Environmental and Experimental Botany 109 (2015) 31–39

Contents lists available at ScienceDirect

Environmental and Experimental Botany

journal homepage: www.elsevier.com/locate/envexpbot

Speciation of antimony and arsenic in the soils and plants in an old antimony mine

Chaoyang Wei[a,*], Zhaofeng Ge[a,b,c], Wangsheng Chu[d], Renwei Feng[e]

[a] Key Laboratory of Land Surface Pattern and Simulation, Institute of Geographic Sciences and Natural Resources Research, Chinese Academy of Sciences, Beijing 100101, China
[b] University of the Chinese Academy of Sciences, Beijing 100049, China
[c] Hebei University, Baoding 071002, China
[d] National Synchrotron Radiation Laboratory, University of Science and Technology of China, Hefei 230029, China
[e] Institute of Agro-Environmental Protection, Ministry of Agriculture, Tianjin 300191, China

ARTICLE INFO

Article history:
Received 23 July 2014
Received in revised form 5 August 2014
Accepted 6 August 2014
Available online 18 August 2014

Keywords:
HPLC-ICP-MS
XANES
Methylation
Soils
Plants

ABSTRACT

The speciation changes of antimony (Sb) in soil–plant system are largely unknown as compared with those of arsenic (As). In this study, indigenous plants and associated soils were sampled at the Xikuangshan Sb mine (XKS), China. The Sb in the soils (441–1472 mg/kg) were far greater than As (32–354 mg/kg), and the Sb and As availabilities in the soils, were 5.5% and 3.9% in average, respectively. HPLC-ICP-MS revealed the presence of four species of Sb in the soils and plants, including Sb^{III}, Sb^{V}, TMSb and UnkSb (unknown). The use of XANES revealed that the UnkSb consisted of inorganic Sb in the form of Sb^{V}. Inorganic Sb were prevalent in the soil and plant samples at the eight sites, whereas TMSb was observed in only a few of the rhizosphere soils, and, in plants at a few of the sites, primarily in the leaves and to a lesser extent in the stems. Arsenic was detected in the soils primarily as inorganic forms, while, DMA was detected in high proportions in all of the plant tissues at all of the sites. The methylation of Sb was far less than that of As in the indigenous plants at XKS. The results suggest that As and Sb differ in transformation characteristics in the soil–plant system in XKS.

1. Introduction

Antimony (Sb) and arsenic (As) are metalloids belonging to Group 15 of the periodic table (Wilson et al., 2010). Arsenic is a toxic and carcinogenic element that is widespread in the environment, and As contamination has been reported worldwide (Sharma and Sohn, 2009). High concentrations of Sb and As are often present simultaneously in sulfide ores (Filella et al., 2002), which have caused the co-contamination of As and Sb (Telford et al., 2009; Wang et al., 2011). Plants inhabited in the vicinity of As and Sb co-contaminated sites have been reported to accumulate high concentrations of As and Sb in their aerial parts. For example, at high contaminated acidic sites, *Agrostis capillaris* L. was found to accumulate up to 240 mg/kg As and 68 mg/kg Sb in the shoots (Bech et al., 2012). Corrales et al. found two fodder species of plant *Trifolium pratense* L. and *Trifolium repens* L. had high tolerance to Sb, and could accumulate as high as 770 mg/kg Sb in their shoots (Corrales et al., 2014). The enrichment of As and Sb in environments could potentially render health risks to humans via food chain, consequently the levels of As and Sb in the environment must be controlled.

Compared to As, very little is known regarding the behavior, ecotoxicology and the environmental distribution of Sb (Telford et al., 2009; Tighe et al., 2005). The chemical similarities between the two metalloids have prompted concerns regarding the enrichment of both metalloids in various environments (Filella et al., 2002; Krachler and Emons, 2001). Sb is often thought of as behaving similarly to As, although this generalization is not always with justification (Casiot et al., 2007; Wilson et al., 2010). Dimethylarsinic acid is very soluble in water, in contrast with dialkylstibinic acid, which is polymeric and relatively insoluble (Parris and Brinckman, 1976).

Sb and As display the same range of oxidation states in the environment (−3 to +5) (Wilson et al., 2010). Both of their levels of toxicity in the environment strongly depend on their speciation (Filella et al., 2002; Gebel, 1997). In general, the order of toxicity of Sb species is as follows: antimonite(Sb^{III}) > antimonate(Sb^{V}) > organoantimonials (e.g., methylated species) (Gebel, 1997; He and Yang, 1999); the toxicity of As species exhibits a similar order: arsenites (As^{III}) > arsenates (Sb^{V}) > organoarsenical (e.g., methylated species) (Wilson et al., 2010).

---

* Corresponding author. Tel.: +86 10 64889465; fax: +86 10 64851844.
E-mail address: weicy@igsnrr.ac.cn (C. Wei).

http://dx.doi.org/10.1016/j.envexpbot.2014.08.002

The speciation transformation process and corresponding mechanisms of As in plants have been well documented (Ma et al., 2001; Tu et al., 2003; Wang et al., 2002). However, those in the case of Sb are far to be resolved, despite that organic Sb have been occasionally detected in some studies. It appears that Sb can be methylated by bacteria and fungus (Filella et al., 2007). For example, biomethylation of Sb by the filamentous fungus *Scopulariopsis brevicaulis* was recently established (Jenkins et al., 1998). Nevertheless, the information on organic species of Sb in plants had rarely been reported, with most current studies on Sb speciation in plants only focusing on Sb^V and Sb^{III} (Okkenhaug et al., 2011). Müller et al. used a chromatographic method to study the Sb speciation in *Pteris vittata* L. spiked with 16 mg/kg Sb^V, they found that Sb^V, Sb^{III}, trimethylated Sb^V and an unidentified Sb compound in the plant (Muller et al., 2009). In their study, the speciation of Sb in the soils of rhizosphere and non-rhizosphere was not known and the relationship between the Sb speciation in soils and in plants was not identified either. It is thus important to identify the location and sources of Sb methylation in plants, which may favor the understanding of the mechanisms on speciation in Sb uptake and transformation in the soil–plant system.

There is evidence that As is detoxified via methylation in biological systems; however, little similar evidence regarding similar processes involving Sb is available (Gebel, 1997). Like As, previous studies also found widespread Sb methylation in biological media. Cullen et al. found, for the first time, the presence of methyl antimony in freshwater fish (Cullen and Reimer, 1989), and Duester et al. reported that monomethylated Sb and As were the dominant species in agricultural and garden soils (Duester et al., 2005). However, due to limited information regarding Sb species and transformation within and between the environment and biological systems, the mechanisms of Sb speciation are still largely unknown (Corrales et al., 2014; Jenkins et al., 2002; Wehmeier and Feldmann, 2005), in contrast with the well documented speciation of As.

The co-existence of As and Sb may affect each other on the uptake by plants. Our previous results showed that the uptake of Sb in *Pteris cretica* L. (Cretan brake fern) was enhanced by increasing As levels, but As was suppressed by high levels of Sb, accompanied with decreased As and enhanced Sb levels in the cytosol fraction (Feng et al., 2011). However, we did not know whether the co-presence of As and Sb in growth media would affect their speciation transformation, as well as whether and where Sb and As methylation occur in the soil–plant system.

Previous studies of Sb speciation primarily involved soils with relatively low levels of Sb (Filella et al., 2007), whereas little work has focused on media with high levels of Sb. In addition, the limited reports of high Sb speciation were based on analyses of only samples of certain types, which may not allow for insights into the speciation and transformation of Sb in the environment and biological systems, e.g., the soil–plant system, and reveal the effect of such bio-factors as rhizospheres.

It is known that heavy metal toxicity depends strongly on the speciation of these elements in the environment. Therefore, knowledge of the distribution, speciation, and transformation of Sb and As in the soil–plant system of the XKS mine area is important for understanding its geochemical and biological cycling and for evaluating the environmental and human health risks. Despite the significance of quantitative speciation, there is only limited information regarding Sb in the soil–plant system (De Gregori et al., 2007; Dodd et al., 1996; Lintschinger et al., 1997, 1998a, 1998b; Nash et al., 2000; Ulrich, 1998a, 1998b; Ulrich et al., 2000). At present, studies of the XKS mine area have primarily involved the total concentrations of Sb and As, and investigations of the Sb and As species in the environment focused only on the inorganic species, particularly in the soil–plant system. It is also unknown whether Sb and As methylation occurred in the soil or plants and whether a rhizosphere environment promotes Sb or As methylation.

Our previous studies have shown that Xikuangshan mine (XKS) is an area of enrichment in Sb and As in the soil–plant system. This situation provides the prerequisite conditions for tracing the Sb species and their translocations from the soils to the plants and making comparisons with the corresponding characteristics of As. Consequently, this study was performed with the goal of estimating the Sb and As speciation, distribution and transformation characteristics in the soil–plant system in the mining and smelting areas of XKS. The methylation of Sb and As in soil and plant extracts was also investigated in this study. The findings are expected to contribute to a better understanding of the behavior of Sb in soils and plants.

2. Materials and methods

2.1. Site description

XKS Sb mine is located in Lengshuijiang County, Hunan province, in south-central China (Fig. 1). The climate in this area is characterized by a typical subtropical continental monsoon, with an average temperature of 16.7 °C and annual rainfall of 1354 mm. The average year-round relative humidity is 53.1%. The XKS Sb mine is the largest Sb mine in the world and measures 70 km^2. The mine consists of two mining areas, i.e., the north mine and south mine, which are accompanied by several Sb smelters in the central area (Fu and Wei, 2013). Antimony mining in this area began in 1897, and the present annual production of Sb is 55,000 tons of ore and 40,000 tons of Sb products (Wang et al., 2011). The long-term, large-scale Sb mining and smelting activities have resulted in Sb, As and other heavy metal contamination of the local environment (Fu and Wei, 2013; He, 2007; Liu et al., 2010; Wang et al., 2011; Wei et al., 2011). The concentrations of Sb in the soils have been measured at 100.6–5045 mg/kg; soil near the Sb mine also contains high concentrations of As (Fu and Wei, 2013; Wei et al., 2011).

2.2. Samples collection and preparation

Initially, we intended to collect samples of the same plant species at various sites and investigate their variations in Sb and As concentrations. However, this goal could not be realized due to the great variation in the vegetation in the mining and smelting areas around XKS. Ultimately, the typical indigenous plant species at XKS were individually sampled at eight sites around the south mine, north mine and central smelters (Fig. 1). Descriptions of the sampling sites and plant species are summarized in Table 1. Samples of the associated rhizosphere and non-rhizosphere soils were also collected. Soils attached to plant roots were carefully collected and labeled as rhizosphere samples, and soils approximately 30 cm from the corresponding plant roots (down to a depth of 20 cm) were collected and labeled as non-rhizosphere samples.

The soil samples were prepared by removing stones and plant debris, were freeze-dried and were then ground and passed through a no. 20 mesh sieve (0.85-mm mesh openings). A 20-g portion of the soil sample was further ground using a mechanical agate grinder to produce fine powders for As and Sb speciation analysis (<150-μm particle size). The plant samples were washed with tap water followed by several rinses with deionized water. Each plant sample was separated into three parts (roots, stems and leaves), freeze dried and cut into pieces using ceramic scissors. The samples were then pulverized using a stainless steel mill to produce homogenous powders. The powdered soils and plants were stored in polyethylene packages at 4 °C prior to the concentration and speciation analyses for Sb and As.