Comparison of three sequential extraction procedures for arsenic fractionation in highly polluted sites

Xiang Wan [a], Haochen Dong [a], Liu Feng [a, *], Zhijia Lin [b], Qiuchen Luo [a]

[a] Department of Environmental Sciences and Engineering, Beijing University of Chemical Technology, Beijing, 100029, PR China
[b] Hunan Institute of Geological Survey, Changsha, Hunan, 410116, PR China

HIGHLIGHTS

- With satisfied total recovery, Shiowatana SEP showed higher extraction efficiency in potentially mobile arsenic fractions.
- Shiowatana SEP was preferred and efficient for the most mobile arsenic extraction.
- Bioavailability evaluation on different arsenic fractions provides an insight to SEPs comparison.
- A case study applied by Shiowatana SEP shows potential risk in relevant areas.

ARTICLE INFO

ABSTRACT

Three sequential extraction procedures (SEPs) including Tessier, Rauret, and Shiowatana SEPs, were compared for arsenic fractionation using highly polluted soils. In the definition context of exchangeable, reducible, oxidizable and residual fractions, with similar arsenic recovery and reproducibility, Tessier and Rauret SEPs were comparable to each other, whereas Shiowatana SEP showed higher extraction efficiency in all the first three arsenic fractions, although it might overestimate the reducible arsenic. Pot experiment indicated three SEPs all could provide an estimation of the most bioavailable arsenic fraction, and the application of Shiowatana SEP should be preferred. Accordingly, a case study with Shiowatana SEP for a site near a realgar mine area is conducted. The results show that although arsenic in this area presents predominantly in the stable fractions, the sum of most bioavailable fractions was accounted around 11% of total arsenic, and moreover, about another 10% of the total arsenic, the fourth fraction in Shiowatana SEP is likely to be transferred into bioavailable species under suitable conditions, such as strong acid impact, revealing a real major risk source being formed. The study indicated that Shiowatana should be more suitable for arsenic fractionation to provide valuable information in the framework of risk assessment.

1. Introduction

Soil arsenic pollution has become a world problem. Many arsenic polluted sites have been found around the world due to human activities (Hibiki and Arimura, 2004; Ahmad and Goni, 2010), and millions of people were exposed to varied degrees of soil pollution (Karim, 2000; Rodríguezlado et al., 2013). Because of their high-toxicity and potential carcinogenic effect, arsenic polluted sites have been increasingly concerned, and many researches on risk assessment for these sites have been reported.

Among them, total-concentration-based methodology has been widely applied for heavy metal polluted sites in early stage (Bech et al., 1997; Chen et al., 1997; Doyle and Otte, 1997). Nevertheless, with the progress in the researches on environmental behaviors and ecological effects of heavy metals, it has been gradually recognized that environmental effects of heavy metals, such as toxicity, migration and geo-chemical cycle, should depend on their chemical forms rather than their total concentration (Georgiadis et al., 2006; Ruiz-Chancho et al., 2007). Due to disregarding the differences in environmental effects and bioavailability among various chemical fractions of heavy metals, the total concentration based method often overestimated the potential risk, and has gradually given way to chemical-form-oriented methods and procedures in latter risk assessment for heavy metal polluted sites

* Corresponding author.
    E-mail address: fengliu-buct@vip.sina.com (L. Feng).

(Hartley et al., 2010; Guillén et al., 2012; Lou et al., 2015).

Many sequential extraction procedures (SEP) can be used to define and extract chemical fractions of heavy metals in soil. These methods classify heavy metals in soil into different operationally defined fractions with increasing metal binding strength. Among them, Tessier SEP is developed for the partitioning of heavy metals into the water soluble and exchangeable fraction, the fraction bound to carbonates, the fraction bound to Fe/Mn oxides, the fraction bound to organic matter and the residual fraction (Tessier et al., 1979), it has been widely used in fractionation partition of mostly heavy metals like Cd, Pb, Cu, Co, Ni, Zn, Fe and Mn in soil/sediment (Pérezcid et al., 1999; Filgueiras et al., 2002; Frankowski et al., 2010), but it is seldom used for arsenic fractionation, and a few researchers found Tessier SEP was not entirely suitable for the determination of arsenic fractions due to incomplete oxidation of some bound arsenic fractions like arsenopyrite by the oxidation agents H_2O_2 used (Mihaljevič et al., 2003).

BCR (shorter form of the Community Bureau of Reference of the European Commission) SEP was first developed in 1993 (Ure et al., 1993) and improved by Rauret et al. (1999). In accordance with this modified BCR SEP, elements of interest are divided in 4 operationally defined steps as the acid extractable fraction, the reducible fraction, the oxidizable fraction and the residual fraction. BCR SEP is another mostly commonly used method after Tessier SEP in present (Albores et al., 2000; Zhang et al., 2010; Mäkelä et al., 2011; Chakraborty et al., 2014; Kerolli−Mustafa et al., 2015). However, similar to Tessier SEP, it has occasionally been used to evaluate arsenic fractionation (Száková et al., 1999; Fernandez et al., 2004; Baig et al., 2009; Otones et al., 2011), and a few researches also indicated that it was not entirely applicable for fractionation of arsenic in soil for similar reasons (Larios et al., 2012).

In contrast with the cationic nature of trace metals, arsenic is predominantly present in soils and sediments as oxyanions. Hence, traditional SEPs have not been recommended for arsenic and procedures especially designed for its study have been advised (Gruebel et al., 1988), and some SEPs (Mclaren et al., 1998; Shiowatana et al., 2001; Wenzel et al., 2001; Cappuyns et al., 2002) specially developed for arsenic fractionation have been proposed and applied in the past years. Among them, the SEP proposed by Mclaren et al. (1998) and improved by Shiowatana et al. (2001) is one of the best methods to date. Within this procedure, arsenic in soil/sediment is divided into the water-soluble fraction, the surface-adsorbed fraction, the Fe/Al associated fraction, the acid extractable fraction and the residual fraction. Up to now, its practical application reported in the literatures is very few (Hartley et al., 2009; Beesley et al., 2010), its efficiency for arsenic fractionation remains to be tested through more real case studies.

In summary, both the well-recognized and experienced SEPs and the developing arsenic-specific SEPs have limitations in arsenic fractionation, and it is indispensable to compare different SEPs, selecting more suitable SEP for arsenic fractionation in arsenic contaminated sites.

To be sure, some studies have already concerned comparisons among different SEPs, but perspectives they have focused on were the recovery rate and reproducibility, the redistribution/re-adsorption during extraction, the selectivity of reagents toward the targeted solid materials and so on (Mihaljevič et al., 2003; Larios et al., 2012). Bioavailability of heavy metals is widely known to be a critical factor to either their transfer from soil to plant or their environmental risks (Bryan and Langston, 1992; Khan et al., 2008), however the evaluation on the bioavailability of different fractions defined by each SEP has hardly or rarely been involved in the comparison studies (Vandenhove et al., 2014), which should be addressed in future.

To improve our understanding of the risks associated with arsenic in soil, this study would compare three SEPs (Tessier, Rauret and Shiowatana) for some arsenic-polluted soil samples and evaluate the bioavailability of each arsenic fraction defined by the three SEPs. As such, it is aimed to find the most appropriate SEP for arsenic-polluted sites and to provide valuable information in the framework of risk assessment.

2. Materials and methods

2.1. Soil source and its physicochemical properties

Shimen realgar (As_4S_4) mine area is one of the five main pollution sources in China. Some studies indicated that total arsenic concentration in soil there reached up to 5240 mg kg^{-1}, revealing a great potential risks for human health (Tang et al., 2016). It could be selected as an ideal case of arsenic polluted sites for this study.

Total 34 topsoil samples (about 0−30 cm in depth, numbered from S1 to S34) were collected by grid sampling method with a grid size of 50 m × 50 m within about 1 km^2 (Fig. 1). All soil samples were air-dried in natural conditions, grinded, and sieved with 2 mm screen for later use.

For all samples, we measured some physical and chemical properties including: pH, organic matter (OM), oxidation-reduction potential (ORP), and the contents of Fe, Mn, S, Ca, Al. For pH and OM measurements, we followed the techniques of a previous study (Sungur et al., 2014). ORP was determined using a depolarization method by an automatic ORP analyser (FJA-5) (Dong et al., 2017). The contents of Fe, Mn, S, Ca, Al was measured by XRF (Jansen et al., 1998; Johnson et al., 1999). Preliminary test indicated that the soil in this region was weakly acidic except only four high pH values was neutral soils (pH ranging from 5.26 to 7.46), with moderate soil fertility (the content of organic matter in soil ranging from 0.35% to 3.59%) and relative high oxidation resistance (soil redox potential ranging from 412 mV to 723 mV). The contents of Fe, Mn, S, Ca and Al in soil range from 1.2% to 15.6%, 0.01% to 0.39%, 0.35% to 6.08%, 0.98% to 4.86% and 1.07% to 6.54% respectively (see supplementary document).

2.2. Extraction of arsenic in soil samples

2.2.1. Extraction of total arsenic

Total arsenic in soil was measured by hydride generation—atomic fluorescence way (Liu, 2005). Proceed as follows: each soil sample was mixed evenly; a certain quantity of sample was taken by quarterly dividing method and ground to 0.149 mm or less, then was digested by chloroazotic acid (aqua regia) for 2 h at water bath of 96 °C. After complete cooling, the digestion was collected through centrifugation and filtration for later arsenic analysis.

2.2.2. Extraction of different arsenic fractions by three SEPs

Nine of the 34 soil samples were selected to conduct comparative study on the three SEPs, based on the distribution of total arsenic concentrations in each soil sample.

The arsenic fractions defined by each SEP and their extraction procedures are listed in Table 1.

All materials which were in contact with the soil samples were soaked overnight in 4 M HNO_3 before use. Like the procedure for extraction of total arsenic, a certain quantity of samples (2 g for each SEP) were taken, air dried at room temperature and sieved (0.149 mm) prior to extraction.

For each SEP, after each step of the procedure, extracts were centrifuged at 4000 rpm for 30 min, and filtered through a 0.1 μm cellulose filter with a vacuum. The soil residue of soil was suspended in 20 mL deionized water, shaken end-over-end for 15 min and centrifuged at 4000 rpm for 5 min before filtration with the