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## Chapter 11.2: Arsenic and Selenium

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### 11.2.1 Introduction

Arsenic (As) and selenium (Se) have become increasingly important in environmental geochemistry because of their significance to human health. Their concentrations vary markedly in the environment, partly in relation to geology and partly as a result of human activity. Some of the contamination evident today probably dates back to the first settled civilizations that used metals.

Arsenic is in Group 15 of the Periodic Table (Table 1) and is usually described as a metalloid. It has only one isotope,  $^{75}\text{As}$ . It can exist in the -III, -I, 0, III, or V oxidation states (Table 2). Selenium is in Group 16 of the Periodic Table and although it has chemical and physical properties intermediate between metals and nonmetals (Table 1), it is usually described as a nonmetal. The chemical behavior of selenium has some similarities to that of sulfur. Formally, selenium can exist in the -II, 0, IV, and VI oxidation states (Table 2). Selenium has six natural stable isotopes, the most important being  $^{78}\text{Se}$  and  $^{80}\text{Se}$ . Although  $^{82}\text{Se}$  is generally regarded as a stable isotope, it is a  $\beta$ -emitter with a very long half-life ( $1.4 \times 10^{21}$  years). Both arsenic and selenium tend to be covalently bonded in all their compounds.

Arsenic is 47th and selenium 70th in abundance of the 88 naturally occurring elements. Much more has become known about the distribution and behavior of arsenic and selenium in the environment since the 1980s because of the increased application of improved analytical methods such as inductively coupled plasma-mass spectrometry (ICP-MS), inductively coupled plasma-atomic emission spectrometry (ICP-AES), and hydride generation-atomic fluorescence spectrometry (HG-AFS). These methods can detect the low concentrations of arsenic and, generally, selenium found in environmental and biological media accurately, and as a result, arsenic and selenium are increasingly included in determinand suites during systematic geochemical mapping and monitoring campaigns (Plant et al., 2003).

Arsenic is highly toxic and can lead to a wide range of health problems in humans. Arsenic has become increasingly important in considering environmental quality because of its high toxicity (Bode'nan et al., 2004) and recent evidence of severe health impacts at the population level, especially in Bangladesh. It is carcinogenic, mutagenic, and teratogenic (National Research Council, 2001). Symptoms of arsenicosis include skin lesions (melanosis, keratosis) and skin cancer. Internal cancers, notably bladder and lung cancer, have also

been associated with arsenic poisoning. Other problems include cardiovascular disease, respiratory problems, and diabetes mellitus. There is no evidence of a beneficial role for arsenic (IOM (Institute of Medicine), 2001; National Research Council, 2001) and it is unclear whether there is any safe dose for humans. Indeed, the precise nature of the relationship between arsenic dose and carcinogenic effect at low arsenic concentrations remains a matter of much debate (Clewell et al., 1999; Smith et al., 2002). It has been shown that normal cells can become cancerous when treated with inorganic arsenic (Waalkes et al., 2007). When cancer cells are placed near normal stem cells, the normal stem cells very rapidly acquire

the characteristics of cancer stem cells (Xu et al., 2012). This finding may explain observations that arsenic often causes multiple tumors of many types to form on the skin or inside the body. Arsenic ranked first on each of the hazardous substances priority lists compiled for the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) between 1997 and 2007 due to its frequency, toxicity, and potential for human exposure at National Priorities List sites (ATSDR, 2010).

The principal public health concern with arsenic is from the development of naturally high-arsenic groundwater resources (Smedley and Kinniburgh, 2002). Extensive arsenicosis from such sources has been reported from Argentina, Bangladesh, Chile, China, Mexico, India, Thailand, and Taiwan. ‘Blackfoot disease,’ a form of gangrene arising from excessive arsenic intake, was first described in Taiwan by Tseng et al. (1968). In contrast to arsenic, trace concentrations of selenium are essential for human and animal health. Until the late 1980s, the only known metabolic role for selenium in mammals was as a component of the enzyme glutathione peroxidase (GSH-Px), a selenoenzyme that plays an important role in the immune system (Johnson et al., 2010; Rotruck et al., 1972). There is now growing evidence, however, that the selenoenzyme is involved in the synthesis of thyroid hormones (Arthur and Beckett, 1989; Combs and Combs, 1986). In the body, selenium is used as part of a group of molecules known as selenoproteins, which contain the amino acid selenocysteine. These selenoproteins have a variety of functions, including acting as components of glutathione peroxidase, selenoprotein SEPS1, selenoprotein P, and thioredoxin reductase, antioxidant defense, cell redox control, and selenium transport in the plasma; they are also anti-inflammatory (Papp et al., 2007). Selenium deficiency has been linked to cancer, Acquired Immune Deficiency Syndrome (AIDS), heart disease, muscular dystrophy, multiple sclerosis, osteoarthropathy, immune system and reproductive disorders in humans, and white muscle disease in animals (Clark et al., 1996; Johnson et al., 2010; Levander, 1986; Rayman, 2008; WHO, 1987, 1996, 2011). A review of selenium in the food chain (Rayman, 2008) and its role in human health and disease was carried out recently (Fairweather-Tait et al., 2011). Selenium deficiency in humans has been implicated in the incidence of a type of heart disease (Keshan disease (KD)) and an osteoarthropathic condition (Kashin–Beck disease (KBD)) over extensive regions of China. Domestic animals also suffer from ‘white-muscle disease’ in these areas (Tan, 1989). In the 1970s and 1980s, the diet of people in the affected regions of China was supplemented with selenium, and sodium selenite was used to treat growing crops. This has resulted in a decline in the incidence of selenium deficiency disease (Liu et al., 2002). Selenium deficiency has been reported from New Zealand and Finland and falling concentrations of selenium in the diet are of increasing concern in many western countries (Oldfield, 1999). In Europe, this trend may have been exacerbated by the increasing use of native low-selenium grains rather than the imported selenium-rich grains of North America (Rayman, 2002). Selenium supplementation of livestock is common. On a global scale, overt selenium toxicity in human subjects is far less widespread than deficiency (Fordyce, 2005),

with between 0.5 and 1 billion people estimated to have an insufficient intake of selenium (Combs, 2001). Despite the essentiality of selenium, the range of intake between the quantities leading to selenium deficiency (<40 µg day<sup>-1</sup>) and toxicity (selenosis) (>400 µg day<sup>-1</sup>) is very narrow in humans (WHO, 1996, 2011). Investigations of the relationships between selenium in the environment and animal health were pioneered by Moxon (1938) in the western United States, where selenium accumulator plants are found and both selenium toxicity and deficiency are of concern. It has since been investigated extensively with regard to toxicity and deficiencies in humans and livestock (Environment Agency, 2009; Kabata-Pendias and Mukherjee, 2007). Longterm exposure to high levels of selenium (1270 µg, 10–20 times higher than normal exposure) can cause selenosis associated with numbness, paralysis, and occasional hemiplegia (ATSDR, 2003). Listlessness and lack of mental alertness were reported in a family who drank well water containing 9 mg l<sup>-1</sup> selenium for about 3 months, but their symptoms disappeared when they ceased drinking well water (ATSDR, 2003). Human selenosis at the population level is rare and is generally related to excesses from food rather than from drinking water. It has been reported from China and Venezuela, where selenium-rich food is grown and consumed locally (Tan, 1989; WHO, 1996, 2011). Cancers of the skin and pancreas have been attributed to high selenium intakes (Vinceti et al., 1998). Selenium sulfide is used in antidandruff shampoos and is potentially carcinogenic, but is not absorbed through the skin unless there are lesions (WHO, 1987). Selenium toxicity can lead to hair and nail loss and disruption of the nervous and digestive systems in humans and to 'alkali' disease in animals. Chronic selenosis in animals is not common, but has been reported from parts of Australia, China, Ireland, Israel, Russia, South Africa, the United States, and Venezuela (Oldfield, 1999). Liver damage is a feature of chronic selenosis in animals (WHO, 1987). Selenium was number 147 on the US 2007 CERCLA hazardous substances priority list (ATSDR, 2010).

It is now recognized that arsenic and selenium interact with each other in various metabolic functions and animal models indicate that each element can substitute for the other to some extent (Davis et al., 2000). This could partly explain the reported protective effect of selenium against some diseases, including some cancers (Shamberger and Frost, 1969). Arsenic was also shown long ago to protect against selenium poisoning in experimental studies with rats (Moxon, 1938). Following the relatively recent discovery of dissimilatory As(V) reduction and the various mechanisms that organisms have evolved to deal with the toxicity of As(V) and As(III), there has been a rapid increase in the understanding of the microbial chemistry of arsenic (see Frankenberger, 2002 and the individual chapters therein) and its consequences for the broader environment.

Selenium chemistry is also closely linked to microbial processes but these are less well understood. Contamination as a result of human activity is of increasing concern for both elements, but especially for arsenic. In the past, the problem was exacerbated by an absence of waste management strategies.

Arsenic concentrations in the natural environment have increased as a result of a number of activities, including mining and smelting, the combustion of arsenical coals, petroleum recovery (involving the release of production waters), refining, chemical production and use, the use of biocides including wood preservatives, the use of fertilizers, the manufacture and use of animal feed additives, and the development of high arsenic groundwater for drinking water and irrigation. Such activities have progressively transferred arsenic from the geosphere into the surface environment and have distributed it through the biosphere, where it poses a potential risk to humans and the wider environment. Endemic arsenic poisoning is associated mostly with naturally high concentrations of arsenic in drinking water, although in China it is a result of burning coal

rich in arsenic (Ng et al., 2003; Sun, 2004). In certain occupational settings, the principal pathway of arsenic to humans can be through inhalation. Arsenicosis caused by the indoor combustion of arsenic-rich coals has also been reported from Guizhou province, China (Aihua et al., 2000; Ding et al., 2000; Finkelman et al., 2003), where open coal burning stoves are used to dry chili peppers, increasing arsenic levels from 1 to 500 mg kg<sup>-1</sup> (Kapaj et al., 2006; Zheng et al., 1996).

Human activities that have increased the concentrations of selenium in the environment include the mining and processing of base metal, gold, coal, and phosphate deposits, the use of rock phosphate as fertilizer, the manufacture of detergents and shampoos, and the application of sewage sludge to land. The increased use of selenium in the pharmaceutical, glazing, photocopying, ceramic, paint, and electronics industries may also be increasing the amount of selenium entering the environment.

In the following sections, the source and occurrence of arsenic in the environment are first reviewed and then its pathways are considered as a basis for an improved understanding of exposure and risk assessment. This should lead to better risk management. A similar format is followed for selenium. In discussing the two elements, and in line with the threats outlined earlier, the emphasis on arsenic is on the behavior of arsenic in water, whereas in the case of selenium it is on the soil–water–plant relationships.

### 11.2.2 Sampling

Selenium and arsenic have been measured in a wide range of environmental media. Here sampling procedures for rocks, soils, sediments, and natural waters are described.

#### 11.2.2.1 Rocks, Soils, and Sediments

In the case of rocks, soils, and sediments, sufficient material representative of the medium to be analyzed should be collected. Soil and sediment samples should be dried at temperatures <35 °C to avoid volatilization losses of arsenic or selenium (Rowell, 1994) and ideally freeze-dried (BGS, 1978–2006). Sampling, analysis, and quality control should be carried out by recognized procedures wherever possible (Darnley, 1995; Salminen and Gregorauskiene, 2000).

#### 11.2.2.2 Water

##### 11.2.2.2.1 Techniques

As with other solutes, sampling natural waters for arsenic and selenium requires (1) the sample to represent the water body under investigation, and (2) that no artifacts are introduced during sampling or storage. Sampling methods vary according to whether ‘dissolved,’ ‘particulate,’ or ‘total’ concentrations are to be determined and whether speciation studies are to be undertaken. Water samples are most commonly analyzed for ‘total’ concentrations of arsenic and selenium. Speciation measurements require additional precautions to ensure preservation of the in situ species until separation or measurement.

As arsenic and selenium are normally present in natural waters at only trace concentrations (<10 µg l<sup>-1</sup> and frequently much lower), considerable care is required to perform reliable trace analyses. Marine chemists were the first to undertake reliable low-level trace analyses of natural waters and develop ‘clean/ultraclean’ sampling procedures (Horowitz et al., 1996). Probably the most thorough accounts of sampling procedures for surface water and groundwaters are those given by the US Geological Survey (USGS) (Wilde and Radtke, 2008). Specific procedures for sampling rainwater, lake water, and seawater are also given. The precautions required in sampling for arsenic and selenium are the same as those for other trace elements present in water at micrograms per liter concentrations. For example, there should be minimal contact between the sample and metallic substances. Sample bottles should be tested first by analyzing deionized water stored in them to ensure that they do not contaminate the sample. They should also be rinsed thoroughly with the sample water before collection.

Ideally, groundwater should be sampled from purpose-built water quality monitoring boreholes or piezometers.

In practice, existing wells or boreholes are frequently used.

As far as practically possible, it is important to purge the borehole by pumping at least three borehole volumes to remove standing water before sampling. Low-flow (<4 lmin<sup>-1</sup>) pumping is preferred to minimize resuspension of colloidal material.

Several procedures have been devised to obtain water quality depth profiles in wells and aquifers. These include depth samplers, nested piezometers, strings of diffusion cells, multilevel samplers, and multiple packers. Each method has its advantages and disadvantages, with very different costs and sampling logistics. As yet, few methods have been devised for arsenic and selenium profiling specifically; probably the most detailed profiling has been carried out in ocean sediments (Sullivan and Aller, 1996). Pore water, including from the unsaturated zone, can be obtained using a high-pressure squeezer or high-speed centrifugation (Kinniburgh and Miles, 1983; Sullivan and Aller, 1996).

There are as yet no methods for the in situ determination or continuous monitoring of arsenic and selenium. However, the diffusive gradient thin-films (DGT) method is a novel sampling method that has been used mainly for cationic metals, but may be adaptable for measuring arsenic and selenium, as it has been for phosphorus (Zhang et al., 1998). In this case, the normal cation exchange resin is replaced by an iron oxide (ferrihydrite) gel. Solutes sorbed by the resin or gel are displaced and subsequently analyzed in the laboratory. In principle, the DGT approach is sensitive with detection limits of the order of nanograms per liter. The method also has the advantage that it can measure a wide range of solutes simultaneously with high spatial resolution (at the mm scale) and determine the average water quality over relatively long timescales (days or longer). Most water samples do not require pretreatment for a total elemental analysis, but where organic arsenic or selenium compounds are suspected, pretreatment by digestion with a strong acid mixture, for example, a 3-min sulfuric acid–potassium persulfate digestion or a nitric acid digestion is necessary. Where preconcentration is required, cold-trapping of the hydrides or liquid–solid extraction has been used, but this is very labor intensive when performed off-line. Groundwater samples usually need no pretreatment.

#### 11.2.2.2 Filtered or unfiltered samples

Studies of the behavior of arsenic and selenium usually require the proportions of their dissolved and particulate components to be identified as this affects their biological availability, toxicity, and transport. It also affects the interpretation of their mineral solubility, adsorption, and redox behavior. Specifications for compliance testing vary with regulatory authority; for example, the US Environmental Protection Agency (US EPA) specifies a 0.45- $\mu\text{m}$  filter while most authorities in developing countries specify (or assume) that water samples are unfiltered. If the water is reducing, it should be filtered before any oxidation occurs. Geochemists typically filter water samples using membrane filters in the range 0.1–0.45  $\mu\text{m}$ , but the effective size of the filter can change as it becomes clogged. There continues to be much discussion about the merits of various filtering strategies (Hinkle and Polette, 1999; Horowitz et al., 1996; Shiller and Taylor, 1996). Small iron-rich particles with adsorbed arsenic, selenium, and other trace elements can pass through traditional filters (Chen et al., 1994; Litaor and Keigley, 1991) and subsequently dissolve when the sample is acidified. Colloids tend to be most abundant in reducing groundwaters and turbid surface waters. In clear groundwater samples that have usually been filtered naturally by movement through an aquifer, differences between concentrations in filtered and unfiltered aliquots are often relatively small. Filtered and unfiltered groundwater samples from high-arsenic areas in Bangladesh were found to have broadly similar arsenic concentrations (within-10%) although larger differences were found occasionally (Smedley et al., 2001b). Similarly, 9 out

of 10 groundwater samples from arsenic-affected wells in Oregon showed little difference (mostly <10%) between filtered and unfiltered samples (Hinkle and Polette, 1999).

Some studies have reported larger differences. A survey of 49 unfiltered groundwater sources in the United States found that particulate arsenic accounted for more than half of the total arsenic in 30% of the sources (Chen et al., 1999) although arsenic concentrations were all relatively small.

#### 11.2.2.2.3 Sample preservation and redox stability

For analysis of total arsenic and selenium, samples are normally preserved by adding ultrapure acid (1 or 2 vol.%), with the choice of acid depending on the analytical procedures to be used. HCl is used before hydride generation-atomic absorption spectrometry (HG-AAS), hydride generation-atomic emission spectrometry (HG-AES), HG-AFS, and HNO<sub>3</sub> before ICP-MS, graphite furnace-atomic absorption spectrometry (GF-AAS), and anodic stripping voltammetry (ASV). Acidification also helps to stabilize the speciation (see later discussions) although Hall et al. (1999) recommended that nitric acid should not be used for acidifying samples collected for speciation. Organic arsenic species are relatively stable and inorganic As(III) species are the least stable (National Research Council, 1999). There are as yet no well-established methods for preserving water samples for arsenic or selenium speciation analysis, although methods are being investigated for arsenic (Kumar and Riyazuddin, 2010; National Research Council, 1999; Rasmussen and Andersen, 2002).

Laboratory observations indicate that the oxidation of As(III) and Se(IV) by air is slow and is often associated with microbial activity. MnO<sub>2</sub>(s), which can precipitate following atmospheric oxidation of manganese-rich water, is also known to be a very efficient catalyst for the chemical oxidation of As(III) (Daus et al., 2000; Driehaus et al., 1995; Oscarson et al., 1983). Iron oxides have also been implicated in increasing the abiotic rate of oxidation of As(III) although the evidence for this is somewhat equivocal and it probably does not occur in minutes or hours unless some H<sub>2</sub>O<sub>2</sub> is present (Voegelin and Hug, 2003). Precipitation of manganese and iron oxides can be minimized by ensuring sufficient acidity (pH 2 or less) and/or adding a reducing/complexing agent such as ascorbic acid, Ethylenediaminetetraacetic acid (EDTA), or phosphate. Recent studies have demonstrated the efficacy of

EDTA (Bednar et al., 2002; Gallagher et al., 2001) and phosphate (Daus et al., 2002) for preserving arsenic speciation. Arsenic speciation in urine is stable for at least 2 months without additives at 4 °C (National Research Council, 1999), though the stability of arsenic species has been found to be dependent on urine matrices (Feldmann et al., 1999). It is reasonable to conclude that natural water samples probably behave in a similar way. As(III) in samples of Ottawa river water survived oxidation for at least 3 days at ambient temperature and without preservatives (Hall et al., 1999). The lowest rates of oxidation occur under slightly acidic conditions (Driehaus and Jekel, 1992) and acidification to pH 3–5 has been found to help stabilize As(III), although it is not always successful (Cabon and Cabon, 2000). HCl normally prevents reduction of As(V) to As(III) and arsenic speciation has recently been shown to be preserved for many months, even in the presence of high Fe(II) concentrations, if water samples are filtered and acidified in the usual way (1 or 2% HCl) (McCleskey et al., 2004). Traces of chlorine in HCl can lead to some long-term oxidation of As(III). One of the critical factors enhancing the oxidation of As(III) is the presence of dissolved Fe(III). On the other hand, the presence of Fe<sup>2+</sup> or SO<sub>4</sub><sup>2-</sup>, two species often found in arsenic rich acid mine drainage (AMD) waters, inhibits the oxidation (McCleskey et al., 2004).

Reduction of As(V) can occur in the presence of air if samples contain dissolved organic carbon (DOC), arsenate reducing bacteria, and no preservatives (Bednar et al., 2002; Hall et al., 1999; Inskeep et al., 2002). Arsenic(V) can then be

reduced rapidly, within a few days. Storage at 3–5 °C and in the dark helps to preserve the speciation (Hall et al., 1999; Lindemann et al., 2000). Ideally, speciation studies for either arsenic or selenium should involve the minimum of time between sampling and analysis.

An alternative approach to the determination of As(III)/As(V) speciation is to separate the As(V) species in the field, using an anion exchange column (Bednar et al., 2002; Vagliasindi and Benjamin, 2001; Wilkie and Hering, 1998; Yalcin and Le, 1998). At near-neutral to acidic pH, typical of most natural waters, uncharged As(III) is not retained by the resin and the retained As(V) can be eluted subsequently with high-purity acid. Providing that total arsenic is known, As(III) can be estimated by difference. Bednar et al. (2002) favored an acetate resin because of its high pH-buffering capacity. Such anion exchange methods do not work for selenium speciation as both the Se(IV) and Se(VI) species are negatively charged and retained by the column.

### 11.2.3 Analytical Methods

#### 11.2.3.1 Arsenic

##### 11.2.3.1.1 Total arsenic in aqueous samples

###### 11.2.3.1.1.1 Laboratory methods

Methods for arsenic analysis in water, food, and biological samples have been reviewed in detail elsewhere (ATSDR, 2007; Irgolic, 1994; National Research Council, 1999; Rasmussen and Andersen, 2002) (Table 3).

Early colorimetric methods for arsenic analysis used the reaction of arsine gas with either mercuric bromide captured on filter paper to produce a yellow–brown stain (Gutzeit method) or with silver diethyldithiocarbamate (SDDC) to produce a red dye. The SDDC method is still widely used in developing countries. The molybdate blue spectrophotometric method that is widely used for phosphate determination can be used for As(V), but the correction for P interference is difficult. Methods based on atomic absorption spectrometry (AAS) linked to hydride generation (HG) or a graphite furnace (GF) have become widely used. Other sensitive and specific arsenic detectors (e.g., AFS, ICP-MS, and ICP-AES) are becoming increasingly available. The accuracy is much better using atomic absorption methods than ICP (Nathanail and Bardos, 2004). HG-AFS in particular is now widely used for routine arsenic determinations because of its sensitivity, reliability, and relatively low capital cost.

Conventional ICP-MS has great sensitivity but suffers from serious interferences. Cl interference leads to the formation of  $^{40}\text{Ar}^{35}\text{Cl}^+$ , which has the same mass/charge ratio as the monoisotopic  $^{75}\text{As}$  ( $m/z=75$ ). Hence, HCl and  $\text{HClO}_4$  should not be used for preservation or dissolution if ICP-MS is to be used. There may also be significant interference in samples with naturally high Cl/As ratios. A Cl concentration of  $1000 \text{ mg l}^{-1}$  gives an arsenic signal equivalent to about  $3\text{--}10 \text{ }\mu\text{g l}^{-1}$ . The use of a high-resolution magnetic sector mass spectrometer, which can resolve the small difference in  $m/z$  for  $^{75}\text{As}^+$  at 74.922 from that of  $^{40}\text{Ar}^{35}\text{Cl}^+$  at 74.931, eliminates the Cl interference. New collision-cell techniques, in which the atomized samples are mixed with a second gas (usually  $\text{H}_2$ ) in a reaction cell, also minimize this interference. Arsenic detection limits of a few nanograms per liter have been reported in matrices containing  $1000 \text{ mg l}^{-1}$  NaCl. The Cl interference can also be avoided by pre-separation using HG, GF, or chromatography.

The American Society for Testing and Materials (ASTM) D 2972-08 standard test methods for arsenic in water cover the photometric and atomic absorption determination of arsenic in most waters and wastewaters. Three test methods are detailed in the standard; that is, silver diethyldithiocarbamate colorimetric; atomic absorption hydride generation; and atomic absorption, graphite furnace (American Society for Testing and Materials, 2010).

Recently, the use of carbon nanotubes has been proposed in several analytical methods, including use as solid-phase extraction

adsorbents for arsenic pretreatment and enrichment from water samples (Li et al., 2009a), and in ASV (Xiao et al., 2008).

#### 11.2.3.1.1.2 Field-test kits

A detailed study of field measurement and sensors for arsenic has been carried out by Melamed (2004). A large number of wells need to be tested (and retested) for arsenic worldwide. Hence, there is a need for reliable field-test kits that can measure arsenic concentrations down to 10 µg l<sup>-1</sup>, the World Health Organization (WHO) guideline value for arsenic in drinking water. Test kits offer the advantage of being relatively inexpensive, portable, and effective for indicating the presence of arsenic. Some of the more recently developed kits based on the Gutzeit method are semiquantitative (Kinniburgh and Kosmus, 2002). Several field-test kits based on this method are available commercially, but their performance is variable (Spear, 2006).

The main limitations of test kits for arsenic in water are that other chemical reactions may interfere; the sensitivity and accuracy of the kits fluctuate depending on the model used and there are differences between field workers, especially as many kits rely on comparison of a test strip to a color chart (Petrusevski et al., 2007).

#### 11.2.3.1.2 Total arsenic in solid samples

X-ray fluorescence spectrometry (XRF) and instrumental neutron activation analysis (INAA) are commonly used for multi-element analysis of rock, soil, and sediment samples as they do not require chemical dissolution. However, the detection limit for arsenic using XRF, for example, is of the order of 5 mg kg<sup>-1</sup> and is too high for many environmental purposes. Once dissolved, arsenic can be determined using many of the methods described earlier for aqueous samples, although the method of digestion must be capable of destroying all solids containing arsenic.

#### 11.2.3.1.3 Arsenic speciation

##### 11.2.3.1.3.1 Aqueous speciation

At its simplest, speciation of arsenic consists of separating it into its two major oxidation states, As(III) and As(V). This can be achieved on unacidified samples by ion chromatography.

More detailed speciation involves determining organic species and less common inorganic species such as sulfide (thio), carbonate, and cyanide complexes, as well as less common oxidation states such as As(III) and As(0). There is increasing interest in the bioavailability of arsenic. Organic speciation usually involves quantifying the two or three major (mainly the methylated) species present. The oxidation state of arsenic in these organic species can be either As(III) or As(V).

Generally, such studies are carried out in research rather than water-testing laboratories.

A two-stage approach to speciation is often used: this involves pre-separation by high-performance liquid chromatography (HPLC) or ion chromatography followed by arsenic detection. The detection methods must be highly sensitive and capable of quantifying inorganic and organic species at the nanograms per liter to micrograms per liter level (Yalcin and Le, 1998). Many combinations of separation and detection methods have been used (Bohari et al., 2001; Ipolyi and Fodor, 2000; Lindemann et al., 2000; Martinez-Bravo et al., 2001; National Research Council, 1999; Taniguchi et al., 1999). All of them require expensive instrumentation and highly skilled operators and none has acquired 'routine' or accredited status. A widely used but indirect method of As(III)/As(V) speciation involves no pre-separation but involves two separate determinations, with and without prereduction. The rate of AsH<sub>3</sub> production by sodium borohydride (NaBH<sub>4</sub>) reduction depends primarily on the initial oxidation state of the arsenic in solution and the solution pH. Under typical operating conditions of about pH 6 where the neutral As(III) species, H<sub>3</sub>AsO<sub>3</sub>, predominates, only As(III) is converted to the hydride (Anderson et al., 1986; Driehaus and Jekel, 1992). For the most part, the negatively charged As(V) species are not converted. For the determination of total arsenic, As(V) to As(III) prereduction can be achieved by adding a mixture of HCl, KI, and ascorbic acid ideally at pH<1 to ensure full protonation



and efficient hydride generation. High concentrations of HCl are particularly effective at this. As(V) can then be estimated by difference. AFS or AAS provide sensitive and fairly robust detectors for the arsine gas produced. High concentrations of some metal ions, particularly Fe<sup>3+</sup> and Cu<sup>2+</sup>, can interfere with the hydride generation, but this can be overcome by adding masking agents such as thiourea (Anderson et al., 1986) or by their prior removal with a cation-exchange resin.

#### 11.2.3.1.3.2 Solid-phase speciation

While most speciation studies have been concerned with redox speciation in solution, speciation in the solid phase is also of interest. Both reduced and oxidized arsenic and selenium species can be adsorbed on minerals, soils, and sediments, albeit with differing affinities (see Sections 11.2.5.3 and 11.2.7.2). Such adsorption has been demonstrated on metal oxides and clays and also probably takes place to some extent on carbonates, phosphates, sulfides, and perhaps organic matter. Structural arsenic and selenium may also be characterized. Solid-phase speciation has been measured both by wet chemical extraction and, for arsenic, by instrumental methods, principally X-ray absorption near edge structure spectroscopy (XANES) (Brown et al., 1999). La Force et al. (2000) used XANES and selective extractions to determine the likely speciation of arsenic in a wetland affected by mine wastes: they identified seasonal effects with As(III) and As(V) thought to be associated with carbonates in the summer, with iron oxides in the autumn and winter, and with silicates in the spring. Extended X-ray absorption fine structure spectroscopy (EXAFS) has been used to determine the oxidation state of arsenic in arsenic-rich Californian mine wastes (Foster et al., 1998b). Typical concentrations of arsenic in soils and sediments (As <20 mg kg<sup>-1</sup>) are often too low for EXAFS measurements, but as more powerful photon beams become available, the use of such techniques should increase. A method for on-site separation and preservation of arsenic species from water using solid-phase extraction cartridges in series, followed by elution and measurement of eluted fractions by ICP-MS for 'total' arsenic, has recently been presented (Watts et al., 2010). Classical wet chemical extraction procedures have also been used to assess the solid-phase speciation of arsenic, but care must be taken not to oxidize As(III) during extraction (Demesmay and Olle, 1997). Extractions should be carried out in the dark to minimize photochemical oxidation.

#### 11.2.3.1.3.3 EPA TCLP test

The US EPA's 'toxicity characteristics leaching procedure' (TCLP) is the most commonly used test for determining the long-term stability of arsenic precipitates. The procedure involves first reacting the solid with a pH-buffered acetate solution (pH 4.93) at a solid-to-liquid ratio of 2:1 to determine solubility. The slurry is agitated for 20 h, and if the concentration of certain toxic elements is found to be above specified thresholds, the material is classified as toxic. The current limit for arsenic is 5 mg l<sup>-1</sup> (Monhemius and Swash, 1999).

Most researchers in the field agree that this test gives only a poor indication of the long-term storage problems that may arise in the case of arsenic (Ghosh et al., 2004, 2006, US EPA, 1999). Moreover, the 5 mg l<sup>-1</sup> limit for arsenic is too high for current and likely future legislation. Arsenic compounds such as scorodite, which are used to immobilize arsenic, often pass the US EPA's TCLP test limit of 5 mg l<sup>-1</sup> arsenic because the lowest solubility for both scorodite and arsenical ferrihydrite is in the weakly acid pH range of 3–4.

#### 11.2.3.2 Selenium

##### 11.2.3.2.1 Total selenium in aqueous samples

Historically, analysis of selenium has been difficult, partly because environmental concentrations are naturally low. Indeed, selenium analysis still remains problematic for many laboratories at concentrations below 0.01 mg l<sup>-1</sup>, a relatively high concentration in many environments (Steinhoff et al., 1999). Hence, selenium has often been omitted from multi-element geochemical surveys, despite its importance (Darnley,

1995). Recent improvements in analytical methods, however, mean that even low levels of selenium can be determined routinely in geological and environmental samples (Johnson et al., 2010). Analytical methods with limits of detection of  $<0.01 \text{ mg l}^{-1}$  include colorimetry, total reflectance-XRF, HG-AFS, gas chromatography (GC) of organic species, ICPMS, and HG-ICP-AES. Of these, HG-AFS and ICP-MS are probably now the most widely used methods. Like arsenic, there are no generally accepted ways of preserving selenium speciation in water samples, and even fewer studies of the factors controlling the stability of the various species. Many of the precautions for arsenic-preserved species (Section 11.2.2.2.3) are also likely to apply to selenium species preservation.

The ASTM D 3859-08 standard test methods for selenium in water include the determination of dissolved and total recoverable selenium in waters and wastewaters. Two of the test methods are atomic absorption procedures, namely gaseous hydride AAS and GF-AAS (American Society for Testing and Materials, 2010).

#### 11.2.3.2.1.1 Pretreatment to destroy organic matter

Organic selenium species are more widespread in the environment than comparable arsenic species. The determination of total selenium by most analytical methods requires samples to be pretreated to remove organic matter, release selenium, and change its oxidation state.

Wet digestion using mixtures of nitric, sulfuric, phosphoric, and perchloric acids, with or without the addition of hydrogen peroxide, has been used for organic samples and natural waters. Nitric acid reduces foaming and/or charring. The trimethylselenonium ion is resistant to decomposition by wet digestion, so a long period of digestion is required for urine and plant materials that may contain the ion.

#### 11.2.3.2.1.2 Laboratory methods

Fluorimetry has been used widely for selenium analysis in environmental samples, but is being superseded by more sensitive instrumental methods. Some of the instrumental methods used for arsenic speciation and analysis can also be used for selenium. In particular, HPLC and HG can separate selenium into forms suitable for detection by AAS, AFS (Ipolyi and Fodor, 2000), or ICP-AES (Adkins et al., 1995). Only Se(IV) forms the hydride and so Se(VI) must be pre-reduced to Se(IV) if total selenium is to be determined. This is normally achieved using warm HCl/KBr followed by coprecipitation with  $\text{La}(\text{OH})_3$  if necessary (Adkins et al., 1995). KI is not used as it tends to produce some Se(0) which is not reduced by HG.  $\text{La}(\text{OH})_3$  collects only Se(IV) so the pre-reduction step to include the contribution from Se(VI) is required before coprecipitation. Other methods of preconcentration include coprecipitation of Se(IV) with hydrous iron oxide or adsorption onto Amberlite IRA-743 resin (Bueno and Potin-Gautier, 2002).

ICP-MS detection of selenium is now favored because of its sensitivity even without HG or other forms of preconcentration. However, selenium can be seriously affected by matrix interferences when using ICP-MS. The polyatomic  $\text{Ar}_2^+$ , with a mass of 80, overlaps with the most abundant isotope of selenium ( $^{80}\text{Se}$ ). Even using hydrogen as a collision gas results in the formation of 2–5% of selenium hydride for which a correction must be applied. For routine analysis of selenium, the hydride-free but less abundant isotopes,  $^{76}\text{Se}$  and  $^{82}\text{Se}$ , are usually determined; however, this results in lower sensitivities and higher detection limits. Detection limits for ICP-MS are around 2–20  $\mu\text{g l}^{-1}$  because of the argon plasma background and interferences. The use of reaction or collision cells or dynamic collision cells can reduce detection limits greatly (Nelms, 2005).

#### 11.2.3.2.2 Selenium in solid samples

Direct analysis of solids for selenium by XRF has a detection limit of about 0.5  $\text{mg kg}^{-1}$  and so is often insufficiently sensitive. Rock, sediment, and soil samples can be dissolved using wet chemical methods (HF, HCl, etc.) followed by  $\text{La}(\text{OH})_3$  coprecipitation to separate hydride-forming elements including selenium. This is present as Se(IV), following acid dissolution

(Hall and Pelchat, 1997). The methods described earlier for aqueous samples can then be used.

Modern thermal ionization mass spectrometry (TIMS) is now sensitive and precise enough to measure individual selenium isotope abundances (e.g.,  $^{80}\text{Se}/^{76}\text{Se}$ ) in solid samples or residues so that it can be used to study environmental cycling/distributions (Johnson et al., 1999). Microbial reduction leads to isotopically lighter products, that is, selenate to selenite reduction has a  $^{80}\text{Se}/^{76}\text{Se}$  fractionation factor,  $\epsilon$ , of about  $-5.5\%$  (Johnson et al., 1999). INAA has been used to determine different selenium isotopes, especially  $^{75}\text{Se}$  in plant tracer studies, and foodstuffs (Combs, 2001; Diaz-Alarcon et al., 1996; Noda et al., 1983; Ventura et al., 2007).

#### 11.2.3.2.3 Selenium speciation

Selenium speciation in waters is poorly understood, although in principle it can be determined using HG with and without a prereduction step (see Section 11.2.3.2.1). Ion-exchange chromatography is used extensively to determine selenium species in plant extracts, and gas chromatography can measure volatile selenium compounds. Recent developments in anion exchange HPLC and MS techniques (ICP-dynamic reaction cell-MS, TIMS, and multiple collector-MS) mean that it is now possible to determine selenium isotope abundances and concentrations in selenamino acids including selenocysteine and selenomethionine (Gomez-Ariza et al., 2000; Sloth and Larsen, 2000; Wang et al., 2007). Electrochemical methods such as cathodic stripping voltammetry (CSV) are highly sensitive and in principle can be used for speciation because only Se(IV) species are electroactive (Lange and van den Berg, 2000). Due to the important role that selenium plays in human nutrition, there is increasing interest in measuring the 'bioavailable' amounts, especially in foodstuffs, using various bioassays (Casgrain et al., 2010; Fairweather-Tait et al., 2010).

#### 11.2.3.3 Quality Control and Standard Reference Materials

Although analysts usually determine the precision of their analyses using replicate determinations, the analysis of arsenic and selenium can be affected seriously by contamination and matrix interferences during sampling and analysis. These can be difficult to identify and are best found by sample randomization and the collection of duplicate samples as part of an objective, independent quality-control system (Plant et al., 1975). The measurement of standard reference materials (SRMs) provides the best method of ensuring that an analytical procedure is producing accurate results in realistic matrices. Many SRMs are now available (Govindaraju, 1994; Rasmussen and Andersen, 2002) but the most widely used are those supplied by the National Institute of Standards and Technology (NIST). Arsenic and selenium concentrations have been certified in a range of natural waters, sediments, and soils (Tables 4 and 5). The certified standards from the National Research Council of Canada (NRC) also include river waters with much lower arsenic concentrations than the NIST standards ( $-0.2$ – $1 \mu\text{g l}^{-1}$ ). Certified standards for As(III)/As(V) and Se(IV)/Se(VI) speciation are available commercially (e.g., SPEX Certiprep® speciation standards).

The Canadian Certified Reference Materials Project (CCRMP) also provides reference materials for lake sediments, stream sediments, and soils (tills) for arsenic, but not for selenium. However, the Institute for Reference Materials and Measurements (IRMM), Geel, Belgium, provides reference materials for estuarine sediments, lake sediments, and channel sediments for arsenic and selenium.

The Geological Survey of Japan (GSJ) provides a wide range of rock SRMs along with 'recommended' arsenic and selenium concentrations. The USGS issues 17 SRMs for which it provides 'recommended' and 'information' (when less than three independent methods have been used) concentrations. Nine of these include data for arsenic and two for both arsenic and selenium (the SGR-1 shale and CLB-1 coal samples). Hall and Pelchat (1997) have analyzed 55 geological SRMs for As, Bi, Sb,

Se, and Te, including SRMs from the USGS, Institute of Geophysical and Geochemical Exploration (IGGE; China), GSJ, CCRMP, and NRC programs. Methods have been developed recently for the determination of selenium in geological materials at nanograms per gram and lower levels (Forrest et al., 2009).

#### 11.2.4 Abundance and Forms of Arsenic in the Natural Environment

##### 11.2.4.1 Abundance in Rocks, Soils, and Sediments

The average crustal abundance of arsenic is 1.5 mg kg<sup>-1</sup> and it is strongly chalcophile. Approximately 60% of natural arsenic minerals are arsenates, 20% sulfides and sulfosalts, and the remaining 20% are arsenides, arsenites, oxides, alloys, and polymorphs of elemental arsenic. Arsenic concentrations of more than 100000 mg kg<sup>-1</sup> have been reported in sulfide minerals and up to 76000 mg kg<sup>-1</sup> in iron oxides (Smedley and Kinniburgh, 2002). However, concentrations are typically much lower. Arsenic is incorporated into primary rock-forming minerals only to a limited extent, for example, by the substitution of As<sup>3+</sup> for Fe<sup>3+</sup> or Al<sup>3+</sup>. Therefore arsenic concentrations in silicate minerals are typically of the order of 1 mg kg<sup>-1</sup> or less (Smedley and Kinniburgh, 2002). Consequently, many igneous and metamorphic rocks have average arsenic concentrations of 1–10 mg kg<sup>-1</sup>. Similar concentrations are found in carbonate minerals and rocks. Arsenic concentrations in sedimentary rocks can be more variable. The highest arsenic concentrations (20–200 mg kg<sup>-1</sup>) are typically found in organic-rich and sulfide-rich shales, sedimentary ironstones, phosphatic rocks, and some coals (Smedley and Kinniburgh, 2002).

Although arsenic concentrations in coals can range up to 35000 mg kg<sup>-1</sup> in some parts of China, concentrations in the range <1–17 mg kg<sup>-1</sup> are more typical (Gluskoter et al., 1977; Palmer and Klizas, 1997; Sun, 2004). Evidence for arsenic enrichment in peat is equivocal. Shotyk (1996) found a maximum of 9 mg kg<sup>-1</sup> arsenic in two 5000–10000-year-old Swiss peat profiles and in the profile with the lower ash content, the arsenic content was 1 mg kg<sup>-1</sup> or lower.

In sedimentary rocks, arsenic is concentrated in clays and other fine-grained sediments, especially those rich in sulfide minerals, organic matter, secondary iron oxides, and phosphates. The average concentration of arsenic in shale is an order of magnitude greater than in sandstones, limestones, and carbonate rocks. Arsenic is strongly sorbed by oxides of iron, aluminum, and manganese as well as some clays, leading to its enrichment in ferromanganese nodules and manganiferous deposits.

Alluvial sands, glacial till, and lake sediments typically contain <1–15 mg kg<sup>-1</sup> arsenic although higher concentrations are found occasionally (Farmer and Lovell, 1986).

Based on a survey of 747 flood-plain sediment samples and 852 stream sediment samples over Europe, median arsenic concentrations of 6.00 and 6.00 mg kg<sup>-1</sup>, respectively, were reported (FOREGS, 2005). Sediments from Qinghai Lake on the Tibetan Plateau have been shown to have arsenic enrichment factors of up to 2- pre-1900 levels; this has been suggested to reflect the burning of arsenical coal for industrial development in western China (Wang et al., 2010).

Stream sediments from England and Wales had a median arsenic concentration of 10 mg kg<sup>-1</sup> (Webb, 1978). A more detailed survey of stream sediments in Wales gave a median concentration of 14 mg kg<sup>-1</sup> (BGS, 1978–2006). Black et al. (2004) state that one grain of arsenopyrite -200 μm across in a 5-g stream sediment sample is equivalent to approximately 1 mg kg<sup>-1</sup> arsenic in the sample. The median arsenic concentration in stream sediments from 20 study areas across the United States collected as part of the National Water-Quality Assessment (NAWQA) program was 6.3 mg kg<sup>-1</sup> (Rice, 1999).

The arsenic concentration in soils shows a similar range to that found in sediments, except where they are contaminated by industrial or agricultural activity. Organic-rich soils tend to have higher concentrations of arsenic due to the presence of

sulfide minerals; for example, peaty and boggy soils have an average concentration of 13 mg kg<sup>-1</sup> (Dissanayake and Chandrajith, 2009; Smedley and Kinniburgh, 2002). A survey of 2600 soils from the Welsh borders had a median arsenic concentration of 11 mg kg<sup>-1</sup> (BGS, 1978–2006). A survey of the concentrations of arsenic in rural soils, thought to reflect ‘background’ conditions in the United Kingdom, reported a range of 0.50–143 mg kg<sup>-1</sup> (Ross et al., 2007). A survey of soil profiles covering 26 countries in Europe gave a median arsenic concentration of 7.03 mg kg<sup>-1</sup> in topsoils (840 samples) and 6.02 mg kg<sup>-1</sup> in subsoils (783 samples) (FOREGS, 2005). Concentrations of 1000 mg kg<sup>-1</sup> or more have been found at contaminated sites close to smelters or industrial sites (Lumsdon et al., 2001). Arsenic and its compounds are used as pesticides, especially herbicides and insecticides, and high arsenic levels in soils over the cotton-growing areas of the United States reflect the past use of such pesticides (US EPA, 2006; see Chapter 11.15). Comparison of soil samples taken following the 2005 flooding of New Orleans with archived soil samples collected in 1998–1999 suggests that the flooding resulted in the deposition of arsenic-contaminated sediments (Rotkin-Ellman et al., 2010).

#### 11.2.4.2 National and International Standards for Drinking Water

National standards for maximum concentrations of arsenic in drinking water have been declining over the last few decades as the toxicity of arsenic has become apparent. The 1903 report of the Royal Commission on Arsenic Poisoning in the United Kingdom set a standard of 150 µg l<sup>-1</sup>. In 1942, the US Public Health Service set a drinking-water standard of 50 µg l<sup>-1</sup> for interstate water carriers and this was adopted nationally by the US EPA in 1975.

The WHO guideline value for arsenic in drinking water was reduced from 50 µg l<sup>-1</sup> to a provisional value of 10 µg l<sup>-1</sup> in 1993, based on a 6×10<sup>6</sup> excess skin cancer risk, 60 times higher than the factor normally used to protect human health (Kapaj et al., 2006). In most western countries, the limit for arsenic in drinking water is now also 10 µg l<sup>-1</sup> (Yamamura, 2003). This includes the European Union (EU) and the United States.

The standard in Switzerland remains at 50 µg l<sup>-1</sup>. While the US EPA maximum contaminant level (MCL) is now 10 µg l<sup>-1</sup>, they have also set an MCL goal of zero for arsenic in drinking water, reflecting the risk to human health.

#### 11.2.4.3 Abundance and Distribution in Natural Waters

Concentrations of arsenic in natural waters vary by more than four orders of magnitude and depend on the source of the arsenic and the local geochemical conditions (Smedley and Kinniburgh, 2002). The greatest range and highest concentrations of arsenic are found in groundwaters, soil solutions, and sediment pore waters because of the presence of favorable conditions for arsenic release and accumulation. Arsenic is mobilized at pH values normally found in groundwaters (pH 6.5–8.5) and under both oxidizing and reducing conditions (Dissanayake and Chandrajith, 2009). Because the range in concentrations of arsenic in water is large, ‘typical’ values are difficult to derive. Concentrations can also vary significantly with time. Oil spills and leakages increase concentrations of arsenic in both fresh and marine water. Moreover, oil prevents underlying sediments from adsorbing the arsenic, which would remove it from the water column (Wainipee et al., 2010).

##### 11.2.4.3.1 Atmospheric precipitation

Arsenic enters the atmosphere as a result of wind erosion, volcanic emissions, low-temperature volatilization from soils, marine aerosols, and pollution. It is returned to the Earth’s surface by wet and dry deposition. The most important pollutant inputs are from smelter operations and fossil-fuel combustion. Concentrations of arsenic in rainfall and snow in rural areas are typically <0.03 µg l<sup>-1</sup> (Table 6), although they are generally higher in areas affected by smelters, coal burning, and volcanic emissions. Andreae (1980) found arsenic concentrations of about 0.5 µg l<sup>-1</sup> in rainfall from areas affected by smelting and coal burning. Higher concentrations (average

16  $\mu\text{g l}^{-1}$ ) have been reported in rainfall 35 km downwind of a copper smelter in Seattle, USA (Crececius, 1975). Values for Arizona snowpacks (Barbaris and Betterton, 1996) are also slightly above baseline concentrations, probably because of inputs from smelters, power plants, and soil dust. A study of sediments in Canada found that profiles of arsenic reflected its deposition as a result of past coal combustion and historical measurements of arsenic in dry and wet atmospheric deposition in rural areas of North America (Couture et al., 2008). In most industrialized countries, sources of airborne arsenic are limited as a result of air pollution-control measures. Unless significantly contaminated, atmospheric precipitation contributes little arsenic to surface waters.

#### 11.2.4.3.2 River water

Concentrations of arsenic in river waters are also low (typically in the range 0.1–2.0  $\mu\text{g l}^{-1}$ ; Table 6; see Chapter 7.7). They vary according to bedrock lithology, river flow, the composition of the surface recharge, and the contribution from baseflow. The lowest concentrations have been found in rivers draining arsenic-poor bedrocks. Seyler and Martin (1991) reported average concentrations as low as 0.13  $\mu\text{g l}^{-1}$  in rivers flowing over karstic limestone in the Krka region of Yugoslavia. Lenvik et al. (1978) also reported average concentrations of about 0.25  $\mu\text{g l}^{-1}$  arsenic in rivers draining basement rocks in Norway.

Relatively high concentrations of naturally occurring arsenic in rivers can occur as a result of geothermal activity or the influx of high-arsenic groundwaters. Arsenic concentrations of 10–70  $\mu\text{g l}^{-1}$  have been reported in river waters from geothermal areas, including the western United States and New Zealand (McLaren and Kim, 1995; Nimick et al., 1998; Robinson et al., 1995). Higher concentrations, up to 370  $\mu\text{g l}^{-1}$ , from the Yellowstone geothermal system have been reported in the Madison River in Wyoming and Montana as a result of geothermal influence. Wilkie and Hering (1998) also found concentrations in the range of 85–153  $\mu\text{g l}^{-1}$  in Hot Creek, a tributary of the Owens River, California. Values higher than 27  $\mu\text{g l}^{-1}$  are reported over the volcanic area of Naples, Italy (FOREGS, 2005). Some river waters affected by geothermal activity show distinct seasonal variations in arsenic concentration. Concentrations in the Madison River are highest during low-flow conditions, reflecting the increased proportion of geothermal water (Nimick et al., 1998). In the Waikato river system of New Zealand, arsenic maxima occur in the summer months, reflecting temperature-controlled microbial reduction of As(V) to the more mobile As(III) species (McLaren and Kim, 1995). Increased arsenic concentrations are also found in some river waters dominated by baseflow in arid areas. Such waters often have a high pH and alkalinity. For example, surface waters from the Loa River Basin of northern Chile (Atacama desert) contain naturally occurring arsenic in the range 190–21800  $\mu\text{g l}^{-1}$  (Ca'ceres et al., 1992). The high arsenic concentrations correlate with high salinity. While geothermal inputs of arsenic are likely to be important, evaporative concentration of the baseflow-dominated river water is also likely to concentrate arsenic in the prevailing arid conditions. Increased arsenic concentrations (up to 114  $\mu\text{g l}^{-1}$ ) have also been reported in alkaline river waters from central Argentina where regional groundwater arsenic concentrations are high (Lerda and Proserpi, 1996).

Although bedrock influences river water arsenic concentrations, rivers with typical pH and alkalinity values (pH 5–7,  $\text{HCO}_3^- < 100 \text{ mg l}^{-1}$ ) generally contain lower concentrations of arsenic, even where groundwater concentrations are high, because of oxidation and adsorption of arsenic onto particulate matter in the stream bed and dilution by surface runoff. Arsenic concentrations in the range of 0.5–2.7  $\mu\text{g l}^{-1}$  have been reported for seven river water samples from Bangladesh, with one sample containing 29  $\mu\text{g l}^{-1}$  (BGS and DPHE, 2001). High arsenic concentrations in river waters can also reflect pollution from industrial or sewage effluents. Andreae and

Andreae (1989) reported arsenic concentrations up to 30  $\mu\text{g l}^{-1}$  in water from the River Zenne, Belgium, which is affected by urban and industrial waste, particularly sewage. The background arsenic concentration was in the range 0.75–3.8  $\mu\text{g l}^{-1}$ . Durum et al. (1971) found that 79% of surface waters from the United States had arsenic concentrations below the detection limit of 10  $\mu\text{g l}^{-1}$ . The highest concentration, 1100  $\mu\text{g l}^{-1}$ , was reported from Sugar Creek, South Carolina, downstream of an industrial complex.

Arsenic can also be derived from mine wastes and tailings.

Azcue and Nriagu (1995) reported baseline concentrations of 0.7  $\mu\text{g l}^{-1}$  in the Moira River, Ontario, upstream of gold mine tailings, with concentrations up to 23  $\mu\text{g l}^{-1}$  downstream.

Azcue et al. (1994) reported concentrations up to 556  $\mu\text{g l}^{-1}$  (average 17.5  $\mu\text{g l}^{-1}$ ) in streams draining mine tailings in British Columbia. Williams et al. (1996) and Smedley (1996) noted high arsenic concentrations (typically around 200–300  $\mu\text{g l}^{-1}$ ) in surface waters from areas of tin and gold mining, respectively. Such anomalies tend to be localized because of the strong adsorption of arsenic by oxide minerals, especially iron oxide, under oxidizing and neutral to acidic conditions typical of many surface waters. Arsenic concentrations are therefore not always very high even in mining areas. For example, stream water arsenic concentrations from the Dalsung Cu–W mining area of Korea ranged from 0.8 to 19.1  $\mu\text{g l}^{-1}$  (Jung et al., 2002).

#### 11.2.4.3.3 Lake water

Arsenic concentrations in lake waters are typically close to or lower than those of river waters. Baseline concentrations of <1  $\mu\text{g l}^{-1}$  have been reported from Canada (Table 6) (Azcue and Nriagu, 1995; Azcue et al., 1995). Higher concentrations in lake waters may reflect geothermal sources or mining activity. Concentrations of 100–500  $\mu\text{g l}^{-1}$  have been reported in some mining areas and up to 1000  $\mu\text{g l}^{-1}$  in geothermal areas. However, arsenic concentrations can be much lower in mining-affected lake waters as a result of adsorption onto iron oxides under neutral to mildly acidic conditions. For example, Azcue et al. (1994) reported concentrations in lake waters affected by mining activity in Canada of about 0.3  $\mu\text{g l}^{-1}$ , close to background values.

High arsenic concentrations can also occur in alkaline, closed-basin lakes. Mono Lake, CA, has dissolved arsenic concentrations of 10000–20000  $\mu\text{g l}^{-1}$  with pH values in the range 9.5–10 as a result of the combined influences of geothermal activity, weathering of mineralized volcanic rocks, evaporation of water at the lake surface, and a thriving population of arsenate-respiring bacteria (Maest et al., 1992; Oremland et al., 2000).

Arsenic concentrations show considerable variations in stratified lakes because of changes in redox conditions or biological activity (Aggett and O'Brien, 1985; Hering and Kneebone, 2002). Arsenic concentrations increase with depth in lake waters in Ontario, probably because of an increasing ratio of As(III) to As(V) and an influx of mining-contaminated sediment pore waters at the sediment–water interface (Azcue and Nriagu, 1995). In other cases, seasonal depletion at the surface parallels that of nutrients such as silicate (Kuhn and Sigg, 1993). Concentrations are higher at depth in summer when the proportion of As(III) is greatest, probably reflecting lower oxygen concentrations as a result of biological productivity.

#### 11.2.4.3.4 Seawater and estuaries

Average arsenic concentrations in open seawater are typically around 1.5  $\mu\text{g l}^{-1}$  (Table 6; see Chapter 8.2). Surface depletion, as with nutrients such as silicate, has been observed in some seawater samples, but not others. Concentrations in estuarine water are more variable because of different river inputs and salinity or redox gradients, but they typically contain less than 4  $\mu\text{g l}^{-1}$ . Peterson and Carpenter (1983) found arsenic concentrations of between 1.2 and 2.5  $\mu\text{g l}^{-1}$  in waters from Saanich Inlet, British Columbia. Concentrations of less than 2  $\mu\text{g l}^{-1}$  were found in Oslofjord, Norway (Abdullah et al., 1995). Higher concentrations reflect industrial or mining

effluents (e.g., Tamar, Schelde, Loire Estuaries) or inputs of geothermal water.

Some studies have reported conservative behavior during estuarine mixing. In the unpolluted Krka Estuary of Yugoslavia, [Seyler and Martin \(1991\)](#) observed a linear increase in total arsenic with increasing salinity, ranging from 0.13  $\mu\text{g l}^{-1}$  in freshwaters to 1.8  $\mu\text{g l}^{-1}$  offshore. Other studies, however, have observed nonconservative behavior in estuaries due to processes such as diffusion from sediment pore waters and coprecipitation with iron oxides or anthropogenic inputs ([Andreae and Andreae, 1989](#); [Andreae et al., 1983](#)). The flocculation of iron oxides at the freshwater–saline interface as a result of increases in pH and salinity can lead to major decreases in the arsenic flux to the oceans ([Cullen and Reimer, 1989](#)).

#### 11.2.4.3.5 Groundwater

The concentration of arsenic in most groundwater is  $<10 \mu\text{g l}^{-1}$  ([Edmunds et al., 1989](#); [Welch et al., 2000](#); see [Chapter 11.1](#)) and often below the detection limits of routine analytical methods.

An analysis of groundwaters used for public supply in the United States showed that only 7.6% exceeded 10  $\mu\text{g l}^{-1}$  with 64% containing  $<1 \mu\text{g l}^{-1}$  ([Focazio et al., 1999](#)). Nonetheless, naturally high-arsenic groundwaters are found in aquifers in some areas of the world and concentrations occasionally reach the milligram per liter range ([Smedley and Kinniburgh, 2002](#)). Arsenic levels are naturally high in groundwaters in Bangladesh, Hungary ([Smedley and Kinniburgh, 2002](#)), and Holland ([Van der Veer, 2006](#)), associated with subsiding Holocene deltaic sediments near recently emergent Himalayan or Alpine mountain ranges. Industrially contaminated groundwater can also give rise to very high dissolved arsenic concentrations, but areas affected are usually localized. For example, [Kuhlmeier \(1997\)](#) found concentrations of arsenic up to 408000  $\mu\text{g l}^{-1}$  in groundwater close to a herbicide plant in Texas.

The physicochemical conditions favoring arsenic mobilization in aquifers are variable, complex, and poorly understood, although some of the key factors leading to high groundwater arsenic concentrations are now known. Mobilization can occur under strongly reducing conditions where arsenic, mainly as As(III), is released by desorption from, and/or dissolution of, iron oxides. Many such aquifers are sufficiently reducing for sulfate reduction, and in some cases for methane generation, to occur ([Ahmed et al., 1998](#)). Immobilization under reducing conditions is also possible: some sulfate-reducing microorganisms can respire As(V) leading to the formation of an  $\text{As}_2\text{S}_3$  precipitate ([Newman et al., 1997a,b](#)). Some immobilization of arsenic may also occur if iron sulfides are formed.

Reducing conditions favorable for arsenic mobilization have been reported most frequently from young (Quaternary) alluvial, deltaic sediments, where the interplay of tectonic, isostatic, and eustatic factors have resulted in complex patterns of sedimentation and the rapid burial of large amounts of sediment together with fresh organic matter during delta progradation.

Thick sequences of young sediments are quite often the sites of high groundwater arsenic concentrations. The most notable example of these conditions is the Bengal Basin which incorporates Bangladesh and West Bengal ([BGS and DPHE, 2001](#)). Other examples include Nepal, Myanmar, Cambodia, parts of northern China ([Luo et al., 1997](#); [Smedley et al., 2003](#); [Wang and Huang, 1994](#)), the Great Hungarian Plain of Hungary and Romania ([Gurzau and Gurzau, 2001](#); [Varsanyi et al., 1991](#)), the Red River Delta of Vietnam ([Berg et al., 2001](#)), Mekong River Delta, Vietnam ([Hoang et al., 2010](#)), and parts of western United States ([Korte, 1991](#); [Welch et al., 2000](#)). Recent groundwater extraction in many of these areas, either for public supply or for irrigation, will have induced increased groundwater flow and this could induce further transport of the arsenic ([Harvey et al., 2002](#)). Probability modeling and measured arsenic concentrations in the Red River Delta, Vietnam, indicate drawdown of arsenical waters from Holocene aquifers to previously uncontaminated Pleistocene aquifers as a result of  $>100$  years of groundwater abstraction ([Winkel et al., 2011](#)).



High concentrations of naturally occurring arsenic are also found in oxidizing conditions where groundwater pH values are high ( $>8$ ) (Smedley and Kinniburgh, 2002). In such environments, inorganic As(V) predominates and arsenic concentrations are positively correlated with those of other anion-forming species such as  $\text{HCO}_3^-$ ,  $\text{F}^-$ ,  $\text{H}_3\text{BO}_3$ , and  $\text{H}_2\text{VO}_4^-$ . Examples include parts of western United States, for example, the San Joaquin Valley, California (Fujii and Swain, 1995), Lagunera region of Mexico (Del Razo et al., 1990), Antofagasta area of Chile (Caceres et al., 1992; Sancha and Castro, 2001), and the Chaco-Pampean Plain of Argentina (Nicolli et al., 1989; Smedley et al., 2002) (Table 6). These high-arsenic groundwater provinces are usually in arid or semiarid regions where groundwater salinity is also high. Evaporation has been suggested to be an important additional cause of arsenic accumulation in some arid areas (Welch and Lico, 1998). High concentrations of arsenic have also been found in groundwater from areas of bedrock and placer mineralization, which are often the sites of mining activities. Arsenic concentrations of up to  $5000 \mu\text{g l}^{-1}$  have been found in groundwater associated with former tin-mining activity in the Ron Phibun area of Peninsular Thailand, the source most likely being oxidized arsenopyrite. Many cases have also been reported from other parts of the world, including the United States, Canada, Poland, and Austria. Examples include the Fairbanks mining district of Alaska, where arsenic concentrations up to  $10000 \mu\text{g l}^{-1}$  have been found in groundwater (Welch et al., 1988), and the Coeur d'Alene district of Idaho, where groundwater arsenic concentrations of up to  $1400 \mu\text{g l}^{-1}$  have been reported (Mok and Wai, 1990). Groundwater arsenic problems in nonmined mineralized areas are less common, but Boyle et al. (1998) found concentrations up to  $580 \mu\text{g l}^{-1}$  in groundwater from the sulfide mineralized areas of Bowen Island, British Columbia. Heinrichs and Udluft (1999) also found arsenic concentrations up to  $150 \mu\text{g l}^{-1}$  in groundwater from a mineralized sandstone aquifer in Bavaria.

#### 11.2.4.3.6 Sediment pore water

Much higher concentrations of arsenic frequently occur in pore waters extracted from unconsolidated sediments than in overlying surface waters. Widerlund and Ingri (1995) reported concentrations in the range  $1.3\text{--}166 \mu\text{g l}^{-1}$  in pore waters from the Kalix River estuary, northern Sweden. Yan et al. (2000) found concentrations in the range  $3.2\text{--}99 \mu\text{g l}^{-1}$  in pore waters from clay sediments in Saskatchewan, Canada. High concentrations are frequently found in pore waters from geothermal areas. Aggett and Kriegman (1988) reported arsenic concentrations up to  $6430 \mu\text{g l}^{-1}$  in anoxic pore waters from Lake Ohakuri, New Zealand. Even higher concentrations have been found in pore waters from sediments contaminated with mine tailings or draining ore deposits. McCreadie et al. (2000) reported concentrations up to  $100000 \mu\text{g l}^{-1}$  in pore waters extracted from mine tailings in Ontario, Canada. High pore water-arsenic concentrations probably reflect the strong redox gradients that often occur over a few centimeters below the sediment–water interface. Burial of fresh organic matter and the slow diffusion of oxygen through the sediment lead to reducing conditions with the consequent reduction of As(V) to As(III) and the desorption and dissolution of arsenic from iron and manganese oxides.

There is much evidence of arsenic being released into shallow sediment pore waters and overlying surface waters in response to temporal variations in redox conditions. Sullivan and Aller (1996) investigated arsenic cycling in shallow sediments from an unpolluted area of the Amazonian offshore shelf. They found pore water-arsenic concentrations of up to  $300 \mu\text{g l}^{-1}$  in anaerobic sediments with nearly coincident peaks of dissolved arsenic and iron. The peaks for iron concentration were often slightly above those of arsenic (Figure 1). The magnitude of the peaks and their depths varied from place to place and possibly seasonally, but were typically between 50 and 150 cm beneath

the sediment–water interface (Sullivan and Aller, 1996). There was no correlation between pore water–arsenic concentrations and sediment–arsenic concentrations (Figure 1).

#### 11.2.4.3.7 Acid mine drainage

Acid mine drainage (AMD), which can have pH values as low as  $-3.6$  (Nordstrom et al., 2000), can contain high concentrations of many solutes, including iron and arsenic. The highest reported arsenic concentration,  $850000 \mu\text{g l}^{-1}$ , was found in an acid seep in Richmond mine, California (Nordstrom and Alpers, 1999). Plumlee et al. (1999) reported concentrations ranging from  $<1$  to  $340000 \mu\text{g l}^{-1}$  in 180 samples of mine drainage from the United States, with the highest values from Richmond mine. Gelova (1977) also reported arsenic concentrations of  $400000 \mu\text{g l}^{-1}$  in the Ural Mountains. Dissolved arsenic in AMD is rapidly removed as the pH increases and as iron is oxidized and precipitated as hydrous ferric oxide (HFO), coprecipitating large amounts of arsenic.

#### 11.2.4.4 Arsenic Species in Natural Waters

The speciation of arsenic in natural waters is controlled by reduction, oxidation, and methylation reactions that affect its solubility, transport, bioavailability, and toxicity (Hering and Kneebone, 2002). The relatively small amount of arsenic released into stream waters during weathering is mobile only if the pH and  $E_h$  are sufficiently low to favor its persistence in trivalent form. Otherwise, dissolved arsenic is rapidly oxidized to insoluble  $\text{As}_2\text{S}_3$  and it becomes sorbed as the arsenate ion ( $\text{AsO}_4^{3-}$ ) by hydrous iron and manganese oxides, clays, and organic matter (Cheng et al., 2009). Inorganic speciation is important because the varying protonation and charge of the arsenic species present at different oxidation states has a strong effect on their behavior, for example, their adsorption. While the concentrations of organic arsenic species are low in most natural environments, the methylated and dimethylated As(III) species are now of considerable interest as they have recently been found to be more cytotoxic, genotoxic, and potent enzyme inhibitors than inorganic As(III) (Thomas et al., 2001).

##### 11.2.4.4.1 Inorganic species

Redox potential ( $E_h$ ) and pH are the most important factors governing inorganic arsenic speciation. The redox behavior of inorganic arsenic species is complex and is mediated by chemical reactions such as ligand exchange, precipitation with iron and sulfide, adsorption to clay and metals, and biotic and abiotic oxidation–reduction reactions (Cullen and Reimer, 1989; Ferguson and Gavis, 1972; Fisher et al., 2007). Under oxidizing conditions, and pH less than about 6.9,  $\text{H}_2\text{AsO}_4^-$  is dominant, while at higher pH,  $\text{HAsO}_4^{2-}$  is dominant ( $\text{H}_3\text{AsO}_4^0$  and  $\text{AsO}_4^{3-}$  may be present in extremely acid and alkaline conditions, respectively) (Figure 2) (Nordstrom and Archer, 2003; Yan et al., 2000). Under reducing conditions where the pH is less than about 9.2, the uncharged arsenite species,  $\text{H}_3\text{AsO}_3$ , predominates. Native arsenic is stable under strongly reducing conditions.

In the presence of high concentrations of reduced sulfur and low pH, dissolved As(III)-sulfide species can be formed rapidly by reduction of arsenate by  $\text{H}_2\text{S}$ . There is now strong evidence for the existence of the trimer,  $\text{As}_3\text{S}_4(\text{SH})_2^-$ , under strongly reducing, acidic and sulfur-rich conditions with the thioarsenite species,  $\text{AsO}(\text{SH})_2^-$ , appearing at higher pHs (Helz et al., 1995; Nordstrom and Archer, 2003; Rochette et al., 2000; Schwedt and Rieckhoff, 1996). Reducing, acidic and sulfur-rich conditions also favor precipitation of orpiment ( $\text{As}_2\text{S}_3$ ), realgar ( $\text{AsS}$ ), or other arsenic sulfide minerals (Cullen and Reimer, 1989). High concentrations of arsenic are unlikely in acidic waters containing high concentrations of free sulfide (Moore et al., 1988). In more alkaline waters, As(III) sulfides are more soluble and higher dissolved arsenic concentrations could persist. There is some evidence for the existence of As(V)–carbonate species (Kim et al., 2000), but their environmental significance has not yet been understood. Examination of the effects of sulfide on aerobic arsenite oxidation in alkaline

lake water samples and in laboratory enrichment culture showed that arsenite oxidation occurred only in treatments with bacteria present; production of arsenate was greatly enhanced by the addition of sulfide or thiosulfate (Fisher et al., 2007). Like dissolved hydrogen, arsine is only expected under extremely reducing conditions. Green rusts, complex Fe(II)–Fe(III) hydroxide minerals that form under reducing conditions, have been shown to be able to reduce selenate to selenite abiotically but not arsenate to arsenite (Randall et al., 2001). The  $E_h$ –pH diagram for the As–O–S system is shown in Figure 3. While such diagrams are useful, they necessarily simplify highly complex natural systems. For example, iron is not included despite its strong influence on arsenic speciation. Hence, scorodite ( $\text{FeAsO}_4 \cdot 2\text{H}_2\text{O}$ ), an important arsenic-bearing mineral found under a wide range of near-neutral, oxidizing conditions, is not represented; neither is the coprecipitation of arsenic with pyrite, nor the formation of arsenopyrite ( $\text{FeAsS}$ ) under reducing conditions. The relative stability of the various As–S minerals is very sensitive to their assumed free energies of formation and the stability of the various soluble As–S species. The  $E_h$ –pH diagram can vary significantly depending on the chosen forms of realgar and orpiment, including their crystallinity.

The extent of redox equilibrium in natural waters has been the cause of considerable discussion. In the case of arsenic, Cherry et al. (1979) suggested that redox equilibrium was sufficiently rapid for As(V)/As(III) ratios to be useful indicators of redox status. Subsequent findings have been somewhat equivocal (Welch et al., 1988) although some recent data for pore water As(V)/As(III) ratios and  $E_h$  measurements have indicated substantial consistency (Yan et al., 2000). While observations of the rate of oxidation of As(III) in groundwater are difficult under field conditions, the rates are believed to be slow. However, biological activity in these waters is also generally low, making redox equilibrium easier to attain than in more productive environments.

#### 11.2.4.4.2 Organic species

Organic arsenic species are important in food, especially fish and marine invertebrates such as lobsters (AsB and arsenosugars), and in blood and urine (monomethylarsonate (MMA) and dimethylarsinate (DMA)), although they usually form only a minor component of arsenic in natural waters (Francesconi and Kuehnelt, 2002; National Research Council, 1999). Their concentrations are greatest in organic-rich waters such as soil and sediment pore waters and productive lake waters and least in groundwaters. The concentrations of organic species are increased by methylation reactions catalyzed by microbial activity, including bacteria, yeasts, and algae. The dominant organic forms found are DMA and MMA in which arsenic occurs in the pentavalent state. Proportions of these two species are reported to increase in summer as a result of increased microbial activity (Hasegawa, 1997). Organic species may also be more abundant close to the sediment–water interface (Hasegawa et al., 1999).

Small concentrations of trimethylarsonate, AsB, AsC, and phenylarsonate have been observed occasionally (Florencio et al., 1997). Arsenic can also be bound to humic material, but this has not been well characterized and may involve ternary complexes with strongly bound cations such as  $\text{Fe}^{3+}$ . There have been reports of ‘hidden’ arsenic species in natural waters. These are organic species that do not form arsine gas with  $\text{NaBH}_4$  and were therefore undetected in early speciation studies. Some, though not all, such arsenic species are detected after UV irradiation of samples (Hasegawa et al., 1999; National Research Council, 1999).

#### 11.2.4.4.3 Observed speciation in different water types

The oxidation states of arsenic in rainwater vary according to source, but are likely to occur dominantly as As(III) when derived from smelters, coal burning, or volcanic sources. Organic arsenic species may be derived by volatilization from soils, and arsine ( $\text{As}(-\text{III})\text{H}_3$ ) may be produced from landfills

and reducing soils such as paddy soils and peats. Arsenate may be derived from marine aerosols. Reduced forms will undergo oxidation in the atmosphere and reactions with atmospheric SO<sub>2</sub> or O<sub>3</sub> are likely (Cullen and Reimer, 1989).

In oxic seawater, the As(V) species predominates, though some As(III) is invariably present, especially in anoxic bottom waters. As(V) should exist mainly as HAsO<sub>4</sub><sup>2-</sup> and H<sub>2</sub>AsO<sub>4</sub><sup>-</sup> in the pH range of seawater (pH around 8.2; Figures 2 and 3) and As(III) mainly as the neutral species H<sub>3</sub>AsO<sub>3</sub>. In fact, relatively high proportions of H<sub>3</sub>AsO<sub>3</sub> occur in surface ocean waters (Cullen and Reimer, 1989) where primary productivity is high, often with increased concentrations of organic arsenic species as a result of methylation reactions by phytoplankton.

The relative proportions of arsenic species in estuarine waters are more variable because of changes in redox, salinity, and terrestrial inputs (Abdullah et al., 1995; Howard et al., 1988). As(V) tends to dominate, although Andreae and Andreae (1989) found increased proportions of As(III) in the Schelde Estuary of Belgium, with the highest values in anoxic zones near sources of industrial effluent. Increased proportions of As(III) also occur near sources of mine effluent (Andreae and Andreae, 1989). Seasonal variations in concentration and speciation have been reported in seasonally anoxic waters (Riedel, 1993). Peterson and Carpenter (1983) reported a clear crossover in the proportions of the two species with increasing depth in the Saanich Inlet of British Columbia. As(III) represented only 5% (0.10 µg l<sup>-1</sup>) of the dissolved arsenic above the redox front but 87% (1.58 µg l<sup>-1</sup>) below it. In marine and estuarine waters, organic forms of arsenic are usually less abundant but are often detected (Howard et al., 1999; Riedel, 1993). Their concentrations depend on the abundance and species of biota present and on temperature.

In lake and river waters, As(V) is generally dominant (Pettine et al., 1992; Seyler and Martin, 1990), although concentrations and relative proportions of As(V) and As(III) vary seasonally according to changes in input sources, redox conditions, and biological activity. The presence of As(III) may be maintained in oxic waters by biological reduction of As(V), particularly during summer months. Higher proportions of As(III) occur in rivers close to sources of As(III)-dominated industrial effluent (Andreae and Andreae, 1989) or where there is a component of geothermal water.

Proportions of As(III) and As(V) are particularly variable in stratified lakes with seasonally variable redox gradients (Kuhn and Sigg, 1993). In the stratified, hypersaline, hyperalkaline Mono Lake (California, USA), As(V) predominates in the upper oxic layer and As(III) in the reducing layer (Maest et al., 1992; Oremland et al., 2000). Oremland et al. (2000) measured in situ rates of dissimilatory As(V) reduction in the lake and found that this could potentially mineralize 8–14% of the annual pelagic primary productivity during meromixis, a significant amount for a trace element, and about one-third of the amount of sulphate reduction. Such reduction does not occur in the presence of NO<sub>3</sub>. In fact, NO<sub>3</sub> leads to the rapid, microbial reoxidation of As(III) to As(V) (Hoefl et al., 2002). Fe(III) acts similarly.

The speciation of arsenic in lakes does not always follow thermodynamic predictions. Recent studies have shown that arsenite predominates in the oxidized epilimnion of some stratified lakes while arsenate may persist in the anoxic hypolimnion (Kuhn and Sigg, 1993; Newman et al., 1998; Seyler and Martin, 1989). Proportions of arsenic species can also vary according to the availability of particulate iron and manganese oxides (Kuhn and Sigg, 1993; Pettine et al., 1992). Sunlight could promote oxidation in surface waters (Voegelin and Hug, 2003).

In groundwaters, the ratio of As(III) to As(V) can vary greatly in relation to changes in the abundance of redox-active solids, especially organic carbon, the activity of microorganisms, and the extent of convection and diffusion of oxygen

from the atmosphere. As(III) typically dominates in strongly reducing aquifers in which Fe(III) and sulfate reduction is taking place. Reducing high-arsenic groundwaters from Bangladesh have As(III)/AsT ratios varying between 0.1 and 0.9 but are typically around 0.5–0.6 (Smedley et al., 2001a). Ratios in reducing groundwaters from Inner Mongolia are typically 0.6–0.9 (Smedley et al., 2003). Concentrations of organic forms of arsenic are generally small or negligible in groundwaters (e.g., Chen et al., 1995; Del Razo et al., 1990).

#### 11.2.4.5 Microbial Controls

The toxicity of arsenic results from its ability to interfere with a number of key biochemical processes. Arsenate can interfere with phosphate biochemistry (oxidative phosphorylation) as a result of their chemical similarity. Arsenite tends to inactivate sulfhydryl groups of cysteine residues in proteins (Oremland et al., 2002; Santini et al., 2002). Microbes have evolved various detoxification strategies for dealing with this (Frankenberger, 2002; Mukhopadhyay et al., 2002; Rosen, 2002). Some microbes have also evolved to use arsenic as an energy source. Certain chemoautotrophs oxidize As(III) by using O<sub>2</sub>, nitrate, or Fe(III) as a terminal electron acceptor and CO<sub>2</sub> as their sole carbon source. A select group of other organisms grows in anaerobic environments by using As(V) for the oxidation of organic matter or H<sub>2</sub> gas (Newman et al., 1998; Oremland and Stolz, 2003; Oremland et al., 2002, 2000; Stolz and Oremland, 1999). Such so-called dissimilatory arsenate reduction (DAsR) was discovered only relatively recently (Ahmann et al., 1994). Fourteen species of Eubacteria, including *Sulfurospirillum* species, have so far been shown to be capable of DAsR (Herbel et al., 2002a) as well as two species of hyperthermophiles from the domain Archaea. Laboratory studies indicate that microbial processes involved in As(V) reduction and mobilization are many times faster than inorganic chemical transformations and that microorganisms play an important role in subsurface arsenic cycling (Ahmann et al., 1997; Bhattacharya et al., 2007; Islam et al., 2004; Jones et al., 2000). In Mono Lake, eastern California, a hypersaline and alkaline water body bacterium strain GFAJ-1 of the Halomonadaceae has been reported, which substitutes arsenic for phosphorus to sustain its growth (Wolfe-Simon et al., 2011). The bacterium *Thiobacillus* has been shown to have a direct role in precipitating ferric arsenate sulfate (Leblanc et al., 1996). Temporal variations between the proportions of arsenate and arsenite have been observed in the Waikato River, New Zealand, and may reflect the reduction of As(V) to As(III) by epiphytic bacteria associated with the alga *Anabaena oscillaroides*. Arsenate reduction does not necessarily take place as an energy-providing (dissimilatory) process (Hoefl et al., 2002). Detoxifying arsenate reductases in the cytoplasm does not provide a means of energy generation. Macur et al. (2001) found active As(V) to As(III) reduction under oxic conditions in limed mine tailings, which they ascribed to a detoxification rather than an energy-producing, respiratory process. This is often combined with an As(III) efflux pump to expel the toxic As(III) from the cell. Purely chemical (abiotic) reduction of As(V) to As(III) has not been documented.

Arsenic can also be released indirectly as a result of other microbially induced redox reactions. For example, the dissimilatory iron-reducing bacterium *Shewanella alga* (strain BrY) reduces Fe(III) to Fe(II) in scorodite (FeAsO<sub>4</sub>·2H<sub>2</sub>O), releasing As(V) but not As(III) (Cummings et al., 1999). This process can be rapid (Langner and Inskip, 2000).

The rapid oxidation of As(III) has also been observed in the geothermally fed Hot Creek in California (Wilkie and Hering, 1998). Oxidation with a pseudo-first-order half-life of approximately 0.3 h was found to be controlled by bacteria attached to macrophytes. Where microbial activity is high, there is frequently a lack of equilibrium between the various redox couples, including that of arsenic (Section 11.2.4.4). This is especially true of soils (Masscheleyn et al., 1991).

#### 11.2.5 Pathways and Behavior of Arsenic in the

## Natural Environment

Most high-arsenic natural waters are groundwaters from particular settings such as mineralized, mined, and geothermal areas, young alluvial deltaic basins, and inland semiarid basins (Smedley and Kinniburgh, 2002). The most extensive areas of affected groundwater are found in the low-lying deltaic areas of Southeast Asia, especially the Bengal Basin, and in the large plains ('pampas') of South America. The sediments of these areas typically have 'average' total arsenic concentrations although concentrations may increase in iron oxide-rich sediments. The chemical, microbiological, and hydrogeological processes involved in the mobilization of arsenic in such groundwaters are poorly understood, but probably involve early diagenetic reactions driven by redox and/or pH changes.

### 11.2.5.1 Release from Primary Minerals

The arsenic in many natural waters is likely to have been derived naturally from the dissolution of a mineral phase. The most important primary sources are sulfide minerals, particularly arsenic-rich pyrite, which can contain up to 10% arsenic, and arsenopyrite (FeAsS). In one study, the greatest concentrations of arsenic were found in fine-grained (<2 μm) pyrite formed at relatively low temperatures (120–200 °C) (Simon et al., 1999). A variety of other sulfide minerals such as orpiment As<sub>2</sub>S<sub>3</sub> and realgar As<sub>2</sub>S<sub>2</sub> also occur in association with gold and base metal deposits. Arsenic is a component of some complex copper sulfides such as enargite (Cu<sub>3</sub>As<sub>4</sub>) and tennantite ((Cu, Fe)<sub>12</sub>As<sub>4</sub>S<sub>13</sub>). Rare arsenides are also found in mineralized areas. All of these minerals oxidize rapidly on exposure to the atmosphere, releasing the arsenic to partition between water and various secondary minerals, particularly iron oxides. Both microbially mediated redox reactions (Section 11.2.4.5) and abiotic processes are involved. Bacteria can influence the oxidation state of arsenic in aquatic environments (Oremland and Stolz, 2003). The microbial oxidation of arsenic minerals such as arsenopyrite, enargite, and orpiment has been discussed by Ehrlich (2002). Oxidation of sulfide minerals can occur naturally or as a result of mining activity. Arsenic-rich minerals around mines may therefore produce arsenic-rich drainage locally, but this tends to be attenuated rapidly as a result of adsorption of various arsenic species by secondary minerals. Some of the best-documented cases of arsenic contamination therefore occur in areas of sulfide mineralization, particularly those associated with gold deposits.

Oxidation is enhanced by mining excavations, mine dewatering, ore roasting, and the redistribution of tailings in ponds and heaps. In the past, this has been the cause of serious environmental damage leading to high arsenic concentrations in soils, stream sediments, surface waters and some groundwaters, and even the local atmosphere. Although these activities have often had a severe impact on the local environment, the arsenic contamination in surface water and groundwater tends to be restricted to within a few kilometers of the mine site. Oxidation of arsenopyrite can be described by the reaction:

$4\text{FeAsS} + 13\text{O}_2 + 6\text{H}_2\text{O} = 4\text{Fe}^{2+} + 4\text{AsO}_4^{3-} + 4\text{SO}_4^{2-} + 12\text{H}^+$   
which involves the release of acid, arsenic, and sulfate as AMD (see Chapter 11.5). Further acidity is released by oxidation of the Fe<sup>2+</sup> and precipitation of HFO or schwertmannite.

These minerals re-adsorb some of the released arsenic, reducing dissolved arsenic concentrations, and may eventually lead to the formation of scorodite (FeAsO<sub>4</sub>·2H<sub>2</sub>O). Experience from bioleaching of arsenic-rich gold ores has shown that the ratio of pyrite to arsenopyrite is an important factor controlling the speciation of the arsenic released (Nyashanu et al., 1999). In the absence of pyrite, about 72% of the arsenic released was As(III) whereas in the presence of pyrite and Fe(III), 99% of the arsenic was As(V). It appears that pyrite catalyzed the oxidation of As(III) by Fe(III) as Fe(III) alone did not oxidize the arsenic (Nyashanu et al., 1999).

**11.2.5.1.1 Examples of mining-related arsenic problems**  
Mining and mineral processing can cause arsenic contamination

of the atmosphere (in the form of airborne dust), sediment, soil, and water. The contamination can be long-lasting and remain in the environment long after the activities have ceased (Camm et al., 2003). Recent estimates suggest that there are approximately 11 million tonnes of arsenic associated with copper and lead reserves globally (USGS, 2005). In developing mines containing significant amounts of arsenic, careful consideration is now given to treatment of wastes and effluents to ensure compliance with legislation on permitted levels of arsenic that can be emitted to the environment. Such legislation is becoming increasingly stringent. Arsenic contamination from former mining activities has been identified in many areas of the world including the United States (Plumlee et al., 1999; Welch et al., 1999, 1988, 2000), Canada, Thailand, Korea, Ghana, Greece, Austria, Poland, and the United Kingdom (Smedley and Kinniburgh, 2002). Groundwater in some of these areas has been found with arsenic concentrations as high as 48000 µg l<sup>-1</sup>. Elevated arsenic concentrations have been reported in soils of various mining regions around the world (Kreidie et al., 2011). Some mining areas have AMD with such low pH values that the iron released by oxidation of the iron sulfide minerals remains in solution and therefore does not scavenge arsenic. Well-documented cases of arsenic contamination in the United States include the Fairbanks goldmining district of Alaska (Welch et al., 1988; Wilson and Hawkins, 1978), the Coeur d'Alene Pb–Zn–Ag mining area of Idaho (Mok and Wai, 1990), the Leviathan Mine (S), California (Webster et al., 1994), Mother Lode (Au), California (Savage et al., 2000), Summitville (Au), Colorado (Pendleton et al., 1995), Kelly Creek Valley (Au), Nevada (Grimes et al., 1995), Clark Fork river (Cu), Montana (Welch et al., 2000), Lake Oahe (Au), South Dakota (Ficklin and Callender, 1989), and Richmond Mine (Fe, Ag, Au, Cu, Zn), IronMountain, California (Nordstrom et al., 2000).

Phytotoxic effects attributed to high concentrations of arsenic have also been reported around the Mina Turmalina copper mine in the Andes, northeast of Chiclayo, Peru (Bech et al., 1997). The main ore minerals involved are chalcopyrite, arsenopyrite, and pyrite. Arsenic-contaminated groundwater in the Zimapán Valley, Mexico, has also been attributed to interaction with Ag–Pb–Zn, carbonate-hosted mineralization (Armienta et al., 1997). Arsenopyrite, scorodite, and tennantite were identified as probable source minerals in this area. Increased concentrations of arsenic have been found as a result of arsenopyrite occurring naturally in Cambro–Ordovician lode gold deposits in Nova Scotia, Canada. Tailings and stream sediment samples show high concentrations of arsenic (39 ppm), and dissolved arsenic concentrations in surface waters and tailing pore waters indicate that the tailings continue to release significant quantities of arsenic. Biological sampling demonstrated that both arsenic and mercury have bioaccumulated to various degrees in terrestrial and marine biota, including eels, clams, and mussels (Parsons et al., 2006).

Data for 34 mining localities of different metallogenic types in different climatic settings were reviewed by Williams (2001). He proposed that arsenopyrite is the principal source of arsenic released in such environments and concluded that in situ oxidation generally resulted in the formation of poorly soluble scorodite, which limited the mobility and ecotoxicity of arsenic. The Ron Phibun tin-mining district of Thailand is an exception (Williams et al., 1996). In this area, arsenopyrite oxidation products were suggested to have formed in the alluvial placer gravels during the mining phase. Following cessation of mining activity and pumping, groundwater rebound caused dissolution of the oxidation products. The role of scorodite in the immobilization of arsenic from mine workings has been questioned by Roussel et al. (2000), who point out that the solubility of this mineral exceeds drinking water standards irrespective of pH.

**11.2.5.1.2 Modern practice in mine-waste stabilization**  
Although large international mining companies now generally

work to high environmental standards, mineral working by uncontrolled and disorganized groups (especially for gold) continues to cause environmental problems in a number of developing countries.

Modern mining practices including waste storage and treatment are designed to minimize the risk of environmental impacts (Johnson, 1995). In most countries, environmental impact assessments and environmental management plans are now a statutory requirement of the mining approval process. Such plans include criteria for siting and management of waste heaps and for effluent control. Closure plans involving waste stabilization and capping to limit AMD generation are also required to reduce any legacy of environmental damage (Lima and Wathern, 1999).

Treatment of AMD includes the use of liming, coagulation, and flocculation (Kuyucak, 1998). Other passive technologies include constructing wetlands that rely on sulfate reduction, alkali generation, and the precipitation of metal sulfides. These are often used as the final step in treating discharged water. More recently, permeable reactive barriers (PRBs) have been advocated. For example, Harris and Ragusa (2001) have demonstrated that sulfate-reducing bacteria can be stimulated to precipitate arsenic sulfides by the addition of rapidly decomposing plant material. Monhemius and Swash (1999) investigated the addition of iron to copper- and arsenic-rich liquors to form scorodite. The arsenic is immobilized by incorporation into a crystalline, poorly soluble compound (Sides, 1995). Swash and Monhemius (1996) have also investigated the stabilization of arsenic as calcium arsenate.

#### 11.2.5.2 Role of Secondary Minerals

##### 11.2.5.2.1 The importance of arsenic cycling and diagenesis

The close association between arsenic and iron in minerals is frequently reflected by their strong correlation in soils and sediments. Iron oxides play a crucial role in adsorbing arsenic species, especially As(V), thereby lowering the concentration of arsenic in natural waters. O'Reilly et al. (2001) suggested that arsenic is specifically sorbed onto goethite through an innersphere complex through a ligand-exchange process. Manganese oxides play a role in the oxidation of As(III) to As(V) and also adsorb significant quantities, although to a much lesser degree than the more abundant iron oxides. HFO is a very fine-grained, high surface area form of iron oxide that is often formed in iron-rich environments in response to rapid changes in redox or pH. It is frequently involved in the cycling of As(III) and As(V). Significant As(V) desorption occurs at pH values of approximately pH 8 and higher (Lumsdon et al., 2001) and this process has been suggested to be important in generating high-arsenic groundwaters (Smedley, 2003; Welch et al., 2000). Arsenic can also be released under reducing conditions (Section 11.2.5.5).

The mobility of arsenic can also be limited in sulfur-rich, anaerobic environments by its coprecipitation with secondary sulfide minerals, and more generally by clays. The precise behavior of arsenic in sediments is poorly understood, but it is likely that important changes occur during sediment diagenesis. Arsenic adsorbed on mineral surfaces is likely to be sensitive to changes in the mineral properties such as surface charge and surface area. A very small mass transfer from solid to solution can lead to a large change in dissolved arsenic concentration. For example, sediments with average arsenic concentrations of less than 5–10 mg kg<sup>-1</sup> can generate milligram per liter concentrations of arsenic when only a small fraction (<1%) of the total arsenic is partitioned into the water.

##### 11.2.5.2.2 Redox behavior

Solid surfaces of many minerals, especially redox-sensitive minerals like iron and manganese oxides, also play an important role in redox reactions and interactions with microbes (Brown et al., 1999; Grenthe et al., 1992). Solid Mn(IV)O<sub>2</sub>, notably birnessite (δ-MnO<sub>2</sub>), assists in the oxidation of As(III) to As(V) while being partially reduced to Mn(II) (Oscarson



et al., 1983; Scott and Morgan, 1995). The rate of oxidation depends on the surface area and surface charge of the MnO<sub>2</sub> and is slightly greater at low pH (pH 4). The Mn(II) and As(V) produced are partially retained or re-adsorbed by the MnO<sub>2</sub> surface, which may lead in turn to a deceleration in the rate of As(III) oxidation (Manning et al., 2002). Reactions with birnessite at very high initial As(III) concentrations may lead to the insoluble mineral krautite (MnHAsO<sub>4</sub>·H<sub>2</sub>O) being formed on the birnessite surface (Tourmassat et al., 2002). The catalytic role of solid MnO<sub>2</sub> in removing As(III) is used to advantage in water treatment (Daus et al., 2000; Driehaus et al., 1995). TiO<sub>2</sub> minerals and Ti-containing clays may also be able to oxidize As(III).

HFO and other iron oxides may also play a significant role in the oxidation of As(III) in natural waters, as the oxidation of As(III) adsorbed by HFO is catalyzed by H<sub>2</sub>O<sub>2</sub> (Voegelin and Hug, 2003). This reaction may be significant in natural environments, with high H<sub>2</sub>O<sub>2</sub> concentrations (1–10 μM) and alkaline pHs, or in water treatment systems where H<sub>2</sub>O<sub>2</sub> is used. Similar surface-catalyzed reactions do not occur with aluminum oxides (Voegelin and Hug, 2003).

The reductive dissolution of Fe(III) oxides in reducing sediments and soils (McGeehan et al., 1998) can also lead to the release of adsorbed and coprecipitated arsenic. Reduction and release of arsenic can precede any dissolution of the iron oxides themselves (Masscheleyn et al., 1991). These processes are likely to be the same as those responsible for the development of high-arsenic groundwaters in the Bengal Basin (Bhattacharya et al., 1997; Kinniburgh et al., 2003; Nickson et al., 2000) and other reducing alluvial aquifers (Korte and Fernando, 1991). The release of sorbed arsenic during diagenetic changes of iron oxides, including loss of surface area, changes in surface structure, and charge following burial, may also be important under both reducing and oxidizing conditions.

The photocatalytic activity of anatase (TiO<sub>2</sub>) has been shown to catalyze the oxidation of As(III) in the presence of light and oxygen (Foster et al., 1998a). Unlike the role of manganese oxides in As(III) oxidation, there is no change in the oxidation state of the surface Ti(IV) atoms.

**11.2.5.3 Adsorption of Arsenic by Oxides and Clays**  
Metal ion oxides are often important in minimizing the solubility of arsenic in the environment in general and more specifically for localizing the impact of arsenic contamination near contaminated sites, especially old mines (La Force et al., 2000; Plumlee et al., 1999; Roussel et al., 2000; Webster et al., 1994). Organic arsenic species tend to be less strongly sorbed by minerals than inorganic species.

There have been many laboratory studies of the adsorption of arsenic species by pure minerals, especially iron and aluminum oxides and clays (Goldberg, 1986; Inskeep et al., 2002).

The general features of the processes involved are now established. Dzombak and Morel (1990) critically reviewed the available laboratory data for the adsorption of a wide range of inorganic species, including those for arsenic, by HFO and fitted the most reliable data to a surface complexation model – the diffuse double-layer model. This model, and the accompanying thermodynamic database, is now incorporated into several general-purpose geochemical speciation and transport models, including PHREEQC2 (Parkhurst and Appelo, 1999) and The Geochemist's Workbench (Bethke, 2002). These software packages enable rapid calculations of the possible role of arsenic adsorption by HFO to be made. Critically, in PHREEQC2, this adsorption behavior can also be automatically linked to the dissolution/precipitation of HFO. The results of such calculations demonstrate the important role of both oxidation states (arsenate vs. arsenite) and pH (Figure 4).

The oxidized and reduced species of arsenic behave very differently on HFO (Figure 4) and this along with the pH dependence of adsorption accounts, at least in part, for their different behavior with oxides and clays and hence their behavior in natural waters. As(V) is very strongly adsorbed by

HFO especially at low pH and low concentrations, but is desorbed as the pH increases as a result of the increasingly strong electrostatic repulsion on the negatively charged HFO surface. The adsorption isotherm for arsenate is consequently highly nonlinear and can be approximated by a pH-dependent Freundlich isotherm; that is, the slope of the adsorption decreases markedly with increasing arsenic concentration (the  $K_a$  varies with concentration). In contrast, As(III) in the pH range 4–9 is present mainly in solution as the neutral  $\text{As}(\text{OH})_3$  species and so electrostatic interactions are not nearly so important. Therefore, arsenite is adsorbed over a wide range of pH and because the adsorbed species is uncharged, arsenite adsorption tends to follow a Langmuir isotherm; that is, the isotherm has an adsorption maximum and approaches linearity at low concentrations. It is also almost independent of pH. Organic arsenic species are weakly adsorbed by oxides, so their formation can increase arsenic mobility. In oxidizing environments, arsenate is more strongly adsorbed than arsenite in neutral to acidic conditions, and especially at low concentrations. Arsenate tends to be much less strongly adsorbed at high pH and this has important environmental consequences. The precise pH where this occurs depends on several other factors (e.g., the total arsenic concentration and the concentrations of other competing anions) but it is in the region pH 8–9. Under these conditions, arsenite may be more strongly bound.

The adsorption of arsenic species also depends to some extent on competition from other anions, which in reducing groundwaters include phosphate, silicate, bicarbonate, and fulvic acids (Appelo et al., 2002; Hiemstra and van Riemsdijk, 1999; Jain and Loeppert, 2000; Meng et al., 2002; Wang et al., 2001; Wijnja and Schulthess, 2000). As(V) and P sorption on HFO are broadly similar although there is usually a slight preference for P (Jain and Loeppert, 2000). Not surprisingly, As(V) is much more strongly affected by P competition than As(III) (Jain and Loeppert, 2000). Cations, such as  $\text{Ca}^{2+}$  and  $\text{Fe}^{2+}$ , may increase arsenic adsorption (Appelo et al., 2002). Once the oxides have an adsorbed load, any change to their surface chemistry or the solution chemistry can lead to the release of adsorbed arsenic, thereby increasing groundwater concentrations. The extremely high solid/solution ratio of soils and aquifers makes them very sensitive to such changes and redox changes are likely to be particularly important (Meng et al., 2001; Zobrist et al., 2000).

Adsorption by aluminum and manganese oxides and clays has not been studied much (Inskip et al., 2002). As(III) binds strongly to amorphous  $\text{Al}(\text{OH})_3$  over pH range 6–9.5, a somewhat greater range than found for HFO. It also binds significantly but somewhat less strongly to montmorillonitic and kaolinitic clays (Manning and Goldberg, 1997). As(V) shows the same declining affinity for clays at high pH as shown by HFO, but in the case of the clays, this decline may begin to occur above pH 7.

#### 11.2.5.4 Arsenic Transport

There are few observations of arsenic transport in aquifers and its rate of movement under a range of conditions is poorly understood. The transport of arsenic, as with many other chemicals, is closely related to adsorption–desorption reactions (Appelo and Postma, 1993). Arsenate and arsenite have different adsorption isotherms and would be predicted therefore to travel through aquifers at different velocities, leading to their separation along the flow path.

Gulens et al. (1979) used breakthrough experiments with columns of sand (containing 0.6% iron and 0.01% manganese) and various groundwaters pumped continuously from piezometers to study As(III) and As(V) mobility over a range of  $E_h$  and pH conditions. Radioactive  $^{74}\text{As}$  (half-life=17.7 days) and  $^{76}\text{As}$  (half-life=26.4 h) were used to monitor the breakthrough of arsenic. The results showed that (1) As(III) moved 5–6 times faster than As(V) under oxidizing conditions with

pH in the range 5.7–6.9; (2) As(V) moved much faster at the lowest pH but was still slower than As(III) under reducing groundwater conditions; and (3) with a pH of 8.3, both As(III) and As(V) moved rapidly through the column but when the amount of arsenic injected was substantially reduced, the mobility of the As(III) and As(V) was greatly reduced. This chromatographic effect (used to advantage in analytical chemistry to speciate arsenic) may account in part for the highly variable As(III)/As(V) ratios found in many reducing aquifers. Chromatographic separation of arsenic and other species during transport would also destroy the original source characteristics, for example, between arsenic and iron, further complicating interpretation of well water analyses.

Few field-based investigations, which allow the partition coefficient ( $K_d$ ) or retardation factor of arsenic species to be determined directly, have been carried out on natural systems. However, the work of [Sullivan and Aller \(1996\)](#) indicates that  $K_d$  values calculated for sediment profiles from the Amazon Shelf are in the approximate range of 11–5000  $\text{kg}^{-1}$ . High-arsenic pore waters were mostly found in zones with low  $K_d$  values (typically  $<100 \text{ kg}^{-1}$ ). Evidence from various studies also suggests low  $K_d$  values ( $<10 \text{ kg}^{-1}$ ) for arsenic in aquifers in which there are high arsenic concentrations ([Smedley and Kinniburgh, 2002](#)). Factors controlling the partition coefficients are poorly understood and involve the chemistry of the groundwater and the surface chemistry and stability of solid phases present.

#### 11.2.5.5 Impact of Changing Environmental Conditions

Arsenic moves between different environmental compartments (rock–soil–water–air–biota) from the local to the global scale partly as a result of pH and redox changes. Being a minor component in the natural environment, arsenic responds to such changes rather than creates them. These changes are driven by the major (bio)geochemical cycles.

##### 11.2.5.5.1 Release of arsenic at high pH

High arsenic concentrations can develop in groundwaters as As(V) is released from oxide minerals and clays at high pH. High pH conditions frequently develop in arid areas as a result of extensive mineral weathering with proton uptake. This is especially true in environments dominated by sodium rather than by calcium, as  $\text{CaCO}_3$  minerals restrict the development of high pHs.

##### 11.2.5.5.2 Release of arsenic on reduction

Flooding of soils generates anaerobic conditions and can lead to the rapid release of arsenic (and phosphate) to the soil solution ([Deuel and Swoboda, 1972](#); [Reynolds et al., 1999](#)). Similarly, arsenic can be released to pore water in buried sediments. The concentration of dissolved arsenic in some north Atlantic pore waters varies inversely with the concentration of easily leachable arsenic in the solid phase and directly with increasing concentrations of solid phase Fe(II) ([Sullivan and Aller, 1996](#)). This reflects a strong redox coupling between arsenic and iron whereby oxidized arsenic is associated with iron oxides in surface sediments and is subsequently reduced and released into pore water with burial. Upward diffusion and reworking of sediment releases the dissolved arsenic to the water column or releases it for readsorption in surface sediments as HFO is formed ([Petersen et al., 1995](#)). Some reducing, iron-rich aquifers also contain high concentrations of arsenic ([Korte, 1991](#)), but there are also many iron-rich groundwaters with low arsenic concentrations.

#### 11.2.5.6 Case Studies

##### 11.2.5.6.1 The Bengal Basin, Bangladesh, and India

In terms of the number of people at risk, the high-arsenic groundwaters from the alluvial and deltaic aquifers of Bangladesh and West Bengal represent the most serious threat to public health from arsenic yet identified. Health problems from this source were first identified in West Bengal in the 1980s but remained unrecognized in Bangladesh until 1993. In fact, the scale of this disaster in Bangladesh is greater than any such previous incident, including the accidents at Bhopal, India, in 1984, and Chernobyl, Ukraine, in 1986 ([Smith et al.,](#)

2000). Concentrations of arsenic in groundwaters from the affected areas have a very large range from  $<0.5$  to  $>3200 \mu\text{g l}^{-1}$

(Kinniburgh et al., 2003). In a survey of Bangladesh groundwater by BGS and DPHE (2001), 27% of shallow ( $<150$  m) tubewells in Bangladesh were found to contain more than the national standard of  $50 \mu\text{g l}^{-1}$

for arsenic in drinking water.

Groundwater surveys indicate that the worst-affected area is in southeast Bangladesh (Figure 5) where more than 60% of the wells in some districts are affected. It is estimated that approximately 30–35 million people in Bangladesh and 6 million in West Bengal are at risk from arsenic concentrations of more than  $50 \mu\text{g l}^{-1}$  in their drinking water (BGS and DPHE, 2001). A study of the data collected by the DPHE–UNICEF (Bangladesh Department of Public Health Engineering–United Nations International Children’s Emergency Fund) arsenic mitigation programme found a prevalence rate of arsenicosis (keratosis, melanosis, and depigmentation) of 0.78 per 1000 people exposed to arsenic levels above  $50 \mu\text{g l}^{-1}$  in 15 heavily affected administrative units in Bangladesh (Rosenboom et al., 2004). The authors state that the data were difficult to interpret as the exposure period has been relatively short and the prevalence rate could increase (Howard et al., 2006). Drinking water is widely accepted as the main exposure route; however, recent studies have reported that rice can be a significant route of exposure to arsenic (Kile et al., 2007; Meharg et al., 2009; Mondal and Polya, 2008), which can be more important than drinking water in the Midnapur area of West Bengal (Mondal et al., 2010).

The affected aquifers of the Bengal Basin are generally shallow (less than 100–150 m deep) and consist mainly of Holocene micaceous sands, silts, and clays associated with the Ganges, Brahmaputra, and Meghna river systems. In West Bengal, the area east of the Hoogli River is affected. The sediments are derived from the Himalayan highlands and Precambrian basement complexes in northern and western West Bengal. In most of the areas with high-arsenic groundwater, alluvial and deltaic aquifer sediments are covered by surface horizons of fine-grained overbank deposits. These restrict the entry of air to underlying aquifers and together with the presence of reducing agents such as organic matter facilitate the development of strongly reducing conditions in the affected aquifers. Mobilization of arsenic probably reflects a complex combination of redox changes in the aquifers, resulting from the rapid burial of the alluvial and deltaic sediments, reduction of the solid-phase arsenic to As(III), desorption of arsenic from iron oxides, reductive dissolution of the oxides, and changes in iron oxide structure and surface properties in the ambient reducing conditions (BGS and DPHE, 2001). Some researchers have also suggested that, in parts of Bangladesh at least, enhanced groundwater flow and redox changes may have been imposed on the shallow aquifer as a result of recent irrigation pumping (Harvey et al., 2002).

Deep tubewells ( $>150$ – $200$  m), mainly from the southern coastal region, and wells in older Plio–Pleistocene sediments from the Barind and Madhupur Tracts of northern Bangladesh almost invariably have arsenic concentrations of less than  $5 \mu\text{g l}^{-1}$  and usually less than  $0.5 \mu\text{g l}^{-1}$  (BGS and DPHE, 2001). It is fortunate that in Calcutta and Dhaka people draw their water from these older sediments and do not face the problem of high arsenic concentrations in drinking water. Dhaka is sited at the southern tip of the Madhupur Tract (Figure 5). Shallow open dug wells also generally have low arsenic concentrations, usually  $<10 \mu\text{g l}^{-1}$  (BGS and DPHE, 2001).

The high-arsenic groundwaters of the Bengal Basin typically have near-neutral pH values and are strongly reducing with measured redox potentials usually less than 100 mV (BGS and DPHE, 2001). The source of the organic C responsible for the reducing conditions has been variously attributed to dispersed

sediment C (BGS and DPHE, 2001), peat (McArthur et al., 2001), or soluble C brought down by a combination of surface pollution and irrigation (Harvey et al., 2002). High concentrations of iron ( $>0.2$  mg l<sup>-1</sup>), manganese ( $>0.5$  mg l<sup>-1</sup>), bicarbonate ( $>500$  mg l<sup>-1</sup>), ammonium ( $>1$  mg l<sup>-1</sup>), and phosphorus ( $>0.5$  mg l<sup>-1</sup>) and low concentrations of nitrate ( $<0.5$  mg l<sup>-1</sup>) and sulfate ( $<1$  mg l<sup>-1</sup>) are also typical of the high-arsenic areas. Some Bangladesh groundwaters are so reducing that methane production has been observed (Ahmed et al., 1998; Harvey et al., 2002). Positive correlations between arsenic and iron in the groundwaters have been reported in some studies at the local scale (e.g., Nag et al., 1996), although the correlations are generally poor on a national scale (Kinniburgh et al., 2003). As(III) typically dominates the dissolved arsenic load, although As(III)/As(V) ratios are variable (BGS and DPHE, 2001). The arsenic-affected groundwaters in the Bengal Basin are associated with alluvial and deltaic sediments with total arsenic concentrations in the range  $<2$ – $20$  mg kg<sup>-1</sup>. These values are close to world average concentrations for such sediments. However, even though the arsenic concentrations are low, there is a significant variation both regionally and locally and the sediment iron and arsenic concentrations appear to be indicators of the concentration of dissolved arsenic (BGS and DPHE, 2001). The mineral source or sources of the arsenic are still not well established. Various researchers have postulated the most likely mineral sources as iron oxides (BGS and DPHE, 2001; Bhattacharya et al., 1997; Nickson et al., 1998), but pyrite or arsenopyrite (Das et al., 1996) and phyllosilicates (Foster et al., 2000) have also been cited as possible sources. High-arsenic groundwaters tend to be associated with relatively arsenic-rich and iron-rich sediments. The solid–solution mass transfers involved are so small that it is difficult to identify, or even eliminate, any particular sources using mass balance considerations alone.

The reasons for the differing arsenic concentrations in the shallow and deep groundwaters of the Bengal Basin are not yet completely understood. They could reflect differing absolute arsenic concentrations in the aquifer sediments, differing oxidation states, or differences in the arsenic-binding properties of the sediments. The history of groundwater movement and aquifer flushing in the Bengal Basin may also have contributed to the differences. Older, deeper sediments will have been subjected to longer periods of groundwater flow, aided by greater hydraulic heads during the Pleistocene period when glacial sea levels were regionally up to 130 m lower than today (Umitsu, 1993). These will therefore have undergone a greater degree of flushing and removal of labile solutes than Holocene sediments at shallower depths.

Isotopic evidence suggests that groundwater in some parts of the Bengal Basin has had a variable residence time. At a site in western Bangladesh (Chapai Nawabganj), tritium was found to be present at 2.5–5.9 TU (tritium units) in two shallow piezometer samples (10 m or less), indicating that they contained an appreciable component of post-1960s recharge (Smedley et al., 2001b). At this site and two others in south and central Bangladesh (Lakshmipur and Faridpur, respectively), groundwater from piezometers between 10 and 30 m depth had tritium concentrations ranging between 0.1 and 9.6 TU, indicating a variable proportion of post-1960s recharge. Some of the low-tritium wells contained high arsenic concentrations suggesting that the arsenic was released before the 1960s; that is, before the recent rapid increase in groundwater abstraction for irrigation and water supply. Groundwater from piezometers at 150 m depth in central and south Bangladesh contained  $<1$  TU, also indicating pre-1960s water. Radiocarbon dating has a longer time frame than tritium and provides evidence for water with ages on the scale of hundreds of years or more. Radiocarbon dating of groundwater sampled from the above piezometers in the 10–40 m depth range typically contained 65–90 percent modern carbon (pmc) while below 150 m the groundwater contained 51 pmc or less (Smedley et al., 2001b). The lowest

observed  $^{14}\text{C}$  activities were in water from deep (>150 m) piezometers in southern Bangladesh. Here, activities of 28 pmc or less suggested the presence of paleowaters with ages of the order of 2000–12000 years.

Taken together with the tritium data, these results indicated that water below 31 m or so tended to have ages between 50–2000 years. Broadly similar results and conclusions were reported by Aggarwal (2000). However, Harvey et al. (2002) drew the opposite conclusion from data from their field site just south of Dhaka. They found that a water sample from 19 m depth contained dissolved inorganic carbon (DIC) with a  $^{14}\text{C}$  composition at bomb concentrations and was therefore less than 50 years old. This sample contained about  $200\ \mu\text{g l}^{-1}$  arsenic and they postulated that the rapid expansion of pumping for irrigation water has led to an enhanced inflow of organic carbon and that this has either produced enhanced reduction and release of arsenic or displacement of arsenic by carbonate. However, a sample from 31 m depth that had a lower  $^{14}\text{C}$  DIC activity and an estimated age of 700 years also contained a high arsenic concentration (about  $300\ \mu\text{g l}^{-1}$ ). This predates modern irrigation activity. Whether, in general, irrigation has had a major impact on arsenic mobilization in the Bengal aquifers is a matter of current debate.

#### 11.2.5.6.2 Chaco-Pampean Plain, Argentina

The Chaco-Pampean Plain of central Argentina covers around 1 million  $\text{km}^2$  and constitutes one of the largest regions of high-arsenic groundwaters known. High concentrations of arsenic have been documented from Córdoba, La Pampa, Santa Fe, Buenos Aires, and Tucumán provinces. Symptoms typical of chronic arsenic poisoning, including skin lesions and some internal cancers, have been recorded in these areas (Hopenhayn-Rich et al., 1996). The climate is temperate with increasing aridity toward the west. The high-arsenic groundwaters are from Quaternary deposits of loess (mainly silt) with intermixed rhyolitic or dacitic volcanic ash (Nicolli et al., 1989; Smedley et al., 2002), often situated in closed basins. The sediments display abundant evidence of postdepositional diagenetic changes under semiarid conditions, with common occurrences of calcrete.

Many investigations of groundwater quality have identified variable and often extremely high arsenic concentrations. Nicolli et al. (1989) found arsenic concentrations in groundwaters from Córdoba in the range of 6–11500  $\mu\text{g l}^{-1}$  (median 255  $\mu\text{g l}^{-1}$ ). Smedley et al. (2002) found concentrations for groundwaters in La Pampa Province in the range of <4–5280  $\mu\text{g l}^{-1}$  (median 145  $\mu\text{g l}^{-1}$ ), and Nicolli et al. (2001) found concentrations in groundwaters from Tucumán province in the range of 12–1660  $\mu\text{g l}^{-1}$  (median 46  $\mu\text{g l}^{-1}$ ). A map showing the distribution of arsenic in groundwaters from northern La Pampa is given in Figure 6.

The geochemistry of the high-arsenic groundwaters of the Chaco-Pampean Plain is quite distinct from that of the deltaic areas typified by the Bengal Basin. The Argentine groundwaters often have high salinity and the arsenic concentrations are generally highly correlated with other anionic and oxyanionic species such as fluorine, vanadium,  $\text{HCO}_3^-$ , boron, and molybdenum.

The WHO guideline value for fluorine in drinking water (1.5  $\text{mg l}^{-1}$ ), as well as that for arsenic, boron, and uranium, is exceeded in many areas. Arsenic is predominantly present as As(V) (Smedley et al., 2002). The groundwaters are also predominantly oxidizing with low dissolved iron and manganese concentrations. There is no indication of reductive dissolution of iron oxides or pyrite oxidation. Under arid conditions, silicate and carbonate weathering reactions are pronounced and the groundwaters often have high pH values. Smedley et al. (2002) found pH values typically of 7.0–8.7. While the reasons for these high arsenic concentrations are unclear, metal oxides in the sediments (especially iron and manganese oxides and hydroxides) are thought to be the main source of dissolved arsenic, although the direct dissolution of volcanic glass has also been cited as a potential source

(Nicolli et al., 1989). The arsenic is believed to be desorbed under high pH conditions (Smedley et al., 2002). A change in the surface chemistry of the iron oxides during early diagenesis may also be an important factor in arsenic desorption.

The released arsenic tends to accumulate where natural groundwater movement is slow, especially in low-lying discharge areas. Evaporative concentration is also a factor, but the lack of correlation between arsenic and chlorine concentrations in the groundwaters suggests that it is not the dominant control (Smedley et al., 2002).

#### 11.2.5.6.3 Eastern Wisconsin, USA

The analysis of some 31350 groundwaters throughout the United States indicates that about 10% exceed the current  $10 \mu\text{g l}^{-1}$  drinking water MCL (Welch et al., 2000). At a broad regional scale (Figure 7), arsenic concentrations exceeding  $10 \mu\text{g l}^{-1}$  are more frequently observed in the western United States than in the east. The Mississippi delta shows a locally high pattern but is not exceptional, when viewed nationally. Arsenic concentrations in groundwater from the Appalachian Highlands and the Atlantic Plain are generally very low ( $<1 \mu\text{g l}^{-1}$ ). Concentrations are somewhat greater in the Interior Plains and the Rocky Mountains and within the last decade, areas in New England, Michigan, Minnesota, South Dakota, Oklahoma, and Wisconsin have been shown to have groundwaters with arsenic concentrations exceeding  $10 \mu\text{g l}^{-1}$ , sometimes appreciably so. Eastern Wisconsin is one such area. The St. Peter Sandstone (Ordovician) aquifer of eastern Wisconsin (Brown, Outagamie, Winnebago Counties) is a locally important source of water for private supplies. Arsenic contamination was first identified at two locations in 1987 and subsequent investigations showed that 18 out of 76 sources (24%) in Brown County, 45 out of 1116 sources (4.0%) in Outagamie County, and 23 out of 827 sources (2.8%) in Winnebago County exceeded the then current MCL for arsenic of  $50 \mu\text{g l}^{-1}$  (Burkel and Stoll, 1999). The highest arsenic concentration found was  $1200 \mu\text{g l}^{-1}$ . A depth profile in one of the affected wells showed that most of the groundwater was slightly acidic (pH 5.2–6.6) and in some places very acidic (pH $<4$ ). There were also high concentrations of iron, cadmium, zinc, manganese, copper, and sulfate, and it was concluded that the arsenic and other elements were released following the oxidation of sulfide minerals (pyrite and marcasite) present in a cement horizon at the boundary of the Ordovician Sinipee Group and the underlying unit, either the St. Peter Sandstone or the Prairie du Chien Group depending on the location. The low pH values are consistent with iron sulfide mineral oxidation.

Subsequent detailed studies in the Fox River valley towns of Algoma and Hobart confirmed the importance of the sulfiderich cement horizon as a probable source of the arsenic (Schreiber et al., 2000) (Figure 8). In the town of Algoma, one well contained  $12000 \mu\text{g l}^{-1}$  arsenic. There was, however, much apparently random spatial variation. Two wells close to the high-arsenic well contained much lower arsenic concentrations ( $12$  and  $34 \mu\text{g l}^{-1}$ ). The highest arsenic concentration found in wells from the town of Hobart was  $790 \mu\text{g l}^{-1}$ . Oxidation of sulfide minerals appears to have been promoted by groundwater abstraction, which has led to the lowering of the piezometric surface at a rate of around  $0.6 \text{ m year}^{-1}$  since the 1950s, leading to partial dewatering of the confined aquifer. The high arsenic concentrations occur where the piezometric surface intersects, or lies close to, the sulfide cement horizon (Schreiber et al., 2000).

### 11.2.6 Abundance and Forms of Selenium in the Natural Environment

#### 11.2.6.1 Abundance in Rocks, Soils, and Sediments

The average crustal abundance of selenium is  $0.05 \text{ mg kg}^{-1}$  (Jacobs, 1989) and like arsenic, selenium is strongly chalcophile and is partitioned into sulfides and rare selenides, such as

crooksite and clausthalite. Selenium generally substitutes for sulfur in sulfide minerals but elemental (native) selenium has also been reported (Alloway, 1995; Davies, 1980; Tokunaga et al., 1996).

Selenium concentrations in coal and other organic-rich deposits can be high and typically range from 1 to 20 mg kg<sup>-1</sup>.

The average selenium concentration in coals from the United States is 4.1 mg kg<sup>-1</sup> (Swanson et al., 1976). Large concentrations of selenium, like arsenic, are often associated with the clay fraction of sediments because of the abundance of free iron oxides and other strong sorbents. The main source to humans is thought to be from bedrock, which affects soil concentrations and availability for plant uptake (Fordyce, 2005). Intrusive igneous and volcanic rocks generally have low concentrations, although the ash and gases from volcanic activity can contain high concentrations (Fergusson, 1990). Selenium concentrations are generally larger in shales than in limestones or sandstones (Neal, 1995) (Table 7). Selenium concentrations of over 600 mg kg<sup>-1</sup> are found in some black shales. Selenium is present in these shales as organoselenium compounds or adsorbed species (Jacobs, 1989). Concentrations exceeding 300 mg selenium per kilogram have also been reported in some phosphatic rocks (Jacobs, 1989). In an area with diverse geology, it is likely that the geographical distribution of selenium will be quite variable due to the occurrence of different rock types or sulfide mineral deposits (Johnson et al., 2010).

There are no selenium mines, but selenium is produced as a by-product of refining other metals such as lead or copper and from sulfuric acid manufacture (Johnson et al., 2010). Soil is a fundamental control on selenium concentrations in the food chain and is a major control of the selenium status of crops and livestock (Fordyce, 2005). Except where there is contamination, there is generally a strong correlation between the selenium content of rocks and the sediments and soils derived from them. Soil selenium concentrations are typically in the range of 0.01–2 mg kg<sup>-1</sup> with a world average of 0.4 mg kg<sup>-1</sup> (Fergusson, 1990; Fordyce, 2005). The selenium concentration in soils rarely exceeds 0.1 mg kg<sup>-1</sup> (Moreno Rodriguez et al., 2005). The geographical distribution of selenium in soils is, however, extremely varied (Wang and Gao, 2001). Extremely high concentrations (up to 1200 mg kg<sup>-1</sup>) have been found in some organic-rich soils derived from black shales in Ireland (Table 8). Soils from England derived from black shales had an average concentration of 3.1 mg kg<sup>-1</sup> compared with an overall average of 0.48 mg kg<sup>-1</sup> for a range of more typical English soils (Thornton et al., 1983). Concentrations of 6–15 mg kg<sup>-1</sup> have been reported in volcanic soils such as those of Hawaii (Jacobs, 1989). High concentrations tend to be found in soils from mineralized areas and in poorly drained soils.

The median selenium concentration in stream sediments from 20 study areas across the United States was 0.7 mg kg<sup>-1</sup> (Rice, 1999) and 0.5 mg kg<sup>-1</sup> in 19000 stream sediments in Wales (BGS, 1978–2006). Selenium levels in sediments of the Lewis and Clark Lake near the Missouri River are in the range of 0.012–9.62 mg kg<sup>-1</sup>, far higher than the toxic-effect threshold of 2 mg kg<sup>-1</sup>. The selenium is thought to be derived from the erosion of shale bluffs containing high levels of the element (Johnson et al., 2010; Lemly, 2002; Pracheil et al., 2010).

Relatively low selenium concentrations are found in well-drained soils derived from limestones and coarse sands.

Selenium-rich vegetation, including the selenium-indicating vetches (*Astragalus* sp.), is widespread in South Dakota and Wyoming, USA. It grows on soils developed over black shales and sandstones with high selenium concentrations (Moxon, 1937). Tuffs are also a source of high Se soils in these areas of the United States. Selenium toxicity was first documented in 1856 near Fort Randall, where a physician in the US Cavalry reported horses experiencing hair, mane, and tail loss and sloughing of hooves. Forage that contains 2–5 mg kg<sup>-1</sup> selenium poses a marginal threat to livestock, and acute effects are likely to occur above 5 mg



selenium per kilogram.

Although geology is the primary control on the selenium concentration of soil, the bioavailability of selenium to plants and animals is determined by other factors including pH and redox conditions, speciation, soil texture and mineralogy, organic matter content, and the presence of competing ions (Fordyce, 2005). Even soils with relatively high total selenium concentrations can give rise to selenium deficiency if the selenium is not bioavailable. The first map of the selenium status of soil and vegetation in relation to animal deficiency and toxicity was prepared by Muth and Alloway (1963).

Several techniques are available to assess selenium bioavailability in soils but the most widely used is the water-soluble concentration (Fordyce et al., 2000b; Jacobs, 1989; Tan, 1989).

In most soils, only a small proportion of the total selenium is dissolved in solution (0.3–7%) and water-soluble selenium contents are generally  $<0.1 \text{ mg kg}^{-1}$  (Table 8).

Selenium is also added to soils as a trace constituent of phosphate fertilizers and in selenium-containing pesticides and fungicides, as well as by the application of sewage sludge and manure (Alloway, 1995; Frankenberger and Benson, 1994; Jacobs, 1989; see Chapter 11.15). Sewage sludge typically contains about 1 mg selenium per kilogram dry weight. Precautionary limits are set for several chemical elements likely to be increased by the application of sewage sludge to land. In the European Union (EU), for example, the banning of the discharge of sewage sludge into the sea since 1999 has increased its application to land. The maximum admissible concentration of selenium in sewage sludge in the United Kingdom is  $25 \text{ mg kg}^{-1}$ , and in soil after application is  $3 \text{ mg kg}^{-1}$  in the United Kingdom and  $10 \text{ mg kg}^{-1}$  in France and Germany (Fordyce 2005; ICRCCL, 1987; Reimann and Caritat, 1998). In the United States, the limit is  $100 \text{ mg kg}^{-1}$ .

#### 11.2.6.2 National and International Standards in Drinking Water

The WHO guideline value for selenium in drinking water is currently  $40 \mu\text{g l}^{-1}$ . The standard adopted by the EC, Australia, Japan, and Canada is  $10 \mu\text{g l}^{-1}$ . The US EPA primary drinking water standard is  $50 \mu\text{g l}^{-1}$ . In California, the MCL for selenium is also  $50 \mu\text{g l}^{-1}$ , but a public health goal of  $30 \mu\text{g l}^{-1}$  for water-soluble and bioavailable selenium compounds in drinking water has been set (California Environmental Protection Agency, 2010).

#### 11.2.6.3 Abundance and Distribution in Natural Waters

The selenium concentration in most natural waters is very low, often less than  $1 \mu\text{g l}^{-1}$  and frequently just a few nanograms per liter. Typical levels of selenium in groundwater and surface water range from 0.00006 to  $0.400 \text{ mg l}^{-1}$ , with some areas having as much as  $6 \text{ mg l}^{-1}$  (Fordyce, 2005; WHO, 1996, 2011). Hence, selenium from drinking water only constitutes a health hazard in exceptional circumstances (Fordyce et al., 2000a; Vinceti et al., 2000). However, occasionally, much greater concentrations are found. Groundwaters containing up to  $275 \mu\text{g l}^{-1}$  have been reported from aquifers in China and  $1000 \mu\text{g l}^{-1}$  selenium from seleniferous aquifers in Montana, USA (Table 9). Selenium concentrations of up to  $2000 \mu\text{g l}^{-1}$  or more have also been reported in lakes from saline, seleniferous areas. Such areas are rare but include some arid parts of the United States, China, Pakistan, and Venezuela. In general, data on selenium concentrations in water are scarce. The mining and processing of gold, base metal, and coal deposits can be an important source of selenium. For example, contamination of the Chayanta River by mine water leached from the nearby Potosi mine in Bolivia resulted in water concentrations of 0.005–0.020  $\text{mg l}^{-1}$  selenium, which exceed the guideline value for freshwater aquatic organisms ( $0.001 \text{ mg l}^{-1}$ ) (Rojas and Vandecasteele, 2007). Reported ranges from the literature are summarized in Table 9.

Waters containing 10–25  $\mu\text{g l}^{-1}$  selenium may have a garlic odor, while waters containing 100–200  $\mu\text{g l}^{-1}$  have an unpleasant taste. Groundwaters generally contain higher

selenium concentrations than surface waters because of more extensive water–rock interactions (Frankenberger and Benson, 1994; Jacobs, 1989).

#### 11.2.6.3.1 Atmospheric precipitation

Selenium in rainfall is derived principally from earth-surface volatilization, volcanic sources, fossil-fuel combustion (especially coal), and the incineration of municipal wastes. Few determinations of selenium in atmospheric precipitation have been reported, but concentrations are usually very low. Hashimoto and Winchester (1967) found concentrations in the range 0.04–1.4  $\mu\text{g l}^{-1}$  (Table 9).

#### 11.2.6.3.2 River and lake water

Selenate (Se(VI)) is only weakly adsorbed by oxides and clays at near-neutral pH. Hence, oxidation of Se(IV) to Se(VI) enhances selenium mobility and persistence in natural waters (see Chapter 7.7). High concentrations of selenate can occur in agricultural drainage waters in arid areas. Seleniferous soils, especially those derived from black shales, are common in central and western United States and irrigation can give rise to concentrations of selenate of several hundred micrograms per liter in drainage water. In water, it exists as selenic and selenious acids (Barceloux, 1999). Further concentration can occur in lakes by evapotranspiration. Well-documented cases of such situations include California (Kesterson Reservoir, Richmond Marsh, Tulare Basin, and Salton Sea), North Carolina (Belews Lake and Hyco Reservoir), Texas (Martin Reservoir), and Wyoming (Kendrick Reclamation Project) in the United States. Problems of selenium toxicity are also found in other semiarid areas. In the Soan-Sakesar Valley of Punjab, Pakistan, average selenium concentrations were 302  $\mu\text{g l}^{-1}$  ( $n=13$ ) in streams and springs and 297–2100  $\mu\text{g l}^{-1}$  in lake water (three lakes) (Afzal et al., 2000). The highest concentrations were reported from low-lying, salinized areas.

The Colorado River catchment, Utah, USA, is also a seleniferous area. Median selenium concentrations in the Colorado River and its major tributaries are in the range of 1–4  $\mu\text{g l}^{-1}$  (Engberg, 1999), although values up to 400  $\mu\text{g l}^{-1}$  have been reported (NAS, 1976). Water samples from the Republican River Basin of Colorado in the United States indicated that nine sites contained concentrations above 0.005 mg  $\text{l}^{-1}$  selenium, which is considered a high hazard for selenium accumulation in the planktonic food chain (May et al., 2001).

Irrigation is believed to have been responsible for about 70% of the selenium reaching Lake Powell (Engberg, 1999). Selenium concentrations in the Cienega de Santa Clara wetlands on the east side of the Colorado River delta, Mexico, are also in the range of 5–19  $\mu\text{g l}^{-1}$  (García-Hernández et al., 2000).

However, high selenium concentrations do not occur in all rivers in arid areas. For example, concentrations in the Jordan River average only 0.25  $\mu\text{g l}^{-1}$  (Nishri et al., 1999). Selenium concentrations in surface waters may be increased locally near sources of waste, including sewage effluent.

#### 11.2.6.3.3 Seawater and estuaries

The main natural flux for selenium is via the marine system. Despite this, selenium concentrations in estuarine water and seawater are generally low. An average concentration of 0.17  $\mu\text{g l}^{-1}$  was estimated for seawater by Thomson et al. (2001). Dissolved concentrations in the range of 0.1–0.2  $\mu\text{g l}^{-1}$  have been reported in San Francisco Bay (Cutter, 1989). Zawislanski et al. (2001b) reported concentrations of 0.07–0.35  $\mu\text{g l}^{-1}$  in the nearby Carquinez Strait. Much of the selenium is thought to have been derived from industrial sources, including historical releases from oil refineries. During low-flow conditions, oil refineries contribute up to 75% of the total selenium load entering San Francisco Bay. Refineries processing oil derived from the neighboring San Joaquin Valley, California, produce effluent-containing selenium concentrations an order of magnitude greater than those in refinery effluent from Alaskan North Slope crude oil (Zawislanski and Zavarin, 1996).

#### 11.2.6.3.4 Groundwater

As in the case of surface waters, the concentrations of selenium

in groundwater are usually low and commonly below analytical detection limits (see [Chapter 11.10](#)). Concentrations tend to be higher in oxidizing groundwaters because the dominant form present, Se(VI), is less prone to adsorption by metal oxides than Se(IV). Elemental selenium is also unstable under oxidizing conditions. High selenium concentrations have been found under oxidizing conditions in groundwaters in some arid and semiarid areas as a result of evaporation. Extremely high concentrations (up to 1300  $\mu\text{g l}^{-1}$ ) have been reported from shallow wells in the upper reaches of the Colorado River catchment, Utah ([Engberg, 1999](#)).

[Deverel and Fujii \(1988\)](#) also reported concentrations in the range of <1–2000  $\mu\text{g l}^{-1}$  ([Table 9](#)) in shallow groundwater from Coast Range alluvial fan sediments near Kesterson Reservoir, California. Concentrations of <20  $\mu\text{g l}^{-1}$  were found in the middle fan deposits, but reached several hundreds of micrograms per liter in the lower fan deposits. Concentrations increased with groundwater salinity, probably as a result of leaching of soil salts by irrigation and subsequent evaporation. [Deverel and Fujii \(1988\)](#) found low concentrations of selenium in groundwater from the eastern side of the San Joaquin valley in alluvial sediments of the Sierra Nevada Formation. Values were generally less than 1  $\mu\text{g l}^{-1}$ , probably as a result of reducing conditions in which selenium occurred in less mobile forms, notably Se(IV).

Selenium-rich groundwaters are also found in the semiarid regions of Argentina ([Table 9](#)). [Nicolli et al. \(1989\)](#) found concentrations up to 24  $\mu\text{g l}^{-1}$  in oxidizing groundwater from Córdoba province. Concentrations were correlated positively with salinity. [Smedley et al. \(2002\)](#) also found selenium concentrations in the range of <2–40  $\mu\text{g l}^{-1}$  (n=34) in oxidizing groundwaters from the neighboring province of La Pampa, with the highest concentrations in high-salinity shallow groundwaters in which selenium was concentrated by evaporation. No speciation studies were carried out, although selenate is likely to dominate. None of the groundwater samples in the [Smedley et al. \(2002\)](#) study exceeded the WHO guideline value of 40  $\mu\text{g l}^{-1}$  for selenium in drinking water.

In the Soan-Sakesar Valley of Punjab, Pakistan, the average selenium concentration in groundwater was 62  $\mu\text{g l}^{-1}$  (n=29) ([Afzal et al., 2000](#)). Again there was a positive correlation between salinity and selenium concentration. Most of the selenium in the groundwater was present as Se(VI).

Selenium concentrations in reducing groundwaters are very low or undetectable as a result of reduction to Se(IV). Concentrations in samples of the strongly reducing high-arsenic groundwaters of Bangladesh were <0.5  $\mu\text{g l}^{-1}$  ([BGS and DPHE, 2001](#)). In the Triassic Sandstone aquifer of the English East Midlands, selenium concentrations varied from less than 0.06 to 0.86  $\mu\text{g l}^{-1}$  ([Table 9](#)). Concentrations were highest in the unconfined oxidizing part of the sandstone aquifer and fell abruptly to less than 0.06  $\mu\text{g l}^{-1}$  at and beyond the redox boundary ([Smedley and Edmunds, 2002](#)).

#### 11.2.6.3.5 Sediment pore water

Few data are available for the selenium content of pore waters. However, [Peters et al. \(1999\)](#) reported concentrations of up to 5  $\mu\text{g l}^{-1}$  in estuarine pore waters from Mannering Bay (Lake Macquarie), New South Wales, Australia. Investigations followed concerns during the 1990s about high selenium concentrations in marine organisms from the area. Concentrations were highest in the upper 5 mm of the profile and were substantially higher throughout the profile than from nearby Nord's Wharf where concentrations were typically <0.2  $\mu\text{g l}^{-1}$  selenium (i.e., below the detection limit). Although redox controls influenced the trends with depth, the high selenium concentrations in the uppermost sediments were thought to reflect contamination from smelter and power station inputs.

#### 11.2.6.3.6 Mine drainage

Since selenium substitutes for sulfur in the structure of sulfide minerals, drainage from mineralized and mined areas may have high dissolved selenium concentrations (see

Chapter 11.5). Acid seeps derived from oxidation of sulfide minerals draining the Moreno Shale in the Coast Ranges, USA, have selenium concentrations up to 420  $\mu\text{g l}^{-1}$  with concentrations of aluminum, manganese, zinc, and nickel in the milligram per liter range (Presser, 1994).

#### 11.2.6.4 Selenium Species in Water, Sediment, and Soil

The behavior of selenium in the environment is similar in many respects to that of arsenic. Importantly, it also occurs naturally in several oxidation states and is therefore redox sensitive. Methylation and hydride formation are important, and sulfur and iron compounds play an important role in the cycling of selenium. Microbiological volatilization of organic selenium, particularly dimethylselenide, is known to be an important factor in the loss of selenium from some selenium-rich soils and waters (Frankenberger and Arshad, 2001; Oremland, 1994; Wu, 2004). Phytoplankton can also promote the production of gaseous selenium compounds in the marine environment (Amouroux et al., 2001).

Selenium occurs in natural waters principally in two oxidation states, Se(IV) and Se(VI). Elemental selenium, Se(0) (red and black forms), and selenide, Se(-II), are essentially insoluble in water and so selenate and selenite are the dominant aqueous forms.  $\text{SeO}_6^{VI+O_4^{2-}}$

occurs mainly in oxidizing waters

while  $\text{HSe(IV)O}_3^-$  and  $\text{Se(IV)O}_3^{2-}$

dominate under reducing

conditions (Figure 9). The concentration ratio of Se(IV) to Se(VI) species in natural waters does not necessarily follow that of other redox couples (e.g.,  $\text{Fe}^{2+}/\text{Fe}^{3+}$ ). This reflects the slow kinetics involved (White and Dubrovsky, 1994).

Elemental selenium, selenides, and selenium sulfide salts are stable only in reducing acidic conditions and are largely unavailable to plants and animals. Zawislanski et al. (2001b) found a strong positive correlation between selenium and organic carbon in suspended particulate matter from San Francisco Bay, possibly reflecting reduction of selenium by organic matter. Strong positive correlations of particulate selenium with particulate iron and aluminum were also noted. The oxidation and reduction of selenium is related to microbial activity. For example, the bacterium *Bacillus megaterium* can oxidize elemental selenium to selenite.

It has been estimated that up to 50% of the selenium in some soils may be present as organic compounds, although few such compounds have been isolated and identified (Jacobs, 1989). In acidic and neutral soils, inorganic selenium occurs as insoluble Se(IV) compounds, and in neutral and alkaline soils as soluble and hence more bioavailable Se(VI) compounds (Allaway, 1968). Se(IV) is adsorbed on to soil particle surfaces with a greater affinity than Se(VI) (Johnson et al., 2000). Selenomethionine has been extracted from soils and is 2–4 times more bioavailable to plants than inorganic selenite, although selenocysteine is less bioavailable than selenomethionine (Allaway, 1995; Davies, 1980; Frankenberger and Benson, 1994; Jacobs, 1989). The bioavailability of the different selenium species in soils can be summarized as: selenate > selenomethionine > selenocysteine > selenite > selenium metal

In general, selenate is more available and more mobile than selenite in the environment, so selenium is much more bioavailable under oxidizing alkaline conditions.

An Eh–pH diagram for the system Se–O–S is given in Figure 10 as a guide but, as in the case of arsenic, it is necessarily an oversimplification of a complex natural system.  $\text{Se}_2\text{S}_3$  is not shown as no thermodynamic data are available for this species. It would probably displace native selenium (black) as the dominant phase under strongly reducing sulfur-rich conditions. The stability of Fe–Se minerals and the effects of selenium adsorption by metal oxides are not represented in the diagram. Selenium is more readily reduced than arsenic. In the solid phase, elemental selenium dominates under strongly reducing conditions with the gaseous  $\text{H}_2\text{Se}$  becoming important under

acid, strongly reducing conditions. Organic selenides occur in biological materials. Some of these selenides are highly volatile. The most detailed studies of selenium distribution and speciation have been carried out for seawater. [Cutter and Cutter \(2001\)](#) found that selenate had generally higher concentrations in marine waters from the southern ( $0.019 \mu\text{g l}^{-1}$ ) than the northern hemisphere ( $0.014 \mu\text{g l}^{-1}$ ). In contrast, selenite had low concentrations in seawater from the southern hemisphere ( $0.005 \mu\text{g l}^{-1}$ ) with the highest concentrations in the equatorial region and below the Intertropical Convergence Zone ( $0.009 \mu\text{g l}^{-1}$ ). Depth profiles of total dissolved selenium, selenite, and selenate in Atlantic seawater all showed surface-water depletion and deepwater enrichment, characteristic of nutrient-like behavior. In North Atlantic Deep Water, the Se(IV)/Se(VI) ratios were generally similar to those found in the eastern Atlantic and North Pacific (0.7), but waters originating in the southern polar regions were enriched in selenate and had low Se(IV)/Se(VI) ratios (-0.4). Organic selenide was found in surface ocean waters but was not detected in mid- or deep-waters.

Selenium profiles in sediments from the northeast Atlantic Ocean indicate concentrations of around  $0.2\text{--}0.3 \text{ mg kg}^{-1}$  in the oxic zone, and typically  $0.3\text{--}0.5 \text{ mg kg}^{-1}$  below the redox boundary, reflecting immobilization under reduced conditions ([Thomson et al., 2001](#)). Similar increases for cadmium, uranium, and rhenium have also been observed in the suboxic zone. As with arsenic, microbiological processes are important in the reduction of selenium, principally through the microbial reduction of Se(IV) and Se(VI) ([Oremland et al., 1990](#)). [Oremland \(1994\)](#) found that the areal rate of dissimilatory selenium reduction in sediments from an agricultural evaporation pond in the San Joaquin Valley was about 3 times lower than for denitrification and 30 times lower than for sulfate reduction. Stable-isotope studies of water in the Tulare Lake Drainage District wetland, California, indicated little selenium isotope fractionation ([Herbel et al., 2002b](#)). This suggested that the primary source of reduced selenium was selenium assimilation by plants and algae, followed by deposition and mineralization rather than the direct bacterial reduction of Se(VI) or Se(IV).

## 11.2.7 Pathways and Behavior of Selenium in the Natural Environment

### 11.2.7.1 Release from Primary Minerals

As noted earlier, the principal natural sources of selenium in water are likely to be sulfides or metal oxides containing adsorbed selenium, especially Se(IV). Coal can be an additional primary source of selenium either directly through oxidation or indirectly via atmospheric precipitation following combustion. Selenium is readily oxidized during the weathering of minerals. Seleniferous groundwater areas such as those occurring in the United States and Pakistan are most common where underlain by selenium- and organic-rich shales that release selenium on weathering. Selenium-rich groundwaters tend to be found in semiarid areas under irrigation. Examples are central and western United States ([Deverel et al., 1994](#)) and parts of Pakistan ([Afzal et al., 2000](#)).

### 11.2.7.2 Adsorption of Selenium by Oxides and Clays

High soil organic matter, iron oxyhydroxide (HFO) and clay mineral content can all absorb or bind selenium to the soil, with the main control on selenium concentration in many soils being the organic matter content. Selenium can become concentrated in organic matter and organic-rich sediments ([Fordyce et al., 2010](#); [Shand et al., 2010](#)). In contrast to arsenic, the reduced form of selenium, Se(IV), is very strongly adsorbed by HFO. This may account in part for the very low selenium concentrations in many strongly reducing environments. Furthermore, also in contrast with arsenic, the oxidized form of selenium, Se(VI), is less strongly adsorbed to HFO than the reduced species. These differences, also reflected by other oxide-based sorbents including clays, account for the markedly

different behavior of arsenic and selenium in natural waters. The behavior of soils mirrors that of pure oxides (Goldberg, 1985). In acidic soils, selenium is likely to occur mainly as Se(IV) strongly adsorbed to iron oxides. Less commonly, Se(IV) may form highly insoluble iron compounds such as ferric selenite ( $\text{Fe}_2(\text{OH})_4\text{SeO}_3$ ) or iron selenide ( $\text{FeSe}$ ). In alkaline, oxidized, and selenium-rich soils, most of the selenium is likely to be present as Se(VI), which is very weakly adsorbed. Furthermore, there are no common insoluble selenate minerals. Hence, selenate accumulates in soluble form, particularly in arid and semiarid areas where evaporation tends to concentrate selenium along with other soluble salts (Deverel et al., 1994). The strong affinity of iron oxides for Se(IV) has been well documented (Dzombak and Morel, 1990) and calculations based on the Dzombak and Morel (1990) diffuse double-layer model and default HFO database show the principal response to pH and redox speciation changes (Figure 11). The selenate species is less strongly adsorbed by iron oxides at near-neutral pH than the selenite species (Figure 11). Clay minerals (Bar-Yosef and Meek, 1987) also adsorb Se(IV). The iron oxide and clay content of soils and sediments can affect the bioavailability of selenium markedly. The strong pH dependence of adsorption is an important control. Maximum adsorption occurs between pH 3–5 and decreases as the pH rises. Organic matter also removes selenium from soil solution, possibly as a result of the formation of organometallic complexes. Addition of phosphate to soils increases selenium uptake by plants because the  $\text{PO}_4^{3-}$  ion displaces selenite from soil particles, making it more bioavailable. Conversely, increasing the concentrations of phosphate in soils can dilute the selenium content of vegetation by inducing increased plant growth (Frankenberger and Benson, 1994; Jacobs, 1989).

#### 11.2.7.3 Selenium Transport

The transport of selenium is related strongly to its speciation. The weak adsorption of selenate by soil and aquifer materials, especially in the presence of high  $\text{SO}_4^{2-}$  concentrations, means that it is relatively unretarded by groundwater flow (Kent et al., 1995). There is also little likelihood that insoluble metal selenates, such as  $\text{CaSe(VI)O}_4 \cdot 2\text{H}_2\text{O}$ , will limit Se(VI) solubility under oxidizing conditions (White and Dubrovsky, 1994). By contrast, the strong adsorption tendency of Se(IV) and low solubility of Se(0) and Se(-II) species mean that transport of selenium is strictly limited under reducing conditions. The strong contrast in selenium mobility between reducing and oxidizing conditions means that changes in redox conditions in soils, sediments, or aquifers can result in significant changes in selenium concentrations in water and crops. For example, the accumulation of selenium in the reduced bottom-sediments of the Salton Sea, California, could be mobilized if engineered changes to transfer water out of the Salton Sea Basin lead to oxidation of the sediments (Schroeder et al., 2002). Such a process has already occurred at Kesterson Reservoir (Section 11.2.7.4.1). The change of land use, for example, from wet paddy soils to dryland agriculture, could also lead to an increase in the uptake of selenium by crops (Yang et al., 1983).

##### 11.2.7.3.1 Global fluxes

Selenium is dispersed through the environment and is cycled by biogeochemical processes involving rock weathering, rock–water interactions, and microbiological activity. Estimates of the selenium fluxes through the atmosphere, land, and oceans indicate that the anthropogenic flux now exceeds the marine flux, the principal natural pathway (Table 10).

The global flux of selenium from land to the oceans via rivers has been estimated as 15380 tonnes per year (Haygarth, 1994). The cycling of selenium from land to water is poorly understood, but approximately 85% of the selenium in rivers is thought to be in particulate rather than dissolved form.

Typical concentrations of selenium in seawater are around 0.1–0.2  $\mu\text{g l}^{-1}$  (Table 9) with an estimated mean residence time of 70 years in the mixed layer and 1100 years in the deep ocean. The oceans are therefore an important sink for

selenium (Haygarth, 1994; Jacobs, 1989). Biogenic volatilization of selenium from seawater to the atmosphere is estimated to be 5000–8000 tonnes per year. Amouroux et al. (2001) have demonstrated that biotransformation of dissolved selenium in seawater by blooms of phytoplankton in the spring is a major pathway for the emission of gaseous selenium to the atmosphere. Hence, oceans are an important part of the selenium cycle.

#### 11.2.7.3.2 Selenium fluxes in air

In air, selenium is mostly bound to particles with volatilization of selenium from volcanoes, soils, sediments, the oceans, microorganisms, plants, animals, and industrial activity, all contributing to selenium in the atmosphere. Natural background concentrations of selenium in nonvolcanic areas are only around 0.01–1 ng m<sup>-3</sup>, but the short residence time, usually a matter of weeks, makes the atmosphere a rapid transport route for selenium. Most urban air has concentrations of 0.1–10 ng m<sup>-3</sup> (WHO, 1996, 2011). Higher levels may be found in the vicinity of coal-fired thermal power stations (90 ng m<sup>-3</sup>; background level, 10 ng m<sup>-3</sup>) with selenium in an amorphous state (Giere et al., 2006; Jayasekher, 2009). For example, in the United Kingdom, soil samples collected between 1861 and 1990 by the Rothamstead Agricultural Experimental Station show that the highest concentrations of selenium were between 1940 and 1970, coinciding with a period of intensive coal use. The decline in selenium in herbage more recently is thought to reflect a switch to fuel sources such as nuclear, oil, and gas (Haygarth, 1994).

Volatilization of selenium into the atmosphere results from microbial methylation of selenium from soil, plant, and water and is affected by the availability of selenium, the presence of an adequate carbon source, oxygen availability, and temperature (Frankenberger and Benson, 1994; Jacobs, 1989).

Most gaseous selenium is thought to be in the dimethylselenide (DMSe) form and it is estimated that terrestrial biogenic sources contribute 1200 tonnes per year of selenium to the atmosphere. Atmospheric dust derived from volcanoes and wind erosion of the Earth's surface (180 tonnes per year) and suspended sea salts (550 tonnes per year) from the oceans are also significant sources of atmospheric selenium. Particle-bound selenium can be transported several thousands of kilometers before deposition. Wet deposition from rain, snow, and other types of precipitation is thought to contribute 5610 tonnes per hectare per year of selenium to the terrestrial environment. In the United Kingdom, for example, wet deposition has been shown to account for 76–93% of the total with >70% in soluble form. Near-to-point sources of selenium, for example, from industry and atmospheric deposition, can account for 33–82% of the selenium present on the leaves of plants (Frankenberger and Benson, 1994; Jacobs, 1989). A study of selenium in plant rings near a village close to coal-fired power stations burning seleniferous coal in China reported much higher concentrations than in plants collected away from the source (Liu et al., 2007).

#### 11.2.7.3.3 Soil–water–plant relationships

Despite selenium being essential for some green algae such as *Chlamydomonas*, it has not been shown to be essential for higher plants (Novoselov et al., 2002; Pilon-Smits and LeDuc, 2009). The selenium concentrations in plants generally reflect those of the soils in which they are grown. An important factor which may determine whether or not selenium-related health problems affect man and animals is the variable capacity of different plant species to accumulate selenium (Alloway, 1995; Frankenberger and Benson, 1994; Jacobs, 1989; Oldfield, 1999). Plants with >25 mg kg<sup>-1</sup> selenium may cause acute poisoning of animals, but these plants are generally distasteful and not eaten unless the animals are especially hungry (Knight and Walter, 2001).

Rosenfield and Beath (1964) classified plants into three groups based on their selenium uptake from seleniferous soils. They are: (1) selenium accumulator plants which can

contain >1000 mg kg<sup>-1</sup> selenium and grow well on high-selenium soils; (2) secondary selenium absorbers with concentrations in the range of 50–100 mg kg<sup>-1</sup>; and (3) others which include grains and grasses that can contain up to 50 mg kg<sup>-1</sup> selenium. Selenium concentrations can range from 0.005 to 5500 mg kg<sup>-1</sup> in selenium accumulators, with most plants containing less than 10 mg kg<sup>-1</sup>.

Plants that require selenium for growth are called obligate accumulators; they are capable of accumulating 10 times the amount of selenium present in soil and include *Astragalus*, *Conopsis*, *Xylorhiza*, and *Stanleya*. Plants known as facultative accumulators do not require selenium for growth, but will bind selenium in its organic forms if it is present in the soil; these plants belong to the genera *Acacia*, *Artemisia*, *Aster*, *Atriplex*, *Castilleja*, *Penstemon*, and *Grindelia* (Knight and Walter, 2001). Accumulators belonging to the plant genera *Astragalus*, *Haplopappus*, and *Stanleya* are commonly found in the semiarid seleniferous environments of the western United States and elsewhere and are used as indicators of high-selenium environments, although other species of these genera are nonaccumulators (Alloway, 1995; Jacobs, 1989).

The exclusion of selenium from the proteins of accumulator plants is thought to be the basis for their selenium tolerance with selenium metabolism based mainly on water-soluble, nonprotein forms such as selenium–methylselenomethionine (Jacobs, 1989). The ‘garlic’ odor characteristic of selenium-accumulating plants reflects the volatile organic compounds DMSe and dimethyldiselenide. Plants can suffer selenium toxicity as a result of selenium competition with essential metabolites for biochemical sites, replacement of essential ions by selenium, mainly major cations, selenate occupation of the sites of essential groups such as phosphate and nitrate, or selenium substitution in essential sulfur compounds.

Experimental evidence suggests that there is a negative correlation between very high soil selenium concentrations and plant growth. Alfalfa yields have been shown to decline when extractable selenium in soil exceeds 500 mg kg<sup>-1</sup>. Yellowing, black spots, and chlorosis of plant leaves and pink root tissue can occur (Frankenberger and Benson, 1994; Jacobs, 1989). Phytotoxicity in nature has been reported only from China, where high selenium concentrations in soil caused discoloration of maize corn-head embryos and also affected the growth and yield of wheat and pea crops, respectively (Yang et al., 1983).

In alkaline soils, selenium is often present as selenite, which is bioavailable to plants and may prevent selenium deficiency in people who eat them. The oxidation state of selenium is critical in determining its availability in the food chain. For example, in neutral to alkaline soils, Se<sup>6+</sup>(selenate) is the dominant state. This form of selenium is generally more soluble and mobile in soils and is readily available for plant uptake than selenite (Se<sup>4+</sup>), which has lower solubility and greater affinity for adsorption on soil particle surfaces (Mikkelsen et al., 1989).

Food crops generally have a low selenium tolerance but most crops have the potential to accumulate selenium in quantities toxic to animals and humans (Jacobs, 1989). In general, root crops contain the highest selenium concentrations (Table 11) with plant leaves containing a higher concentration than the tuber. For example, Yang et al. (1983) noted that selenium concentrations in vegetables (0.3–81.4 mg kg<sup>-1</sup>) were generally higher than in cereal crops (0.3–28.5 mg kg<sup>-1</sup> in rice and maize) in seleniferous regions of China. Brassicas are unable to distinguish selenium from S and so tend to accumulate selenium. Turnip leaves can have particularly high concentrations with an average of 460 mg kg<sup>-1</sup> ranging up to 25000 mg kg<sup>-1</sup> compared to an average of 12 mg kg<sup>-1</sup> in the tuber. *Boletus pinicola* and *Boletus edulis* species of edible mushroom collected in Galicia, Spain, were found to have mean selenium concentrations in the hymenophore of 74.93 and 52.7 mg kg<sup>-1</sup> dry weight, resulting in a recommendation



to consume in moderation (Melgar et al., 2009).

In moderate to low selenium environments, alfalfa (*Medicago* sp) has been shown to take up more selenium than other forage crops. Crop species grown in low-selenium soils generally show little difference in selenium uptake, so changing the type of crop grown makes little impact. An exception has been reported from New Zealand, where changing from white clover to the grass *Agrostis tenuis* increased the selenium content of fodder (Davies and Watkinson, 1966).

#### 11.2.7.4 Case Studies

##### 11.2.7.4.1 Kesterson Reservoir, USA

One of the best-documented cases of selenium toxicity in animals occurred at Kesterson Reservoir, California, USA (Jacobs, 1989; Wu et al., 2000). Soil irrigation in the western San Joaquin valley of California began in the late 1800s and accelerated particularly in the 1930s–1940s. Irrigation water was taken from both surface water and groundwater (Deverel and Fujii, 1988). During the 1970s, flow into the reservoir was mainly surface water, but over the period 1981–1986 almost all the inflow was from shallow agricultural drainage for which the reservoir acted as a set of evaporation ponds. This inflow contained 250–350  $\mu\text{g l}^{-1}$  selenium, mostly present as bioavailable selenate (Se(VI)).

The primary source of the Se is believed to have been pyrite in shales, particularly the Upper Cretaceous–Paleocene Moreno Shale and the Eocene–Oligocene Kreyenhagen Shale. Concentrations of selenium in these formations range up to 45  $\text{mg kg}^{-1}$  with median concentrations of 6.5 and 8.7  $\text{mg kg}^{-1}$ , respectively (Presser, 1994). The concentration of selenium in the surface sediments (0–0.3 m depth) of the old playas is in the range 1–20  $\text{mg kg}^{-1}$ , reflecting the historical accumulation of selenium from the selenium-rich drain water. Deeper sediments typically contain much lower selenium concentrations of 0.1–1  $\text{mg kg}^{-1}$  (Tokunaga et al., 1994).

Between 1983 and 1985, the US Wildlife Service compared the biological impact of the high selenium in the Kesterson Reservoir region to that of the adjacent Volta Wildlife area, which was supplied with water containing normal selenium concentrations. The research showed that the high concentrations of selenium in the irrigation waters were having a detrimental effect on the health of fish and wildlife (Tokunaga et al., 1994). Health effects on birds in the Kesterson Reservoir area were very marked, with 22% of eggs containing dead or deformed embryos. The developmental deformities included missing or abnormal eyes, beaks, wings, legs, and feet, as well as hydrocephaly. It has been estimated that at least 1000 adult and young birds died between 1983 and 1985 as a result of consuming plants and fish containing 12–120 times the normal amount of selenium. No overt adverse health effects were noted in reptile or mammalian species, but the concentrations of selenium present were of concern in terms of bioaccumulation through the food chain.

These findings led the US Bureau of Reclamation to halt the discharge of agricultural drainage to the reservoir. The reservoir was also dewatered and the lower parts were infilled to prevent groundwater rising to the soil surface. Bioremediation based on microbial reduction of selenite and selenate to insoluble Se(0) or methylation of these species to DMSe was used to immobilize the selenium. Field trials demonstrated that microorganisms, particularly *Enterobacter cloacae*, were effective in reducing selenium to insoluble Se(0) and that the process was stimulated by the addition of organic matter (Wu et al., 2000). The area was planted with upland grass. Biological monitoring has demonstrated that selenium concentrations in the water and vegetation at Kesterson are now much lower and largely within safe limits. By 1992, concentrations of selenium in surface pools that formed after periods of rainfall were in the range 3–13  $\mu\text{g l}^{-1}$ .

##### 11.2.7.4.2 Enshi, China

Human selenosis has been reported from Enshi district, Hubei province, China. Between 1923 and 1988, 477 cases of human

selenosis were reported, 338 resulting in hair and nail loss and disorders of the nervous system. In one small village, the population was evacuated after 19 out of 23 people suffered nail and hair loss and all the livestock had died from selenium poisoning. Cases of selenosis in pigs reached a peak between 1979 and 1987, when 280 out of 2238 pigs were affected in one village.

No human cases of selenium toxicity have been reported in recent years, but animals continue to show health problems as a result of the high concentrations of selenium in the environment (Fordyce et al., 2000b; Yang et al., 1983).

Yang et al. (1983) were the first to compare concentrations of selenium in soil, crops, drinking water, human urine, blood, nail, and hair samples from the Enshi area with other regions of China. They demonstrated that the endemic selenium poisoning was related to the occurrence of selenium-enriched Permian coal deposits. These contained selenium concentrations of up to 6470 mg kg<sup>-1</sup>. Selenium concentrations in the soil, food, and human samples from areas underlain by these rocks were up to 1000 times higher than in samples from nearby low-selenium areas and dietary intakes of selenium greatly exceeded the recommended international and Chinese thresholds (Table 12). Locally grown crops constituted 90% of the diet in the Enshi area with cereal crops (rice and maize) accounting for 65–85% of the selenium intake. In addition to exposure through the food chain, villagers also mined the coal for fuel and used the residues as a soil conditioner.

Concentrations of selenium in the soils and foodstuffs can vary markedly from deficient to toxic in the same village, depending on the outcrop of the coal-bearing strata (Fordyce et al., 2000b). Villagers were therefore advised to avoid cultivating areas underlain by the coal or using coal ash to condition the soil. The outbreaks of human selenosis in the late 1950s and early 1960s coincided with drought and failure of the rice crop, leading to an increased dependence on locally produced vegetables and maize. As the source of food crops diversified, incidence of the disease diminished.

#### 11.2.7.4.3 Soan-Sakesar Valley, Pakistan

The Soan-Sakesar valley is situated in the center of the Salt Range mountains in Punjab, northeast Pakistan. The geochemistry of the waters in the area has been studied extensively by Afzal et al. (1999, 2000). The average altitude of the Soan-Sakesar valley is 762 m and the mean annual rainfall (1984–1994) is 613 mm. The average summer temperature is 33 °C and average winter temperature 3 °C, with periods below freezing. Average evaporation is estimated to be about 950 mm year<sup>-1</sup>. The area is essentially a closed basin, although ephemeral streams and rivers, including the River Soan, flow seasonally westwards toward the River Indus.

The area is covered by sedimentary rocks mainly of Tertiary age. The valley lies between two parallel east–west ridge systems. Wheat and maize are grown in the area. Three quite large brackish-saline lakes (3–14 km<sup>2</sup>) occur within synclinal structures formed by the folding of Eocene rocks. The largest and most saline lake, Lake Uchhali, has a TDS (total dissolved solids) of about 36 g l<sup>-1</sup>, a nitrate concentration of 28 mg l<sup>-1</sup>, and a boron concentration of nearly 1 mg l<sup>-1</sup>. It also contains a selenium concentration of 2.1 mg l<sup>-1</sup>. The major-element chemistry is dominated by Na–Mg–Cl–SO<sub>4</sub>. The majority of surface waters in the region exceeded the WHO guideline value of 40 µg l<sup>-1</sup> for selenium in drinking water, with an observed mean concentration in streams and springs of 302 µg l<sup>-1</sup> (Table 13).

The Soan-Sakesar aquifer consists of two major formations, a freshwater Sakesar limestone (Chharat Group) of the Eocene age and a brackish formation (Rawalpindi Group). Groundwater recharge is mainly from infiltration through the alluvial fans during times of stream flow. Groundwater has been used extensively for irrigation and has led to substantially altered groundwater flow patterns. The water table is generally 4–7 m bgl and varies by 1–2 m seasonally.

The groundwaters of the area also contain a high salt content with a large majority of selenium concentrations in excess of the WHO guideline value for drinking water and the FAO (Food and Agriculture Organization) guideline value for irrigation water (20  $\mu\text{g l}^{-1}$ ). The median concentrations of  $\text{NO}_3$  and boron in groundwaters from the area were 27.5 and 0.52  $\text{mg l}^{-1}$ , respectively. The Sakesar Formation is dominated by shale. This probably forms the ultimate source of selenium. Selenium concentrations, as well as the overall dissolved salt concentration, were greatest in low-lying areas where a shallow water table existed and where intense evaporation of soil water had occurred.

Selenium speciation confirmed that all the waters were dominated by selenate with 10–20% selenite (Afzal et al., 2000). A small percentage of the selenium was present as organic selenium in the surface waters but this was absent from the groundwaters. Volatilization of selenium from the lakes was suspected but not proven. It is likely that selenate was reduced to selenite or elemental selenium in the anoxic sediments.

#### 11.2.7.4.4 Selenium deficiency, China

In contrast, selenium deficiency has been implicated in several human diseases, most notably KD and KBD. KD is an endemic selenium-responsive cardiomyopathy that mainly affects children and women of child-bearing age and is named after Keshan County in northeast China (Wang and Gao, 2001). During the years of peak KD prevalence (1959–70), 8000 cases and up to 3000 deaths were reported annually (Tan, 1989). The disease occurred in a broad belt from northeast to southwest China where subsistence farmers depended on local food supplies. White muscle disease in animals occurred in the same areas. In areas with KD in China, selenium levels in the soil are around 0.112  $\text{mg kg}^{-1}$  compared to an average of 0.234  $\text{mg kg}^{-1}$  in nonendemic areas of the world (WHO, 1986) where selenium may occur in its inorganic form as selenide, selenate, and selenite. Grain crops in the affected areas contained <0.04  $\text{mg kg}^{-1}$  selenium, which led to extremely low dietary intakes (10–15  $\mu\text{g}$  selenium per day) in the local population. A very low selenium status in the affected population was indicated by selenium concentrations in hair of <0.12  $\text{mg kg}^{-1}$  (Tan, 1989; Xu and Jiang, 1986; Yang and Xia, 1995). In Tibet, soil selenium concentrations in KBD areas were lower than those in nondisease areas, and the mean concentrations of soil selenium in Tibet were lower than the average of China (0.29  $\text{mg kg}^{-1}$ ), with a close relationship between soil selenium concentrations and KBD in Tibet (Li et al., 2009b). Supplementation with 50  $\mu\text{g}$  selenium per day prevented the condition, but had no effect on those already showing signs of disease.

The precise biological function of selenium in KD is unclear and seasonal variations in prevalence suggested the involvement of a virus. High levels of the Coxsackie B virus were found in KD patients (Li et al., 2000). Work by Beck (1999) showed that a normally benign strain of the Coxsackie B3 virus becomes virulent in selenium- or vitamin E-deficiency conditions.

The incidence of the disease has fallen in recent years as a result of selenium supplementation and improved economic conditions in China generally (Burk, 1994). The evidence of viral mutageny in the presence of selenium deficiency has important implications for many infections. Selenium deficiency may increase the likelihood of dying from Human Immunodeficiency Virus (HIV)-related diseases (Baum et al., 1997) and may have exacerbated the incidence of AIDS in parts of Africa.

The relation between selenium deficiency and KD in Zhangjiakou District, China, has been described in detail by Johnson et al. (2000). Soils in the villages with a high prevalence of KD were found to be black or dark brown, with a high organic matter content and lower pH than other soils in the region. Although the soil in the KD-affected areas contained a

high total selenium concentration, the selenium was strongly bound by soil organic matter and it was not in a bioavailable form (Johnson et al., 2010). Water-soluble selenium concentrations in the villages with a high prevalence of KD were lower than deficiency threshold values (geometric mean, 0.06  $\mu\text{g l}^{-1}$ ; threshold, 3  $\mu\text{g l}^{-1}$ ).

The study concluded that when the bioavailability of selenium is low, any factor that further reduces its bioavailability and mobility may be critical. Adding selenium fertilizer to crops rather than to soils was recommended to increase the selenium concentrations in local diets. No cases of KD have been reported since 1996 as the diet has become more diversified as a result of improvements in economic conditions and transport.

KBD, named after the two Russian scientists who first described it in the late 1800s, is an endemic osteoarthropathy which causes deformity of joints. It is characterized by impaired movement, commonly with shortened fingers and toes and in extreme cases, dwarfism (Levander, 1986; Tan, 1989; WHO, 1993). In China, the distribution of the disease is similar to KD in the north, but the links with selenium deficiency are less clear. Iodine supplementation of the diets of children and nursing mothers, together with 0.5–2.0 mg sodium selenite a week for 6 years, reduced the disease prevalence from 42% to 4% in children aged 3–10 years (WHO, 1987). As with KD, other factors have been implicated in the pathogenesis of KBD. These include drinking water high in humic acids, greater fungal (mycotoxin) contamination of grain, and iodine deficiency (Peng et al., 1999; Suetens et al., 2001). KBD also occurs in Siberia, North Korea, and, possibly, parts of Africa.

#### 11.2.8 Concluding Remarks

The recent surge of research on the behavior of arsenic in the environment has followed the discovery of human health problems linked to high concentrations of the element in some groundwaters, soils, and contaminated land. Fewer studies of selenium have been undertaken, although serious health problems related to selenium toxicity or deficiency have been reported. There have also been many studies on the distribution of arsenic, and more recently selenium, for metalliferous, especially gold, exploration.

This chapter has outlined the main effects of arsenic and selenium on human and animal health, their abundance and distribution in the environment, sampling and analysis, and the main factors controlling their speciation and cycling. Such information should help to identify aquifers, water resources, and soils at risk from high concentrations of arsenic and selenium, and areas of selenium deficiency. Human activity has had, and is likely to continue to have, a major role in releasing arsenic and selenium from the geosphere and in perturbing the natural distribution of these and other elements over the Earth's surface.

Arsenic and selenium demonstrate many similarities in their behavior in the environment. Both are redox-sensitive and occur in several oxidation states under different environmental conditions. Both partition preferentially into sulfide minerals and metal oxides and are concentrated naturally in areas of mineralization and geothermal activity. Also, both elements occur as oxyanions in solution and, depending on redox status, are potentially mobile in the near-neutral to alkaline pH conditions that typify many natural waters. However, some major differences also exist. Selenium is immobile under reducing conditions, while the mobility of arsenic is less predictable and depends on a range of other factors. Selenium also appears to partition more strongly with organic matter than does arsenic.

While concern with arsenic in the environment relates principally to toxicity conditions, concerns with selenium relate to both deficiency and toxicity conditions. The optimum range of selenium concentrations for health is narrow. In certain environments, high intakes of arsenic or selenium, or very low intakes of selenium, can occur, potentially leading to a wide

range of disease conditions, not all of which are well understood and some of which may not yet have been recognized. Many of the health and environmental problems caused by arsenic and selenium were not predicted until recently because of a lack of knowledge of the distribution and behavior of arsenic and selenium in the environment. Recent improvements in understanding have been aided by improved and cost-effective analytical techniques and more powerful data processing, which have made it easier to prepare high-resolution geochemical maps. Also, modern digital datasets of geochemical and hydrochemical data are used increasingly in modeling studies to estimate element speciation, bioavailability, and risk.

The discovery of high concentrations of arsenic in groundwater from parts of the Bengal Basin of Bangladesh and West Bengal and elsewhere after several years of groundwater development has highlighted the need to analyze for a wide range of water-quality parameters before using such water sources. With the advent of modern multi-element analytical techniques capable of measuring arsenic and selenium at environmentally relevant concentrations on an almost routine basis, it should be possible to include arsenic and selenium in more geochemical and hydrochemical surveys and thereby acquire a much better picture of their distribution, behavior, and role in the environment.

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Table 1 Physical properties of arsenic and selenium.

Name	Arsenic		Selenium	
Symbol	As		Se	
Atomic number	33		34	
Periodic Table group	15		16	
Atomic mass	74.9216		78.96	
Classification	Metalloid		Non-metal	
Pauling electronegativity	2.18		2.55	
Density (kg m <sup>-3</sup> )	5727		4808	
Melting point (°C)	817 (at high pressure)		220	
Boiling point (°C)	614 (sublimes)		685	
Natural isotopes & abundance	<sup>75</sup> As	100%	<sup>74</sup> Se	0.87%
			<sup>76</sup> Se	9.02%
			<sup>77</sup> Se	7.58%
			<sup>78</sup> Se	23.52%
			<sup>80</sup> Se	49.82%
			<sup>82</sup> Se	9.19%

Table 2 Chemical forms of arsenic and selenium.

Element and formal oxidation state	Major chemical forms
As(-III)	Arsine [H <sub>3</sub> As]
As(-I)	Arsenopyrite [FeAsS], loellingite [FeAs <sub>2</sub> ]
As(0)	Elemental arsenic [As]
As(III)	Arsenite [H <sub>2</sub> AsO <sub>3</sub> <sup>-</sup> , H <sub>3</sub> AsO <sub>3</sub> ]
As(V)	Arsenate [AsO <sub>4</sub> <sup>3-</sup> , HAsO <sub>4</sub> <sup>2-</sup> , H <sub>2</sub> AsO <sub>4</sub> <sup>-</sup> , H <sub>3</sub> AsO <sub>4</sub> ]
Organic As (V and III)	Dimethylarsinate [DMA, (CH <sub>3</sub> ) <sub>2</sub> AsO(OH)], monomethylarsonate [MMA(V), CH <sub>3</sub> AsO(OH) <sub>2</sub> or MMA(III), CH <sub>3</sub> As(OH) <sub>2</sub> ], arsenobetaine [AsB, (CH <sub>3</sub> ) <sub>3</sub> As <sup>+</sup> ·CH <sub>2</sub> COO <sup>-</sup> ], arsenocholine [AsC, (CH <sub>3</sub> ) <sub>3</sub> As <sup>+</sup> ·CH <sub>2</sub> CH <sub>2</sub> OH]
Se(-II)	Selenide [Se <sup>2-</sup> , HSe <sup>-</sup> , H <sub>2</sub> Se]
Se(0)	Elemental selenium [Se]
Se(IV)	Selenite [SeO <sub>3</sub> <sup>2-</sup> , HSeO <sub>3</sub> <sup>-</sup> , H <sub>2</sub> SeO <sub>3</sub> ]
Se(VI)	Selenate [SeO <sub>4</sub> <sup>2-</sup> , HSeO <sub>4</sub> <sup>2-</sup> , H <sub>2</sub> SeO <sub>4</sub> ]
Organic Se	Dimethylselenide [DMSe, CH <sub>3</sub> SeCH <sub>3</sub> ]; dimethyldiselenide [DMDSe, CH <sub>3</sub> SeSeCH <sub>3</sub> ], selenomethionine [H <sub>3</sub> N <sup>+</sup> CHCOO <sup>-</sup> ·CH <sub>2</sub> CH <sub>2</sub> SeMe], selenocysteine [H <sub>2</sub> N <sup>+</sup> CHCOO <sup>-</sup> ·CHSeH]

Table 3 Recognised methods of arsenic analysis (from Rasmussen and Anderson (2002))

Technique	LoD (µg L <sup>-1</sup> )	Sample size (mL)	Equipment cost (US\$)	Analytical throughput per day	Comments	Accredited Procedure
HG-AAS	0.05	50	20–100,000	30–60	Single element	ISO 11969 SM 3114
GF-AAS	1–5	1–2	40–100,000	50–100		ISO/CD 15586 SM 3113
ICP-AES	35– 50	10–20	60–100,000	50–100	Multi-element; requires Ar gas supply. Can reduce LoD with HG	ISO/CD 11885 SM 3120
ICP-MS	0.02– 1	10–20	150– 400,000	20–100	Multi-element	SM 3125 U.S. EPA 1638
HG-AFS	0.01	40–50	20–25,000	30–60	Single element but can be adapted for Se and Hg	
ASV	0.1	25–50	10–20,000	25–50	Only free dissolved As	U.S. EPA 7063
SDDC	1–10	100	2–10,000	20–30	Simple instrumentation	SM 3500 ISO 6595

Table 4 Standard Reference materials for natural waters from various suppliers.

SRM	Supplier	Medium	Arsenic ( $\mu\text{g L}^{-1}$ )	Selenium ( $\mu\text{g L}^{-1}$ )
TMRAIN-04	NWRI	Rainwater	1.14	0.83
SLRS-5	NRC	River water	0.413*	–
CASS-5	NRC	Seawater	1.24	
NASS-6	NRC	Seawater	1.43	
SLEW-3	NRC	Estuarine Water	1.36	
SRM 1640a	NIST	Natural water	8.075	20.13
SRM 1643e	NIST	Fresh water	60.45	11.9
BCR-609	IRMM	Ground water	1.20*	–
BCR-610	IRMM	Ground water	10.8*	
CRM 403	IRMM	Seawater	9.9*	–
CASS-4	NRC	Seawater	1.1	–

NWRI= National Water Research Institute, Environment Canada; NIST= National Institute of Standards and Technology, Gaithersburg, Maryland, USA; IRMM=Institute for Reference Materials and Measurements; NRC=National Research Council of Canada.

\* $\mu\text{g kg}^{-1}$

Table 5 Standard Reference materials for soils, sediment and sludges from the National Institute of Standards and Technology (NIST).

SRM	Medium	As ( $\text{mg kg}^{-1}$ )	Se ( $\text{mg kg}^{-1}$ )
1646a	Estuarine Sediment	6.23	0.193
1648a	Urban Particulate Matter	115.5	28.4
1944	New York/New Jersey Waterway Sediment	18.9	1.4
2586	Trace Elements in Soil (contains lead from paint)	8.7	0.6
2587	Trace Elements in Soil (contains lead from paint)	13.7	
2702	Inorganics in Marine Sediment	45.3	4.95
2703	Sediment for Solid Sampling (Small, Sample) Analytical Techniques	45.5	4.9
2709a	San Joaquin Soil	10.5	1.5
2710a	Montana I Soil	0.15%	1
2711a	Montana II Soil	107	2
2780	Hard Rock Mine Waste	48.8	5
2781	Domestic Sludge	7.82	16

2782	Industrial Sludge	166	0.44
8704	Buffalo River Sediment	17	

Concentrations in mg kg<sup>-1</sup> unless noted as %

Table 6 Concentration ranges of arsenic in various water bodies (modified from a compilation by Smedley and Kinniburgh, 2002).

Water body and location	Arsenic concentration: average or range ( $\mu\text{g L}^{-1}$ )
<b>Rain water:</b>	
Maritime	0.02
Terrestrial (w USA)	0.013–0.032
Coastal (Mid-Atlantic, USA)	0.1 (<0.005–1.1)
Snow (Arizona)	0.14 (0.02–0.42)
Terrestrial rain	0.46
Seattle rain, impacted by copper smelter	16
<b>River water:</b>	
Various	0.83 (0.13–2.1)
Norway	0.25 (<0.02–1.1)
South-east USA	0.15–0.45
USA	2.1
Dordogne, France	0.7
Po River, Italy	1.3
Polluted European rivers	4.5–45
River Danube, Bavaria	3 (1–8)
Schelde catchment, Belgium	0.75–3.8 (up to 30)
<i>High-As ground water influenced:</i>	
Northern Chile	190–21800
Northern Chile	400–450
Córdoba, Argentina	7–114
<i>Geothermally influenced:</i>	
Sierra Nevada, USA	0.20–264
Waikato, New Zealand	32 (28–36)
	44 (19–67)
Madison and Missouri Rivers, USA	10–370
<i>Mining influenced:</i>	
Ron Phibun, Thailand	218 (4.8–583)
Ashanti, Ghana	284 (<2–7900)
British Columbia, Canada	17.5 (<0.2–556)
<b>Lake water:</b>	
British Columbia	0.28 (<0.2–0.42)
Ontario	0.7
France	0.73–9.2 (high Fe)
Japan	0.38–1.9
Sweden	0.06–1.2
<i>Geothermally influenced:</i>	
Western USA	0.38–1000
<i>Mining influenced:</i>	
Northwest Territories, Canada	270 (64–530)
Ontario, Canada	35–100

Water body and location	Arsenic concentration: average or range ( $\mu\text{g L}^{-1}$ )
<b>Estuarine water:</b>	
Oslofjord, Norway	0.7–2.0
Saanich Inlet, British Columbia	1.2–2.5
Rhône Estuary, France	2.2 (1.1–3.8)
Krka Estuary, Yugoslavia	0.13–1.8
<i>Mining and industry influenced:</i>	
Loire Estuary, France	up to 16
Tamar Estuary, UK	2.7–8.8
Schelde Estuary, Belgium	1.8–4.9
<b>Seawater:</b>	
Deep Pacific and Atlantic	1.0–1.8
Coastal Malaysia	1.0 (0.7–1.8)
Coastal Spain	1.5 (0.5–3.7)
Coastal Australia	1.3 (1.1–1.6)
<b>Ground water:</b>	
Various USA aquifers	<1–2600
Various UK aquifers	<0.5–57
Bengal Basin, West Bengal, Bangladesh	<0.5–3200
Chaco-Pampean Plain, Argentina	<1–5300
Lagunera, northern Mexico	8–620
Inner Mongolia, China	<1–2400
Taiwan	<10 to 1820
Great Hungarian Plain, Hungary, Romania	<2–176
Red River Delta, Vietnam	1–3050
Mining-contaminated ground waters	50–10,000
Geothermal water	<10–50,000
Mineralised area, Bavaria, Germany	<10–150
Herbicide-contaminated ground water, Texas	408,000
<b>Mine drainage:</b>	
Various, USA	<1–850,000
Ural Mountains	400,000
<b>Sediment pore water:</b>	
Baseline, Swedish estuary	1.3–166
Baseline, clays, Saskatchewan, Canada	3.2–99
Baseline, Amazon shelf sediments	up to 300
Mining-contam'd, British Columbia	50–360
Tailings impoundment, Ontario, Canada	300–100,000

Table 7 Selenium concentrations in selected rock types.

Material	Selenium (mg kg <sup>-1</sup> )
<b>Earth's Crust</b>	0.05
<b>Igneous rocks</b>	
Ultramafic rocks	0.05
Mafic rocks	0.05
Granite	0.01–0.05
Volcanic rocks	0.35
Volcanic rocks, USA	<0.1
Volcanic rocks, Hawaii	<2.0
Volcanic tuffs	9.15
<b>Sedimentary Rocks</b>	
Marine carbonates	0.17
Limestone	0.03–0.08
Sandstone	<0.05
W. USA shale	1–675
Wyoming shale	2.3–52
S Korean shale	0.1–41
Carbon-shale China	206–280
Mudstone	0.1–1500
Phosphate	1–300
USA Coal	0.46–10.7
Australian coal	0.21–2.5
Chinese stone-coal	<6500
Oil	0.01–1.4

Sources: Jacobs (1989), Fordyce et al. (2000b), WHO (1987), Oldfield (1999), Alloway (1995), Davies (1980).



Table 8 Selenium concentrations in soils.

Soil	Total Se (mg kg <sup>-1</sup> )	Water-soluble Se (mg kg <sup>-1</sup> )
World general	0.4	
World seleniferous	1–5000	
USA general	<0.1–4.3	
USA seleniferous	1–10	
England/Wales general	<0.01–4.7	0.05–0.39
Ireland seleniferous	1–1200	
China general	0.02–3.8	
China Se deficient	0.004–0.48	0.00003–0.005
China Se adequate	0.73–5.7	
China seleniferous	1.49–59	0.001–0.25
Finland	0.005–1.25	
India Se deficient	0.025–0.71	0.019–0.066
India seleniferous	1–20	0.05–0.62
Sri Lanka Se deficient	0.11–5.2	0.005–0.043
Norway	3–6	
Greece Se deficient	0.05–0.10	
Greece Se adequate	> 0.2	
New Zealand	0.1–4	

Sources: Davies (1980), Thornton et al. (1983), Jacobs (1989), WHO (1987), Alloway (1995), Oldfield (1999), Fordyce et al. (2000a), Fordyce et al. (2000b).

Table 9 Concentration ranges of Se in various water bodies.

Water body and location	Se concentration and range ( $\mu\text{g L}^{-1}$ )	Reference
<b>Rain water</b>		
Various	0.04–1.4	Hashimoto and Winchester (1967)
Polar ice	0.02	Frankenberger and Benson (1994)
<b>River and lake water</b>		
Jordan River, Jordan	0.25	Nishri et al. (1999)
River Amazon, Brazil	0.21	Jacobs (1989)
Colorado River, USA	<1–400	NAS (1976); Engberg (1999)
Mississippi River, USA	0.14	Jacobs (1989)
Lake Michigan, USA	0.8–10	Jacobs (1989)
Gunnison River, USA	10	Jacobs (1989)
Cienaga de Santa Clara wetland, Mexico	5–19	García-Hernández et al. (2000)
<b>Seawater and estuaries</b>		
Seawater	0.09; 0.17	Hem (1992); Thomson et al. (2001)
San Francisco Bay, USA	0.1–0.2	Cutter (1989)
Carquinez Strait, San Francisco Bay, USA	0.07–0.35	Zawislanski et al. (2001a)
<b>Ground water</b>		
East Midlands Triassic Sandstone, UK	<0.06–0.86	Smedley and Edmunds (2002)
Chaco-Pampean Plain, loess aquifer, Argentina	<2–40	Nicolli et al. (1989); Smedley et al. (2002)
Bengal Basin alluvial aquifer, Bangladesh	<0.5	BGS and DPHE (2001)
Soan-Sakesar Valley alluvial aquifer, Punjab, Pakistan	Avg 62	Afzal et al. (2000)
Colorado River catchment, USA	up to 1300	Engberg (1999)
Coast Range alluvial aquifer, San Joaquin Valley, California, USA	<1–2000	Deverel et al. (1994)
Sierra Nevada alluvial aquifer, San Joaquin Valley, California	<1	Deverel et al. (1994)
Central Barents ground water, Norway	0.01–4.82	Reimann et al. (1998)
Slovakian ground water	0.5–45	Rapant et al. (1996)
<b>Pore water</b>		
Baseline, estuarine Lake Macquarie, Australia	<0.2	Peters et al. (1999)
Smelter and power-station-impacted, Lake Macquarie, Australia	0.3–5.0	Peters et al. (1999)

Table 10 Global selenium fluxes.

Source	Pathways	Se flux (tonne yr <sup>-1</sup> )
Anthropogenic releases	Mining, anthropogenic releases to atmosphere, water, land and oceans	76000–88 000
Marine loss	Volatilisation, sea salt suspension, into marine biota, sediment transfer to land	38250
Terrestrial loss	Volatilisation, particle resuspension, dissolved and suspended load to oceans	15380
Atmospheric loss	Wet and dry deposition to the oceans and land	15300

Source: Haygarth (1994).

Table 11 Examples of Se contents in various crops grown in the USA.

USA crop type	Average Se (mg kg <sup>-1</sup> dry wt)
Roots and bulbs	0.407
Grains	0.297
Leafy vegetables	0.110
Seed vegetables	0.066
Vegetable fruits	0.054
Tree fruits	0.015

Source: Jacobs (1989).

Table 12 Deficiency and toxicity thresholds for selenium in various media.

Medium	Units	Deficient	Marginal	Moderate	Adequate	Toxic	Criterion	Reference
<b>Soils:</b>								
Worldwide	mg kg <sup>-1</sup>	0.1–0.6					Animal health	Various
Chinese soils	mg kg <sup>-1</sup>	0.125	0.175	0.400		>3	Human health	Tan (1989)
Chinese soil water-soluble	mg kg <sup>-1</sup>	0.003	0.006	0.008		0.020	Human health	Tan (1989)
<b>Vegetation:</b>								
Worldwide	mg kg <sup>-1</sup>	<0.1			0.1–1.0	3–5	Animal health	Jacobs (1989); Levander (1986)
Chinese cereals	mg kg <sup>-1</sup>	0.025	0.040	0.070		>1	Human health	Tan (1989)
<b>Animals:</b>								
Food, chronic exposure	mg kg <sup>-1</sup>	<0.04			0.1–3	3–15	Animal health	Jacobs (1989); Mayland (1994)
Cattle and sheep liver	mg kg <sup>-1</sup>	0.21					Animal health	WHO (1986)
Cattle and sheep blood	mg kg <sup>-1</sup>	<0.04	0.05–0.06		0.07–0.10		Animal health	Mayland (1994)
<b>Humans:</b>								
Chinese Human hair	mg kg <sup>-1</sup>	0.200	0.250	0.500		>3	Human health	Tan (1989)
Urinary excretion rate	µg day <sup>-1</sup>				10–200		Human health	Oldfield (1999)
Food	mg kg <sup>-1</sup>	<0.05				2–5	Human health	WHO (1996)
Ref. Dose U.S. EPA	mg kg <sup>-1</sup> day <sup>-1</sup>				0.005		Human health	U.S. EPA (2011)
Human Diet (WHO)	µg day <sup>-1</sup>	<40			55–75	>400	Human health	WHO (1996)
Drinking water (WHO)	µg L <sup>-1</sup>					>10	Maximum admissible concentration	WHO (1993)

Table 13 Average concentrations of ground water and stream/spring samples from the Soan-Sakesar valley, Pakistan (from Afzal et al., 2000).

Parameter	Lake Uchhali n=3	Ground waters n=29	Streams/Springs n=13
	mg L <sup>-1</sup>		
Ca	159	22	64
Mg	1770	62	104
Na	9890	130	323
K	254	14	25
Alkalinity	584	234	577
Cl	9530	89	216
SO <sub>4</sub>	14300	243	551
NO <sub>3</sub>	28	30	20
Li	2.86	0.3	0.65
B	0.96	0.61	0.36
P	0.48	0.17	0.52
SiO <sub>2</sub>	5.1	3.7	5.2
Se	2.10	0.062	0.302
Mo	0.02	0.021	0.019

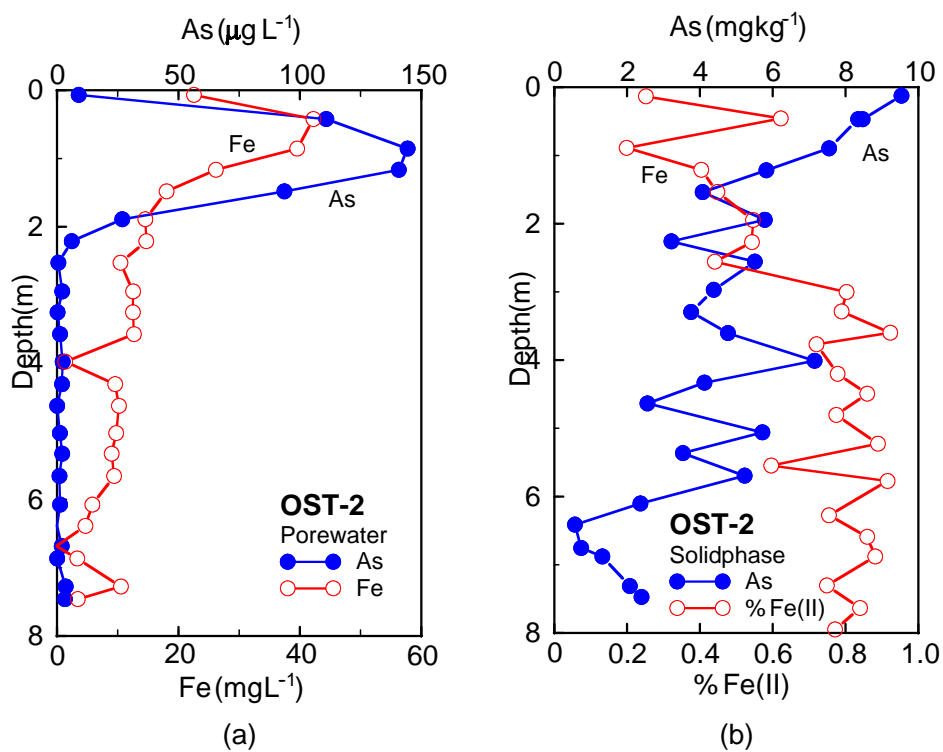




Figure 2 Speciation of As(V) and As(III) in a 0.01M NaCl medium as a function of pH at 25°C (from Smedley and Kinniburgh, 2002).



Figure 3 Eh-pH stability diagram for arsenic in the presence of sulfur at 25°C, 1 bar total pressure. The stability field for water is shown by the dashed lines. The grey area represents a solid phase.

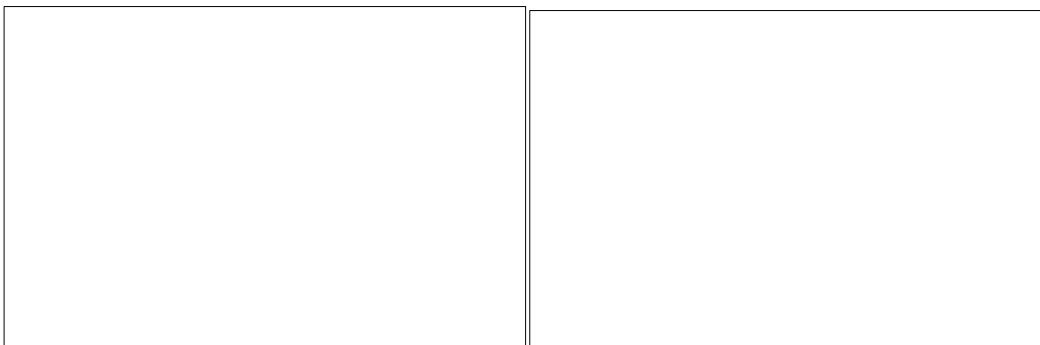


Figure 4 Calculated percent adsorption of (a) oxidised and (b) reduced arsenic species by hydrous ferric oxide (HFO). Infilled areas show the adsorption for a range of total As concentrations (0.1–10  $\mu\text{mol L}^{-1}$ ) and ionic strengths (1–100  $\text{mmol L}^{-1}$ ).

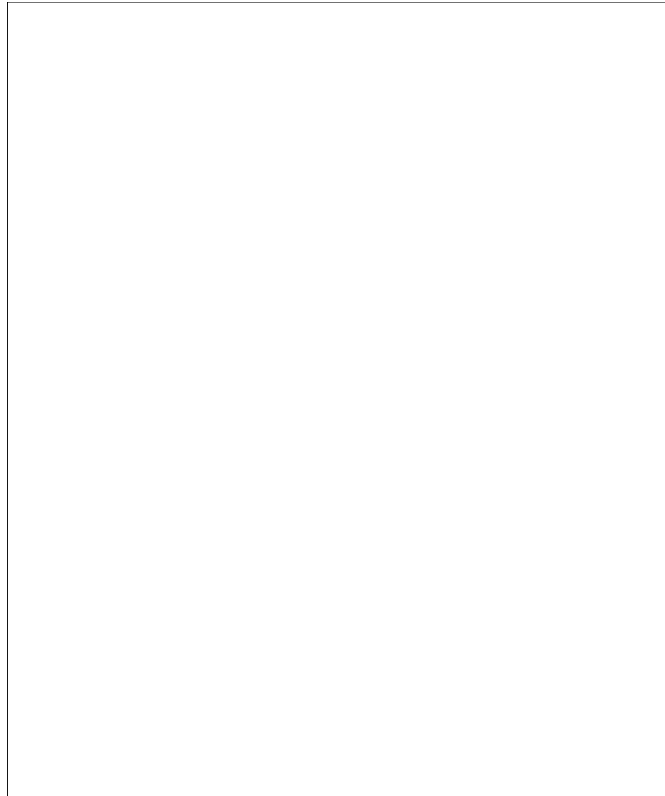


Figure 5 Map showing the distribution of arsenic in shallow (<150 m) Bangladesh ground waters based on some 3200 ground water samples (from BGS and DPHE, 2001, <http://www.bgs.ac.uk/Arsenic/bphase2/home.html>).



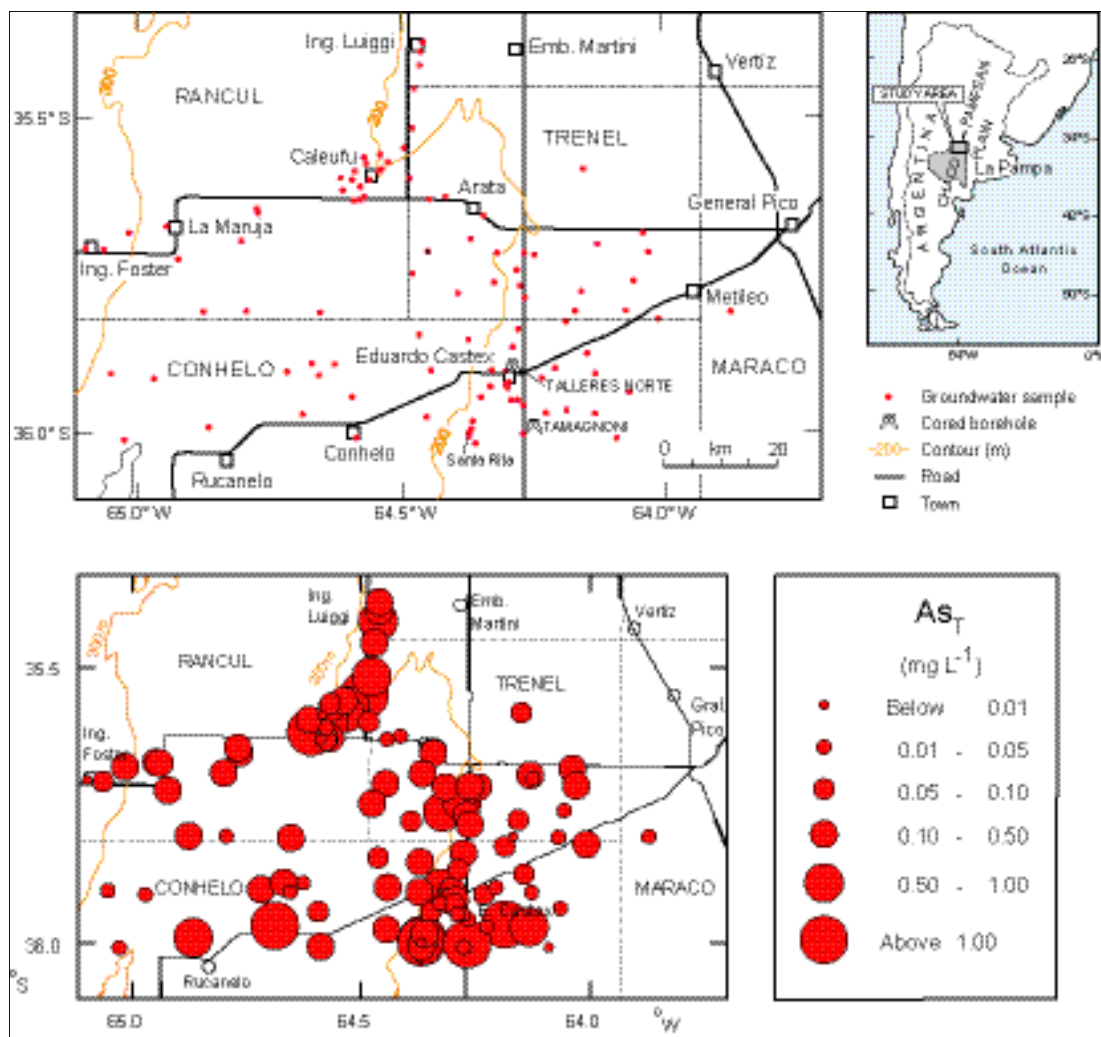


Figure 6 Map showing (top) ground water sampling locations and (bottom) observed arsenic concentrations in the Chaco-Pampean Plain of central Argentina (from Smedley et al., 2002).

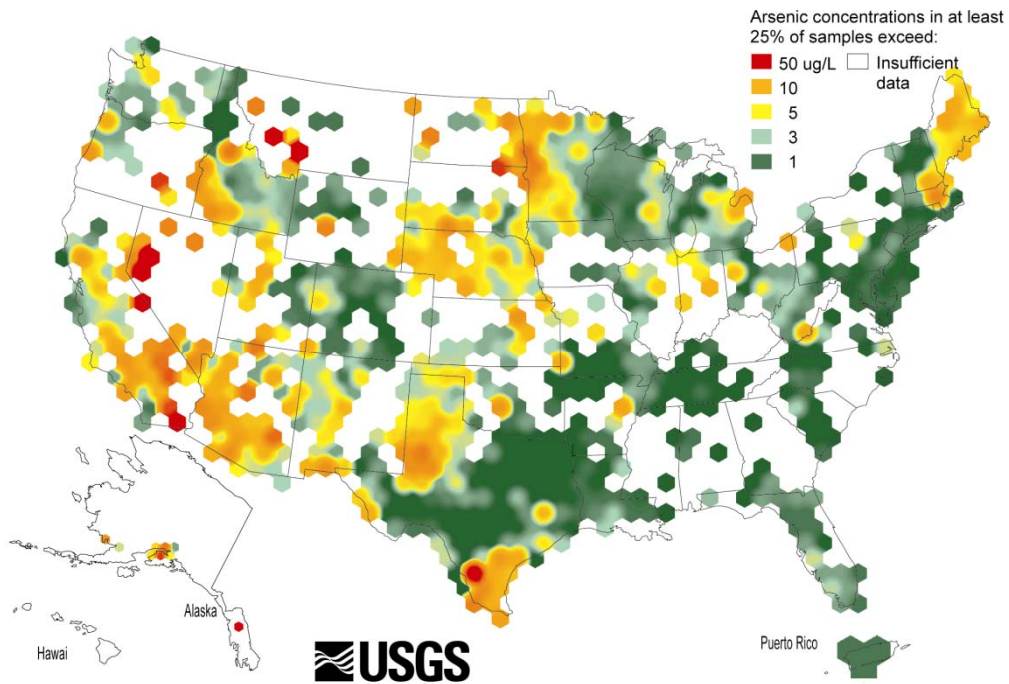


Figure 7 Map of the USA showing the regional distribution of arsenic in wells (from [http://water.usgs.gov/nawqa/trace/pubs/geo\\_v46n11/fig3.html](http://water.usgs.gov/nawqa/trace/pubs/geo_v46n11/fig3.html) after Ryker, 2001). This shows where 25% of water samples within a moving 50 km radius exceed a certain arsenic concentration. It is computed from 31,350 water samples and updated from the results presented by Welch et al. (2000).



Figure 8 Hydrogeological section through part of Algoma, Winnebago County, Wisconsin showing the arsenic concentration in various wells in relation to the cemented sulfide-rich horizon and the static water level (after Schreiber et al., 2000). AMSL = above mean sea level

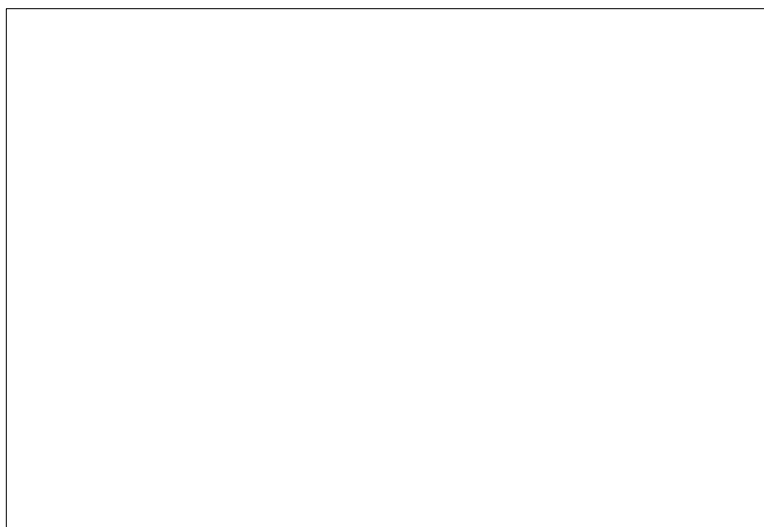


Figure 9 Speciation of selenium in a 0.01M NaCl medium as a function of pH at 25°C. The plot for Se(VI) is not shown since this is always dominated by  $\text{SeO}_4^{2-}$ .



Figure 10 Eh-pH stability diagram for selenium at 25°C, 1 bar total pressure. The stability field for water is shown by the dashed lines.

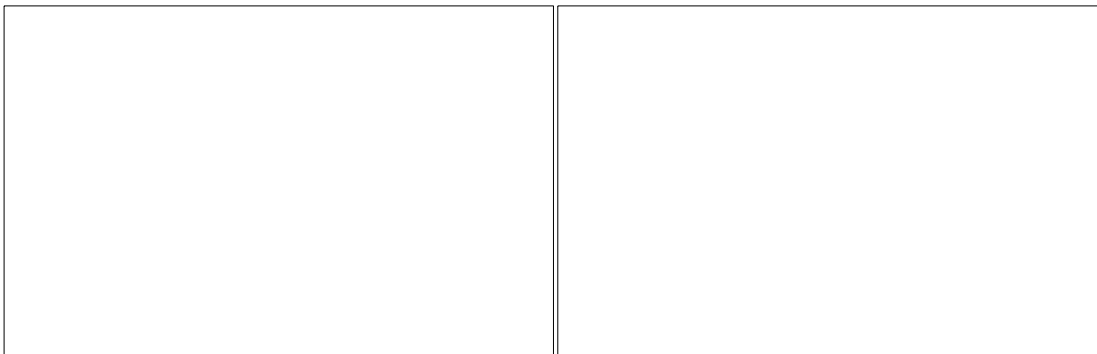


Figure 11 Calculated % adsorption of (a) oxidised and (b) reduced selenium species by hydrous ferric oxide (HFO). Infilled areas show the adsorption for a range of total Se concentrations (0.1–10  $\mu\text{mol L}^{-1}$ ) and ionic strengths (1–100  $\text{mmol L}^{-1}$ ).