Bioavailability and risk assessment of arsenic in surface sediments of the Yangtze River estuary

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ABSTRACT

The bioavailability and risk assessment of As were studied in sediments of the Yangtze River estuary (YRE). Results showed that residual fractions dominated the As partition (>85%), which attenuated overall bioavailability. After the residual fraction, As mainly partitioned into the Fe-Mn oxides fraction (3.16–4.22%). Arsenic bound to Fe-Mn oxides was higher in wet seasons. The carbonate fraction was minimal, which may result from the negative state presence of As in sediments. According to the risk assessment code, the YRE was classified as low risk. Additionally, the reduction of As(V) to As(III) may occur due to the reducing condition in wet seasons. Considering As(III) is more toxic and mobile, As bound to the exchangeable and Fe-Mn oxides fractions may have more potential ecological risk. Thus, the speciation and fraction should be both considered on the ecological risk of As in sediments of the YRE.

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1. Introduction

Arsenic (As) is a toxic metalloid that poses a health threat in many countries (Amstaetter et al., 2010). Arsenic has acute and chronic toxic and carcinogenic effects on aquatic organisms and humans (Oremland and Stolz, 2003). Elevated levels of arsenic present in the environment have caused public concern (Yang et al., 2009). Arsenic is ubiquitous in groundwater, soil and sediments as a result of natural processes including mineral weathering, dissolution and geothermal activities (Manning et al., 1998; Yamamura et al., 2013). Anthropogenic sources include insecticides, pigment production, leaded gasoline manufacture, fossil fuel combustion, mining and electronic industries. Of these, mining and the use of groundwater abundant in As for crop irrigation are the main sources of higher levels of As in the environment (Ehlert et al., 2014). The sources in estuarine environment include terrestrial input, wet and dry atmospheric deposition, release during the resuspension of sediments, decomposition and regeneration of phytoplankton, and anthropogenic activities (Li et al., 2014). In an aquatic environment, As is typically much more concentrated in sediments than in water (Ahmann et al., 1997). Sediments act as both a source of groundwater contamination and a sink for As, which can be re-partitioned to the water column due to changes in the chemical environment (Choi et al., 2009).

To quantify the extent of pollution, total concentration is widely used for assessing contamination in sediments. However, total concentration provides insufficient information to estimate the potential environmental effect on sediments (Nemati et al., 2011; Sundaray et al., 2011). A metal's mobility, bioavailability and toxicity depend considerably on the chemical fraction (Díaz-de Alba et al., 2011; Huang et al., 2013; Fan et al., 2014). According to sequential extraction procedure, metals in sediments can be classified into exchangeable, carbonate, Fe-Mn oxide, organic and residual fractions (Tessier et al., 1979). Arsenic, when bound to different fractions, exhibits different bioavailabilities. The metal bound to the exchangeable fraction is the most mobile and bioavailable, as well as the most harmful to aquatic organisms (Feng et al., 2014). Many studies have assessed metal pollution using different methods (Díaz-de Alba et al., 2011; Nemati et al., 2011). Use of the risk assessment code (RAC) is one of the methods that has been applied to assess the potential ecological risk of a metal with the consideration of bioavailability to a marine ecosystem by considering the exchangeable and carbonate fractions (Sundaray et al., 2011; Duan et al., 2013; Huang et al., 2013).

In sediments, As predominantly exists in two speciations: (1) arsenate (As(V)), which dominates in oxidizing conditions, and (2) arsenite (As(III)), which dominates in reducing conditions (La Force et al., 2000). In natural conditions, As is preferentially adsorbed on Fe-oxides and Mn-oxides. Many studies have investigated the micro mechanism of As, including sorption and desorption on the surface of mineral oxides, the process of partitioning between the solid and aquatic phases and the transformation between As(III) and As(V) under different redox conditions (Jay et al., 2005; Kocar and Fendorf, 2009; Ying et al., 2011; Muehe et al., 2013; Ohtsuka et al., 2013; Singer et al., 2013). However, these studies mainly focus on the speciation of As overall whereas less attention has been paid to the speciation in different fractions. Considering that arsenite is much more mobile and toxic than arsenate (Keon et

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al., 2001; Ying et al., 2011), each fraction of As with different ratio of arsenite and arsenate may have a different bioavailability.

In order to manage environmental pollution, it is not sufficient to study only the sorption and desorption on the surface of mineral oxides, the process of partitioning between the solid and aquatic phases and the transformation between As(III) and As(V) under different redox conditions. The spatio-temporal changes of As also should be carried out to analyse the distribution, seasonal variation, and pollution assessment. The combination of both approaches on mechanism and spatio-temporal studies could give a better understanding of the behavior of As in the environment. Geostatistics and geographic information system (GIS) are also useful tools to study the distribution of contaminants and analyse the extent of pollution in large scale regions (Mamat et al., 2014; Wang et al., 2015). Geostatistics has been proven to be an effective methodological approximation for studying metal pollution in soil, sediment, mining areas and groundwater (Lee et al., 2009; Antunes and Albuquerque, 2013; Chica-Olmo et al., 2014). Ordinary Kriging is also widely used in predicting pollution and has also been utilized in the present study (Liu et al., 2014; Wang et al., 2014; Wang et al., 2015).

An estuary is an environmentally sensitive area with varying environmental attributes, which may have an influence on the partitioning of a metal into different fractions. The large amounts of organic and inorganic effluents in an estuary and the interaction between these complexes result in an estuary presenting multiple redox conditions (Yao et al., 2006). In addition, seasonal variations might change the oxidizing environment in estuary (Wang et al., 2012). An estuary also contains distinctive particle sizes due to various environmental conditions, hydrological events and human activities (Yao et al., 2007; Balzer et al., 2013; Feng et al., 2014). Particle size is very important in the transportation and cycling of metals. The process of transformation between exchangeable and residual fractions has reportedly been observed on clay minerals (Lim et al., 2002).

In this study, the Yangtze River estuary (YRE) was chosen to investigate the behavior of As in estuarine sediment. The aims of this study were to: (1) describe the fraction distributions in three seasons; (2) investigate the impact of seasonal variations on fractions; (3) analyse bioavailability by examining the relationship between fraction and speciation; (4) assess the potential ecological risk of As in the YRE.

2. Materials and methods

2.1. Study area

The YRE is on the eastern coast of China (Fig. S1). The YRE is located in a very important industrial area, and is the receiving waterbody for a large volume of industrial effluent and domestic sewage. It has been reported that 5×10^6 tons of wastewater per day are discharged into the YRE (Zhang et al., 2009). The YRE has also experienced metal pollution resulting from rapid economic development (Feng et al., 2004; Du et al., 2013). In addition, the construction of the Three Gorges Dam in the upper portion of the YRE has influenced some chemical and physical properties of coastal waters, which may affect the toxicity and distribution of metals (Christophoridis et al., 2009; Wang et al., 2015). It has been reported that the sources of As in the YRE include water discharge, remobilisation of bedrock and anthropogenic inputs, and the YRE receives about 234.8×10^5 mol of dissolved inorganic As per year (Yao et al., 2007). The total concentration of As in the YRE ranges from 1.70 to 22.1 μg g^{-1} with an average of 11.5 μg g^{-1} (Duan et al., 2013).

2.2. Sampling collection and analytical methods

Surface sediments were collected to a depth of 2-5 cm from 30 sampling sites in the YRE in August 2010, November 2010 and May 2011. (Fig. S1). At each site, three surface sediment samples were collected and mixed into a composite sample. Samples were freeze dried and sieved through a 1 mm clean plastic net to remove coarse debris and fragments of shells, and then ground to pass through a 63 μm mesh. The analyses of As concentrations and fractions were conducted for the grain size fraction within 63 μm, which has been adopted by many other researches (Huang et al., 2013; Qiao et al., 2013; Fan et al., 2014)

A sequential extraction procedure was used to measure As fractions according to Tessier's method (Tessier et al., 1979). The freeze dried samples were ground in agate mortar, homogenised and stored at 4 °C. (1) Exchangeable fraction: the sediments were extracted for 1 h with 8 mL of 1 M MgCl$_2$ pH 7.0 with continuous agitation. (2) Carbonate fraction: the residual was agitated continuously for 5 h with 8 mL of 1 M NaOAc adjusted to pH 5.0 with HOAc. (3) Fe-Mn oxides fraction: the residual was extracted at 96 °C for 6 h with 20 mL of 0.04 M NH$_2$OH HCL in 25% (v/v) NaOAc. (4) Organic fraction: to the residual were added 3 mL of 0.02 M HNO$_3$ and 5 mL of 30% H$_2$O$_2$ adjusted to pH 2.0 with HNO$_3$, and the mixture was agitated at 85 °C for 2 h. Another 3 mL of 30% H$_2$O$_2$ (pH 2.0 with HNO$_3$) was then added, and the mixture was agitated at 85 °C for 3 h. Subsequently 5 mL of 3.2 M NH$_4$OAc in 20% (v/v) HNO3 was added, and the sample was diluted to 20 mL and agitated for 0.5 h. (5) Residual fraction: the residual was digested with HNO$_3$ (70%) and HClO$_4$ (60%).

Following each extraction, the extractants were centrifuged at 800g for 30 min at room temperature. Then 1 mL of HNO$_3$ (70%) was added after each extraction. The solution was heated to dryness at 140 °C. The residual was digested in 10 mL of 2% HNO$_3$ at 70 °C for 1 h. Extracted fractions were measured using inductively coupled plasma-atomic emission spectrometry (ICP-AES). More details can be found in Fan et al. (2014). The recovery (cumulative concentration of As in extracted steps and total concentration) calculated for each sample was between 86 and 102% of the certified reference materials values, which were two standard samples of specified reference sediments from the Institute of Geophysical and Geochemical Exploration of the Chinese Academy of Geological Sciences.

2.3. Risk analysis and geostatistics

The risk assessment code (RAC) was applied to assess the potential ecological risk of As with the consideration of bioavailability in sediments by applying a scale to the percentage of exchangeable and carbonate fractions. The results of the RAC analysis were classified into categories based on the criteria below (Sundaray et al., 2011) (Table 1).

ArcGIS was used to analyse the spatial distribution and perform the environmental risk assessment based on As fractions. Ordinary Kriging with geostatistics tools in ArcGIS was used to predict the values of concentrations at unsampled locations. Ordinary Kriging was estimated by a linear combination of observed values with weights (Wang et al., 2014):

$$Z^*(x_0) = \sum_{i=1}^{n} \lambda_i Z(x_i)$$

where $Z^*(x_0)$ was the estimated value of Z at point x_0, $Z(x_i)$ was the sampled value at point x_i and λ_i was the weight placed on $Z(x_i)$.

Table 1
Risk assessment code categories and corresponding risk descriptions.

Risk categories	The proportion of exchangeable and carbonate fractions
No risk	<1%
Low risk	1%–10%
Medium risk	11%–30%
High risk	31%–50%
Very high risk	>50%