Section 4

Characteristics and Behaviour of Individual Elements

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16

Arsenic and Antimony

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16.1 Introduction

Arsenic (As) and antimony (Sb) are chalcophilic metalloids that share numerous similarities in biogeochemical properties. This chapter reviews the chemical properties, environmental/geochemical reactions, phytoaccumulation and toxicology of the two elements.

Arsenic belongs to Group 15 in the periodic table. The electron configuration is $[Ar]3d^{10}\ 4s^2\ 4p^3$, and it has four major oxidation states (+5, +3, 0, and −3). Arsenic has multiple isotopes, and most of them have very short half-life ($t_{1/2}$) of microseconds to milliseconds. Of these, ^{71}As, ^{72}As, ^{73}As, ^{74}As and ^{74}As have $t_{1/2}$ of approximately 65 h to 80 days, and ^{75}As is the only stable isotope. In the soil and water environment, inorganic As is mainly present in two oxidation states (+3 and +5). Arsenite, As(III), commonly exists as arsenious acid, $As(OH)_3$, in reduced environments. Conversely, an oxidized environment contains more arsenate, As(V), as arsenic acid (for example, $HAsO_4^{2-}$). Antimony also belongs to Group 15 in the periodic table. The electron configuration is $[Kr]\ 5s^2\ 4d^{10}\ 5p^3$, and it has four major oxidation states (+5, +3, 0 and −3). The most common oxidation states in low temperature environments are +5 and +3. Although Sb has multiple isotopes, most of them have short $t_{1/2}$ of <1 day. Only a few of its isotopes have $t_{1/2}$ of more than a few days: ^{122}Sb (2.7 days), ^{124}Sb (60.2 days), ^{126}Sb (12.3 days), and ^{127}Sb (3.85 days). Antimony has two stable isotopes, ^{121}Sb and ^{123}Sb. Antimony-125 is a fission product of ^{235}U, and has a half life of ~2.76 years. While antimonite, Sb(III), commonly exists as antimonous acid,

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$Sb(OH)_3$, in reduced environments, antimonate, Sb(V), as $Sb(OH)_6^-$ is commonly present in oxidized environments.

These elements have commonly been used in industrial, medical, and agricultural applications. One of the common industrial uses of As is in tanneries for preserving animal hides. Arsenic has also been used in agriculture as a component of insecticides, herbicides, fungicides, algaecides, sheepdips, wood preservatives, deworming agents for livestock, and vaccinations for poultry and swine [1,2].

Antimony was historically used in the gold extraction processes. The Sb sulfide stibnite (Sb_2S_3) is the principal ore of antimony, and has a brilliant metallic luster. The color was used for cosmetic purposes (for example, eyeliner) in ancient times. In more recent years, stibnite is used in the semiconductor industry to produce diodes and infrared detectors. It is also commonly used as a mixing compound with lead to strengthen the hardness of batteries, alloys, bullets, cable sheathing, matches, medicines, plumbing, and soldering [3,4]. It can be found in flame-retardants in plastics and textiles, and medical drugs to treat some tropical diseases (for example, visceral leishmaniasis).

Arsenic and Sb in soil and water environments originate from indigenous sources (for example, mineral weathering) and anthropogenic inputs (for example, mining, industrial processes, and pesticide application). Due to their undesirable toxicological effects, these metalloids pose threats to human health and the wider environment. In particular, As contamination occurs worldwide, with hotspots in Thailand, Taiwan, mainland China, Argentina, and Chile. There are also many watersheds and drinking water sources in the United States affected by As contamination. In some parts of South East Asia, Bangladesh and West Bengal, the total As level can be as high as 150 $\mu g\, l^{-1}$ in drinking water [5], while the maximum concentration level (MCL) set by the US Environmental Protection Agency (USEPA) and the World Health Organization (WHO) is 10 $\mu g\, l^{-1}$ [6,7].

The maximum drinking water limit for Sb was set to 5 $\mu g\, l^{-1}$, though this is considered provisional until a greater understanding of its toxicity is achieved [7]. While the MCL of Sb is low, typical Sb concentrations in uncontaminated waters are less than 1 $\mu g\, l^{-1}$ [7]. However, there are some reports of elevated Sb levels in natural geothermal systems ranging from 500 to 100, 000 mg kg^{-1} [8–11].

Arsenic can have negative impacts on both human and ecological health, because of the carcinogenicity (for example, skin, lung, and bladder), phytotoxicity and biotoxicity [12,13]. Arsenate, As(V) is known to replace phosphate in substituted monosaccharides, along with inhibiting ATP synthesis by uncoupling oxidative phosphorylation, leading to the breakdown of energy metabolism [14]. Arsenite, As(III), is generally more toxic than As(V) due to its preferential reaction with sulfhydryl groups in mammalian enzymes [15], resulting in inhibition of the pyruvate and succinate oxidation pathways and the tricarboxylic acid cycle, impaired gluconeogenesis, and reduced oxidative phosphorylation. Labile As(III) as arsenious oxide (As_2O_3) is absorbed through the lungs and intestines, and biochemically acts to coagulate proteins, form complexes with coenzymes, and inhibit the production of the essential enzyme andenosine triphosphate (ATP) in metabolic processes [16]. Arsine gas is known to cause a dose-dependent intravascular hemolysis and multisystem cytotoxicity in rodents (for example, [17]).

The sudden infant death syndrome drew public attention to Sb toxicity [18,19]. It was hypothesized that stibine (SbH_3) gas formed by fungal transformation of fire retardants containing Sb in cot mattresses might be a cause of sudden death syndrome [19]. However, there is insufficient epidemiological evidence to support the theory [20]. In adult humans, inhalation of stibine gas is known to cause hemolytic anemia, hemolysis, myoglobinuria, hematuria, renal failure, nausea, vomiting, and headache. Pneumoconiosis, other respiratory effects, and cutaneous effects (for example, a transient and pustules known as 'antimony spots') have been reported in workers occupationally exposed to dusts and fumes containing Sb [21,22]. Cardiovascular mortality and morbidity have been attributed to inhalation of the Sb trisulfide [23]. Patients treated with antileishmaniasis agents, sodium stibogluconate, showed side-effects of renal tubular acidosis, thrombocytopenia, and pancreatitis [24–26]. However, the mechanism of toxicity of Sb(V) compounds is not clearly understood.

16.2 Geogenic Occurrence

16.2.1 Arsenic

The average total As content in uncontaminated soils is approximately 5 mg As kg^{-1} [27,28]. Volcanic soils may contain up to 20 mg As kg^{-1} [15]. Due to the application of As-containing pesticides and defoliants, the As content of contaminated soils can range up to 2553 mg As kg^{-1} [29]. The average As level in agricultural soils in 12 US states was approximately 165 mg As kg^{-1} [30].

Naturally occurring As is found in about 245 mineral species including arsenides, sulfides, sulfosalts, and oxidation products such as oxides, arsenites, and arsenates. These are generally associated with basin-filled deposits of alluvial-lacustrine origin, and volcanic deposits [2,31]. Naturally occurring As-S minerals are arsenopyrite (FeAsS), enargite (Cu_3AsS_4), orpiment (As_2S_3), and realgar (AsS). In terrestrial environments, inorganic forms are generally predominant over organic forms. The speciation of the inorganic forms (arsenite and arsenate) is highly affected by pH and redox conditions. Most of the organic fractions are associated with methyl groups ($–CH_3$) such as methanearsonic acid (MAA) and dimethylarsinic acid (DMAA) [32]. In agricultural drainage/evaporation ponds, approximately 40 % and 15 % of total As are found as DMAA and MAA, respectively [33]. Eventually organic As species are converted into CO_2 and inorganic As by oxidative degradation, or into volatile As compounds or arsine (AsH_3) gas by reduction and further methylation. Due to the low solubility of the volatile compounds, they readily complex with atmospheric particulates before being deposited on the ground [2].

16.2.2 Antimony

In geothermal systems, antimony is commonly associated with gold and sulfur [34]. The average total Sb content in uncontaminated soils is in the order of a few micrograms per kilogram [35,36]. Martin and Whitefield [37] reported the average Sb concentration in soils of approximately 1 $\mu g\ kg^{-1}$. The majority of natural Sb sources are mineral deposits from hot springs, volcanic ore deposits, boreholes, and gold mines in schist [9,11].

Elevated concentrations (8–61 mg Sb kg^{-1}) of Sb have been observed near smelting plants and outfalls of sewage and fertilizer facilities [38–41]. There is a report about Sb-enriched sandstone from Zimbabwe containing total Sb of up to ~5000 mg kg^{-1} [42]. Areas near old mining and Cu and Pb smelting can have residual Sb levels of 103–260 mg kg^{-1} [39,43,44].

Naturally occurring antimony is commonly combined with S, Pb, and As to form over 100 different minerals. In hydrothermally altered rocks, Sb is often found in stibnite [Sb_2S_3] and/or kermisite [Sb_2S_2O], guettardite, [$Pb(Sb,As)_2S_4$], cervantite [$Sb(III)Sb(V)O_4$] and paradocrasite [$Sb(III)_2(Sb(III),As)_2$]. Of these minerals, only stibnite (SbS_3) is commercially mined as a source for metallic antimony. A trace quantity of Sb is generally present in Ag, Cu, and Pb ores. Like As, Sb can be volatilized as SbH_3 or methylated species in the environment [45].

16.3 Sources of Soil Contamination

Arsenic contamination sources originate from both indigenous and anthropogenic inputs, including atmospheric deposition. Weathering of As-containing primary minerals, the main natural source of contamination, could yield an annual global input of 45 000 Mg As y^{-1} [14]. While shales and coal contain mean As concentration of 13 mg kg^{-1} and 25 mg kg^{-1}, respectively, sedimentary rocks could contain As concentrations as high as 2000 mg kg^{-1}. The major anthropogenic sources of As originate from industrial processes such as smelting of As-containing ores and by-products of fossil fuel combustion (for example, fly coal ash), and agricultural uses. Approximately 60 % of the anthropogenic As emissions are largely associated with two sources: Cu-smelting and coal combustion [46]. The total As input into the atmosphere including volcanic activity, wood preservatives grassland fires marine aerosols and biogenic liberation is estimated to be approximately 2.8×10^7 kg As y^{-1} [46,47].

Agricultural applications of As include insecticides, herbicides, fungicides, algaecides, sheepdips, wood preservatives, deworming and antibacterial agents for livestock, vaccination for poultry and swine, and recycled poultry litter [1,48]. Poultry litter containing an organic As compound (Roxasone) as an antibacterial agent has been used in agriculture at the rate of 8.96–20.16 Mg ha^{-1}, with total As inputs in three US states (Delaware, Maryland, and Virginia) estimated at between 20 and 50 Mg As y^{-1}[49].

Most Sb soil pollution originates from mining and smelting industries and from the outfalls of sewage, shooting ranges and fertilizer facilities [1,38–41]. In the United States alone, approximately 5.5×10^6 kg of Sb-associated compounds were released into the aquatic and terrestrial environments between 1993 and 1997, with more than 97 % released onto the land [50]. In addition to the terrestrial inputs, significant amounts of air-borne Sb have also contributed to overall Sb inputs. Global atmospheric input of Sb can be as high as 6.1×10^3 Mg y^{-1}. While ~60 % of the atmospheric inputs are from anthropogenic sources including the incineration of waste, fossil fuel combustion, and the smelting of metal, the rest are from natural sources including wind-blown dust, sea salt spray, volcanic activity, and forest fires [51–54].

16.4 Chemical Behavior in Soils

16.4.1 Arsenic Speciation and Solubility

In general, the solubility of inorganic As increases in reduced environments. Adsorbed As can be released through reductive dissolution of the adsorbent, for example conversion from the ferric ion to the ferrous ion. A direct reduction of As(V) to As(III) also increases the solubility of total As due to weak As(III) sorption on soil components. Arsenic can form solubility products with calcium, aluminum, sulfur and iron in the soil/water environment. The solubility constant values (10^{-11}) for iron and aluminum arsenates are smaller compared to that of calcium arsenate (10^{-5}), indicating that iron and aluminum control the availability of As in soils [29]. In oxic environments, the predominant chemical species is arsenate, which readily binds to clay minerals. pH also affects the solubility of arsenate. While arsenate ions precipitate out with trivalent metals, for example Al(III) and Fe(III)) to form scorodite and amorphous aluminum arsenate at acidic pH, calcium arsenate precipitates (for example, $Ca_3(AsO_4)_2$) at alkaline pH conditions [55]. Barium arsenate ($Ba_3(AsO_4)_2$) is known to be most insoluble of the As precipitates. In reduced systems, arsenite forms solubility products with sulfides (for example, realgar, AsS, and orpiment, As_2S_3).

In low-temperature geochemical environments, inorganic As is mainly present in two oxidation states (+3 and +5). Figure 16.1 shows the effects of redox potential

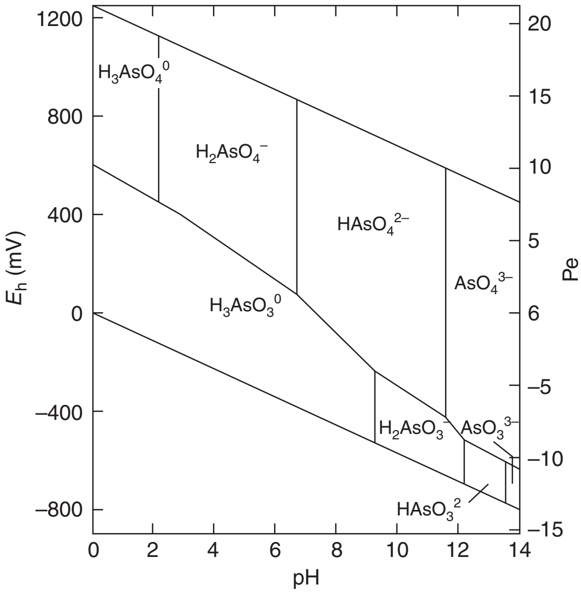

Figure 16.1 *E_h–pH diagram for aqueous As species in the system As–O_2–H_2O at 25 °C and 1 bar total pressure (Reprinted from Applied Geochemistry, 17, P.L. Smedley and D.G. Kinniburgh,* A review of the source, behavior and distribution of arsenic in natural waters, *517–568. Copyright 2002, with permission from Elsevier [56].)*

(E_h) and pH on aqueous As speciation. Arsenite, As(III), commonly exists as arsenious acid, $As(OH)_3$, in reduced environments (for example, E_h -200 mV $< +300$ mV over a pH range of 4 to 8) [2]. It has weak acid characteristics similar to boric acid (Equation 16.1):

$$As(OH)_3 + H_2O \longleftrightarrow As(OH)_4^- + H^+, \quad \log K = -9.29 \tag{16.1}$$

A fully protonated form is expected to be predominant in reduced soil environments due to the high pK values (pK_1 = 9.22, and pK_2 = 12.13). Conversely, oxidized environments contain more arsenate, As(V), as arsenic acid. Dissociation constants of arsenic acid (pK_1 = 2.20, pK_2 = 6.97, and pK_3 = 13.4) predict deprotonated forms of arsenic ($H_2AsO_4^-$ and $HAsO_4^{2-}$) in acidic to neutral environments.

In neutral oxygenated aquatic systems, As(III) oxidation has been reported to have a half-life of 1 year [57], and no oxidation occurred over a 37-day period in distilled, deionized water [58]. Arsenite oxidation in a 0.0005 M NaCl solution was stable below pH 9 after 72 h [59].

In soil and water environments, As solubility is controlled not only by the redox potential but also by the types of sorbent available, that is Fe(III) and Mn(IV) hydroxides, and the As minerals themselves. In general, reducing conditions and/or the presence of reductants readily promote sorbent dissolution, causing the release of sorbed As. Increased As solubility in reduced soils has been reported by many researchers [60–63]; however, decreased As solubility in long-term flooded soils has also been observed [63,64]. Resorption of As on solids [65] and co-precipitation of $Mn_3(AsO_4)_2$-like phases [61] were suggested to explain the decreased As solubility under long-term and moderately reduced conditions (0–100 mV).

The influence of redox potential on the solubility of As from several metal-arsenate minerals was investigated in a Santa silt loam soil from northern Idaho using an equilibrium thermodynamic study coupled with XANES (X-ray absorption near edge structure) analysis of arsenic oxidation [66]. Arsenic solubility decreased under oxidized conditions as: $Ca_3(AsO_4)_2 = Na_2AsO_4 > AlAsO_4 > Mn_3(AsO_4)_2 > Fe(AsO_4)_2$. In contrast, under anoxic conditions (<0 mV), the relative solubilities were: $Fe(AsO4)_2 > Ca_3(AsO_4)_2 = Na_2AsO_4 > AlAsO_4 > Mn_3(AsO_4)_2$. XANES analysis showed that aluminum arsenate is rapidly converted to solid-phase arsenite, indicating the most susceptible metal-arsenate phase occurs under reducing conditions [66].

16.4.2 Arsenic Retention in Soils

The retention of As on soils is highly dependent on the physicochemical properties of the soils, especially the nature and abundance of crystalline and amorphous iron and aluminum oxides, and clay and calcium contents. Several researchers have reported that As(III) and As(V) retention in soils are highly associated with ammonium oxalate-extractable iron (Fe_{ox}) and/or aluminum (Al_{ox}) and dithionite–citrate–bicarbonate (DCB)-extractable iron and/or aluminum [67–74]. High As(V) retention in calcium rich soils with pH > 7 has also been reported [75]. The sorption of As(III) and As(V) on three California soils was studied at varying As concentration, pH, and ionic strength [69]. The soils with the highest DCB-extractable Fe and the highest clay content had the highest affinity for As(III) and

As(V). Sorption isotherms showed that As(V) species sorbed more strongly than As(III) under most conditions.

Ionic strength (*I*) can have an influence on both the rate of the elementary reaction and the type of surface complexation (inner- and/or outer-sphere complexation) [76,77]. Gupta and co-workers [78] investigated the effects of ionic strength on As(III) and As(V) sorption kinetics on alumina. As(V) sorption kinetic experiments (pH ~6.6) showed that an initial sorption rate in seawater was much slower than that in (nonsaline) water. The sorption of As(III) at pH ~8 in seawater was also slower than that in water. Arai *et al.* [79] also reported two different *I* dependencies on As reactivity on alumina; while As(V) was insensitive to changes in *I* at pH 4–8, As(III) sorption decreased with increasing *I* and pH.

Arsenate sorption on soil minerals is influenced by the surface charge density of solids and the speciation of As(V). In general, As(V) sorption on inorganic minerals increases with decreasing pH of bulk fluid (pH_b) due to (i) the negatively charged chemical species, that is $HAsO_4^{2-}$ and (ii) the positively charged mineral surfaces, when $pH_b < PZC$ (point of zero charge) of the solids. The first dissociation constant of As(V) is approximately 2.2, followed by constants of ~7 and ~12.8. At most environmental pH values (4–8), the arsenic species are predominantly in deprotonated forms (negatively charged species), and the charge properties of metal oxides are positive due to the PZC of the solids (that is, 6.5–8.5 for iron oxides, 8.2–9.1 for aluminum oxides, an exception is manganese oxides, for example birnessite ~2.8). Therefore, As(V) is expected to sorb onto metal oxide surfaces strongly via electrostatic interaction when $pH_b - PZC$ is less then zero, and to predominantly sorb via ligand exchange when $pH_b - PZC$ is greater than zero.

pH-dependent sorption behavior of As(V) has been observed for ferrihydrite, hematite and aluminum oxyhydroxides [80–85]. In general, As(V) sorption is maximized at acidic pH, and gradually decreases with increasing pH. Figure 16.2 shows the pH-dependent As(V) sorption on hematite surfaces.

As metal oxyhydroxides (for example, ferrihydrite, hematite, and schwertmannite) exhibit a strong affinity for As(V) at acidic pH values [86–88], various phyllosilicate minerals also show a similar pH-dependent As(V) sorption behavior. Arsenate sorption on alumina, kaolinite, illite, and montmorillonite gradually increases from pH 3 to 5, and then decreases with increasing pH up to 10 [75,82,85,89]. Conversely, the As(V) sorption envelope on quartz showed no significant adsorption (less than 15 % of net adsorption) between pH 2.8 and 9.5 [85]. Arai and co-workers [79] investigated As(V) sorption complexes forming at the γ-Al_2O_3–water interface using X-ray absorption spectroscopy (XAS). The XAS data indicates that As(V) forms inner-sphere complexes with a bidentate binuclear configuration, as evidenced by an As(V)–Al bond distance of ~ 3.11–3.15 Å. A similar molecular configuration was reported on allophone surfaces. Several other XAS studies indicated that arsenate inner-sphere sorption mechanisms on metal hydroxide surfaces [91,93–96]. The results of inner-sphere surface species are consistent with the findings of Arai and co-workers' study [79]. The results of spectroscopic investigations are summarized in Table 16.1.

While the sorption of As(V) on metal oxides and phyllosilicate minerals is highly dependent on the relation between pH of the bulk solution and the PZC of solids, As(III) sorption is more dependent on its speciation. At most environmental pH values (4–8),

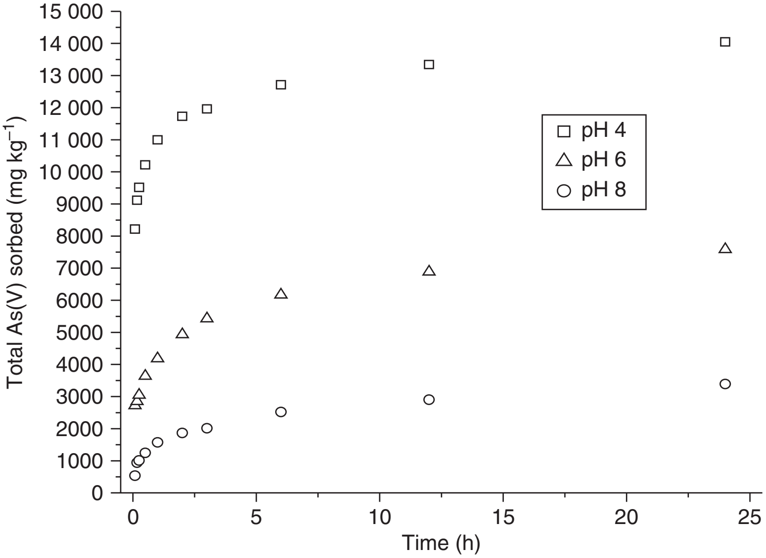

Figure 16.2 *Arsenate sorption kinetics at the hematite–water interface, with suspension density 4g l^{-1}, ionic strength = 0.01 M NaCl, and [As(V)]$_{total}$ = 1.35 mM.*

arsenite (as $As(OH)_3$)(aq) does not have any charge, and the negative charge increases with increasing pH due to its weak acidity ($pK_1 = 9.22$, and $pK_2 = 12.13$). As(III) sorption on metal oxides and phyllosilicate minerals increases with increasing pH, whereas As(V) sorption decreases with increasing pH. Figure 16.3 shows the contrasting pH dependent sorption behavior of As(III) and As(V) on γ-Al_2O_3 surfaces.

The As(III) sorption envelope and isotherms on goethite, kaolinite, illite, montmorilloinite, and aluminum hydroxide were investigated earlier [59,83,109]. Although there were slight differences in As(III) uptake in different sorbents, As(III) sorption generally increased with increasing pH from 4 to 6, and then gradually decreased. A similar pH-dependent As(III) sorption was also observed in goethite and in arid soils that had high (> 4000 mg kg^{-1}) DCB-extractable iron [97]. Raven and co-workers [86] reported the biphasic As(III) sorption reactions on ferrihydrite; the initial fast sorption was nearly completed within the first few hours, and followed by slow uptake. At initial As concentrations of 0.27–13.3 mol As mol^{-1} Fe ferrihydrite, the As(III) sorption was greater at higher pH. At the highest initial arsenite concentration of 13.3 mol As kg^{-1} of ferrihydrite, a distinct sorption maximum was observed for arsenite adsorption at approximately pH 9.0, which corresponds closely to the first pK_a ($\sim$9.2) of H_3AsO_3.

The presence of As(III) inner-sphere surface species on aluminum oxide, goethite, and birnessite has been reported in several spectroscopic studies (see Table 16.2). While most mineral surfaces retain As(III) via ligand exchange mechanisms, there are a few reports about the formation of As(III) outer-sphere surface complexes on aluminum oxide and ferrihydrite surfaces [79,101].

The oxidation of As(III) in geomedia containing oxidants (for example, manganese oxides) has been reported by several researchers [99,110–113]. Arsenite can be readily

Table 16.1 *A summary of sorption mechanisms of arsenate, arsenite, antimonite, and antimonate in geomedia*

Adsorbate	Adsorbent	Suggested surface species	References
As(III)	γ-Al_2O_3	Inner-sphere bidentate and outer-sphere	[79]
As(III)	Goethite	Inner-sphere bidentate	[97]
		Inner-sphere bidentate	[98]
As(III)	Birnessite	Inner-sphere bidentate	[99]
As(III)	Hydrous Mn oxides	Inner-sphere bidentate	[100]
As(III)	Ferrihydrite	Inner-sphere bidentate and outer-sphere	[101]
		Inner-sphere bidentate	[102]
As(III)	Amorphous Al oxides	Outer-sphere	[101]
As(V)	γ-Al_2O_3	Inner-sphere bidentate	[79]
As(V)	Gibbsite	Inner-sphere bidentate	[100]
		Inner-sphere bidentate	[103]
As(V)	HFO	Inner-sphere bidentate	[104]
	Ferrihydrite		[93,105]
As(V)	Goethite Lepidocrocite, and Akagenite	Inner-sphere bidentate	[93,105]
	Goethite	Inner-sphere bidentate and Inner-sphere monodentate	[94]
	Goethite	Inner-sphere bidentate	[92]
	Goethite	Inner-sphere bidentate	[96]
	Goethite	Inner-sphere bidentate	[98]
As(V)	Amorphous Fe oxides		[101]
As(V)	Hematite	Inner-sphere bidentate	[86]
As(V)	Green rust and Lepidocrocite	Inner-sphere bidentate	[106]
As(V)	Birnessite	Inner-sphere bidentate	[95]
As(V)	Birnessite	Inner-sphere bidentate	[91]
As(V)	Allophane	Inner-sphere bidentate	[90]
Sb(III)	Goethite	Inner-sphere bidentate	[107]
Sb(V)	Goethite	Inner-sphere bidentate	[107]
Sb(V)	Amorphous Fe oxyhydroxide	Inner-sphere	[108]

oxidized to As(V) at the mineral surface and the mineral–water interface either by surface catalysis or direct oxidation. For example, Scott and Morgan [110] reported that the uptake of As(III) by synthetic birnessite (δ-MnO_2) increased with decreasing pH, and oxidation products [110]. The reaction, which was independent of oxygen concentration, indicated that birnessite acted as a direct oxidant for As(III). The reaction rate was positively correlated to the molar ratio of MnO_2/As(III), and the respective reaction order was 1.5 [111].

Surface-catalyzed As(III) oxidation on birnessite was shown in molecular scale analysis, using XANES [99,112,114]. To explain the reaction mechanisms, several researchers suggest the importance of Mn(IV) and/or Mn(III) in birnessite contributing to the initial reactivity of manganese oxides in the experimental systems [115–118].

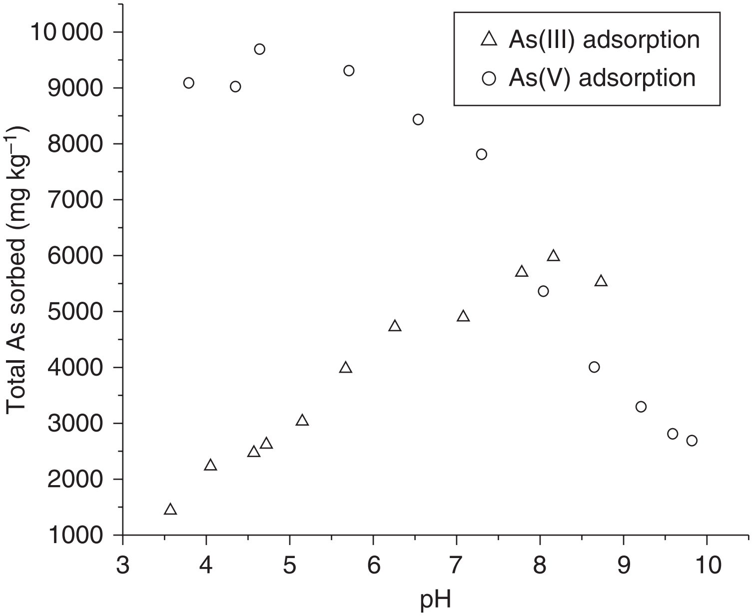

Figure 16.3 *Arsenate and arsenite sorption envelopes on* γ*-*Al_2O_3 *(As(III) and As(V))*$_{total}$ *= 1 mM, suspension density = 5g* l^{-1}*, and ionic strength = 0.01 M NaCl)*

16.4.3 Arsenic Desorption in Soils

The extent of contaminant release greatly affects the bioavailability and transport processes in aquatic and terrestrial environments. Slow desorption and irreversible/hysteretic reactions have been reported in several studies. Slow As(V) desorption was observed in goethite and aluminum oxide [92,119,120]. The desorption rate was significantly slower than the rate of adsorption under similar reaction conditions. Some have found that incubation times strongly influence the reversibility of adsorbed As(V) from soils and soil components (aluminum oxide, goethite, halloysite, kaolinite, illite, montmorillonite, and chlorite) [113,119–121]. The As(V) recovery decreased with increasing aging time. Arai and Sparks [119] reported that the As(V) release from aluminum oxide decreased with increasing aging time from 3 days to 1 year at pH 4.5 and 7.8. The longer the residence time (3 days–1 year), the greater the decrease in As(V) desorption at both pH values, suggesting irreversible reactions. Lin and Puls [122] also reported the irreversible As(V) sorption on clay mineral surfaces. The As(V) recovery decreased with increasing aging time from 1 to 75 days, and the effect was most pronounced in halloysite and kaolinite.

Several researchers tested the effects of ligands on As(V) release from soil components. O'Reilly and co-workers [92] reported that phosphate was more effective than sulfate in removing As(V). Jackson and Miller compared the ability of phosphate and hydroxyl ions to remove various As compounds (that is, As(III), As(V), dimethylarsenic acid, monomethylarsonic acid, *p*-arsanilic acid, and roxasone) from goethite and amorphous iron oxyhydroxide [123]. Although phosphate released As(III) from goethite surfaces, it was not as effective as hydroxyl ions. They reported that hydroxyl ions removed >70 % of all As compounds on these mineral surfaces. The effect of alkaline pH on As release was also documented by Masscheleyn *et al.* [61].

16.4.4 Antimony Speciation and Solubility

Like arsenic, the valence state of Sb greatly affects the solubility in the low-temperature geochemical environments. This means the solution speciation of Sb(III) and Sb(V) influences its retention and transport processes in soils. As discussed above, the speciation of oxyanions is influenced by pH. Oxyanion sorption on soil components is a function of both the net surface charge density of the sorbent and the chemical speciation of the sorbate, which in turn are dependent on the pH of the bulk fluid (pH_b). Antimonite (Sb(III)) commonly exists as antimonous acid, $Sb(OH)_3$, in the reduced environment [35,124,125]. It has weak acid characteristics similar to boric acid as shown in Equation (16.2).

$$Sb(OH)_3 + H_2O = Sb(OH)_4^- + H^+, \log K{=}{-}11.82 \tag{16.2}$$

A fully protonated form is expected to be predominant under reduced conditions due to the high p*K* value. In the presence of aqueous sulfide under reduced conditions, thioantimony complexes (for example, $Sb(III)S_2^-$ and $Sb(III)_2S_4^{2-}$) are known to readily form at neutral to alkaline conditions [10,126]. Under reducing conditions, solubility of Sb is limited by the solubility of Sb(III) sulfides (for example, stibnite) and oxides (for example, $Sb(OH)_3$, Sb_2O_3 (valentinite, senarmontite), Sb_2O_4 (cervantite)). Krupka and Serne [127] demonstrated the solubility calculation of these species under the total Sb concentration (Sb_t) of $10^{-14.6}$ mol l^{-1}. The system was undersaturated with respect to these solids (Figure 16.4). When Sb_{total} increases to 10^{-7} mol l^{-1}, the solubility products (Sb_2O_4, Sb_2S_3, Sb_2O_4, and/or $Sb(OH)_3$) readily form at acidic to alkaline pH values under reducing conditions (−500 mV to 750S mV) (Figure 16.5).

In addition to the sulfide complexes, Sb(III) is also known to make complexes with chlorine at high chloride concentrations. Under reducing conditions, the aqueous species of Sb(III) readily complex with dissolved Cl^- to form $SbCl^{2+}$, $SbCl_2^+$, $SbCl_3^0(aq)$, and $SbCl_4^-$ in acidic aqueous solutions [128].

Conversely, in oxidized environments antimonite, Sb(V) is the dominant Sb species [35,129]. Due to its larger atomic size, the coordination of Sb(V) is different from that of arsenate. It is octahedrally coordinated with six oxygen atoms. A protonation constant of antimonite is shown in Equation (16.3).

$$Sb(OH)_5 + H_2O = Sb(OH)_6^- + H^+, \log K = -2.47 \tag{16.3}$$

This equation predicts negatively charged species ($Sb(OH)_6^-$) in acidic to neutral environments. Antimonate is very soluble in oxic environments [130]. Although the general thermodynamic prediction of Sb(III) species can be applied to reduced environments, Sb(III) species can also be detected in oxic conditions [35]. Researchers have suggested that the metastability of Sb(III) under oxic conditions may have been linked to biotic processes and/or a slow kinetic effect of Sb(III) oxidation. Similarly, Sb(V) is frequently found in anoxic systems [35]. Metastability of Sb(V) might be attributed to the formation

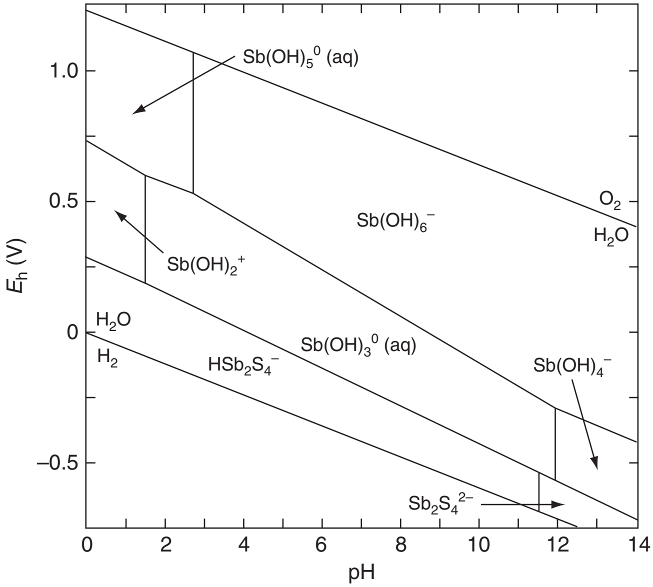

Figure 16.4 *E_h–pH diagram of aqueous speciation of antimony (calculated at 25 °C and a concentration of $10^{-14.6}$ mol l^{-1} total dissolved antimony (Reproduced with permission from K.M. Krupka and R.J. Serne,* Geochemical factors affecting the behavior of antimony, cobalt, europium, technetium, and uranium in vadose sediments, *Pacific Northwest National Laboratory, 2002 [127].)*

of Sb(V) thiocomplexes (for example, SbS_4^{3-}) and/or a slow Sb(V) reduction process in anoxic environments. The presence of Sb(V) sulfide complexes under reducing conditions have been reported by several researchers [131–133].

While the aqueous speciation at low concentrations of total dissolved Sb (<100 μM) can be explained by the studies mentioned above [131–133], Sb(V) may undergo polymerization when dissolved antimony concentration is >0.001 M under acidic conditions, resulting in polynuclear species such as $Sb_{12}(OH)_{64}^{4-}$ and $Sb_{12}(OH)_{66}^{6-}$ [129]. No polymerized Sb(III) aqueous species have been reported.

16.4.5 Antimony Adsorption and Desorption in Soils

Unlike arsenic, the sorption and desorption processes of Sb in geomedia have not been extensively investigated. However, several researchers have studied the macroscopic Sb(III) and Sb(V) sorption in metal oxyhydroxides, phyllosilicate minerals and soils [108,134–137].

In an earlier investigation, Crecelius *et al.* [135] reported strong sorption of anionic Sb(V) hydrolytic species in uncontaminated Puget Sound sediments from Washington, USA. The sorption increased with decreasing pH, and the sorbed Sb(V) fraction was associated with extractable iron and aluminum components in the sediments. Ambe [134] investigated the sorption kinetics of Sb(V) on α-Fe_2O_3 surfaces at pH 4. The rate of sorption was proportional to the square of both the concentration of $Sb(V)_t$ and the

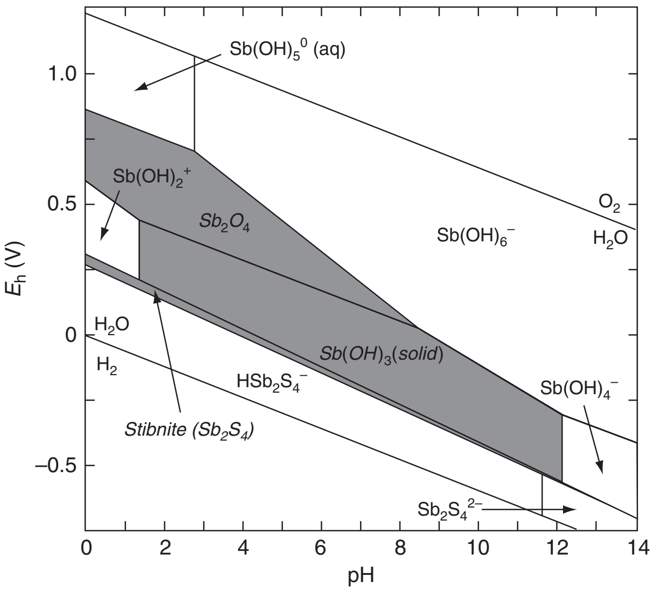

Figure 16.5 *E_h–pH diagram of aqueous speciation and solubility products of antimony. (The diagram was calculated at 25 °C and a concentration of 10^{-7} mol/L total dissolved antimony.) Solubility products are shown shaded (Reproduced with permission from K.M. Krupka and R.J. Serne,* Geochemical factors affecting the behavior of antimony, cobalt, europium, technetium, and uranium in vadose sediments, *Pacific Northwest National Laboratory, 2002 [127].)*

surface area of α-Fe_2O_3. The sorption capacity of the α-Fe_2O_3 sample for Sb(V) ions was ~ 7 mg g^{-1}, which is much less than the calculated value of monolayer coverage (45 mg g^{-1}). Subsequent desorption studies indicated the slow desorption of Sb(V) from the α-Fe_2O_3 surfaces at pH 4–10.

Tighe *et al.* [136] studied Sb(V) sorption in two organic rich soils, and two model phases mimicking those dominant in these soils, namely a solid humic acid and an amorphous $Fe(OH)_3$, at pH 2.5–7 [136]. Antimonate sorption increased with decreasing pH in these soils and in the humic acid. In contrast, the amorphous ferric oxyhydroxide showed less pH dependency of Sb(V) sorption within the pH range examined.

Effects of ionic strength and pH on Sb sorption were investigated on goethite surfaces [137]. Antimonate sorption on goethite decreases with increasing pH from 4 to 10. However, the uptake of Sb(V) was reduced at pH > 6 when ionic strength was increased from 0.01 M to 0.1 M $KClO_4$. The authors suggested that the sorption phenomena in the higher ionic strength solutions was caused by the formation of $KSb(OH)_6^0$ ion pair [137]. On the contrary, antimonite, Sb(III) sorption was not strongly affected by changes in the pH or ionic strength [137]. Antimonite adsorption was insensitive to changes in I at pH 2–6. A modified triple-layer model was successfully used to describe the inner-sphere Sb(III) and Sb(V) sorption processes in goethite under the reaction conditions studied [137].

More recently, a few spectroscopic studies were conducted to investigate the sorption mechanisms of Sb(III) and Sb(V) on mineral surfaces [106,107]. Scheinost *et al.* [107]

reported that the presence of specific Sb–Fe interatomic distances corresponded to the edge sharing inner-sphere surface species of Sb(III) and Sb(V) on goethite surfaces (Table 16.1). McComb and co-workers [108] used Attenuated Total Reflectance infrared (IR) spectroscopy to understand Sb(V) retention at the amorphous iron oxyhydroxide–water interface. The chemisorption of Sb(V) increased with decreasing pH from 8 to 3. They suggested a ligand exchange reaction (that is, inner-sphere sorption mechanism) based on the Fourier transform infrared (FTIR) spectra observation; the loss of an OH stretching mode upon the Sb(V) reaction on the mineral surfaces (Table 16.1). They also observed an increase in the extent of Sb(V) release at alkaline pH values.

Belzile *et al.* [138] studied the Sb(III) sorption in amorphous iron oxyhydroxides and birnessite. They reported rapid surface catalyzed Sb(III) oxidation on these surfaces at different pH values, determined via differential pulse adsorptive stripping voltammetry analysis. Leuz and co-workers [137] also reported the surface catalyzed oxidation of Sb(III) on goethite surfaces.

16.5 Risks from Arsenic and Antimony in Soils

Due to various anthropogenic inputs to (for example, mining, smelting industries) and indigenous sources in (for example, mineral weathering) soils, As and Sb are often transported to surface waters and groundwaters, resulting in aqueous concentrations of these elements greater than the current MCL in many parts of the world [2,8,9,11,139]. High concentrations of As and Sb in drinking water supplies raise serious concerns regarding protection of human and ecological health. In recent years many researchers have assessed the environmental risks of As and Sb accumulation in terrestrial biota, such as plant species at contaminated sites.

As described above in Section 16.4, solubility and mobility of As and Sb are highly influenced by pH, redox status and types of adsorbents in soils. Antimony and As are considered relatively immobile under oxidizing conditions due to the strong fixation mechanisms of their pentavalent species in soil matrices. However, some studies have shown that a fraction of these elements may be bioavailable in oxic environments, depending on soil contamination levels and the specific plant species growing at contaminated sites. Arsenic and Sb in soils can be readily taken up by a wide variety of plant species [140,141]. Background As and Sb content in terrestrial vascular plants ranges from 0.2–50 μg g^{-1} and 0.009–1.5 μg g^{-1}, respectively [140,142–144]. In terrestrial vascular plants, the background Sb content was found to range from 0.2 to 50 μg g^{-1} [140,142,145]. Tyler and co-workers [146] reported the amounts of As and Sb in developing, maturing, and wilting leaves. The amounts of As and Sb were very low in leaves (<1 μg per 100 leaves). However, total element concentrations gradually increased throughout the growing season and usually in the subsequent winter.

While the above studies show a wide range of the background As and Sb concentrations in plants growing at uncontaminated sites, bioaccumulation of As and Sb can be elevated in some plant species at or near mining sites [38,147,148]. Some plant species (for example, *Agrostis canina, Achillea tenuis, Pseudosuga taxifolia,* and *Pityrogramma calomelanos, Pteris vittata,* and moss species (for example, *Pohlia wahlenbergii* and

Table 16.2 *A summary of arsenic and antimony accumulation in plant species at metalloid-contaminated sites*

Study sites	Total metalloid conc. in soils (mg kg^{-1})	Plant species	Metalloid uptake in plant tissues (mg kg^{-1})	References
Abandoned Portuguese mines	As: 76 Sb: 663	*Digitalis purpurea*	Sb: 139	[158]
		Erica umbellate	Sb: 1.74	
		Calluna vulgaris	Sb: 1.25	
		Cistus ladanifer	Sb: 3.65	
		Old needles of *Pinus pinaster*	As: 30	
		Calluna vulgaris	As: 0.62	
		Chamaespartinum tridentatum	As: 0.54	
		leaves of *Cistus ladanifer*	As: 2.77	
		Erica umbellate	As: 0.64	
		Quercus ilex subsp. ballota	As: 3.6	
An abandoned Sb-mining area in southern Italy	Sb: 139	*Achillea ageratum* basal leaves	Sb: 1367	[141]
		Achillea orescences	Sb: 1105	
		English Plantain (*Plantago lanceolata*) in roots	Sb: 1150	
		Maidenstears (*Silence vulgaris*) in shoots	Sb: 1164	
Arsenic-contaminated soils in southwest England	As: 8500–26,500	Old leaves of velvet bentgrass (*Agrostis canina*) and bentgrass (*Agrostis tenuis*)	As: 6,640	[150]
Chromated copper arsenate-contaminated soils in Central Florida	As: 18.8–1,603	Brake fern (*Pteris vittata*)	As: 3,280–4,980	[151]
Arsenic-contaminated sites in Thailand that are affected by mine tailings	As: 21–16,000	Dixie silverback fern (*Pityrogramma calomelanos*) and ferns (*Pteris vittata*)	As: up to 8,350 As: 24–76	[155]
		Herb (*Mimosa pudica*)	As: 18–37	
		Shrub(*Melastoma malabrathricum*)	As: 15–32	
		Tree (*Bauhinia glauca Wall.*)		
Former Sb-mining areas	As: 5.3–2035	Roots and leaves of (*Mentha aquatica*)	540 and 216	[141]
		Roots of (*Phragmites australis*)	688	
Historic gold-mining sites in northern Westland, New Zealand	As: 2000–40,000	Manuka, (*Leptospermum scoparium*)	As: <10	[156]
		Gorse (*Ulex europaeus*)	As: <10	
		Tree fuchsia (*Fuchsia excorticate*)	As: <10	
		Broadleaf (*Griselinia littoralis*)	As: <10	
		Reeds (*Juncus spp.*)	As: <100	
		Mosses (*Pohlia wahlenbergii*)	As: Up to 30,000	

Table 16.3 *A summary of arsenic and antimony chemical speciation in different plant species in metalloid-contaminated environments*

Study sites	Total metalloid conc. in soils	Biota/plant species	Chemical species	References
Abandoned As, Sb and Zn mines	As: 51.9–21 200 mg kg^{-1}	Scots pine needles, *Pinus sylvestris*	Arsenite and/or arsenate	[157]
		Hard rush shoots (*Juncus inflexus L.*), boxtree leaves (*Buxus sempervire*n), and Ferns (*Dryopteris filix-max*)	Methylarsonate (0.012–0.585 mg kg^{-1}), dimethylarsinate (0.013–0.569 mg kg^{-1}), trimethylarsine oxide (0.02–0.5 mg kg^{-1}) and tetramethylarsonium ion (<0.19 mg kg^{-1})	
Laboratory study	Switzerland soils (Sb >1000 mg kg^{-1})	Microbes and filamentous fungi	Volatile trimethylantimony [$(CH_3)_3S$] species	[159]
	0.1 mg kg^{-1} of Sb in liquid culture			[160]
Keg Lake and Kam Lake, near Yellowknife, Northwest Territories, Canada	Sb in pondweeds: 48–68 mg kg^{-1}	Pondweed (*Potamogetan pectinatus*)	Sb as Sb(III), methylstibine, CH_3SbH_2, dimethylstibine $(CH_3)_2SbH$, and trimethylantimony $(CH_3)_3Sb$	[161]
NaH_2AsO_4-spiked uncontaminated soils	As: 50 mg kg^{-1}	Fern (*Pteris vittata L.*)	As(III)/As(III)-S in the leaves	[162]
Arsenic-contaminated mine waste, and arsenic-amended liquid cultures	Six hydroponic treatments: 0, 1, 2, 5, 15, 30 and 60 mg kg^{-1}, and As contaminated soil samples(< 1,100 mg kg^{-1})	Radish (*Rhaphanus sativus*)	Arsenite, arsenate, and As(III)– sulfur compounds in leaf, stem and root sections of plants	[163]

Streams and puddles receiving mine effluent	Sb: 3.7–380 µg kg^{-1}	Moss (*Funuria hygmmerrica and Drepanocladus sp.*), cattail (*Typha lutifoliu*) and burmarigold (*Bidens cernuu*), duckweed (*Lemna minor*), water milfoil (*Myriophyllum sp.)* Pondweed (*Potomogetan richanisonii*), and bur-reed (*Spurgunium augustifolium*) and fungi lichen, pixie cup lichen (*Cladoniu sp.*), puffball mushroom (*Lycopenion sp.*) and shaggy mane mushroom (*Coprinus comatus*).	Sb (V), Sb(III) and methylated (Me) antimony species in all samples Me_3Sb ranged from 5 to 170 µg kg^{-1} Sb(III) and Sb(V) concentrations were from 5 to 12 and 28 to 5000 µg kg^{-1}, respectively	[164]
Former mining sites in Catalonia, Spain	Not available	Moss (*Hypnum cupressiforme* Hedw), fern (*Dryopteris filix-max* (L.) Schott.), stitchwort (*Stellaria halostea*), *Dryopteris filix-max* (L.) Schott. and figwort (*Chaenorhinum asarina*)	A sum of Sb(III), Sb(V) and trimethyl Sb species in these plant species yielded <28 % of total Sb. Sb(V) was a major Sb species in moss Sb(III) was a dominant Sb species (1.75 mg kg^{-1}) in stitchwort	[165]
Laboratory study	40 µg kg^{-1} of Sb(III) in river and sea water	*Spirulina platensis* (cyanobacterium) and *Phaseolus*	Sb(III) and Sb(V) species	[166]

Brachythecium cf. reflexum) can accumulate high levels (>1000 mg kg^{-1}) of As and Sb from soils [149–157]. The results of metalloid phytoaccumulation studies are summarized in Table 16.2. While many focused on the measurements of operationally defined chemical extractable and/or total As and Sb concentrations in plant tissues, some researchers pointed out the importance of chemical speciation with respect to toxicity and phytoaccumulation processes. Recent research has shown the presence of As(III), As(V), Sb(III), Sb(V), and methylated As and Sb species in plant tissues (Table 16.3). It is apparent that phytoaccumulation of As and Sb differs across plant species growing at contaminated sites. However, the relationship between phytoaccumulation mechanisms and the chemical speciation found in plants and soils is not well understood.

16.6 Conclusions and Future Research Needs

This chapter has discussed the chemical properties of As and Sb, toxicity, and reactivity in soil–water–plant systems. Although these elements share numerous similarities in biogeochemical properties, their reactivity is highly influenced by changes in environmental conditions. Whereas the trivalent states of As and Sb are mobile in the reduced soil–water systems, the pentavalent species are relatively immobile under oxidizing conditions due to the strong fixation mechanisms in soil matrices.

The metalloid accumulation in plant species readily occurs at As and Sb naturally contaminated sites. Some shrubs, grasses, reeds, and mosses can tolerate As and Sb and largely remove these metalloids from surface soils. Populations of a variety of plant species colonized at contaminated sites are responding to these metalloids by exclusion or accumulation.

The extent/rate of bioaccumulation and sorption/desorption processes are highly influenced by the chemical species specific in the plant–water–soil systems. Unfortunately, the chemical speciation of As and Sb in soils and plant tissues are rarely correlated with reaction processes (for example, plant uptake and desorption processes) at the field scales and soil physicochemical properties (for example, redox status, pH, and hydrologic properties). Using modern microscopic and spectroscopic techniques (for example, transmission electron microscope spectroscopy, synchrotron based X-ray techniques), solid-state speciation in soils and biological-media can be better characterized, and these research findings will further lead to better toxicological/risk assessment of As and Sb in field-scale settings. These comprehensive research results will be helpful in making better regulatory decisions, and in designing effective *in situ* remediation technologies and environmental management programs to enhance environmental quality and ecological health.

References

[1] Adriano, D.C., Trace Elements in the Terrestrial Environment; Springer-Verlag, New York, 1986.

[2] Gao, S.; Tanji, K.K.; Goldberg, S., Session 1: Potentially toxic trace elements in soils and sediments Paper 4: Reactivity and transformation of arsenic; in: Dudley LM, Guitjens J (eds), Agroecosystems: Sources, Control, and Remediation of Oxyanions. Symposium on Sources,

Control, and Remediation of Oxyanions in Agroecosystems, 19–22 June, 1994; San Francisco: Proc. Symp., Pacific Div., Am. Assoc. Adv. Sci., 1997.
[3] Carlin, J.F. Jr., Antimony; U.S. Geological Survey Mineral Commodity Summaries. 2000. http://minerals.usgs.gov/minerals/pubs/commodity/antimony/(accessed 7 December 2009).
[4] Onish, H., Antimony; Springer Verlag, Heidelberg, 1969.
[5] Berg, M.; Tran, H.C.; Nguyen, T.C.; Pham, H.V. Schertenleib, R; Giger, W., Arsenic contamination of groundwater and drinking water in Vietnam: A human health threat; Environ Sci Technol. 2001, 35, 2621–2626.
[6] United States Environmental Protection Agency. EPA to implement 10ppb standard for arsenic in drinking water; Report No. EPA 815-F-01-010, 2001.
[7] WHO. Guidelines for Drinking-water Quality, vol. 2: Health Criteria and Other Supporting Information; World Health Organization, Geneva, 1996.
[8] Ritchie, J.A., Arsenic and antimony in some New Zealand thermal waters. NZJ Sci. 1961, 4, 218–29.
[9] Weissberg, B.G.; Browne, P.R.L.; Seward, T.M., Ore metals in active geothermal systems; in: Barnes H.L. (ed.), Geochemistry of Hydrothermal Ore Deposits; John Wiley & Sons, Inc., New York, 1979, pp. 738–7380.
[10] Kolpakova, N.N., Laboratory and field studies of ionic equilibria in the Sb_2S_3–H_2O–H_2S system; Geochem Int. 1982, 19, 46–54.
[11] Stauffer, E.; Thompson, J.M., Arsenic and antimony in geothermal waters of Yellowstone National Park, Wyoming, USA; Geochim. Cosmochim. Acta 1984, 48, 2547–2561.
[12] DaCosta, E.W.B., Variation in the toxicity of arsenic compounds to microorganisms and the suppression of the inhibitory effects by phosphate; Appl. Microbiol. 1972, 23, 46–53.
[13] Sheppard, S.C., Summary of phytotoxic levels of soil arsenic; Water Air Soil Pollut. 1991, 64, 539–550.
[14] Tamaki, S.; Frankenberger, Jr. W.T., Environmental biochemistry of arsenic; in: Whitacre, D.M. (ed.), Reviews of Environmental Contamination and Toxicology; Springer-Verlag, New York, 1992, vol. 124, pp. 79–110.
[15] Faust, S.D.; Aly, O.M., Chemistry of Natural Waters; Science Publishers Inc., Ann Arbor, MI, 1981.
[16] Manahan, S.E., Toxicological chemistry of chemical substances; Environmental Chemistry, 6th edn; Lewis Publishers, Ann Arbor, 1994, pp. 675–704.
[17] Blair, P.C.; Thompson, M.B.; Morrissey, R.E.; Moorman, M.P.; Sloane, R.A.; Fowler, B.A., Comparative toxicity of arsine gas in B6C3F1 mice, Fischer 344 rats, and Syrian Golden Hamsters: system organ studies and comparison of clinical indices of exposure; Toxicol. Sci. 1990, 14, 776–787.
[18] Flemming, P.J.; Cooke, M.; Chantlet, S.M.; Golding, J., Fire retardants, biocides, plasticisers, and sudden infant deaths; Brit. Med. J. 1994, 309, 1594–1596.
[19] Richardson, B.A., Sudden infant death syndrome: a possible primary cause; J. Forensic Sci. Soc., 1994, 34, 199–204.
[20] Blair, P.; Fleming, P.; Bensley, D.; Smith, I.; Bacon, C.; Taylor, E., Plastic mattresses and sudden infant death syndrome; Lancet 1995, 345, 720.
[21] Apostoli, P.; Porru, S.; Alessio, L., Antimony, biological indicators for the assessment of human exposure to industrial chemicals; European Commission, Luxembourg, 1994.
[22] McCallum, R.I., Occupational exposure to antimony compounds; J. Environ. Monit. 2005, 7, 1245–50.
[23] ATSDR AfTSaDR, Toxicological Profile for Antimony; US Public Health Service, US Department of Health and Human Services, Altanta, 1992.
[24] Horber, F.F.; Lerut, J.; Jaeger, P., Renal tubular acidosis, a side effect of treatment with pentavalent antimony; Clin Nephrol. 1991, 36:213.
[25] Braconier, J.H.; Miorner, H., Recurrent episodes of thrombocytopenia during treatment with sodium stibogluconate; J Antimicrob. Chemother. 1993, 31, 187–8.
[26] Gasser, R.A.; Magill, A.J.; Oster, C.N.; Franke, E.D. Grogel, M; Berman, J.D., Pancreatitis induced by pentavalent antimonial agents during treatment of leishmaniasis. Clin. infect. Dis. 1994 18, 83–90.

[27] Colburn, P.; Alloway, B.J.; Tompson, I., Arsenic and heavy metals in soil associated with regional geochemical anomalies in Southwest England; Sci. Total Environ. 1975, 4, 359–63.

[28] Voigt, D.E.; Brantley, S.L., Chemical fixation of arsenic in contaminated soils. Appl Geochem. 1996, 11, 633–43.

[29] Walsh, L.M.; Keeny, D.R., Behavior and phytotoxicity of inorganic arsenicals in soils; in: Woolson, E.A. (ed.), Arsenical Pesticides; ACS, Washington, DC, 1975, pp. 35–52.

[30] Woolson, E.A.; Axley, J.H.; Kearney, P.C., Correlation between available soil arsenic, estimated by six methods, and response of corn (*Zea Mays L.*); Soil Sci. Soc. Am. Proc. 1971, 35, 101–5.

[31] Committee on Medical and Biological Effects of Environmental Pollutants NRC. Chemistry and distribution of arsenic in the environment. Arsenic, Medical and Biological Effects of Environmental Pollutants, National Academy of Science, Washington, DC, 1977, pp. 4–79.

[32] Braman, R.S., Environmental reaction and analysis method; in: Fowler, B.A. (ed.), Biological and Environmental Effects of Arsenic; Topics in Environmental Health; Elsevier Science Publishers, New York, 1983, pp. 141–154.

[33] Tanji, K.K.; Dalgren, R.A., Acidification of evaporation ponds to reduce contaminant hazards to wildlife-phase I (Chemical aspects). DWR Agreement #: B58194; 1993.

[34] Bagby, W.C.; Berger, B.R., Geologic characteristics of sediment-hosted, disseminate precious metal deposits in the western United States; in: Berger, B.R., Bethke, P.M. (eds), Geology and Geochemistry of Epithermal Systems; Rev. Econ., 1985, 165–202.

[35] Filella, M.; Belzile, N.; Chen, Y.W., Antimony in the environment: a review focused on natural waters I. Occurrence; Earth Sci. Rev. 2002, 57, 125–176.

[36] Fink, C.R., A perspective on metals in soils; J. Soil Contam. 1996, 5, 329–359.

[37] Martin, J.-M.; Whitefield, M., The significance of the river input of chemical elements to the ocean; in: Wong, C.S., Boye, E., Bruland, K.W., Burton, J.D., Goldberg, E.D. (eds), Trace Metals in Sea Water; NATO Adv. Res. Inst., Plenum, New York, 1983, pp. 265–296.

[38] Ainsworth, N.; Cooke, J.A.; Johnson, M.S., Biological significance of antimony in contaminated grassland; Water, Air Soil Pollut. 1991, 57–58, 1993–1999.

[39] Crecelius, EA, Johnston, CJ, Hofer, GC., Contamination of soils near a copper smelting by arsenic, antimony and lead. Water, Air, Soil Pollut. 1974, 3, 337–342.

[40] Asami, T, Kubota, M, Saito, S., Simultaneous determination of anitimony and bismuth in soils by continuous hydride generation-atomic absorption spectrometry. Water Air Soil Pollut. 1992, 62, 349–355.

[41] Papakostidis, G.; Grimanis, A.P.; Zafiropoulos, D., Heavy metals in sediments from the Athens sewage outfall area; Mar Pollut Bull. 1975, 6, 136–139.

[42] Wild, H., Geobotanical anomalies in Rhodesia: 4. The vegetation of arsenical soils. Kirkia 1974, 9, 243–264.

[43] Li, X.; Thornton, I., Arsenic, antimony and bismuth in soil and pasture herbage in some old metalliferous mining area in England. Environ; Geochem. Health. 1993, 15, 135–144.

[44] Ragaini, R.C.; Ralston, H.R.; Roberts, N., Environmental trace metal contamination in Kellogg, Idaho, near a lead smelting complex; Environ. Sci. Technol. 1977, 11, 773–781.

[45] Andreae, M.O.; Asmodi, J.-F.; Foster, P.; Van't dack, l., Determination of antimony(III), antimony(V), and methylantimony species in natural waters by atomic absorption spectrometry with hydride generation; Anal. Chem. 1981, 53, 1766–1771.

[46] Matschullat, J., Arsenic in the geosphere-a review; Sci. Total Environ. 2000, 249, 297–312.

[47] Chilvers, D.C.; Peterson, P.J., Lead, mercury, cadmium and arsenic in the environment; in: Hutchinson, T.C., Meema, K.M. (eds), Global Cycling of Arsenic; John Wiley & Sons, Inc., New York, 1987, pp. 279–301.

[48] Anderson, C.E., Arsenicals as feed additives for poultry and swine; in: Lederer, W.H., Fensterheim, R.J. (eds), Arsenic: Industrial, Biomedical, Environmental Perspectives; Van Nostrand Reinhold, New York, 1983, pp. 89–97.

[49] Christen, K., Chickens, manure, and arsenic; Environ. Sci. Technol. 2001, 35(5), 184A–5A.

[50] United States Environmental Protection Agency. Toxics Release Inventory, USEPA, Washington, DC, 1998.

[51] Nriagu, J.O.; Pacyna, J.M., Quantitative assessment of worldwide contamination of air, water and soils by trace metals; Nature 1988, 333, 134–139.

[52] Nriagu, J.O., A global assessment of natural sources of atmospheric trace metals; Nature 1989, 338, 47–49.

[53] Nriagu, J.O. Global metal pollution. Poisoning the biosphere? Environment 1990, 32, 28–33.

[54] Maeda, S., Safety and Environmental Effects, John Wiley & Sons, Inc., New York, 1994.

[55] Fergusson, J.E., The Heavy Metals: Chemistry, Environmental Impact and Health Effects, Pergamon Press, Oxford, 1990.

[56] Smedley, P.L. and Kinniburgh, D.G., A review of the source, behavior and distribution of arsenic in natural waters. Appl. Geochem. 2002, 17, 517–568.

[57] Tallman, D.E.; Shaikh, A.U., Redox stability of inorganic arsenic(III) and arsenic(V) in aqueous solution; Anal. Chem. 1980, 52, 196–199.

[58] Eary, L.E.; Schranke, J.A., Chemical modeling of aqueous systems II, American Chemical Society, Washington, DC, 1990.

[59] Manning, B.A.; Goldberg, S., Adsorption and stability of arsenic (III) at the clay mineral–water interface; Environ. Sci. Technol. 1997, 31, 2005–2011.

[60] Deuel, L.E.; Swoboda, A.R., Arsenic solubility in a reduced environment; Soil Sci. Soc. Am. Proc. 1972, 36, 276–278.

[61] Masscheleyn, P.H.; Delaune,R.D.W.H.; Patrick, J., Effect of redox potential and pH on arsenic speciation and solubility in a contaminated soil; Environ. Sci. Technol. 1991, 25(8), 1414–1418.

[62] Masscheleyn, P.H.; Delaune, R.D.W.H.; Patrick, J., Arsenic and selenium chemistry as affected by sediment redox potential and pH; J. Environ. Qual. 1991, 20, 522–527.

[63] McGeeham, S.L.; Naylor, D.V., Sorption and redox transformation of arsenite and arsenate in two flooded soils; Soil Sci. Soc. Am. J. 1994, 58, 337–342.

[64] Onken, B.M.; Hossner, L.R., Plant uptake and determination of arsenic species in soil solution under flooded conditions; J. Environ. Qual. 1995, 24, 373–381.

[65] Onken, B.M.; Adriano, D.C., Arsenic availability in soil with time under saturated and subsaturated conditions; Soil Sci. Soc. Am. J. 1997, 61, 746–752.

[66] Rochette, E.A.; Li, G.C.; Fendorf, S.E., Stability of arsenate minerals in soil under biotically generated reducing conditions; Soil Sci. Soc. Am. J. 1998, 62, 1530–1537.

[67] Arai, Y.; Lanzirotti, A.; Sutton, S.; Newville, M; Dyer, J.; Sparks, D.L., Spatial and temporal variability of arsenic solid-state speciation in historically lead arsenate contaminated soils; Environ. Sci. Technol. 2006, 40, 673–679.

[68] Jacobs, L.W.; Syers, J.K.; Keeney, D.R., Arsenic sorption by soils; Soil Sci. Soc. Am. Proc. 1970, 34, 750–754.

[69] Manning, B.A.; Goldberg, S., Arsenic(III) and arsenic(V) adsorption on three California soils; Soil Sci. 1997, 162, 886–895.

[70] Livesey, N.T.; Huang, P.M., Adsorption of arsenate by soils and its relation to selected chemical properties and anions; Soil Sci. 1981, 131, 88–94.

[71] Sakata, M., Relationship between adsorption of As(III) and boron by soil and soil properties. Environ. Sci. Technol. 1987, 21, 1126–1130.

[72] Violante, A.; Colombo, C.; Buondonno, A., Competitive adsorption of phosphate and oxalate by aluminum oxides; Soil Sci. Soc. Am. J. 1991, 55, 65–70.

[73] Fordham, A.W.; Norrish, K., Arsenate-73 uptake by components of several acidic soils and its implications for phosphate retention, Aust. J. Soil Res. 1979, 17, 307–316.

[74] Norrish, K.; Rosser, H., Mineral Phosphate; Academic Press, Melbourne, 1983.

[75] Goldberg, S.; Glaubig, R.A., Anion sorption on a calcareous, montmorillonitic soil-arsenic; Soil Sci. Soc.Am. J. 1988, 52, 1297–1300.

[76] Hayes, K.F.; Papelis, C.; Leckie, J.O., Modeling ionic strength effects of anion adsorption at hydrous oxide/solution interface; J Colloid Interface Sci. 1988, 125, 717–726.

[77] Stumm, W.; Morgan, J.J., Theory of elementary processes. Aquatic Chemistry, Chemical Equilibria and Rates in Natural Water, John Wiley & Sons, Inc., New York, 1995, pp. 69–76.

[78] Gupta, S.K.; Chen, K.Y., Arsenic removal by adsorption; J. Water Pollut. Cont. Feder. 1978, 50, 493–506.

[79] Arai, Y.; Elzinga, E.J.; Sparks, D.L., X-ray absorption spectroscopic investigation of arsenite and arsenate adsorption at the aluminum oxide–water interface; J. Colloid Interface Sci. 2001, 235, 80–88.

[80] Anderson, M.A.; Ferguson, J.F.; Gavis, J., Arsenate adsorption on amorphous aluminum hydroxide; J. Colloid Interface Sci. 1976, 54, 391–399.

[81] Bleam, W.F.; Pfeffer, P.E.; Goldberg, S.; Taylor, R.W.; Dudley, R., A ^{31}P solid-state nuclear Magnetic resonance study of phosphate adsorption at the boehmite/aqueous solution; Langmuir 1991, 7, 1702–1712.

[82] Chen, Y.R.; Butler, J.N.; Stumm, W., Adsorption of phosphate on alumina and kaolinite from dilute aqueous solutions; J. Colloid Interface Sci. 1973, 43, 421–436.

[83] Pierce, M.L.; Moore, C.B., Adsorption of arsenite and arsenate on amorphous iron hydroxide; Water Res. 1982, 16, 1247–1253.

[84] Shang, C.; Stewart, J.W.B.; Huang, P.M., pH effect on kinetics of adsorption of organic inorganic phosphates by short-range ordered aluminum and iron precipitates; Geoderma 1992, 53, 1–14.

[85] Xu, H.; Allard, B.; Grimvall, A., Influence of pH and organic substance on the adsorption of As(V) on geologic materials; Water Air Soil Pollut. 1988, 40, 293–305.

[86] Arai, Y.; Sparks, D.L.; Davis, J.A., Effects of dissolved carbonate on arsenate adsorption and surface speciation at the hematite-water interface; Environ. Sci. Technol. 2004, 38, 817–824.

[87] Raven, K.P.; Jain, A.; Loeppert, R.H., Arsenite and arsenate adsorption on ferrihydrite: Kinetics, equilibrium, and adsorption envelopes; Environ. Sci. Technol. 1998, 32, 344–349.

[88] Fukushi, K.; Sato, T.; Yanase, N., Solid-solution reactions in As(V) sorption by schwertmannite; Environ. Sci. Technol. 2003, 37, 3581–3586.

[89] Edzwald, J.K;, Toensing, D.C.; Leung, M.C. Phosphate adsorption reaction with clay minerals; Environ. Sci. Technol. 1976, 10, 485–490.

[90] Arai, Y.; Sparks, D.L.; Davis, J.A., Arsenate adsorption mechanisms at the allophane-water interface; Environ. Sci. Technol. 2005. 39, 2537–2544.

[91] Manning, B.A.; Fendorf, S.E.; Bostick, B.; Suarez, D.L., Arsenic(III) oxidation and arsenic(V) adsorption reactions on synthetic birnessite; Environ. Sci. Technol. 2002, 36, 976–981.

[92] O'Reilly, S.E.; Strawn, D.G.; Sparks, D.L., Residence time effects on arsenate adsorption/desorption mechanisms on goethite; Soil Sci. Soc. Am. J. 2001, 65, 67–77.

[93] Waychunas, G.A.; Rea, B.A.; Fuller, C.C.; Davis, J.A., Surface chemistry of ferrihydrite: Part 1. EXAFS studies of the geometry of coprecipitated and adsorbed arsenate; Geochim. Cosmochim. Acta 1993, 57, 2251–2264.

[94] Fendorf, S.E.; Eick, M.J.; Grossl, P.; Sparks, D.L., Arsenate and chromate retention mechanisms on goethite. 1. Surface structure; Environ. Sci. Technol. 1997, 31, 315–320.

[95] Foster, A.L.; G.E.; Brown, J.; Parks, G.A., X-ray absorption fine structure study of As(V) and Se(IV) sorption complexes on hydrous Mn oxides; Geochim. Cosmochim. Acta 2003, 67, 1937–1953.

[96] Lumsdon, D.G.; Fraser, A.R.; Russell, J.D.; Livesey, N.T., New infrared band assignments for the arsenate ion adsorbed on synthetic goethite (α-FeOOH); J. Soil Sci. 1984, 35, 381–386.

[97] Manning, B.A.; Fendorf, S.E.; Goldberg, S., Surface structure and stability of arsenic(III) on goethite: spectroscopic evidence for Inner-sphere complexes; Environ Sci Technol. 1998, 32, 2383–2388.

[98] Sun, X.; Doner, H.E., An investigation of arsenate and arsenite bonding structures on goethite by FTIR; Soil Sci. 1996, 161, 865–872.

[99] Tournassat, C.; Charlet, L.; Bosbach, D.; Manceau, A., Arsenic(III) oxadation by birnessite and precipitation of manganese(II) arsenate; Environ. Sci. Technol. 2002, 36, 493–500.

[100] Foster, A.L.; Brown, Jr. G.E., Tingle, T.N.; Parks, G.A., Quantitative arsenic speciation in mine tailing using X-ray absorption spectroscopy; Am. Mineral. 1998, 83, 553–568.

[101] Goldberg, S.; Johnston, C.T., Mechanisms of arsenic adsorption on amorphous oxides evaluated using macroscopic measurements, vibrational spectroscopy, and surface complexation modeling; J. Colloid. Interface Sci. 2001, 234, 204–216.

[102] Suarez, D.L.; Goldberg, S.; Su, C., Evaluation of oxyanion adsorption mechanisms in oxides using FTIR spectroscopy and electrophoretic mobility; in: Sparks D.L., Grundl T.J. (eds), Mineral–Water Interfacial Reactions Kinetics and Mechanisms, ACS, Washington, DC, 1998, pp. 136–178.

[103] Ladeira, A.C.Q.; Ciminelli, V.S.T.; Duarte, H.A.; Alves, M.C.M.; Ramos, A.Y., Mechanism of anion retention from EXAFS and density functional calculation: arsenic (V) adsorbed on gibbsite; Geochim. Cosmochim. Acta 2001, 65, 1211–1217.

[104] Manceau, A., The mechanism of anion adsorption on iron oxides: Evidence for the bonding of arsenate tetrahedra on free $Fe(O, OH)_6$ edges; Geochim. Cosmochim. Acta 1995, 59, 3647–3653.

[105] Waychunas, G.A.; Davis, J.A.; Fuller, C.C., Geometry of sorbed arsenate on ferrihydrite and crystalline FeOOH: Re-evaluation of EXAFS results and topological factors in predicting sorbate geometry, and evidence for monodentate complexes; Geochim Cosmochim Acta 1995, 59, 3655–3661.

[106] Randall, S.; Sherman, D.M.; Ragnarsdottir, K.V., Sorption of As(V) on green rust ($Fe_4(II)Fe_2(III)(OH)12SO_4\ 3H_2O$) and lepidocrocite ($\gamma$-FeOOH): Surface complexes from EXAFS spectroscopy; Geochim. Cosmochim. Acta 2001, 65, 1015–1023.

[107] Scheinost, A.C.; Rossberg, A.; Vantelon, D. *et al.*, Quantitative antimony speciation in shooting-range soils by EXAFS spectroscopy; Geochim Cosmochim Acta 2006, 70, 3299–3312.

[108] McComb, K.A.; Craw, D.; McQuillan, A.J., ATR-IR spectroscopic study of antimonate adsorption to iron oxide; Langmuir 2007, 23(24), 12125–12130.

[109] Frost, R.R.; Griffin, R.A., Effect of pH on adsorption of arsenic and selenium from landfill leachate by clay minerals; Soil Sci. Soc. Am. J. 1977, 41, 53–57.

[110] Scott, M.J.; Morgan, J.J., Reactions at oxide surface. 1. oxidation of As(III) by synthetic birnessite; Environ Sci Technol. 1995, 29, 1898–1905.

[111] Oscarson, D.W.; Huang, P.M.; Liaw, W.K., The oxidation of arsenite by aquatic sediments; J. Environ. Qual. 1980, 9, 700–703.

[112] Sun, X.; Doner, H.E.; Zavarin, M., Spectroscopy study of arsenite [As(III)] oxidation on Mn-substituted goethite; Clays Clay Miner. 1999, 47(4), 474–480.

[113] Driehaus, W.; Seith, R.; Jekel, M., Oxidation of arsenate(III) with manganese oxides in water treatment;Water Res. 1995, 29, 297–305.

[114] Foster, A.L.; G.E.; Brown, J.; Parks, G.A., X-ray absorption fine structure spectroscopy study of photocatalyzed, heterogeneous As(III) oxidation on kaoline and anatase; Environ. Sci. Technol. 1998, 32, 1444–1452.

[115] Kostka, J.E.; George, W.; Luther, I.; Nealson, K.H., Chemical and biological reduction of Mn (III)-pyrophosphate complexes: potential importance of dissolved Mn (III) as an environmental oxidant; Geochim. Cosmochim. Acta 1995, 59, 885–894.

[116] Nico, P.S.; Zasoski, R.J., Importance of Mn(III) availability on the rate of Cr(III) oxidation on d-MnO_2; Environ. Sci.Technol. 2000, 34, 3363–3367.

[117] Nesbitt, H.W.; Canning, G.W.; Bancroft, G.M., XPS study of reductive dissolution of 7Å-birnessite by H_3AsO_3, with constraints on reaction mechanism; Geochim. Cosmochm. Acta 1998, 62, 2097–2110.

[118] Chiu, V.Q.; Hering, J.G., Arsenic adsorption and oxidation at manganite surfaces. 1. Method for simultaneous determination of adsorbed and dissolved arsenic species; Environ. Sci Technol. 2000, 34, 2029–2034.

[119] Arai, Y.; Sparks, D.L., Residence time effects on arsenate surface speciation at the aluminum oxide–water interface; Soil Sci. 2002, 167, 303–314.

[120] Grossl, P.R.; Sparks, D.L., Evaluation of contaminant ion adsorption/desorption on goethite using pressure-jump relaxation kinetics; Geoderma 1995, 67, 87–101.

[121] Woolson, E.A.; Axley, J.H.; Kearney, P.C., The chemistry and phytotoxicity of arsenic in soils: II. Effects of time and phosphorus; Soil Sci. Soc. Am. Proc. 1973, 37, 254–259.

[122] Lin, Z.; Puls, R.W., Adsorption, desorption and oxidation of arsenic affected by clay minerals and aging process; Environ. Geol. 2000, 39, 753–759.

[123] Jackson, B.P.; Mille, W.P., Effectiveness of phosphate and hydroxide for desorption of arsenic and selenium species from iron oxides; Soil Sci. Soc. Am. J. 2000, 64, 1616–1622.

[124] Gayer, K.H.; Gerrett, A.B., The equilibria of antimonous oxide(rhombic) in dilute solutions of hydrochloric acid and sodium hydroxide at 258 °C; J. Am. Chem. Soc. 1952, 72, 2353–2354.

[125] Ahrland, S.; Bovin, J., The complex formation of antimony(III). in perchloric and nitric acid solutions – a solubility study; Acta Chem. Scand A 1974, 28, 1089–1100.

[126] Wood, S.A., Raman spectroscopic determination of the speciation of ore metals in hydrothermal solutions: I. Speciation of antimony in alkaline sulfide solutions at 25 °C; Geochim Cosmochim Acta 1989, 53, 237–244.

[127] Krupka, K.M.; Serne, R.J., Geochemical factors affecting the behavior of antimony, cobalt, europium, technetium, and uranium in vadose sediments; Pacific Northwest National Laboratory, Richland, Washington, 2002.

[128] Oelkers, E.H.; Sherman, D.M.; Vala Ragnarsdottir, K.; Collins, C., An EXAFS spectroscopic study of aqueous antimony(III)-chloride complexation at temperatures from 25 to 250 °C; Chem. Geo. 1998, 151, 21–27.

[129] Baes, C.F.R.E.M., The Hydrolysis of Cations. John Wiley & Sons, Inc., New York, 1976.

[130] Rai, D.; Zachara, J.M.; Schwab, A.P.; Schmidt, R.L.; Girvin, D.C.; Rogers, J.E., Chemical Attenuation Rates, Coefficients, and Constants in Leachate Migration. Volume 1: A Critical Review; Electric Power Research Institute; Palo Alto, 1984.

[131] Helz, G.R.; Valerio, M.S.; Capps, N.E., Antimony speciation in alkaline sulfide solutions: Role of zerovalent sulfur; Environ. Sci. Technol. 2002, 36, 943–948.

[132] Mosselmans, J.F.W.; Helz, G.R.; Pattrick, R.A.D.; Charnock, J.M.; Vaughan, D.J., A study of speciation of Sb of bisulfide solutions by X-ray absorption spectroscopy; Appl. Geochem. 2000, 15, 879–989.

[133] Sherman, D.M.; Ragnarsdottir, K.V.; Oelkers, E.H., Antimony transport in hydrothermal solutions: an EXAFS study of antimony(V) complexation in alkaline sulfide and sulfide-chloride brines at temperatures from 25 °C to 300 °C at Psat; Chem. Geo. 2000, 167, 161–167.

[134] Ambe, S., Adsorption-kinetics of antimony(V) ions onto alpha-Fe_2O_3 surfaces from an aqueous solution; Langmuir 1987, 3, 489–493.

[135] Crecelius, E.A.; Bothner, M.H.; Carpenter, R., Geochemistries of arsenic, antimony, mercury, and related elements in sediments of Puget Sound; Environ. Sci. Technol. 1975, 9, 325–333.

[136] Tighe, M.; Lockwood, P.; Wilson, S., Adsorption of antimony(V) by floodplain soils, amorphous iron(III) hydroxide and humic acid; J. Environ. Monit. 2005, 7, 1177–1185.

[137] Leuz, A.K.; Monch, H.; Johnson, C.A., Sorption of Sb(III) and Sb(V) to goethite: influence on Sb(III) oxidation and mobilization; Environ. Sci. Technol. 2006, 40, 7277–7282.

[138] Belzile, N.; Chen, Y-W.; Wang, Z., Oxidation ofatimony(III) by amorphous iron and manganese oxyhydroxides; Chem. Geo. 2001, 174, 379–387.

[139] Meharg, A., Venomous Earth. How Arsenic Caused the World's Worst Mass Poisoning; Macmillan Science, New York, 2005.

[140] Coughtrey, P.J.; Jackson, P.J.; Thorne MC. Radionuclide distribution and transport in terrestrial and aquatic ecosystems; AA Balkema, Rotterdam, 1983.

[141] Baroni, F.; Boscagli, A.; Protano, G.; Riccobono, F., Antimony accumulation in *Achillea ageratum, Plantago lanceolata* and *Silene vulgaris* growing in an old Sb-mining area; Environ. Pollut. 2000, 109, 347–352.

[142] Brooks, R.R., Geobotany and biogeochemistry in mineral exploration; Harper and Row, New York, 1972.

[143] Bowen, H.J.M., Environmental Chemistry of the Elements; Academic Press, London, 1979.

[144] Kabata-Pendias, A.; Pendias, H., Trace Elements in Soils and Plants; CRC Press, Boca Raton, FL, 1984.

[145] Bowden, J.W.; Nagarajah, S.; Barrow, N.J.; Posner, A.M.; Quirk, J.P., Describing the adsorption of phosphate, citrate and selenite on the variable charge mineral surface; Aust. J. Soil Res. 1980, 18, 49–60.

[146] Tyler, G.; Olsson, T., The importance of atmospheric deposition, charge and atomic mass to the dynamics of minor and rare elements in developing, ageing, and wilted leaves of beech (*Fagus sylvatica* L.); Chemosphere 2006, 65, 250–260.

[147] Shacklette, H.T.; Erdman, J.A.; Harms, T.F., Trace elements in plant foodstuffs; in: Oehme F.H. (ed.), Toxicity of Heavy Metals in the Environment, Part 1; Marcel Dekker, New York, 1978, 25–43.

[148] Istas, J.; De Temmeran, L.; Dupire, S.; Hoenig, M., Luchtverontreiniging door een metallurgisch bedrijf: een systematisch onderzoek (Final Report). Belgian National Research and Development Programme on Environment – Air; Brussels, Belgium, 1982.

[149] Peterson, P.J., Unusual accumulation of elements by plants and animals; Sci. Prog. 1971, 59, 505–526.

[150] Porter, E.K.; Peterson, P.J., Arsenic accumulation by plants on mine waste (United Kingdom); Sci. Total Environ. 1975, 4, 365–371.

[151] de Koe, T., Agrostis castellana and Agrostis delicatula on heavy metal and arsenic enriched sites in NE Portugal; Sci. Total Environ. 1994, 145, 103–109.

[152] de Koe, T.; Beek, M.A.; Haarsma, M.S.; Ernst, W.H.O., Heavy metals and arsenic in grasses and soils of mine spoils in North East Portugal, with particular reference to some Portuguese goldmines; in: Nath B. (ed.), Environmental Pollution, Proc. Int. Conf, ICEP-1, 1991, pp. 373–380.

[153] Ma, L.Q.; Komar, K.M.; Tu, C.; Zhang, W.; Cai, Y.; Kennelley, E.D., A fern that hyperaccumulates arsenic; Nature 2001, 409, 579.

[154] Warren, H.V.; Delavault, R.E.; Barasko, J., The arsenic content of Douglas Fir as a guide to some gold, silver and base metal deposits; Can. Mining Metall. Bull. 1968, 7, 1–9.

[155] Visoottiviseth, P.; Francesconi, K.; Sridokchan, W., The potential of Thai indigenous plant species for the phytoremediation of arsenic contaminated land; Environ. Pollut. (Series B) 2002, 118, 453–461.

[156] Craw, D.; Rufaut, C.; Haffert, L.; Paterson, L., Plant colonization and arsenic uptake on high arsenic mine wastes, New Zealand; Water Air Soil Pollut. 2007, 179, 351–364.

[157] Ruiz-Chancho, M.J.; Lopez-Sanchez, J.F.; Schmeisser, E.; Goessler, W.; Francesconi, K.A.; Rubio, R., Arsenic speciation in plants growing in arsenic-contaminated sites; Chemosphere. 2008, 71, 1522–1530.

[158] Pratas, J.; Prasad, M.N.V.; Freitas, H.; Conde, L., Plants growing in abandoned mines of Portugal are useful for biogeochemical exploration of arsenic, antimony, tungsten and mine reclamation; J Geochem. Explor. 2005, 85, 99–107.

[159] Gürleyük, H.; Van Fleet Stalder, V.; Chasteen, T.G., Confirmation of the biomethylation of antimony compounds; Appl. Organomet. Chem. 1997, 11, 471–483.

[160] Jenkins, R.O.; Craig, P.J.; Miller, D.P.; Stoop, L.C.A.M.; Ostah, N.; Morris, T.A., Antimony biomethylation by mixed cultures of micro-organisms under anaerobic conditions; Appl. Organomet. Chem. 1998, 12, 449–455.

[161] Dodd, M.; Pergantis, S.A.; Cullen, W.R.; Li, H.; Eigendorf, G.K.; Reimer, K.J., Antimony speciation in freshwater plant extracts by using hydride generation–gas chromatography–mass spectrometry; Analyst 1996, 121, 223–228.

[162] Webb, S.M.; Gaillard, J.F.; Ma, L.Q.; Tu, C., XAS speciation of arsenic in a hyperaccumulating fern; Environ. Sci. Technol. 2003, 37, 754–760.

[163] Smith, P.G.; Koch, I.; Reimer, K.J., Uptake, transport and transformation of arsenate in radishes (*Raphanus sativus*); Sci. Total Environ. 2008, 390, 188–197.

[164] Koch, I.L.W.; Feldmann, J.; Andrewes, P.; Reimer, K.J.; Cullen, W.R. Antimony species in environmental samples; Int. J. Environ. Anal. Chem. 2000, 77, 111–131.

[165] Miravet, R.; Bonilla, E.; López-Sánchez, J.F.; Rubio, R., Antimony speciation in terrestrial plants. Comparative studies on extraction methods; J Environ. Monit. 2005, 7, 1207–1213.

[166] Madrid, Y.; Barrio-Cordoba, M.E.; Cámara, C., Biosorption of antimony and chromium species by *Spirulina platensis* and *Phaseolus*. Applications to bioextract antimony and chromium from natural and industrial waters; Analyst 1998, 123, 1593–1598.