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Antimony as a global dilemma: Geochemistry, mobility, fate and transport[☆]

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ABSTRACT

Elevated concentrations of antimony (Sb) in environmental, biological and geochemical systems originating from natural, geological and anthropogenic sources are of particular global concern. This review presents a critical overview of natural geochemical processes which trigger the mobilization of Sb from its host mineral phases and related rocks to the surrounding environments. The primary source of Sb contamination in the environment is geogenic. The geochemical characteristics of Sb are determined by its oxidation states, speciation and redox transformation. Oxidative dissolution of sulfide minerals and aqueous dissolution are the most prevalent geochemical mechanisms for the release of Sb to the environment. Transformation of mobile forms of Sb is predominantly controlled by naturally occurring precipitation and adsorption processes. Oxyhydroxides of iron, manganese and aluminum minerals have been recognized as naturally occurring Sb sequestrating agents in the environment. Antimony is also immobilized in the natural environment via precipitation with alkali and heavy metals resulting extremely stable mineral phases, such as schafarzikite, tripuhyite and calcium antimonates. Many key aspects, including detection, quantification, and speciation of Sb in different environmental systems as well as its actual human exposure remain poorly understood. Identification of global distribution of most vulnerable Sb-contaminated regions/countries along with aquifer sediments is an urgent necessity for the installation of safe drinking water wells. Such approaches could provide the global population Sb-safe drinking and irrigation water and hinder the propagation of Sb in toxic levels through the food chain. Hence, raising awareness through the mobility, fate and transport of Sb as well as further transdisciplinary research on Sb from global scientific communities will be a crucial stage to establish a sustainable Sb mitigation on a global scale.

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1. Introduction

The existence of elevated levels of antimony (Sb) in soils, sediments, surface/ground-water and biological systems have received considerable attention worldwide in the present decade due to its adverse consequences on human food chain, drinking and irrigation water sources as well as agricultural crop productivity (Ahmad et al., 2014; Cai et al., 2016a; Filella et al., 2009). Antimony belongs to the 15th group of the periodic table, having an atomic number of 51, an atomic weight of 122 and a density of 6.697 kg/m^3 at 26 °C (Anderson, 2012). Antimony occurs naturally in rocks, water and soils at the levels of 0.15–2 mg/kg, < 1 µg/mL and 0.3–8.6 mg/kg, respectively (Pierart et al., 2015). However, the Sb is present at elevated concentrations in different environmental, biological and geological compartments due to its mobilization from minerals and related rocks as well as human induced activities such as mining, military training, smelting and use of pharmaceuticals and pesticides (Ahmad et al., 2014; Okkenhaug et al., 2016; Rajapaksha et al., 2015; Wang et al., 2011). Countries of particular concern where the contamination of Sb has been described so far to be significantly

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associated with geogenic sources, such as mine ores, geothermal and volcanic systems include the USA, China, Australia, New Zealand, Japan, Mexico, Spain and Slovakia (Ashley et al., 2006; Henckens et al., 2016; McNamara et al., 2016; Simmons et al., 2016; Wang et al., 2011). However, due to geological similarities among different countries, Sb occurrence and its adverse effects can be expected in many other countries around the world where the problem has not been described so far. Therefore, the determination of actual exposure of global population to Sb requires more attention in the near future.

Antimony often coexists with arsenic (As) in the natural environment due to their similar geochemical behavior (Arai, 2010). With regard to historical practices, Sb together with As have been processed at a larger scale because of elevated mining activities during the past decades. For instance, Hillgrove Sb-gold mine in New South Wales (NSW), Australia and the stibnite ore of Xikuangshan, China are associated with an extensive release of both metalloids to the environment (Okkenhaug et al., 2012; Telford et al., 2009). It has been reported that Sb possesses similar toxicity as arsenic, nevertheless the Sb present in mammals is not detoxified by methylation (Gebel, 1997). Although As has been subjected to numerous in-vitro and in-vivo studies and proven carcinogenicity of its different species for humans (Bailey et al., 2016; Kurosawa et al., 2016; Yin et al., 2017), there is limited information on toxicity of Sb species and their actual exposure to ecological and human health (Gebel, 1997; Multani et al., 2016). Thus, a mechanistic toxicological approach should urgently be developed for future risk assessment of a variety of Sb species in environmental and biological systems.

Much concerns regarding the occurrence, and analyses of Sb in different geological, environmental, and biological systems emerged over recent decades (Aksoy et al., 2009; Alvarez-Ayuso et al., 2013; Filella et al., 2002b; Filella and May 2005; Gebel, 1997; He, 2007; Henckens et al., 2016; Krachler et al., 2001). A series of critical reviews on the occurrence of Sb, its characteristic features of solution chemistry and microbiota relevant interactions has been published making the global scientific community more interested in Sb contamination over different environmental, biological and geological compartments (Filella et al., 2002a, b; Filella et al., 2007). A critical review of various techniques and methodologies which are used for the quantification of different chemical forms of Sb in atmospheric aerosols was presented by (Smichowski, 2008). Another attempt has been taken to reveal a comprehensive overview of issues related to the existing state of knowledge on the behavior of Sb in the environment (Filella et al., 2009). Moreover, the literature on human exposure to Sb through air, air dust, drinking water and foods has been critically reviewed for identifying different pathways of Sb intake by humans (Belzile et al., 2011). Very recently, Multani et al. (2016) reviewed the chemical behavior of Sb in the effluents of metallurgical industry with an emphasis on treatment strategies (Multani et al., 2016). Such a growing interest on Sb related studies over recent decades has endeavored to understand the existing knowledge gaps in Sb research.

Up to date, little information is available regarding mobilization mechanisms of Sb from host mineral phases and its transformation through different environmental compartments. Furthermore, global distribution of Sb contaminated aquifer sediments are still not fully understood, so that the groundwater in Sb contaminated regions such as Xikuangshan, China, NSW, Australia, ZlataIdka, Slovakia, etc. may exceed the safe Sb guidelines of 10 μg/L for drinking water (WHO, 2003). Hence, a substantial research gap exists in studying the release mechanisms of Sb from host minerals and related rocks as well as the analysis of toxic inorganic and organic Sb species in various environmental systems, including groundwater and geothermal fluids. Furthermore, many vital aspects of bio-geochemical behavior of Sb are poorly understood, so that Sb mobilization mechanisms from primary and secondary mineral phases are not well documented in comparison with As. Therefore, critical areas of Sb research, including its ecotoxicology, biogeochemical cycle and chemical species in different environmental systems need to be addressed by the future research.

The main objective of the present review is to bring a critical overview on geochemical mechanisms that involve in the mobilization of Sb from its host mineral phases as well as in controlling its transformation over different environmental systems and their interfaces. Moreover, this review attempts to claim the Sb in a holistic approach emphasizing its physical, geochemical, and microbial/biological aspects based on available data published mostly in the period of 2000–2016. Overall, this provides a comprehensive discussion on (i) speciation (ii) redox transformation (iii) mobilization mechanisms, and (iv) sequestration of Sb in different environmental compartments.

2. Antimony as a global threat

2.1. Field screening for antimony

Antimony and natural Sb-bearing sulfides were found as early as 4000 BCE. Up to date, a variety of industrial operations such as production of paint pigments, flame retardants, plastics, glassware and ceramics, and alloys in ammunition and battery manufacturing plants extensively utilize Sb; as a result the global consumption of Sb has increased to more than 1.4×10^5 tons each year (Guo et al., 2014b; Henckens et al., 2016). Moreover, ore mining (geogenic source, but anthropogenically released) and smelting industries have been recognized as the major anthropogenic source of Sb pollution in soil and water systems over the past ten decades (Guo et al., 2014a). Generally, Sb has been derived from mineral ores of gold, silver and mercury sulfides mining in over 15 countries worldwide (Anderson, 2012). During the past 110 years, China has been the main Sb provider in the world, accounting for over 87% of the global Sb production which is predominantly associated with the major mined ore deposit located in the province of Hunan (the center of eastern China). In this ore deposit, $1.2–1.5 \times 10^4$ metric tons of Sb have been produced annually within a period of 2009–2013 (Henckens et al., 2016; Pierart et al., 2015). With regard to the global Sb production, over the period from 1900 to 2013 (113 years), the average annual Sb yield has been annually increased by 5.6% (Henckens et al., 2016). Such a massive annual consumption of Sb worldwide (Table 1) may pose the generation of a large amount of Sb-contaminated solid wastes, such as water-quenched slag, desulfurized slag, metal-alkali residues, and blast furnace dust to the environment (Guo et al., 2014a).

Table 1
Major Sb mine production in the world from 2010 to 2015 (in metric tons) (Survey, 2012, 2013, 2014, 2015, 2016).

Country	Antimony mine production / Metric tons					
	Year					
	2010	2011	2012	2013	2014	2015
China	120,000	150,000	145,000	120,000	120,000	115,000
Russia	3000	3300	6500	7000	9000	9000
Australia	–	–	–	–	5800	5500
Bolivia	3000	3900	4000	5000	5500	5000
Tajikistan	2000	2000	2000	4700	4700	4700
Turkey	–	–	–	–	4500	4500
Burma	–	–	–	9000	3300	3500
South Africa	3000	4700	3800	3100	1600	–

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2.2. Toxicology and epidemiology

Antimony has been recognized as one of the genotoxic elements; thus it is not considered as an essential element either in plants or animals (Smichowski, 2008). The permissible limits of Sb in drinking water as recommended by the United States Environmental Protection Agency (USEPA) and European Union (EU) are 6 μg/L (49 nM) and 5 μg/L (41 nM), respectively (Directive, 1976; Ungureanu et al., 2015; USEPA, 2001, 2009). The current guideline for Sb in drinking water recommended by the World Health Organization (WHO) is 10 μg/L (82 nM) (WHO, 2003). Non-observed adverse effect levels (NOAEL) in the sub-chronic drinking water is estimated to be 6.0 mg/kg of body weight per day (Poon et al., 1998). Median lethal dose (LD_{50}) for the oral uptake of Sb(V) in the form of potassium antimony tartrate in animals is nearly 115 mg/kg of body weight in rabbits and rats to 600 mg/kg of body weight in mice, while Sb_2O_3 was known as practically non-toxic ($LD_{50} > 20,000$ mg/kg of body weight), which is due to its very low solubility in water (Gebel, 1999).

Inorganic compounds of Sb are more toxic than its organic species and the Sb(III) compounds are predicted to be approximately 10-fold more toxic than Sb(V) oxo-anionic species (Nakamaru and Altansuvd, 2014; Smichowski, 2008; Ungureanu et al., 2015). Antimony trioxide (Sb_2O_3) is possibly carcinogenic to humans (Group 2B), while carcinogenic effects of antimony trisulfide (Sb_2S_3) on humans has not been identified (group 3) with regard to the classification of the International Agency for Research on Cancer (IARC) (Ungureanu et al., 2015). It is reported that total daily intakes of Sb generally ranges 1.0–80 μg for people those who are living in Sb-contaminated areas (Belzile et al., 2011). Daily oral uptake of Sb (10–70 μg/day) by humans has been considerably higher than its exposure via inhalation, although the total exposure from environmental sources, foods and drinking water is quite lower than the occupational exposure (Belzile et al., 2011). Contamination of terrestrial and aquatic systems around nuclear waste disposal sites is more life-threatening due to gamma emitting radionuclide; ^{125}Sb which is a fission product of ^{253}U (half-life - 2.8 years) (Scheinost et al., 2006).

Acute exposure to Sb through inhalation by humans may cause the irritation of the skin and eyes. Antimony spots which are a type of rash infecting around sweat and sebaceous glands are the worst impact of skin irritation (USEPA, 1999). Effects of Sb exposure to human eye include ocular conjunctivitis. These acute toxicity symptoms of Sb have been confirmed based on *in vivo* studies in rats, mice, and guinea pigs (ATSDR, 1992). Oral uptake of water-soluble Sb salts through drinking water or food may cause the irritation of gastrointestinal mucosa, thereby resulting in various adverse health effects such as vomiting, abdominal cramps, diarrhea and cardiac toxicity in the human body. The minimal lethal dose (LD) for oral inebriation by Sb(V) in the form of potassium antimony tartrate has been reported as 300 and 1200 mg for a child and an adult, respectively. Volatile species of Sb, particularly inorganic Sb hydrides (SbH_3) and a lipophilic gas may contaminate the atmosphere and thereby leading to inhalation of volatiles or insoluble particulates in humans (Fort et al., 2016). Chronic inhalation of such Sb containing dusts causes the infection of the respiratory tract, myocardial as well as the liver. Moreover, oral exposure of Sb(III) species may lead to the destruction of optic nerves, uveitides and retinal bleeding and the specific symptoms include headache, coughing, anorexia, troubled sleep and vertigo (Winship, 1987).

The dissolution of Sb_2O_3 in synthetic gastric juice which is analogous to human gastric fluid has been reported to be 20 mg/L after 24 h (Elinder, 1986). The abdominal adsorption of Sb_2O_3 in humans has been reported to be in the range of 5–20%, whereas Sb(V) in the form of potassium antimony tartrate possess an absorption rate of 5% (Lauwers et al., 1990). Human exposure to Sb_2O_3, mostly by intake of contaminated food and drinking water is directly linked with carcinogenic incidences, including lung cancer (Fort et al., 2016; Okkenhaug et al., 2016). Antimony is highly attracted by human spleen and blood cells and can easily be accumulated in vascularized organs and tissues, mainly the liver and kidney resulting in serious risks to human health, such as cardiovascular diseases, liver diseases and respiratory diseases (Feng et al., 2013; Gebel, 1997). The Sb(III) in the form of $Sb(OH)_3$ is capable of easily penetrating through cell membranes due to its neutral pH, so that it acquires a long elimination half-life compared to As(V) (24 vs 94 h, respectively) (Stemmer, 1976). On the other hand, $Sb(OH)_3$ can form complexes with thiol groups, and thereby accumulating in body cells (Gebel, 1997). Therefore, Sb has been recognized as an emerging contaminant by the WHO, USEPA and EU (Guo et al., 2014b).

2.3. Bioaccumulation and bioaccessibility of antimony

Bioaccumulation of Sb may reflect its bioavailability to living organisms (Fu et al., 2011). Bioaccessibility is the fraction of total amount of Sb that is potentially available to be absorbed by an organism, and this fraction represents the maximum amount of Sb available for intestinal absorption (Peijnenburg et al., 2007). Bioaccessibility along with bioavailability may result the bioaccumulation of Sb in living organisms, including plants and animals. Thus, both bioaccumulation and bioaccessibility considerations are important tools to assess the extent of hazard associated with Sb contaminated sites as well as probable human health risks (Fu et al., 2011; Li et al., 2014).

Bioaccessible concentrations of Sb have been commonly determined by using two *in vitro* chemical extraction methods, namely the Simplified Bioaccessibility Extraction Test (SBET) and Physiologically Based Extraction Test (PBET) (Li et al., 2014). Soils of Xikuangshan Sb mine areas, China were contaminated with Sb in an average concentration of 3061 mg/kg and the bioaccessibility values of Sb in this soil were reported to be 5.89 ± 6.44% and 7.83 ± 9.82% for SBET and PBET (gastric) extractions, respectively (Li et al., 2014). Interestingly, the overall bioaccessibility of Sb in the most of tested soil samples were lower than 30% that may be due to either immobilization of Sb by iron oxyhydroxides, and sulfides present in soils or association of the most of Sb in the residual fraction of soil. A similar study conducted in shooting ranges in Australia demonstrated that the bioaccessibility of Sb in the gastric phase of humans ranges from 10 to 80% that is slightly higher than that of the intestinal phase (6–50%) (Sanderson et al., 2012). Moreover, the bioaccessibility of Sb in a lead contaminated mine soil was determined to be 1.5–12% of the total Sb concentrations (26–1150 mg/kg) by using an *in vitro* Bioaccessibility Group Research Europe (BARGE) digestion test (Denys et al., 2009). However, in contrast to As, limited studies have been found regarding the bioaccessibility of Sb in contaminated soils up-to-date (Denys et al., 2009; Li et al., 2014; Sanderson et al., 2012). Accessing bioaccessible concentrations of Sb in a variety of multi-metal contaminated soil systems is essential in the near future as it is supposed to be providing more applicable guidelines for risk assessments as well as clues to preserve various biological species in food chains. Soluble forms of Sb can readily be taken up by plant species depending on several processes including, speciation, adsorption/desorption, precipitation/dissolution, and Sb-ligand complex formation (Müller et al., 2013; Pierart et al., 2015). More mobile species of Sb, such as $SbCl_2$, $[Sb(OH)_6]^-$, etc. that are available in soils/waters at or adjacent to mining sites, shooting range and ore processing facilities may enter the plant tissues via natural food

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chains and subsequently accumulate in human body cells which may lead to severe health risks. The toxicity levels of Sb in plants generally lie in the range of 5–10 mg/kg, so that increased concentrations of Sb in edible plant tissues may lead to adverse phytotoxicity effects such as, growth retardation, inhibition of photosynthesis, decrease in the uptake of certain essential elements and synthesis of certain metabolites (Alvarez-Ayuso et al., 2013; Feng et al., 2013; Pérez-Sirvent et al., 2012; Vaculík et al., 2013). For example, lettuce plants grown in soil that is spiked with Sb (up to 82 mmoL/kg) in the form of Sb_2O_3 showed a 10% inhibition of their shoot biomass after 31 weeks from the metal treatment, due to the stress of high concentrations of Sb in plant tissues (Oorts et al., 2008).

It has been recently reported that some medicinal plants such as *Fragaria vesca, Taraxacum officinale, Tussilago farfara, Plantago major, Veronica officinalis, Plantago media,* and *Primula elatior* that are naturally growing around an old Sb mining sites in Slovakia (Central Europe) can accumulate high Sb concentrations (10–920 mg/kg) in plant tissues (Vaculík et al., 2013). However, these plants possessed a great tolerance against such high amounts of Sb without showing phytotoxic symptoms. A high accumulation of Sb (2–507 mg/kg) was found in pine and birch plants growing in the tailing of an old Sb mine site located in Ouche (France) (Jana et al., 2012). Furthermore, some plant species such as *Cistus ladanifer. L.* and *Carduus tenuiflorus* Curtis growing in neighboring areas impacted by a stibnite mine exploitation in southwest of Alburquerque village (Spain) have accumulated Sb in their edible parts of up to 152–340 mg/kg (Alvarez-Ayuso et al., 2013). These findings may evident that many crops cultivated adjacent to mining sites are subjected to the accumulation of high concentrations of Sb in the edible parts of crops which subsequently brings adverse impacts in human health due to direct and indirect exposure via food chains (Feng et al., 2013). For instance, people living around Xikuangshan Sb ore mining area (China) daily intake Sb in the amounts of 554 μg that is 1.5-fold higher than the tolerable daily intake (TDI) of Sb (360 μg/day) (Wu et al., 2011). The consumption of Sb contaminated drinking water, rice, vegetables, and meat/poultry, account for nearly 19, 33, 26, and 19% of the total Sb intake, respectively (Feng et al., 2013). Although the concentrations of Sb in soils from Xikuangshan Sb mine were high, the bioaccessibility values of Sb were lower than 30% (Li et al., 2014). Such an interesting behavior of Sb may be due to its co-occurrence with oxy-hydroxides of iron, manganese and aluminum phases which are not readily dissolved by the synthetic digestive fluids (Li et al., 2014). A similar study conducted in shooting ranges in Australia has demonstrated that the bioaccessibility of Sb in the gastric phase of humans ranges from 10 to 80% that is slightly higher than that of the intestinal phase (6–50%) (Sanderson et al., 2012).

3. Geochemical aspects of antimony

Antimony can predominantly be found in mineralized rocks and mesothermal quartz vein related deposits in the natural environment (Ashley et al., 2003; Craw et al., 2004). It typically exits as stibnite (Sb_2S_3) which is the primary source of Sb in mesothermal quartz veins (Craw et al., 2004; Emons et al., 2004). Furthermore, the Sb often coexists with other metal(loid)s such as Cu, Ag, Au, Zn, Cd, Hg, Ba, U, Sn, Pb, P, As, Bi, S, Se, Te, Nb, Ta, Mo, W, Fe, Ni, Co, and Pt (Roper et al., 2012; Smichowski, 2008). Arsenic is the major metalloid that is often co-associated with Sb-bearing minerals due to its similar geochemical properties. For example, primary Sb-minerals including, annivite [$(Cu_{12}(As,Bi,Sb)_4S_{13}$], gabrielite [$Tl_6Ag_3Cu_6(As,Sb)_9S_{21}$], gerstleyite [$Na_2(As,Sb)_8S_{13}\cdot 2H_2O$], geocronite [$Pb_5(As,Sb)_{12}S_8$], stibiodomeykite [$Cu_3(As,Sb)$], etc. are associated with As at considerable extent (Venkateswarlu et al., 2016). Fig. 1 illustrates some common primary and secondary Sb minerals which occur in the natural environment at considerable amounts. Geochemical processes of Sb are a suite of complex phenomena in the natural environment. Thus the understanding of speciation and redox transformation of Sb is very important to assess its toxicological effects as well as adverse consequences in the environment.

3.1. *Chemical speciation*

Species analysis of Sb may theoretically determine all chemical species that can be formed in a certain system. The toxicity, mobility and transformation of Sb entirely depend upon its speciation, which is often a function of pH, and redox potential (Wilson et al., 2010). Common chemical species of Sb which can be found in different environmental systems are illustrated in Fig. 2. Antimony can commonly occur in four oxidation states as Sb(V), Sb(III), Sb(0), and Sb(-III), while it is typically present in environmental, biological and geochemical systems as inorganic antimonites [Sb(III)] and antimonates [Sb(V)] (Fig. 3) (Kang et al., 2000). It can also exist as organic compounds (methylated species); however, its inorganic species are more prevalent than organic forms in many environmental systems. The harmfulness of Sb compounds varies in the order of organoantimonials < Sb(V) < Sb(III) (Wilson et al., 2010).

Positively charged species of Sb can only exist under very acidic conditions (<2 pH), whereas antimonite ion [$Sb(OH)_6^-$] and antimony hydroxide [$Sb(OH)_3$] are recognized as commonly occurring inorganic forms in natural waters (Ungureanu et al., 2015). Antimony pentoxide (Sb_2O_5) is readily dissolved in aqueous solutions producing [$Sb(OH)_6$], which can exist over a wide range of pH (2.7–10.4), whereas antimony trioxide (Sb_2O_3) is less soluble in aqueous solutions regardless of the pH due to the formation of insoluble antimony hydroxide [$Sb(OH)_3$] (Fig. 3) (Kang et al., 2000; Krachler et al., 2001). In high alkaline solutions (pH > 10.4), Sb_2O_3 tends to be dissociated as either $H_2SbO_3^-$ or $Sb(OH)_4^-$ and hence the trivalent Sb always prevails as a neutral compound over a wide range of pH as expressed by the following equation (Kang et al., 2000).

$$Sb(OH)_{3(s)} + 3H_2O_{(l)} \rightarrow Sb(OH)^-_{6(aq)} + 3H^+_{(aq)} + 2e \quad (1)$$

Generally, Sb occurs in mineral phases as its sulfides and oxides such as Sb_2S_3, valentinite (Sb_2O_3, orthorhombic), senarmontite (Sb_2O_3, cubic), cervantite ($Sb^{3+}Sb^{5+}O_4$), kermesite (Sb_2S_2O) stibiconite [$Sb_3O_6(OH)$], etc. and most of these phases may release various Sb species via oxidation and aqueous dissolution, and thereby distributing them over different environmental systems (Roper et al., 2012). Kermesite is a product of partial oxidation between stibnite and valentinite or stibiconite and is often co-exist with several mineral phases including, senarmontite, valentinite, cervantite and stibiconite (Kharbish et al., 2009). Senarmontite is thermodynamically predicted to be stable at 298.2 K. Although Sb_2O_5 is not considered as a mineral, it is known as two synthetic phases due to its hydrated form, $Sb_5O_{12}(OH)\cdot H_2O$ (Roper et al., 2012). In natural hydrothermal systems, Sb can be found as trivalent hydroxide and sulfide complexes, whereas its chloride complexes can exist only in strongly acidic solutions (Zotov et al., 2003).

Organic Sb speciation is still not fully understood, however organic Sb species have been recognized as less toxic compared to inorganic compounds (Müller et al., 2009). Methylated Sb species including, mono-di- and tri-methylated compounds are the most widespread Sb organic species that can be found in soil, water and biotic systems (Duester et al., 2005; Müller et al., 2009; Wilson et al., 2010). Methylated Sb species, trimethylantimony dichloride [$(CH_3)_3SbCl_2$], methylstibonic acid, $(CH_3)SbO(OH)_2$,

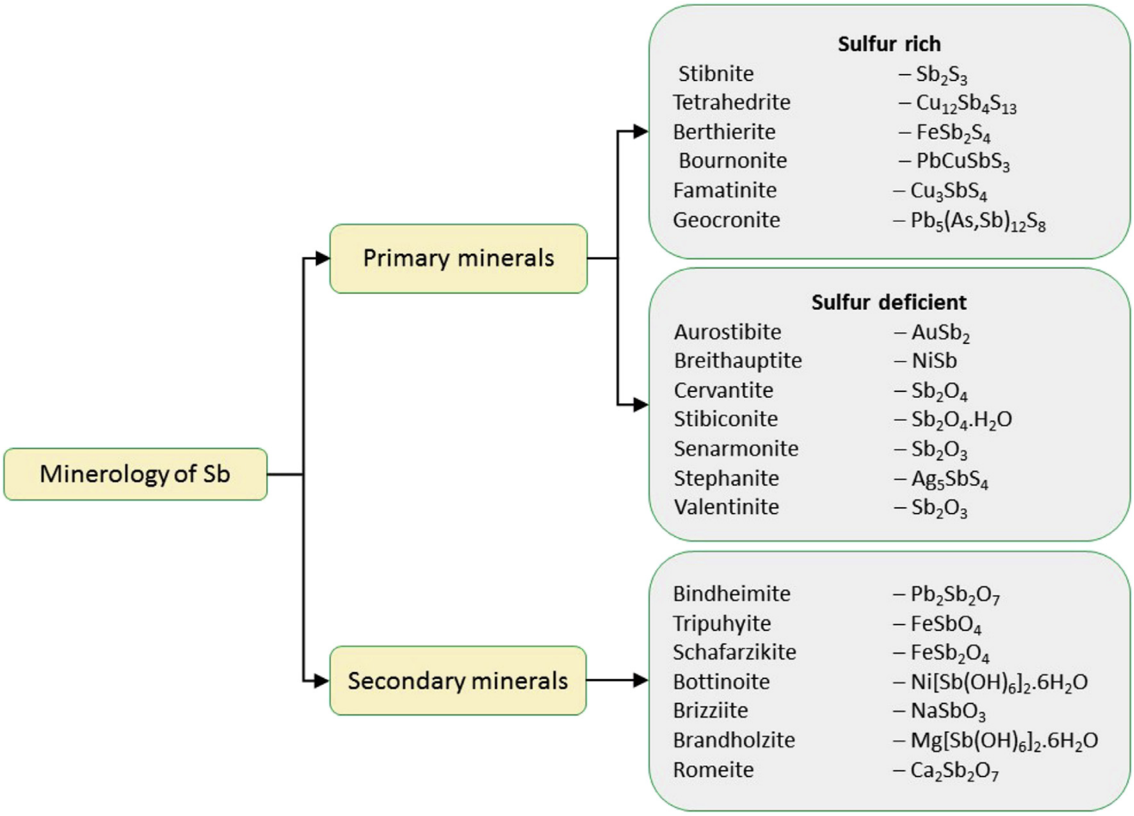

Fig. 1. Primary and secondary Sb minerals that are commonly found in the environment. [Adapted from (Multani et al., 2016)].

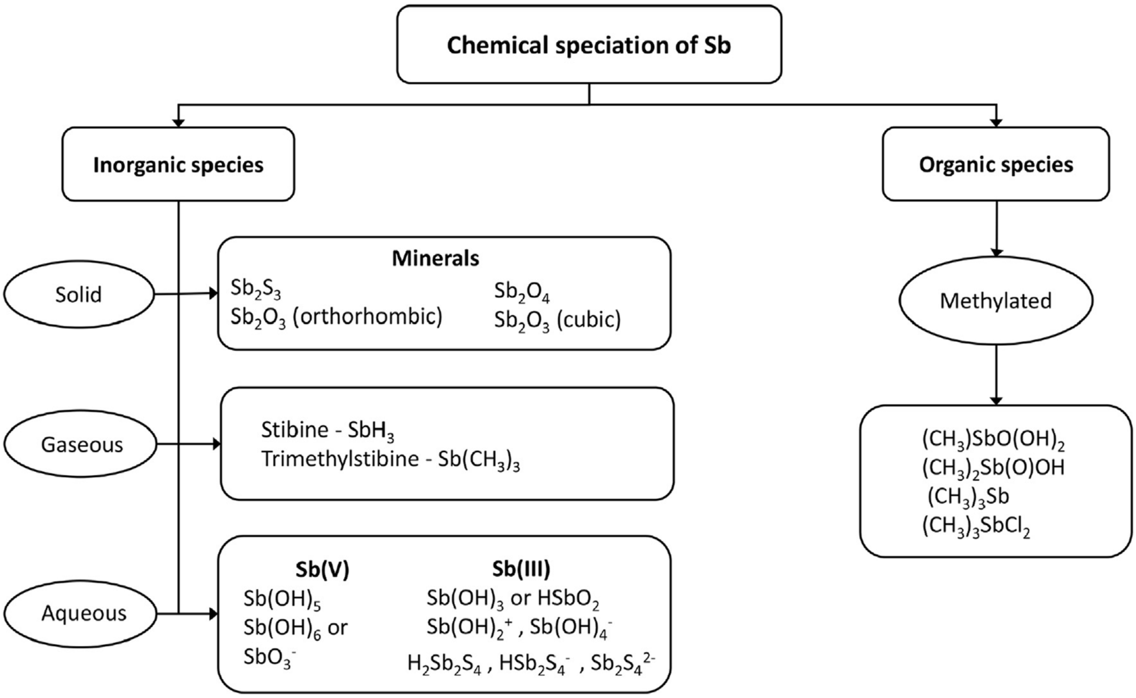

Fig. 2. Chemical species of Sb that can be commonly found in the environment (Okkenhaug et al., 2011; Planer-Friedrich and Scheinost, 2011; Wilson et al., 2010).

dimethylstibonic acid, $(CH_3)_2Sb(O)OH$, and trimethylstiboxide $(CH_3)_3Sb$ have been observed in various environmental samples, including marine biota, sea water, waterlogged soils and urban soils (Lintschinger et al., 1998; Wilson et al., 2010). The $[(CH_3)_3SbCl_2]$ species is likely to be occurring in aqueous solutions in the form of $[(CH_3)_3Sb(OH)]^+$ (Lintschinger et al., 1998). Besides, several Sb-

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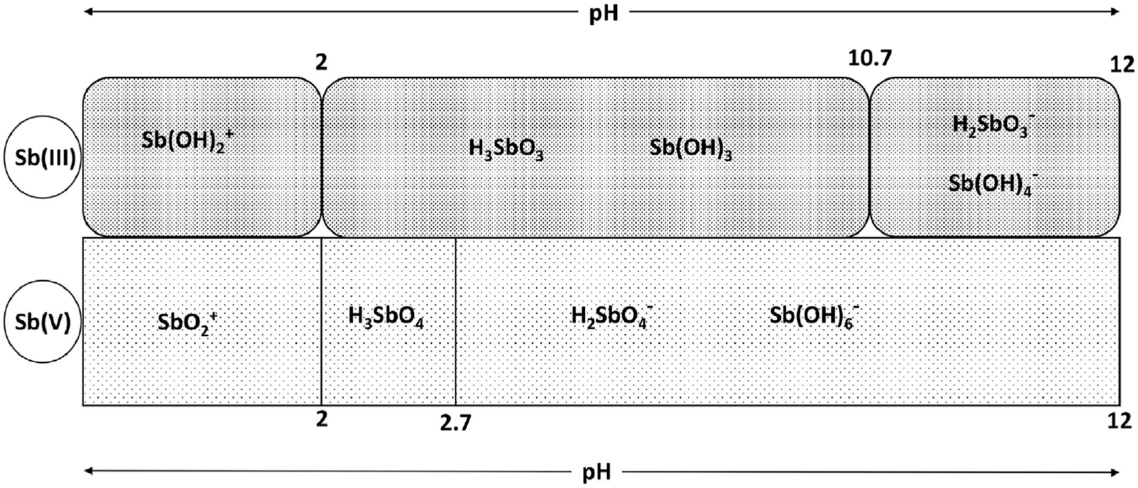

Fig. 3. Schematic representation of chemical speciation of Sb at different pHs.

sulfur (thio-antimony) complexes such as trithioantimonate and tetrathioantimonate have been identified in geothermal waters (Mosselmans et al., 2000; Planer-Friedrich and Scheinost, 2011). Species, $HSb_2S_4^-$ and $Sb_2S_4^{2-}$ have been identified as the thermodynamically most stable forms of thioanimonite complexes at lower temperatures (<120 °C), while hydroxothioantimonite complex, $Sb_2S_2(OH)_2^{\circ}$ is dominates at higher temperatures (>120 °C) (Planer-Friedrich and Scheinost, 2011).

3.2. Redox transformation

The mobility, bioavailability and transport of Sb are directly linked with redox transformation from one Sb species to another and hence, understanding redox processes of Sb species is important for their risk assessment. Redox transformation of Sb species takes place via oxidation and reduction processes under aerobic (oxic) as well as anaerobic (anoxic) conditions.

3.2.1. Aerobic conditions

In oxic environments, Sb(V) $[Sb(OH)_6^-]$ is the predominant form of Sb, so that it is expected to have high concentrations of Sb(V) compared to thermodynamically unstable Sb(III) in oxygen enriched water and soil systems (Filella et al., 2002a). The Sb(V) is predominant under oxic and mildly reducing conditions due to the oxidation of iron and manganese oxyhydroxides or complexation with dissolved sulfides (Chen et al., 2003). The mobility of Sb(V) is relatively higher compared to the Sb(III) at neutral pH (Mitsunobu et al., 2009). It has been investigated that Sb can entirely be present as Sb(V) (74–100%) over a wide redox potential (Eh) ranging from 360 to −140 mV at pH 8 in a soil-water interface around Ichinokawa mine in Japan (Mitsunobu et al., 2006). These findings indicated that Sb(III) gets oxidized to Sb(V) at more negative Eh values and hence Sb(V) is very stable (100%) in the oxic environment compared to Sb(III) (Mitsunobu et al., 2006).

The oxidation of more toxic Sb(III) to less toxic Sb(V) is enhanced by Fe and Mn oxyhydroxides, O_2 and H_2O_2 present in natural water and sediments and this detoxification process is rapid (completing after a few days) following the pseudo-first order kinetic rate model (reaction 2) (Belzile et al., 2001; Leuz and Johnson, 2005).

$$2Fe(OH)_{3(s)} + Sb(OH)_{3(aq)} \rightarrow 2Fe(OH)_{2(s)} + H_3SbO_{4(aq)} + H_2O_{(l)} \tag{2}$$

The oxidation of Sb(III) and adsorption of Sb(V) on goethite [FeO(OH)] is strongly pH dependent and, the oxidation reaction is highly favored at 3–5.9 pH with the pseudo-first-order rate constant ranging from $0.9–5.0 \times 10^{-6}\ s^{-1}$ (Leuz et al., 2006). Moreover, Sb(III) associated with natural organic matter, dissolved organic carbon (DOC) and humic acids is easily oxidized by photo-oxidants such as hydrogen peroxide (H_2O_2) and these processes can be beneficial in transforming high toxic Sb(III) species into less toxic Sb(V) species in contaminated aquatic and terrestrial areas (Belzile et al., 2001; Fan et al., 2014; Steely et al., 2007). Photo-oxidation of Sb(III) on goethite was investigated with the aid of kinetic measurements and X-ray photoelectron spectroscopy (XPS) techniques and this study indicated that the Sb(III) can be adsorbed and oxidized on goethite after the irradiation with simulated solar light (Fan et al., 2014).

The oxidation processes of Sb(III) to Sb(V) by O_2 and H_2O_2 also is strongly pH dependent (reaction 3); however, the rate of this reaction is slower than those of the oxidation on Mn(IV) and Fe(III) (hydro)oxides (Leuz and Johnson, 2005). The oxidation reaction of Sb(III) with O_2 in homogeneous aqueous solutions followed the pseudo-first order kinetics with respect to the concentrations of Sb(III) and inversely proportional to the concentrations of H^+ at a constant O_2 concentration of 0.22×10^{-3} M and a pH > 10. In contrast to this, the oxidation by H_2O_2 was pseudo-first order depending on the total contents of both Sb(III) and H_2O_2 and inversely proportional to the H^+ concentrations at 8.1–11.7 pH. This oxidation process in the presence of H_2O_2 can be expressed by the reactions (4), (5) and (6).

$$Sb(OH)_{3(aq)} + H_2O_{(l)} \leftrightarrow \begin{array}{c} Sb(OH)_{4(aq)}^- + H_{(aq)}^+ \\ pKa = 11.8 \end{array} \tag{3}$$

$$H_2O_{2(aq)} + H_{(aq)}^+ \leftrightarrow HO_{2(aq)}^- \quad pKa = 11.6 \tag{4}$$

$$Sb(OH)_{4(aq)}^- + H_2O_{2(aq)} \leftrightarrow Sb(OH)_{6(aq)}^- \tag{5}$$

$$Sb(OH)_{3(aq)} + HO_{2(aq)}^- + H_2O_{(l)} \rightarrow Sb(OH)_{6(aq)}^- \tag{6}$$

3.2.2. Anaerobic conditions

The speciation of Sb in anoxic environments has still not been fully understood. The Sb(III) in the form of $[Sb(OH)_3^{\circ}]$ is the most prevailing species in alkaline anoxic environments and it may also

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exist as SbS_2^- based on theoretical thermodynamic predictions (Chen et al., 2003). However, Sb(V) in the form of SbS_4^{3-} has also been observed under anoxic conditions due to its slow reaction kinetics (Filella et al., 2002a; Wilson et al., 2010). Reduced sulfur compounds that are likely to be occurring in anoxic water and sediments act as reducing agents governing the redox transformation of Sb(V) to the more toxic form of Sb(III) (reaction 7) (Polack et al., 2009).

$$H_2S_{(aq)} + Sb(OH)^-_{6(aq)} + H^+_{(aq)} \rightarrow Sb(OH)_{3(aq)} + 1/8S_{8(s)} + 3H_2O_{(l)} \tag{7}$$

The possibility of this process has been confirmed by laboratory experiments under a controlled anaerobic environment and the findings revealed that at room temperature, the reduction of Sb(V) [$Sb(OH)_6^-$] by aqueous sulfide is widespread at the beginning of the reaction and it then becomes much rapid (<400 min) at acidic pHs (<5 pH) following first order reaction kinetics (Polack et al., 2009). Under slightly acidic solutions (pH 5–6), the $Sb(OH)_6^-$ tends to be dissociated into several less stable and very reactive Sb complexes and this reaction may be expressed as same as the dissociation of $Sb(OH)_5$ in acidic medium (reaction 8, where n = 0–5) (Polack et al., 2009).

$$\begin{aligned} Sb(OH)_{5(aq)} + nH_2O^+_{(aq)} &\rightarrow Sb(OH)_{5-n}(OH_2)^{n+}_{n(aq)} + H_2S_{(aq)} \\ &\rightarrow 1/8S_{8(aq)} + 2H_2O_{(l)} + nH^+_{(aq)} \end{aligned} \tag{8}$$

Furthermore, Sb(V) can be reduced to Sb(III) by Fe(II) contained in minerals such as magnetite and mackinawite (Kirsch et al., 2008). Recent studies have also found that even in anoxic environments, thioantimonite species can be oxidized to thioantimonates by sulfur; the reaction may be expressed by equation (9) (Helz et al., 2002; Planer-Friedrich and Scheinost, 2011).

$$Sb(III)_{(aq)} + S^{2-}_{n(s)} + H^+ \rightarrow Sb(V)_{(aq)} + HS^-_{(aq)} + S^{2-}_{(n-1)(s)} \tag{9}$$

As the reaction implies, the transformation of insoluble sulfur into polysulfide compounds (HS^-) could be of particular concern in surface and groundwater systems that are used for drinking purposes.

3.3. Microbial interactions

Microbial redox processes can directly control the speciation, mobility and transport of Sb species in the environment. Several studies have reported the biological oxidation of Sb(III) as a cellular detoxification mechanism in bacteria and algae (Hamamura et al., 2013; Li et al., 2013; Sun et al., 2011). Antimony oxidizing bacteria such as *Stibiobacter senarmontii*, *Pseudomonas, Agrobacterium tumefaciens,* etc. play a crucial role in the biogeochemical cycling of Sb, transforming toxic Sb(III) to less toxic Sb(V) species (Li et al., 2013). Table 2 summarizes the significance of several types of microbial species in controlling the redox transformation and mobility of Sb in different environmental systems.

4. Mechanisms of antimony mobilization

Naturally occurring geochemical processes in minerals and mineral phases associated with rocks, sediments, soils and solid rocks/sediments of aquifer and unsaturated zone are directly linked with the extent of Sb contaminations in soils, sediments, ground- and surface waters. Chemical/physical weathering, naturally occurring oxidation and microbial processes are often responsible for converting primary Sb mineral phases, predominantly sulfides and sulfosalts, to secondary Sb minerals which are soluble in water and more mobile in the environment. The mobilization of Sb from its native mineral phases and related rocks is governed by several mechanisms including, dissolution, particulate transport, and oxidation and the released Sb species are transformed by gravitational, fluvial and atmospheric pathways (Hu et al., 2016a). Therefore, the knowledge of Sb release mechanisms and their interactive effects on/with other organic and inorganic phases are essential to predict the fate and transformation of its toxic species in different environmental systems.

4.1. Dissolution of antimony bearing minerals

Investigation of solubility properties of Sb bearing minerals in aqueous solutions is of particular concern in order to assess the extent of dissolution and distribution of toxic Sb species in the environment. Temperature, pH and Eh of the medium are the key factors which can have significant impact on the solubility of Sb species from Sb rich ores and related soil and sediments (Hu et al., 2016a). The dissolution reactions of Sb bearing minerals including valentinite, senarmontite, stibnite, stibiconite and native metallic Sb in pure water and acidic solutions have been documented (Biver and Shotyk, 2013; Obolensky et al., 2007; Roper et al., 2012; Zotov et al., 2003). The solubility of valentinite takes place over a wide range of pH (1.5–12) at 25 °C, forming neutral $Sb(OH)_3$ complex, which is capable of prevailing in the environmental systems over a wide pH range as long as the temperature does not exceed 350 °C (Obolensky et al., 2007; Zotov et al., 2003). The reaction may be expressed as follows (Pokrovski et al., 2009; Zotov et al., 2003):

$$Sb_2O_{3(s)} + 3H_2O_{(l)} \rightarrow 2Sb(OH)_{3(aq)} \tag{10}$$

The solubility of senarmontite in pure water also follows the same way as the above equation, (10) but under different conditions such as slightly acidic pH (4–5 pH), wide range of temperature (80–400 °C) and pressure (0.1–100 MPa) (Zotov et al., 2003). The dissolution reaction of stibiconite may formally be expressed by equation (11) (Biver and Shotyk, 2013).

$$Sb_3O_6OH_{(s)} + 6H_2O_{(l)} \rightarrow Sb(OH)_{3(aq)} + 2Sb(OH)_{5(aq)} \tag{11}$$

Since $Sb(OH)_3$ is a weak acid, it can further dissociate in aqueous solutions to hexahydroxoantimonate $[Sb(OH)_6]^-$ which is the principal species of Sb(V) above pH 2.47 (Reaction 12) (Arai, 2010; Biver and Shotyk, 2013).

$$\begin{aligned} Sb(OH)_{5(aq)} + H_2O_{(l)} \rightarrow\ & [Sb(OH)_6]^-_{(aq)} + H^+_{(aq)} \\ & \log K = -2.47 \end{aligned} \tag{12}$$

The dissolution of metallic Sb in aqueous solutions occurs at >450 °C and 50–100 MPa (reaction 13) (Obolensky et al., 2007).

$$Sb_{(metal)} + 3H_2O_l \rightarrow Sb(OH)_{3(aq)} + 1.5H_{2(g)} \tag{13}$$

The pH is one of the key parameters controlling the mobilization of Sb from its solid sources. Recent laboratory experiments have revealed that the release of Sb from its ores is highly favorable in basic pHs (9–10 pH) rather than acidic (<4 pH) or neutral media (Hu et al., 2016a). The Sb bearing ores containing Sb_2S_3 can mobilize Sb, producing its hydroxide complexes (reaction 14) (Biver and Shotyk, 2012b; Hu et al., 2016a)

$$Sb_2S_{3(s)} + 6H_2O_{(l)} \rightarrow 2Sb(OH)_{3(aq)} + 3H_2S_{(aq)} \tag{14}$$

Batch reactor experiments have been conducted in order to derive the kinetics for the proton promoted dissolution of the main natural antimony oxides over the range of $2 \leq pH \leq 11$ (Table 3)

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Table 2
Significance of microbial species in controlling the redox transformation and mobility of Sb in different environmental systems.

Type of micro-organism	Species	Environment/system	Significance	Reference
Bacteria	*Acinetobacter* sp. *Comamonas* sp. *Stenotrophomonas* sp. *Variovorax* sp.	Mined soils	Detoxification via oxidation of Sb(III) to Sb(V)	(Li et al., 2013; Sun et al., 2016)
Cyanobacteria	*Microcystis*	Aqueous solutions, under laboratory conditions (pH 2.5–2.6)	Biosorption of Sb(V)	(Sun et al., 2011)
Bacteria	*Stenotrophomonas* *Pseudomonas*	Mine tailing (pH 5.9–7.2)	Oxidation of Sb(III) to Sb(V)	(Hamamura et al., 2013)
Bacteria Algae	*Agrobacterium tumefaciens* *Cyanidiales*	Culture media (pH 6)	Oxidation of Sb(III) to Sb(V)	(Lehr et al., 2007)
Bacteria	*Hydrogenophaga taeniospiralis* *Variovorax paradoxus*	Stibnite mine sediments	Oxidation of Sb(III) to Sb(V)	(Terry et al., 2015)
Protozoa	*Leishmania*	In *Leishmania* cells	Reduction of Sb(V) to Sb(III) and accumulation	(Brochu et al., 2003; Manzano et al., 2013)
Microbes	–	Fresh water sediments in mined sites and lake	anaerobic microbiological respiration via reduction of Sb(V) to Sb(III)	(Kulp et al., 2014)
Fungi (yeast)	*Cryptococcus humicolus*	Culture media under oxic conditions	Methylation of Sb	(Hartmann et al., 2003)
Thermoacidophilic bacteria	*Sulfobacillus* *Leptospirillum* *Ferroplasma* strains	Gold ores and antimony containing sulfide minerals	Oxidation of Sb(III) to Sb(V)	(Tsaplina et al., 2014; Tsaplina et al., 2010; Zhuravleva et al., 2011)

Table 3
Estimated values for the dissolution rates of Sb released by common natural mineral oxide phases at $2 \leq pH \leq 11$ under standard conditions and ionic strength $(I) = 0.01$ moL/L.

Mineral oxide phase	Rate of Sb release (mol/m^2s^1)	Activation energy (kJ/mol^1)
Stibnite	$(2.2 \pm 0.2) \times 10^{-9}\ a(H^+)^{0.11 \pm 0.01}$ $(2 \leq pH \leq 4.74)$	-10.6 ± 1.9 (2.0 pH)
	$(4.3 \pm 0.2) \times 10^{-10}\ a(H^+)^{-0.030 \pm 0.003}$ $(4.74 \leq pH \leq 10.54)$	53 ± 14 (8.7 pH)
Senarmontite	$(5.3 \pm 2.2) \times 10^{-7}\ a(H^+)^{-0.54 \pm 0.05}$ $(2.0 \leq pH \leq 6.93)$	46.6 ± 4.7 (3.0 pH)
	$(1.4 \pm 0.3) \times 10^{-14}\ a(H^+)^{-0.53 \pm 0.07}$ $(6.93 \leq pH \leq 10.83)$	68.1 ± 6.1 (9.9 pH)
Valentinite	$(6.3 \pm 0.2) \times 10^{-8}\ a(H^+)^{-0.052 \pm 0.003}$ $(1.97 \leq pH \leq 6.85)$	41.9 ± 1.1(3.0 pH)
	$(2.79 \pm 0.05) \times 10^{-8}$ $(6.85 \leq)$	39.0 ± 4.6 (9.9 pH)

(Biver and Shotyk, 2013). Different aqueous Sb complexes such as $Sb(OH)_5$, $Sb(OH)_3$, and $Sb(OH)_2^+$ are capable of equilibrating in aqueous media as expressed by equations 15–17 (Vithanage et al., 2015). With the increase of pH, more of the $Sb(OH)_3$ tends to be dissolved into its anionic forms and the $Sb(OH)_4^-$ is the most soluble Sb complex in aqueous solutions:

$$Sb(OH)_{5(aq)} + H_2O_{(l)} \leftrightarrow \quad Sb(OH)^-_{6(aq)} + H^+_{(aq)} \quad \log K = -2.7 \tag{15}$$

$$Sb(OH)_{3(aq)} + H_2O_{(l)} \leftrightarrow \quad Sb(OH)^-_{4(aq)} + H^+_{(aq)} \quad \log K = -11.82 \tag{16}$$

$$Sb(OH)^+_{2(aq)} + H_2O_{(l)} \leftrightarrow \quad Sb(OH)_{3(aq)} + H^+_{(aq)} \quad \log K = -1.42 \tag{17}$$

4.2. Oxidative dissolution of sulfide minerals

Antimony is naturally mobilized into the environment from mesothermal mineral deposits and the release is predominantly from sulfur bearing minerals, particularly Sb_2S_3 (Ashley et al., 2003; Craw et al., 2004). The pH, oxygen and sulfur concentrations, presence of other organic and inorganic ligands such as humic substances, organic acids, hydroxyl ions, Fe and Mn complexes, etc. are the main factors that govern the rate of mobilization from its natural sources as well as anthropogenic systems (Biver and Shotyk, 2012a; Hockmann et al., 2014; Hu et al., 2016a). The typical aqueous complexes which can be in equilibrium with Sb_2S_3 are $H_2Sb_2S_4$, $HSb_2S_4^-$ and $Sb_2S_4^{2-}$ (Helz et al., 2002). Based on theoretical calculations, it has been found that the $H_2Sb_2S_4$ is thermodynamically more stable than $Sb_2S_4^{2-}$ and both Sb(III) and Sb(V) possess the same Sb–S stretching frequencies according to the evidences of Raman spectroscopic data (Tossell, 1994). In sulfur enriched solutions, the release of Sb occurs via an equilibration between Sb_2S_3 and orthorhombic sulfur producing two soluble complexes which might control the mobility and transformation of Sb in anaerobic environments (Helz et al., 2002). The first complex (equation (18)) is comprised of both Sb(III), and Sb(V) valences and the second complex (equation (19)) is an Sb(V) compound:

$$HS^-_{(aq)} + S_{(s)} + Sb_2S_{3(s)} \rightarrow \quad HSb_2S^-_{5(aq)} \quad \log K = -1.47 \pm 0.17 \tag{18}$$

$$HS^-_{(aq)} + 2S_{(s)} + Sb_2S_{3(s)} \rightarrow \quad {Sb_2S_{6(aq)}}^{2-} \quad \log K = -9.55 \pm 0.07 \tag{19}$$

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Stibnite is dissolved in pure water and acidic solutions (3–7 pH) in the presence of hydrogen sulfide (H_2S = 0.02–0.1 M) at, 200–350 °C and 50 MPa (equation (4)). On the other hand, in H_2S enriched solutions, over a wide range of pH and temperature, the dissolution of stibnite is attributed to the formation of different Sb complexes such as thioantimonite ($H_nSb_2S_{6-n}$, n = 0–2) and hydroxothioantimonite [$Sb_2S_2(OH)_2$] (Zotov et al., 2003).

Oxidative dissolution of natural Sb_2S_3 may lead to acid rock drainage (acid mine) generating protons and thereby making the system more acidic, which promotes the release of Sb from parent rocks to the surrounding ecosystems (Biver and Shotyk, 2012b, 2013). Hence, the acid rock drainage in Sb-bearing minerals may result in elevated concentrations of Sb in surface and groundwater as well as in adjacent soils. The kinetic behavior of the release of Sb from Sb_2S_3 has been reported by (Biver and Shotyk, 2012b); this study investigated that several factors including pH, concentrations of dissolved oxygen, elemental sulfur and other inorganic species (Fe^{3+}, Ca^{2+}, Mg^{2+}, Al^{3+}, and Ce^{3+}) that are associated with the mineral surfaces can have an impact on the dissolution of natural Sb_2S_3. Generally, the oxidative dissolution process releases Sb(III) species into their soluble form ($Sb(OH)_3$) under abiotic conditions and the corresponding reaction may be represented by equation (20) (Biver and Shotyk, 2012b):

$$Sb_2S_{3(s)} + 6O_{3(aq)} + 6H_2O_{(l)} \rightarrow 2Sb(OH)_{3(aq)} + 3H_2SO_{4(aq)} \tag{20}$$

The rate of this dissolution reaction is proportional to the concentrations of protons and dissolved oxygen at the Sb_2S_3 surface under both acidic and alkaline conditions. In acidic solutions, this dissolution takes place via a diffusion control mechanism, whereas in basic solutions, it occurs via surface control. Moreover, the dissolution process is greatly catalyzed by Fe^{3+} and Al^{3+} ions in acidic solutions, while in basic media, Ca^{2+} and Mg^{2+} ions tend to increase the dissolution rate. In a similar study, the oxidative dissolution of Sb_2S_3 in Sb-bearing ores in China was explained with regard to following reaction sequence (Hu et al., 2016b).

$$Sb_2S_{3(s)} + 6H_2O_{(l)} \rightarrow 2Sb(OH)_{3(aq)} + 3H_2S_{(aq)} \tag{21}$$

$$2Sb(OH)_{3(aq)} + O_{2(aq)} + 4H_2O_{(l)} \rightarrow 2Sb(OH)^-_{6(aq)} + 2H^+_{(aq)} \tag{22}$$

$$H_2S_{(aq)} + 2O_{2(aq)} \rightarrow H_2SO_{4(aq)} \tag{23}$$

5. Naturally occurring control strategies

Sequestration of mobile Sb species by naturally occurring processes is an essential phenomenon to control their mobility over different environmental, geological and biological systems. Formation of stable secondary Sb minerals via precipitation and adsorption on metal oxyhydroxides is known as the most prominent naturally occurring processes that can control the mobility and transformation of Sb species in various environmental systems including, ground- and surface-water, soil and sediments (Liu et al., 2015; Multani et al., 2016).

5.1. *Antimony sequestration via precipitation*

In soils, mobile species of Sb can readily be complexed with alkali metals such as, calcium, magnesium, sodium and potassium, thereby precipitating as alkali metal hydroxyantimonate salts which possess exceptionally low solubilities under ambient conditions (Multani et al., 2016). For instance, the solubility of some Sb-alkali metal complexes including, mopungite, $Na[Sb(OH)_6]$, brandholzite, $[Mg(H_2O)_6][Sb(OH)_6]_2$, and potassium hexahydroxoantimonate, $K[Sb(OH)_6]$ are reported to be 0.4, 0.5 and 15.0 g/L, respectively (Selim, 2012). It is investigated that the solubility of Sb in the soils affected by active Sb mine of Xikuangshan, China is predominately attenuated by a complex of calcium antimonate, $Ca[Sb(OH)_6]_2$ due to its extremely low solubility ($K_{sp} = 10^{-12.55}$) (Johnson et al., 2005; Okkenhaug et al., 2011). In Xikuangshan Sb ore deposit, the Sb(III) gets oxidized to $Sb(OH)_6^-$ by oxidation and dissolution of Sb_2S_3 which is an acidification process making the soil very acidic (reaction 24) (Okkenhaug et al., 2011). Simultaneous dissolution of $CaCO_3$ deposits may neutralize such soil systems (reaction 25). The produced $Sb(OH)_6^-$ which is the predominant water soluble Sb species in the soils of Xikuangshan area can be co-precipitated with aqueous Ca^{2+} ions present in soils, thereby forming highly stable $Ca[Sb(OH)_6]_2$ (Okkenhaug et al., 2011).

$$Sb_2S_{3(s)} + 7O_{2(g)} + 10H_2O_{(l)} \rightarrow 3SO^{2-}_{4(aq)} + 2Sb(OH)^-_{6(aq)} + 8H^+_{(aq)} \tag{24}$$

$$CaCO_{3(s)} + H^+_{(aq)} \rightarrow Ca^{2+}_{(aq)} + HCO^-_{3(aq)} \tag{25}$$

Naturally occurring calcium antimonite minerals such as $Ca[Sb(OH)_6]_2$ and romeite, $Ca_2Sb_2O_7$, having the solubility of 16.0 and 0.040 g/L have been identified as the most insoluble secondary Sb minerals in soils (Diemar et al., 2009; Multani et al., 2016; Selim, 2012).

Despite aforementioned very stable Sb-alkali mineral phases, water soluble Sb can also be precipitated with other heavy metals such as Ni, Fe and Pb forming insoluble secondary mineral phases particularly, bottinoite, $Ni(H_2O)_6[Sb(OH)_6]_2$, bindheimite, $Pb_2Sb_2O_7$, iron antimonates schafarzikite ($FeSb_2O_4$), and tripuhyite ($FeSbO_4$) (Multani et al., 2016). The extreme stability of these minerals is mainly due to their very low solubility ranging from few μg/L to 9.3 μg/L (Diemar et al., 2009). The schafarzikite and tripuhyite minerals have been recognized as crucial sinks of Sb in the natural environment due to their excellent stabilities, so that such minerals play a critical role in reducing elevated concentrations of Sb in the supergene enrichment of Sb ore deposits (Leverett et al., 2012). Solubility tests based on thermodynamic analyses demonstrated that the stability constants (log K) of tripuhyite and schafarzikite at 298 K are (−10.68 ± 0.10) and (−0.81 ± 0.01), respectively which prove high stabilities of these mineral phases (Leverett et al., 2012). The calculated gift free energy values (ΔG°_f) of tripuhyite and schafarzikite at 298 K were −836.8 ± 2.2 and −959.4 ± 4.3 kJ/mol, respectively and such high negative values of ΔG°_f further corroborate with the feasibility of Sb immobilization. Therefore, it is clear that the formation of such stable secondary Sb minerals via precipitation play a vital role in the sequestration of mobile species of Sb in the natural environment.

5.2. *Antimony sequestration via adsorption*

Redox active oxide phases including, iron, aluminum and manganese oxide minerals, clay minerals and natural organic matter are the most important environmental sorbents which can control the mobility of dissolved Sb species present in water and soil/sediments (Ilgen et al., 2012; Tighe et al., 2005). A variety of environmental factors, particularly temperature, pH, redox potential (Eh), DOC and organic and inorganic ligands directly affect the adsorption of Sb on specific mineral surfaces (Gustafsson and Sjöstedt, 2016). The adsorption of metals on these mineral phases are predominately governed by a ligand exchange mechanism with surface structural OH_2 or OH^- groups at the adsorption sites (Jain et al., 1999). Naturally occurring such processes, particularly in

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aquifer sediments tend to control the transport of mobile species of toxic contaminants, including Sb to the groundwater.

5.2.1. *Sorption on iron oxides*

The term "iron oxides" is considered to be a mixture of iron oxides, hydroxides and oxyhydroxides which are highly reactive mineral phases in the natural environment. Iron containing minerals such as goethite, hematite and ferrihydrite that are widely exist in soils and sediments play a vital role in immobilizing toxic Sb species through oxidation processes (Cui et al., 2015; Fan et al., 2014; Mittal et al., 2013; Ogawa et al., 2016; Rakshit et al., 2011). Dissolution of Sb bearing minerals may lead to elevated concentrations of Sb in mine waters and such dissolved Sb species can easily be adsorbed by hydrated iron oxides, thereby limiting their distribution in the environment (Craw et al., 2004). For instance, iron oxyhydroxides that are accumulated in mine tailing waters around the Hillgrove mine site in New South Wales (Australia) adsorbed aqueous Sb with a distribution coefficient (K_d) of up to 10^5 at near neutral pH. Hence, the adsorption of soluble Sb on iron oxides is one of the most prominent mechanisms in order to attenuate high levels of aqueous Sb found in contaminated sites (Craw et al., 2004).

Batch and kinetic experiments performed under controlled laboratory conditions have studied the feasibility of the adsorption reaction of Sb on ferric hydroxides [$Fe(OH)_3$] (Leuz et al., 2006; Thanabalasingam and Pickering, 1990). Goethite has been found to be a prominent sorbent for the immobilization of both Sb(III) and Sb(V) species and Sb(III) strongly adsorbs on goethite over a wide range of pH (3–12), while the maximum adsorption of Sb(V) occurs on the surface below 7 pH (Leuz et al., 2006). The mechanism of Sb adsorption on amorphous iron oxyhydroxides involves four major steps, (i) the formation of a surface complex between Fe(III) oxyhydroxide and Sb(III), (ii) the transfer of two electrons from Sb(III) to two Fe atoms, (iii) the discharge of oxidized Sb(V) and (iv) the release of reduced Fe(II) (Fig. 4) (Belzile et al., 2001). A hematite coated magnetic nanoparticle also showed a great adsorption capacity for Sb(III) (36.7 mg/g) present in aqueous solution, suggesting the effectiveness of such hematite modified nanoparticles for the decontamination of Sb polluted waters (Shan et al., 2014).

Iron plaques containing both ferrihydrite and goethite, found in waterlogged or flooded paddy soils, have also been recognized as a suitable adsorbent for the sorption and immobilization of Sb(III), thereby reducing the phytotoxicity in rice (*Oryza sativa* L.) plants (Cui et al., 2015; Thanabalasingam and Pickering, 1990). Kinetics for the sorption of Sb(III) on a composite of quartz sand coated with Fe_3O_4 and graphene oxide in aqueous media appeared to be followed by the pseudo-first order kinetic model indicating the involvement of physisorption mechanisms in the adsorption process (Yang et al., 2015). Green rusts are a composite of Fe(II)–Fe(III) layered double hydroxides, which exist as a natural mineral in many sub-oxic soils and sediments and which have a great affinity to Sb(V), thereby reducing Sb(V) to the Sb(III) species on their surface (Mitsunobu et al., 2009). It has been found that the Sb(V) is adsorbed on the surface of green rust incorporated with sulfate through two binding sites with different sorption mechanisms, (i) the edge sites with inner-sphere complex and (ii) the interlayer surface with outer-sphere complex (Mitsunobu et al., 2009). The effectiveness of ferrihydrite for simultaneous adsorption and oxidation of Sb(III) in the presence of Sb(V) in binary systems has also been demonstrated in a recent study (Qi and Pichler, 2016). With regard to the finding of this research, under competitive conditions, Sb(V) does not effect on the adsorption of Sb(III) on ferrihydrite, whereas Sb(V) adsorption is noticeably suppressed by Sb(III) over a wide pH range (4–10 pH). Hence the speciation of Sb and adsorption of its more toxic Sb(III) form by ferrihydrite is an environmentally friendly phenomenon, as it permits to control the mobility and transport of the more toxic forms of Sb in aquatic environments.

5.2.2. *Sorption on manganese oxides*

Manganese oxides also are a combination of manganese oxides, hydroxides and oxyhydroxides which are considered to be strong oxidizing agents in the natural environment (Milová-Žiaková et al., 2016). Oxyhydroxides of manganese (Mn) play a vital role in reducing the mobility of Sb via oxidation and adsorption mechanisms (Wang et al., 2012). Several previous studies have revealed

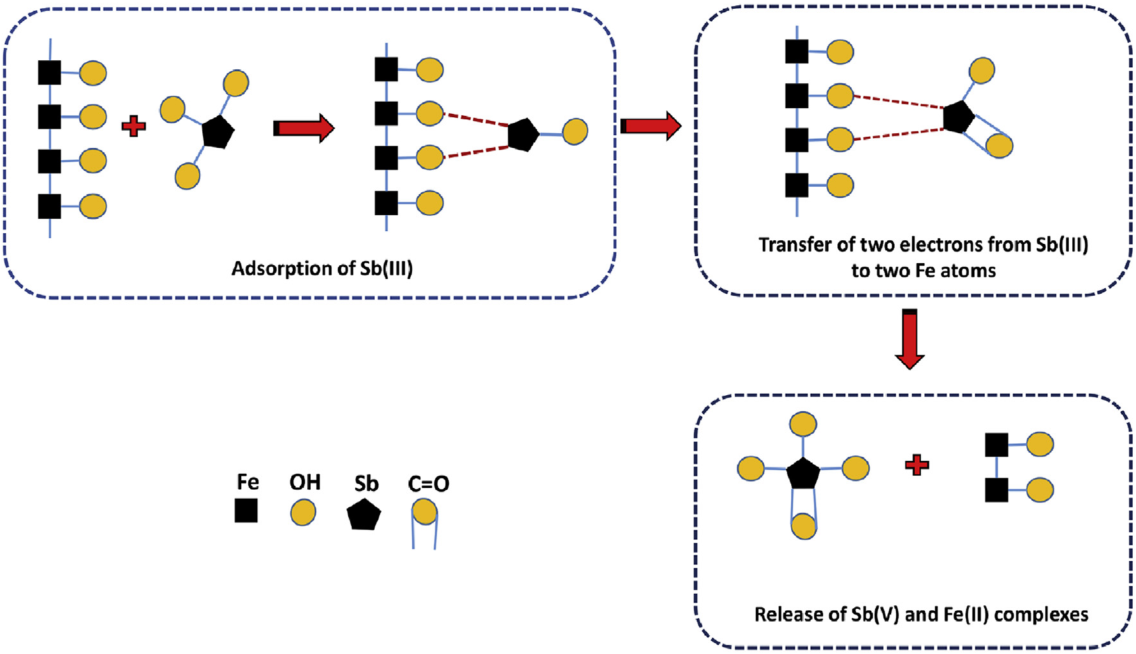

Fig. 4. Schematic representation of potential mechanisms for the adsorption of Sb(III) on amorphous iron oxyhydroxides [adapted from (Belzile et al., 2001)].

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the relevance of manganese oxides to immobilize Sb present in water, soil and sediments under natural as well as laboratory and green house conditions (Cai et al., 2016b; Essington and Vergeer, 2015; Ettler et al., 2015; Mok and Wai, 1990; Nakamaru and Altansuvd, 2014). It is reported that the mobility of Sb from sediments of the Coeur d'Alene river, United States located around silver, lead and zinc mining areas is controlled by manganese oxides present in river sediments (Mok and Wai, 1990). Naturally occurring birnessite (δ-MnO_2) has been recognized as a suitable reactive mineral phase for the immobilization of Sb(V) in contaminated soils (Essington and Vergeer, 2015). Moreover (Bagherifam et al., 2014), investigated that naturally occurring manganese oxides is capable of reducing the mobility and bioavailability of Sb in agricultural soil.

The adsorption of Sb(III) by a synthetic Mn oxyhydroxide in anoxic environments has been reported according to (Belzile et al., 2001):

$$MnO_{2(s)} + Sb(OH)_{3(aq)} + H_2O_{(l)} \rightarrow Mn(OH)_{2(aq)} + H_3SbO_{4(aq)} \tag{26}$$

This study demonstrated that the capacity of Mn oxides for oxidizing Sb(III) was much higher than that of Fe oxyhydroxides (Belzile et al., 2001). The mechanism of the adsorption process was found to be the same as that of the iron oxyhydroxides. In contrast to the adsorption mechanism on Fe oxyhydroxides, the adsorption of Sb(III) and the formation of a surface complex with the Mn(IV) oxide often takes place through only one Sb(III) on one Mn binding site.

Liu et al. (2015) have investigated the potential of an outer-sphere complex of Mn-oxide incorporated with Mn^{2+} which is formed by the reductive dissolution of Mn(IV) oxide by K_2SO_3 for the adsorption of Sb(V). The reductive dissolution of Mn(IV) leads to the release of Mn^{2+}, thereby forming outer-sphere surface complexes as represented by following equations (Liu et al., 2015).

$$Mn(IV)O_{2(s)} + SO^{2-}_{3(aq)} + 2H^+_{(aq)} \rightarrow Mn^{2+}_{(aq)} + SO^{2-}_{4(aq)} + H_2O_{(l)} \tag{27}$$

$$\equiv Mn - O - OH_{(s)} + Mn^{2+}_{(aq)} \rightarrow [\equiv Mn - O - O - Mn]^+_{(s)} + H^+_{(aq)} \tag{28}$$

$$2[\equiv Mn - O - OH]_{(s)} + Mn^{2+}_{(aq)} \rightarrow [\equiv Mn - O - O - Mn - O - O - Mn\equiv]_{(s)} + 2H^+_{aq} \tag{29}$$

The released Mn^{2+} tends to be interfaced with Mn(IV) oxide surface forming a Mn(III) complex (reaction 30) which is attributed to creating more binding sites for the adsorption of Sb(V). The adsorption of Sb(V) on the outer-sphere surface of the Mn-oxide complex occurred through the substitution of −O−Mn groups within ≡Mn−O−O−Mn by Sb(V), thereby releasing adsorbed Mn^{2+} into the solution due to the competition of Sb(V) and Mn^{2+} ions for the binding sites (reaction 31). Furthermore, the adsorption can be attained by the formation of inner surface complexes and the replacement of hydroxyl groups which are attached on the Mn-oxide surfaces (reaction 32) (Liu et al., 2015).

$$\equiv Mn(IV) - OH_{(s)} + Mn^{2+}_{(aq)} + H_2O_{(l)} + H^+_{(aq)} \rightarrow 2\left(\equiv Mn(III) - OH_{2(s)}\right) \tag{30}$$

$$\equiv Mn - O - O - Mn_{(s)} + Sb(V)_{(aq)} + 2H^+_{(aq)} \rightarrow \equiv Mn - O - Sb(V)_{(s)} + Mn^{2+}_{(aq)} + H_2O_{(l)} \tag{31}$$

$$\equiv Mn - O - OH_{(s)} + Sb(V)_{(aq)} + H^+_{(aq)} \rightarrow \equiv Mn - O - Sb(V) + H_2O_{(l)} \tag{32}$$

In a similar study, a Fe−Mn binary oxide phase showed much higher adsorption capacity (1.76 mmoL/g) for Sb(III) than those of FeOOH (0.83 mmoL/g) and MnO_2 (0.81 mmoL/g); in this system the MnO_2 facilitates the oxidation of Sb(III) to Sb(V), while the FeOOH provides binding sites for the adsorption of Sb(III) and Sb(V) (Xu et al., 2011). Hence, the adsorption of Sb(III) by naturally occurring Mn oxyhydroxides could be a natural detoxification process, by which toxic inorganic Sb(III) found in anoxic aquatic systems is oxidized into the less toxic Sb(V) during its transport to the oxic environment (Belzile et al., 2001).

5.2.3. *Sorption on clay minerals and Al-oxides*

Few studies have reported the interaction mechanism of Sb species with clay materials and Al-oxides (gibbsite) (Kameda et al., 2009; Rakshit et al., 2011; Xu et al., 2001). A recent research has attempted to study the sorption effects of a clay mineral namely bentonite on the adsorption of Sb(III) and Sb(V) in aqueous solutions using batch sorption experiments (Xi et al., 2011). This study showed that the rate of Sb(III) adsorption on bentonite is fairly faster than that of Sb(V) and the maximum adsorption capacities for Sb(III) and Sb(V) were 370–555 and 270–500 μg/g, respectively; this indicates a high adsorption capacity of bentonite for the removal of Sb(III) from aqueous solutions (Xi et al., 2011). The sorption of Sb(V) was strongly affected (reduced) by the presence of other anions such as NO_3^-, SO_4^{2-}, and PO_4^{3-} due to the competitive adsorption effect with negatively charged $Sb(OH)_{6-}$ This may enhance the mobility, bioavailability, and toxicity of Sb species in the presence of such competitive anions typically found in the natural environment. Xi et al. (2009) investigated that the adsorption of Sb(V) on kaolinite clay mineral is strongly dependent on pH and the maximum adsorption occurs (75%) at 3.6 pH while decreasing it by 20% with the increase of pH up to 9.2 (Xi et al., 2009).

Gibbsite (Al-oxide) is a common mineral in soils and the Sb(V) strongly interacts with it through its surface via adsorption mechanisms (Rakshit et al., 2011). Furthermore, a commercially available activated alumina has shown an increased adsorption capacity for Sb(V) (Xu et al., 2001). In acidic solutions, Al-oxides can be protonated making the surface positively charged and thereby generating electrostatic interactive forces with negatively charged Sb(V) species on the surface (Xu et al., 2001). The surface complexation reaction for the sorption of Sb(V) on gibbsite can be formally expressed as reactions (33) and (34) (Rakshit et al., 2011; Xu et al., 2001). Previous studies have demonstrated that the variation in the adsorption capacities of Mn, Fe and Al hydroxides for the adsorption of Sb(III) decreases in the order of MnOOH > $Al(OH)_3$ > FeOOH (Thanabalasingam and Pickering, 1990).

$$Al - OH_{(s)} + H^+_{(aq)} \leftrightarrow Al - (OH)^+_{2(s)} \tag{33}$$

$$2Al - OH_{(s)} + Sb(OH)^-_{6(aq)} \rightarrow (AlO)_2Sb(OH)^-_{4(s)} + 2H_2O_{(l)} \tag{34}$$

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5.2.4. *Interactions with natural organic matter*

Interactions of Sb with natural organic matter also are important interfaces for the fate, mobility and transformation of Sb in aquatic systems (Buschmann et al., 2005; Dousova et al., 2015). Interactions of Sb with a variety of organic ligands such carboxylic acids, alcohols, phenols (catechol), and amino acids of natural organic matters have been published (Buschmann and Sigg, 2004; Filella and May 2005; Filella and Williams, 2012; Tella and Pokrovski, 2009; Tserenpil and Liu, 2011). Analyses of lake waters have indicated that nearly 85% of total Sb in these systems is associated with natural organic matter, such as humic and fulvic acids and the rest is in the forms of inorganic Sb(III) and Sb(V) (Tella and Pokrovski, 2009). Complexation of Sb(III) species such as $[Sb(OH)_{3-n}]^{n+}$, $Sb(OH)_{3,}$ and $[Sb(OH)_4]^-$ with mono-functional organic ligands (acetic) or those having non adjacent carboxylic groups (adipic, malonic) is negligible, whereas the Sb(III) is capable of complexing with poly-functional carboxylic and hydroxyl-carboxylic acids and catechol over a wide range of pH ($3 < pH < 9$) in natural waters (Tella and Pokrovski, 2009). This study found that nearly 35% of total aqueous Sb tends to be bound with DOC via carboxylic and hydroxy-carboxylic groups in an aqueous solution containing Sb (1 µg/L) and DOC (5 mg/L), at 2–10 pH.

Humic acids have been recognized as an efficient adsorbent for Sb(III) at 4 pH with a sorption capacity of 23 µmoL/g in aqueous solutions (Pilarski et al., 1995) and the sorption is supposed to be through the hydroxy-carboxylic functional groups of humic acid forming bidendate complexes (Tella and Pokrovski, 2009). Under environmentally applicable conditions, (DOC = 5 mg/L), pH = 7, $[Sb(OH)_3]$ = 1 µg/L, up to 30% Sb(III) is likely to be bound with aquatic humic acids trough two binding sites (i) a phenolic group forming a neutral complex and (ii) a carboxylic group forming a negatively charged complex (Buschmann and Sigg, 2004). In addition, humic acids can catalyze the oxidation of Sb(III) to Sb(V) as it can act as an electron acceptor. For instance, humic acids found in shooting range soil have shown a critical function in immobilizing Sb, thereby controlling its mobility, fate and transport over the surrounding environments (Van Vleek et al., 2011).

6. Gaps in existing research and future perspectives

Existing knowledge and understanding upon the limitations of current research on Sb could enrich the mitigation of its environmental and health consequences. The relatively brief history, mostly in the present decade, researching the occurrence, distribution, (hydro)geochemistry and remediation of Sb has endeavored to alleviate the problems of different Sb species, which are of different toxicity, in various environmental systems. However, on global level, Sb has by far not attracted much public concern compared with As, some other toxic metals (e.g. Pb, Cd, Cr, Hg, etc.) or some organic contaminants; this is despite that its significance for human health as well as natural environment is of particular concern as the present review has been proven.

The present critical review has demonstrated that very little efforts have been undertaken on field scale analyses and determination of different inorganic and organic Sb species in biological, geological and environmental systems. Moreover, reporting on the distribution of Sb, particularly its species through the global groundwater and other environmental suites as well as its direct and indirect impacts on the populations those who are living in the most vulnerable locations around the globe have been insignificant. Therefore, fundamental researches based on the analysis of total Sb concentrations should be extended upon a variety of toxic Sb species, including methylated and thio-Sb complexes in soils, sediments, surface and groundwater systems. Modern geological approaches interfaced with existing technologies would be more beneficial to detect widespread distribution of Sb in global surface and groundwater systems, which could pave the way to reduce the toxicological effects of Sb on public and environmental health.

7. Summary

The present critical review provides a general context of Sb geochemistry and its mobilization from host mineral phases and related rocks. The primary source of Sb is often natural which is derived mainly from the weathering, dissolution, and particulate transport of Sb bearing minerals particularly stibnite, antimonite and valentinite. The geochemistry of Sb is a multifaceted phenomenon in the environment, which is a function of oxidation state, speciation and redox transformation. The mobilization of Sb from its native rock minerals to the environment is governed by oxidative dissolution of sulfide minerals and aqueous dissolution. The mobility of Sb and its transformation is predominantly controlled by naturally occurring precipitation and adsorption processes. At the present, the occurrence and distribution of elevated concentrations of Sb in terrestrial and aquatic systems of the countries including, the USA, China, Australia, New Zealand, Spain, Mexico and Slovakia are of particular concern. However, due to geological similarities, Sb occurrence and its adverse effects can be expected in many other countries around the world where the problem has not been described so far. The Sb-related health problems within affected population all over the world have still not been documented considerably. Hence, the multiplication of future research on fate, speciation, distribution and remediation of Sb is an urgent necessity in order to establish a sustainable Sb extenuation on a global scale, which will provide the growing world population Sb-safe freshwater and food in the near future.

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