



## Arsenic characteristics in the terrestrial environment in the vicinity of the Shimen realgar mine, China

Fen Yang<sup>a,b,c</sup>, Shaowen Xie<sup>a,b,c</sup>, Chaoyang Wei<sup>a,b,\*</sup>, Jinxin Liu<sup>a,b,c</sup>, Hongzhi Zhang<sup>a</sup>, Tao Chen<sup>c,d</sup>, Jing Zhang<sup>d</sup>

<sup>a</sup> Institute of Geographic Sciences and Natural Resources Research, Chinese Academy of Sciences, Beijing 100101, China

<sup>b</sup> Key Laboratory of Land Surface Pattern and Simulation, Chinese Academy of Sciences, Beijing 100101, China

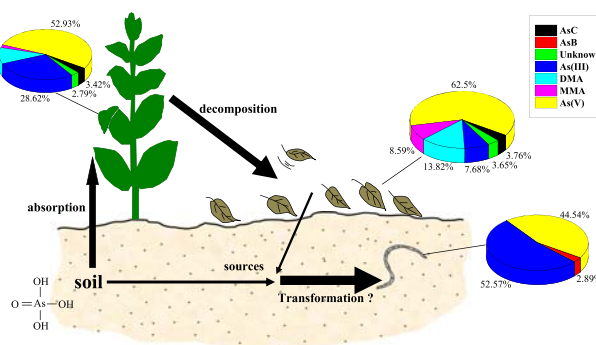
<sup>c</sup> University of Chinese Academy of Sciences, Beijing 100049, China

<sup>d</sup> Institute of High Energy Physics, Chinese Academy of Sciences, Beijing 100049, China

### HIGHLIGHTS

- Arsenic characterization in a soil-plant-litter-earthworm system were examined.
- Samples from contaminated and uncontaminated areas were compared.
- Arsenate [As(V)] was almost the only detected As form in all soil samples.
- Dominant inorganic As and various organic As were detected in plants and litter.
- Primarily inorganic As and minor amounts of AsB were detected in earthworms.

### GRAPHICAL ABSTRACT



### ARTICLE INFO

#### Article history:

Received 29 October 2017

Received in revised form 25 December 2017

Accepted 8 January 2018

Available online xxxx

Editor: F.M. Tack

#### Keywords:

Arsenic speciation

HPLC-ICP-MS

XANES

Earthworms

Terrestrial plants

Biotransformation

### ABSTRACT

In this study, multiple types of samples, including soils, plants, litter and soil invertebrates, were collected from a former arsenic (As) mine in China. The total As concentrations in the soils, earthworms, litter and the above-ground portions of grass from the contaminated area followed the decreasing order of 83–2224 mg/kg, 31–430 mg/kg, 1–62 mg/kg and 2–23 mg/kg, respectively. X-ray absorption near-edge structure (XANES) analysis revealed that the predominant form of As in the soils was arsenate (As(V)), while no arsenite (As(III)) was detected. In the grass and litter of the native plant community, inorganic As species (As(V) and As(III)) were the main species, while minor amounts of DMA, MMA, AsC, and an unknown As species were also detected in the extracts analyzed with high-performance liquid chromatography inductively coupled plasma mass spectrometry (HPLC-ICP-MS). The As speciation and As concentrations varied with the plant species, and very high As levels (197–584 mg/kg) and proportions of inorganic As (>99%) were found in two As-hyperaccumulating ferns, *Pteris vittata* and *Pteris cretica*. The major As species extracted from earthworms were inorganic, with proportions of 51–53% As(III) and 38–48% As(V). AsB was the only organic species present in the earthworm samples, although at low proportions (<8.99%). The internal bioconversion of other As species is hypothesized to contribute greatly to the formation and accumulation of AsB in earthworms, although the direct external absorption of organic As from soils might be another source. This study sheds light on the potential sources of complex organoarsenicals, such as AsB, in terrestrial organisms.

© 2018 Elsevier B.V. All rights reserved.

\* Corresponding author at: Institute of Geographic Sciences and Natural Resources Research, Chinese Academy of Sciences, A11 Datun Road, Chaoyang District, Beijing 100101, China. E-mail address: [weicy@igsnrr.ac.cn](mailto:weicy@igsnrr.ac.cn) (C. Wei).

## 1. Introduction

Arsenic (As) is a toxic metalloid element that is widely distributed in the environment (Ng, 2005). Recent studies suggest that exposure to As may increase the risk of certain diseases, including skin lesions, peripheral artery disease, hypertension, cardiovascular disease, diabetes, skin cancer, urothelial cancer, and reproductive system damage (Shen et al., 2016). The As toxicity is known to depend on the total concentration and on the chemical species (Ng, 2005). In general, inorganic As species are more toxic than organic forms. Among the inorganic forms, arsenite (As(III)) is considered to be more toxic than arsenate (As(V)). Methylated organic species, such as monomethylarsonic acid (MMA) and dimethylarsinic acid (DMA), are less toxic than other forms (Mandal and Suzuki, 2002). However, the trivalent forms of the methylated metabolites, MMA(III) and DMA(III), are generally regarded as extremely toxic (Hughes, 2002). Organoarsenicals, such as arsenobetaine (AsB), arsenocholine (AsC) and arsenosugars (AsS), are generally considered non-toxic (Kaise et al., 1985). Therefore, it is essential to monitor both the total As concentration and As speciation in environmental and biological samples.

Mining and smelting activities have been reported to be major sources that contribute significantly to the elevation of As levels in soils (Smedley and Kinniburgh, 2002; Garelick et al., 2008). Soil contamination with As can represent an important source of As in terrestrial ecosystems near mining areas and can eventually harm the ecosystem structure and functioning; hence, this contamination has become an increasing concern worldwide (Maunoury-Danger et al., 2017). A variety of plant species growing in As-contaminated soils have been reported to accumulate high concentrations of As in their aboveground parts (Ma et al., 2001; Wei et al., 2015). It has been reported that the main species detected in terrestrial plants are As(V), As(III), DMA, MMA, and other organic species; additionally, AsB, TMA, and AsC, have also been detected (Amaral et al., 2013). Although many plant species with high As accumulation abilities have been identified, the knowledge regarding the As characteristics of native plant communities in As-contaminated soils remains relatively limited (Otones et al., 2011).

Earthworms are reported to increase the water-soluble As in soil and to enhance the ability of plants to tolerate contaminants (Sizmur et al., 2011a; Jusselme et al., 2013). Earthworms constitute up to 80% of the total biomass of the soil fauna and spend most of their life in the soil (Sivakumar, 2015), thereby playing a major role in the functioning of the soil ecosystem (van Gestel et al., 2009). Earthworms become exposed to heavy metals through ingestion and dermal contact and are often used as model species and biomarkers in terrestrial ecotoxicological risk assessments since they are readily available and easy to handle (Pierce et al., 2002; Shin et al., 2007; Dada et al., 2013). Additionally, terrestrial invertebrates, which have the ability to accumulate high levels of As, are potential vehicles for trophic transfer to higher organisms such as frogs, birds, moles and shrews and thus form an important part of terrestrial food webs (Moriarty et al., 2009; Button et al., 2011, 2012). For these reasons, the study of biomarkers in earthworms has received increasing attention in recent years (Sizmur et al., 2011b; Calisi et al., 2013). However, most studies have been carried out under laboratory conditions, while investigations of earthworm biomarkers under field conditions have been scarce (Calisi et al., 2013; Wang et al., 2016).

Plant litter decomposition is a key process in the matter cycling and energy flow of ecosystems (Jonczak et al., 2014; Berg and McClaugherty, 2014). Particularly, over the life span of a plant, the dispersion of As via leaf litter to contiguous ecosystems might be far from negligible (Maunoury-Danger et al., 2017). The suggested sources of the As observed in earthworms include accumulation from both soils and leaf litter (Langdon et al., 2003b; Button et al., 2011). Generally, in the terrestrial environment, As can enter plants through their root systems and can be dispersed by leaf litter, posing a threat to soil invertebrates

living in As-contaminated soils (Pulford and Watson, 2003; Dedeke et al., 2016; Wang et al., 2016). To the best of our knowledge, the literature has primarily focused on the relationships between soils and plants or earthworms in terrestrial ecosystems, but such a limited scope is insufficient (Van Nevel et al., 2014; da Silva Souza et al., 2014; Lucisine et al., 2015; Kramar et al., 2017). To further understand the As cycling in the terrestrial environment, comprehensive studies on As bioaccumulation and biotransformation via a soil-plant-leaf litter-terrestrial fauna approach are highly desired.

The objectives of the present study were to investigate both the total As concentrations and As speciation in various media (soils, plants, leaf litter and earthworms) from a former As mining area in China. Particular attention was paid to the native plant community growing in the study area. Additionally, the potential sources and pathways of some organic As species within the terrestrial environment were expected to be elucidated through this study.

## 2. Materials and methods

### 2.1. The site and sampling procedures

The Shimen realgar mine (29°38'11"–29°38'43" N, 111°2'06"–111°2'23" E) is located in Shimen County, Hunan Province, China (Fig. 1). This mine contains the largest reserves of realgar in Asia, with a mining history of >1500 years until it closed in 2011. The long-term, large-scale mining and smelting activities resulted in As contamination of the local environment. Soils from the mining area have been measured to contain As concentrations in the range of 475–5240 mg/kg (Tang et al., 2016). In this study, a total of seventeen sampling sites were established at different distances from the center of the mine. Among these sites, eleven sites were in the contaminated area (around the smelter and tailings dam), while six sites were in the uncontaminated area (>4 km from the upper part of the smelter). Fig. 1 shows the locations of the sampling sites, and the descriptions are summarized in Table 1.

Soils, earthworms, snails, leaf litter, and plant samples were collected from around the closed mining area in Shimen in May 2015 and June 2016. For the soil samples, a composite soil sample consisting of three subsamples from the top soil layer (0–15 cm depth) in an area of approximately 1 m<sup>2</sup> was collected with a spade. Prior to analysis, the soil samples were air dried at room temperature, separated from stone and plant debris, ground and sieved through a 0.84 mm nylon sieve (20 mesh). The pH was measured using a 1:2.5 ratio of soil to deionized water, and the total organic matter (TOM) was determined using the Walkley-Black method. For chemical analysis, a portion of the soil samples (~15 g) was ground to 100 mesh (150 μm). In this study, we collected leaf litter consisting of a mixture of partially decomposed grass and the aboveground parts of these grasses from the upper layer of soils. The dominant plant communities were composed of *Pennisetum alopecuroides*, *Digitaria sanguinalis*, *Cynodon dactylon*, *Eleusine indica* and *Plantago asiatica*. The vegetation samples were separated into leaves, roots, fruit, seeds and stems; washed thoroughly with tap water; and rinsed in deionized water three times. Approximately 10–20 individuals of earthworms were handpicked at each sampling site if available and left on wet filter paper for 48 h to allow them to void their bowels. After depuration, the earthworms were sacrificed and rinsed with deionized water. Surviving snails (n = 6) were sampled at site J; the soft tissues were carefully removed after gently crushing the cleaned shells and collected using tweezers and latex gloves. A previous study showed that oven drying resulted in the same As(III)/As(V) ratio in biological samples as fresh and freezing drying, indicating that oven drying did not cause the oxidation of As(III) to As(V) (Jedynak et al., 2010). Consequently, in this study, all samples were dried in an oven at 70 °C to constant weight and pulverized to 100 mesh prior to analysis.

Download English Version:

<https://daneshyari.com/en/article/8860742>

Download Persian Version:

<https://daneshyari.com/article/8860742>

[Daneshyari.com](https://daneshyari.com)