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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 trans-disciplinary research on Sb from global scientific communities will be a crucial stage to establish a sustainable Sb mitigation on a global scale.

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 × 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	–