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Comparison of diffusive gradients in thin-films (DGT) and chemical extraction methods for predicting bioavailability of antimony and arsenic to maize

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ABSTRACT

Antimony (Sb) and arsenic (As) are hazardous metalloids that cause much attention. Assessing the bioavailability is essential for understanding the potential risk and toxicity of Sb and As in soils. In this study, a set of methods were tested to assess the bioavailability of Sb and As to field/potted maize. Twelve soils, 7 maize (*Zea mays* L.) samples and corresponding root soils were collected from the world's largest active Sb mining area (Xikuangshan, China). The soils contained average 1074 mg/kg Sb and 65 mg/kg As with the pH varied from 4.78–7.70. Eight soil samples with a gradient of Sb and As concentration were selected for pot experiments of maize. Diffusive gradients in thin-films (DGT) and traditional chemical extraction methods, including six single-step extractions (H_2O, 0.01 M $CaCl_2$, 1 M NH_4NO_3, 0.1 M Na_2HPO_4, 0.05 M EDTA and 0.005 M DTPA) and modified-BCR sequential extraction were used to predict the bioaccumulation of Sb and As by maize. Sb and As measured by DGT, DTPA and modified-BCR correlated better with Sb and As in the shoots and roots of field/potted maize compared to H_2O, $CaCl_2$, NH_4NO_3, Na_2HPO_4 and EDTA. The correlation coefficients of DGT, DTPA and modified-BCR were at least 0.869 ($p < 0.01$), 0.866 ($p < 0.01$) and 0.831 ($p < 0.05$), respectively. These three techniques are well applicable for simultaneous prediction of Sb and As bioavailability to both field and potted maize in soils.

1. Introduction

Antimony (Sb) and arsenic (As) are toxic metalloid assumed to behave similarly at times and frequently co-occur in sulfide ores, such as stibnite (Sb_2S_3), which leads to Sb-As combined pollution (Filella et al., 2002; He et al., 2018; Wilson et al., 2010). Both Sb and As have been listed as priority pollutants of interest by the United States (USEPA, 1979) and European Union (EU, 1976), and hazardous wastes by the Basel Convention (Kim et al., 1998). Xikuangshan Sb mine in China is a super-large Sb mine over the world with serious Sb-As co-contamination (He et al., 2012). Investigations into effects of Sb and As on plants have been carried out (Garg and Singla, 2011; Tschan et al., 2009b). High concentration of Sb can inhibit the growth of rice (He and Yang, 1999), barley and lettuce (Oorts et al., 2008), maize, wheat, clover, sunflower and Indian mustard (Tschan et al., 2009a). Similarly, high concentration of As is toxic to rice (Abedin and Meharg, 2002), maize (Gulz et al., 2005), wheat (Yoon et al., 2015) and *Spartina alterniflora* Loisel (Carbonell et al., 1998).

Chemical methods are widely used to assess bioavailability of metal (loid) pollutants, which are generally divided into two types depending on whether they're based on chemical extraction or mechanistic modeling (Kim et al., 2015). The most common traditional chemical extraction methods are single-step extraction and sequential extraction procedure. Based on extraction of targets from environment, diffusive gradients in thin-films (DGT) can be seen as a passive sampler, whose essential part consists of a diffusive layer and a binding layer. The binding layer of DGT devices acts as a plant/root taking up the metals, breaking the equilibrium established by other usual passive samplers. Therefore, DGT can measure not only the metals in soil solution but also the resupply from the solid phase after depletion of the soil solution. The DGT concentration is calculated according to equations (listed in Section 2.5.2) and to some extent represents the effective concentration (Zhang et al., 2001). The DGT technique has been proved to be an effective method to determine the bioavailability of elements in soil in many cases (Six et al., 2014; Tandy et al., 2011; Zhang and Davison, 2015).

For measurement of Sb and As, DGT equipped with a ferrihydrite binding layer (FH-DGT) has been used in a natural stream, ground water and sediment (Lucas et al., 2014; Okkenhaug et al., 2015; Österlund et al., 2010; Stockdale et al., 2008). Nowadays, DGT with a

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binding layer of other materials, such as titanium dioxide and zirconia, is also available for Sb and As determination (Guan et al., 2015; Panther et al., 2013). Previous work mostly focused on aquatic environment due to the critical role of water content during deployment of DGT. Little has been done concerning the measurement of Sb and As by DGT in soils. Ngo et al. (2016) first demonstrated the suitability of DGT to predict bioavailable Sb and As in contaminated soils to radish (*Raphanus sativus*) through pot experiments, where the soils were obtained by mixing a contaminated soil with an uncontaminated soil at different ratios, resulting in the very similar soil properties, which can bring in significant influence in plant uptake and extraction process (Anawar et al., 2008; Ettler et al., 2007; Feng et al., 2013; Rosas-Castor et al., 2014). Therefore, it remains unknown whether DGT is still suitable in the face of various soil properties.

The aims of this study were to investigate whether bioavailable Sb and As to maize (*Zea mays* L.) can be simultaneously predicted by chemical extraction or DGT technique via both potted and sampled maize. Labile Sb and As were extracted by H_2O, $CaCl_2$, NH_4NO_3, Na_2HPO_4, EDTA, DTPA, modified-BCR and DGT, and were compared with Sb and As bioaccumulated by maize, an important crop worldwide. The soils used in the pot experiments were selected to obtain a gradient of both total Sb and As concentration. In addition, a link was tried to be established between potted plants and field samples, which is implicational for future study on predicting bioavailability of plants in the field based on results obtained in the laboratory. This is the first study to compare DGT, a series of single-step extractions and modified-BCR sequential extraction to simultaneously predict Sb and As bioavailability to maize via not only pot experiments but also field samples, facing various soil properties.

2. Materials and methods

2.1. Site description and sample collection

The study area, Xikuangshan is located between 27.7°N and 111.4°E near Lengshuijiang city of Hunan Province, central-south of China. The antimony deposit is hosted by dark-gray chert in the black shale series of the Upper Devonian Shetianqiao Formation. The deposit consists of the south mine and the north mine, which are located on the east limb of the anticline. Stibnite (Sb_2S_3) is the major ore mineral, along with trace amounts of pyrite, pyrrhotite and sphalerite, and As is one associated element (Fan et al., 2004; He, 2007; Liu et al., 2010). Long history of mining and smelting has led to Sb-As pollution in this area (Fu et al., 2010; He et al., 2012). There're two main rivers, Qingfeng River and Lianxi River, tributaries of Zijiang River. They both flow through the mining area and receive large amount of mining and smelting sewage water. There is no obvious boundary between the mining and residential area. Contaminated soil is extensively used in agricultural production, which results in a serious threat to the health of the local people as well as the local ecosystem.

In the Xikuangshan area, 12 soil, 7 maize (*Zea mays* L.) and corresponding root soil (at 0–20 cm depths of the plant rhizosphere) samples were collected in June 2015. The sample sites were chosen near the two local mines (South mine and North mine), a Sb smeltery and along the two rivers. The sampling sites are shown in Fig. 1 and the site description is shown in Table 1. The maize plants were all in mature period with similar growth and were collected in croplands at site 1–3, 6 and 8–10. In order to distinguish, those are numbered as S1–S3, S6 and S9–S11, including both plant and root-soil samples. The maize's shoots, roots and root soil were separated. The plant parts were oven-dried (80 °C) and ground. The soil samples were air-dried, crushed with a wooden roller and then passed through a 10-mesh (< 2 mm) sieve. For physicochemical properties analysis and determination of total amount of metals, some soil samples were sieved through 150 μm and 74 μm mesh.

2.2. Sample analysis

Following microwave-assisted digestion (MARS, CEM, USA) of the soil and plant samples with HCl + HNO_3 + $HClO_4$ (3:1:1), the total Sb and As concentrations were determined by hydride generation atomic fluorescence spectrometry (HG-AFS) (AFS 9700, Titan Instrument Co., Ltd., China). Total Fe, Mn, Zn, Cu, Cr, Cd and Pb concentrations in soil samples were determined by inductively coupled plasma atomic emission spectrometer (ICP-AES) (NexION300x, PerkinElmer, USA). Soil pH was measured at solid/water ratio of 1:5 by use of pH meter (PB-10, Sartorius, Germany) according to soil quality-determination of pH (ISO 10390:2005). Total organic matter content was determined using elemental analyzer (EA3000, Leeman, China) following a procedure of removing inorganic carbon by 10% HCl. Maximum water holding capacity (MWHC) was determined by: (i) weighing some dried soil in a cutting ring with filter paper beneath the soil and porous cap of the cutting ring at the bottom; (ii) immersing soil in MQ water for a day with the water surface just at the same height of the soil surface and then weighing; (ii) drying the soil by placing it on dry sand and then weighing; (iii) calculating the MWHC. Particle size was determined using laser particle size analyzer (S3500, Microtrac, USA).

2.3. Pot experiments

Maize seeds (*Zea mays* L.) were immersed in 75% alcohol for 10 min to sterilize and then soaked for 3 days in ultrapure water. The 8 soil samples (< 2 mm) were chosen from site 4, 5, 6, 7, 8, 10, 11 and 12 in order to establish a gradient of both Sb and As concentration. However, soils form the croplands where maize plants were sampled were with similar total As concentration (Table 2). Before plantation, the soils were wet to approximately 80% of the MWHC and kept at dark for 1 week. Subsequently, the maize seeds were sown in the pots containing 1.5 kg of soil. There were 5 seeds in each pot and only 3 were selected after germination. All pots were placed in an illumination incubator (PQX-3500-30, Saifu, China) with preset conditions (light: dark = 14:10 h, temperature was 30 and 25 °C). After 6 weeks, the whole plants were harvest, carefully washed with ultrapure water, separated into shoot and root and then oven-dried at 80 °C. The plant samples were ground and microwave-assisted digested with HCl + HNO_3 + $HClO_4$ (3:1:1). The total Sb and As concentrations were determined by HG-AFS.

2.4. Chemical extraction

Several single-step extractions were performed referring to previous studied (Ettler et al., 2007; Feng et al., 2005; Pueyo et al., 2004). The extracts were filtered through 0.45 μm filter before Sb and As determination by HG-AFS. The detailed operating procedures are described briefly below:

(1) H_2O extraction: 2.5 g soil in 25 mL of ultrapure water, shaking for 2 h, 20 °C;
(2) $CaCl_2$ extraction: 2.5 g soil in 25 mL of 0.01 M $CaCl_2$, shaking for 2 h, 20 °C;
(3) NH_4NO_3 extraction: 10 g soil in 25 mL of 1 M NH_4NO_3, shaking for 2 h, 20 °C;
(4) Na_2HPO_4 extraction: 2.5 g soil in 25 mL of 0.1 M Na_2HPO_4, shaking for 2 h, 20 °C;
(5) EDTA (ethylenediaminetetraacetic acid) extraction: 5 g soil in 25 mL of 0.05 M EDTA, shaking for 2 h, 20 °C, where several drops of 1 M NaOH was added to EDTA solution in order to enhance the solubility;
(6) DTPA (diethylene triamine pentaacetic acid) extraction: 5 g soil in 25 mL of 0.005 M DTPA and 0.01 M $CaCl_2$ and 0.1 M TEA (triethanolamine), pH 7.3, shaking for 2 h, 20 °C.