Reviews in Mineralogy & Geochemistry
Vol. 79 pp. 1-16, 2014

The Environmental Geochemistry of Arsenic
— An Overview —

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INTRODUCTION

Arsenic is one of the most prevalent toxic elements in the environment. The toxicity, mobility, and fate of arsenic in the environment are determined by a complex series of controls dependent on mineralogy, chemical speciation, and biological processes. The element was first described by Theophrastus in 300 B.C. and named arsenikon (also arrhenicon; Caley and Richards 1956) referring to its "potent" nature, although it was originally considered an alternative form of sulfur (Boyle and Jonasson 1973). Arsenikon is believed to be derived from the earlier Persian, *zarnik* (online etymology dictionary, *http://www.etymonline.com/index.php?term=arsenic*). It was not until the thirteenth century that an alchemist, Albertus Magnus, was able to isolate the element from orpiment, an arsenic sulfide (As_2S_3). The complex chemistry required to do this led to arsenic being considered a "bastard metal" or what we now call a "metalloid," having properties of both metals and non-metals. As a chemical element, arsenic is widely distributed in nature and can be concentrated in many different ways. In the Earth's crust, arsenic is concentrated by magmatic and hydrothermal processes and has been

1529-6466/14/0079-0001$05.00 http://dx.doi.org/10.2138/rmg.2014.79.1

used as a "pathfinder" for metallic ore deposits, particularly gold, tin, copper, and tungsten (Boyle and Jonasson 1973; Cohen and Bowell 2014). It has for centuries been considered a potent toxin, is a common poison in actual and fictional crimes, and has led to significant impacts on human health in many areas of the world (Cullen 2008; Wharton 2010).

ARSENIC TOXICITY IN DRINKING WATER

The potential issues associated with elevated As concentrations in water supplies have led to a large body of published research in the last few years related to:

- arsenic impacts in the environment (Chappell et al. 1994, 1999, 2001, 2003; Nriagu 1994a,b; Abernathy et al. 1997; Nordic Ministers Council 1999; Frankenberger 2002; Naidu et al. 2006; Garelick and Jones 2009)
- advances in arsenic chemistry and microbiology (O'Day et al. 2005; Henke 2009; Santini and Ward 2012; Zhu et al. 2014)
- arsenic in groundwater and drinking water (NRC 1977, 1999, 2001; Anwar 2000; Bianchelli 2003; Welch and Stollenwerk 2003; Bhattacharya et al. 2007; Meliker 2007; Aphuja 2008; Bundschuh et al. 2005, 2009; Sorlini and Collivignarellli 2011)
- the health effects of arsenic (Nriagu et al. 1994b; Murphy and Guo 2003; Le and Weinfeld 2004; Parker and Parker 2004; Meharg 2005; Cullen 2008; Ravenscroft et al. 2009; Jean et al. 2010; Wharton 2010; Chen and Chiou 2011; Ng et al. 2012)
- improved methods of arsenic analysis (Le 2001; Clifford et al. 2004; Francesconi and Kuehnelt 2004; Samanta and Clifford 2006).

Based on the mounting evidence for the acute and chronic toxicity of As, the WHO recommended a more stringent drinking water limit for total As which was provisionally reduced in 1993 from 50 μg L^{-1} to 10 μg L^{-1} (NRC 1999). The recommended value, however, is still based largely on analytical capability (NRC 2001). If the standard basis for risk assessment applied to industrial chemicals was applied to As, the maximum permissible concentration would be lower based on toxicology and water consumption. The recommendations are based on an average body weight and water intake per day. Those with hard manual work in tropical regions surpass the average daily water intake by a factor of 2-3 and for them, the limit would still have to be decreased (Chakraborti et al. 2010).

Although many national authorities are bringing limits in line with the WHO guideline value, many developing countries still operate at the 50 μg L^{-1} standard, in part because of lack of adequate testing facilities for lower concentrations. Despite the substantial body of literature, research on As is still continuing and many recent papers have focused on groundwater with little interconnection to understanding the fundamental source(s) of As, its variable speciation in both solid and aqueous form, and its interaction with the biosphere. The purpose of this short course volume is to provide a summary of the current state of knowledge in these areas.

ARSENIC MINERALOGY AND PRIMARY OCCURRENCE

Arsenic is mobilized in the environment through a combination of natural processes such as weathering reactions, biological activity, and volcanic emissions, as well as through a range of anthropogenic activities. It has only one stable isotope (^{75}As) and is the 47th most abundant natural element. The average crustal abundance is 2.5 mg kg^{-1} although it is even more abundant in the upper continental crust (5.7 mg kg^{-1}; Hu and Gao 2008) and generally more abundant in marine shales and mudstones (Tourtelot 1964), with high concentrations associated with hydrothermal ore deposits, coal, and lignite deposits (Table 1).

Table 1. Range of arsenic concentrations in the environment.

Rock/soil type	Average As (mg kg^{-1})	Range As (mg kg^{-1})	Refs.
Ultrabasic	1.5	0.03 – 15.8	[1]
Granite	1.3	0.2 – 15	[1]
Andesite	2.7	0.5 – 5.8	[1]
Basalt	2.3	0.18 – 113	[1]
Slate/phyllite	18	0.5 – 143	[1]
Mudstone/marine shale	3 – 15	<490	[1]
Hornfels	5.5	0.7 – 11	[1]
Sandstone	4.1	0.6 – 120	[1]
Limestone	2.6	0.1 – 20.1	[1]
Phosphorite	21	0.4 – 188	[1]
Coal		0.3 – 35,000	[1]
Alluvial sands (Bangladesh)	2.9	1 – 6.2	[1]
Alluvial muds (Bangladesh)	6.5	2.7 – 14.7	[1]
River bed (Bangladesh)		1.2 – 5.9	[1]
Tropical soils (Ghana)	0.3	0.2 – 1.2	[2]
Tropical baseline soils, gold deposit (Ghana)		2 – 35,600	[2]
Great Basin Alluvium (Nevada, USA)		13.6 – 54	[3]
Loess Silt (Argentina)		5.4 – 18	[1]
Mine-contaminated soil (Cornwall)	1,800	4 – 9,000	[4]
Gold mine waste (California, USA)		10.1 – 15,300	[5][6]
Mine-contaminated sediment (USA)	342	80 – 1,104	[1]
Mine-contaminated reservoir sediment (California, USA)		54 – 301	[7]
Soil, sulfide deposit	126	2 – 8,000	[1]
Glacial till, Canada	9.2	1.9 – 170	[1]
Sewage sludge	9.8	2.4 – 39.6	[1]

References: [1] Smedley and Kinniburgh (2002); [2] Bowell (1994); [3] Theodore et al. (2003); [4] Bowell et al. (2013); [5] MFG (2009); [6] Alpers et al. (2014, this volume); [7] Savage et al. (2000)

As of July 2014, there are 568 known minerals for which arsenic is a critical component. These include elemental arsenic, arsenides, sulfides, oxides, arsenates, mixed-anion arsenates, and arsenites (IMA 2014). High arsenic concentrations are also found in many oxide minerals and hydrous metal oxides, either as part of their periodic structure or as sorbed and occluded species. Iron oxides are particularly well known to accumulate As up to concentrations of several weight per cent. Arsenic (as As(III) or As(V)) can substitute for P(V), Si(IV), Al(III), Fe(III), and Ti(IV) in various mineral structures and is therefore present in many rock-forming minerals, albeit at much lower concentrations. The element is primarily concentrated in sulfide minerals where it can occur as an arsenide or sulfarsenide anion bound to transition metals (e.g., löllingite, $FeAs_2$; arsenopyrite, FeAsS) or more rarely in minerals where arsenic forms nominally a cation (e.g., realgar, AsS).

Despite the large number of known As minerals, the largest reservoir of arsenic in crustal rocks is probably pyrite (Nordstrom 2000) which contains trace to minor contents (up to 16.5 wt% in synthetic marcasite and 10 wt% in natural pyrite; Reich et al. 2005; Neumann et al. 2013; Simon et al. 2013) of this element. Besides being an important constituent of ore bodies, pyrite is also formed in low-temperature sedimentary environments under reducing conditions.

Authigenic pyrite is present in the sediments of many rivers, lakes, oceans, and aquifers and plays a very important role in the present-day geochemical cycles of various elements. Through a series of intermediate phases, pyrite commonly forms in zones of intense reduction such as around buried and decomposing organic matter or in microenvironments where the sulfate-reducing bacteria generate appreciable amounts of sulfide. It is sometimes present in a characteristic form as framboidal pyrite (Roberts 1982; Wilkin and Barnes 1997; Alpers et al. 2002). During the formation of this pyrite, it is likely that As will also be incorporated. Pyrite is not stable in aerobic systems and oxidizes to hydrous iron oxides with the release of large amounts of sulfate, acidity, and associated trace constituents, including As (Nordstrom and Alpers 1999). The presence of pyrite as a minor constituent in sulfide-rich coals is ultimately responsible for the production of "acid rain" and coal mine associated acid mine drainage (AMD), and for the presence of As problems around coal mines and areas of intensive coal burning (e.g., Tourtelot 1964; Finkelman et al. 1999, 2002; Finkelman 2004).

ARSENIC IN THE WEATHERING ENVIRONMENT

Arsenic in secondary minerals and soils

Arsenic behavior is typical of many chalcophile elements in that it is released by sulfide oxidation, modified by various biogeochemical processes, and attenuated by adsorption and co-precipitation with Fe-minerals, clays, and organic matter. It can form a large number of secondary As minerals including native arsenic, arsenates, and in rare cases arsenites (Drahota and Filippi 2009) such as in the Tsumeb deposit of Namibia (Bowell 2014, this volume). The attenuation and concentration of As in surface soils can be a useful indicator of sulfide mineral deposits (Boyle and Jonasson 1973). For example in the northern part of Nevada, As concentrations in soils define zoned anomalies or "chalcophile corridors" around major bedrock gold deposits (Theodore et al. 2003; Fig. 1).

District-scale As geochemical trends in the vicinity of major Carlin-type deposits in alluvium, surface rocks, and stream sediments define "corridors" of anomalous values with a northwest-trending lobate pattern that mimics the distribution of the major gold deposits. Here As occurs in concentrations up to 54 mg kg^{-1} and reflects the concentration of As in pyrite that occurs within the gold-bearing zones (Thompson et al. 2002). Arsenic concentration in exposed surface rocks (up to 90 mg kg^{-1}) correlates to As in derivative stream sediments. The application of X-ray absorption near-edge spectra (XANES) of selected light-density minerals from the stream-sediment samples indicated As is associated with Al-bearing phases, such as gibbsite, amorphous Al oxyhydroxides, or aluminosilicate clay minerals as As(V) (Theodore et al. 2003). This association occurred through chemical weathering of mineralized rock fragments and migration of As in groundwater with fixation in the supergene environment as As(V).

Arsenic in water

The geochemical behavior of As in the surficial environment is characteristic of oxyanion-forming metalloids in that it is mobile not only at the pH values typically found in groundwaters (pH 6.5-8.5) but also under both oxidizing and reducing conditions. Arsenic can occur in the environment in several oxidation states although in most natural groundwaters, it occurs either as the trivalent arsenite [As(III)] or pentavalent arsenate [As(V)]. Organic arsenic forms may be produced by biological activity, mostly in surface waters, but are rarely quantitatively important except in biological tissues where they may be dominant (for example arsenobetaine; Cullen and Reimer 1989). Arsenic is generally present as an oxysalt or oxyanion in oxic environments. In anaerobic soils, on the other hand, it is typically found combined with sulfur. Thus, in uncontaminated aerobic sediments and soils arsenate ($As^{V}O_4^{3-}$) is the predominant species, whereas in anaerobic sediments and soils arsenite ($As^{III}O_3^{3-}$) is the dominant species (Nordstrom and Archer 2003; Campbell and Nordstrom 2014, this volume).

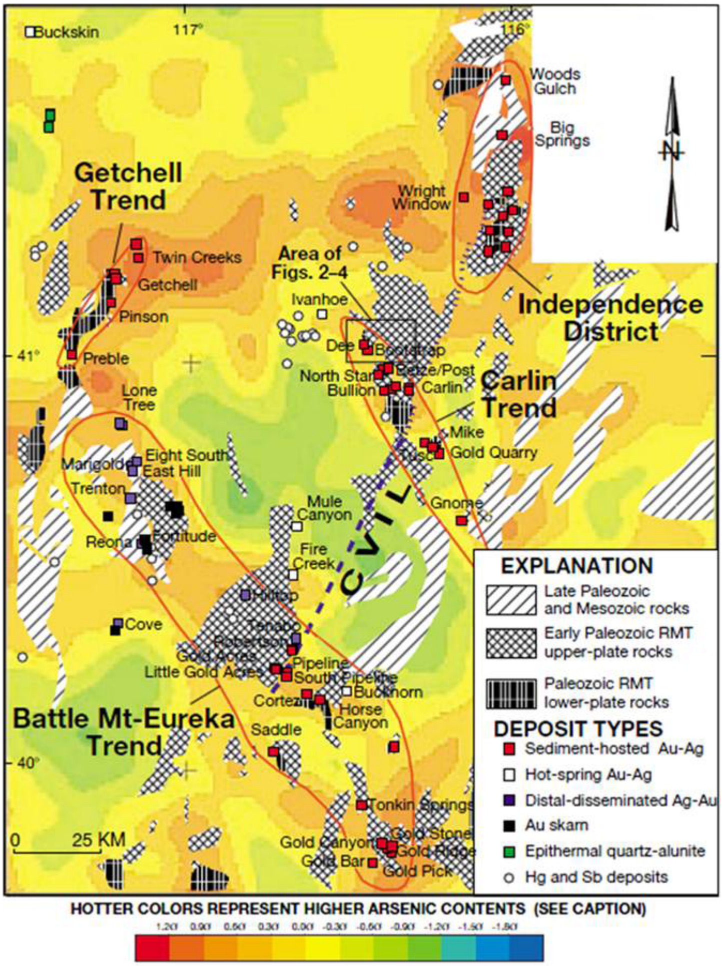


Figure 1. (*for color see Plate 1*) Index map showing relationship of alluvium As concentrations in northernmost Carlin trend to bedrock, Crescent Valley-Independence Lineament (CVIL), and major mineral deposits in north-central Nevada (Theodore et al. 2003). Distribution of arsenic contents in sediment samples is in normalized log scale. Reported As contents in approximately 4,300 sediment samples are gridded (1,000-m-wide cells) and filtered (z = 5,000 m) resulting in contours showing standard deviations from the mean of log-transformed metal concentrations. [Reproduced with permission of the Society of Economic Geologists from Theodore et al. (2003), *Econ Geol*, Vol. 98, Fig. 1, p. 288.]

Methylated forms of As can also form in surficial environments and are also pH sensitive. Over the natural range of Eh and pH in soils, both As(III) and As(V) can occur in a range of stable aqueous and solid forms. Commonly both forms occur together in waters and some minerals due to redox disequilibrium. The equilibrium constants for selected As species in aqueous solution are given in Table 2.

Thus, As dispersion in water can be extensive and concentrations can vary considerably in naturally occurring waters (Welch and Stollenwerk 2003) as shown in Table 3. Typically rainwater carries few trace elements except in highly industrialized environments where local conditions can impact rainwater chemistry (Hem 1985). River-water As content is likewise

Table 2. Aqueous speciation of arsenic (from Lewis et al. 1976; Nordstrom et al. 2014, this volume)

Arsenic acid	
$H_3AsO_4 \rightleftharpoons H_2AsO_4^- + H^+$	$pK_a = 2.25$
$H_2AsO_4^- \rightleftharpoons HAsO_4^{2-} + H^+$	$pK_{a2} = 6.98$
$HAsO_4^{2-} \rightleftharpoons AsO_4^{3-} + H^+$	$pK_{a3} = 11.58$
Arsenous acid	
$H_3AsO_3 \rightleftharpoons H_2AsO_3^- + H^+$	$pK_a = 9.24$
Monomethylarsonic acid	
$CH_3AsO(OH)_2 \rightleftharpoons CH_3As(OH)O_2^- + H^+$	$pK_a = 4.19$
$CH_3As(OH)O_2^- \rightleftharpoons CH_3AsO_3^{2-} + H^+$	$pK_{a2} = 8.77$
Dimethylarsinic acid	
$CH_3AsO(OH) \rightleftharpoons (CH_3)_2AsO_2^- + H^+$	$pK_a = 6.14$

Table 3. Range of arsenic concentrations in natural waters.

Type	**Range As ($\mu g\ L^{-1}$)**	**Refs.**
Terrestrial rain water	0.013 – 0.032	[1]
Seawater (deep Pacific/Atlantic)	1 – 1.8	[1]
River water	<1 – 12,400	[1]
Lake, mine pit lake	<1 – 508	[1]
Lake water	<0.2 – 0.42	[1]
Groundwater (UK)	<0.5 – 10	[1]
Groundwater (Bangladesh)	<0.5 – 2,500	[1]
Groundwater (West Bengal)	<0.5 – 3,200	[1]
Groundwater (Antofagasta, Chile)	100 – 1,000	[1]
Groundwater, mine impacted (Coeur d'Alene, Idaho, USA)	<1400	[1]
Groundwater, mine impacted (Northern Bavaria, Germany)	<10 – 150	[1]
Yellowstone geothermal water (Wyoming, USA)	160 – 10,000	[2]
Waiotapu geothermal (New Zealand)	710 – 6,500	[2]
Wairakei geothermal (New Zealand)	230 – 3,000	[2]
El Tatio geothermal (Chile)	45,000 – 50,000	[3]
Salton Sea (USA)	30 – 12,000	[1]

References: [1] Smedley and Kinniburgh (2002); [2] Webster and Nordstrom (2003); [3] Ellis and Mahon (1977)

a product of local conditions in which point-source discharges, such as a mine, can impact local river-water chemistry adversely but the area impacted is typically limited and dilution tends to reduce the impact with distance. In addition, such changes can also occur in response to localized changes over time in the physical and chemical conditions of the receiving environment. For example the Mokrsko stream in central Czech Republic is a neutral oxic stream that drains a natural As-Au anomaly with As concentrations decreasing away from this point source and also shows diel and seasonal variations (Drahota et al. 2006, 2009, 2013).

Groundwater arsenic concentrations can vary significantly (Table 3). Apart from volcanic and geothermal inputs and anthropogenic impacts including mining-influenced water (Smedley and Kinniburgh 2002; Webster and Nordstrom 2003), some large aquifers, demonstrate natural concentrations above 50 μg L^{-1} (Table 3). These aquifers have been reported from Bangladesh, West Bengal, Chile, Argentina, China, Mexico, Vietnam, and parts of Canada and the U.S.A. (Smedley and Kinniburgh 2002; McGuigen et al. 2010; Chappells et al. 2014). Although the presence of As concentrations above 50 μg L^{-1} is not uncommon, it is not typical. The conditions controlling these elevated As levels are complex and relate to bedrock type (although not always), past and present hydrogeology, and geochemical environment. The most studied area of natural high As groundwater is in Bangladesh and West Bengal where high As in alluvial and deltaic aquifers has resulted in a significant human-health impact. Here, more than a quarter of all shallow drinking-water wells contain As above 50 μg L^{-1} (Smedley and Kinniburgh 2002).

The impacted aquifers are generally shallow (100-150 m deep) and developed in Holocene age micaceous sands, silts and clays. The sediments were most likely derived from upland Himalayan catchments and West Bengal basement complex. The aquifers are capped by a layer of clay or silt that restricts the ingress of atmospheric oxygen and, together with organic matter in the sediments, has produced reducing conditions that favor the mobilization of As. The As is believed to be derived mainly by desorption and reduction of arsenate from rapidly buried Fe oxides.

Deeper aquifers in Bangladesh tend to show lower concentrations of As. The differences between the two aquifers may relate to variations in the total As reservoir available in host sediments, oxidation state of As, and the speciation of As in the sediments. In addition, groundwater recharge and flushing of the aquifers in the Bengal basin are also contributing factors. Older, deeper sediments have most likely been subject to prolonged periods of groundwater flow assisted by greater hydraulic driving forces during the Pleistocene (Smedley and Kinniburgh 2002). Older sediments are often oxidized and have sufficient hydrated ferric oxides to immobilize As through sorption.

ANTHROPOGENIC ARSENIC CONTAMINATION

Human activity contributes to the mobilization of As through mining and mineral processing, combustion of fossil fuels, and the use of As in pesticides, herbicides, crop desiccants, wood preservatives, and as an additive to livestock feed, particularly for poultry and swine. It was once common practice to dip sheep and cattle in As-rich solutions to rid them of parasites and other pests. Examination of these solutions led to the discovery of arsenate-reducing and arsenite-oxidizing microorganisms. Although the use of arsenical products such as pesticides and herbicides has decreased significantly in the last few decades, their use for wood preservation is still common in developing countries and for municipal use (Matschullat 2000, 2011). The impact on the environment of the use of arsenical compounds, at least locally, will remain for many years.

These anthropogenic outputs can be observed on local- to continent-scale mapping of soil and sediment geochemistry (e.g., Reimann et al. 2009). For example in the Kola region of Russia, the dispersion of As from smelting operations generates localized hot spots of As in the vicinity of the Norilsk Smelter (Fig. 2). Elevated As is also seen in the gold-mining region near Kittilä, Finland, especially in the C-horizon soils (Fig. 2).

Perhaps the most commonly identified source and concern for As in the environment and its toxicity are the impacts related to mining (Craw and Bowell 2014, this volume). Under the extremely acidic conditions of acid mine drainage (AMD), high concentrations of arsenic (up to 850 mg L^{-1}) have been reported (Nordstrom and Alpers 1999). The highest values of

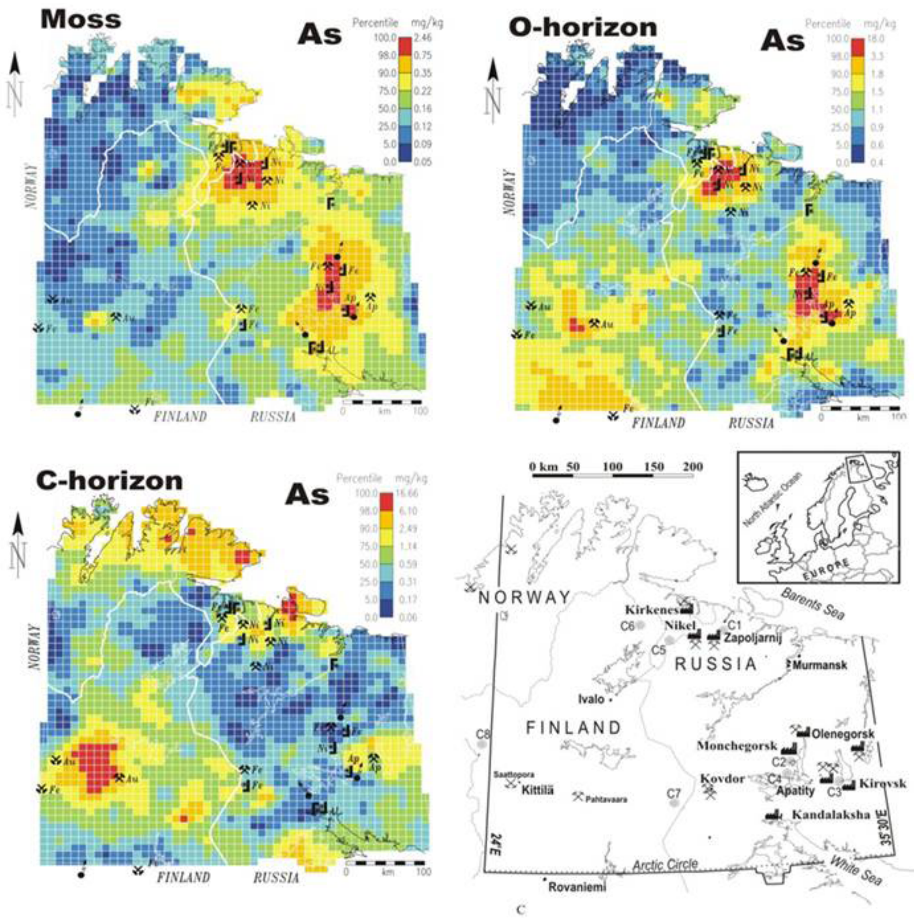


Figure 2. (*for color see Plate 2*) Regional distribution of As in moss and O- and C-horizon soil samples in the Kola Project area. [Reproduced with permission of Elsevier from Reimann et al. (2009) *Appl Geochem*, Vol. 24, Fig. 9, p. 1158.]

dissolved As reported in the literature (130,000 mg L^{-1}) were found at the Jáchymov mine in Czech Republic in highly acidic waters with a pH around 0 (Majzlan et al. 2014). Very-high As concentrations (4,000 mg L^{-1}) have also been measured in pH-neutral waters associated with arsenic trioxide produced from ore roasting (Jamieson 2014, this volume). Extensive study has been made of methods to mitigate the impacts of mining on the environment with respect to As pollution including management of future potential discharges (Riveros et al. 2001; Bowell and Craw 2014, this volume).

ARSENIC IN THE BIOSPHERE

Arsenic is also present in the biosphere and can be transferred through the food chain. Although the element is not an essential nutrient it can be taken up by pathways mimicking that of beneficial nutrients, for example arsenate via the phosphate transporters and arsenite via the aquaglyceroporin channels (Bhattacharjee et al. 2008; Zhao et al. 2010; Yang et al. 2012). The total arsenic content of terrestrial plants is estimated to be 1.8×10^5 tons, approximately four orders of magnitude less than that in soil (Matschullat 2011). This difference reflects generally limited As bioaccumulation because of the low bioavailability of As in soil. There are exceptions, however, such as ferns that can accumulate more than 1,000 mg kg^{-1} As and rice species that have been reported as being hyperaccumulators (Ma et al. 2001; Srivastava et al. 2006; Zhu et al. 2014).

In the tissue of living organisms, As occurs as As(III) or As(V) with As(III) predominant in reduced environments. Biological transformation can also lead to stabilization of As(III) in oxic environments as methylated As or arsenosugar compounds (Zhu et al. 2014).

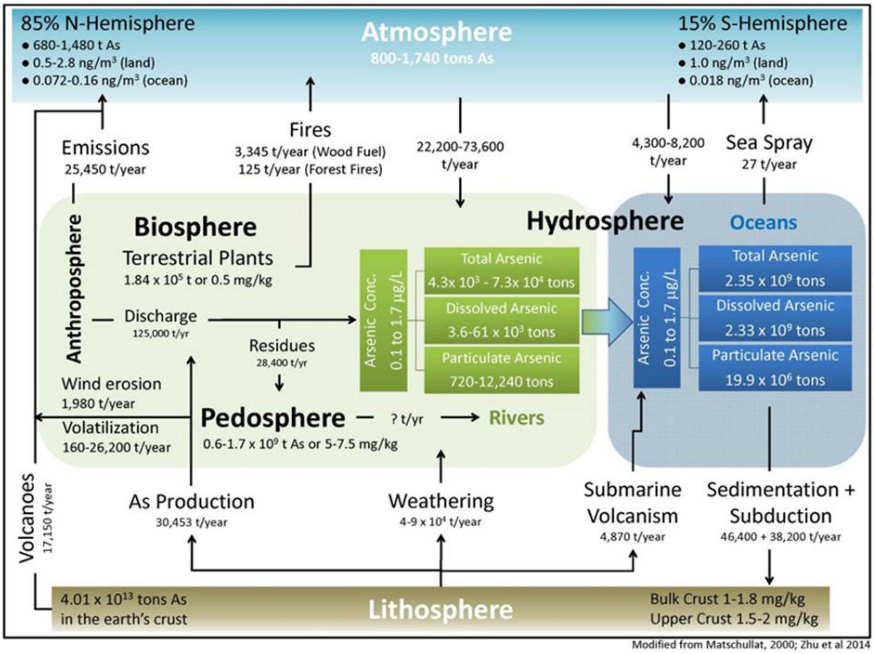
In marine organisms, As is commonly present as arsenobetaine (AB) and arsenosugars (Francesconi and Edmonds 1996). Arsenic (III) is predominant in reduced environments, although it can occur in oxic environments as a result of biological transformation and redox disequilibrium (Zhu et al. 2014). In most living organisms, arsenite is predominant due to the prevailing low redox conditions. The activity of microbial methylation reactions is well understood. In the presence of microorganisms, methylation of the arsenic oxyanion may occur to form monomethylarsonic acid (MMAA), dimethylarsinic acid (DMAA), trimethylarsinic acid (TMAA), and dimethylarsine (DMA) (Zhu et al. 2014). The reduction of arsenate to arsenite may have been an important process in primeval biological cycles (van Lis et al. 2013; Zhu et al. 2014).

In general, the thermodynamically most stable aqueous As species over the general groundwater pH range of 4-8 is $H_2AsO_4^-$. Under reducing conditions, H_3AsO_3 will be the most stable aqueous arsenic species in the absence of complexing ions and methylating organisms. However, the rate of change in the oxidation state of As is not rapid unless microbially mediated, and microbial catalysis can change the distribution of redox species substantially from equilibrium (Zhu et al. 2014). Although some organisms can fully methylate As over a wide Eh-pH range, others are more specific in the As species with which they can react. These processes are also pH dependent and consequently pH variations affect the distribution of organic as well as inorganic As species (Amend et al. 2014, this volume).

BIOGEOCHEMICAL CYCLING OF ARSENIC

The majority of As in Earth's crust-ocean-atmosphere system is present in the lithosphere (Fig. 3). The size of the lithospheric pool is approximately five orders of magnitude larger than that in the ocean (Matschullat 2011). Weathering of rocks, geothermal and volcanic activities, mining, and smelting release As from the lithosphere to the terrestrial and oceanic environments (Fig. 3). The biosphere reservoir appears to be fairly well characterized (e.g., Ma et al. 2011; Zhu et al. 2014). However the detection of hyperaccumulating plant species and highly variable results still present challenges to providing accurate predictions of As budgets. The shortest-term reservoir, the atmosphere, presents more of an issue. Limited data exist for As in the atmosphere and even less for the anthroposphere, so related estimates of global flux are not very reliable. Due to the very low concentrations observed in atmospheric media compared with soils, the impact of airborne pollution may be difficult to detect except in extreme examples (e.g., Reimann et al. 2009; Jamieson 2014, this volume).

The concentrations of As in natural waters vary by more than four orders of magnitude depending on the source of As, the amount available and the local geochemical environment (Fig. 3). Under natural conditions, the greatest range and the highest concentrations of As are found in groundwaters as a result of the strong influence of water-rock interactions and the greater tendency in aquifers for the physical and geochemical conditions to be favorable for As mobilization and accumulation. The reported ranges are therefore extreme and unrepresentative of natural waters as a whole. Concentrations are commonly higher when riverine inputs are affected by industrial or mining effluent or by geothermal water. Unlike some other trace



Modified from Matschullat, 2000; Zhu et al 2014

Figure 3. (*for color see Plate 3*) Global arsenic cycle. Redrawn and simplified from Matschullat (2000), Zhu et al (2014).

elements such as boron, saline intrusion of seawater into an aquifer is unlikely to lead to a significant increase of arsenic in the affected groundwater. In lake and river waters, As(V) is generally the predominant species (Pettine et al. 1992), though significant diel and seasonal variations in speciation as well as absolute concentration have been found (Gammons et al. 2007). Concentrations and relative proportions of As(V) and As(III) vary according to changes in input sources, redox conditions and biological activity. The presence of As(III) may be maintained in oxic waters by biological reduction of As(V), particularly during summer months (Lloyd and Oremland 2006; Santini and Ward 2012). Higher relative proportions of As(III) have been found in rivers close to inputs of As(III)-dominated industrial effluent and in waters with a component of geothermal water (Webster and Nordstrom 2003; Morin and Calas 2006).

Proportions of As(III) and As(V) are particularly variable in stratified lakes where redox gradients can be large and seasonally variable (e.g., Kuhn and Sigg 1993). As with estuarine waters, distinct changes in As speciation occur in lake profiles as a result of redox changes. For example, in the stratified, hypersaline and hyperalkaline Mono Lake (California, U.S.A.), there is a predominance of As(V) in the upper oxic layer and of As(III) in the lower reducing layer (Maeda 1994; Oremland et al. 2000). Rapid oxidation of As(III) occurs during the early stages of lake turnover as a result of microbial activity (Oremland et al. 2000). This event precedes Fe(II) oxidation although the speciation of As in lakes does not always follow that expected from thermodynamic considerations.

Welch et al. (1988) found that the Eh calculated from the As(V)-As(III) couple neither agreed with that from the Fe(II)-Fe(III) and other redox couples nor with the measured Eh. Therefore, the As redox couple is not reliable as a redox indicator except in a qualitative manner. Kempton et al. (1990) showed that only the Fe(II/III) and the $Fe(CN)_6^{3-}/Fe(CN)_6^{4-}$ redox couples respond quantitatively to a platinum electrode in a Nernstian equilibrium manner.

Therefore, redox species have to be measured; they cannot be calculated reliably from Eh measurements. Much of this redox disequilibrium has been attributed to the role of microorganisms in the cycling of As (Zhu et al. 2014).

As a molecular analogue of phosphate, arsenate uses a phosphate transport system to enter cells. Once inside, it inhibits the phosphorylation of ADP and thereby the synthesis of ATP, leading to its toxic legacy. Arsenate can also substitute for phosphate in various biomolecules, thus disrupting key pathways, including glycolysis. Arsenite is even more toxic than arsenate and enters the cell much like glycerol molecules (Meng 2004). Arsenite binds with glutathione, a key enzyme in mammalian metabolism, inhibiting its function and it binds to thiolates in cysteine residues, disrupting the function of many proteins (Mukhopadhyay et al. 2002).

Arsenic levels in edible plants are generally low, even in crops grown on contaminated land with lower levels in Fe-rich and clay-rich soils and higher levels in plants grown on sandy or organic-rich soils such as aridisols, alluvium, or peat (Abrahams and Thornton 1987). The degree of uptake is variable from species to species. Unlike marine and freshwater organisms grown in contact with sediments, the As level in plants remains below that of the associated soils. In plants, roots show higher As levels than stems, leaves, or fruit and lower plants and grasses have a greater uptake than higher-order plants. For example in SW England, crops growing directly on As-contaminated spoil rarely exceed 1 mg kg^{-1} As while grass growing on identical substrate can have levels in excess of 2000 mg kg^{-1} As. In urban areas, similar grass species growing on soil with 20 mg kg^{-1} As were found to have a maximum of 3 mg kg^{-1} As dry weight (Abrahams and Thornton 1987).

Arsenic uptake by plants tends only to be significant in alkaline soils or where extremely high As levels (>10,000 mg kg^{-1} As) occur in the substrate (Table 4). In the Bau area of Sarawak, Malaysia, high As levels in the soil (15-50,000 mg kg^{-1} As) coupled with an alkaline soil pH (7.5-8.4) has led to high As uptake in bamboo species (up to 4,500 mg kg^{-1} in roots and 2,650 mg kg^{-1} in leaves). In the Kutna Hora district, Czech Republic, a strong As uptake from mine-impacted soils and root vegetables has been demonstrated in laboratory tests (Száková et al. 2010). The highest As concentrations occur around areas where the soil is comprised of lime (used in the kilns) and mine spoil.

Table 4. Biogeochemistry of arsenic in vegetation from mine sites.

Region	**Range As (mg kg^{-1})**	**Refs.**
Ashanti, Ghana	18 – 4,800	[1]
South West England	3 – 2,700	[2]
Kilimafeza, Tanzania	0.5 – 26.3	[3]
Flin Flon, Manitoba, Canada	400	[4]
Nova Scotia, Canada	36 – 738	[4] [5]

References: [1] Bowell (1991); [2] Abrahams and Thornton (1987); [3] Bowell et al. (1995); [4] Brooks et al. (1981); [5] Wong et al. (1999)

Arsenic uptake in plants can occur through aqueous transfer at the roots or from absorption of colloids or dissolved species through leaves. The cycling of As in the near-surface environment thus occurs not only through solution transfer but also through the decay of As-bearing vegetation and recycling of this material (Fig. 4).

SUMMARY

Arsenic is common in the near-surface environment but concentrations in water, solids, and biota are highly variable. The distribution of As in the environment is dependent on source, mineralogy, speciation, biological interactions, and geochemical controls. This paper

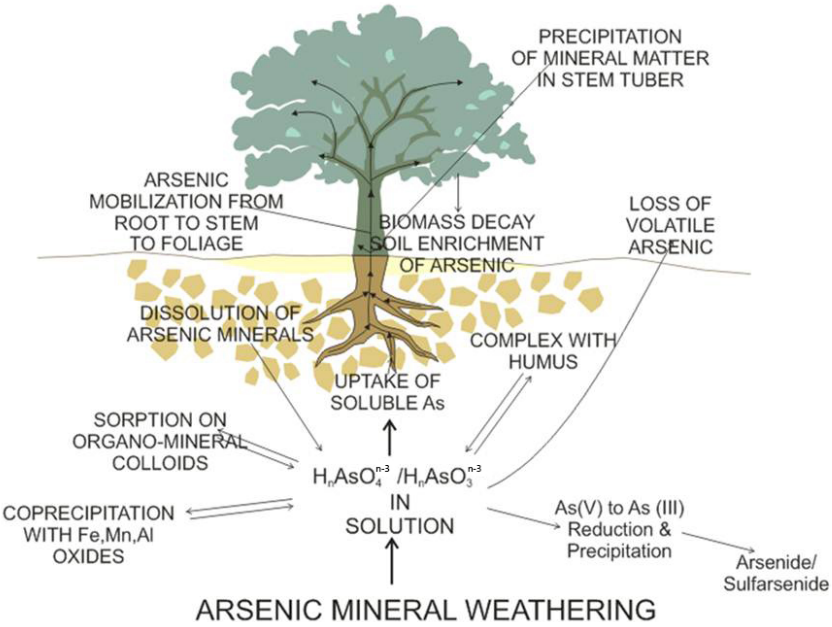


Figure 4. Conceptual model of arsenic cycling in the near-surface environment (after similar schemes by Stopinski 1976).

has attempted to characterize the distribution and cycling of As in the environment and to introduce the main biogeochemical controls on its speciation and mobilization.

Arsenic-rich environments are typically associated with chalcophile mineral deposits or geothermal activity. However, As-rich sediments and soils can also occur due to sedimentary and hydrogeological cycling of As-rich materials. The biological transformation and cycling of As can lead to oxidation or reduction of species that mobilize or attenuate As. Methylation and demethylation may also occur and this may promote transfer of As in the food chain, affecting ecological toxicity.

Predictive calculations of arsenic cycling are limited by the accuracy and precision of thermodynamic data for some minerals and aqueous species (Nordstrom et al. 2014, this volume). Data for global fluxes are limited for some natural processes, such as volcanism and soil degassing. Pedosphere and hydrosphere studies have tended to focus on areas of known “enriched” arsenic anomalies but regional mapping studies (such as Reimann et al. 2009) have greatly improved estimates for baseline or background estimates of As. The natural variation in As concentrations is large (2-3 orders of magnitude) and typically displays little variation in a vertical soil profile. Anthropogenic contamination is highly localized and provides notable hot spots.

In understanding the dispersion of As in the environment, geological materials provide a basic framework for characterizing As concentrations in ecosystems. Large variations can be observed on all spatial scales influenced by a variety of natural processes including non-geological influences such as climate and vegetation. These natural variations must be documented and the processes causing them understood before reliable estimates of the anthropogenic impact on the natural environment can be made.

ACKNOWLEDGMENTS

The authors wish to thank Stephen Day and Michael Parsons for reviews that greatly improved the manuscript.

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