1999a) suggests a sense of fatalism. Likewise, the value a poor person puts on having a sanitary latrine, or sending a child to school, may be linked to perceptions of economic cost and benefit, or social status. Beliefs and values do not take place in a vacuum, but are shaped and respond to the context of people's lives. Fatalism, for example, often comes from a lack of viable options and a feeling of lack of control over one's life.

- ***A behaviour is likely to be repeated if the benefit is rewarding, and less likely if the experience is punishing or unpleasant.*** A pilot project in Argentina investigated a home-based solution to the arsenic problem by providing arsenic removal salts directly to poor families. Government sanitation workers followed up with house-to-house visits to show people how to use the salts and to emphasise the importance of changing their drinking water habits. The salts effectively lowered arsenic levels by 70 per cent. The success of this technology was due to its easy use in the home. This facilitated behavioural change in the short term (Rivero *et al.*, 1999). Unfortunately, the new behaviour could not be sustained because the supply of salts ended with the project.

- ***Individuals are not passive responders, but have a proactive role in the behaviour change process.*** Public health officials in the United States use advances in communication technology to interact directly with people affected by arsenic. Web pages and 'open meetings' on the Internet provides a forum for a two-way flow of information, letting people decide on their role in the communication process, ascribe meaning to messages and control the process of behaviour change.

- ***Social relations and social norms have a substantial and persistent influence on how people behave.*** Communication strategies targeting social groups (e.g., family, co-workers and youth clubs) may contribute to substantial and sustainable behavioural change. The stronger the affiliation with a group, the more responsive a person is to the group's norms. The national arsenic communication strategy in Bangladesh, for example, aims to leverage the influence of Muslim *imams* (religious leaders) to promote a norm of sharing arsenic-safe tubewell water (Asiatic, 1999b).

- ***Behaviour is not independent of context. People influence, and are influenced, by their physical and social environments.*** This principle emphasises that health behaviour is influenced by a vast array of biological, environmental, social, physical, spiritual, economic and regulatory factors. In the Indian state of West Bengal, strong resistance to an arsenic removal technology was overcome when villagers travelled to a nearby community to talk to their neighbours who had already adopted the innovation.

Managing the communication process - lessons from Bangladesh

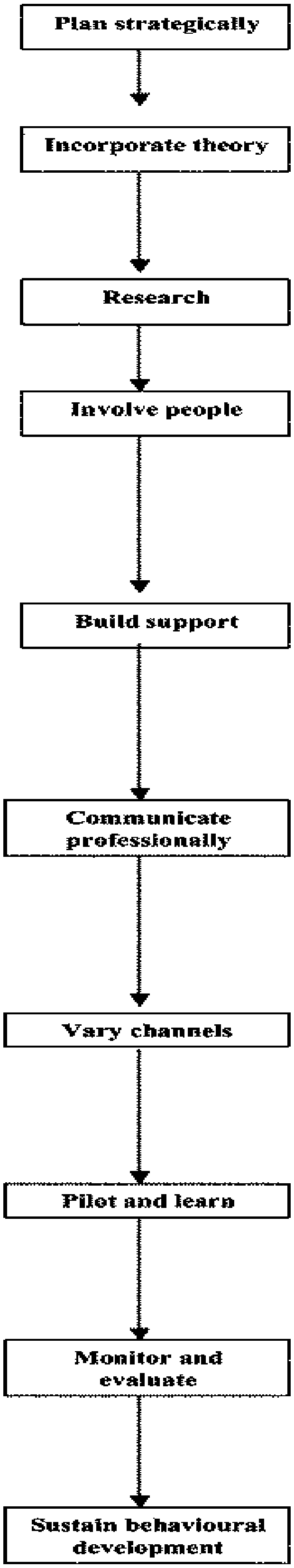
No single universal strategy exists for changing complex human behaviour. However, the experience of developing a national communication strategy for arsenic in Bangladesh provides some best practices for planning and managing processes of communicating about arsenic in drinking water supplies.

Up until 1998, relatively little communication work for arsenic had been done in Bangladesh. As a result, awareness was low, despite the severity of the problem. A baseline survey indicated that only 7 per cent of 1,839 people interviewed had heard of arsenic (OMQ, 1998).

There were also disagreements on what would be technically correct to communicate. Misinformation was a serious concern. A small working group of government scientists and technical advisors filled this void by reviewing the available literature and coming to a consensus on a set of 'technical parameters' to guide the communication strategy "see Annex 7.1".

These parameters ensured that the information communicated was technically accurate, leaving communicators free to get on with the work of deciding how best to communicate. The Bangladesh example helps to demonstrate the importance of ensuring that the information disseminated is accurate and consistent. Time and resources need to be invested in ensuring that the content of the communication passes the most stringent technical scrutiny.

The approach to developing a communication strategy on arsenic in Bangladesh is relevant to communicators in other countries. While the social, political, economic and technical context will be different, the following critical path can inform the development of an arsenic strategy.


Plan strategically
Incorporate theory
Research
Involve people
Build support
Communicate professionally
Vary channels
Pilot and learn
Monitor and evaluate
Sustain behavioural development

Figure

A number of conceptual models exist for planning communication strategies. The Bangladesh strategy adopted the ***ACADA planning process*** (assessment, communication analysis, programme design, action) used by UNICEF.

Communication and behavioural science theory provides communication planners with a framework for planning a strategy to change behaviour. In Bangladesh, ***diffusion theory*** was applied to identify the various stages large groups of people pass through in adopting a new behaviour and technology.

The communication process began with a rigorous investigation of ***knowledge, attitude and practice***. Rapid rural assessments, using standard qualitative methodologies, were used.

Participatory rural appraisal techniques were used to give villagers a voice in identifying their needs and solutions. This included mapping exercises to identify local resources and special meetings to try to include all the different groups in a village to determine how best to communicate about arsenic. The challenge in Bangladesh, as elsewhere, is to turn over communication processes and methods to local people, putting them at the core of communication analysis, planning and action. This approach relies on accountable and flexible institutions, considerable resources, trained facilitators and recognition that changing behaviour is a long-term process.

The Bangladesh example demonstrates that a ***broad, multi-sectoral approach*** to arsenic is needed for behavioural development and social change. The strategy included an advocacy plan to ensure high-level support from senior policy makers and politicians at the national and sub-national level. Social mobilisation at the grassroots complements advocacy by moving entire segments of a society towards the goal of drinking safe water.

UNICEF and the Government of Bangladesh engaged a ***full-service social marketing agency*** to produce and manage the communication strategy. This approach proved more efficient and cost-effective than hiring staff to provide specialised services in media production, media planning, research and strategy development. Creating one team to develop the campaign also ensured that all media and communication materials were consistent and mutually reinforcing.

Television and radio commercials were used to generate general awareness and support for the arsenic project in Bangladesh. However, ***interpersonal communication*** was the key to behaviour change. Communication tools were developed for health workers, NGO volunteers and tubewell testers coming into direct contact with the household.

Important lessons were learned in Bangladesh during the pilot phase in four *upazillas* (an administrative unit). The pilot highlighted problems in coordinating activities across various government departments, identified training gaps and confirmed acceptance of the various communication materials.

As the Bangladesh strategy is fully implemented, ongoing process monitoring will measure the responsiveness and efficiency of various government institutions to carry out the communication strategy. Qualitative and quantitative assessments at mid-term and the end of a communication strategy indicate whether the strategy is successful in changing behaviour.

Getting people to change their behaviour and maintain that new practice or attitude is the essential task of the communication strategy in Bangladesh. It will require a continual flow of new ideas and support. It will also require more targeted communication to those resisting change, or left out of the process. Communicators will need to upgrade their skills and capacity to move beyond raising awareness to working with communities and families in ways that support long-term behavioural development.

7.1 Introduction

There is limited information about attempts to communicate with families and communities about arsenic in drinking water supplies. Despite the global nature of the problem, little documentation exists about efforts in different countries to communicate with people about the risk to their health from arsenic. This chapter fills that void by providing a synthesis of the global experience to date.

The single largest communication initiative related to arsenic at present is in Bangladesh. A multi-media, multi-level communication strategy launched in 1999 with assistance from UNICEF aims to help people switch from arsenic-contaminated water to safer sources for drinking and cooking. Radio and television commercials are being aired for free by state-owned media outlets. Interpersonal communication and outdoor media are being used initially in limited areas as the project scales up.

The Bangladesh example, presented here as a case study, provides insight into some best practices for developing and managing complex processes of communicating about arsenic.

Other experiences from India, Argentina and the United States point to lessons on how to communicate effectively about arsenic. There is also a brief introduction to risk communication, an approach commonly used in developed countries to respond to critical environmental and public health problems.

These initiatives are augmented by the rich experience of public health communicators globally in managing processes of behavioural and social change. Experiences from Asia, Latin America and Africa in other fields, such as sanitation and hygiene, reproductive health and HIV/AIDS, provide important lessons to communicators working on arsenic.

The global experience in public health communication informs approaches on how best to communicate about arsenic. The chapter begins by examining communication within an historical context so as to understand the dramatic evolution in approaches and practices over the past several decades. The chapter then traces the evolution in theory and practice from its top-down origins to more popular models of participatory communication. Finally, experiences from the field - successes and failures - are presented. The reader will find that these broad themes and lessons are particularly relevant to communicators and policy makers in developing countries concerned about arsenic.

7.1.1 A brief historical overview

Notions of how we communicate with families and communities about their health are evolving in radical ways. The concept of communicating ***to*** someone is giving way to fundamentally more democratic and egalitarian ideas of communicating ***with*** a person whose health is at risk.

Fifty years ago, communication in the development sector was a simple, ***one-way flow*** of information from sender to receiver usually through the mass media. This approach reflected the norms of the modernisation paradigm that emphasised transferring technology and norms from the 'developed' to the 'developing'. By the 1960s, a ***two-step flow model*** emerged, recognising the importance of social networks and opinion leaders as go-betweens for the media.

A more influential model grew out of ***diffusion*** studies in the United States "see section 7.2.1". Diffusion theory suggests that people pass through a series of stages as they take up - or reject - a new idea or practice (Valente and Rogers, 1995). At least ten popular models of these 'stages of change' are in practice in communication today. Rogers (1995) suggests that people becomes aware, then concerned, acquire knowledge, are motivated, intend to act, try out the new behaviour, evaluate and then decide to keep up the new behaviour or not.

Communicators use diffusion as a planning tool in deciding which approaches and media to use - and at what stage - to encourage people to take up a new practice. In recent years, communicators have included more participatory techniques, in response to criticism that diffusion is a top-down, hierarchical approach to behavioural development (McKee, 1992).

By the mid-1970s, communication practice began to reflect wider shifts in global development. Top-down began to give way to the practice and rhetoric of ***participatory approaches***. Chambers (1994) and others wrote of the need for 'reversals' in development so that local people, especially the poor, could be active participants in their own development. Values that promoted a focus on income-poverty and economic development broadened to include social development and good government, eliminating poverty, and decentralisation and democracy (Singhal and Sthapitanonda, 1996). Making participation meaningful, however, has often proved elusive (Rahnema, 1992).

Participatory communication projects aim to 'empower' individuals and communities to take control of their lives. Information flows both ways between sender and receiver. Local beneficiaries are involved in designing the message and share in the responsibility of being the sender. Low cost technologies such as low-power VHF FM radio, camcorders, desk-top publishing and the Internet all open up opportunities for people to be in charge of their own communication. In the participatory model, communication is a process, not a series of products.

7.1.2 Some definitions

New acronyms and terms keep coming up to describe the evolution in methods and approaches to communication. These changes often reflect paradigm shifts in the development sector.

IEC refers to *information, education, communication* and is often associated with hierarchical, top-down approaches to development (Burgers, 1999). In contrast, many communication practitioners today advocate *behavioural change communication (BCC)*. ***BCC*** shifts the emphasis from making people aware to bringing about new attitudes and practice. BCC tries to understand people's situations and influences, develops messages that respond to these concerns and uses communication processes and media to persuade people to increase their knowledge and change risky behaviour (UNICEF, 1999b).

Social marketing is an approach to communication in the development sector that adapts some of the techniques used in commercial marketing. It relies on segmenting the market, 'consumer' research, concept development and the mass media in particular to bring about acceptance for a social idea, cause or practice (Berry, 1993).

Social mobilisation differs from social marketing because it aims to muster national and local support for a general goal or programme through a more open and uncontrolled process. It is often less concerned with attempting to bring about behavioural change by researching and communicating specific messages than it is with mobilising large segments of society to a goal (such as universal immunisation, literacy or family planning). The idea is to use as many channels as possible at an accelerated rate (McKee, 1992).

In practice, there is often not a clear division between these various approaches. Communicators often mix elements from each of these strategies. As a result, communication in the development sector is evolving into a multi-disciplinary mix of communication, sociology, anthropology, education, social marketing and social mobilisation.

7.1.3 Advances and challenges in communication

Communication is frequently taken to mean spreading information or generating media materials *ad hoc*. These approaches often lead to disappointing results. Empirical evidence shows that simply raising awareness can fail to make an impact on what people think and do (FHI, 1999, Seidel, 1992, Jackson 1997).

Measuring success is also a challenge. Communication and social mobilisation require considerable resources and a long-term view. There is usually no quick pay-off in terms of sustained behavioural change. As a result, the number of posters printed and radio commercials broadcast are often used as proxy indicators for whether communication strategies work or not (Chatterjee, 1999).

Many communication initiatives - particularly around behaviour change - attract support because they claim they can change something. In the field of HIV/AIDS, for example, much of the funding for communications initiatives has gone into attempts to change individual behaviours. Much of this work has had a substantial impact. However, some critics assert it has not sought to change the underlying factors that are driving a still escalating epidemic - poverty, social exclusion, prejudice and discrimination, migration and poor health systems (Gray-Felder and Deane, 1999; Airhihenbuwa *et al*., 1998).

Behavioural science and communication theories can play a useful role in the design and implementation of communication strategies (Jackson, 1997). Theory provides communicators with a conceptual framework for why people act the way they do and how best to respond. Yet many communication strategies often start without a firm theoretical footing (Witte, 1998). Strategies that are developed without a clear notion of why people act the way they do are unlikely to result in the desired change in attitudes and behaviour.

Despite these limitations, there are numerous examples from around the globe of successful strategies that promote good health and change behaviour “see section 7.3”. These experiences provide important insight into how best to develop an effective communication strategy.

All communicators, for example, agree that research on knowledge, attitude and practice (KAP) is an important preliminary step. Generating baseline data is equally important in allowing communicators to measure progress.

Communicators also rely increasingly on tools for participatory learning and research. Many also see the need to address gender issues as part of any communication strategy in an attempt to address inequity and inequality. Lessons from social marketing point to the importance of carefully segmenting a target audience and reaching people through a wide variety of media. In many communication strategies, social mobilisation is key to achieving certain goals.

7.1.4 Holistic approaches

These issues have led some communicators to look at more holistic approaches to communication. United Nations agencies, such as UNICEF and UNFPA in particular, emphasise a ‘rights-based’ approach to communication for development “see section 7.3.5”. Advocacy is an important approach in ensuring that universal declarations of human rights translate into services (UNICEF, 1999a).

Communicators are looking increasingly to integrate a gender perspective into communication strategies. This includes promoting and ensuring the participation of women and girls in all stages of a programme, including research and social analysis. It means moving away from a traditional approach where health and development messages are directed only to girls and women - ignoring roles and responsibilities of men and boys. Gender progressive communication also includes boys and men as communication audiences and participants. It builds consensus on root causes of gender inequality within a particular social context and tries to equip men and women with the tools and skills to advocate for structural change.

Communication for development is an amalgamation of the approaches mentioned so far. In practice, communication for development is a researched and planned process crucial for social transformation. It operates through three main strategies; *advocacy* to raise resources and political and social leadership commitment for development goals; *social mobilisation* to build partnerships and alliances with civil society organisations and the private sector; and *programme communication* for changes in knowledge, attitude and practice of participants in programmes.

Communication can play a central role in changing the behaviour of individuals and groups when combined with the development of appropriate *skills* and *capacities* and the provision of an *enabling environment*. Communication also plays a key role in *behavioural development*, a term used in this chapter to describe the process of putting a principal focus on children, encouraging early habits and attitudes that result in healthy behaviour (UNICEF, 1999b).

In summary, communication needs to be understood and used as a *process* - and not simply a collection of print materials, radio commercials and television ads - to change what people think and do (Chatterjee, 1999).

7.2 Strategies for communicating for development

7.2.1 Communication models

Communication professionals - and those working in public health in particular - are known for generating models to chart the process of behaviour change (Bowes, 1997). These various models reflect historical developments in approaches to communication. Some of these models, and the lessons they offer, are presented here.

Diffusion

In the 1940s, sociologists in the mid-west state of Iowa developed a theory to explain why farmers were reluctant to take up new hybrid corn varieties. The general picture was that farmers would only gradually give up their resistance to the new corn after talking with neighbours who were already satisfied 'adopters'. Diffusion studies have since laid the groundwork for a variety of behaviour change models across the social sector. Communicators find these models particularly useful in determining strategic approaches to large population groups (UNICEF, 1999a).

Diffusion is a process by which a new practice or behaviour gets communicated through certain channels over time among individuals and groups (Rogers, 1995). In theory, there are six types of groups. *Innovators* act on information they get through the media and peers outside their community. *Early adopters* act if convinced by the media and innovators that the new practice 'works'. *Early* and *late majority adopters* rely heavily on information from their peers "see box 7.1". Mass media and traditional media are also important in modelling new behaviour to this group. *Late acceptors* and *resistors* require extensive peer group education (Rogers, 1995 and UNICEF, 1999).

These groups move through different stages of change as people decide on a new behaviour or practice. Although there are several versions of these stages, the principle remains the same. People do not suddenly begin to do something they have never done before. They learn, weigh the benefits and see if anyone else is doing it. They acquire the skills needed for the new behaviour, apply it to their own lives and evaluate whether it is worthwhile continuing. They may reject the behaviour, or encourage others to follow their lead.

A basic notion of diffusion is that a new idea is adopted slowly during the early stages, builds steam and then flattens out again. When plotted over time, the rate of adoption is typically S-shaped as early adopters tell others about their experience and encourage them to take up the new practice. A critical mass builds and then levels off as fewer individuals or groups remain to adopt the behaviour (Backer *et al*, 1998). At each stage, experience shows that people need different kinds of information, emotional support and skills.

Box 7.1 Diffusing an arsenic removal technology in India

In 1998, a large non-governmental organisation in West Bengal, India initiated a pilot project to provide drinking water to 115 villages. Ram Krishna Mission Lok Shiksha Parishad (RKMLSP) developed a ‘demand-driven’ approach to try to heighten community ownership and responsibility for water supply schemes. Villagers were asked to participate in selecting appropriate technologies, contribute 30 per cent of capital costs and provide funds for operation and maintenance. This was in sharp contrast to several decades of government-led planning to provide drinking water to rural areas free of cost (Dey and Sengupta, 1999).

Twenty-six villages in two districts covered under the project had to contend with an additional challenge - arsenic in the groundwater supply. RKMLSP worked through an informal network of community organisations to generate awareness about the arsenic problem. A water and sanitation committee was established in each village to discuss various technological options to ensure an arsenic-safe supply of water for drinking and cooking. Domestic household filters and arsenic removal units attached to hand pump tubewells were new technologies put before the communities.

To diffuse this technology, RKMLSP organised a series of ‘awareness camps’ to bring villagers together to talk about arsenic. Scientists explained why the water was contaminated, while doctors gave graphic accounts of the effect on health. Water from various tubewells was tested. Contaminated wells were marked with a red ‘x’ as a visual prompt to villagers not to drink that water.

Discussions between the villagers and the NGO were intensive and time-consuming. At the outset of the project, RKMLSP projected that it would take approximately two to three months to create institutions in the village to take up the new arsenic technologies. In reality, this process often stretched into six months (DMC, 1999).

Some communities were reluctant to try the new technologies. In the Baruipur area, people responded negatively to the idea of attaching arsenic removal units to public tubewells. They complained that the capital outlay was too high and were suspicious that not everyone who used the tubewell would contribute to operation and maintenance costs.

RKMLSP overcame the resistance by bringing community leaders from Baruipur to neighbouring villages so that ‘early adopters’ could demonstrate the new technology and explain the arrangements for sharing costs. The treatment unit was also redesigned for Baruipur to make it smaller and cheaper. An independent evaluation concluded that modelling the new behaviour, and improving the cost, played a critical role in the decision by villagers in Baruipur to install 12 arsenic removal units (DMC, 1999).

Social learning models

Health Belief Model

According the health belief model, two main factors are likely to influence whether an individual will adopt a particular behaviour to protect his or her health. One, they have to feel personally susceptible to the disease. There has to be a perception of ***risk***. Second, the person must believe that the recommended action will be ***effective*** in reducing the perceived risk and that the benefits outweigh the costs of not acting (Rhodes and Fishbein, 1997). The health belief model identifies certain barriers that influence health behaviours. Barriers may be thought of as psychological (e.g., embarrassment), structural (e.g., lack of transportation, lack of access), or financial (Witte, 1998).

Theory of Reasoned Action

This theory says ***intention*** is the primary determinant of behaviour. A person's intention to perform a particular behaviour is a function of two determinants. First, there is the person's attitude towards performing the behaviour. Attitudes are shaped by beliefs about the consequences of performing the behaviour, such as the cost and benefits of taking preventive action. Secondly, intention is influenced by social, or normative, pressure. This theory suggests that communication is usually more successful when it focuses on specific behaviours ("don't drink water from this red marked tubewell") rather than broader categories of behaviour ("always drink safe water").

Social learning theory

Social learning theory proposes that two key factors influence behaviour. A person must believe the benefits outweigh the costs. More importantly, the person must have a sense of personal agency, or ***self-efficacy*** (Bandura 1995). A person with a developed sense of self-efficacy holds strong convictions that he or she has the skill and abilities to act consistently to protect his or her health, despite various obstacles.

Self-efficacy builds when people set goals, monitor their behaviour and enlist incentives and social support. Bandura's research shows that if people are not convinced of their personal efficacy, they rapidly abandon the skills they have been taught when they fail to get quick results.

Another central concept is that individuals can acquire cognitive skills and new patterns of behaviour ***vicariously*** by observing others. Bandura emphasises the power of mass media, particularly television, in creating a 'symbolic environment' in which new ideas and social practices are rapidly diffused within and between societies.

Box 7.2 Putting theory to work in Kenya - the case against fear tactics

An example from Kenya helps to demonstrate the limitations of using fear to promote behavioural change. Witte *et al.* (1998) applied behavioural theory to evaluate the effectiveness of 16 different HIV/AIDS communication campaigns at various sites along the Trans-Africa Highway in Kenya. The investigators looked at the different strategies for ***threat*** and ***efficacy***.

Threat was used to make the target group feel susceptible to risk. If the threat was perceived as serious, investigators wanted to know whether people would take action to protect their health. Their response was evaluated in terms of self-efficacy ("Am I able to protect myself from HIV infection?") and response-efficacy ("Does wearing a condom protect me from HIV?").

The evaluation found that none of the materials promoted threat and efficacy at the same time. The study concluded that a communication strategy could fail when people perceive the threat to be trivial and/or not pertinent to them. In the Kenyan case, some materials simply drew no reaction from the audience.

Where it generated fear, the study found that people were not left with a sense that they could action to protect their health. Respondents felt unable to perform a recommended action ("I cannot bring up the issue of condoms with my partner") or believed the response would be ineffective ("Condoms don't work; they have holes in them"). They then gave up trying to control the danger. Instead, some controlled their fear by denying the risk of infection, defensively avoid the issue, or perceive manipulation ("AIDS is a hoax; it's really a government plot") (Witte *et al.*, 1998). Theory in this case helped to demonstrate that a fear-based communication strategy fails when it triggers fear control processes.

Process model

The 'process model' is a straightforward, linear path of health education. It was first adopted in the 1980s in rural Honduras to promote oral rehydration therapy, using an extensive print, broadcast and interpersonal communication campaign. Process models focus on education, how people learn and social marketing. The main difference from learning models is that process models focus on specific communication inputs and learning, rather than a person's motivational state and perceived self-efficacy. Process models also stress assessments at several points in a campaign to make sure there is a fit between the message and the information people need to change their behaviour (Bowes, 1997).

PRECEDE model

PRECEDE (Predisposing, Reinforcing, Enabling Causes in Educational Diagnosis) shifts the focus from messages, media and audience to the social, political, organisational and regulatory issues that affect public health. It uses a complex scheme moving backwards through six phases to get at the root causes of a health problem. Social and epidemiological outcomes are traced back to behaviour, which in turn are traced back to social, educational and administrative roots. Health education is divided into three components: targeting individuals, health workers and the community (Bowes, 1997).

Risk communication

Risk communication is a term frequently used in 'developed' countries to describe the process of communicating with people about risk factors associated with industrial technologies, natural hazards and human activities. It adheres to many of the same principles of behavioural change described in this chapter.

However, strategic approaches frequently differ given the wide disparity between 'developed' and 'developing' countries in terms of people's access to media, levels of education and media literacy, socio-economic profiles, institutional norms and structural issues. Risk communication relies heavily on the mass media, public relations and interactive communication technologies, such as the Internet, to create an informed dialogue with the public to identify and avoid risk (ATSDR, 1999).

Risk communication is part of the wider discipline of *risk management*, which strives for some *quantitative* expression of hazard and the exposure of different populations. This is then summed up in a calculated probability for various outcomes and relative risk trade-offs. Yet, the public often uses different, and legitimate, criteria to evaluate the same facts. The response is usually *qualitative*: “Is this safe to do, yes or no?” “Will my children be harmed if they are exposed to this?” “What a horrible way to die.” (Leiss, 1999).

Under certain circumstances, for example, some expert assessors may regard low-level exposure to a known carcinogen as an insignificant threat to public health. The public’s perception of the meaning of this information could be quite different. Risk communication looks to bridge not only the communication gap, but the gap in credibility as well. This credibility often depends on how risk communicators ‘frame’ information.

Slovic (1997) argues that risk communication only gains legitimacy and acceptance if the public is actively involved in the assessment and risk decision-making.

7.2.2 Principles to guide communication

A number of key principles derived from the global experience of public health communication can guide efforts to address the arsenic problem in various countries. These principles (Jackson, 1997) are useful in amalgamating theory with practice.

· ***Developing new behaviours is a process, not an event. Learning often requires repeated attempts at the desired behaviour.*** This principle underscores the importance of setting specific objectives for behavioural development. Change will be gradual. Individuals will move at different paces and should set their own goals. Communication strategies need to keep in step with people’s intention to act and provide the proper inputs to create an enabling environment for change. Empirical evidence shows that simply raising awareness will not lead to long-term behavioural change. Sustaining behaviour change - moving from awareness to action to long-term behavioural maintenance - requires ongoing and systematic approaches to communication.

· ***Beliefs and values influence how people behave.*** Beliefs involve how people think about consequences or what is likely to happen. Values are qualitative judgements about outcomes or events. Strategies to target beliefs need to address risk, self-efficacy and perceived social norms. Perceptions of benefits, costs and social relevance all target values. There are likely to be a multitude of beliefs and values under the belief and value of primary interest. For example, the belief that “I am not likely to get sick from drinking arsenic affected water” could have several underlying beliefs: “Only old people get sick” and “It’s in God’s hands whether I get sick” (Asiatic, 1999a).

· ***A behaviour is likely to be repeated if the benefit is rewarding; it is less likely if the experience is punishing or unpleasant***. Communicators must not assume that people are content to change their behaviour. Collecting water from a new, but distant source because it is arsenic-free will result in more drudgery for women in Bangladesh (Asiatic, 1999a). Communicating the perceived benefits needs to precede or accompany mitigation activities. Behaviour can also be reinforced through the experience of personal control, success and social recognition.

· ***Individuals are not passive responders, but have an active role in the behaviour change process.*** Fundamentally, it is people, not health educators, who control the process of change. They decide to take part in communication activities. People assign meaning to messages. They evaluate their experience with new behaviour. The implication of this principle is that effective strategies for behavioural development are deeply rooted in research of existing knowledge, attitude and practices (UNICEF, 1999). Community participation is key to this communication process. It relies on dialogue, consultation with and empowerment of people in a community to identify and decide how best to overcome the problems. In 1993, CARE Bangladesh launched a nine-month pilot project to improve hygiene behaviour in 9,100 households. The project relied on intensive interpersonal communication using innovative games, stories and songs developed with villagers, based on their beliefs and practices. The number of interventions was kept small, involving all family members. At the end of the project, diarrhoea prevalence had dropped by two thirds and dramatic improvements were reported in proper hand washing and safe disposal of children's faeces (Bateman, 1995).

· ***Social relations and social norms have a substantial and persistent influence on how people behave.*** These norms extend from individuals to social groups (e.g., family, work group, club). The stronger the affiliation with a group, the more responsive a person is to the group's norms. Communication strategies targeting social groups may achieve substantial and sustainable behavioural change. The national arsenic communication strategy in Bangladesh leverages the influence of religious leaders to promote a norm of sharing arsenic-safe tubewell water (Asiatic, 1999b).

· ***Behaviour is not independent of the context in which it occurs. People influence, and are influenced, by their physical and social environments.*** This principle emphasises that health behaviour is influenced by a vast array of biological, environmental, social, physical, spiritual, economic and regulatory factors. Existing theories and models commonly ignore this context and focus on the individual. Evaluations of HIV/AIDS campaigns in Africa, Asia and Latin America suggest communication strategies to change individual behaviour without addressing these wider issues are inadequate to promote behavioural development (Airhihenbuwa *et al.*, 1998). Social mobilisation and advocacy are key interventions to widen the acceptance for new norms and values, creating an environment for individuals to make healthy choices.

7.3 Strategies in action

Programme communication, advocacy and social mobilisation are key strategies in communication for development. This section reviews some of the global experiences of communicators. Where possible, reference is made to field experiences about arsenic communication. The global experience on other key public health issues, such as reproductive health, HIV/AIDS and sanitation, are presented.

7.3.1 Programme communication - strategies for arsenic & HIV/AIDS

Arsenic

In mid-1998, the Government of Bangladesh and a consortium of Dutch consulting firms launched a limited public information campaign in six district towns to tell people about arsenic in the drinking water supply. Most people in the town were using hand pump tubewells, drawing water from 'shallow' aquifers contaminated by high levels of arsenic.

While there was a wide variation in the extent of contamination, the project estimated that some 150,000 people were at risk of chronic arsenic poisoning from drinking from tubewells (Hanchett *et al.*, 1999). Tubewells were marked red (unsafe) and green (safe) based on the results of a field test. Local women were recruited and trained to communicate with users on the importance of drinking water safe from arsenic.

By 1999, the project launched a more ambitious and intensive series of ‘arsenic weeks’ to mobilise key influential people and to broaden the reach of communication. Some 30 primary school teachers, community leaders and influential residents from each town were brought together to learn about the arsenic problem, ask questions and consider options. Groups of approximately 50 caretakers responsible for tubewells installed as part of the project in each town were mobilised. They were trained during two half-day workshops on how to communicate with water users about arsenic. Up to 500 people in each town turned out for open meetings. Primary school children were given colourful stickers with simple messages about the need to drink water only from a green-marked tubewell (van Agthoven *et al.*, 1999).

A survey showed that the strategy did raise awareness. Almost two-thirds of the population reported having had some exposure to the campaign. 80 per cent of these people could explain the meaning of the colour coding on tubewells. Those who had not been reached by the communication activities were more likely to drink unsafe water.

Raising awareness, however, was not sufficient to bring about the hoped-for changes in behaviour. Six months after the campaign ended, more than 50 per cent of those who knew the meaning of red-marked tubewells continued to drink that water despite the health risk (Hanchett *et al.*, 1999). The evaluation highlighted the difficulty in changing firmly entrenched behaviour. Not only were the arsenic-related messages unfamiliar, they also contradicted more than a decade of government and non-government communication efforts promoting tubewell water as safe to drink.

The evaluation revealed other problems. Paint faded over time, leaving people confused about which tubewells were safe and which were not. Some people confused the colours, especially children and poorly educated women. The situation was aggravated by long queues at ‘safe’ tubewells, leading to flare-ups and arguments over shared facilities.

Some of these issues are programmatic in nature. A better paint would address the fading problem, while more water points would address the lack of supply. However, the Bangladesh experience also demonstrates the importance of a more systematic and comprehensive approach to communication. The interventions in the towns were limited, with few communication materials, inadequate levels of interpersonal communication and no reinforcing mass media. Importantly, the communication strategy was not designed to address the wider socio-economic and cultural context that plays a critical role in behaviour change.

HIV/AIDS

The experience of AIDSCAP, the most ambitious international HIV/AIDS project to date, provides insight into the need for strategic and comprehensive approaches to communication. AIDSCAP was implemented by Family Health International and its partners in 45 countries between 1991 and 1997. Funding was provided by USAID.

The project supported the production and dissemination of some 5.8 million pieces of communication material, including printed items, advertisements, copies of videos, dramas, television and radio programmes. These materials reached almost 19 million people.

Evaluations of AIDSCAP projects in 19 countries suggest that behaviour change communication can have a significant impact on what people think and do. In Cameroon, the number of male students who reported having more than one sex partner dropped from 53 to 36 per cent in three years. 62 per cent of sex workers in the AIDSCAP intervention area in Nepal reported using condoms with their most recent client in 1996 -up from 35 per cent in 1994. Condom use among sex workers outside the project area actually decreased. In Jamaica, the majority of the population now reports some kind of behaviour change to avoid HIV (FHI, 1999).

Certain time-tested elements of health communication remain the foundation of behaviour change communication for HIV/AIDS prevention - and are equally applicable to communicating about arsenic. These include identifying and segmenting target audiences, using multiple communication channels and involving target audiences in developing materials and messages.

Through technical assistance, training and distribution of a series of handbooks, the project promoted a shift from the top-down IEC model to a more systematic approach that gives people the knowledge, skills, encouragement and support they need for HIV risk reduction. Communication specialists working in HIV/AIDS have begun to broaden their approach to address the social, political and environmental factors that influence risk behaviour. Experience with HIV/AIDS has made it clear that an individual can rarely sustain a change in behaviour without a supportive environment. The project offers some important lessons to communicators about arsenic:

· In addition to encouraging individual behaviour change, programme communication can create environmental conditions to make it easier for people to reduce their risk. A carefully designed information campaign targeted businesses, religious leaders and the media to secure their backing for a more supportive environment for Jamaicans to discuss safe sex.

· Contracting out communication services to local social marketing agencies and communication consultants can be more cost effective than training project staff in specialised communication skills.

· AIDSCAP used a ‘stages of change’ model to plan communication activities. In this construct, people go from being aware of a risk, to getting motivated, trying a new behaviour and then adopting it full-time (or not). A study in eight countries showed that planners using the model could design specific interventions most suited to where people were on the continuum.

· Peer counsellors and grassroots communicators need to upgrade their skills continually in order to be effective. A study in 21 countries showed that as people moved past the awareness stage, counsellors did not have the skills to promote behaviour change and maintenance. An effective communication strategy on arsenic needs to anticipate this evolution in training needs.

7.3.2 Social mobilisation - Latin America and South Asia

Social mobilisation attempts to bring together a wide coalition around a particular goal. Citizens, communities, various groups and institutions are all encouraged to rally behind a specific cause, such as universal sanitation coverage, children's immunisation or food-for-all.

A social mobilisation campaign to encourage breastfeeding in Brazil in the mid-1980s targeted mothers as well as health services, the infant food industry, employers, decision-makers and local communities. An evaluation revealed a dramatic increase in the duration of breastfeeding in Greater Sao Paulo and a reduction in infant mortality due to diarrhoea and other infections (McKee, 1992).

The best-planned communication strategy can have little impact if there are problems with the project itself. An example from Bangladesh demonstrates the point. Between 1972 - 1997, various donors contributed some US$ 175 million for a rural water supply and sanitation programme in rural Bangladesh. In addition to sinking tubewells and building latrines, the project relied on social mobilisation to promote behavioural change. The aim was to generate demand for latrines, change people's hygiene practices and to promote the safe use of water. Communication materials were developed and public sector and NGO workers were trained to mobilise villagers at the grassroots level. The strategy included community planning and building local political support (Danida, 1999).

The results were limited. An evaluation shows that one fourth of latrines in use were not sanitary, adding to environmental pollution. People's practices and understanding of personal hygiene remained poor. Hand washing after defecation was not followed assiduously. Bathing in polluted pond water continued. People persisted in the belief that children's faeces was not harmful and did not dispose of the waste safely A number of factors undermined the efforts at social mobilisation. The impact of training tubewell mechanics to carry out social mobilisation was limited because of their low education levels. At the same time, more qualified government workers, NGO staff, local leaders, schoolteachers and *imams* trained for mobilisation lacked the necessary incentives and professional dedication to disseminate health and hygiene messages. Supply was an issue. While the numbers of private latrine producers did increase, sales centres remained far away from most villages, driving costs up and buyer interest down.

Strategies to address institutional issues could have been strengthened. Mobilisers often lacked the skills or means to motivate local politicians mostly concerned with rent seeking and getting votes. The government department responsible for the project also failed to recruit staff quickly or to set up management structures to monitor and coordinate the work (Danida, 1999).

Overall, evaluators found that the project needed more effective strategies to target the poorest people in a community and to address gender inequities. Decisions on where to situate a tubewell fell to the most rich and influential. Public tubewells often ended up away from the homes of poor people and closer to those already well served. While communicators were delivering the correct message, there was not a supportive environment for people to make choices that could protect their health.

7.3.3 Social marketing - getting the right media mix in Bolivia

Fertility and infant mortality rates in Bolivia are among the highest in Latin America. In 1990, the government launched a national reproductive health programme to promote healthy reproductive practices, improve services and increase acceptance for modern family planning methods. Health communication was a key programme strategy.

In 1994, the government launched an intensive mass media campaign directed at four major cities. More than 40 radio and 11 television commercials were aired over seven months and rebroadcast a year and a half later. Posters, videos for health clinics and a comprehensive set of print materials for health workers to discuss with clients were prepared. The major campaign themes were “Reproductive health is in your hands”, “Get information and services where you see this (programme) logo” and “You decide when and how many children to have” (Valente et al., 1996). The strategy promoted birth spacing, family planning, pre and postnatal care, breastfeeding and prevention of unsafe abortions.

An impact survey showed that overall exposure to the campaign, and recall of messages, was high. Practically all Bolivians in urban areas reported being aware of some aspect of the campaign. There were also significant changes in behaviour. Family planning use reported by those highly exposed to the campaign increased by 61 per cent. Misunderstanding about the details of specific family planning methods did persist and the evaluation showed more research was needed on how partners communicate with each other on family planning.

Many scholars argue that the mass media are effective at disseminating information, but that interpersonal communication is necessary for behaviour change. Many communication projects use mass media to advertise new ideas and products, and rely on outreach and peer education programmes for adoption (Berry, 1993; McKee, 1992; Seidel, 1992). Similar principles were applied in deciding what channels to use in the Bolivian campaign. Mass media would raise awareness and knowledge, change attitudes and encourage people to act. Interpersonal communication and detailed family planning use would push people to the next step of changing their behaviour. The efficacy of mass media and interpersonal communication also depends on the quality of the content, treatment and dissemination.

An evaluation of the campaign (Valente and Saba, 1998) looked closely at the relative importance of mass media and interpersonal relations. The results support prior research that shows the mass media influence the information-related steps to behaviour change. At the same time, people’s exposure to personal networks (including friends, community leaders and health professionals) was associated with all steps to behaviour change.

7.3.4 Advocacy - reproductive rights

Advocacy, in its broadest sense, is an effective way to use information to bring issues and problems into the public domain for discussion and action. The first task of advocacy often is to raise awareness in general, yet its ultimate objective is to spark action - either from decision-makers or their constituents (UNICEF, 1999a).

Advocacy requires gathering, organising and formulating information into argument and then communicating that through various interpersonal and media channels to political and social leaders. The aim is to gain commitment and active support for a development objective and prepare society for its acceptance over the long-term.

Many United Nations and other development agencies frame development and communication objectives within a human rights context. They use advocacy tools to raise awareness generally, bring about policy change and to mobilise resources. International Plan Parenthood (IPPF)'s global field experiences with advocacy demonstrate some of these strategies in action.

IPPF's Charter on Reproductive Rights is based on the legal framework of CRC and CEDAW. It reiterates the extent to which sexual and reproductive rights are already recognised as human rights. It looks to ensure more choice in health services as a key strategy in fulfilling rights and to increase the capacity of NGOs to monitor and ensure the fulfilment of these rights (UNICEF, 1999b).

Hungary, Lithuania, Bulgaria, Russia, Latvia and Slovakia have used the Charter as a background reference for input into draft legislation on reproductive health and sex education. China, Korea, Thailand, Vanuatu and Tonga have translated the Charter into their own language. Following advocacy from IPPF, the medical associations of Kenya and Tanzania have requested copies of the Charter for their members as part of a campaign on medical ethics. Family planning advocates in Colombia, Palestine and Senegal now offer legal services related to the Charter.

Rights-based advocacy is a time-consuming process, often complicated by the gap between the international discourse and the context of national and local realities. The legal terminology used in international rights conventions and how local people talk about their own lives are often at odds. More fundamentally, Western constructions of individual human rights can conflict with notions of community and collective interests in developing countries (Blanchet, 1995).

7.3.5 Advances in communication technologies - Australia and the U.S.

Advances in technology are changing the shape and form of how communication, particularly in developing countries. The idea of the community as a physical place is shifting in favour of "virtual" communities (Bowes, 1997). The development and spread of interactive, computer-based media have removed some of the geographical constraints of traditional broadcast and print media. The Internet and direct broadcast satellites are leapfrogging structural and social barriers to communication.

Government agencies are capitalising on the growing access to the newer technologies to communicate about arsenic in drinking water supplies. Examples from the United States and Australia provide just two of a multitude of web sites developing in response to the public's demand for information about arsenic.

Health officials in Australia use the Internet as one component in a larger strategy to communicate publicly about the risk to health from arsenic in mine tailings (http://www.hna.ffh.vic.gov.au). Government web sites provide information for 'question and answer' sessions, newsletters, press releases and policy announcements. In 1998, this was supplemented by a series of community forums in five centres to bring together government experts and community people to discuss the problem. No evaluation of the impact this approach is available.

Recent studies from Minnesota indicate the cancer risk from arsenic in drinking water is similar to the cancer risk from indoor radon and tobacco smoke. Updates on the impact on health are regularly posted on the state health department's web site (http://www.health.state.mn.us), along with consumer confidence reports, results of public hearings and health profiles.

These technologies are yet to make the same inroads in developing countries. Lack of infrastructure, costs, media literacy, perceived utility, as well as class, age and gender biases, hinder the rapid diffusion of new ways of communicating. Yet even this is changing because of the interlocking forces of media liberalisation and deregulation, as well as a changing global political and economic context.

Box 7.3 Communicating with children

A vast array of literature points to the importance of early childhood care and development. Empirical evidence shows that child development begins well before birth and is influenced by a myriad of cognitive, physical, psycho-social, environmental and cultural forces from conception to adolescence (Berk, 1994).

Certain principles adopted from Foster (1998) and Kolucki (1998) provide a useful guide to communicators working with children on public health issues. All children have a right to participate in communication strategies that impact on their lives. These can include child-to-child strategies and media especially for children.

The following principles and guidelines derive from research and experience, the *Convention on the Rights of the Child* (CRC) and what children themselves have taught communicators.

· Physical health, intellectual achievement, social skills and emotional well-being all work together in child development. These factors are ***interdependent***. The most healthful child-rearing style balances high expectations with high responsiveness to the child's needs. These children come to know their parents believe in them and will guide them away from harm. Children also know that their parents will respond sensitively to their problems.

· Communication for, by and about children needs to ***model positive behaviour***. This is less confusing to a child than portraying a negative behaviour and telling not to do it. Child-to-child communication can portray younger children learning from older children and vice versa.

· It is important to discuss and challenge ***gender stereotyping***. Communication also needs to challenge stereotypes of class, ethnicity, disability and religion.

· Children need praise, encouragement and respect for their own unique temperaments, challenges and talents. Children with disabilities, in particular, need to be presented in the media as equal partners in societies, as opposed to hapless victims. Children's communication needs to promote ***self-esteem***.

· An enriched, stimulating home environment, school or care centre significantly improves a child's intellectual, physical, social and emotional development, especially when provided from birth onwards. Children's media needs to be as ***interactive*** as possible, encouraging learning, questioning and experimentation. Self-efficacy develops by letting children tell their own stories, through their own voices and in the development of their own media.

· Children's ***play*** provides the brain with the best foundation for all future learning and relationships. Children's communication needs to promote learning through play, instead of rigid or rote learning.

Child development is relevant to communicators working on arsenic in drinking water supplies for two reasons. It is a principle of development communication that children have a right to participate in communication activities affecting their health. Children are not invisible or passive recipients of information.

A focus on children in arsenic communication strategies is a long-term investment in healthy living and processes of social change. Children are often more enthusiastic consumers of information than adults, willing to try new practices and engage in activities that form good health habits (UNICEF, 1996).

7.4 Communicating about arsenic: a case study from Bangladesh

The Government of Bangladesh (GOB), with assistance from UNICEF, launched a comprehensive multi-media, multi-level communication strategy on arsenic in December 1999. The nature, origin and scale of the arsenic problem in Bangladesh are arguably unique in a global context. However, an approach to communicating about arsenic in that country can offer some lessons to other communicators dealing with arsenic in drinking water supplies.

7.4.1 Method of building a strategy

For many years, UNICEF used the Triple-A steps of assessment, analysis and action to plan and implement programmes. This familiar model was recently expanded to **ACADA** - **a**ssessment, **c**ommunication **a**nalysis, programme **d**esign and **a**ction (UNICEF, 1999a) and was used as a methodology to guide the design and implementation of the arsenic communication strategy in Bangladesh.

Assessment

Assessment refers to the research stage required in any communication strategy. In spite of the severity of the problem in Bangladesh, awareness about the arsenic problem was low. A 1998 baseline survey indicated that only 7 per cent of 1,839 women interviewed had heard of arsenic - 5 per cent in rural areas and 20 per cent in urban areas (OMQ, 1998). Only four per cent of respondents in another survey knew that it was important to drink from sources safe from arsenic in order not to get sick (Mitra and Associates, 1998).

A report by a social marketing agency based on group discussions and interviews among about 700 respondents (representing a wide variety of target groups) provided further insights into the challenges of communication.

· While there are wide variations in what people knew about arsenic contamination and its consequences on health, awareness levels were very low.

· The level of awareness was relatively higher in those areas where some arsenic mitigation activities had been conducted.

· The predisposition to behaviour change was relatively higher in those areas where there were known cases of arsenicosis.

· The differentiation between pathogen free and arsenic free water was not clearly understood.

· There was a general resistance to change water consumption and water management behaviour (Asiatic, 1999b).

The assessment stage also included an important step that was unique in the Bangladesh context. Up until 1998, relatively little communication work had been done on arsenic. As a result, there was little agreement on what would be technically correct to communicate. Misinformation was a serious concern. A small working group of government scientists and technical advisors filled this void by reviewing the available literature and coming to a consensus on a set of 'technical parameters' to guide the communication strategy "see Annex 7.1". These parameters ensured that the information communicated was technically accurate, leaving communicators free to get on with the work of deciding how best to communicate.

Communication analysis

The research findings had significant implications for the communication strategy. A series of exercises for a *communication analysis* identified key objectives for desirable behaviour, audiences to target and involve, appropriate strategies and the most effective communication channels.

A 'changeability grid' was used to identify behaviours along four parameters. Behaviours that were important from a health and social perspective - and easily changed - were considered the first priority. Important behaviours but less easily changed were the second priority. Less important and easily changed, and less important and less easily changed, were priorities three and four respectively. Strategic communication objectives followed from this exercise (Asiatic, 1999b).

In areas most affected, the priority was to convince people most at risk to collect their water for drinking and cooking from a safe source. The key shift in behaviour was for villagers to share water from tested and safe tubewells. Sharing water was portrayed in communication material as a short-term, emergency response to the problem. This was complemented by communication that promoted a longer-term response - informing people about the need to convert to new, safe sources of water, such as pond water filtered through roughing media and sand.

Resistance was evident. Two decades of successfully communicating that tubewell water was safe needed to be unravelled. The research exercise revealed gaps in credibility that needed to be filled: 'First you tell us to give up our pond water because it was polluted. Now you are telling us the tubewell water is not fit to drink. Why should we believe what you say next?'.

In affected areas, villagers - particularly women - needed to be more involved in choosing alternate water supply sources. Men and boys had to share in the extra workload. Each of these communication objectives was addressed within the socioeconomic dynamic of rural Bangladesh where women's mobility is often restricted and the gender division of labour excuses men from water collection. Unresponsive and hierarchical government systems are yet to be decentralised in ways that are accountable to villagers. Literacy rates and media access are lowest for those most at risk.

Communication planners in Bangladesh adapted diffusion theory as a conceptual framework for the strategy. Five stages of change were identified. The preliminary stages were to be addressed during the first year and a half of the communication campaign.

In this first phase, communication would provide input to address the general lack of knowledge. Those who were aware, but complacent, would be targeted with communication designed to penetrate indifference by highlighting the risk to health. The strategy would also address the needs of villagers concerned about the problem, but unable to act because of socio-cultural barriers. Communication targeted local politicians and community leaders to motivate them to provide solutions for people unable to access a safe source of water.

A mid-course review will reveal what communication activities are needed to address the final two stages of behavioural change. Diffusion theory recognises that late acceptors or resistors need special attention to bring about behavioural change. The positive experience of people who have accepted new drinking habits and water management will be modelled to those still drinking arsenic contaminated water. More intensive interpersonal communication will also address specific gaps in information that will be identified through ongoing research activities. Maintaining behavioural change will rely on a constant flow of information that reinforces new practice.

Programme design

A social marketing agency was selected through a competitive bidding process to produce the strategy. Standard practices for pre-selecting, contracting and working with an agency were followed (Gill and Galway, 1999; Greenberg, R. *et al*., 1996). Rigorous evaluation tools were used to pre-test communication materials for comprehension, appeal, ability to create intent to act and perceptions of efficacy. Exit interviews with some 400 participants in focus groups in six districts revealed no gross negatives in the materials. Simple recall tests showed that people understood and remembered information (RCS, 1999).

The communication *programme design* for the first phase of the strategy called for an extensive multi-media campaign to target a national audience to raise awareness generally. Radio, television and print media presented information in a neutral, non-sensational manner to avoid generating fear or over-stimulating demand for services not yet available across the country.

The mass media campaign addressed the credibility gap by using spokespersons deemed reliable and believable to a rural audience. Public services announcements were built around teachers, religious leaders and health workers, using a factual approach to reassure viewers and listeners that the situation was serious, but that people could take certain steps to protect their health. Television commercials also modelled gender progressive behaviour, with men taking on a greater role in the household to collect and manage water.

A different approach was adopted in areas where there was a programme in place to test all wells, ensure an alternate safe water source and provide appropriate health care. Communication was initially limited to four rural areas in the pilot phase. Interpersonal communication materials were more graphic and pictorial in presenting the impact on health, while providing information about what people could do to protect their health. The same credible spokespersons used in the mass media were carried through to communication materials used in face-to-face meetings. For example, *imams* in this predominantly Muslim country were enrolled to institute a social norm to share safe water as an auspicious act during their call for prayers and sermons.

Access to women in the home was, and remains, a significant barrier. Grassroots level health workers offer the only direct entry for communicating with women in most homes in rural Bangladesh. At the same time, health workers are burdened with carrying communication messages for a host of other health and social issues, often without the capacity or support needed to move beyond simply raising awareness. A simple, low-literacy flip chart on arsenic was developed as a communication tool. Similar materials were also developed for other grassroots level workers coming into the village, including tubewell testers, agriculture extension workers, teachers and NGO volunteers.

Research showed that children knew little about arsenic and few had heard of the word. Fewer still could connect arsenic with their tubewell water or make the association with arsenic-related illnesses. Supplementary reading materials were designed for school children aged 6-11 to introduce the arsenic problem in a staged manner, matching sophistication of the materials with different stages of a child's cognitive and psychosocial development.

The materials designed for use with children in the earliest classes created simple word associations between arsenic and tubewell water. The materials also encouraged children to develop a habit to drink water only from a tubewell marked with green paint, signifying it was arsenic safe. A picture book for class three children promoted a greater understanding of the problem and what drinking the water would do to health.

A classroom planner developed for class nine students provided key messages on what their village could do to ensure a safe water supply. It was designed to facilitate the transition of older students into active participants in the wider community (Asiatic, 1999b).

The Bangladesh experience underscored the importance of not underestimating the amount of time and resources needed to produce quality materials that are acceptable to a wide variety of stakeholders. The process of developing communication materials for children involved more than a year of intensive interaction with government education officials on content and presentation.

Action

It was recognised early that the arsenic problem in Bangladesh would require a multi-sectoral approach to communication. The Public Health Engineering Department (PHED) responsible for rural water supply relied on the assistance of various other government departments, including health, religious affairs, primary and secondary education, mass communication and state-controlled television and radio broadcasters.

Partners in the NGO sector, including some of the largest organisations in Bangladesh, were also enrolled in an extensive consultation process.

These various stakeholders were brought together at various stages during 1998-99 to arrive at a consensus on the approach and implementation for a communication strategy. Individual ministries were responsible for sending appropriate instructions down through the chain of command to enrol grassroots workers in the communication activities. State-run broadcasters began to air the television and radio commercials based on a media plan prepared by the social marketing agency.

The agency was also responsible for monitoring media placements and field-level activities during the pilot phase at the sub-district level in 2000. Wide scale dissemination of communication materials, and training for grassroots workers, in various districts of the country will coincide with the expansion of tubewell testing and the provision of alternate sources beginning in 2001.

Other development players, including the World Bank, UNDP and international NGOs, are also engaged in significant arsenic mitigation activities. These groups participated in the process of consultation to develop the GOB-UNICEF communication strategy. Many have since decided to incorporate communication materials and methodologies from this strategy into their own programme activities.

7.4.2 Learning from Bangladesh

An initial evaluation of the communication campaign piloted in the four rural *upazillas* (administrative unit) indicates that the arsenic communication strategy in Bangladesh is raising awareness and helping to change behaviour.

In-depth interviews in mid-2000 with 224 respondents, including children, adults, grassroots government workers and service providers, provide some insight into the change in thinking about arsenic. 10 focus group discussions were also held in each of the four *upazillas*.

Awareness levels, which nationally were extremely low in 1998, increased dramatically. 95% of respondents could now explain that a red-painted tubewell indicated unsafe levels of arsenic, while a green-marked tubewell indicated that the water was safe for drinking and cooking. More than three-quarters of respondents understood that arsenic is a poison and were able to trace the origin to groundwater. 85% of respondents were also familiar with the symptoms of arsenic poisoning.

Behaviour in the four *upazillas* was also changing. Most respondents now attempted to collect and use water from a source they know is safe from arsenic. However, 16% said that they still drank from arsenic contaminated tubewells because a safe source was not available or was too far away (personal communication, Hussain, 2000).

The evaluation was helpful to communication planners in validating some of the approaches and activities under the campaign. It also highlighted weaknesses, providing planners with opportunities to refine the strategy. Grassroots workers, for example, were enthusiastic about using the communication materials but needed more training and motivation in order to meet all the original targets for interacting with villagers on arsenic. Other groups identified as potential communicators, such as the elected heads of local government bodies, were less enthusiastic in assuming a role in the campaign. The evaluation also pointed to the importance of matching communication with the efficient availability of services - in this case, alternative sources of safe water. The principle remains that communication alone cannot lead to sustained behavioural change.

More experiences will be forthcoming as the Bangladesh campaign expands in 15 additional *upazillas*. Until those results are available, communicators can draw lessons from the methodology and approach used in Bangladesh. These can be broadly split into two areas: ***programme transformation*** and ***management excellence*** (Gill and Galway, 1997).

Programme transformation

Programme transformation looks at methods to ensure that communication is part of a process of social change and reform. This requires working actively with communities and families to identify problems and solutions that are appropriate to local realities. Social change also requires approaches to communication that promote equity along gender, class and ethnic lines. In the Bangladesh strategy, programme transformation is being addressed in several key ways.

Strategic planning using the ACADA planning process. A distinct campaign identity, focused activities and measurable outputs are hallmarks of the Bangladesh strategy. Research activities and the application of diffusion theory were important planning tools for selecting the most effective communication intervention.

Professional approaches to communication. The Bangladesh experience showed the importance of a multi-sectoral approach to communicating about arsenic. It also demonstrated the efficiency of working with professional communication agencies in putting together multi-media, multi-level campaigns. Professional standards in production were achieved, with the materials hitting high benchmarks for appeal, comprehension and efficacy. Over time, the materials will become more targeted to audiences where change is still slow.

Innovation in strategies, processes and products. The communication materials in Bangladesh were carefully designed to build on the experiences of past strategies. Products for grassroots workers were made less bulky and heavy, and more user-friendly. The strategy also aimed to enrol ‘new’ grassroots workers, such as agriculture extension workers and sales agents of pharmaceutical companies, to penetrate deeper into communities affected by arsenic.

Core values. The arsenic communication strategy promoted core values related to gender and equality. Women were portrayed in print and broadcast media as pro-active decision-makers. Materials also ensured that at least half the people portrayed were girls or women. Research activities and pre-testing ensured that half the respondents were women Ethnic minorities from Bangladesh’s hilly areas. The strategy made deliberate attempts to reach women in the home through as many channels as possible.

Management excellence

Management excellence refers to the processes followed in developing and implementing communication strategies. It identifies the institutional strengths and weaknesses often associated with communicating for development.

Outsourcing. The bulk of UNICEF's communication activities in Bangladesh are contracted out to full-service social marketing agencies, including the development of the GOB-UNICEF arsenic communication strategy. This approach ensured access to the best and most competitive private sector resources for research, market segmentation, production and monitoring and evaluation. The strategy also built the social marketing capacity of the advertising agency, moving away from the narrow pursuit of promoting a 'brand'.

Capacity building. UNICEF provided key support to GOB in developing the arsenic strategy. It also managed the bidding process for hiring a social marketing agency and production of materials. UNICEF's overall assistance expedited the process of putting together a strategy. It also supported ongoing efforts to sustain and build the capacity of the government's Public Health Engineering Department to manage complex 'software' interventions to change behaviour.

Creating institutional and organisational mechanisms within the public sector requires considerable time, funds and expertise on the part of the donor agency, as well as time and resources from the private sector agency. These are difficult to ensure over an extended period of time.

Training. The Bangladesh strategy called for the intensive involvement of grassroots government and NGO workers. This required extensive training and orientation that were often built into regular training schedules. The training modules focused on helping communicators understand their role in creating processes to raise awareness. These will be modified as the campaign progresses to raise the skills of communicators in facilitating processes of behavioural change.

Flexible teams. The strategy envisaged that flexible teams of professionals from different disciplines would come together to manage the process of building this communication strategy. This was largely successful as the strategy was developed with inputs from engineers, health professionals, educators, religious experts, anthropologists and communicators.

Getting people to change their behaviour and maintain that new practice or attitude remains the essential task of the communication strategy in Bangladesh. It offers lessons to communicators on best practices for developing and implementing a communication strategy for arsenic. The experience of that country will continue to be instructive to communicators as evaluations are completed on the impact of the approach.

7.5 A brief chapter summary

Experience demonstrates the need to ***plan strategically*** and link communication to available services. ***Theory*** can inform the development of a strategy and provide a framework for explaining why people act the way they do. This is complemented by ***research*** to ensure any strategy on arsenic communication is firmly rooted in local cultural and social norms. ***Involving the community*** moves communication away from a top-down approach to a more sustainable, effective flow of information between people.

The experience of communicating about arsenic and other pubic health issues clearly demonstrates the need for a broad, ***multi-sectoral approach*** to bring about sustained behavioural development. Social marketing agencies can offer a full range of services in producing and managing a communication strategy. Up-front costs are often expensive and managing these services requires experienced and trained staff. However, this approach can be more ***efficient and cost-effective*** than retaining a large number of staff to provide specialised services in research and strategy development, media planning and media production.

Mass media and interpersonal communication are an effective combination in changing attitudes that lead to behavioural change. Yet, face-to-face communication is generally recognised as the most effective way to move people from being aware to trying and then adopting new behaviours.

Important lessons can be learned by taking a proposed strategy and ***piloting the approach*** in a limited area for a specific period of time. The pilot will confirm whether the strategy is effective in changing behaviour. It also reconfirms earlier pre-testing findings. Adjustments at this stage lead to a final strategy and an implementation plan for scaling up activities. ***Qualitative and quantitative assessments*** at the mid-term and end of a communication strategy indicate whether a strategy is successful and what adjustments are needed to ensure behavioural development.

Getting people to ***change*** their behaviour, and ***maintain*** that new practice or attitude, are essential objectives of communication for development. To reach these objectives, communicators need the skills and training to move beyond raising awareness to working with communities and families in ways that support long-term behavioural development.

These lessons derive from the numerous examples of communication strategies in action from across the globe. The range in approaches and methodologies is vast, as is the degree of success and failure in bringing about long-term behavioural change. While there is no single universal strategy for changing complex human behaviour, the experiences profiled in this chapter point to some best practices for communicators managing processes of communication for arsenic in drinking water supplies.

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Annex 7.1 Technical parameters for communication about arsenic

The following is a *guide to the social marketing agency developing a communication strategy for the UNICEF-assisted Safe Water Programme of the Department of Public Health Engineering. It sets technical parameters for what can be communicated, based on current understandings on arsenic. These parameters were developed after a review of available literature and with input from DPHE, MOH&FW, BAMSWP, UNICEF, WHO and World Bank. The technical parameters are not the actual messages to be promoted. The social marketing agency will use these parameters to develop messages which are appropriate to the relevant target audience (families, grassroots workers, doctors, government officials) and channels (mass media, outdoor media, interpersonal communications). The left-hand column indicates the technical parameter of what is being communicated. The right-hand column gives the appropriate reference (UNICEFb, 1999)*.

Technical parameters	References/citations
BACKGROUND	
Arsenic is a substance that occurs naturally in the environment. It is part of the rocks and soil.	Arsenic is a ubiquitous element with metalloid properties. In nature, it is widely distributed in a number of minerals, mainly as the arsenides of copper, nickel and iron, or as arsenic sulfide or oxide. In water, arsenic is usually found in the form of arsenate (arsenic V) or arsenite (arsenic III). (**Special report on Arsenic. WHO 1981**)
You cannot see, taste or smell arsenic in water.	

HEALTH EFFECTS OF ARSENIC

Arsenic is a poison. The body will try to expel arsenic through urine, faeces, hair and nails. If a person drinks arsenic-contaminated water over a long period of time, it can damage the body. In some cases, it can be fatal.	Arsenic in drinking water has been linked to elevated rates of bladder, kidney, skin and liver cancer, as well as other non-cancerous conditions such as nausea, abdominal pain and diarrhoea (**Guidelines for drinking-water quality, WHO, 1993**)
It can take years for symptoms to develop. You can drink arsenic contaminated water and not look or feel sick right away.	Signs of chronic arsenicalism, including dermal lesions, have been observed in populations ingesting arsenic-contaminated drinking water. Dermal lesions were the most commonly observed symptoms, occurring after minimum exposures of 5 years. (**WHO, 1993**)
If a person stops drinking arseniccontaminated water, some of the visiblesymptoms - such as thickening of the skinon the palms and soles (keratosis), dry, cracked skin on the feet and palms, andblackening and spotting of the skin (melanosis and leukamelanosis) - can be reversed in some cases. If patients continue to drink arsenic contaminated water, they can develop ulcers, gangrene and various kinds of cancer, which can be fatal. Some other non-cancer effects from drinking arsenic contaminated water include flushing of the face, conjunctivitis, generalised weakness, liver enlargement, chronic cough or respiratory difficulty, solid oedema of legs and hands, periperhal neuropathy. ***NB: Symptoms will not be indicated as sequential.***	**(Vahter, Metabolism of Arsenic in Fowler, ed., Biological and Environmental Effects of Arsenic, 1983)**
Symptoms include skin lesions, dark spots on hands and palms, and hardening of skin into nodules. There is no medicine to cure arsenic poisoning. However, patients showing various clinical symptoms could be managed by symptomatic treatment in some cases. Localised skin cancer, if detected early, can be cured by surgical excisions. Having continued surveillance of those people showing skin symptoms may help detection of early cancer and treatment.	**Arsenic in Drinking Water, NIPSOM, 1997. WHO, 1981. Marked increase..., Smith et al., American Journal of Epidemiology 1998. Manifestations: clinical (skin lesions, melanosis, keratosis, oedema); complications (skin symptoms more pronounced, internal organs affected); malignancy (tumours, cancer, gangrene).**

The skin symptoms can be painful if they become infected. Antibiotic lotions can be used for cracked skin to stop infection. Medicated ointments can ease the visible symptoms, such as dry, cracked skin. In the case of keratosis, the ointments keep the skin softer and may keep the nodules from getting larger. However, these problems will not go away if the person continues to drink arsenic contaminated water.	**NIPSOM, 1997** **As advised by Dr. Iftekhar Hussain, Deputy Programme Manager, Arsenic, Ministry of Health & Family Welfare, 21/2/99.**
Susceptibility to arsenicosis depends on how much arsenic contaminated water you drink, the extent of the period you have been drinking that water and the concentration of arsenic in the water.	According to Chakraborti and Saha, the lowest arsenic concentration in water producing dermatosis was found to be 200 ppb. However, the total quantity of arsenic consumed per day and the duration of exposure are important factors. **(Biswas et al, 199**8)
A better diet may increase your resistance to some of the early effects of arsenic poisoning.	Both Vitamin C and methionine reduce the toxicity of arsenic. **(Biswas et al, 199**8, citing **(Harding, 198**3) and **(USEPA, 198**8)
Arsenic contaminated tubewell water can still be used for washing, clothes, utensils, bathing and other household purposes. Touching water that has arsenic is not hazardous.	For appreciable dermal absorption of arsenic, the skin has to be very hydrated - i.e., well over an hour of direct exposure to water. However, there is no firm data from human subject experimentation. **Dr. Buck Grisson, ATSDR & Charles Abernathy, EPA.**
Arsenicosis is not contagious. You will not get the symptoms of arsenicosis by touching or embracing a person who is suffering from arsenicosis.	**(WHO 1981)**

HYDROGEOLOGY, OCCURRENCE

Arsenic is a naturally occurring geological phenomenon. In Bangladesh, arsenic is being found in groundwater at different depths and in different concentrations underground.	**BGS/MMI, 1998** found arsenic concentrations ranging from 2 to 167 parts per billion. Distinct spatial variations were found both on regional and local scales.
There are different theories as to the cause of the arsenic problem in Bangladesh. One theory claims that as	**BGS/MMI, 1998**

groundwater is pumped out for irrigation and drinking water, mineral like pyrite containing more than normal amount of arsenic are exposed to oxygen and dissolve, releasing arsenic. In this view, fluctuations of the water table are the cause of arsenic contamination in groundwater. The other main theory is that arsenic was present in iron coatings in the aquifer. As aquifers became oxygen poor over time, the iron coatings dissolved, releasing arsenic naturally. This probably happened thousands of years ago. Many hydrogeologists believe that the latter theory is the cause in a large part of Bangladesh. Widespread arsenic contamination in Bangladesh is not caused by power poles, pesticides or fertiliser.

The accepted limit for arsenic in drinking water in Bangladesh is less than 50 parts per billion (ppb) (.05 mg/L). People should not drink or cook with water if a test shows 50 ppb or more.

Tubewells that test negative for arsenic will still need to be monitored periodically. Concentrations of arsenic in that tubewell water may increase naturally over time. A tubewell with unsafe levels of arsenic (50 ppb or above) does not need retesting. The arsenic in that water supply will not go away.

MMI, 1998 indicates that older wells were more likely to be contaminated than younger ones. This suggests that wells can be safe at one time and gradually become contaminated. Anecdotal evidence also supports this. However, this is thought to be a slow process, taking years.

** NB: the retesting protocol needs to be developed*

Once a tubewell is tested, the following protocol is to be followed: safe tubewells are those with less than 50 ppb and the spout will be painted green; contaminated tubewells are those with arsenic concentrations of 50 ppb or more. Its spout will be painted red.

** NB: the painting protocol needs to be informed to the private manufacturers of tubewells. Department of Environment. Environmental Conservation Act 1997.*

ALTERNATE SOURCES

Rainwater does not have unsafe levels of arsenic. If rainwater is properly stored - in a dark, closed container with a lid to keep people or animals from touching the water

Heijnen and Mansur, 1998 showed that rainwater stored in properly designed jars can remain pathogen-free for months. They found no faecal coliform in stored rainwater

- it will be safe to drink. The water can be stored this way for months. The tank, rooftop and gutter should be cleaned once a year using bleaching powder.	after 6-18 months of use. **DPHE (unpublished)** have made water quality tests on stored rainwater and found it pathogen free.
Water from ponds is often heavily contaminated with germs that can cause diarrhoeal diseases. Pond water is not safe for drinking without treatment.	**Bilqis et. al 1995**
Most pond water can be made safe to drink by filtering it through a pond sand filer. The sand filter needs regular cleaning. This will require a lot of community participation to keep the system clean and functioning. Water collectors need to pump water into the filter before filling their container so that the next user does not have to wait for the water to filter through the system.	It is well known that pathogens will die off naturally with storage. More than 50% of the pathogens in water will die within two days and 90 percent will die by the end of one week. **Linsley et al. 1994.** **DPHE (unpublished)** has made water quality tests on PSF water and found it pathogen free. * *NB: do not encourage people to boil their water due to the environmental damage this may cause.*
Protect the area around the pond to reduce the risk of contamination. There are four simple steps. Latrines/disposal of faeces must be 10 meters away from the water source; do not allow animals (livestock) into the pond; do not bathe, wash utensils, soiled napkins or bedding in the pond; build an embankment at least one foot high around all sides of the pond to prevent surface water run-off draining into the pond. This advice needs to be promoted in conjunction with promotion of the pond sand filter.	
ARSENIC REMOVAL AND SLUDGE DESTABILIZATION AT THE HOUSEHOLD LEVEL	*NB: the Safi filter, activated alumina are still unconfirmed as options; these could be included as options once verified as safe and effective.*
Phitkiri (alum) is a short-term, emergency response for people who have no alternate source of safe water. It removes some arsenic, but not all. It may also not make the water safe if the original concentration is quite high. It should only be used until the family can get safe water from another source (e.g., a	**NIPSOM 1997** reports that the alum method removes about 70% of arsenic. Steps for use are outlined in pages 37-38. **Khoe and Emett 1999** A field demonstration of arsenic removal process in Sonargaon showed that dosing tubewell water in a kolshi with alum (20-30 mg/l)

neighbour's safe tubewell, deep tubewells, RWH, PSF). Alum promotion needs to be closely linked with messages to keep the kolshi (container) well cleaned, using an abrasive, to prevent a build up of germs. Letting water sit overnight in a kolshi may remove a small amount of arsenic in some but not all cases. Again, this should only be promoted as a short-term, emergency response.

removed 50-75% of arsenic.

Bilqis et al. 1995 demonstrated that water stored in kolshis experiences exponential growth in fecal coliform levels over a matter of hours (from 2 to 2510 CFU/100 ml in 10 hours). Scrapings from the bottom of kolshis yielded high FC counts (up to 75,000 CFU/100 ml).

Passive sedimentation removes only a limited amount of arsenic - allowing precipitation of naturally occurring iron (5 mg/l) could only remove 25% of arsenic **Khoe and Emett 1999. UNICEF/DPHE 1999** Action Research Report finds 60% removal over 24 hours - but only at four inches from the surface.

MYTHS

Boiling does not remove arsenic. It can make the problem worse because the water boils down, leaving less water but the same amount of arsenic.

OTHER

In the case of diarrhoea, follow the three golden rules: increased fluids; continued feedings; if the diarrhoea persists after three days seek medical help.

CDD case management. Messages developed as part of government ORT communication campaign.

Chapter 8. Strategies to mitigate arsenic contamination of water supply

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Chapter Summary

The preceding chapters in this volume have presented the best available knowledge on the contamination of water sources by low concentrations of arsenic, and some of the technologies and tools available for its mitigation. The objective of this chapter is to apply this knowledge in the development of a strategic framework to help planners and

policy makers design effective and sustainable mitigation programmes. The discussion in the chapter draws on the lessons learned over the years in the water supply sector, and introduces institutional and economic factors in the development of this framework.

While presenting general information applicable to all instances of arsenic contamination world-wide, the discussion focuses on the specific constraints faced by the poor and isolated rural communities that are most severely affected.

The discussion in the chapter begins with a brief summary of the water supply and quality situation world-wide, a review of arsenic in relation to other water quality issues, including its consequences and global scope. It then presents the following key design principles to be considered in the development arsenic mitigation strategies: inform affected people and other stakeholders in a timely fashion; take immediate steps to determine the extent and seriousness of the problem through testing; prepare separate, but compatible, emergency and long-term programme phases; prioritise reductions in arsenic intake, even if standards are not met immediately; involve all relevant sectors in a coordinated mitigation programme; involve other stakeholders in a multi-partner effort; and recognize uncertainty by using flexible programme designs.

The chapter goes on to present a series of case studies on responses to arsenic contamination of water supplies in middle- and low-income countries. The objective of the case studies is to illustrate the application of design parameters in different geographic and socio-economic contexts. The discussion concludes with a brief review of the key design principals specific to arsenic mitigation programming.

8.1 Introduction: water quality and arsenic

The contamination of drinking water sources by low concentrations of naturally occurring arsenic presents governments, public and private utilities, and the development community with a significant new challenge. The design and implementation of arsenic mitigation programmes must be carried out under conditions of imperfect knowledge, especially in areas where arsenic contamination affects the rural poor.

As the preceding chapters in this volume show, much is already known about the geochemical, epidemiological, clinical and mitigation technology aspects of the problem and its solutions. However, as the same chapters point out, much more needs to be learned. The goal of this chapter is to integrate the various areas of arsenic contamination knowledge into a multi-sectoral strategic framework for intervention on the ground.

Global experience with successful mitigation is, however, limited and governments (in both developing and industrialized countries) have only recently taken up the challenge of addressing the problem of naturally occurring arsenic contamination. In the absence of well-tested “models” for the definition and implementation of arsenic mitigation strategies, this chapter presents (i) key physical and socio-economic aspects that define the arsenic problem and its mitigation strategy; (ii) examples of mitigation strategies in selected countries; and (iii) a framework of lessons learned to help to prioritise the components of comprehensive mitigation strategies at the community, national and global levels. Such a prioritisation is of key importance given the limited resources available, and the urgency of the problem.

This chapter is aimed at a broad audience of professionals involved in arsenic mitigation world-wide. However, its focus is clearly on those areas that present the greatest challenge for the development of effective and sustainable strategies: poorer isolated rural communities - whether in Bangladesh, Chile or the USA.

8.1.1 The nature, cost and consequences of unsafe water

Safe water for domestic use is a priority in all countries and for all people. In industrialised countries, reliable and safe water supply at a reasonable cost is taken for granted by most. In developing countries, this is not the case. Despite significant expenditures on water supply in developing countries by government and external support agencies over the last ten years - from $10 to $25 billion a year (WHO/UNICEF 2000; WSSCC 1999) - almost 20 per cent of the world's population, or about one billion people, still do not have access to a safe source of water. And, as shown in Table 8.1, progress over the last 10 years has been slow.

Table 8.1 Global water supply coverage
(percent of world population with access to improved water supply)

	1990	**2000**
Urban	95 %	94 %
Rural	66 %	71 %
Total	79%	82 %

(WHO/UNICEF 2000)

People themselves recognize the importance of safe water and are willing to pay for it. Households routinely spend up to three percent of their income on water, and in situations of shortages or exploitation, people are often forced to pay much more. Against intuitive expectation, the poor tend to lose out: they are often not connected to the subsidized water distribution systems, and are forced to purchase expensive water from vendors at high prices, up to twenty times higher than what their neighbours are paying (WSSCC 1999).

The water supply challenge is as much one of quantity as of quality. The value of safe and adequate water supply resides in several factors. In many regions of the world, it means bringing water closer to the house, thus dispensing women and children from the (expensive) chore of hauling it from a distant well. As discussed in Chapter Six, some estimates put the cost of hauling water at 40 billion hours of labour a year in Africa alone. In addition to reducing drudgery, easy access to water of reasonable quality can stimulate an array of small-scale commercial activities such as vegetable growing and animal husbandry. If the water supply is of good quality and replaces old contaminated wells or supplies, it also contributes towards improvements in public health. Finally, water is increasingly seen by many to be a basic human right and thus the provision of water to all, at a reasonable cost, is an imperative that must be fulfilled by governments and other duty-bearers (see, for example, Article 24 of the Convention of the Rights of the Child -United Nations 1989).

However, if that water is of dubious quality or is easily contaminated during transportation or handling, it may actually increase health risks. For example, a persistent problem confronted by water supply authorities for many years is the presence of lead. This contaminant is absent from natural water but dissolves under certain circumstances from lead pipes that until recently were the material of choice for in-house plumbing. Two thousand years ago Romans used it even for longer-distance transport of drinking water, which caused widespread lead poisoning. Arguably, that was the worst case of water poisoning until arsenic was identified as a major concern.

Such chemical contamination of water supplies remains a very serious problem. However, the most serious water quality problem is contamination by pathogens (bacteria, viruses, amoebae, helminths, etc.) which remains the major cause of morbidity and mortality. Worldwide, there are 3-3.5 million deaths per year from gastro-intestinal diseases (WHO 1995, Murray and Lopez 1996, Van der Hoek *et al.* 1999). While some of these deaths are caused by poor quality water sources, more are caused by the contamination of water during transportation and household storage, by poor hygiene, and by the lack of sanitary means for excreta disposal.

As discussed in Chapter Five, drinking water is never pure H_2O - it always contains dissolved salts, some of which are of natural origin, and others introduced through pollution or contamination. Some of these constituents are innocuous or even necessary dietary supplements, while others, even when of natural origin, can be detrimental to health. Calcium, for example, originates from calcareous rock dissolving in the aquifer. Its presence in drinking water not only adds to one's requisite daily intake of this element, but it also forms a thin calcium carbonate layer in distribution pipelines which helps prevent the contamination of water from undesirable pipe material such as lead or copper. Fluoride, on the other hand, also originates from dissolved minerals but has different health impacts. In large concentrations it stains teeth after a few months of ingestion and if taken over prolonged periods it will lead to painful and debilitating skeletal deformation. This occurs in rural water supply systems in several countries such as India and Ghana[2].

[2] In contrast, health authorities in some industrialized countries allow the deliberate addition of very small quantities of fluoride because it helps arrest tooth decay, and fluoride is added to toothpaste for the same reason. Whether or not this practice should continue is the subject of some debate.

Table 8.2 attempts to summarize and compare the magnitude, effects and responses to key water supply problems worldwide. Although figures are purely indicative, they illustrate the seriousness of water supply problems.

Table 8.2 A tentative global comparison of water-related health problems

Problem faced	**People affected[1] (order of magnitude)**	**Health effect[2]**	**Remedies available[3]**	
			Type	**Technical complexity**
Limited access to drinking water	*Only developing countries:* 1.1 billion	Various	Increase coverage by replicating water supply	Moderate

			programmes	
Gastro-intestinal diseases due to water-carried pathogens (usually related to surface water)	*Only developing countries:* 1.5 billion cases/yr 3.0 million deaths/yr (burden: 120 million DALY/yr)[4]	Diarrhoea, cholera, worm infestation, etc; Often fatal	Improve hygiene behaviour, improve sanitation, apply disinfection of water	Low
Lead in water supply (related to distribution pipes)	1 million	Neural and cerebral disorders	Replace lead pipes and fixtures	Low
Fluoride in water supply (groundwater)	*Mostly in developing countries:* Tens of millions	Tooth decay and debilitating skeletal deformation - irreversible	Remove fluoride, or provide water from alternative source	Moderate
Arsenic in water supply (groundwater)	*Mostly in developing countries:* Tens of millions	Skin diseases, intestinal cancers; often fatal	Remove arsenic, or provide water from alternative source	Moderate to high

Notes:

[1]. Various data sources: 1990-1995, 1999. People affected: people suffering from disease or great inconvenience.

[2]. In some cases there can be more than one causative agent, but water is always a major factor

[3]. The institutional complexity of remedy implementation is generally high in most developing countries

[4]. DALY = Disability-adjusted Life Years (WHO 1995, Murray and Lopez 1996, Van der Hoek *et al.* 1999)

Three developments in the past few decades have begun to change how governments and programme planners approach the issue of water supply and contamination. First, the capacity to analyse ever smaller amounts of constituents in water has advanced substantially. In the past, concentrations could typically only be measured in the mg/L (parts per million) range, while now measurements are routinely carried out for concentrations a thousand to a million times smaller. Second, the health status and life expectancy have risen substantially across most countries (with some noticeable exceptions in Africa due to AIDS). Third, health and epidemiological research have advanced: more information is available on the nature and treatment of longer-term health effects of prolonged ingestion of low-concentration contaminants. Taken together, these developments mean that more information is available on such contaminants and their public health repercussions, there is a greater need to confront these problems, and responses are within easier reach.

8.1.2 Arsenic: an emerging challenge

As shown above in Table 8.2, the potential global impact of arsenic contamination on public health makes it today's top priority water quality issue, second in importance only to the microbiological contamination of water[3]. Arsenic's acute toxicity has been known for thousands of years, but the enhanced capability to detect very low concentrations in water (see Chapter Two for more information on arsenic analysis) has clarified the links between arsenic in low concentrations and the incidence of some types of cancer (see Chapter Three for more information on health effects). The disease symptoms caused by arsenic toxicity are now being termed *arsenicosis*. As field workers and scientists are discovering that arsenic, even at very low concentrations, seriously affects health *if ingested over prolonged periods*, we come to conclude that arsenic contamination is much more prevalent in the world than we thought a decade ago (see Chapter One and Table 8.3 below on the global incidence of arsenic contamination of water sources). This is especially worrisome because, in contrast to many other contaminants, there are no simple and inexpensive technologies to mitigate the problem, especially in the case of isolated rural households. In Chapter Six, currently available arsenic removal technologies are analysed and compared to technologies for tapping alternative arsenic-free water sources. The overall conclusion of the analysis is that in rural areas of developing countries, source substitution is more feasible than arsenic removal in most cases.

[3] Fluoride may affect as many or more people than does arsenic (although the lack of information makes it impossible to give reliable figures - especially for arsenic). However, arsenic will likely cause far more fatalities than fluoride, and thus it is seen as being more serious. What is cliar is that both contaminants casue a great deal of human suffering, and thus both should be the subject of active mitigation programmes by governments and external support agencies.

Until recently, most sectoral programmes were centred around the lack of access to water supplies, a problem could be addressed effectively by installing comparatively cheap handpumps, dug wells or through approaches such as the introduction of communal taps. Although this required a significant financial outlay as well as institutional capacity building, the strategy is in itself reasonably well established and risk-free if implemented properly.

The emerging importance of arsenic and other naturally-occurring toxicants places a new burden on water supply authorities and policy makers. Large cities in industrialized countries, which are connected to centralized water treatment and reticulation systems, can afford the added expense and technical knowledge necessary to implement arsenic removal programmes. However, in virtually all other situations, arsenic removal is much more problematic. Cities and towns in middle-income countries, and even smaller towns in industrialised countries, find it difficult to raise the technical and financial resources to set up arsenic removal systems. In rural areas of developing countries that rely almost exclusively on handpump-equipped tubewells, the situation is much more serious. The combined repercussions of the high prevalence of arsenic contamination, the isolation and poverty of rural households in developing countries, and the high costs and relative complexity of arsenic removal systems is creating a programmatic and policy challenge on a scale never before seen in the water sector. While Table 8.3 provides some perspective on the scale of the arsenic problem, too little is known currently about the full extent of the problem and the real costs of mitigation systems to attempt an estimate of the cost of global remediation. What is clear is that the poor, and especially the rural poor, are the most vulnerable.

While there are many unknowns, knowledge and tools are available to help to begin to meet the challenge. The preceding chapters in this volume represent a wealth of information that can immediately be applied to assist in the design and implementation of arsenic mitigation programmes. Another knowledge base that must be tapped is the lessons learned in over thirty years of working in the sector in rural and poor environments which emphasize that success can only be achieved if the approach is locally-based, relies on the participation of truly empowered communities, and is driven by an explicit and committed demand from the community (Sara and Katz 1998, WSSCC 1999).

8.1.3 Arsenic contamination world-wide

The extent of the arsenic problem world-wide is as yet unknown. Before arsenic was identified as the unambiguous cause of wide-scale health problems in Bangladesh, such occurrences were considered relatively isolated. However, since the 1990s, efforts by governments, external support agencies, and academic institutions to identify other potential contamination areas have dramatically increased. Although it is far too early to definitively outline the extent of the problem globally, it is possible to present a preliminary analysis. This has been attempted in Table 8.3.

The first case of a large-scale health problem caused by naturally-occurring arsenic to be identified and recorded was in Taiwan in 1968. Chile's contamination case became recognized as such in the seventies. In the eighties, the problems in West Bengal, India, as well as in Ghana, Mexico and several other countries were documented. The largest contamination case to date is clearly Bangladesh. In the early nineties patients from western districts in Bangladesh started to cross the border to visit hospitals in Calcutta, but it was not until 1995 before official exploration of the problem was initiated. After 1997 the number of studies and initiatives rapidly grew leading to the discovery that most of the country should be considered at serious risk.

Table 8.3 Overview of major arsenic contamination situations in the world (all figures are estimates collected from a large number of sources)

Country/Region	Number of people at risk	Spatial distribution and nature of the contamination
Taiwan *South west and north east coastal zones*	200,000	Rural and small townships depending on well water of which many are contaminated at medium to high levels, some up to 1,800µg/L
China *Inner Mongolia Shaanxi,* *Xinjiang*	600,000 1,100,000	Dispersed incidence of low and medium and occasionally high concentrations in wells. Some regions (e.g. Baotou, I-M): high incidence of contaminated wells at high concentration

USA *>50µg/L (esp. in Western part)* *>25µg/L*	200,000 2,500,000	Origin of arsenic varies. Arsenic occurs primarily in groundwater and in some rivers (California) fed by geothermal sources. In mid-west and eastern plains low concentrations and disperse incidence.
Mexico *Lagunera Region: towns of Torreón, Matamoros, Viesca, Francisco, Madero, San Pedro, Tlahualilo, Gomez Palacio, Mapimi, Lerdo, Nazas and Ceballos (Coahuila and Durango States)*	400,000	An enclosed basin with primarily calcareous formations, arsenic was first found in the east corner of the aquifer, but dissipated to other sides probably under suction of groundwater pumping. Low to medium concentrations in a large number of wells in the affected zone.
Chile *Loa and Salado regions (north Chile): cities of Antofagasta, Colama, Chuquicamato, Salar de Atacama; Arica Province*	400,000	Associated with quaternary volcanism in the sparsely populated and arid Central Andean Cordilleras. Many rivers and lakes contaminated by thermal springs or dissolution of salts. Many enclosed basins with evaporative lakes *(salares*). In some regions contaminated shallow wells. Low to high concentrations with sometimes well above 1,000µg/L in river water (Ch: Loa R.). In north-western Argentinean plains also in sedimentary soils.
Argentina *Salta Province: Puna and Chaco Salteño regions*	200,000	
Bolivia *Southern Altiplano (Dept. Potosí)*	50,000	
Greece *Thessaloniki*	150,000	In particular aquifers. Hydrothermal origin. Low to high concentration.
Hungary	400,000	Mostly artesian wells in peaty and sedimentary soils. Low to medium concentrations.
Ghana *Obuasi*	100,000	Some shallow wells and streams contain low to medium concentrations. Gold mining, and possibly some arsenopyrite oxidation.
India *West Bengal State*	In 8 Districts, out of total pop. of 40	West Bengal: Out of 17 Districts, 8 have affected wells in various

(suspected occurrence in Bihar, Gangetic and Brahmaputra plains)	million, 5 million “live close to contaminated well”	zones. Within these zones half of wells (medium depth) contain arsenic at low to medium levels. Origin not conclusively established but not likely due to arsenopyrite oxidation.
Bangladesh *In most Districts*	80-90 million people live in affected Districts, of which 20-30 million “live close to contaminated well”	Low to high concentration in groundwater wells of 5-150m deep. Some areas have 80-100% of wells contaminated, others much less; across the affected Districts 30-40% of wells affected (>50µg/L). Aquifers appear reductive alkaline environment, with arsenic displaced from clay adsorption sites by cations such as phosphate
Vietnam *Red River delta region, including Hanoi*	Arsenic confirmed in some wells. Number of people affected unknown.	Preliminary testing in Hanoi and Red River districts has indicated a significant arsenic problem in shallow tubewells used for drinking water. There are an estimated 150,000 shallow tubewells used for drinking in these regions.

Note: [1] Low/medium/high concentration: in order of magnitude of 10-50/50-250/above 250µg/L.

[2] “People at risk”: living in direct vicinity and/or actually drinking water with 50µg/L.

Large epidemiological studies conducted first in Taiwan and later in Chile suggested that what was considered the safe level (standard) at 50µg/L may have to be revised downward. As described in Chapter Five, on the basis of such studies WHO set a provisional guideline value of 10µg/L, down from an earlier figure of 50µg/L. If such downward revisions are adopted as national standards, the number of people to be considered at risk will grow per country by a factor 2 to 10, depending on the local situation[4].

An additional complication in this discussion, that will only be alluded to here, is the contention that arsenic (and possibly also other dissolved salts) are significantly correlated statistically at very low concentrations with an array of non-specific diseases, especially cancers, that develop only over a very long exposure time. If this were proved to be true, it would signal a fundamentally more complex approach to

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[4] Currently the countries of the European Union and seven other countries have adopted standards of 10µg/L or lower. Most other countries - including Bangladesh - maintain standards of 50µg/L. See Chapter Five, and Section 8.2.3 in this chapter, for further discussion on the setting of standards for arsenic.

include these types of “third generation” issues in the relationship between water supply and public health, as it could mean that many micro-constituents that are normally present in groundwater pose serious health risks.

8.2 Developing a mitigation strategy: key factors

The development of a mitigation strategy in developing and industrialized countries is guided by similar considerations, although developing countries face additional constraints on financing and on technical and administrative capacity. In both cases, a wide range of multi-disciplinary factors must be considered in the development of sustainable strategies.

Although all relevant disciplines must be considered in strategy development, the focus of mitigation efforts must clearly be on water. In the current large-scale public health crises related to arsenic, water is the principal cause, and water is only the “cure”.

Currently there is no specific medical therapy for the prevention or treatment of arsenicosis. As detailed in Chapter Four of this volume, medical interventions are limited to alleviating the effects of symptoms and treating diseases, such as cancer, that can ultimately result from arsenic exposure. The only way to prevent arsenicosis in the first place is to ensure that arsenic ingestion does not occur. And the first and most important step in the treatment of arsenicosis when it does occur, is also to eliminate or reduce arsenic exposure.

As discussed in Chapter Three, exposure to arsenic occurs through a variety of environmental media, including food, soil and air. However, in cases - such as in Bangladesh - where arsenic is present in water in significant concentrations, water is the principle contributor to the daily intake of arsenic in humans (see Chapters Three and Four). Therefore, efforts to reduce arsenic intake should concentrate on the provision of arsenic-free water.

Arsenic mitigation strategies have to address the conflict between the need to fill a comparatively large knowledge gap (which calls for ample study prior to action) and the need to bring in immediate remedial action (which calls for early operational and investment decisions). Any strategy will have to be conceived in a sufficiently adaptable way and will inevitably have to determine a first course of action based on a preliminary classification of the nature of the local contamination case. A rough typology is summarized below, based on a number of differentiating factors.

8.2.1 The hydrogeological factor

Arsenic in natural waters

Arsenic is found in low concentrations in rocks, soils and sediments throughout the world. Under certain conditions, arsenic is released into natural waters resulting in a wide range of concentration levels. As described in Chapter One, high arsenic concentration levels are principally restricted to groundwater, with some exceptions.

Cases of large scale naturally-occurring arsenic contamination of groundwater are mainly confined to hydrogeological environments characterised by young sediment deposits (often alluvium), and low-lying flat conditions with slow-moving groundwater such as in deltaic areas (such as in much of Bangladesh). High concentrations of arsenic in groundwater also occurs in regions where sulphide oxidation has occurred, in geothermal areas, and as a result of mining activity. Geothermal activity and mining can also result in serious - but usually localised - occurrences of surface water contamination.

See Chapter One for a more comprehensive discussion of the sources of arsenic in natural waters.

The variability of arsenic contamination

Hard rock and calcareous formations carry groundwater in fissures and cracks. The available water, therefore, is unevenly distributed in the formation. Loamy or sandy sediments, on the other hand, tend to be more homogeneously porous to water, and water is more evenly distributed. These sediments, however, were not deposited in even layers one atop the other. As rivers eroded and silted up, sediment packets of varying composition and granulometry were deposited and shifted along. Therefore, their arsenic content and release potential may vary, even within distances as short as 10 m. This situation is encountered, for example, in Bangladesh, where handpumps draw water with very different arsenic levels even though they are located in each other's vicinity in a corner of a village (see also Chapter One). In other places, such as Inner Mongolia, China, most wells are arsenic-free, but some "hot spots" exist with very high concentrations.

In some areas arsenic contamination varies significantly, and more predictably, with depth. In Bangladesh, for example, almost all wells testing positive for arsenic are in aquifers shallower than 150m (see Figure 6.1 in Chapter Six). However, as discussed further below, deeper wells may become contaminated over time.

The implications of this high degree of variability in the context of mitigation strategy development is that all wells must be tested separately for arsenic. On the other hand, it also means that in a given area there is a good chance that some wells are uncontaminated and can be used as safe sources of drinking water.

Availability of an alternative water sources

The mitigation strategy for arsenic contamination can entail arsenic removal, but because of the costs and operational complexity of the technologies involved, it is often preferable to seek an alternative water source of good quality. This is especially the case, as discussed earlier, for rural areas of developing countries. Options include surface water, harvested rain water, or arsenic-free groundwater. The latter, if available, is generally the preferable option. While appropriate in some cases, surface water generally requires extensive treatment and rainwater harvesting, while feasible, is usually technically difficult to achieve for the provision of year round water supplies. See Chapter Six for a comprehensive analysis of alternative sources of drinking water.

Arsenic-free groundwater is either transferred from a more distant source, or, as in the case of Bangladesh, may be abstracted from arsenic-free groundwater "pockets" or deeper aquifers in the neighbourhood of the contaminated well. In the latter case, where arsenic contamination is a widespread phenomenon, the arsenic concentration in the new wells should be checked at least annually because "safe" wells could gradually start aspirating contaminated layers. This has happened in Mexico (see below) and was also reported in West Bengal, where deep wells, originally arsenic-free, over time started to draw from contaminated layers. In addition, if deep wells are improperly grouted (sealed), arsenic-contaminated water from shallow aquifers may directly enter the well.

8.2.2 The water supply technology factor

As discussed earlier, two technical choices are available to planners of arsenic mitigation programmes: remove arsenic from existing contaminated sources of water, or develop and deliver alternative, arsenic-free water sources. The decision will be based on a variety of factors and will vary from case to case. In Section 6.4 of Chapter Six, a protocol for the selection of an arsenic-free water supply technology (both arsenic removal and source substitution technologies) is developed, based on a set of five technical criteria and six socio-economic criteria. The discussion below presents the key points to be considered in the development of mitigation strategies.

The availability of feasible technical options for arsenic removal

Arsenic is difficult to remove in simple, inexpensive ways, especially at concentrations above 100µg/L. Most technological research has been geared at either lowering the already low concentrations that are typically found in Western Europe (20-80mg/L) by optimising common treatment processes such as coagulation with iron or alum, or at more advanced and expensive processes that are typically destined for low flow rates, such as ion exchange and adsorption.

What is to be considered feasible depends on a variety of factors such as: (1) the existing basic water supply system, e.g. whether it is an “urban” piped system with centralized treatment, or one consisting of handpumps shared by a number of families as is typical in many rural environments; (2) the amount of arsenic in the water and the percentage that needs to be removed - the smaller the size of, and the more basic this system, the more unlikely it is that arsenic removal is feasible; (3) the level of technical and managerial capacity available to install and maintain the treatment units; and (4) the level of income and the willingness to contribute financially to operation and maintenance of the equipment - usually communities fail to maintain systems that are installed for free by the government. The importance of such considerations implies that any strategy for arsenic mitigation will need to be site-specific to avoid the seduction of looking for a “magic bullet” that will solve the problem in all instances.

The availability of feasible alternative water sources

Given that arsenic removal is prohibitively expensive in many circumstances, much will depend on the availability of feasible alternative water sources. Again, feasibility must be judged against several criteria, among which the capability and the willingness to pay of the households are critical. Also, the quality of these alternative sources must be thoroughly checked.

In Bangladesh, for instance, several regions have easy access to surface water ponds. It is argued that resorting to these ponds would be quite feasible, as Bangladeshis traditionally drew water from a protected pond before the general conversion to groundwater in the seventies. However, nowadays many of these ponds have been unprotected or derelict, collecting waste and sewage. Other ponds are dowsed with chemicals and used for fish cultivation, and are also unsuitable as a drinking water source. In addition, the population pressure in the rural areas has increased drastically thus rendering these ponds a much less obvious alternative. Re-introducing the protection of communal ponds will require a substantial change of attitude in the rural population. It runs the risk of reversing the recent progress in significantly reducing the mortality and morbidity caused by waterborne pathogens.

8.2.3 The health factor

Uncertainties in the epidemiology of arsenicosis

With only few incidences thoroughly investigated over longer time horizons (several decades) the chronic health effects of long-term exposure to small dosages seem adequately documented to confirm that health risks do exist, but there remains ample scope for debate on the risk calculation. Nonetheless, from the previously generally agreed 50mg/L, the standard for the maximum allowable arsenic concentration in water has been lowered to 10mg/L by a number of countries and, as a guideline, by WHO. In 2000, the US EPA lowered its standard from 50 to 10 mg/L, but it had contemplated 8 or even 5 mg/L (it has since revoked this new standard, see below). These lower standards, however, would have implied what some consider a prohibitively large increase in the cost of water treatment and/or abstraction of alternative safe water sources, and analysis showed that this burden would have affected primarily the smaller rural water supply systems. Physical chemical laws dictate that it is always much less expensive to remove the first 90% of the contamination (when at high concentrations) than the last 10% (which corresponds to very low concentrations). At the same time, the validity of extrapolating epidemiological data to effects at much lower concentration levels is contested notably by the American water utilities (Black et al., 1999). The fact that in 2001 the new US administration revoked the 10mg/L US standard only months after it was first announced illustrates - in part - the lack of consensus on what the safe level of arsenic in drinking water should ultimately be.

These point raise two issues:

- Rich countries that already have achieved near-100% coverage of their population with good water supply may find it expensive to meet the new standards, but for poorer countries the cost is prohibitive and they must therefore prioritise and phase their financial effort. For example, in Bangladesh the World Bank-supported Arsenic Mitigation - Water Supply programme recognizes the long-term goal of meeting the Bangladeshi standard (50mg/L) in each household, but in the intermediate emergency period aims at approaches to reduce by as much as possible the excess intake of arsenic, even though this not always guarantees that the standard is achieved immediately.

- The levels of intake that are to be considered safe vary with, among others, body weight, average water ingestion, nutritional condition, and predisposition of individuals. For example, Bangladeshi agricultural labourers working under the sun drink 3-4L of water daily, against 1-2L for the average American. Equally important, the trajectory of arsenic from the underground water into the body varies a lot and can introduce physical chemical phenomena that neutralize or exacerbate the toxic effect. In Bangladesh, for instance, which witnesses almost country-wide poisoning of groundwater, there is not always a correlation between the typical level of the arsenic concentration as measured in the groundwater and the incidence of disease.

Preliminary observation suggests that areas south-east of Dhaka (such as Laksmipur and Chandpur, see Fig. 8.2) experience among the highest concentrations (well into the 100s and even 1,000mg/L) yet few casualties are reported. Areas north-west of Dhaka, on the other hand, such as Ruppur and Bagga, face concentrations 5-10 times lower, yet morbidity and mortality are higher. This discrepancy has not been explained so far. Differences in nutrition, or different water source use patterns (some people may make more use of surface water for drinking or cooking), may also play a role. This region also has groundwater with high dissolved iron levels, which spurs women to always let pitchers with water stand for a night after which the iron precipitate is decanted - precipitate that is known to effectively bind arsenic (see also Box 8.2, below). Epidemiological results, therefore, need to account for such effects, for these can help target the strategy significantly better.

Arsenicosis as priority in the local health picture

The image and reputation of arsenicosis as a slow poison may distort a candid assessment of the burden the disease imposes on a population. As discussed above and detailed in Chapter Four, the best treatment strategy when symptoms start emerging is the provision of arsenic-free water. Planners and affected populations should be made aware of the fact that introducing arsenic-free drinking and cooking water is the first and most important single step to be taken: this will reduce the chances of escalating health problems amongst affected people, and may, in some cases, reverse the symptoms and some of the clinical manifestations of arsenic toxicity. The fact that there is some symptomatic reversibility in the disease, at least in the early stages, may allow more time for appropriate preventive action than acute emergencies, such as, diarrhoeal diseases. Nonetheless, in most cases arsenic poisoning is a localized phenomenon which makes the larger population vulnerable to slow recognition of the problem, and inadequate response by national health authorities.

At the same time, mitigation strategies should be careful to not overemphasize the arsenic burden, because it risks a possible neglect of other important health threats. For instance, substituting arsenic contaminated groundwater with water from ponds or shallow dug wells in poor rural areas may actually *reduce* the quality of health in that region because of the potential to increase the incidence of gastro-intestinal diseases[5].

[5] Although reliable data is scarce, in Bangladesh the mortality rate due to diarrhoeal diseases is estimated at 120,000-200,000 per annum, of which possibly half can be attributed to drinking of pathogen-contaminated water (Dewier and Islam 1997). The best estimates so far for arsenicosis mortality suggest an order of magnitude of 20,000-40,000. These figures are by themselves insufficient to warrant a definitive prioritization, but they do highlight the need for careful consideration of priorities.

Need for parallel health/curative efforts

Although arsenic-free water is in many respects the best “antidote” for the majority of people at risk or even for those in the first stages of intoxication, in some of the population arsenic may have already damaged their health irreversibly. For these people a separate strategy for adequate curative effort should be developed, comprising at least identification and diagnostic capabilities at the local level, referral systems, and provision of treatment, possibly at more centralized locations. In addition, programmes to enhance the health and nutritional situation of the local population are likely to render people more resilient and may lower the incidence or seriousness of the health impact. However, as described in Chapter Four, the treatment of advanced stages of arsenicosis is still in its infancy. Nonetheless, the very fact that a diagnostic system is in place already helps to restore confidence, and, importantly, it is the only way to provide an accurate assessment of the health impact, which in turn is essential to develop an effective strategy. Until now, the problem assessment is very often founded on arsenic concentration levels in the water, or on the number of patients with visible (skin) defects. Yet, the most serious health impacts concern internal tumours that are not easily detected or are not recognizable as related to arsenic.

8.2.4 The economic and institutional factor

Capacities and institutional strengths required at the levels of households, local governments and utilities, and national governments

Industrialized countries dispose of elaborate institutional capacities, and finance and cost recovery mechanisms, that allow them to (1) identify and assess arsenic poisoning cases at an early stage; (2) set up a working health support system; (3) conduct high-quality research to come up with technically feasible solutions for arsenic removal or provision of alternative sources for water; (4) involve both local government in proper local planning, and national government in policy making, standard setting, monitoring and providing financial stimulus; (5) depend on water supply utilities to construct, operate and maintain all requisite infrastructure, and recover all costs; (6) rely on a private sector capable of delivering a wide array of quality services and goods; and (7) depend on households that are generally well educated about environment and water quality issues, and about the necessity to pay the utility fees and taxes to sustain operations. Developing countries, on the other hand, though perhaps stronger on the institutional “quality” of family and community cohesion, commonly experience serious weaknesses in one or more of the above institutional characteristics.

Mitigation costs and affordability

The provision of “safe” drinking water close to home has been and still is a major policy priority in most developing countries (see above). Bangladesh, like many other developing countries, has made great progress towards achieving the goal of full water supply coverage over the past three decades, drastically lowering the incidence of diarrhoeal diseases and contributing to economic growth. The cost of providing the basic service level of one handpump per 10-20 households is high (at US$100-300), but over the past decade income has risen enough to allow families to pay for the pump installation themselves. A vigorous private sector of manufacturers, drillers and pump mechanics has sprung up to meet this demand. Clearly, the financial and technical-institutional capacity of the Bangladeshi society has grown commensurate to this type of technology. Arsenic - removal systems, and alternative water supply, however, are options that pose new constraints for either rural or urban settings: they are decidedly more costly than regular water supply; and they require higher levels of technical-managerial capacity. As discussed earlier, even in the United States - a rich country with strong institutions - a debate was sparked during the revision review process of the arsenic standard. Although larger cities would be able to afford and operate the required technologies, smaller towns and rural communities would face serious financial and operational problems in conforming to a standard of 10mg/L or below.

The "rural" and "urban" agendas

From the above discussion it is clear that small and rural communities are at particular risk. They tend to be less wealthy than urban ones, and typically cannot benefit from large economies of scale to finance water treatment processes. Rural households, especially in developing countries, commonly rely on their own handpump-fitted private well, or a shared local well. Installing arsenic removal filters on such handpumps present a number of technical and institutional problems, and this has yet to be attempted on any significant scale. Bringing in alternative water, by piping, tanker or by walking to a more distant source, adds considerably to the economic cost. In addition, rural communities in developing countries have less developed local institutions such as local governments or water utilities, and transaction costs are higher to have the private sector involved as service provider. Mitigation strategies must allow for this difference in the environment.

Another factor to consider is the disposal of spent arsenic-laden filter media (or sludge water) from arsenic removal systems. In centralized systems this media can be relatively easily collected and stored in protected landfill sites. It becomes significantly more difficult when dealing with a large number of scattered household or community systems in rural areas, especially in countries with poor transportation networks[6].

8.3 Mitigation Strategies

Arsenic contamination of drinking water supplies occurs in high, middle and low-income countries. Wherever it arises, the technical parameters which form the basis for developing mitigation strategies remain the same. Thus, there are general facets of mitigation programme design which will be common in all programmes and countries. However, the social, economic, geographic and cultural differences between affected countries dictate differences in approaches and strategic choices in the final shape of the programme design. To best illustrate both the similarities and differences in mitigation programming, this section is divided into three parts: a description of a general approach to programming design, and case studies of specific approaches from middle and lower income countries.

Readers with an interest in more information on how socio-economic factors specifically influence technology choice in the development of arsenic mitigation strategies should also read Section 6.4 of Chapter Six.

8.3.1 A general approach to developing a mitigation strategy

Arsenic contamination occurs in a wide variety of forms, as so does the societal context in which the contamination must be addressed. A check-list of strategic issues to consider in developing site-specific interventions is suggested in Table 8.4 below. If recent experience gained from arsenic mitigation efforts to date is combined with the experience obtained from addressing related sectoral problems and other "crisis"

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[6] There is some debate on whether the disposal of spent media in rural areas constitutes a potential threat to public health or not. See Box 6.8 in Chapter Six for more information.

situations (water supply, health emergencies, disaster relief, etc.), a set of general principles for the design of arsenic mitigation strategy can be devised, as outlined below.

Inform affected people and other stakeholders in a timely fashion

In most cases the arsenic problem was recognized first by health officials alerted by the unusual high incidence of skin diseases. In many of these situations little remedial action ensued and often the local affected communities were not informed about these developments. This may seem inappropriate in hindsight, but a lack of understanding of the problem's significance and of the underlying phenomena, and a traditional reluctance to work across government sectors commonly contributed to the inertia. In some countries this even led to a period where government officials denied the existence of a problem.

A transparency policy engenders its own set of difficulties. A risk exists that people will panic, although prolonged absence of information is even more certain to stir panic. Also, government and other officials may feel vulnerable due to accountability issues. However, wide consensus exists that only informed people can make proper choices, and that successful strategies critically depend on the fact that the affected people and other stakeholders "buy into" the proposed programmes. This cooperation is especially important in the arsenic case because a successful strategy depends on a series of actions regarding water use and hygiene, and many of them are of a strictly behavioural nature within the affected communities and households and well out of control of government.

Therefore, any strategy must include, on a priority basis, a comprehensive and participatory information programme stressing immediate actions that can be taken by affected communities and that allows feedback from these communities to programme managers in government and civil society organizations. Such programmes typically include radio and TV broadcasts, contributions to newspapers and other publications, public hearings, activities geared at schools and youth organizations, involvement of religious institutions, staging of plays, facilitation of interpersonal communication, and other methodologies. Box 8.4 in this chapter briefly outlines the communication strategy employed by the government and UNICEF in Bangladesh as an example. Detailed recommendations for understanding, developing and implementing communication programmes for arsenic mitigation are covered in Chapter Seven.

Box 8.1
The Right to Information

The provision of comprehensive information about arsenic to affected communities is not just a good programming strategy. Access to information is a basic human right that governments and other duty-bearers are obligated to fulfil.

This right has been stated and reaffirmed in different ways in several widely ratified international conventions and charters beginning with Article 19 of the Universal Declaration of Human Rights, and including Article 17 of the Convention of the Rights of the Child and Article 15 or the Declaration on

Social Progress and Development (United Nations, 1948, 1969 and 1989).

Testing: take immediate steps to determine the extent and seriousness of the problem

Due to the high degree of spatial variability of arsenic contamination of groundwater (as described earlier), the field testing of wells for arsenic is a programming priority. This is especially true in countries - such as Bangladesh - where people rely on individual handpump-equipped tubewells for their drinking and cooking needs. Without testing it is difficult to judge the real scale of the problem at the national level and thus it is difficult to design a rational programme strategy. At the community level, it is impossible for people to make informed choices about how to use and share existing sources of water - or to construct new systems - if the extent of the problem is not known.

In reality, field testing in low income countries has proven to be extremely problematic. The development of the inexpensive, robust and user-friendly arsenic test kits that are essential for a successful field testing programme has been slower than expected. This means that programmes have been designed and launched - necessarily due to the urgency of the confronting the problem - without the benefit of the key data that a field test programme could provide. See Chapter Two for more information about arsenic measurement and analysis and the field and laboratory levels.

After wells have been tested once, they will have to be re-tested again on a periodic basis due to the possibility of migration of arsenic across aquifers as described in Chapter One and elsewhere. Periodic arsenic testing as part of a national groundwater surveillance programme (also see Section 5.6 of Chapter Five) should be an integral component in long-term national arsenic and groundwater quality programmes.

Prepare separate, but compatible, emergency and long-term programme phases

The very fact that the contamination is detected by the presence of patients suggests that rapid action is required. However, the characteristics of emergency and sustainable programmes differ considerably, and both phases must be clearly distinguished. Rapid action programmes can rely on extensive subsidies and on executive agencies that are good at effective fast delivery of a service or product (such as identification of contaminated wells, and emergency relief and distribution of safe water or medicine). Longer term programmes that seek to establish a sustainable system to address the problem require a more time-consuming process of institutional capacity building with a focus on local authorities and organizations. The process includes the development and definition of financial and managerial commitments on the part of these institutions and the full participation of all stakeholders in the final programmatic framework. It is now widely recognized that emergency relief is most effective when it is not in contradiction with the sustainability requirements of long-term mitigation strategies. Local conditions should be the predominant determining factor on how the emergency and the longer-term programmes are made to co-exist.

Prioritise reductions in arsenic intake, even if standards are not met immediately

All other factors being equal, people drinking water with higher concentrations of arsenic will more likely contract arsenicosis. It is thus an imperative, from both a strategic and ethical perspective, to focus immediate relief efforts on those communities with higher levels of arsenic concentrations in their domestic water supplies. Such efforts, given time and resource constraints, may focus on reducing arsenic levels to some interim standard above the national standard, but far below the elevated levels found in many sources. Such a strategy, by seeking out communities in arsenic “hot spots” and providing immediate solutions, will ensure that resources are used to help the greatest number of affected people.

As emergency interventions develop into longer-term programmes, and as additional financial resources are raised to fund such programmes, arsenic mitigation efforts can be re-directed towards ensuring that national standards are met for all domestic water sources.

Involve all relevant sectors in a coordinated mitigation programme

Effective strategies that relate to health and behavioural habits require, by definition, a multi-sectoral approach. Such an approach necessitates the coordinated participation of government agencies from different sectors and different levels of government, as well as other institutions and stakeholders from civil society:

- Typically, health agencies are the first to be confronted with the effects of contamination. When the public health problem is water-related, normally the agencies responsible for water supply and/or for water resources management should play a leadership role given their mandate and their access to expertise and finance. These agencies are also most familiar with the administrative procedures for commissioning of works. Although local conditions may impose specific constraints, a typical distribution of roles among key stakeholders in an arsenic contamination strategy is as follows. At the local level, the urban or rural municipality or district is the prime actor in the provision of water supply and similar services. It is also the most appropriate level from which to coordinate the activities in different sectors (water supply, health, information, etc.). In the rural context, sufficiently strong technical and financial capacities are often still absent at this local-government level, and little experience may exist regarding sustained provision of such services. In such cases, strong village - or community-based water organizations may better represent the community, and may have more success in successfully implementing cost sharing programmes. Whether at the level of local government, or in the form of a village based organization or water committee, it is essential that a “water utility” in whatever form can operate in close reciprocal relationship with its “customers”. This implies that the utility can operate in a financially and managerially autonomous fashion, that it derives at least the operation and maintenance costs from local tariffs, and that it is seen as fully accountable to its community, with all major decisions transparent and subject to scrutiny. Where there are potential gains in economies of scale, local utilities should cooperate.

- At the central level, leadership roles need to be fulfilled with respect to development of overall policy and priority-setting, conflict resolution among regions and main stakeholders, initiation, coordination and supervision of the national arsenic mitigation programmes, development of scientific support mechanisms of high quality, and provision of financial support. Such support can take the form, for example, of a partial subsidy of the capital costs of arsenic treatment works, or for offsetting those additional costs to water supply that are caused by the arsenic.

- The Ministry of Health and regional health authorities are commonly the first to be informed about an arsenic contamination case, for the simple reason that until now arsenic is not one of the key contaminants for which water utilities monitor water supply and wells routinely (despite the fact that arsenic has been a listed toxic substance in WHO literature and guidelines since the 1950s - see Chapter Five). The health sectors, therefore, need to be better equipped and prepared to identify and diagnose arsenicosis. This information should be channelled into a national steering or coordination committee that would allow other sectoral agencies to take action. Similarly, health agencies need to keep full records on incidence and possible causation of the arsenicosis to detect trends over time, as the contamination may spread and as populations may become more or less vulnerable, and to ensure detailed follow-up of the nation's mitigation programmes (see Chapter Two for a more detailed discussion on public health surveillance for arsenicosis). In coordination with the medical system, curative approaches for arsenicosis must be put in place as well as systems to minimize any secondary effects (such as skin infections - see also Chapter Four). Finally, the Ministry (or the environmental regulatory agency) usually retains the critical task of setting and monitoring drinking water quality standards, as described more fully in Chapter Five.

- Typically the Ministry of Water Resources, Public Works or Local Government is the national agency responsible for supervising and assisting the water supply utilities. In most countries, therefore, these ministries commonly take the lead in establishing an arsenic mitigation strategy where it concerns water supply.

- The Ministry of Agriculture plays the key role in the activities geared at the agricultural impact of the presence of arsenic in irrigation water. This relates to essentially three issues: (1) arsenic may enter the food chain; (2) arsenic may inhibit proper crop growth[7]; and (3) heavy groundwater abstraction discharges large quantities of arsenic on irrigated fields and may change the hydrochemistry of the aquifer[8]. Typically the agricultural agencies have a strong stake in accurate understanding of groundwater flow and availability.

- The geological services, and the academic research establishment must play a key role in a development effort with such a high science and technology input requirements. Geological services are needed to evaluate the extent and progress of the contamination problem, develop and test hypotheses on the source of the arsenic, conduct research and modelling on feasible mitigation interventions, and provide reliable information to private citizens and entities. Many of these knowledge-based responsibilities are also shared by universities and research centres. An important element is the role that the scientific community plays in a country's policy-making or day-to-day life. Where strong academic and scientific societies exist, there is openness in sharing of information and more confident confrontation of new and emerging problems such as the arsenic contamination. As detailed in Chapter One, outstanding questions on the hydrogeology and geochemistry of arsenic mobilisation and contamination may very well outnumber known facts, underscoring the need for such organizations and for information sharing.

- As full partners, the international community can share its knowledge, technology, funding and technical assistance. However, past mistakes have to be addressed squarely and national and local stakeholders have to be in control of the design and implementation of development efforts such as for arsenic mitigation.

[7] Arsenic, for example, substantially lowers the productivity of rice plants at concentrations above 50µg/L (causing "straight-stem" disease due to small rice grains).

[8] Likely much of the arsenic will be adsorbed onto oxidized iron particles when discharged under aerobic conditions. However, as biomass is collected on the ground and starts rotting in the topsoil during subsequent seasons, the arsenic may be released again.

Involve other stakeholders (communities, NGOs, private sector) in a multi-partner effort

As described above, the nature of arsenic contamination necessitates well-coordinated contributions from different partners both in and outside of government. Especially when dealing with dispersed and poorly informed rural communities, the success of a strategy depends on the cooperation of civil society organizations, the willingness of stakeholders to participate in an effective way, and on the role of the private sector to provide a wide array of services to the communities.

Recognize the uncertainty: design for flexibility

Few water supply programmes present so many uncertainties up-front, yet maintain such a high sense of urgency. The uncertainties pertain to the hydrogeology, the epidemiology, the water supply and treatment options, and the behavioural and institutional aspects at the national and community level. The latter is especially of concern in countries, such as Bangladesh, where rural communities have not had a history of dealing with complex and expensive water supply systems. Will these communities be willing and able to organize themselves and provide finance to properly and sustainably manage new water systems? Clearly, any mitigation strategy will have to rely on high-quality studies - thereby avoiding delays - but still be able to drastically improve the focus and effectiveness of the next phases in the implementation programme. Any programme should minimize up-front costs to contain expenses in case the strategy must be amended. Strong links must be built with a scientific advisory committee, or equivalent, to attract the best analytical and research capacity, and develop a high-quality data base of all relevant parameters, that will be maintained as long as the arsenic problem exists, and that will be able to detect changes in the situation.

Table 8.4 Check-list on key issues in the development of an integrated strategy for arsenic mitigation

Determinants of the gravity of arsenic contamination	Possible strategic intervention
Measurable, physical symptoms of arsenic contamination: Extent and intensity of contamination, sources and valences of As, etc.	• National data collection; • Improvement of field and laboratory protocols for As measurement.
Economic impact of As contamination: Health, environment, agriculture, etc.	• Integration of information on the impact of As on key economic/social sectors to establish priorities and appraise solutions.
On-site actions that promote As ingestion directly or through bio-accumulation: This is especially important where	• Provision of on-demand testing of individual wells; • Provision of information on health and emergency alternative sources of water;

large numbers of affected rural people rely on contaminated water for themselves, their animals and their crops.	• Long term technical assistance to decrease reliance on As contaminated sources.
Off-site actions that promote As contamination: Rates of pumping and overall flows of groundwater in one place could be affecting the quality of water of individual farmers in another place.	• Research on and modelling of groundwater dynamics; disseminate data; • Include As (and overall water quality parameters) in the routine environmental impact evaluation of water development projects.
Level of knowledge of people and institutions: In many cases, there are simple on-site solutions that can be introduced, in others, more research is needed. (see, for example, Box 8.2)	• With information on the extent of the problem, disseminate existing technologies; • Prioritise research and dissemination themes for capacity building of key actors in an As situation.
Legal, institutional, policy framework: In most cases, groundwater management is left to individual users, with government maintaining overall stewardship.	• Clarify the roles and empower institutions that can address groundwater quality issues, starting with local-level institutions; • Integrate As mitigation in overall water supply, water management, health, agriculture and environmental strategies.
International considerations: For developing countries, external assistance often constitutes the bulk of investment into specific sectors, such as water supply.	• Include As in routine environmental impact assessment of water-related investments; • Promote local ownership of interventions by keeping the national and local stakeholders in the "driver's seat" at all time in planning, designing, implementing and monitoring of As mitigation. • Promote international networking in support of As mitigation.

Box 8.2
Dug wells: Traditional knowledge for arsenic mitigation in West Bengal, India

Dr. Dipankar Chakraborti (Jadavpur University, Calcutta, India) has been one of the earliest voices around the world for recognizing the epidemic nature of arsenic as a naturally occurring contaminant. His teams have now more than 13 years of field experience in West Bengal and Bangladesh. One of their observations was initially puzzling but arguably points to one of the more cost-effective water treatment methods for the millions living in rural areas with arsenic in their groundwater.

In West Bengali villages known to have arsenic in the groundwater, virtually no *arsenicosis* incidences were found where people drank mainly from the common dug wells, which are shallow hand-excavated wells. However, *arsenicosis* was found in people who drank from deeper tubewell water in the same areas, although dug well water was often as rich in arsenic as tubewell water. Field and lab work suggested a correlation between the iron content of dug well water and the lower levels of arsenic in the water that got eventually consumed. It could be surmised that dug wells, with their higher exposure to air, allow iron and arsenic to co-precipitate out of the water.

Dr. Chakraborti thinks this is consistent with traditional behaviour in rural West Bengal: Bengalis say *“Jal basi kore khab*i” which translates into “drink water after letting it settle overnight”. Such a simple procedure, accepted as local wisdom, would indeed allow to lower arsenic levels in water (if iron is present at significant levels) and have it settle out at the bottom of the water jar. Filtration of the supernatant water with a simple home strainer, readily available in rural households, would further enhance separation of the settled arsenic from the drinking water (see Chapter Six for a comprehensive analysis on the pros and cons of all arsenic removal techniques, including the one described here).

8.3.2 Arsenic mitigation strategy in middle-income countries: Mexico and Chile

Background

Local health authorities were the first to detect arsenicosis in both countries in the sixties and seventies. However, it took several years before recognition grew that this was indeed arsenic-induced, that it was related to water contamination, and that many more casualties would be caused if no rapid remedial action was taken.

In Mexico, one of the principal areas where the contamination was found to be occurring was the Lagunera Region in the country’s mountainous centre, north of the capital and straddling the Coahuila and Durango States. The Region is a large enclosed basin with a small population of approximately 400,000 (Table 8.2; Fig. 8.1) and intensive agricultural activity, notably grain production. Crops are irrigated from groundwater wells and from water reservoirs on rivers on the outskirts of the region.

In Chile, contamination was reported in the northern provinces of the sparsely populated central Cordilleras and the nearby coastal plain. This region has a few larger towns and cities (notably Antofagasta) in the coastal plain. In addition, several dozen small hamlets, each with a population of approximately one hundred, are located more inland. The region has numerous local depressions that collect the scarce run-off and from where the water evaporates leaving salt layers *(salare*s). The rural communities are very poor and remote in relation to the towns.

Mitigation strategies

Although local health authorities had been aware since 1964 of the arsenicosis incidence in the Lagunera Region (Mexico), little action was taken. In 1986-87 the (then) Ministry of Agriculture and Water Resources took the lead in drafting a mitigation strategy together with the Ministries of Health and of Urban Construction (the latter typically being responsible for water supply). A three-phase strategy was developed:

1. Emergency response of a temporary nature:
o Make the situation public and explain to the local communities the implications of the contamination and the government’s actions;

o Provide rapid health response to identify patients, provide information, and offer medical assistance where feasible;

o Bring in reverse osmosis treatment plants mounted on trucks to treat local well water and distribute free of cost at selected locations in the towns;

o Initiate studies regarding the origin and possible dissipation of arsenic contamination in the groundwater.

2. Sustainable mid-term solution: Finance a pipeline *(acuaducto)* to convey safe groundwater from distant wells to the affected towns, from where it can be tapped by the local utilities. (Early studies had shown that the arsenic originated from one corner of the aquifer and was dissipating to other zones under the influence of water abstraction. The continuing groundwater use would after several years cause these safe wells to become contaminated as well.)

3. Longer-term sustainable solution: If the *acuaducto* starts to yield contaminated groundwater, the initial pipeline design would allow an extension to tap water from surface water reservoirs in the mountains.

Insert Figure 8.1 Map of the Lagunera Region in Mexico

The *acuaduct*o's length is approximately 100km and involved substantial expenditure. Over negotiations with the local governments that normally are responsible for water supply, the national government agreed to finance the construction of the new wells, pumping stations and pipeline given the exceptional nature of the water supply situation. The local authorities agreed to (1) set up a joint regional corporation (owned by the two States involved and the municipalities) to operate and maintain the *acuaducto,* and to ensure local cost recovery for this through tariffs; and (2) assume the responsibility for investment, operation and maintenance for the distribution of the water starting from the respective abstraction points on the *acuaduct*o. The national government transferred ownership of the infrastructure to this new corporation. The main operational cost of the *acuaducto* is for pumping. Isolated farms that were not connected to the local distribution networks would have to purchase drinking water from the utility by container or tanker.

In Chile, the affected region is arid and sparsely populated. The water supply task rests solely with local governments. The major affected city of Antofagasta (population: 200,000) draws water from the Toconce River via a 300km pipeline. Most rivers in this region, as well as in the Arica Province, have elevated arsenic concentrations. Some six conventional treatment plants for surface water are operational in the region serving a total population of approximately 330,000 and have been upgraded to remove arsenic to the threshold of 50mg/L. Although originally this goal proved difficult to achieve, optimised operation has recently allowed the production of water at this quality level in the larger plants. However, performance remains variable. Treatment typically consists of oxidation with chlorine followed by direct filtration or flocculation with alum, and final filtration. However, the small rural communities of *atacameño* settlements of 100-400 people are too dispersed and too poor to be easily reached. Experiments with small-scale on-site treatment have been initiated using iron sponges as adsorbent and double sand filters, but no satisfactory solution has been achieved so far. Interestingly, mummified bodies of native Indians have been discovered in the mountain range, dating back several centuries, and many of these show high arsenic levels in their tissue.

8.3.3 Arsenic mitigation strategy in low-income countries: case studies from Bangladesh

The characteristics of the arsenic contamination in Bangladesh differ substantially from those in the two Latin American countries described above. Bangladesh is decidedly poorer, with a GNP per capita of US$270 compared to US$3,700-5,000 for Chile and Mexico. Its population density is very high, and most people live in small to medium sized villages, with populations generally ranging from 500-3,000.

Most of the country is a flat deltaic area with soft soils and high water table. This allowed the successful introduction of shallow and medium-deep handpump-equipped tubewells since the seventies. Current estimates indicate that there are now between 2.5 and 5 million such wells used for domestic water supply and an additional 5 to 6 million wells drilled for irrigation purposes but also used, at least in part, for drinking water (DCH/Uposhon 2000; UNICEF 2000a; WHO 1999). The majority of the tubewells were drilled by the private sector, and a vigorous market exists of part suppliers, well drill crews and mechanics.

Bangladesh's government structure is still very centralized. However, since 1997, new legislation is gradually promoting the devolution of power to local levels, although it is unclear to what extent the lowest administrative unit (the Gram Parishad, which is an association of one to three villages) will be enabled to assume decision-making powers. Local authorities are very weak and many have no prior experience with infrastructure and with water service delivery.

The contamination is nearly country-wide (Fig. 8.2) with up to four-fifths of the territory sitting atop contaminated aquifers. The size of the affected area, the very large numbers of people "at risk", and the often very high arsenic concentrations (well above 500mg/L) make it decidedly a priority concern at the national scale. An important complicating factor is that the contamination degree varies widely from one spot to another, and one well may be contaminated whilst another one at 10m distance yields good quality water (although it is reported that good wells can turn bad over time, as discussed earlier in this chapter).

Insert Figure 8.2 Map of Bangladesh

Caption: "Map of Bangladesh indicating the distribution and intensity of contamination. The data are compiled from a variety of reliable well studies conducted by the Government, NGOs and others. The map reflects the status of the understanding in 1998; new information broadly confirms this pattern (World Bank 1998)."

Preliminary reports of arsenicosis emerged in the early nineties in the western Districts bordering West Bengal in India (where widespread arsenic contamination of groundwater was just being recognised). First field tests on randomly sampled wells, notably by the Dhaka Community Hospital and Jadavpur University's School of Environmental Studies, and later by the Department of Public Health Engineering, confirmed an unexpectedly large incidence of arsenic contamination. In 1996 the Minister of Health and Family Welfare took the initiative to set up an inter-ministerial committee to review the situation. WHO fielded a number of individual experts to help assess the situation but it soon transpired that the dimension and complexity of the problem necessitated a broader effort.

The two case studies presented below describe some of the programmes currently being implemented in Bangladesh. The first case study is on the Bangladesh Arsenic Mitigation - Water Supply Program (BAMWSP), a large national-level programme implemented by the government of Bangladesh and financed primarily through a World Bank loan. The second case-study describes a smaller "action research" initiative supported by WHO and UNICEF in Bangladesh, financed by the United Nations Foundation.

The case studies presented here describe only a portion of ongoing activities in Bangladesh. There are many external support agencies, local and international NGOs, academic institutions, and branches of government active in arsenic mitigation activities in the country. A recent WaterAid report lists 35 such organizations (Jones 2000).

It should also be noted that this plethora of agencies and initiatives, while welcomed and necessary, can create its own set of problems. The coordination of mitigation strategy development and implementation in Bangladesh has been problematic. One of the purposes of the BAMWSP programme as described below was to assist the Government of Bangladesh in developing the capacity and institutional infrastructure to effectively coordinate all mitigation activities in the country. This has been more difficult then originally envisaged and, to date, efforts are still ongoing by governments and a number of agencies (including WHO) to set-up effective coordination mechanisms.

Case study: The World Bank-supported Bangladesh Arsenic Mitigation - Water Supply Program (BAMWSP)

In 1997 the government requested the World Bank to assist in working out a national strategy and in assisting in the coordination of the international cooperation effort.

When the programme was being designed, the degree of urgency was inversely proportional to the amount of information on hand. Very limited insight existed into the extent, cause, and impact of the contamination; no simple technological answers were available nor did the country have much experience with low-cost water supply systems beyond shallow handpumps. Millions of measurements of arsenic would have to be conducted in the field, yet world-wide only the first steps were being taken to develop a cheap and reliable field test kit. In 1997, not even a reliable estimate of the number of wells existed. Most difficult of all, the local nature of the contamination would force the teams to work closely with the local affected communities, yet there was no proven methodology in Bangladesh to develop sustainable service delivery at the grass-roots level. Under such challenging circumstances, a phased approach was opted for, with plenty of room for "learning-by-doing".

In 1998 the government adopted a national strategy for implementing the programme, for which support was provided through a soft credit from the World Bank complemented with a grant from the Swiss Development Corporation. Various coherent support and complementary activities, all as grants, from the British, Danish, Dutch and Japanese Governments, as well as from UNDP, WHO, UNICEF, IAEA (and others) were also taken into account in the programme development process. A number of major NGOs, both international and national, were also active preparing their own responses, and some participated in the strategy development and implementation of the World Bank-supported programme.

Partly to start understanding the precise nature of the problem at field level, and partly to provide field assistance, a preliminary emergency initiative was conducted in 1997-1998 to complement the planned World Bank-supported programme. With UNDP funding, a national health agency, the Dhaka Community Hospital and NGOs held one-week-per village extensive visits, first in 200 and thereafter in 600 villages that were carefully selected. The local health situation and all wells were analysed and recorded, and basic information and medicine given. This field study confirmed earlier hypotheses about the high incidence of contamination, and the commitment of villagers to deal with it.

The main principles and components of the strategy developed are as follows (programme policies and illustrative technical, institutional and financial details of project implementation are compiled in a manual; BAMWSP 1998):

1. The consensus among experts is that it is priority to provide arsenic-free drinking water, partly because it is a *preventive* measure, and partly because in many arsenicosis patients clean water flushes out excess arsenic from the body and may reverse disease symptoms, to a certain extent (see e.g. WHO 1997). Therefore, the strategy concentrates in the first instance on water service delivery rather than strictly on health care. The main initiative, thus, is placed with the Ministry of Local Government, Rural Development and Cooperatives, as well as with local authorities, village communities and NGOs to the extent that they play a role in water supply. Nonetheless, a second separate activity concerns health care and curative action and falls under the purview of the health authorities and medical colleges. The Minister of Health remains the Chair of the overarching policy coordinating committee.

2. With most Bangladeshi households fully depending on their handpump-equipped well for water, these households have, at least, the right to be informed about (1) the current status of their own well, (2) the availability of an alternative safe water source in their immediate vicinity, (3) basic rules to minimize the exposure and the health impact, and (4) the quality of their well water in the further future through the provision of an arrangement that would allow annual re-testing. Providing this information can be done in a reasonably expedient way, and it would arguably be a very cost-effective first approach to reduce the net intake of arsenic. Similarly, such transparency would help prevent panic given that rumours on the contamination were spreading quickly.

3. The most appropriate strategy would be to lower as quickly as possible the net arsenic intake by applying low-cost, simple approaches, even if these do not immediately meet the drinking water standard. Such a strategy is justified by the fact that the sheer scale of the contamination and the intrinsic cost of mitigation technologies pose an excessive financial burden on households and government, and because the arsenicosis risk is reduced more or less proportionally to arsenic intake. For example, a backyard flocculation-and-filtration double bucket system costs less than US$5 and can be reliably operated in households; removing only 80% of the arsenic, it would lower the concentration of well water with 300 to 60mg/L - still above the standard of 50, but now with much reduced health risk.

4. The first four-year implementation phase includes a nation-wide rapid emergency component that comprises (1) the testing of all wells (at the same time recording these wells in a GIS data base), (2) a rapid health survey with referral for diagnosis and treatment, (3) the provision of short-term relief where feasible, and (4) nation-

wide as well as village-based information (see the second Bangladesh case study below, and Box 8.4 for a description of national information campaigns). A second, parallel component aims at providing more sustainable alternative water supply options, which may imply some construction and procurement. This component will progress more slowly as it has to build community demand and participation at village level. Possibly 10-15 years may be necessary to cover all affected villages, and identification of the “hot spots” (in terms of local health impact) would be eminently important.

5. In towns, the programme helps local authorities (that normally would already exist but may have limited experience with utility functions) to set up water quality monitoring, and design and finance remedial actions. Utilities will be supported and trained to improve service delivery and cost recovery to ensure sustainable operation.

6. In the rural areas as well as in the urban fringes, community-based organizations will be set up. In close coordination with the local official administrations, these will decide on their local strategies, select their alternative water supply technology, have a design formulated, conduct local procurement, and carry out and/or supervise construction. They will take charge and finance the operation and maintenance of any infrastructure and, importantly, finance part of the investment as well. The programme finances the other part of the investment. Water supply alternatives include rainwater harvesting, ponds, dug wells and shrouded wells, deep groundwater, and where feasible, arsenic removal techniques. Many of these options will also require sanitation to prevent recurrence of diarrhoeal diseases, since the alternative water source would be again surface or pond water that are very liable to bacterial contamination. An uncommon partnership between local and national government, and NGOs, has been forged to implement the programme. Local NGOs act as the direct partners for the local authorities and for the communities when these form their community-based organizations and devise and implement their strategy.

7. One of the unknowns in the strategy is whether communities and local authorities will be strong and accountable enough to assume the task of sustaining the delivery of water services within the community. These doubts notwithstanding, the programme design assumes that greater effectiveness and sustainability will be achieved by keeping management and implementation at the local level as much as possible. Compelling arguments that support working directly through the communities are (1) positive experiences with service delivery in projects in neighbouring countries; (2) the demonstrated ability of Bangladeshi communities and private entrepreneurs to develop a vigorous handpump market without government support; and (3) the unusually high awareness and concern among the population, at least in some parts of the country, that arsenic is dangerous to health. Nonetheless, the programme’s strategy is flexible enough to allow simultaneous piloting and implementation of different institutional approaches and then replication of what works best.

8. A major constraint in optimising the strategy is the lack of information on the epidemiology (see, for example, Chapter Three), the extent and causes of the arsenic release and the related hydrogeology (see Chapter One for details of outstanding questions and further research needs), the institutional arrangements and behavioural aspects of the water service, and the appropriate low-cost water supply technologies[9]. To address this, two supportive entities are being set up. The National Arsenic Mitigation Information Centre to collect, interpret and disseminate all relevant hydrogeological, water quality, health and socio-economic data. Secondly, a

Technology Assessment Group of experts was established to review technology options, allocate funds to local researchers to undertake specified studies, and provide academic input in the policy development. Several bilateral donors fund specific fundamental studies, such as on the geochemistry of the problem, the development of a cheap and reliable field test kit, and on the epidemiological dimension.

9. The strategy provides substantial capacity building efforts, especially to assist communities and local authorities in developing their skills as well as their internal administrative procedures. In addition, training for medical colleges on arsenic diagnosis and referral is included. Finally, a substantial effort is made to inform and educate the population at large through a variety of the media channels about appropriate ways of dealing with arsenic.

[9] As described in Chapter Six, there is no shortange of information on alternative water supply technologies in general, but there are questions about applying the technolgies in Bangladesh. In addition, there are many outstanding questions on arsenic removal technologies.

Case study: Who- and Unicef-supported Programmes in Bangladesh10

[10] Information sources for this case study include UNF 2000, WHO/UNICEF 2001 and other WHO and UNICEF sources.

UNICEF and WHO have been key partners with the Government of Bangladesh in the area of rural water supply and sanitation for several decades. As such, these two agencies have been at the forefront of national arsenic research and response programmes since the crisis emerged. Both agencies are supporting a number of ongoing initiatives in the area of arsenic in Bangladesh with a variety of partners[11].

[11] UNICEF, for example, is working with the Department of Public Health Engineering (DPHE) in the area of water supply at the national level, and has supported DPHE's large-scale arsenic testing programme (UNICEF 2000). UNICEF has also helped to develop a national arsenic communication campaign (see Box 8.2). WHO has supported the Government of Bangladesh's response to the arsenic situation since 1994, primarily through the provision of technical expertise. WHO is also active, with a variety of local partners, in the area of research and development of alteranative water supply systems. WHO's global role as the focal point for water quality issues within the UN system, and the publisher of the Guidelines for Drinking-water Quality, has allowed it to act as a kind of knowledge base for all agencies working in the area of arsenic in Bangladesh (WHO 1999).

For the purposes of this case study, a new WHO/UNICEF joint project will be described. The fact that it has recently been developed (2000/2001), has allowed it to capitalize on lessons learned from other arsenic mitigation projects in Bangladesh, and can thus be considered to be a kind of state-of-the-art project design for arsenic research and mitigation in the context of Bangladesh. The most important input to the design of the WHO/UNICEF joint project are the lessons learned from previous initiative, notably from the DPHE/UNICEF Action Research Project described below.

DPHE/UNICEF Action Research Project: Lessons Learned

The DPHE/UNICEF arsenic mitigation Action Research Project was implemented in 1999 and 2000 in five upazillas[12]. The project's achievements at the field level included the testing of over 100,000 tubewells, the construction of over 500 alternative water systems (deep tubewells, pond sand filters, rainwater harvesters and dug wells), the distribution of 14,000 home arsenic removal filters (four different household filter designs were used in the project) and the construction of 3 community filter plants. The project also identified more than 900 arsenic patients and provided palliative care for symptom relief.

[12] Sub-district administrative divisions, previously known as thanas.

The DPHE/UNICEF project provided a valuable set of information and data on the effectiveness, real costs and sustainability of technology choices for arsenic mitigation under actual field conditions. Several technologies - notably household arsenic filters - were modified as the project progressed in response to field-level conditions. The project also reinforced expectations of planners that there is no single "best" technology for arsenic removal or alternative water supply in Bangladesh - rather it helped to narrow and improve the set of effective, acceptable and inexpensive technologies available for application by local authorities to respond to local conditions.

Perhaps the most important lessons learned from the UNICEF/DPHE Action Research project were at the institutional level. Like the World Bank-funded BAMWSP project described in the case study above, the design of this project emphasized the importance of working at the local level. However, instead of attempting to work directly with a large number of small, local NGOs as was envisaged by the BAMWSP project, the Action Research project designers instead opted for forging partnerships with four large national NGOs. Each of the NGOs chosen (BRAC, Grameen Bank, Dhaka Community Hospital and Rotary) had extensive country-wide networks of extension workers with well-established systems of supervision and feedback. This proved to be a successful model, allowing the project to immediately concentrate on pursuing objectives rather than spending time establishing new institutional infrastructures necessary for working with larger numbers of scattered NGOs.

On the other hand, the project did not go far enough to establish and formalize links with local government authorities at the upazilla and village levels. This is now seen to be potentially detrimental to long-term sustainability. In addition, no system of community contribution towards the construction, maintenance and operation of the new water supply systems was put in place. This, also, would impede the eventual expansion of the model to the national level.

Building Community-based arsenic mitigation response capacity in three sub-districts: an outline of the WHO/UNICEF joint project

The United Nations Foundation has funded the two-year project, which will be implemented by DPHE, the Directorate General of Health Services (DGHS), WHO and UNICEF in cooperation with the World Bank-funded BAMWSP project, local governments in the sub-districts (upazillas), and six national NGOs and research institutions.[13] In terms of funding and size, the project is an order of magnitude smaller than the World Bank-supported project (roughly $2.5 million versus $42 million) and is restricted to a small area of the country. As such, the project's key objective is not to mitigate the arsenic problem on a national scale, but to develop an approach to arsenic mitigation at the local level that can ultimately be used by larger government and external support agency initiatives. However, the project is not a study, it is “action research” that will, as it develops strategic approaches, also help communities provide solutions to the arsenic public health problem in the project area.

[13] National Institute for Preventive and Social Medicine (NIPSOM), Bangladesh Rural Advancement Committee (BRAC), Grameen Bank, Dhaka Community Hospital, NGO Forum for Drinking Water Supply and Sanitation, ICDDR, B - Centre for Health and Population Research.

A key concept behind the project is the promotion of empowerment for local action for arsenic mitigation. As such, it builds on recent Government of Bangladesh movements in this direction as described, in part, in the above case study. It also is in accordance with government’s 1998 National Policy for Safe Water and Sanitation which emphasizes greater user participation through local governments. As described earlier in this chapter and elsewhere in this volume (notably in Chapters One and Six), there is a high degree of spatial variability of arsenic contamination of tubewells in Bangladesh and technological and institutional solutions must also differ from area to area. Thus, an approach that emphasizes local solutions to local problems is highly suited to this issue.

The project will promote an integrated approach including awareness raising, water supply testing, choosing and constructing alternative safe water sources, and patient identification. Capacity-building efforts will be focussed on the upazilla and sub-upazilla government authorities for the provision of communication, advice and action in arsenic-affected villages.

At the institutional level, the project’s design reflects the lessons learned from the DPHE/UNICEF Action Research Project described above. Planning and implementation of activities at the upazilla and sub-upazilla level will be the responsibility of local government authorities supported by DPHE, UNICEF’s field-based staff, and national NGOs. Technology choice will be made on the basis of local conditions and preferences out of a changing pool of acceptable technologies defined by DPHE, WHO and UNICEF based on the results of the Action Research Project, ongoing research and information from other agencies active in the sector.

Activities implemented at the upazilla-level range from awareness-creation and tubewell testing to monitoring and evaluation (see Box 8.3). The roles and responsibilities of all implementing partners differ from activity to activity and are pre-determined in the project design. The focus of the project on capacity building is reflected in the number of activities that include training and the development of institutional infrastructure. The design of upazilla-level activities also stress the need to monitor, evaluate and document lessons learned during the implementation period.

Box 8.3
Joint WHO/UNICEF Project: List of Upazilla-level activities

1. Training/awareness creation for NGO, DPHE, Local govt., Health complex staff, communication campaign counterparts

2. Carry out baseline survey/study

3. Formation of upazilla arsenic mitigation committee

4. Training on use of communication materials and implementation of communication campaign

5. Training for tube well testing

6. Blanket tubewell testing

7. Arsenicosis patient identification and management

8. Formation of Village Arsenic Mitigation Committees

9. Provision of technical advice on alternative water supply technologies (with emphasis on gender considerations) and community selection of appropriate technologies

10. Training on construction of alternative safe water technologies

11. Construction or distribution of alternative water supply technologies

12. Training for caretakers on alternative water supply technology maintenance

13. Monitoring of alternative water supply technologies

14. Evaluation: changes in baseline data, assessment of effectiveness

15. Consolidation and dissemination of knowledge generated and lessons learnt

(source: WHO/UNICEF 2001)

The multi-faceted nature of the arsenic crisis as described earlier in this chapter was a key factor in the design of the joint project. The design was careful to include implementing partners and cooperating institutions that could bring a variety of skills and experience to project implementation. NGO partners were chosen not only for their field presence, but for the mix of skills and experience they offer which include: primary health care, grass-roots mobilisation, micro-credit, epidemiological research, and rural water supply. Similarly, both the public health engineering (DPHE) and health (DGHS) wings of government are participating in the project. On the same note, the implementing partners (WHO and UNICEF) will operate within their comparative competencies in the management of the project: UNICEF will use its water supply and communication experience, and its field presence in Bangladesh, to take the lead on managing the upazilla-level project activities, while WHO will take primary responsibility for the management and implementation of the research component of the project described below.

The project's research component has two objectives: one, to support and inform implementation of the project itself, and two, to expand the general knowledge base on arsenic and mitigation, for the use in other projects in Bangladesh and elsewhere. The project will sponsor studies and research on the causes and effects of arsenicosis.

Topics to be studied will include case detection and management, and suspected associated co-factors such as nutrition and dose-response relationships. The research activities will be undertaken in collaboration with national institutions (notably, the Centre for Health and Population Research) and in cooperation with complementary research activities at the national and global levels.

Box 8.4: Information, education and communication in addressing Bangladesh's arsenic crisis

Community involvement is a fundamental aspect of arsenic mitigation in Bangladesh. The population is largely rural and supplied with water through community or private tubewells. Lessons in Bangladesh and elsewhere had already shown that these conditions dictate a community-based approach - in planning, design and implementation - for the success and long-term sustainability of overall interventions in water supply and sanitation.

Mass awareness techniques that had already proven successful in dramatically reducing the incidence of water-borne microbial diseases are being re-introduced; this time to confront a "new", chemical, contaminant: dissolved arsenic in groundwater.

Historically unique challenges are, however, constraining the effectiveness of mass awareness campaigns targeting arsenic contamination. Previous water-quality related campaigns such as during the Water Decade have targeted well-understood human-induced water degradation processes (e.g. faecal contamination) with the use of readily available mitigation interventions (oral re-hydration saline, low-cost tubewells). In the case of arsenic, however, the source of contamination is natural and continuous --arsenic is colour-, odour-and taste-less-- and the technology for field testing and treating of arsenic is still under development. Under these circumstances, incomplete or erroneous information could lead to panic, misinformation, and a worsening of the situation, such as, for example, rural people reverting to highly microbially-contaminated surface water once they know that their underground water source is contaminated with arsenic.

Communication initiatives: Arsenic contamination in Bangladesh has triggered an unprecedented level of mobilization of local NGOs, government organizations and external support agencies. Among the early and most active organizations in Bangladesh that focused on the preparation and evaluation of community-level communication strategies were the Dhaka Community Hospital, the Bangladesh Rural Advancement Committee, and Integrated Services for Childhood. With external support from UNICEF and in collaboration with central and local government agencies (Directorate of Public Health Engineering, the Ministry of Health and others) communication packages have been prepared and are being widely disseminated to communities. In particular, in December 1999 a the UNICEF-designed National Communication Campaign on Arsenic Mitigation was launched, aiming at the dissemination of available material on key aspects of the problem. Because of the gravity and geographical extent of the problem, the communication campaign has to rely on the widest range possible of NGO participation in collaboration with 5 levels of decentralized government entities. As in other aspects of arsenic mitigation, coordination among such a large number of institutions is a major challenge. See the case study in Chapter Seven for a complete description of the development of the national communication campaign.

Technical Parameters: Given the knowledge gaps and degree of uncertainty in the area of arsenic, it is of key importance to ensure that the technical information that form the basis for communication messages are clearly defined. In Bangladesh, a small group of international experts was convened to define and come to a consensus on a set of basic technical information that was then used as the technical underpinning for the development of the national campaign. See the annex of Chapter Seven for the full text of these technical parameters.

Vital Information that is being disseminated through pamphlets, site visits and mass media outlets, include the following:

- Test water for arsenic;

- Do not drink from contaminated wells (usually marked with red paint);

- Improve diet to include protein, vitamin supplement etc.;

- Collect rain water for drinking and cooking;

- Explanation/demonstration of currently available low-cost technologies for: household and community-level arsenic removal, surface water filters for microbial/sediment treatment, and rain water harvesting;

- Explanation of external symptoms of arsenicosis;

- Information on options for referral of affected people to health personnel.

From Development to Dissemination: As new research refines technical knowledge about arsenic, and as arsenic mitigation strategies evolve, it is important that messages disseminated through communication campaigns to communities be updated on a regular basis. It is therefore essential to revise technical parameters for communication through networks of researchers, planners and field workers. Such networks are being established in Bangladesh and will require concerted and long-term support to ensure their effectiveness in changing the situation on the ground.

(From Chapter Seven of this volume and various reports by UNICEF-Dhaka, e.g. UNICEF 2000b, and other agencies)

8.4 Conclusions

It is now clear that the chronic effects of low concentrations of arsenic in drinking water have been underestimated. Large populations in various parts of the world are exposed to levels of arsenic above safe limits. The full epidemiological implications of arsenic contamination are only now emerging, and it is likely that over the coming decade more arsenicosis cases will be identified.

This adds substantially to the complexity of water service provision. Arsenic removal is - in general - expensive and technically difficult, and alternative water sources may either be unavailable or can pose their own serious health risks (such as increased diarrhoeal disease incidence). Such complexity in the provision of safe water supply is especially acute in rural and poor urban areas, and also in regions where arsenic levels are relatively high (above 200mg/L).

Importantly, the degree of complexity and the commensurate expenditure greatly depend on what is considered to be a “safe” standard for drinking water. Technological and financial complexity of arsenic mitigation skyrocket once standards are lowered below 50mg/L. It is doubtful that setting standards at the safest possible level is an effective health policy for developing countries because the resulting costly arsenic mitigation is likely to divert funds from other health related programmes that may have a greater impact on public health. Whatever national standards are, it is of key importance that priority be given to measures that reduce the absolute intake of arsenic as much as possible, even if the standard is not met immediately.

Arsenic contamination can occur in a wide variety of geographic and socio-economic contexts. Therefore, any mitigation strategy will have to be tailored to suit the local hydrogeological, institutional and financial situation. That said, it is also important to not develop national or sub-national arsenic mitigation programmes in isolation. Many of the lessons learned over the years in water supply programme implementation are highly applicable in situations where arsenic is a factor. One of the most important of these lessons is that to achieve effectiveness and sustainability communities must be fully involved in the planning and development of water supply systems, and they must be fully committed to take an appropriate level of managerial and financial responsibility for the construction, operation and maintenance of those systems. Often, such institutional and social factors are a greater determinant of the ultimate success of water supply programmes than are technological factors. Similarly, real, long-term health benefits do not automatically flow from new water supply systems, they must be accompanied by communication and education programmes that promote behavioural change.

The government plays a critical role. It must develop national plans of action, and ensure that mitigation efforts by external support agencies and civil society organisations are implemented in a coordinated fashion. Governments must also ensure that the affected population is fully and properly informed about the situation, so that people themselves can immediately initiate precautionary measures. Governments should work with academic and research institutions to improve the understanding of the causes, extent and impact of arsenic contamination. Most importantly, governments should immediately provide emergency relief as far as is feasible, and, in many cases, provide financial support for the construction of mitigation facilities if these prove beyond the means the communities.

It is now abundantly clear that groundwater should be carefully analysed for arsenic before it is used as a source for domestic water supply systems - or even for irrigation. Although the ultimate global impact of arsenic contamination on public health is as yet unknown, there is little doubt that it constitutes a serious threat and arsenic analysis should thus be included in water quality monitoring surveillance programmes. Perhaps more importantly, the arsenic crisis in Bangladesh and elsewhere has highlighted the need for including comprehensive water quality surveys as integral components of all water supply programmes. Finally, the experience from arsenic has indicated that additional research is necessary on the potential health effects of other inorganic elements present in low concentrations in water sources.

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