ARSENIC IN DRINKING-WATER

1. Exposure Data

1.1 Chemical and physical data

Arsenic is the 20th most common element in the earth's crust, and is associated with igneous and sedimentary rocks, particularly sulfidic ores. Arsenic compounds are found in rock, soil, water and air as well as in plant and animal tissues. Although elemental arsenic is not soluble in water, arsenic salts exhibit a wide range of solubilities depending on pH and the ionic environment. Arsenic can exist in four valency states: –3, 0, +3 and +5. Under reducing conditions, the +3 valency state as arsenite (As^{III}) is the dominant form; the +5 valency state as arsenate (As^{V}) is generally the more stable form in oxygenized environments (Boyle & Jonasson, 1973; National Research Council, 1999; O'Neil, 2001; WHO, 2001).

Arsenic species identified in water are listed in Table 1. Inorganic As^{III} and As^{V} are the major arsenic species in natural water, whereas minor amounts of monomethylarsonic acid (MMA) and dimethylarsinic acid (DMA) can also be present. The trivalent monomethylated (MMA^{III}) and dimethylated (DMA^{III}) arsenic species have been detected in lake water (Hasegawa *et al.*, 1994, 1999). The presence of these trivalent methylated arsenical species is possibly underestimated since only few water analyses include a solvent separation step required to identify these trivalent species independently from their respective

Table 1. Some arsenic species identified in water[a]

Name	Abbreviation	Chemical formula	CAS No.	pKa
Arsenous acid (arsenite)	As^{III}	$As(OH)_3$	13464-58-9	9.23, 12.13, 13.4
Arsenic acid (arsenate)	As^{V}	$AsO(OH)_3$	7778-39-4	2.22, 6.98, 11.53
Monomethylarsonic acid	MMA^{V}	$CH_3AsO(OH)_2$	124-58-3	4.1, 8.7
Monomethylarsonous acid	MMA^{III}	$CH_3As(OH)_2$	25400-23-1	
Dimethylarsinic acid	DMA^{V}	$(CH_3)_2AsO(OH)$	75-60-5	6.2
Dimethylarsinous acid	DMA^{III}	$(CH_3)_2AsOH$	55094-22-9	
Trimethylarsine oxide	TMAO	$(CH_3)_3AsO$	4964-14-1	

[a] From National Research Council (1999); Francesconi & Kuehnelt (2002); Le (2002)

pentavalent analogues. Other unidentified arsenic species have also been reported in seawater and fresh water, and could represent up to 20% of the total arsenic (Francesconi & Kuehnelt, 2002; Le, 2002).

1.2 Analysis

Studies of human exposure to arsenic and its consequences for human health require two different kinds of arsenic analyses depending on whether quantitative or qualitative results are required. Several methods have been developed and improved for the measurement of total arsenic, and have been widely used for the evaluation of drinking-water contamination and the resulting concentrations of arsenic in humans. On the other hand, analytical methods allowing arsenic speciation have gained increasing interest. The environmental fate and behaviour, bioavailability and toxicity of arsenic vary dramatically with the chemical form (species) in which it exists, the inorganic As^{III} and As^{V} being, for example, far more toxic than MMA and DMA. Thus selective methods that determine the relative concentration of the different arsenic species in drinking-water are required when more precise assessments of their impact on human health are needed.

Analytical methods for arsenic have been reviewed (National Research Council, 1999; WHO, 2001; Goessler & Kuehnelt, 2002).

The most commonly used methods for the analysis of arsenic and arsenic compounds in water and biological samples are described below, and their characteristics are summarized in Table 2.

1.2.1 *Preservation of samples*

Assessment of human exposure to arsenic through drinking-water relies on the analysis of arsenic in water and in biological samples. Biological markers may more accurately reflect total dose of exposure in populations exposed to low, but potentially carcinogenic levels of arsenic in drinking-water. Many tissues contain arsenic following exposure to the element, but not all represent useful biomarkers. For example, arsenic is removed from blood within a few hours and excreted through the kidneys and urine within a few days. Determination of arsenic in urine is commonly used as a measure of recent exposure. Hair and nails have been shown to provide reliable biomarkers for long-term chronic exposure to arsenic in humans (Karagas *et al.*, 1996, 2000). However, nails are preferred to hair since their contamination with arsenic from the air is negligible, whereas hair can adsorb 9–16% exogenous inorganic arsenic (Mandal *et al.*, 2003). Karagas *et al.* (2001a) found that measurements of arsenic in both toenails and water were reproducible over a 3–5-year period.

Depending on the sample studied and the type of analysis to be performed, particular caution must be taken to overcome problems related to sample contamination and stability of the arsenic species. For determining total element concentrations, the main considerations for sample collection and storage are to prevent contamination and to minimize

Table 2. Most commonly used analytical methods for arsenic and arsenic compounds in water and biological samples

Methodology	Sample analysed	Detection	Detection limit	Advantages	Disadvantages	References
Colorimetric/spectrophotometric methods	Water Urine, serum Hair, nails	Total arsenic	~ 40 µg/L	Low cost, very simple, uses a simple spectrophotometer		Kingsley & Schaffert (1951); Vogel *et al.* (1954); Dahr *et al.* (1997); Pillai *et al.* (2000); Goessler & Kuehnelt (2002)
Inductively coupled plasma–atomic emission spectrometry (ICP–AES)	Water	Total arsenic	~ 30 µg/L			SM 3120 (1999); Environmental Protection Agency (1994a); Goessler & Kuehnelt (2002)
Inductively coupled plasma–mass spectrometry (ICP–MS)	Water Nails	Total arsenic	0.1 µg/L	Analytical method approved by US EPA	Spectral and matrix interference	Environmental Protection Agency (1994b); Chen *et al.*, 1999; Goessler & Kuehnelt (2002)
High resolution (HR)–ICP–MS	Water Urine Nails	Total arsenic	0.01 µg/L	Solves spectral interferences in samples with complex matrices		Gallagher *et al.* (2001); Karagas *et al.* (2001, 2002)
Instrumental neutron activation analysis (INAA)	Hair, nails Tissues	Total arsenic	~ 0.001 µg/g	Reference method for detection of arsenic		Garland *et al.* (1993); Nichols *et al.* (1993); Pan *et al.* (1993); Pazirandeh *et al.* (1998); Karagas *et al.* (2001)
Electrothermal atomization laser–excited atomic fluorescence spectrometry (ETA–LEAFS)	Serum	Total arsenic	0.065 µg/L	Requires only minimal sample volume, sample pretreatment and measurement time		Swart & Simeonsson (1999)
Graphite furnace–atomic absorption spectrometry (GF–AAS)	Water, urine Hair, nails, tissues	Total arsenic	~ 0.025 µg/g	Analytical method approved by US EPA	Pre-atomization losses, requires the use of matrix modifyers	Agahian *et al.* (1990); SM 3113 (1999); WHO (2001)

Table 2 (contd)

Methodology	Sample analysed	Detection	Detection limit	Advantages	Disadvantages	References
Hydride generation–atomic absorption spectrometry (HG–AAS)	Water Urine Hair, nails	Total arsenic and arsenic speciation	0.6–6 µg/L	Analytical method approved by US EPA		Braman & Foreback (1973); Crecelius (1978); Le *et al.* (1994a,b); Chatterjee *et al.* (1995); Lin *et al.* (1998); Ng *et al.* (1998); Wyatt *et al.* (1998a,b); Shraim *et al.* (1999, 2000); SM 3114 (1999)
Hydride generation–quartz furnace–atomic absorption spectrometry (HG–QF–AAS)	Water Tissues	Total arsenic and arsenic speciation	0.003–0.015 µg/L	Inexpensive		Environmental Protection Agency (1996c)
High-performance liquid chromatography (HPLC)–HG–AAS	Urine	Total arsenic and arsenic speciation	1–47 µg/L			Lamble & Hill (1996); Kurttio *et al.* (1998)
HPLC or solid-phase cartridge separation combined with hydride generation–atomic fluorescence spectrometry (HPLC–HG–AFS)	Water, urine	Arsenic speciation	0.05–0.8 µg/L	Rapid, inexpensive No need for sample pretreatment		Le & Ma (1997); Aposhian *et al.* (2000); Le *et al.* (2000a,b); Gong *et al.* (2001); Yalcin & Le (2001)
HPLC–ICP–MS	Water Water, urine Hair, nails	Total arsenic	0.01 µg/L 0.14–0.33 µg/L	No need for sample pretreatment	Expensive and often time-consuming Spectral and matrix interference	Shibata & Morita (1989); Londesborough *et al.* (1999); Chatterjee *et al.* (2000); Mandal *et al.* (2001); Shraim *et al.* (2001); Karagas *et al.* (2002); Mandal *et al.* (2003)

loss of trace amounts of analytes. High-density polyethylene containers are usually preferred to glass containers because they are less adsorptive for arsenic. These are precleaned with nitric acid and then rinsed with distilled water.

Groundwater sampling is carried out by allowing the well-water to flow through the pumping pipe for approximately 10 min before collection.

Traditionally, water and urine samples are acidified with sulfuric or nitric acid to reduce potential adsorption of trace elements onto the surface of the sample container and to prevent bacterial proliferation. Samples can then be kept at +4 °C or at room temperature and preferably measured within 7 days (Lin *et al.*, 1998; Rahman *et al.*, 2002). Pande *et al.* (2001) reported, however, that all the field kits they evaluated were subject to negative interference if samples were acidified with nitric acid for preservation; they showed that acidification using 5% ascorbic acid instead of nitric acid eliminates interference.

In iron-rich waters, the stability of As^{III} and As^{V} can be affected by the formation of iron precipitates (iron oxides and/or hydroxides designated by 'FeOOH'). These precipitates can form during transport to the laboratory for analysis of arsenic. Studies of laboratory reagent water containing both As^{III} and Fe^{III} indicated that, within 18 h at room temperature, the resulting FeOOH precipitates contained a mixture of As^{III} and As^{V} with near quantitative removal of aqueous arsenic. Addition of a chelating agent such as ethylenediamine tetraacetic acid (EDTA), by sequestering Fe^{III}, inhibits the formation of FeAsOH precipitates and preserves the stability of arsenic species in iron-rich waters for more than 10 days (Gallagher *et al.*, 2001).

Reliable information from speciation analysis requires that the concentration of individual species of the element be unchanged by handling and treatment of the sample. Although traditionally used for their preservation, acidification of samples is not suitable since it leads to changes in arsenic speciation.

For urine specimens, low temperature (4 °C and –20 °C) conditions are required if they are to be stored up to 2 months without substantial changes in arsenic speciation (except for MMA^{III} and DMA^{III} species). For longer storage times, the stability of arsenic species varies with the complex matrix and pH of the urine, and accurate measurement of inorganic As^{III} and As^{V} separately is more difficult since As^{V} is rapidly reduced to As^{III}. MMA^{V} and DMA^{V} are more stable (for up to 4.5 months). The trivalent arsenic species, monomethylarsonous acid (MMA^{III}) and dimethylarsinous acid (DMA^{III}), suspected to be key metabolic intermediates in human urine, are extremely unstable. It was shown that over 90% of MMA^{III} was rapidly oxidized to MMA^{V} in urine samples when stored at +4 °C or –20 °C over a 5-month period, while DMA^{III} was completely oxidized to DMA^{V} within 1 day (Gong *et al.*, 2001). In a recent review, these authors found that the use of a complexing agent, diethylammonium diethyldithiocarbamate (DDDC), improved the stability of MMA^{III} and DMA^{III} in urine samples. In the presence of DDDC (1–10 mM), MMA^{III} was found to be stable for 4 months at –20 °C (with a recovery of 85–95%) and DMA^{III} was partially preserved. Approximately 80% of DMA^{III} remained after 3 weeks of storage and 10–24% remained after 4 months (Jiang *et al.*, 2003). The use of other additives (such as hydrochloric acid, sodium azide, benzoic acid, benzyltrimethylammonium chloride and cetylpyridinium chloride) has no particular benefit (Feldman *et al.*, 1999; Chen *et al.*, 2002).

For arsenic speciation, well-water is usually filtered at the sampling site using a 0.45 μm filter (Lin *et al.*, 1998).

Methods for on-site separation of As^{III} and As^{V} species immediately after water-sample collection using solid disposable cartridges can be efficiently used for speciation of particulate and soluble arsenic. A measured volume of the sample is passed through the 0.45-μm membrane filter, then serially through a connected silica-based strong anion-exchange cartridge. The filter captures particulate arsenic, while the anion-exchange cartridge retains As^{V}. Arsenite is not retained and is detected in the effluent. Arsenate is subsequently eluted with 1 M hydrochloric acid (HCl) from the anion-exchange cartridge and then analysed for concentration (Le *et al.*, 2000a).

In hair and nail samples, the arsenic species are less prone to change. For analysis of total arsenic, as for speciation methods, these specimens are usually prepared according to the International Atomic Energy Agency (IAEA) procedure (Ryabukhin, 1978).

Following extensive washing to eliminate exogenous arsenic resulting from air contamination, approximately 100 mg of each hair sample are usually placed in a Teflon beaker, mixed with acetone and then washed with distilled water. Nails are treated similarly to hair following brushing. Samples are weighed prior to analysis (Lin et *al.*, 1998; Mandal *et al.*, 2003). More stringent washing procedures have also been described for complete removal of surface contamination, by incubating nails for 20 min in 1% Triton X100 before analysis (Chen *et al.*, 1999).

1.2.2 *Analytical methods for measurement of total arsenic*

Determination of total arsenic in biological samples in most cases requires the complete destruction of the organic matrix. During this process, all the organic arsenic compounds should be converted into inorganic arsenic by oxidative digestion. Acid digestion (or wet ashing) (Kingsley & Schaffert, 1951) and dry ashing (George *et al.*, 1973) are the two basic methods that have been widely employed for oxidative digestion of samples prior to analysis. A microwave-assisted digestion technique has been developed recently and is currently used as a rapid preparation for sample analysis (Le *et al.*, 1994c; Goessler & Kuehnelt, 2002). For analysis of soft biological tissues using inductively coupled plasma (ICP) techniques, a simple partial digestion in a closed vessel at low temperature and pressure is often sufficient for the sample preparation and pretreatment step (WHO, 2001).

Historically, colorimetric/spectrophotometric methods have been used to determine total arsenic concentration. Several commercial field kits have been based on these methods. At present, laboratories often prefer more sensitive methods such as atomic absorption spectrometry (AAS), neutron activation analysis (NAA), atomic emission spectrometry (AES), mass spectrometry (MS) or atomic fluorescence spectrometry (AFS).

(*a*) *Colorimetric/spectrometric methods*

These methods take advantage of the formation of volatile arsine (AsH_3) gas to separate arsenic from other possible interference with the sample matrix. The colorimetric methods are easy to use and inexpensive in terms of equipment and operator cost. They are useful for the semi-quantitative determination of high concentrations of arsenic in water.

The silver diethylthiocarbamate (AgDDTC) method is the most popular spectrophotometric method for the determination of arsenic in water. The method is based on the generation of arsine either with zinc and hydrochloric acid or sodium borohydride in acidic solutions. The arsine gas is then flushed through a solution of diethylthiocarbamate in pyridine or pyridine/chloroform. The red-coloured complex can be measured at 520 nm. Using a modification of this method, Dhar *et al.* (1997) reported a detection limit of 40 µg/L for arsenic in water samples, with a 95% confidence.

Pillai *et al.* (2000) reported a new simple and reliable spectrophotometric method to determine total arsenic in environmental and biological samples. It involves bleaching the pinkish-red dye Rhodamine-B (measured at 553 nm) by the action of iodine released from the reaction between potassium iodate and arsenic in a slightly acidic medium.

The classic Gutzeit test (Vogel, 1954) is derived from the historical Marsh test. It is based on the generation of arsine (AsH_3) from arsenic compounds by the addition of zinc granules to concentrated sulfuric acid. The arsine can be detected by its reaction on a strip of filter moistened with silver nitrate or mercuric chloride, which produces a grey or a yellow to reddish-brown spot, respectively.

Field test kits

The high concentrations of arsenic currently found in groundwater in many parts of the world pose an important challenge because of the large number of wells that must be tested. This is particularly true in Bangladesh and other Asian hot spots such as Myanmar, Nepal, Cambodia, Laos, Viet Nam and India. Although less accurate than laboratory-based methods, field kits that allow on-site semi-quantitative determination of arsenic concentrations in well-water are of vital importance, since in these countries, the current laboratory capacity cannot cover the high level of analytical needs. Field testing has several advantages. In Bangladesh and other hot climates, attempts to keep samples cool over a long period of transport to a laboratory can be difficult. With field kits, there is no need for transport, no storage and therefore no need for preservation, which in addition reduces the cost of analysis and the time required for the well owner to be informed. Field kits are also simple to use after reasonable training of technicians.

These tests, however, must be accurate and sensitive enough to assess the level of arsenic contamination.

Much concern about the reliability of field kits recently led to careful evaluations of commercially available kits (Pande *et al.*, 2001; Rahman *et al.*, 2002a,b; Environmental Protection Agency-Battelle, 2002a,b; Erickson, 2003). The original field kit widely used in Bangladesh had a stated minimal detectable concentration of 100 µg/L, which largely exceeded the maximum permissible arsenic concentration defined by WHO (10 µg/L) and even the maximum stated by most developing countries (50 µg/L). Fortunately, the newer field test kits are more sensitive. Evaluations of these kits are summarized in Table 3.

A modification of the Gutzeit method using mercuric bromide is the basis of most commercial field kits. A test strip moistened with mercuric bromide is exposed to arsine gas derived from the sample solution, to form complex salts of arsenic and mercury. These reactions give a yellow [$H(HgBr_2)As$] to brown [$(HgBr)_3As$] to black [Hg_3As_2] stain. The intensity of the yellowish-brown colour developed on the test strip is proportional to the arsenic concentration in the sample. When the reaction is completed, the test strip is compared with a colour chart provided with the kit and allows semi-quantitative determination of total arsenic concentration.

More recent field kits include digital measurement of arsenic levels without depending on the judgement of the technician's eyes to detect the difference between colour shades of the coloured strip (Arsenator, PeCo test). The improvement in reading results in higher sensitivity and reliability (Environmental Protection Agency-Battelle, 2002a,b; Durham & Kosmus, 2003).

In addition, promising biological tools (bacterial biosensors) may lead to new kits for quantitative and qualitative measurement of arsenite and arsenate in aqueous solution (Flynn *et al.*, 2002; Stocker *et al.*, 2003).

(*b*) *Inductively coupled plasma–atomic emission spectrometry (ICP–AES)*

ICP–AES involves the use of plasma, usually argon, at temperatures between 6000 and 8000 °K as the excitation source. The analyte is introduced into the plasma as an aerosol. A typical detection limit achievable for arsenic with this technique is 30 µg/L. Because of the rather high detection limits, ICP–AES is not frequently used for the determination of arsenic in biological samples (Goessler & Kuehnelt, 2002).

In August 2002, ICP–AES was withdrawn from the US Environmental Protection Agency (US EPA)-approved analytical methods for arsenic since this technique is inadequate to meet the requirements of the new EPA standard for arsenic in drinking-water of 10 µg/L (10 ppb), effective since February 2002 (Environmental Protection Agency, 2002).

(*c*) *Inductively coupled plasma–mass spectrometry (ICP–MS)*

ICP–MS is superior to ICP–AES with respect to detection limits, multi-element capabilities and wide linear dynamic range. This technique combines the ICP as the ion source with a mass analyser. Quadrupole mass filters are the most common mass analyser; double-focusing magnetic/electrostatic sector instruments and time-of-flight mass analysers are also used (Goessler & Kuehnelt, 2002).

ICP–MS is classified among the US EPA-approved analytical methods for arsenic (Environmental Protection Agency, 2002), with a detection limit of 0.1 µg/L.

The sensitivity can be further improved by the use of hydride generation (HG) techniques leading to a more efficient sample introduction and to matrix removal. The use of a high-resolution mode with HG–ICP–MS allows a 10-fold decrease in the detection

Table 3. Evaluation of some field test kits for analysing arsenic in water

Field test kits	Kit capability	Minimum detection limit of arsenic	Detection range	Rate of false positive/false negative	Effects of interferences (sodium chloride, iron, sulfate, acidity)	Occupational hazard potential (OH)	Time required per test	Evaluation reference
Quick^{TM} (industrial test kit, Rock Hill, USA)	Semi-quantitative	~ 5–20 µg/L	5, 10, 20, 40, 60, 100, 200, … 500 µg/L	0–4%/5–16%	ND	Safe	< 15 min	Environmental Protection Agency-Battelle (2002a)
AS75 (PeCo test kit) (Peters Engineering, Graz, Austria)	Semi-quantitative	~ 15–50 µg/L	10, 20, 30, … 100 µg/L 2.5, 5, 10, 20, … 60 µg/L	0–3%/0%	None	Safe	ND	Environmental Protection Agency-Battelle (2002b)
AAN (Asia Arsenic Network, Japan)	Semi-quantitative	~ 20 µg/L	20, 50, 100, 200,… 700 µg/L	19%/71%	Some with sulfide	Accidental escape of arsine gas may cause OH.	15 min	Pande *et al.* (2001); Rahman *et al.* (2002)
E. Merck (Germany)	Qualitative for arsenic concentration > 50 µg/L	~ 50–100 µg/L	100, 500, 1000, 1700, 3000 µg/L	21%/60%	Some with sulfide	Accidental spillage of acid and escape of arsine gas may cause OH.	30 min	Pande *et al.* (2001); Rahman *et al.* (2002)
NIPSOM (National Institute of Preventive and Social Medicine, Bangladesh)	Qualitative for arsenic concentration > 50 µg/L	~ 10–20 µg/L	10, 20, 50, 100, 200, 300 … 700 µg/L	21%/33%	Some with sulfide	Accidental spillage of acid and escape of arsine gas may cause OH.	5 min	Pande *et al.* (2001); Rahman *et al.* (2002)
AIIH-PH (All India Institute of Hygiene and Public Health, India)	Semi-quantitative	~ 50 µg/L	> 50 µg/L	25%/1%	Sulfide interference eliminated	Accidental spillage of acid and escape of arsine gas may cause OH.	30 min	Pande *et al.* (2001); Rahman *et al.* (2002)
GPL (General Pharmaceuticals Ltd, USA)	Semi-quantative	~ 10 µg/L	10, 50, 100, 200, 400, 500 … 1500 µg/L	10%/32%	ND	Accidental spillage of acid and escape of arsine gas may cause OH.	20 min	Rahman *et al.* (2002)
Aqua (Aqua Consortium, Calcutta, India)	Semi-quantitative	~ 100 µg/L	> 50 µg/L	ND	Sulfide interference eliminated	Accidental spillage of acid and escape of arsine gas may cause OH. Contact with HgBr2 paper affects fingers of the user.	15 min	Pande *et al.* (2001)

limit (0.01 µg/L) for arsenic in water samples. HG–ICP–MS can be used for biological samples such as urine and nails (Chen *et al.*, 1999; Gallagher *et al.*, 2001; Karagas *et al.*, 2001a, 2002).

(*d*) *Neutron activation analysis (NAA)*

Instrumental NAA is an accurate and sensitive means to measure arsenic. The method can analyse relatively small biological samples, and has been used efficiently to measure total arsenic in hair, nails and other tissues, with a detection limit of approximately 0.001 µg/g (Pan *et al.*, 1993; Garland *et al.*, 1996; Nichols *et al.*, 1998; Pazirandeh *et al.*, 1998; Karagas *et al.*, 2001a).

(*e*) *Electro-thermal atomization laser–excited atomic fluorescence spectrometry (ETA–LEAFS)*

ETA–LEAFS is a highly sensitive and selective method that has been developed by the combination of laser-excited atomic fluorescence spectrometry with electro-thermal atomization in graphite cup or tube furnaces. The technique provides excellent analytical performance at ultra-trace levels, with a detection limit of 0.065 µg/L for arsenic in undiluted serum. This approach allows measurements to be taken directly on the serum samples after a simple dilution step. It also minimizes the amounts of sample required and can provide multiple measurements when only limited amounts of sample are available (Swart & Simeonsson, 1999).

(*f*) *Atomic absorption spectrometry (AAS)*

AAS is one of the most common analytical procedures for measuring arsenic in both environmental and biological materials. The main methods are flame AAS (FAAS), electro-thermal AAS (ET–AAS), also referred to as graphite furnace AAS (GF–AAS), and HG–AAS.

FAAS, with a relatively high detection limit (~1 mg/L), was never seriously considered for determining arsenic in environmental and biological samples.

The principal difference among the various AAS techniques is the means and form of presentation and atomization of the sample.

In GF–AAS, a small aliquot, rather than a continuous flow of sample, is deposited in a graphite furnace in which it is completely dissolved and mineralized *in situ*. The analyte is vaporized to form volatile hybrids. Matrix modifiers, such as a mixture of palladium and magnesium, must be used to protect the analyte from premature volatilization before vaporization, and therefore loss of arsenic. GF–AAS is classified among the approved US EPA analytical methods for arsenic in water (Environmental Protection Agency, 2002). It has been used for the determination of total arsenic in water and many biological samples (Agahian *et al.*, 1990).

HG–AAS uses the hydride generation technique, which can easily be connected to various detection systems and greatly improves the detection limit of all methods. The HG technique is based on the production of volatile arsines (by the addition of either zinc/hydrochloric acid or a sodium borohydrate/acid mixture) which are transported by an inert gas to the detection system. HG–AAS is probably the most widely used method to determine total arsenic in water (Rahman *et al.*, 2001; Chakraborti *et al.*, 2002) and various matrices (Wyatt *et al.*, 1998a; Das *et al.*, 1995). HG–AAS is also classified among the US EPA-approved analytical methods for arsenic in water (Environmental Protection Agency, 2002). Detection limits for total arsenic in water achievable by this technique are around 0.6 μg/L.

1.2.3 *Analytical methods for arsenic speciation*

The combination of high-performance separation methods with highly sensitive instrumental detection systems is necessary to determine arsenic species (arsenic speciation) at trace levels. These combinations, referred to as hyphenated techniques, have been extensively described by Goessler and Kuehnelt (2002).

Three steps are required for arsenic speciation: the extraction of arsenic from the sample, the separation of the different arsenic species and their detection/quantification. The extraction procedure should be as mild and complete as possible. A combination of various extractants is often necessary to remove all the arsenic; polar and organic solvents or water are commonly used for this purpose. In many cases (water or urine samples), extraction may not be necessary. In the next step, a combination of separation procedures is usually required because of the different chemical properties of the arsenic compounds (anionic, neutral, cationic). Selective HG and high-performance liquid chromatography (HPLC) are the most commonly used. After the different arsenic compounds have been separated, they must be detected with a suitable detector. All the methods cited in Section 1.2.2 have been used more or less successfully to identify and determine arsenic compounds. Some efficient and sensitive hyphenated methods, commonly used or recently developed, are described below and presented in Table 2.

(*a*) *AAS–derived hyphenated methods*

Hydride generation quartz furnace atomic absorption spectrometry (HG–QF–AAS) is an improved modification of GF–AAS, described by the US Environmental Protection Agency (Environmental Protection Agency, 1996c), in which the graphite furnace is replaced by a quartz furnace. The method is designed to measure both total arsenic and arsenic species in water (range, 0.01–50 μg/L) and in tissue (range, 0.01–500 μg/g dry weight for arsenic and arsenic species). The detection limits for total inorganic arsenic, As^{III} and As^{V} have been determined to be 3 ng/L and 15 ng/L for DMA and MMA, respectively, when no background element or interference is present.

Modifications of the HG–AAS method have also been described that allow the determination of arsenic species (As^{III}, As^{V}, MMA, DMA) in water and biological samples (Braman & Foreback, 1973; Crecelius, 1978; Le *et al.*, 1994a,b,c; Hasegawa *et al.*, 1994; Lin *et al.*, 1998; Ng *et al.*, 1998). These modifications, which involve trapping the arsine species at liquid nitrogen temperature (–196 °C), allow the elution by chromatography of each compound at room temperature. Ng *et al.* (1998) described, for example, an optimized HG–cold trap–AAS procedure for the speciation of arsenic in urine, with detection limits of 0.25 µg/L, 0.325 µg/L and 0.75 µg/L for inorganic arsenic species, MMA and DMA, respectively. On the other hand, using the HG–AAS method after cold trapping and chromatographic separation, Hasegawa *et al.* (1994) were able, for the first time, to separate the trivalent MMA^{III} and DMA^{III} species from the pentavalent DMA and MMA species in natural water following solvent extraction using DDDC.

A system that can separate arsenic species using on-line HPLC prior to their on-line decomposition by microwave digestion, prereduction with L-cysteine and analysis by HG–AAS (HPLC–HG–AAS) has been developed (Lamble & Hill, 1996), and enables the full speciation of arsenobetaine, MMA, DMA, As^{III} and As^{V} in biological samples. A simple modification of the system can determine total arsenic in the sample. A comparable system was used to determine total arsenic and arsenic species in urine specimens, with detection limits of 1.0, 1.6, 1.2 and 4.7 µg/L for As^{III}, As^{V}, MMA and DMA, respectively (Kurttio *et al.*, 1998).

(*b*) *Atomic fluorescence spectrometry (AFS)-derived hyphenated techniques*

AFS is an excellent detector of arsenic compounds; it is, in addition, rather simple and inexpensive. AFS has been used to detect arsenic hybrids in the ultraviolet spectral region because of the small background emission produced by the relatively cool hydrogen diffusion flame. The use of cold vapour or HG, together with an intense light source, enables very low detection limits to be reached.

A rapid method for speciation of As^{III}, As^{V}, MMA and DMA (and also arsenobetaine) has been developed based on the rapid separation of the target arsenic species on one or two 3-cm HPLC guard columns, followed by HG–AFS (Le & Ma, 1997). This simple method provides the complete speciation of arsenic present in water and urine samples within 1.5 min with no need for treatment of the sample. Detection limits for the four arsenic species in urine samples are 0.4–0.8 µg/L.

More recently, a solid-phase extraction cartridge linked to HG–AFS was described for speciation of arsenic in water and urine, with detection limits of 0.05 µg/L in water. The disposable cartridges are inexpensive and specific for selective retention of arsenic species, and the method is suitable for routine determination of trace levels of arsenic species in drinking-water to comply with the more stringent environmental regulations (Yalcin & Le, 2001).

HPLC–HG–AFS has led to the speciation in urine of trace levels of trivalent MMA^{III} and DMA^{III} together with the other arsenic species (Gong *et al.*, 2001).

(*c*) *Inductively coupled plasma–mass spectrometry (ICP–MS)-derived hyphenated methods*

Among the detector methods, ICP–MS is certainly not the cheapest. The advantage of ICP–MS lies in its multi-element capabilities, excellent detection limits and wide linear range. Moreover, low detection limits are not restricted to the hybrid-forming arsenic compounds (Goessler & Kuehnelt, 2002).

Numerous methods have been developed for the speciation of arsenic using the separation power of HPLC combined with the sensitivity of ICP–MS detection (Shibata & Morita, 1989; Le *et al.*, 1998; Londesborough *et al.*, 1999; Chen *et al.*, 1999; Chatterjee *et al.*, 2000; Mandal *et al.*, 2001, 2003).

High-temperature (column temperature at 70 °C) HPLC–ICP–MS was used to determine 13 arsenic and selenium species in urine (Le *et al.*, 1998). The high temperature achieved an improved resolution and faster separation. The speciation of six arsenosugar metabolites in urine can be completed in 19 min at 70 °C compared with 37 min at room temperature.

Londesborough *et al.* (1999) reported an improved HPLC–ICP–MS method for the speciation of eight anionic, cationic or neutral arsenic species (As^{III}, As^{V}, MMA, DMA, arsenobetaine, arsenocholine, trimethylarsine oxide (TMAO) and tetramethylarsonium ion (TMA)) using a single ion-exchange column, with detection limits of 0.19, 0.52, 0.29, 0.16, 0.16, 0.58, 0.6 and 0.38 µg/L, respectively. In this method, the matrix of biological samples noticeably affects the column efficiency.

High sensitivity was also obtained with the development of the HPLC–ultrasonic nebulizer high-power nitrogen-microwave–ICP–MS method, which could be particularly useful for arsenic speciation in samples with high chloride concentrations since no chloride interference (as$^{40}Ar^{35}Cl$) was observed in urine with a chloride matrix of up to 10 000 mg/L (Chatterjee *et al.*, 2000).

Using optimized HPLC–ICP–MS, Mandal *et al.* (2001) detected the trivalent MMA^{III} and DMA^{III} species for the first time in urine samples, with no prechemical treatment, with detection limits in the range of 0.14–0.33 µg/L.

In conclusion, depending on the specific need, reliable results should be obtainable provided that special care is taken in the preservation and preparation of samples and the method of analysis is chosen carefully.

1.3 Natural occurrence

Arsenic is a metalloid that occurs naturally; it is the component of more than 245 minerals. Examples of arsenic levels in some geological materials are given in Table 4. Arsenic is commonly concentrated in sulfide-bearing mineral deposits, especially those associated with gold mineralization, and it has a strong affinity for pyrite, one of the more ubiquitous minerals in the earth's crust. It is also concentrated in hydrous iron oxides. Arsenic and its compounds are mobile in the environment. Weathering of rocks converts

Table 4. Levels of arsenic in geological materials

Materials	Concentration (mg/kg)	Source
Earth crust total	1–1.8	Matschullat (2000)
Upper crust	1.5–2	Matschullat (2000)
Igneous rocks		
Basic basalt	02–113	Mandal & Suzuki (2002); Smedley & Kinniburgh (2002)
Gabbro, dolorite	0.06–28	Mandal & Suzuki (2002); Smedley & Kinniburgh (2002)
Acidic granite	0.2–13.8	Mandal & Suzuki (2002); Smedley & Kinniburgh (2002)
Sedimentary rocks		
Phosphorites	0.4–188	Smedley & Kinniburgh (2002)
Sandstones	0.6–120	WHO (1981); Mandal & Suzuki (2002)
Shale and argillite	0.3–500	Hale (1981)
Schist and phyllite	0.5–143	Hale (1981)
Carbonates	0.1–20	Matschullat (2000); Mandal & Suzuki (2002)
Coals	0.3–35 000	Smedley & Kinniburgh (2002)
Sulfide minerals		
Pyrite	100–77 000	Smedley & Kinniburgh (2002)
Pyrrhotite	5–100	Boyle & Jonasson (1973)
Chalcopyrite	10–5000	Smedley & Kinniburgh (2002)
Galena	5–10 000	Smedley & Kinniburgh (2002)
Sphalerite	5–17 000	Smedley & Kinniburgh (2002)
Marcasite	20–126 000	Smedley & Kinniburgh (2002)
Oxide minerals		
Haematite	up to 160	Smedley & Kinniburgh (2002)
Iron oxide	up to 2000	Smedley & Kinniburgh (2002)
Iron(III) oxyhydroxide	up to 76 000	Smedley & Kinniburgh (2002)
Sulfate minerals		
Jarosite	34–1000	Smedley & Kinniburgh (2002)

arsenic sulfides to arsenic trioxide, which enters the arsenic cycle as dust or by dissolution in rain, rivers or groundwater. Arsenic can also enter the food chain, causing widespread distribution throughout the plant and animal kingdoms. The occurrence and behaviour of arsenic in the environment have been extensively reviewed (Cullen & Reimer, 1989; Tamaki & Frankenberger, 1992; Matschullat, 2000; Mandal & Suzuki, 2002; Nordstrom, 2002; Smedley & Kinniburgh, 2002).

A limited range of geological environments can result in significant natural elevation of arsenic in water supplies (Nordstrom, 2002). These include: organic rich (black) shales, Holocene alluvial sediments with slow flushing rates, mineralized and mined zones (most often gold deposits), volcanogenic sources, thermal springs, closed basins in arid-to-semi-arid climates, particularly in volcanic regions, and strongly reducing aquifers with low sulfate concentrations.

Depending on prevailing climatic and hydrological conditions, soils and sediments, surface waters, groundwaters and air can become enriched in arsenic where these geological conditions prevail.

1.3.1 *Arsenic speciation in natural materials*

Mineral forms in which arsenic is present in soils are approximately 60% arsenates and 20% sulfides and sulfosalts; the remaining 20% includes arsenides, arsenites, oxides, silicates and elemental arsenic.

These mineral forms are generally weathered to the inorganic water-soluble species, arsenate (As^{V}) and arsenite (As^{III}), with arsenate dominating under oxidized conditions and arsenite under reduced conditions (Cullen & Reimer, 1989). Under both aerobic and anaerobic conditions, micro-organisms can transform inorganic arsenic into organic forms such as MMA, DMA and volatile TMA. TMA in the air is then rapidly converted into water-soluble species, As^{V} and TMAO (Pongratz, 1998; Turpeinen *et al.*, 1999, 2002). These compounds can also be degraded by microflora. In certain materials, organic arsenic compounds naturally build up to high concentrations (Mandel & Suzuki, 2002; Smedley & Kinniburgh, 2002).

1.3.2 *Abundance and distribution of arsenic*

(*a*) *Soils and sediments*

Measurements of background arsenic levels in surface soil are all compromised by atmospheric deposition of anthropogenically derived arsenic. Anthropogenic sources to soil include use and resuspension of arsenic-based pesticides, mining, smelting, manufacturing and waste-disposal activities. Shotyk *et al.* (1996) showed that arsenic levels were 20-fold higher in surface horizons of ombrotrophic (rain-fed) peat bogs than in lower horizons. This high level was due to industrially derived inputs of arsenic. Centuries of mining activities can result in an extremely high concentration of arsenic in soils. This is the case in South-West England where arsenic concentrations in some old smelter and/or mine areas range from 24 to 161 000 mg/kg (Farago *et al.*, 1997).

Koljonen (1992) estimated a global average level of arsenic in soils of 5 mg/kg, but concentrations vary considerably among geographical regions. Arsenic concentrations in sediments in lakes, rivers and streams in the USA ranged from 0.1 to 4000 mg/kg. Levels of arsenic in a detailed survey of Finland, which has a low population density and is remote from major centres of pollution, ranged up to 60 mg/kg for the 1164 samples tested (Lahermo *et al.*, 1998). Soils formed from arsenic-enriched geological substrates can have naturally higher levels than the ranges quoted. These ranges must therefore be considered as typical background levels rather than absolute ranges.

Soils formed on top of arsenic-rich bedrocks have elevated levels of this element. Colbourn *et al.* (1975) reported mean arsenic levels of 88 mg/kg (range, 24–250 mg/kg; *n* = 18) in soils formed naturally from parent material consisting of metamorphic aureole around a granitic intrusion. The Strassegg area in Gasen (Styria, Austria) has extensive arsenopyrite (FeAsS) mineralization, with the ore body running close to the surface (Geiszinger *et al.*, 2002). The soils formed on top of this ore vein are enriched in arsenic, with levels ranging from 700 to 4000 mg/kg, and are used for agronomic cultivation.

Soils formed in and around ancient and modern hot springs with elevated arsenic in geothermal fluids have naturally elevated levels of arsenic due to enrichment of the parent material of the soil (Ballantyne & Moore, 1988). The ancient hot-spring system at Rhynie, north-eastern Scotland, has cherts with arsenic levels ranging from 15 to 300 mg/kg (Rice *et al.*, 1995). Sinter from active hot springs in the Taupo Volcanic Zone, New Zealand, have arsenic levels ranging from below detection limits to 1646 mg/kg (McKenzie *et al.*, 2001). An area of at least 10 km^2 in St Elizabeth, Jamaica, has a geochemical anomaly, whereby arsenic concentrations in soil reach 400 mg/kg (Lalor *et al.*, 1999). The anomalous values may result from an ancient hot-spring environment responsible for the introduction and deposition of pyrite and arsenopyrite in the limestone bedrock, which were subsequently oxidized and weathered, leading to arsenic-rich soils.

Sediment levels of arsenic in the Waikato River, New Zealand, ranged from 7.9 to 1520 mg/kg dry wt, resulting in high levels of arsenic in sediment living biota, such as the freshwater mussel, *Hyridella menziesi* (Hickey *et al.*, 1995).

In a number of delta environments in South-East Asia, deep fluvial and deltaic Pleistocene-Holocene sediments have accumulated (up to 10 km thick in Bangladesh) (Nickson *et al.*, 2000). During glaciation, river levels were 100 m lower than in interglacial times, and at this time of low sea level, the sediments were flushed and oxidized, leading to iron (Fe^{III}) oxyhydroxide precipitation on sediment surfaces. These sedimentary iron oxyhydroxides scavenge arsenic, with arsenic levels reaching up to 517 mg/kg in FeOOH phases (Nickson *et al.*, 2000). Under reducing conditions caused by microbial metabolism of sedimentary organic matter (present at up to 6% as C), in which sulfate levels are low, insoluble Fe^{III} is converted to soluble Fe^{II}, leading to the mobilization of arsenic from the dissolved FeOOH phase. Although traces of arsenic-rich pyrites are found in the sediments, they are present in quantities that are too small for pyrite oxidation to contribute significantly to arsenic in groundwaters.

Water percolating from hot-spring systems into the surrounding soil or sediment also causes a rise in arsenic concentrations (Langner *et al.*, 2001; Koch *et al.*, 1999).

The Antofagasta Region, northern Chile, is characterized by volcanism (Queirolo *et al.*, 2000a). High levels of arsenic are found in soils and river sediments in this region (Caceres *et al.*, 1992), and crops (maize and potato) grown on these soils have high levels of arsenic, reaching 2 mg/kg in maize (Queirolo *et al.*, 2000b).

Arsenic concentrations in mineralized zones rich in arsenic are further elevated, often severely, by mineral extraction and processing (Smedley & Kinniburgh, 2002).

(*b*) *Groundwaters*

Under natural conditions, the greatest range and the highest concentrations of arsenic are found in groundwater as a result of the strong influence of the water–rock interactions and the favourable physical and geochemical conditions in aquifers for the mobilization and accumulation of arsenic. Arsenic is particularly mobile at pH values typically found in groundwater (pH, 6.5–8.5) under both oxidizing and reducing conditions.

Background concentrations of arsenic in groundwater in most countries are less than 10 μg/L and sometimes substantially lower. However, values quoted in the literature show a very wide range, from < 0.5 to 5000 μg/L. Most high levels of arsenic in groundwater are the result of natural occurrences of arsenic. Cases of arsenic pollution caused by mining are numerous but tend to be localized.

Arsenic can occur in the environment in several oxidation states (–3, 0, +3 and +5) but, in natural waters, is mostly found in inorganic forms as oxyanions of trivalent arsenite (As^{III}) or pentavalent arsenate (As^{V}). Redox potential (Eh) and pH are the most important factors controlling arsenic speciation. Under oxidizing conditions, arsenate is dominant, as the $H_2AsO_4^-$ form at low pH (less than approximately 6.9), or as the $HAsO_4^{2-}$ form at higher pH. Under reducing conditions at pH less than approximately 9.2, the uncharged arsenite species H_3AsO_3 predominates (Smedley *et al.*, 2002).

In two recent reviews, Smedley and Kinniburgh (2002) and Smedley *et al.* (2002) focused extensively on the factors that control arsenic concentration in groundwater.

In relatively pristine habitats where anthropogenic activity can be excluded as a contributor to arsenic levels in aquifers, Lahermo *et al.* (1998) found that arsenic levels in groundwaters in Finland reached up to 1040 μg/L, with a median of 0.65 μg/L ($n = 472$). The highest levels of arsenic were found in groundwaters from wells drilled in Precambrian bedrock.

In an extensive groundwater survey in the USA, Welch *et al.* (2000) reported that approximately half of the 30 000 samples analysed had naturally occurring arsenic levels ≤ 1 μg/L, with about 10% exceeding 10 μg/L. Geothermal water and high evaporation rates are associated with arsenic concentrations ≥ 10 μg/L in ground- and surface waters.

There are three major types of natural geological condition giving rise to high levels of arsenic in groundwaters:

(i) aquifers composed of rocks or sediments enriched with arsenic-containing minerals of geogenic origin, such as sulfide mineralization;

(ii) aquifers containing sediments coated with iron oxyhydroxide-(FeOOH) phases enriched in arsenic through hydrological action, where arsenic is mobilized into porewater by reducing conditions;

(iii) aquifers enriched in arsenic through high rates of evaporation in arid areas, leading to increased mineral concentration in groundwaters; the arsenic is mobile in such aquifers because of the high pH (> 8.5) caused by concentration of alkali and alkali earth metals in solution.

Geochemical conditions similar to the alluvial sediments in Bangladesh exist in the Red River alluvial tract in the city of Hanoi, Viet Nam, where FeOOH reduction is thought to have led to the high arsenic levels recorded in groundwaters (Berg *et al.*, 2001). Smedley and Kinniburgh (2002) outline that the reducing conditions observed in Bangladesh/West Bengal and Viet Nam aquifers are similar to those in the regions of Taiwan, China, northern China and Hungary that suffer from high levels of arsenic in groundwaters.

Smedley *et al.* (2002) studied the geochemistry of arsenic in groundwaters from Quaternary loess aquifers, which were high in arsenic, in an area thought to spread over 10^6 km^2 in La Pampa province, central Argentina. Dissolved arsenic ranged from 4 to 5300 µg/L, with 73% of samples exceeding 50 µg/L. The conclusions drawn for La Pampa province may be applicable elsewhere in determining which regions are vulnerable to arsenic and related water-quality problems: "Under oxidising conditions, vulnerable aquifers potentially occur where several important criteria coincide: semi-arid climatic conditions with limited recharge where high-pH groundwater can be generated; young (Quaternary) sediments or volcanic sediments; and slow groundwater-flow conditions. Such aquifers are likely to have been poorly flushed over the geologically-short timescale since deposition and hence will have had little opportunity for removal of trace elements such as arsenic from the aquifer." Similar conditions exist in the Lagunera and Sonora regions of Mexico and in the Atacama Desert, Chile (Smedley & Kinniburgh, 2002).

(*c*) *Surface waters*

Matschullat (2000) collated measurements of arsenic in surface waters. Levels of arsenic dissolved in uncontaminated stream waters ranged from 0.1 to 1.7 µg/L, and those in seawaters were 1.5–1.7 µg/L. Concentrations in open seawater show little variation from the value of 1.5 µg/L (Smedley & Kinniburgh, 2002).

Arsenic in surface stream waters in Finland, which could be considered a pristine environment because of its low population density and remote geographical location, ranged from 0.06 to 1.6 µg/L (median, 0.36 µg/L; $n = 1157$) (Lahermo *et al.* 1998). These levels correlated well with arsenic levels in glacial till, with the highest stream water levels occurring in catchments with metamorphic, volcanic and sedimentary geologies. Levels in the more geographically remote part of Finland were lower than those in the south, which is nearer to continental Europe. Arsenic levels in Finnish water were lower than those for continental Europe, again emphasizing the pristine nature of the Finnish environment.

The Ciwidey River, West Java, drains a catchment dominated by the Quaternary volcano Patuha, which contains an acid crater lake (pH < 1) (Sriwana *et al.*, 1998). Arsenic in the crater lake was recorded to be 279 µg/L, with the stream draining this lake having levels of 57 µg/L. In the tributary river of the stream, levels dropped to below 1 µg/L. In a crater lake with naturally elevated levels of arsenic, such as Lake Xolotlan in Nicaragua, mean arsenic concentrations ranged from 10.23 to 30.13 µg/L (Lacayo *et al.* 1992).

Takatsu and Uchiumi (1998) studied water from Lake Usoriko, Japan, which is acidified by hot springs. The sediments of this lake contained 1.6% by mass of arsenic, with arsenic levels in the open lake waters ranging from 10 to 450 µg/L.

Levels of arsenic in drinking-water extracted from the Waikato River, New Zealand, for the city of Hamilton averaged 32 μg/L. Arsenic concentrations appear to follow a regular seasonal variation, being approximately 10–25 μg/L higher in the summer months, and fall to 6 μg/L after water treatment (McLaren & Kim, 1995). The elevated levels of arsenic in the Waikato river are of natural origin, as its catchment is the volcanic region of the Central Plains (Hickey *et al.*, 1995).

Natural surface waters in the Antofagasta region of Chile, originating from springs, have very high levels of arsenic because of zones mineralization associated with volcanic activity (eruptions, vents, geysers and thermal springs). Surface water is used as drinking-water and to irrigate crops (Queirolo *et al.*, 2000a,b). Arsenic levels reached 3000 μg/L in rivers and canals in this region, with many rivers routinely having levels over 100 μg/L.

In an area with similar volcanic activity in the Salta Province, Argentina, high levels of arsenic have been recorded in thermal springs, tap-water and river water (Vahter *et al.*, 1995).

High levels of arsenic have been recorded in rivers in arid areas of Chile and Argentina where surface water is dominated by base-flow (whereby groundwater flows into the river from surrounding rock) (Caceres *et al.*, 1992; Lerda & Prosperi, 1996). Caceres *et al.* (1992) found concentrations in surface water up to 22 mg/L. The high degree of evaporation that occurs in these regions concentrates the arsenic leached from weathered rocks. Such surface waters have high pH, due again to high rates of evaporation that lead to concentration of alkaline and alkaline earth cations leached from the rocks.

(*d*) *Air*

Concentrations of arsenic in ambient air in remote locations range from < 1 to 3 ng/m^3, but concentrations in cities may range up to 100 ng/m^3. Arsenic in ambient air is usually a mixture of arsenite and arsenate, with organic species being of negligible importance except in areas of arsenical pesticide application or other industrial activity (WHO, 2001). Sources of arsenic to air include use and resuspension of arsenic-based pesticides, mining, smelting, manufacturing and waste-disposal activities. Arsenic may be introduced into the atmosphere directly from these processes, or it may be derived from sediment and soil particles being entrained into the atmosphere or the production of volatile arsenic metabolites, such as arsines, from soils (Woolson, 1977; Turpeinen *et al.*, 2002). Defining what constitutes natural levels is, therefore, difficult.

(*e*) *Other*

Arsenic has been detected in rainwater at concentrations ranging from < 0.005 to 45 μg/L, with higher levels occurring in contaminated areas (WHO, 2001).

Arsenic compounds are abundant in certain seafoods at concentrations as high as several hundred milligrams per kilogram. Although marine animals contain many arsenic compounds, most species contain arsenobetaine as the major arsenical. Arsenobetaine is not metabolized by humans and is believed to have low or negligible toxicity. Inorganic arsenic and arsenosugars can, however, be present in some marine algae, seaweeds, oysters, mussels and clams (reviewed by Francesconi & Kuehnelt, 2002).

Dimethylarsinate is often the major arsenical constituent of species of fungi. Arsenite and arsenate are also commonly found in fungi (Francesconi & Kuehnelt, 2002).

Inorganic arsenic species are dominant in the chemistry of arsenic in terrestrial plants (Francesconi & Kuehnelt, 2002) and, although less studied, the concentration of arsenic in wheat and vegetables grown in countries highly contaminated with arsenic could be relevant to human health. Most of the vegetables cultivated in the Antofagasta Region (northern Chile), which is characterized by volcanic events (eruptions, thermal springs), are found at local markets of a population of approximately 4000 people. In this region, very high arsenic contents have been reported in Socaire and Talabre (1850 µg/kg in corn and 860 µg/kg in potatoes, including potato skins, respectively), two towns situated close to the Lascar volcano (Queirolo *et al.*, 2000b). These values exceed the national standard for arsenic (500 µg/kg) by approximately 400% and 180%, respectively.

In Bangladesh, contamination of agricultural soils from long-term irrigation with arsenic-contaminated groundwater led to phyto-accumulation in food crops. Various vegetables harvested in Samta village in the Jessore district have been reported to contain high concentrations of arsenic (range, 306–489 µg/kg) (Alam *et al.*, 2003). In West Bengal (India), high arsenic contents have also been reported in many vegetables and spices, especially in the skin of most vegetables, as a result of the dependence of the agricultural system on groundwater (Roychowdhury *et al.*, 2002, 2003).

Moreover, high concentrations of arsenic have been reported in fruit, vegetables, grain and meat in regions contaminated by anthropogenic pollution; this is the case in the Moscow region (Russia), which has been shown to be contaminated by fertilizer industry plants (Zakharova *et al.*, 2002). High levels of arsenic have also been reported in plants, vegetables and cow's milk, as a consequence of heavy contamination of soils, surface and groundwaters by arsenic attributed to industrial sources (veterinary chemicals, pharmaceuticals, pesticide industries) in the area of Patancheru, Andhra Pradesh (India) (Sekhar *et al.*, 2003).

Interestingly, rare plants are able to accumulate exceedingly high concentrations of arsenic (in the order of 1% dry mass). Brake fern (*Pteris vittata*) in particular is extremely efficient at extracting arsenic from soils and translocating it into its fronds. Arsenic concentrations in fern fronds, growing in soil spiked with 1500 mg/kg arsenic, increased from 29.4 to 150 861 mg/kg within 2 weeks. Since it acts as an arsenic hyperaccumulator, brake fern could be used in the remediation of arsenic-contaminated soils (Ma *et al.*, 2001).

1.4 Human exposure

The natural and anthropogenic occurrence of arsenic in drinking-water has been recognized as a major public health issue in several regions of the world over the past two or three decades. Areas affected by arsenic span the globe, and significant exposures have been identified in Bangladesh, India, Taiwan, China, Mexico, Argentina, Chile and the

USA. Table 5 summarizes the geological characteristics of the regions of the world with naturally elevated levels of arsenic in the drinking-water.

Recent reviews have outlined the worldwide problem of arsenic in drinking-water (WHO, 2001; Mandal & Suzuki, 2002; Nordstrom, 2002; Smedley & Kinniburgh, 2002; Chakraborti *et al.*, 2003b).

1.4.1 *Exposure in Bangladesh*

In terms of the population exposed, the problem of arsenic contamination in much of southern and eastern Bangladesh is the most serious in the world, and occurs in groundwater from the alluvial and deltaic sediments that make up much of the area. In addition, it is complicated by large variability in arsenic levels at both local and regional scales.

In Bangladesh, tubewells began to be used for drinking-water in the 1970s to control the problem of gastrointestinal disease linked to contamination of shallow wells and surface waters. In the 1990s, it was discovered that the water from many of these wells was contaminated with arsenic. Since then, extensive research has been carried out to characterize the extent of the problem. Figure 1 shows the districts in Bangladesh affected by arsenic and Table 6 gives an overall picture of the database. Table 7 shows the distribution of concentrations of arsenic in hand tubewells, and Table 8 summarizes the levels of arsenic measured in biological samples.

The level of contamination with arsenic of tubewells in Bangladesh exceeded both the World Health Organization guideline of 10 μg/L and the Bangladesh permissible limit of 50 μg/L (Dhar *et al.*, 1997; Smith *et al.*, 2000a; Kinniburgh & Smedley, 2001: Alam *et al.*, 2002).

A survey of 27 districts in Bangladesh up to January 1997 analysed over 3000 water samples and revealed that 38% of them contained more than 50 μg/L arsenic (Dhar *et al.*, 1997). In another survey examining 294 tubewells, 85 samples (29%) were contaminated by arsenic at levels above 50 μg/L (Ahmad *et al.*, 1997). Between September 1996 and June 1997, all functioning wells (n = 265) in the village of Samta in the Jessore District were tested for arsenic (Biswas *et al.*, 1998). Approximately 91% of the wells contained arsenic at levels higher than 50 μg/L. Furthermore, 600 people-were examined clinically, and a few hundred hair, nail and urine samples were tested using flow injection HG–AAS. The data obtained showed that 99% of urine samples and 98% of nail samples of the population studied in Samta village contained levels of arsenic above normal and 78% of hair samples above toxic levels. The arsenic problem of Bangladesh became highlighted when an international conference was held in Dhaka, Bangladesh, in 1998 (Dhaka Community Hospital Trust and School of Environmental Studies, 1998).

By March 1998, it was reported that 4196 of 9024 wells in Bangladesh tested for arsenic contained levels higher than 50 μg/L and 884 wells had levels higher than 500 μg/L (Mandal *et al.*, 1999). A Rapid Action Programme (RAP) was performed by field kit in a sample of 500 villages with a total population of 469 424. Approximately 62% of the 32 651 tubewells sampled had levels of arsenic above 100 μg/L (Quamruzzaman *et al.*, 1999).

Table 5. Regions of the world with naturally elevated levels of arsenic in groundwater

Country/region	Affected area (km^2)	Potentially exposed population	Arsenic concentration (µg/L)	Environmental conditions	Reference
Bangladesh	118 849	$\sim 3 \times 10^7$	< 0.5–2500	Hollocene alluvial/deltaic sediments; abundance of organic matter; strongly reducing, neutral pH, high alkalinity, slow groundwater flow rates	Chakraborti *et al*. (2002); Smedley & Kinniburgh (2002)
India/West Bengal	38 865	6×10^6	< 10–3200	Same as Bangladesh	Chakraborti *et al*. (2002); Smedley & Kinniburgh (2002)
Viet Nam				Pleistocene and Holocene sediments; strongly reducing conditions	Berg *et al*. (2001)
China/ Taiwan	4 000	$\sim 10^5$	10–1820	Coastal zones, sediments, including black shales; strongly reducing, artesian conditions, some groundwaters contain humic acids	Smedley & Kinniburgh (2002)
China/ Xinjiang, Shanxi	38 000	~ 500	40–750	Holocene alluvial plain; reducing	Smedley & Kinniburgh (2002); Cao (1996)
Thailand	100	1.5×10^4	1–< 5000	Dredge quarternary alluvium; oxidation of disseminated arsenopyrite due to mining	Smedley & Kinniburgh (2002)
Mongolia/ Inner Mongolia	4 300	$\sim 10^5$	< 1–2400	Holocene alluvial and lacustrine sediments; strongly reducing, neutral pH, high alkalinity, some groundwaters contain humic acids	Cao (1996); Smedley & Kinniburgh (2002); Sun *et al*. (2001)

Table 5 (contd)

Country/region	Affected area (km^2)	Potentially exposed population	Arsenic concentration (µg/L)	Environmental conditions	Reference
Argentina/ Chaco-Pampean Plain	10^6	2×10^6	< 1–7550	Holocene and earlier loess with rhyolitic volcanic ash; oxidizing, neutral to high pH, high alkalinity; groundwaters often saline	Nordstrom (2002); Smedley & Kinniburgh (2002)
Northern Chile/ Antofagasta	35 000	5×10^5	100–1000	Quaternary volcanogenic sediments; generally oxidizing, arid conditions, high salinity	Queirolo *et al*. (2000a); Smedley & Kinniburgh (2002)
Bolivia		5×10^4		Same as Argentina and Northern Chile	Nordstrom (2002)
Mexico	32 000	4×10^5	8–620	Volcanic sediments; oxidizing, neutral to high pH	Smedley & Kinniburgh (2002)
Germany/ Bavaria	2 500		< 10–150	Mineralized sandstone	Nordstrom (2002)
Hungary, Romania/ Danube Basin	110 000	4×10^5		Quaternary alluvial plain; reducing conditions, some high in humic acid	Smedley & Kinniburgh (2002)
Spain		$> 5 \times 10^4$	< 1–100	Mineralization; alluvial sediments	Nordstrom (2002)
Greece		1.5×10^5		Mineralization; thermal springs; mining	Nordstrom (2002)
Ghana		$< 1 \times 10^5$	< 1–175	Sulfide mineralization, particularly arsenopyrite; gold mining	Nordstrom (2002)

Table 5 (contd)

Country/region	Affected area (km^2)	Potentially exposed population	Arsenic concentration (µg/L)	Environmental conditions	Reference
Canada/Moira Lake, Ontario	100		50–3000	Mine tailing; ore mining	Smedley & Kinniburgh (2002)
Canada/British Columbia	50		0.5–580	Sulfide mineralization in volcanic rocks; neutral to high pH groundwater	Smedley & Kinniburgh (2002)
USA/Arizona	200 000		< 1300	Alluvial basins, some evaporites; oxidizing, high pH	Smedley & Kinniburgh (2002)
USA/ California	5 000		< 1–2600	Holocene and older basin-fill sediments; internally drained basin, mixed redox conditions, high salinity	Smedley & Kinniburgh (2002)
USA/Nevada	1 300		< 2600	Holocene mixed aeolian, alluvial and lacustrine sediments; mainly reducing, some high pH, some with high salinity due to evaporation	Smedlley & Kinniburgh (2002)

Figure 1. Degree of arsenic contamination in 64 districts in Bangladesh

From Chakraborti *et al.* (2002)

Table 6. Status of contamination of groundwater by arsenic in Bangladesh

	Bangladesh
Total area (km^2)	148 393
Population (millions)	120
Total number of districts	64
Total number of water samples analysed	34000
Samples containing > 10 µg/L arsenic (%)	56.35
Samples containing > 50 µg/L arsenic (%)	37.38
Number of districts affected by arsenic (> 50 µg/L)	50
Population of districts affected by arsenic (millions)	104.9
Area of districts affected by arsenic (km^2)	118 849
Number of villages affected by arsenic (arsenic in drinking-water > 50 µg/L)	2000
Number of people drinking arsenic-contaminated water > 50 µg/L (millions)	25

From Chakraborti *et al.* (2002)

Table 7. Distribution of arsenic concentrations in water samples from hand tubewells

Total no. of water samples analysed	Arsenic concentration range (µg/L)							
	< 10	10–50	51–99	100–299	300–499	500–699	700–1000	> 1000
34 000	14 991	6429	2949	5812	2174	894	479	272
	44.1%	18.9%	8.7%	17.1%	6.4%	2.6%	1.4%	0.8%

From Rahman *et al.* (2001)

In continuing surveys of 42 districts affected by arsenic in Bangladesh, Chowdhury *et al*. (2000a,b) reported the analysis of 10 991 water samples of which 59% contained arsenic levels above 50 µg/L.

Of the 34 000 drinking-water samples collected in Bangladesh up to August 2001, 272 contained ≥ 1000 µg/L arsenic (Table 6; Chakraborti *et al*., 2002). The highest concentration of arsenic measured in drinking-water in Bangladesh was 4700 µg/L. In the Chiladi village of Senbagh Thana in the Noakhali district, 100% of tubewell-water samples contained arsenic concentrations ≥ 50 µg/L, 94% contained ≥ 300 µg/L and 28% contained ≥ 1000 µg/L.

Table 8. Concentrations of arsenic in samples of hair, nails, urine (metabolites) and skin scale collected from the areas in Bangladesh affected by arsenic

Parameter	Arsenic in hair[a] (µg/kg)	Arsenic in nails[b] (µg/kg)	Arsenic in urine[c] (µg/L)	Arsenic in skin scale[d] (µg/kg)
No. of observations	4 386	4 321	1 084	705
Mean	3 390	8 570	280	5 730
Median	2 340	6 400	116	4 800
Minimum	280	260	24	600
Maximum	28 060	79 490	3 086	53 390
Standard deviation	3 330	7 630	410	9 790
% of samples having arsenic above normal	83.15	93.77	95.11	–

From Rahman *et al.* (2001)

[a] Normal levels of arsenic in hair range from 80 to 250 µg/kg; 1000 µg/kg indicates toxicity.

[b] Normal levels of arsenic in nails range from 430 to 1080 µg/kg

[c] Normal levels of arsenic in urine range from 5 to 50 µg/1.5 L (per day)

[d] Normal value for skin scale arsenic not defined

Thousands of hair, nail and urine samples from people living in villages affected by arsenic have been analysed (Table 8). Approximately 90% of children under 11 years of age living in the affected areas show levels of arsenic in hair and nails above the normal level (Rahman *et al.*, 2001).

A comparative study reported analyses of arsenic species in urine samples ($n = 42$) from one affected village of Madaripur district, where the average concentration of arsenic in drinking-water was 376 µg/L, and a non-affected village ($n = 27$), where the concentration of arsenic in drinking-water is known to be below 3 µg/L (Chowdhury *et al.*, 2003). The average urinary levels of arsenic of children were higher than those of adults. The ratios of MMA to inorganic arsenic and of DMA to MMA were 0.93 and 4.11 in adults and 0.74 and 8.15 in children, respectively.

Chakraborti *et al.* (1999a) reported arsenic concentrations in hand tubewells from 100 to 415 m in depth in all geographical regions in Bangladesh. The report indicated that 99% of the tubewells analysed that were deeper than 300 m had an arsenic concentration below 50 µg/L. Understanding the mechanism of arsenic release to groundwater in Bangladesh should help to provide guidance for the placement of safe new water wells (Nickson *et al.,* 1998, 2000).

1.4.2 *Exposure in India*

(*a*) *Contamination by arsenic of groundwater in northern India*

A preliminary study was reported in 1976 on arsenic in dug wells, hand pumps and spring water from Chandigarh and different villages of the Punjab, Haryana and Himachal Pradesh in northern India (Datta & Kaul, 1976). A value as high as 545 µg/L arsenic was obtained in one water sample from a hand pump. Datta (1976) further reported high arsenic content in the liver of five of nine patients with non-cirrhotic portal hypertension who had been drinking arsenic-contaminated water. To date no further information on arsenic poisoning in northern India is available.

(*b*) *Contamination by arsenic of groundwater in West Bengal*

Since 1984, extensive research in West Bengal has revealed that this region has one of the most serious problems with groundwater contamination by arsenic in wells used for drinking-water. Figure 2 shows the districts in West Bengal affected by arsenic and Table 9 gives an overall picture of the database and the extent of the problem. Table 10 shows the distribution of concentrations of arsenic in hand tubewells in areas of West Bengal, and Table 11 summarizes the levels of arsenic measured in biological samples.

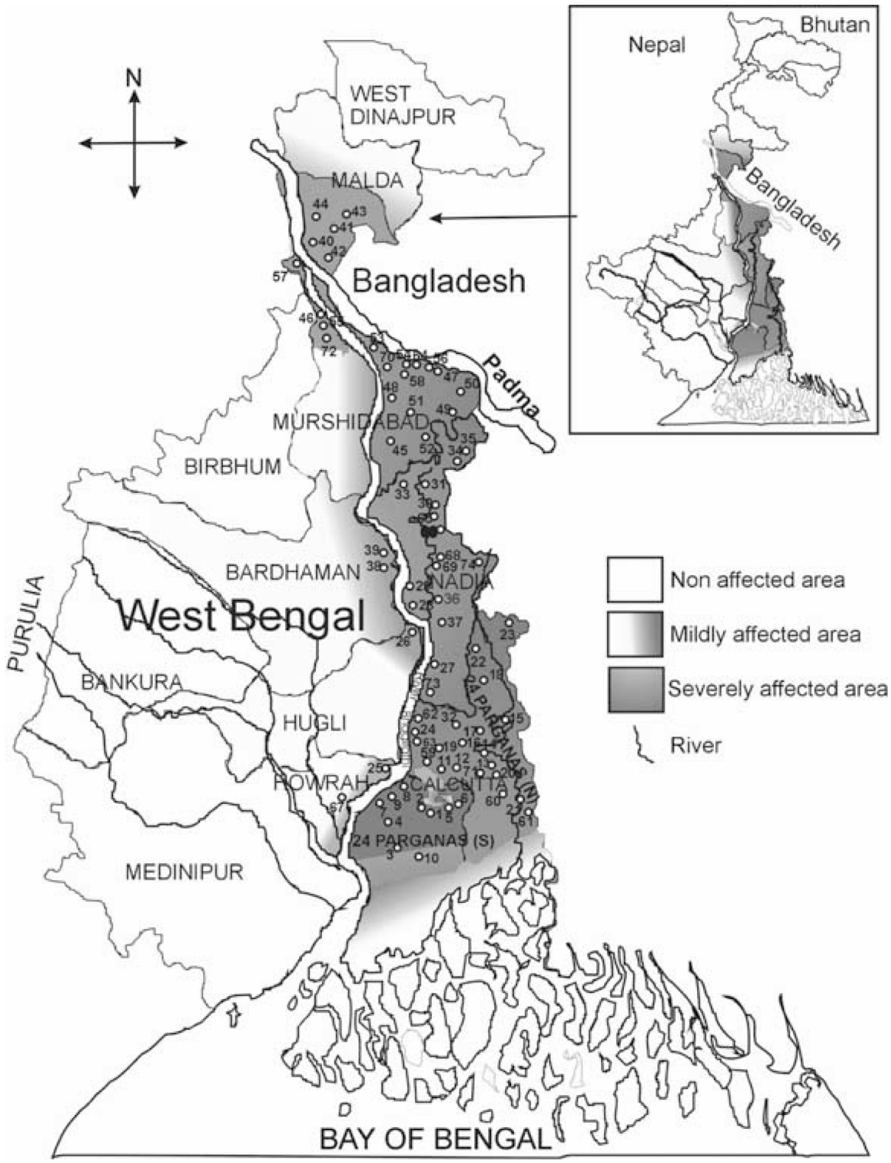
Contamination of groundwater by arsenic was first detected in the state of West Bengal, India, in 1983 (Garai *et al*., 1984). Sixteen people whose drinking-water came from two hand tubewells in one village in the district of 24-Parganas were identified as having arsenical skin lesions. Arsenic concentrations in these tubewells were 1250 and

Table 9. Status of contamination of groundwater by arsenic in West Bengal, India

	West Bengal
Total area (km^2)	89 193
Population (millions; according to 1991 Census)	68
Total number of districts	18
Total number of water samples analysed	105 000
Samples containing > 10 µg/L arsenic (%)	51
Samples containing > 50 µg/L arsenic (%)	25
Number of districts affected by arsenic (> 50 µg/L)	9
Population of districts affected by arsenic (millions)	42.7
Area of districts affected by arsenic (km^2)	38 865
Number of blocks/police stations affected by arsenic	74
Number of villages (approx.) affected by arsenic (arsenic in groundwater > 50 µg/L)	2700
Number of people drinking arsenic-contaminated water > 50 µg/L (millions)	6

From Chakraborti *et al* (2002)

Figure 2. Areas of West Bengal in which drinking-water is contaminated with arsenic



From Chakraborti *et al.* (2002)

Table 10. Concentrations of arsenic in water samples from hand tubewells in West Bengal, India

No. of water samples analysed	Arsenic concentration range (µg/L)							
	< 10	10–50	51–99	100–299	300–499	500–699	700–1000	> 1000
101 934	49 310	27 309	10 005	11 782	2354	724	334	116
	48.4%	26.8%	9.8%	11.6%	2.3%	0.7%	0.3%	0.1%

From Rahman *et al.* (2001)

Table 11. Concentrations of arsenic in samples of hair, nails, urine (metabolites) and skin scale collected from the areas in West Bengal (India) affected by arsenic

Parameters	Arsenic in hair[a] (µg/kg)	Arsenic in nails[b] (µg/kg)	Arsenic in urine[c] (µg/L)	Arsenic in skin scale[d] (µg/L)
No. of observations	7 135	7 381	9 795	165
Mean	1 480	4 560	180	6 820
Median	1 320	3 870	115	4 460
Minimum	180	380	10	1 280
Maximum	20 340	44 890	3 147	15 510
Standard deviation	1 550	3 980	268	4 750
% of samples having arsenic above normal	57	83	89	–

From Rahman *et al.* (2001)

[a] Normal levels of arsenic in hair range from 80 to 250 µg/kg; 1000 µg/kg indicates toxicity.

[b] Normal levels of arsenic in nails range from 430 to 1080 µg/kg

[c] Normal excretion of arsenic in urine ranges from 5 to 40 µg/1.5 L (per day)

[d] Normal value for skin scale arsenic not defined

700 µg/L. Saha and Poddar (1986) reported that 36 villages from 18 police stations/blocks of six districts were affected in 24-Parganas, Murshidabad, Nadia, Barddhaman, Midnapur and Maldah. Water samples from 207 hand tubewells were analysed and 105 (50.7%) showed arsenic concentrations above 50 µg/L; the highest concentration recorded was 568 µg/L. Analysis of arsenic in hair, nails and skin-scale from people in the affected villages confirmed exposure to arsenic.

In 1987, an epidemiological survey in six villages of three districts (24-Parganas, Barddhaman and Nadia) revealed 197 patients with arsenical dermatosis in 48 families

(Chakraborty & Saha, 1987). Of 71 water samples collected from tubewells of the affected villages, the concentration of arsenic in 55 (77.5%) was higher than the permissible limit (50 μg/L) for arsenic in drinking-water in India. The mean arsenic concentration in 31 water samples collected from tubewells of affected families was 640 μg/L and that in 40 water samples collected from tubewells of unaffected families was 210 μg/L. Another epidemiological investigation (Guha Mazumder *et al*., 1988) in a village in 24-Parganas also found evidence of effects of arsenic in 62 (92.5%) of 67 members of families who drank contaminated tubewell-water (level of arsenic, 200–2000 μg/L). In contrast, only six (6.25%) of 96 persons from the same area who drank water with a level of arsenic < 50 μg/L showed any effects.

In 1991, a report from the government of West Bengal (Steering Committee, Arsenic Investigation Project, 1991) concluded that water of the intermediate aquifer in areas of West Bengal was polluted with arsenic. Neither the shallow (first) nor the deep (third) aquifers had reported arsenic contamination. The sand grains in the arsenic-contaminated aquifer were generally coated with iron and material rich in arsenic.

In October 1994, a committee constituted by the government of West Bengal (Committee Constituted by Government of West Bengal, 1994) reported arsenic contamination in 41 blocks in six districts of West Bengal. The committee analysed about 1200 water samples from these six districts for arsenic and other common water-quality parameters, and the highest concentration of arsenic reported was 3200 μg/L.

The expanding database on the problem of arsenic contamination in West Bengal has been documented in a continuing series of publications. By December 1994, it was reported that 312 villages from 37 blocks/police stations in six districts in West Bengal were affected by contamination of groundwater with arsenic. From extrapolation of the data, it was predicted that more than 800 000 people were drinking arsenic-contaminated water from these districts, and based on the analysis of several thousand water samples, average arsenic concentrations in the wells sampled ranged from 193 to 737 μg/L (Das *et al.*, 1994; Chatterjee *et al*., 1995). The highest arsenic concentration of 3700 μg/L was found in a hand tubewell from a village in South 24-Parganas district. Groundwater and urine samples from affected villages were also analysed for arsenite, arsenate, MMA and DMA. Groundwater contained arsenate and arsenite in a ratio of approximately 1:1. In urine, DMA and MMA were the predominant species, together with some arsenite and arsenate. Das *et al.* (1995) reported high arsenic levels in the hair, nails, urine, skin-scale and a few liver tissues (biopsy) of people from arsenic-affected villages who had arsenical skin lesions.

Based on the analysis of 20 000 water samples from areas of West Bengal, Mandal *et al.* (1996) reported that seven districts (North 24-Parganas, South 24-Parganas, Nadia, Barddhaman, Murshidabad, Maldah, Hugli) were affected by arsenic. Approximately 45% of these samples had arsenic concentrations above 50 μg/L, and the average concentration was approximately 200 μg/L.

Groundwater contamination was reported in 985 villages from 69 police stations/ blocks in nine districts of West Bengal on the basis of analyses of 58 166 water samples.

The nine districts were Maldah, Murshidabad, Barddhaman, Hugli, Howrah, Nadia, North 24-Parganas, South 24-Parganas and Calcutta. After extrapolation of data from the water analyses and screening villagers for arsenical skin lesions, it was estimated that about 5 million people were drinking-water contaminated with levels of arsenic above 50 µg/L. The total population in the nine districts of West Bengal affected by arsenic is about 43 million (Chowdhury *et al.,* 2000a,b).

On the basis of an analysis of 101 394 hand tubewells and approximately 25 000 biological samples, and screening of 86 000 persons in affected villages of West Bengal, Rahman *et al.* (2001) reported that 2600 villages were affected by arsenic in groundwater at levels of > 50 µg/L and that approximately 6 million people drank water contaminated with arsenic at levels above 50 µg/L. Mandal *et al.* (2001) identified DMA^{III} and MMA^{III} for the first time in urine from the affected areas of West Bengal.

Roychowdhury *et al.* (2002) reported total arsenic in food composites collected from a few arsenic-affected villages in Murshidabad district, West Bengal, where arsenic-contaminated groundwater was used for agricultural irrigation. The report showed average daily dietary intake of arsenic from foodstuffs for adults and children of 180 and 96.5 µg, respectively.

Rahman *et al.* (2003) studied North 24-Parganas, one of the nine affected districts of West Bengal, for 7 years. On the basis of analyses of 48 030 water samples and 21 000 hair, nail and urine samples, and screening of 33 000 people in North 24-Parganas, it was estimated that about 2 million and 1 million people are drinking water contaminated with arsenic at levels above 10 and 50 µg/L, respectively.

(i) *Source of contamination of groundwater by arsenic in West Bengal*

When the contamination of drinking-water by arsenic was first discovered in West Bengal, tubewell strainers, pesticides, insecticides and other anthropogenic sources were first considered as possible origins of the groundwater contamination (Chakraborty & Saha, 1987). However, Das *et al.* (1994) showed that a single deep tubewell supplying water to a few villages in Maldah, one of the nine arsenic-affected districts, was drawing nearly 150 kg arsenic per year, indicating that the source of arsenic was geological. Analyses of bore-hole sediments showed high concentrations of arsenic in only a few soil layers and the arsenic therein was found to be associated with iron pyrites. Das *et al.* (1995, 1996) also confirmed analytically the existence of arsenic-rich pyrites in bore-hole sediment. It was proposed that heavy drawing of groundwater and aeration of the aquifer leads to the decomposition of arsenic-rich pyrites and consequently contamination of groundwater with arsenic. Similar conclusions were reached by Mallick and Rajagopal (1995).

Bhattacharya *et al.* (1997, 1998) reported an association between arsenic and hydrated ferric oxide (HFO) and its mobilization to the aquifer due to changes in redox conditions during the development of groundwater. Ahmed *et al.* (1998) and Nickson *et al.* (1998, 2000) also suggested that reduction of HFO resulted in the mobilization of arsenic from absorbed HFO.

(ii) *Contamination of groundwater by arsenic in the residential area of Behala-Calcutta due to industrial pollution*

In Calcutta, chronic arsenicosis was first reported by Guha Mazumder *et al.* (1992). The study of Chatterjee *et al.* (1993) on the source of arsenic and the magnitude of the contamination revealed that a chemical factory producing several chemical compounds, including the insecticide Paris-Green (copper acetoarsenite), was responsible for the contamination. This factory had been producing about 20 tonnes of Paris-Green per year for approximately 20 years. Analysis of soil surrounding the production waste-dumping ground showed very high concentrations of arsenic (as high as 10 000 μg/g). Nineteen hand tubewells, used for drinking and cooking in the immediate area, showed very high concentrations of arsenic (up to 39 000 μg/L). The concentration of arsenic in hand tubewells decreased the farther the wells were located from the dumping ground. A follow-up study in the affected areas (Chakraborti *et al.*, 1998) showed that the total average concentration of arsenic in the 19 hand tubewells sampled previously had decreased by only 10–15% from the levels observed 8 years before.

(*c*) *Contamination of groundwater by arsenic in Chhattisgarh State*

Contamination of groundwater by arsenic was reported in a few villages of Rajnandgaon district of Chhattisgarh by Chakraborti *et al.* (1999b). The present State of Chhattisgarh had been within the State of Madhya Pradesh 2 years previously. The source of arsenic in groundwater is natural and geological both for the alluvial Bengal Basin and the rocky belt of Dongargarh-Kotri zone of Rajnandgaon district. The total population of the district is 1.5 million. Except for two towns — Rajnandgaon and Khairagarh — the entire district depends on tubewells and dugwells. Water samples (n = 146) were collected from 22 villages of Chowki block, Rajnandgaon district, and levels of arsenic in groundwater were found to be above 10 μg/L in eight villages and above 50 μg/L in five villages, with the highest concentration being 880 μg/L. From 150 hair samples examined, approximately 75% of people were found to have levels of arsenic in hair above toxic levels. Pandey *et al.* (1999) also reported contamination of groundwater by arsenic in the Rajnandgaon district of Chhattisgarh. Of 390 samples analysed, 26 sites were found to be contaminated with arsenic, with the highest concentration being 1010 μg/L. The number of people at risk was estimated at 10 000. Pandey *et al.* (2002) established that the extent of the arsenic contamination in this area is even greater; about 30 000 people residing in 30 villages and towns are directly exposed to high levels of arsenic in drinking-water (up to 3050 μg/L arsenic) and more than 200 000 people are at risk. The source and mobilization process of arsenic from affected areas of Rajnandgaon district Chhattisgarh was reported by Acharyya (2002).

(*d*) *Contamination of groundwater by arsenic in Middle Ganga Plain, Bihar*

In the Middle Ganga Plain, Bihar, tubewells replaced dugwells about 20 years ago. Analyses of the arsenic content of 206 tubewells from Semria Ojha Patti (95% of the total in the village) showed that 56.8% exceeded concentrations of 50 μg/L, with 19.9% > 300 μg/L. The distribution indicated that, of the 5000 residents of Semria Ojha Patti, 18.8% used safe water (< 10 μg/L arsenic), 24.7% used water containing 10–50 μg/L arsenic, 56.8% used water containing > 50 μg/L, and 19.9% used water containing > 300 μg/L. The concentrations of arsenic in urine, hair and nail correlated significantly ($r = 0.72$–0.77) with concentrations in drinking-water. Of the 51 urine samples analysed, 98% had levels of arsenic above that of the normal secretion, with 47% > 500 mg/L, 33% > 1000 mg/L and 5.9% > 3000 mg/L; 57.6% of hair samples and 76.3% of nail samples were found to be above the normal range (Chakraborti *et al.*, 2003a).

(*e*) *Contamination of groundwater and surface water by arsenic in the industrial region of Patancheru, Andhra Pradesh*

Patancheru, in the Medak District of Andhra Pradesh, is one of the major industrial estates, situated 30 km from Hyderabad. The main source of arsenic has been identified as Park Trade Centre, Gaddapotharam Bulk Drug Factory, which makes veterinary drugs based on arsonic acid, as well as other sources such as the pesticide and drug intermediate industries. The solid wastes of these industries are dumped indiscriminately near Kazipally Lake, and represent a source of contamination of nearby waters and soils. Arsenic contamination was evaluated in 14 villages in this area. Very high levels of arsenic were found in the range of 80–8960 μg/L and 140–7350 μg/L in surface water and groundwater, respectively. In both surface water and groundwater, the average arsenite (As^{III}) concentration was about 20% of total arsenic (Sekhar *et al.*, 2003).

Samples of blood, urine, hair and nails from 193 inhabitants of these 14 contaminated villages were analysed. Arsenic levels in the biological samples were very high, ranging from 400 to 1400 μg/kg in blood (control, 6–10 μg/kg), from 60 to 160 μg/L in urine (control, 6–10 μg/L), from 300 to 940 μg/kg in hair (control, 10–130 μg/kg) and from 500 to 1630 μg/kg in nails (control, 120–160 μg/kg). High concentrations of arsenic were also detected in vegetables, plants and cow's milk in this area and represent a second possible source of exposure for the population (Sekhar *et al.*, 2003).

1.4.3 *Exposure in Central and South America*

In South America, the main source of exposure to arsenic has been the natural contamination of drinking-water. In this area, arsenic originates from the geological formations associated with volcanoes, affecting Chile, Bolivia, Peru and Argentina in the Andean region (Queirolo *et al.*, 2000a). The largest populations affected are the Antofagasta Region in northern Chile, with approximately 400 000 exposed inhabitants, and the Córdoba Province in Argentina, with approximately 630 000 people exposed. Mexico also has naturally occurring arsenic in drinking-water, which is best characterized in the Lagunera region, in central northern Mexico, where approximately 400 000 people are exposed. The mean levels in drinking-water for these populations range from 50 to 500 µg/L; in isolated wells, levels reach as high as 6897 µg/L arsenic. Exposure has been recorded since the beginning of the last century. Currently, most areas in these regions receive water with levels of arsenic below 50 µg/L.

Exposures to arsenic due to contaminated air, soils and water as a result of copper, gold or silver mining have been described in Mexico (Díaz-Barriga *et al.*, 1993; Calderón, 1999; Mejía *et al.*, 1999), Chile (Romo-Kroger & Llona, 1993; Romo-Kroger *et al.*, 1994; Santolaya *et al.*, 1995; Sancha, 1997; Flynn *et al.*, 2002), Brazil (Romo-Kroeger & Llona, 1993) and Nicaragua (Cruz *et al.*, 1994). The area affected in central Mexico is San Luis de Potosí. In Chile, environmental and occupational exposures to arsenic in air have been reported in the Andes Mountains in Regions II, III, V and VI and the Metropolitan Region, where five major copper mining plants are located (Ministerio de Salud, 1986; Santolaya *et al.*, 1995; Ferreccio *et al.*, 1996), but no secondary contamination of drinking-water.

(*a*) *Mexico*

In Mexico, most studies of arsenic in drinking-water have been conducted in the States of Durango and Coahuila, which constitute the Lagunera Region (Table 12). Del Razo *et al.* (1990) studied 128 wells from 11 counties and found arsenic contents of 8–624 µg/L; 50% of the wells had arsenic levels > 50 µg/L. They estimated that at least 400 000 people, mostly from the rural areas of the region, have been exposed to levels of arsenic > 50 µg/L. Since the 1960s, when arsenic contamination was first identified, the polluted wells have gradually been replaced and, by the end of 1989, most of the population was receiving water with arsenic levels below 20 µg/L (Cebrián *et al.*, 1994). Some contamination of drinking-water by arsenic has been reported in the State of Hidalgo in the Zimapan Valley, where the exposed population has been estimated at 35 000, and levels of arsenic in the drinking-water ranged from 21 to 1070 µg/L (Armienta *et al.*, 1997; Gomez-Arroyo *et al.*, 1997).

In San Luis de Potosí, in central Mexico, exposure to arsenic associated with mining activities arises from drinking-water, soil and dust, and the estimated exposed population is 600 000. Mean arsenic concentrations in air have been measured at 0.48 µg/m^3 (0.36–0.88 µg/m^3) (Díaz-Barriga *et al.*, 1993), and concentrations of arsenic in drinking-water vary from 9.9 to 20.9 µg/L (with some wells near the smelter having concentrations that range from 105 to 6897 µg/L). Studies of soil in San Luis de Potosí have demonstrated extremely high levels of arsenic in the vicinity of the mines (188–944 µg/g, Díaz-Barriga *et al.*, 1993; 2215–2675 µg/g, Mejía *et al.*, 1999), and also in the dust of the nearby households (800–1182 µg/g, Díaz-Barriga *et al.*, 1993; 1780–9950 µg/g, Mejía *et al.*, 1999). By 1991, the copper mining companies that caused the air, soil and water contamination of the area implemented dust control technologies and other measures to control soil pollution (Cebrián *et al.*, 1994).

Table 12. Exposure to arsenic in drinking-water in Mexico

Location	Source of water	No. of samples studied	Year	Total arsenic in water (µg/L; range)	Reference
Sonora, Hermosillo	Wells of 29 cities	173	NR	2–305	Wyatt *et al*. (1998a)
Lagunera Region	Wells, different towns	171	1970s–1980s	7–624	Cebrían *et al*. (1983); Del Razo *et al*. (1990); García-Vargas *et al*. (1994); Gonsebatt *et al*. (1997); Hernández-Zabala *et al*. (1999)
Zimapán, Hidalgo	Aquifer, 6 different towns		(Since 1970)	21–1070	Gomez- Arroyo *et al*. (1997)
San Luis de Potosí	Tap-water, Morales and Graciano	19	NR	9.9–20.9	Díaz-Barriga *et al*. (1993)
	Wells near smelter	NR	NR	106–6897	Meíja *et al.* (1999)

NR, not reported

Levels of arsenic in urine and hair are presented in Tables 13–14. Levels of arsenic in hair were high in samples from subjects exposed to arsenic in water in Zimapán, and were twice those in samples from subjects in Mexico City, which were also above the reference value, probably due to air pollution (Armienta *et al*., 1997).

(*b*) *Argentina*

In Argentina, the main source of arsenic in drinking-water has been from wells, with concentrations ranging from 40 to > 4500 µg/L (Table 15), and arsenic was first reported in well-water in 1917 (Arguello *et al*., 1938). In 1970 and 1980, aqueducts from rivers with low levels of arsenic were built to replace the use of well-water, but some populations continued to be exposed (Hopenahyn-Rich *et al*., 1996a,b,c). The provinces with high levels of arsenic in their well-water are: Córdoba, Salta, La Pampa, Santa Fé, Tucuman, Santiago del Estero, San Luis and part of Buenos Aires. The best characterized is Córdoba, a region in central Argentina, that extends over an area of 165 000 km^2 and has a population of 2 750 000, distributed in 26 counties. In some counties of Córdoba, high levels (between 100 and 2000 µg/L) of arsenic were recorded in drinking-water during the 1930s (Hopenhayn-Rich *et al*., 1996a).

In Córdoba, Hopenhayn-Rich *et al*. (1996a) obtained data from various sources, including measurements of arsenic in drinking-water from official national health reports made in the 1930s, a survey in 1942, two studies reported in 1968 and 1985 and a water survey reported in 1973. Based on the available measurements, average exposure of the population of each town was estimated, assuming that all people drank the same concentration

Table 13. Total arsenic in human urine samples in Mexico, Argentina and Chile

Location	No. of exposed subjects studied	Year	Mean arsenic in urine	Range	Reference
Mexico					
Lagunera, Santa Ana	36 adults		489 µg/gc	109–1829 µg/gc	García-Vargas *et al*. (1994);
	35 adults		548 µg/gc	295–849 µg/gc	Del Razo *et al*. (1997);
	37 adults		848 µg/L	88–2058 µg/L	Hernández-Zavala *et al*. (1999)
San Luis de Potosí	80 children		51.6 µg/gc	18.2–186.2 µg/gc	Calderón *et al*. (2001)
	112 children		70.5 µg/gc	17.7–497.7 µg/gc	Meíja (1999)
	133 children		117.6 µg/gc	33–594 µg/gc	Díaz-Barriga *et al*. (1993)
Argentina					
Córdoba province, MJ	282		160 µg/L	60–410 µg/L	Lerda (1994)
Santa Fe, Tortugas	155		70 µg/L	10–600 µg/L	Lerda (1994)
San Antonio	11		274 µg/L	126–440 µg/L	Vahter *et al*. (1995)
Other towns	15		36 µg/L	13–89 µg/L	Vahter *et al*. (1995)
San Antonio	10 lactating women		400 µg/L	250–610 µg/L	Concha *et al*. (1998a)
	11 pregnant women		335 µg/L	116–439 µg/L	Concha *et al*. (1998c)
San Antonio and Taco	34 children	1994	382 µg/L	125–621 µg/L	Concha *et al*. (1998b)
San Antonio	23 women		344 µg/L	90–606 µg/L	
Chile					
Region I	93 general population	1984–95	45 µg/L	10–92 µg/L	Venturino (1987); Sancha (1997)
Rest of Chile	2472 general population	1984–2000	13 µg/L	5–49 µg/L	Venturino (1987); Sancha (1997); CONAMA (2000)
Antofagasta	164 general population	1968	NR	1–700 µg/L	Gonzalez (1970)
Antofagasta	262 general population	1994–2000	69 µg/L	18–99 µg/L	Sancha (1997); CONAMA (2000)
Calama	239 general population	1977–95	76 µg/L	21–124 µg/L	Borgoño *et al*. (1980); Sancha (1997)
San Pedro	265 general population	1997	611.7 µg/L	61–1893 µg/L	Hopenhayn-Rich *et al*. (1996b,c); Moore *et al*. (1997a,b)

gc, grams of creatinine; NR, not reported

Table 14. Arsenic in human hair samples in Mexico and Chile

Location (source of exposure)	Year of sample	No. of subjects	Total arsenic in sample (µg/g)		Reference
			Mean	SD (range)	
Mexico					
Zimapán	NR	120	8.5	3.56	Armienta *et al.* (1997)
Mexico City (water)		17	4.6	1.96	
San Luis de Potosí	NR				Díaz-Barriga *et al.* (1993)
(smelter (1.5 km))		75	9.9	(1.4–57.3)	
(smelter (25 km))		25	0.5	(0.2–1.2)	
Lagunera (wells)	NR	35	NR	(0–23.3)	Chávez *et al.* (1964)
Chile					
Iquique	1969	26	0.8	NR	Borgoño & Greiber (1971)
Antofagasta	1968–76	607	7.7	4.2–14.8	Gonzalez (1970); Borgoño & Greiber (1971); Sandoval & Venturino (1987)
Antofagasta	1986–92	293	0.42	0.01–3.68	Jamett *et al.* (1992); Peña *et al.* (1992)
Calama	1977	203	3.75	0–10	Borgoño *et al.* (1980)
Calama	1986–92	60	4.28	0.98–14.2	Jamett *et al.* (1992); Peña *et al.* (1992)
Chuquicamata	1986–92	60	17.19	3.03–54.77	Jamett *et al.* (1992); Peña *et al.* (1992)
Puchuncaví	1990	151	2.178	0.103–18.023	Chiang *et al.* (1990)
Valparaíso	1990	NR	0.434	0.015–1.525	Chiang *et al.* (1990)

SD, standard deviation

of arsenic. It was estimated that 273 014 people had been exposed to an average of 178 µg/L arsenic and another 406 000 people had been exposed to some arsenic (at least one measurement of 120 µg/L in water). A report available through CEPIS/PAHO (Penedo & Zigarán, 2002) described the arsenic content of 100 water samples from wells in Córdoba and confirmed Hopenhayn's estimations: they estimated that 625 861 people were exposed to arsenic, with regional averages ranging from 70 to 180 µg/L and individual well measurements from 10 to 1900 µg/L.

The Salta Province is the only area where high levels of arsenic have also been found in surface waters (Penedo & Zigarán, 2002). In the provinces of Salta and Jujui, in north-western Argentina, samples from five rivers had arsenic levels ranging from 52 to 1045 µg/L, and samples from three surging thermal springs had arsenic levels of 128–10 650 µg/L (de Sastre *et al.*, 1992). The population of San Antonio de los Cobres is the best studied in this province (Vahter *et al.*, 1995; Concha *et al.*, 1998a,b,c). San Antonio de los Cobres is a village in the Salta Province, 3800 m above sea level, with

Table 15. Exposure to arsenic in drinking-water in Argentina

Location	Source of drinking-water wells	No. of samples (year)	Total arsenic in water (µg/L)		Reference
			Average	Range	
Córdoba Province	Bell-Ville	NR (1917–20)	NR	1120–4500	Arguello *et al.* (1938)
Córdoba Province	Marcos Juárez	282 (NR)	130	10–660	Lerda (1994)
Córdoba Province	2 counties	118 (1942)	178	40–533	Hopenhayn-Rich *et al.* (1996a)
Córdoba Province	5 counties	67 (NR)	70–180	10–1900	Penedo & Zigarán (2002)
Santa Fe Province	Tortugas	155 (NR)	20	0–70	Lerda (1994)
Salta Province	School pipes	18 (NR)	592	4–1490	Astolfi (1971)
Salta Province	San Antonio San Antonio	2 areas (NR) 1 well	NR NR	93–440 8250–10 650	de Sastre *et al.* (1992)
	San Antonio	10 (1994)	167	117–219	Vahter *et al.* (1995); Concha *et al.* (1998a); Del Razo *et al.* (1999)

NR, not reported

approximately 5000 inhabitants (Vahter *et al.*, 1995). Until recently, this population had been drinking-water from wells with arsenic contents varying from < 1 to 440 µg/L, with one well reaching 9450 µg/L on average. Arsenic levels in urine are presented in Table 13 and other biomarkers in Table 16.

There are no studies of arsenic in air in Argentina. High levels of arsenic have been found in prepared food and soups in San Antonio de los Cobres (soup, 259–427 µg/g; prepared food, 131–418 µg/g; Concha *et al.*, 1998b).

(*c*) *Chile*

Northern Chile (Regions I–III) is an expanse of 250 000 km^2, of which 35 000 are quaternary volcanic rocks rich in arsenic (Queirolo *et al.*, 2000a). Arsenic reaches the population through drinking-water and through contamination of air and soil, as a result of mining activities.

In Chile, the main sources of drinking-water are rivers that originate in Cordillera de los Andes and reach the Pacific Ocean. Rivers in northern Chile (Regions I and II) have high natural arsenic concentrations, particularly those from the Region of Antofagasta. Arsenic concentrations in rivers in Region II vary along its course, depending on the arsenic content of its tributaries, and range from 30 to 3310 µg/L but reach 14 250 µg/L in some hot springs (Table 17) (Alonso, 1992; Queirolo *et al.*, 2000a). Exposure of the

Table 16. Arsenic in other biological samples in Salta Province, Argentina

Location	No. of subjects	Type of sample (year)	Total arsenic in sample		Reference
			Median	Range	
San Antonio de los Cobres	9 women	Breast milk	2.3 µg/kg[a]	0.83–7.6 µg/kg	Concha *et al.* (1998a)
		Blood	9.8 µg/L	4.4–19 µg/L	
		Urine	390 µg/L	250–610 µg/L	
		Blood	µg/L	µg/L	Vahter *et al.* (1995)
San Antonio	15		7.6	2.7–18.3	
Santa Rosa	5		1.5	1.1–2.0	
Olacapato	5		1.3	1.2–2.4	
Tolar Grande	5		1.3	1.0–1.3	
	Children	Blood (1994)	µg/L	µg/L	Concha *et al.* (1998b)
San Antonio and T Pozo	36		9.1	5.5–17	
Rosario de Lerma	20		0.8	0.27–1.5	
	Women				
San Antonio and T Pozo	27		9.3	2.7–18	
Rosario de Lerma	11		0.95	0.69–1.8	
San Antonio de los Cobres	Pregnant women				Concha *et al.* (1998c)
	11	Blood	11 µg/L	5.6–13 µg/L	
	11	Cord blood	9.0 µg/L	6.0–12 µg/L	
	11	Placenta	34 µg/kg	17–54 µg/kg	
	10	Maternal milk	3.0 µg/kg[a]	2.3–4.8 µg/kg	

[a] µg/kg fresh weight

Table 17. Concentration of arsenic in surface waters in Chile, Region II, 1983–86

River studied and location	Mean total arsenic in water (µg/L)
Salado River	
Tatio Hot Springs	14 250
Codelco Mine Reservoir	7 500
Before Toconce River	3 310
Toconce River Before Salado	600
Before Curti	860
Ayquina	980
Before Loa River	760
Loa River	
Before Salado	270
Yalquincha	800
Finca	910
Before San Salvador River	1 380
San Salvador Before Loa	1 270
La Posada Bridge	1 500
Quillagua	1 440
Outlet of River	1 360
Upper Loa River Basin	210–330
Gorges south of Salado river	30–60
Spring north of Salado river	190–370

From Alonso (1992)

population in this region has ranged from 40 to 860 µg/L, depending on the rivers used for its water supply; 1958–70 was the highest exposure period for the largest population (approximately 300 000) (Table 18).

Sancha (1997) estimated the total number of people exposed in 1996 to specific levels of arsenic in the drinking-water in Chile: 7 million inhabitants (53.3%) were exposed to less than 10 µg/L; 5.5 million (41.9%) were exposed to 10–30 µg/L; 450 000 inhabitants (3.4%) were exposed to 30–50 µg/L; 170 000 inhabitants (1.3%) were exposed to 50–60 µg/L; and 1500 (0.01%) were exposed to 600–800 µg/L.

There are a few studies of arsenic in general environmental air in Chile (Romo-Kroger & Llona, 1993; Romo-Kroger *et al.*, 1994; Sancha, 1997; COSUDE, 2000). Sancha (1997) and COSUDE (2000) covered a large part of the country from 1994 to 1999. They found that cities not in the vicinity of copper smelting operations had arsenic levels in the air ranging from 0.001 to 0.057 µg/m^3, with a population of approximately 6 million people. The cities located 30–45 km from a copper smelter had arsenic levels in the air ranging from 0.01 to 0.14 µg/m^3 and had approximately 755 000 inhabitants. The cities in the vicinity (within 10 km) of smelters had arsenic levels in air ranging from 0.03

Table 18. Average concentration (µg/L) of arsenic in drinking-water in Regions II and I and the rest of Chile

Region	Town	Population (2002 census) living in exposed areas	1930–57	1958–70	1971–77	1978–80	1981–87	1988–94	1995–2002	Reference
II	Tocopilla and Elena	31 175	250	250	636	110	110	40	–	Ferreccio *et al*. (2000)
	Calama	136 739	150	150	287	110	110	40	– 38	Ferreccio *et al*. (2000) Sancha (1997)
	San Pedro	4 883	600	600	600	600	600	600	–	Ferreccio *et al*. (2000)
	Chiu Chiu	250	–	–	–	–	–	–	753	Smith *et al*. (2000b)
	Caspana	275	–	–	–	–	–	–	13	Smith *et al*. (2000b)
	Antofagasta and Mejillones	306 548	90	860	110	110	70	40	– 32	Ferreccio *et al*. (2000) Sancha (1997)
I	Arica-Iquique	426 351	–	–	–	–	–	–	32	Sancha (1997)
III–XIII	Rest of Chile	14 213 266	–	–	–	–	–	–	5	Sancha (1997)

Averages supplied by Empresa Servicios Sanitarios de Antofagasta for 1950–67 and Servicio de Salud Antofagasta for 1968–94
For 1995–2000, data and ranges published in studies

to 2.4 µg/m^3, with an estimated 60 000 people exposed. The rest of the country that was not sampled has a population of approximately 6 million people whose exposure is estimated to be in the lowest range of < 0.010 µg/m^3 (COSUDE, 2000).

Mean levels of arsenic in the air inside the Chuquicamata copper mine, the world's largest open copper mine, for the period 1952–91 ranged from 1.6 µg/m^3 in the administrative areas to 201.72 µg/m^3 in the smelting areas (Ferreccio *et al.*, 1996). This exposure has decreased in the last decade in correlation with the implementation of new technologies in smelting to avoid arsenic contamination. Workers exposed to arsenic had urinary levels ranging from 40 to 490 µg/L in 1992; between 1987 and 1990, 32–58% of workers in exposed areas had levels of urinary arsenic above 300 µg/L.

In Region II, 1020 people were examined between 1987 and 2002; the mean total arsenic in urine was 225 µg/L, ranging from 1 to 1893 µg/L. In comparison, in Region I which has intermediate exposure to arsenic in water (40 µg/L), 91 people were examined and their urinary arsenic averaged 45.5 µg/L, ranging from 10 to 92 µg/L. In the rest of Chile (arsenic in drinking-water, < 10 µg/L), 2472 people were sampled and mean urinary arsenic was 13 µg/L, ranging from 5 to 49 µg/L (Table 13). Arsenic measured in hair from people in Chile is presented in Table 14.

(*d*) *Other*

In Nicaragua, there has been concern regarding contamination with heavy metal of Lake Asososca, which is a source of drinking-water for Managua. The level of arsenic in sediment was found to be 4.1 µg/g, and that in water ranged from 0 to 18.07 µg/L, with a mean concentration of 5.86 µg/L, well below current water standards. Higher values of 25 µg/L were found in Lake Monte Galán (Cruz *et al.*, 1994). An earlier study conducted in Lake Xolotlán found arsenic levels in surface water ranging from 10.2 to 30.1 µg/L; wastewater from a thermal plant discharging into the river contained concentrations of 5295–16 700 µg/L (Lacayo *et al.*, 1992).

In Brazil, concerns have been raised regarding arsenic contamination as a result of gold mining in the zone of Minas Gerais, in south-eastern Brazil. In 1998, urinary arsenic was measured in 126 schoolchildren, and a mean concentration of 25.7 µg/L (range, 2.2–106 µg/L) was found. Environmental studies in the surrounding areas found mean levels of arsenic in surface water of 30.5 µg/L (range, 0.4–350 µg/L); levels of arsenic in soils ranged from 200 to 860 mg/kg; and sediments had a mean concentration of 350 mg/kg, ranging from 22 to 3200 mg/kg (Matschullat *et al.*, 2000).

1.4.4 *Exposure in South-East Asia*

There are many reports on the human exposure to arsenic in the drinking-water in South-East Asia. High concentrations of arsenic in drinking-water have been documented in China (Cao, 1996), Taiwan, China (Tseng *et al.*, 1968; Chiou *et al.*, 1997a), Thailand (Choprapawon & Rodcline, 1997), and Viet Nam (Berg *et al.*, 2001). The use of artesian wells, which were later shown to have high levels of arsenic in the water, began in the early 1920s in southern Taiwan, China (Tseng *et al.*, 1968), in the early 1950s in Inner Mongolia (Ma *et al.*, 1996), in the late 1950s in north-eastern Taiwan, China (Chiou *et al.*, 1997a, 2001), in the early 1960s in Xinjiang, China (Wang, 1996), in the late 1980s in Ronbipool, Thailand (Choprapawon & Rodcline, 1997), in the early 1990s in Shanxi, China (Cao, 1996) and in the mid-1990s in Viet Nam (Berg *et al.*, 2001). There have been several reports on industry-related exposure to arsenic through drinking-water contamination from tin mining in Ronpibool, Thailand (Choprapawon & Rodcline, 1997).

Table 19 summarizes data on arsenic contamination of drinking-water in various regions of South-East Asia.

(*a*) *China*

Several geographical areas in mainland China have a high content of arsenic in the drinking-water, including Xinjiang, Inner Mongolia and Shanxi (Cao, 1996). The villages with high concentrations of arsenic in the drinking-water in Inner Mongolia are clustered in Bamen and Huhehot. Ma *et al.* (1996) reported the arsenic concentration in the water of 9733 wells in Bamen: 2465 had levels of arsenic > 50 μg/L; in five counties of Bamen, the percentage of wells with an arsenic concentration > 50 μg/L varied, ranging from 11 to 59%; more than 500 villages had at least one well with an arsenic concentration > 50 μg/L; and the level of arsenic in drinking-water from all wells from the two areas ranged from < 50 to 890 μg/L. The water from a total of 497 wells in Huhehot were tested for arsenic: 111 had an arsenic level > 50 μg/L; 48 villages had at least one well with arsenic concentration > 50 μg/L; and the level of arsenic in drinking-water ranged from < 81 to 890 μg/L (Ma *et al.*, 1996). Sun *et al.* (2001) reported a survey on the concentration of arsenic in 303 wells in a village in Inner Mongolia: 77 wells (25.4%) had a level of arsenic < 10 μg/L, 85 (28.1%) had levels of 10–49 μg/L, 131 (43.2%) had levels of 50–499 μg/L and 10 (3.3%) had levels of ≥ 500 μg/L.

In the highly contaminated area of Xinjiang, located in Tunguei, arsenic concentrations in well-water in 15 villages of the area ranged from 50 to 850 μg/L, and were mostly between 100 and 500 μg/L (Wang, 1996).

Sun *et al.* (2001) reported a survey of 2373 wells in 129 villages in the Basin of Datong and Jinzhong, Shanxi, in 1994–95. Levels of arsenic in drinking-water ranged from < 50 to 4440 μg/L and 833 wells had an arsenic concentration > 50 μg/L. The percentage of wells with an arsenic concentration > 50 μg/L in seven counties of the area varied from 6.3 to 54.7%.

(*b*) *Taiwan, China*

There are two endemic areas of arseniasis in Taiwan, China. One is located in the south-western coastal area where Blackfoot disease, a unique peripheral vascular disease associated with long-term ingestion of arsenic from artesian well-water, is endemic. There are four townships in this area: Peimen, Hsuehchia, Putai and Ichu. High levels of arsenic in artesian wells and patients with Blackfoot disease have also been documented in two neighbouring townships, Hsiayin and Yensui. Another endemic area of chronic arsenic

Table 19. Contamination of drinking-water by arsenic in various regions of South-East Asia

Country	Area/population	Sample	Level of arsenic (range; µg/L)	Source of arsenic	Reference
Taiwan (China)	South-western Blackfoot disease-endemic area (Peimen, Hsuehchia, Putai, Ichu)	13 artesian well-water	240–960	Natural	Blackwell *et al.* (1961)
		34 artesian well-water	350–1100	Natural	Chen *et al.* (1962)
		11 artesian well-water	340–896	Natural	Yeh (1963)
		97 artesian well-water	10–1100	Natural	Kuo (1968)
	North-eastern endemic area of chronic arsenic poisoning (Chuangwei, Wuchieh, Chiaohsi, Tungshan)	3901 well-water	< 0.15–3590	Natural	Chiou *et al.* (2001)
	Taiwan (314 townships)	83 656 well-water	< 10–> 1000	Natural	Lo (1975)
Thailand	Thammarat Province	Surface water	< 0.5–583 < 0.5–28.4 As^{III}	Arsenopyrite wastes	Williams *et al.* (1996)
		Shallow water	1.25–5114 < 0.5–125 As^{III}		
		Surface water	4.8–583	Mining	Choprapawon & Porapakkham (2001)
		River	541–583		
China	Inner Mongolia	497 well-water (Huhhot)	< 10–1860	Natural	Ma *et al.* (1996); Luo *et al.* (1997)
		9733 well-water (Bamen)	< 50–890	Natural	Ma *et al.* (1996)
	Xinjiang	Well-water in 15 villages (Tunguei)	50–850	Natural	Wang (1996)
	Shanxi	2373 well-water in 129 villages (Datong, Jinzhong)	< 50–4440	Natural	Sun *et al.* (2001)

Table 19 (contd)

Country	Area/population	Sample	Level of arsenic (range; µg/L)	Source of arsenic	Reference
Japan	Fukuoka	67 well-water	1–293 11–220 As^{V} 15–70 As^{III}	Natural	Kondo *et al.* (1999)
	Sendai		1–35		
	Takatsuki		3–60		
	Kumamoto		5–66		
Viet Nam	Red River Basin	68 tubewells,	1–3050 (72% > 10 µg/L)	Natural	Berg *et al.* (2001)
		8 treatment plants	11–190		

toxicity is located in the Lanyang Basin of north-eastern Taiwan, in which there are four townships: Chiaohsi, Chuangwei, Tungshan and Wuchieh (Table 19).

In the area of south-western Taiwan where Blackfoot disease is endemic, Blackwell *et al.* (1961) reported levels of arsenic of 240–960 μg/L in 13 artesian wells, Chen *et al.* (1962) reported levels ranging from 350 to 1100 μg/L in 34 artesian wells and Yeh (1963) found levels ranging from 340 to 900 μg/L in water samples from 11 wells. Kuo (1968) carried out a larger survey of 97 artesian wells in 42 villages of the six townships in the endemic area and found concentrations in well-water ranging from 10 to 1100 μg/L, with a median of 500 μg/L. In this south-western area, the arsenic concentration was higher in water from deep artesian wells than in that from shallow wells, showing a correlation coefficient of $r = 0.627$ ($p < 0.01$). Arsenate was the dominant species of arsenic in the artesian well-water.

Lo (1975) reported a nationwide survey of arsenic content in drinking-water from 83 656 wells in 314 precincts and townships. In total, 15 649 (18.7%) wells had an arsenic concentration ≥ 50 μg/L and 2224 (2.7%) had an arsenic concentration ≥ 350 μg/L. Most townships with high arsenic concentration in well-water were found to cluster in south-western and north-eastern Taiwan.

Chiou *et al.* (2001) tested the water from 3901 tubewells in 18 villages of four townships in the north-eastern endemic area of chronic arsenic toxicity by the HG–FAAS method in 1991–94. The arsenic content ranged from undetectable (< 0.15 μg/L) to 3590 μg/L.

(*c*) *Thailand*

The Ronpibool district is situated approximately 70 km south of Nakorn Sri Thammarat Province, in the southern part of Thailand, and had a total population of approximately 23 000 in 1998. A geological survey found that the potential sources of arsenic contamination in the mining areas were from high-grade arsenopyrite waste piles in bedrock mining localities, sub-ore grade waste-rock piles, sulfide-rich wastes from ore-dressing plants, disseminated sulfide waste from small-scale prospecting and floatation activities and alluvial tin workings (Choprapawon & Porapakkham, 2001).

In 1994, a collaborative study was initiated to establish the distribution and geochemical form of arsenic in surface drainage and aquifer systems in the area. Surface waters were sampled at 26 stations and groundwater samples were collected from 23 shallow wells and 13 deep boreholes. Concentrations of arsenic in samples of surface water ranged from < 0.5 (limit of detection) to 583 μg/L and As^{III} levels ranged from < 0.5 to 28.4 μg/L. Concentrations in shallow groundwater samples ranged from 1.25 to 5114 μg/L and As^{III} levels ranged from < 0.5 to 125 μg/L. Concentrations in deep borehole samples ranged from 1.25 to 1032 μg/L and As^{III} levels ranged from < 0.5 to 53.6 μg/L (Williams *et al.*, 1996).

In another study, significant concentrations of arsenite (As^{III}) were detected in several of the water samples with the highest levels of arsenic (28.4, 25.6 and 24.9 μg/L), although arsenate (As^V) remained the dominant species (more than 92% of the total) (Choprapawon & Porapakkham, 2001).

(*d*) *Viet Nam*

Berg *et al.* (2001) reported arsenic contamination of the Red River alluvial tract in the city of Hanoi, Viet Nam, and in the surrounding rural districts. Because of naturally occurring organic matter in the sediments, the groundwaters are anoxic and rich in iron. In rural groundwater samples from private small-scale tubewells, contamination levels ranged from 1 to 3050 µg/L, with an average concentration of 159 µg/L arsenic. In a highly affected rural area, the groundwater that is used directly as drinking-water had an average concentration of 430 µg/L. Analysis of raw groundwater pumped from the lower aquifer for the Hanoi water supply yielded arsenic levels of 240–320 µg/L in three of eight treatment plants and 37–82 µg/L in another five plants. Aeration and sand filtration that are applied in the treatment plants for the removal of iron lowered the arsenic content to levels of 25–91 µg/L, but 50% remained above 50 µg/L. The high arsenic concentrations found in tubewells (48% above 50 µg/L and 20% above 150 µg/L) indicate that several million people consuming untreated groundwater might be at a considerable risk for chronic arsenic poisoning.

(*e*) *Japan*

In March 1994, high concentrations of arsenic (> 10 µg/L) were detected in 29 of 67 well-water samples in the southern region of the Fukuoka Prefecture, Japan. The range of arsenic concentrations was 1–293 µg/L: As^V ranged from 11 to 220 µg/L; As^{III} ranged from 15 to 70 µg/L; and MMA and DMA were both < 1 µg/L. The maximum concentration was lower than the figures recorded in Taiwan, China, and India, but higher than those reported in Sendai (range, 1–35 µg/L), Takatsuki (range, 3–60 µg/L) and Kumamoto (range, 5–66 µg/L), Japan (Kondo *et al.*, 1999).

Arsenic concentrations in water from 34 wells in the Niigata Prefecture were measured between 1955 and 1959 as part of a historical cohort study using the Gutzeit method, and ranged from non-detectable to 3000 µg/L: six wells had a non-detectable concentration; 17 wells contained < 1000 µg/L; and 11 wells contained ≥ 1000 µg/L. All wells with arsenic concentrations > 100 µg/L were located within a distance of 500 m from a factory that produced arsenic trisulfide (Tsuda *et al.*, 1995).

(*f*) *Other*

In a recent United Nations Economic and Social Commission for Asia and the Pacific–United Nations International Children's Emergency Fund–World Health Organization (UNESCAP-UNICEF-WHO, 2001) expert group meeting, contamination of groundwater by arsenic was also reported from other countries including Lao People's Democratic Republic, Cambodia, Myanmar and Pakistan. It has also been reported from Nepal (Tandukar *et al.*, 2001; Shreshta *et al.*, 2002).

1.4.5 *Exposure in other countries*

Exposure in other countries is summarized in Table 20.

(*a*) *Africa (Egypt, Ghana) and the Middle East (Iran)*

In a 1999 study of 100 subjects in Cairo, Egypt, arsenic was measured by HG–AAS (detection limit, 1 μg/L) in hair samples and drinking-water. Levels of arsenic in hair samples ranged from 40 to 1040 μg/kg and levels in drinking-water samples were less than 1 μg/L (Saad & Hassanien, 2001).

Concentrations of arsenic in groundwaters from two areas in Ghana — the Obuasi area in the Ashanti region and the Bolgatanga area of the Upper East region — ranged from < 1 to 64 μg/L [As^{III} range, 6–30 μg/L] and < 1 to 141 μg/L [As^{III} range, < 1–9 μg/L], respectively. Sulfide minerals such as arsenopyrite and pyrite were present in the Birimian basement rocks of both areas and these constitute the dominant sources of arsenic. Concentrations were lowest in the shallowest groundwaters, and increased at greater depths. The lateral and vertical variations in dissolved arsenic concentrations were controlled by ambient pH and redox conditions and by the relative influences of sulfide oxidation and sorption (Smedley, 1996).

Concentrations of arsenic were measured in the scalp hair of three groups of people from a village in western Iran using NAA. One group consisted of healthy subjects, the second of subjects with suspected arsenic poisoning, and the third of subjects with confirmed arsenic poisoning. The arsenic content of water sources used by the inhabitants was also measured. The average arsenic concentration in hair was 200 μg/kg in the healthy group, 4900 μg/kg in the group with suspected poisoning and 5600 μg/kg in the group with arsenic poisoning; arsenic concentrations in water samples varied between 30 μg/L and 1040 μg/L (Pazirandeh *et al.*, 1998).

(*b*) *Australia*

Australia is a country rich in minerals that present a significant source of natural arsenic contamination to the environment, in addition to anthropogenic sources such as mining activities and pesticide use. In 1991, survey data showed elevated levels of arsenic in the surface water and groundwater in Victoria, particularly around gold mining areas. Concentrations of arsenic in groundwater ranged from < 1 to 300 000 μg/L (n = 109) and those in surface water ranged from < 1 to 28 300 μg/L (n = 590). In a follow-up study of the same region in the mid-1990s, arsenic concentrations ranged from 1 to 12 μg/L in groundwater samples (n = 18), from 1 to 220 μg/L in surface water samples (n = 30) and from 1 to 73 μg/L in drinking-water samples (n = 170) (Hinwood *et al.*, 1998).

In an investigation of the relationship between environmental exposure to arsenic from contaminated soil and drinking-water and the incidence of cancer in the Victoria region, median arsenic concentrations in groundwater ranged from 1 to 1077 μg/L (total range, 1–300 000 μg/L; n = 22 areas) (Hinwood *et al.*, 1999).

Table 20. Concentrations of arsenic (As) in drinking-water in other countries

Country	Population	Date	Sample (no.)	Levels (µg/L)	Source of arsenic	Reference
Africa						
Egypt	Cairo	1999	Tap water (5 districts)	1	NR	Saad & Hassanien (2001)
Ghana	Obuasi area	NR	Groundwater	< 1–64 (total As) 6–30 (As^{III})	Natural	Smedley (1996)
	Bolgatanga area	NR		1–141 (total As) 1–9 (As^{III})		
Middle East						
Iran	West Iran	NR	Spring water (20)	30–1040	Natural	Pazirandeh *et al.* (1998)
Australia						
Victoria	Victoria	mid-1990s	Groundwater (18) Surface water (30) Drinking-water (170)	1–12 1–220 1–73	Natural anthropogenic (mining, pesticide)	Hinwood *et al.* (1998)
			Ground- and surface water (22 geographical areas)	1–300 000 (1–1077 medians)		Hinwood *et al.* (1999)
Europe						
Finland		1993–94	Groundwater (69)	17–980		Kurttio *et al.* (1998)
		1996	Wells (72) Control population	< 0.05–64 (median, 0.14)	Natural	Kurttio *et al.* (1999)
Spain	Madrid	1998	353 water supplies Wells (< 2% of population uses wells)	74% < 10 23% 10–50 3.7% > 50	Natural	Aragones Sanz *et al.* (2001)
Romania (Transylvania)	Bihor and Arad counties	1992–95	Drinking-water	0–176	Natural	Gurzau & Gurzau (2001)
Switzerland	Grisons Canton Valais Canton	1998	Public water supplies (336) 14 000 people	< 10–170 12–50	Natural	Pfeifer & Zobrist (2002)
United Kingdom	South-west		Private supplies (3)	11–80		Farago *et al.* (1997)

Table 20 (contd)

Country	Population	Date	Sample (no.)	Levels (µg/L)	Source of arsenic	Reference
North America						
Canada	Nova Scotia	NR	Well-water (94 households)	1.5–738	Natural	Meranger *et al.* (1984)
		1981–85	Communities (121)	< 2–34		Health Canada (1992)
	Rural areas (Saskatchewan)	NR	Private wells and municipality wells (61 wells)	< 1–117	Natural	Thompson *et al.* (1999)
USA						
Western USA		NR	Rainwater and snow	< 0.002–0.59		Welch *et al.* (1988)
			Rivers	0.20–264		
			Lakes	0.38–1000		
			Seawater	0.15–6.0		
			Groundwater	130–48 000	Mining area	
				50–2750	Basin fill deposits	
				170–3400	Volcanic areas	
				80–15 000	Geothermal area	
Maine, Michigan, Minnesota, South Dakota, Oklahoma, Wisconsin			Groundwater 17 496 samples	40% > 1 5% > 20		Welch *et al.* (1999)
National Survey		NR	Surface water (189)	68 max	Natural	Chen & Edwards (1997)
			Groundwater (239)	117 max		
Arizona	Verde Valley		Groundwater (41)	10–210 µg/L		Foust *et al.* (2000)
Illinois	Groundwater	1994–2001	Deep glacial drift aquifer	> 5–83	Natural	Warner (2001)
			Shallow glacial drift aquifer	1–28		
Montana, Wyoming		1988–95	Madison River	35–370	Natural	Nimick *et al.* (1998)
		1973–95	Missouri River	2–69		
National survey	National	mid 1990s	Drinking water supplies (21 120)	6–17% > 5 1–3% > 20		Frey & Edwards (1997)
National survey	36% population of US population	1992–93	Water companies (140 utilities)	56% > 0.5 16% > 2 5% > 5	Natural	Davis *et al.* (1994)

Table 20 (contd)

Country	Population	Date	Sample (no.)	Levels (µg/L)	Source of arsenic	Reference
Missouri and Iowa		NR	Family wells (11)	34–490	Natural	Korte & Fernando (1991)
New Jersey		1977–79	Groundwater (1064) Surface water (591)	1 (median) 1160 (max.) 1 (median) 392 (max.)	Natural	Page (1981)
Ohio		NR	88 wells	0–96	Natural	Matisoff *et al.* (1982)
Alaska		1976	Well-water (59)	1–2450		Harrington *et al.* (1978)
Oregon		1968–74	Tap-water (558)	0–2150 8% > 50		Morton *et al.* (1976)
New Hampshire		1994	Drinking-water (793)	< 0.01–180		Karagas *et al.* (1998, 2002)
Utah		1978–79	Community water supplies (88)	0.5–160	Natural	Bates *et al.* (1995)
Utah		1976–97	151 drinking-water (151)	3.5–620	Natural	Lewis *et al.* (1999)
National survey	25 states		Groundwater systems Surface water systems	5.3% > 10 0.8% > 10	Natural	Environmental Protection Agency (2001)

NR, not reported

(*c*) *Europe (Finland, Romania, Spain, Switzerland, United Kingdom)*

Samples of well-water were collected in Finland between July and November 1996. The final study population (144 627 from a register-based cohort) consisted of 61 bladder cancer cases and 49 kidney cancer cases diagnosed between 1981 and 1995, as well as an age- and sex-balanced random sample of 275 subjects (reference cohort). To evaluate the validity of water sampling, two water samples were taken from each of 36 randomly selected wells at two different times (on average 31 days apart; range, 2 h–88 days). The arsenic concentrations in the original samples and field duplicates were not significantly different. The arsenic concentrations in the wells of the reference cohort ranged from < 0.05 to 64 μg/L (median, 0.14 μg/L). Five per cent of the reference cohort had arsenic concentrations > 5 μg/L and 1% (4/275) had consumed well-water containing levels of arsenic that exceed the WHO drinking-water quality guideline value of 10 μg/L (Kurttio *et al.*, 1999). Locally in Finland, drinking-water from privately drilled wells contains high concentrations of arsenic up to 980 μg/L (Kurttio *et al.*, 1998). The arsenic is of geological origin.

In the north-west region of Transylvania, Romania, drinking-water contains arsenic as a result of the geochemical characteristics of the land. The geographical distribution of arsenic in drinking-water in this region, sampled between 1992 and 1995, was heterogeneous, with a mixture of high (mostly in rural areas) and low concentrations in contiguous areas (range, 0–176 μg/L arsenic). Estimates indicated that about 36 000 people were exposed to concentrations of arsenic in the drinking-water ranging from 11 to 48 μg/L, and about 14 000 inhabitants were exposed to arsenic levels exceeding 50 μg/L (Gurzau & Gurzau, 2001).

In 1998 in Madrid, Spain, arsenic concentrations of more than 50 μg/L, the maximum permissible concentration for drinking-water in Spain, were detected in some drinking-water supplies from underground sources. In the initial phase, water samples from 353 Madrid water supplies were analysed. In a second phase, 6 months later, analyses were repeated on those 35 water supplies that were considered to pose a possible risk to public health. Seventy-four per cent of the water supplies studied in the initial phase had an arsenic concentration of less than 10 μg/L, 22.6% had levels of 10–50 μg/L and 3.7% had over 50 μg/L. Most of the water supplies showing arsenic levels greater than 10 μg/L were located in the same geographical area. In the second phase, 26 of the 35 water supplies were in the same range (10–50 μg/L arsenic) as in the first survey; nine had changed category, six of which had less than 10 μg/L and three had more than 50 μg/L. In Madrid, less than 2% of the population drinks water from underground sources (Aragones Sanz *et al.*, 2001).

In Switzerland, areas with elevated levels of arsenic have been found primarily in the Jura mountains and in the Alps. Weathering and erosion of rocks containing arsenic releases this element into soils, sediments and natural waters. The limit for drinking-water (50 μg/L) in Switzerland is not generally exceeded but, in the cantons of Ticino, Grisons and Valais, concentrations of arsenic above 10 μg/L have been found in the drinking-water. The canton of Grisons tested all of the 336 public water supplies in 1998. In 312 drinking-water supplies, arsenic concentrations were below 10 µg/L (93%), while 21 samples had arsenic concentrations between 10 and 50 µg/L (6%). Three samples exceeded the Swiss limit of 50 µg/L (0.9%); the maximum concentration found was 170 µg/L. Ore deposits and sediments in the canton of Valais have also been known for some time to contain arsenic. The drinking-water in this area was not tested for arsenic until 1999. Since then, it has been determined that in this canton approximately 14 000 people live in areas where the drinking-water contains between 12 and 50 µg/L (Pfeifer & Zobrist, 2002).

Although levels of arsenic in public water supplies are low, there is concern about the 20 000–30 000 private well-water supplies in South-West England, particularly those in old mining areas, which undergo limited or no treatment. From limited available data, three private supplies of those tested in Cornwall had arsenic levels above the 5-µg/L detection limit, and contained 11, 60 and 80 µg/L (Farago *et al.*, 1997).

(*d*) *North America*

(i) *Canada*

Samples from 61 groundwater sources, including 25 privately owned wells and 36 wells operated by rural municipalities, in Saskatchewan, Canada, were tested for arsenic. For virtually all of the rural municipal wells, no chemical or physical water treatment was performed other than periodic chlorination, whereas approximately half of the private wells underwent some form of water treatment. The most commonly used forms of water treatment included water softening with an ion exchange device, filtration and removal of iron. Arsenic was not detected in 25 samples (10 private wells and 15 rural municipal wells) using a method with a detection limit of 1 µg/L; 34 samples (13 private wells and 21 rural municipal wells) had levels between 1 and 50 µg/L; only two wells (private) had levels greater than 50 µg/L (maximum concentration, 117 µg/L) (Thompson *et al.*, 1999).

In an earlier survey of water supplies from 121 communities in Saskatchewan sampled between 1981 and 1985, arsenic levels were below 10 µg/L in 88% and below 2 µg/L in 42% of the samples taken; the maximum level recorded was 34 µg/L (Health Canada, 1992).

The concentration of total soluble inorganic arsenic (arsenate plus arsenite) was measured in duplicate water samples from the wells of 94 residents in seven communities in Halifax County, Nova Scotia, where arsenic contamination of well-water was suspected. Levels of arsenic exceeded 50 µg/L in 33–93% of wells in each of the communities; in 10% of the wells sampled, concentrations were in the range of 500 µg/L. The total measured levels ranged from 1.5 to 738.8 µg/L (Meranger *et al.*, 1984).

(ii) *USA*

The occurrence of arsenic in groundwater has been reported in the USA for areas within the states of Alaska, Arizona, California, Hawaii, Idaho, Nevada, Oregon and Washington. High concentrations are generally associated with one of the following geochemical environments: (*a*) basin-fill deposits of alluvial-lacustrine origin, particularly in semi-arid areas; (*b*) volcanic deposits; (*c*) geothermal systems; and (*d*) uranium and gold mining areas. Arsenic concentrations ranged from < 0.002 to 0.59 μg/L in rainwater and snow, from 0.20 to 264 μg/L in rivers, from 0.38 to 1000 μg/L in lakes and from 0.15 to 6.0 μg/L in seawater. Maximum observed concentrations of arsenic ranged from 130 to 48 000 μg/L in groundwater from mining areas, from 50 to 2750 in basin-fill deposits, from 170 to 3400 in volcanic areas and from 80 to 15 000 μg/L in geothermal areas. Total inorganic arsenic ranged from 1.1 to 6000 μg/L, arsenite ranged from 0.6 to 4600 μg/L and arsenate ranged from 0 to 4300 μg/L (Welch *et al.*, 1988).

Within the last decade, high concentrations of arsenic exceeding 10 μg/L in groundwater have been documented in many other areas of the USA (Morton *et al.*, 1976; Harrington *et al.*, 1978; Page, 1981; Matisoff *et al.*, 1982; Korte & Fernando, 1991; Davis *et al.*, 1994; Bates *et al.*, 1995; Chen & Edwards, 1997; Frey & Edwards, 1997; Karagas *et al.*, 1998; Nimick *et al.*, 1998; Lewis *et al.*, 1999; Foust *et al.*, 2000; Warner, 2001; Karagas *et al.*, 2002) (Table 20). The US Geological Survey reported that these high concentrations most commonly result from: (*a*) upflow of geothermal water; (*b*) dissolution of, or desorption from, iron oxide; and (*c*) dissolution of sulfide minerals. Overall, analyses of approximately 17 000 groundwater samples in the USA suggest that about 40% of both large and small regulated water supplies have arsenic concentrations greater than 1 μg/L. About 5% of regulated water systems are estimated to have arsenic concentrations greater than 20 μg/L (Welch *et al.*, 1999).

Using a 25-state database of compliance monitoring from community systems, the Environmental Protection Agency (2001) found that 5.3% of groundwater systems and 0.8% of surface water systems had concentrations > 10 μg/L.

In a national retrospective groundwater study of 18 850 drinking-water samples (2262 from community wells and 16 602 from private wells), the US Geological Survey found the 90th percentiles for community wells and private wells to be 8 μg/L and 13 μg/L, respectively (Focazio *et al.*, 2000). A study in New Hampshire found that drinking-water from private wells contained significantly more arsenic than that from community wells. In addition, this study found that deep wells had higher arsenic concentrations than superficial wells and that samples voluntarily submitted to the state for analysis had higher concentrations than randomly selected household water samples (Peters *et al.*, 1999).

1.5 Regulations and guidelines

Arsenic has been a contaminant of concern in drinking-water for several years. For example, in the USA in 1942, a maximum permissible concentration for arsenic was set at 50 μg/L by the Public Health Service. This standard was reaffirmed in 1946 and 1962; however, in 1962, the Public Health Service advised that concentrations in water should not exceed 10 μg/L when “more suitable supplies are or can be made available” (Smith *et al.*, 2002). In 2002, the maximum contaminant level for arsenic in the USA was lowered from 50 μg/L to 10 μg/L (Environmental Protection Agency, 2001). Table 21

Table 21. Regulations and guidelines for arsenic in drinking-water

Region	Guideline/ regulation (μg/L)	Reference
World	10	WHO (1998)
Europe	10	European Commission (1998)
USA	10	Environmental Protection Agency (2001)
Canada	25	Health Canada (2003)
Australia	7	National Health and Medical Research Council and Agriculture and Resource Management Council of Australia and New Zealand (1996)
South-East Asia (Bangladesh, India, Viet Nam, China)	50	WHO (2000)
Laos, Mongolia, Japan and Taiwan	10	WHO (2000); Taiwan Environmental Protection Agency (2000)
Argentina, Bolivia, Brazil and Chile	50	WHO (2000); Penedo & Zigarán (2002); Chilean Institute of National Standards (1984)
Philippines and Indonesia	50	WHO (2000)
Sri Lanka and Zimbabwe	50	WHO (2000)
Namibia	10	WHO (2000)
Bahrain, Egypt, Oman and Saudi Arabia	50	WHO (2000)
Jordan and Syria	10	WHO (2000)

details the various regulations and guidelines that have been established for arsenic in drinking-water.

The WHO (1998) guideline of 10 μg/L is a provisional value. A provisional guideline is established when there is some evidence of a potential health hazard but for which available data on health effects are limited, or when an uncertainty factor greater than 1000 has been used in the derivation of the tolerable daily intake.

The Canadian guideline (Health Canada, 2003) is an interim maximum acceptable concentration, again, due to the limited data on health effects.

Several other countries have also established standards for arsenic, and several developing countries have established a standard for arsenic of 50 μg/L (WHO, 2000).