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Bioaccessibility of antimony and arsenic in highly polluted soils of the mine area and health risk assessment associated with oral ingestion exposure

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ABSTRACT

In this study, the bioaccessibility and the human health risks of Sb and As in soils from Xikuangshan (XKS) Sb mine, Hunan, China were investigated using two commonly used *in vitro* extraction methods, Simplified Bioaccessibility Extraction Test (SBET) and Physiologically Based Extraction Test (PBET). Soils in the XKS Sb mine area were mainly co-contaminated by Sb (74.2–16,389; mean: 3061 mg kg^{-1}) and As (7.40–596; mean: 216 mg kg^{-1}). The bioaccessibility values of Sb and As in most cases were less than 30%, and the average bioaccessibility values of Sb and As were $5.89 \pm 6.44\%$ and $2.13 \pm 2.55\%$ for the SBET extraction; $7.83 \pm 9.82\%$ and $6.62 \pm 6.37\%$ for the PBET (Gastric) extraction; and $3.03 \pm 3.53\%$ and $2.40 \pm 2.01\%$ for the PBET (Intestinal) extraction, respectively. The bioaccessible Sb and As were significantly positively correlated with the total concentrations, but negatively correlated with the Fe, Al, Mn and organic matter (OM) contents in soils. Risk assessment results based on total concentrations might overestimate the risk existing in the studied area. After considering the bioaccessibility, the Hazard Quotient (HQ) values of Sb for most of the sampling sites and of As for all of the sampling sites became lower than 1. The Carcinogenic Risk (CR) values of As were also significantly reduced, 8.77E−06 and 1.74E−05 on average for the SBET and PBET methods, respectively. Considering the bioaccessibility can provide more applicable guidelines for risk assessments and more rational suggestions in the management of the soils contaminated with Sb and As.

1. Introduction

Antimony (Sb) is a nonessential toxic metalloid of the global concern (Filella et al., 2009; Amarasiriwardena and Wu, 2011). Sb is considered to be toxic to humans and it could cause diseases to liver, skin, and respiratory and cardiovascular systems (Schnorr et al., 1995). In the mid-1990s when Sb was claimed to be involved in the Sudden Infant Death Syndrome (Filella et al., 2009), it was the first time that it had attracted the attention of the public. Like arsenic (As), Sb and its compounds are also considered to be pollutants of priority interest by the United States Environmental Protection Agency (United States, Environmental Protection Agency (USEPA), 1979). However, contrary to the widespread interest on understanding the environmental behavior of As, which has been studied for decades, the behavior of Sb has received relatively little attention (Okkenhaug et al., 2012).

It has been reported that serious Sb pollution usually occurs in the mining and smelting areas, and it generally co-occurs with As pollution (Telford et al., 2009; Wilson et al., 2009; Fu et al., 2010). Soils enriched with Sb and As can pose a potential threat to human health via soil ingestion. Traditional human health risk assessment calculations are most often based on total (or pseudo-total) concentrations, implying that the entire ingested contaminant is available for uptake into the bloodstream (Pelfrêne et al., 2012). However, only the bioaccessible part of the contaminants, defined as the fraction of contaminant that is soluble in the gastrointestinal environment, is potentially available for human absorption (Ruby et al., 1999; Oomen et al., 2002). Therefore, assessments based on the total or pseudo-total concentrations may overestimate the risk; a bioaccessibility adjustment factor may be necessary to accurately assess the potential health risks associated with the ingestion of contaminated soils.

Several *in vitro* digestion models have been used to assess the Sb and As bioaccessibility in a variety of contaminated soils (Navarro et al., 2006; Juhasz et al., 2009; Denys et al., 2008, 2012; Meunier et al., 2011; Mingot et al., 2011; Jeong et al., 2013).

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The Sb and As bioaccessibility values varied greatly in these studies. This suggests that a variety of parameters, including Sb and As solid phase distributions and soil properties, influence the bioaccessibility which in turn has implications on human health risk assessment. Nevertheless, at present, limited research has focused on whether these models result in similar Sb and As bioaccessibility values. In addition, few studies have investigated the difference of the bioaccessibility between Sb and As. The As bioaccessibility results have recently been applied to health risk assessment and it has been proved to be valid and useful (Lee et al., 2006; Hu et al., 2011; Das et al., 2013; Martínez-Sánchez et al., 2013). However, there is little information available on the application of Sb to the health risk assessment. Often, Sb is assumed to behave similarly to As (Casiot et al., 2007), and the observed behaviors of Sb may be predicted and explained by the observations of As (Filella et al., 2007). However, this assumption has not been confirmed, and it has limitations under many environmental conditions (Wilson et al., 2009; Fu et al., 2011). Therefore, it is required to study the difference between the Sb and the As bioaccessibility and their application to risk assessment. Furthermore, an improved understanding of the influence of soil properties on the bioaccessibility of Sb and As is also needed.

China is one of the largest Sb producers in the world, and its average annual production has accounted for about 80% of the global requirements in 2012 (U.S. Geological Survey, 2013). Xikuangshan (XKS) Sb mine is the largest Sb mine in the world, located near Lengshuijiang city, Hunan province in the central China. It is consisted of the south mine and the north mine. It covers an area of 70 km^2 on a large Sb deposit and is nicknamed as the “World's Antimony Capital”, where there are 16 villages with a combined total of more than 10,000 residents in the surrounding rural and mountainous area (Wu et al., 2011). To date, many studies have been conducted on this area and serious co-pollution of Sb and As has been found around the XKS soils, mine tailings, mine drainage, drinking water, crops and local biota (He, 2007; Zhu et al., 2009; Fu et al., 2010, 2011; Qi et al., 2011; Wu et al., 2011). Health risk associated with the dietary co-exposure to the high levels of antimony and arsenic in the XKS has been previously investigated by Wu et al. (2011). Yet, the human health risk through oral ingestion of Sb and As in the soils of this area has not been investigated. This investigation is important to be considered, especially when the bioaccessibility results are involved. Taking the XKS antimony mine as the study area, the objectives of this study are (1) to study the antimony and the arsenic bioaccessibility in the soils with serious co-pollution of Sb and As using different *in vitro* digestion models; (2) to investigate the effect of selected soil properties on the magnitude of the Sb and As bioaccessibility; and (3) to assess the exposure and characterize the risk to adults exposed to soils of these localities.

2. Materials and methods

2.1. Description of sampling sites

Soil samples were collected from the Xikuangshan Sb mine and its surrounding area in September 2012 (Fig. 1). In the Xikuangshan Sb mine, stibnite (Sb_2S_3) is the dominant ore mineral present. A comprehensive description of the mineralogy of the mining area is given by He (2007). As shown in Fig. 1, 6 samples were randomly collected from the control point (S1) called Zhadu, far away from the mine area, where there were no mining and smelting activities there; 4 samples from the South Sb mine (S2); 6 samples from the North Sb mine (S3); 5 samples from the S4 which is called Qilijiang area, located between the South mine and the North mine; 2 samples from a waste rock dump (S5) and 6 smelting residue samples were collected near a tailing dam (S6). Samples from S1, S2, S3 and S4 are classified as mine soils while samples from S5 and S6 are classified as mining waste.

2.2. Characterization of top soils

At each sampling site, five sub-samples were collected from the surface layer (0–20 cm) and bulked together to form one composite sample. All the samples were placed in polyethylene bags and transported to the laboratory. In the laboratory, the soil samples were air-dried, gently crushed and sieved through 2-mm nylon sieve to remove stones, coarse materials, and other debris. Parts of <2 mm soils were used for analysis of selected soil properties, portions of soils were ground by an agate grinder to pass a 0.25-mm sieve for *in vitro* analysis of arsenic and antimony. This particle size (<250 μm) is believed to be most likely to adhere to human hands and become ingested or directly available for ingestion during a hand-to-mouth activity (Ruby et al., 1996; Denys et al., 2008). The basic physiochemical properties of the soils are given in Table 1 and detailed description of analytical methods can be found in the Supplementary material.

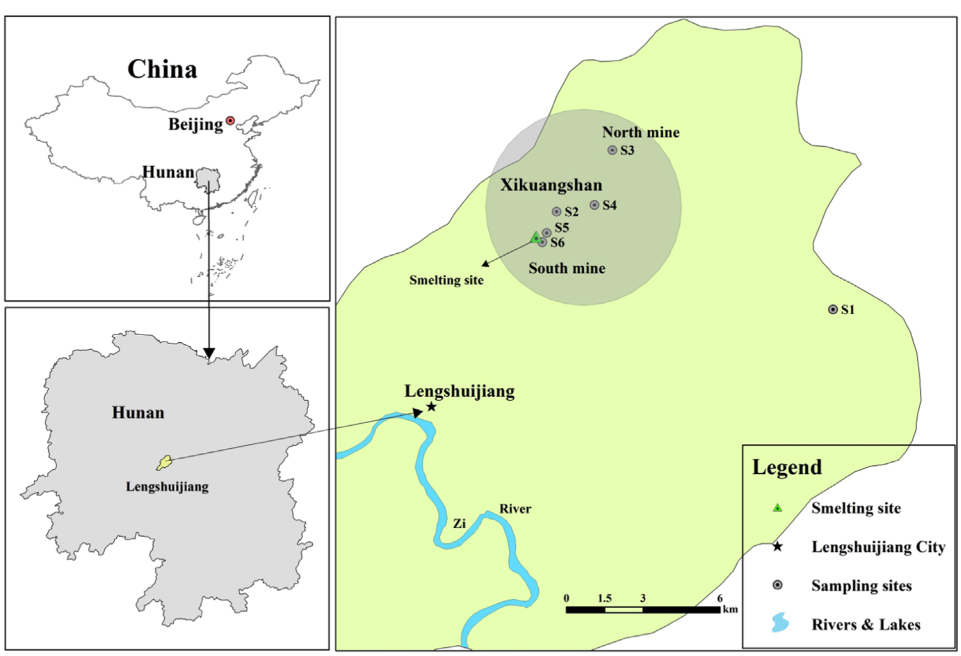

Fig. 1. Locations of sampling sites in Xikuangshan area, Hunan, China.