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Rapid evaluation of arsenic contamination in paddy soils using field portable X-ray fluorescence spectrometry

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ABSTRACT

Arsenic (As) in paddy fields is deteriorating food security and human health through rice ingestion. Rice is the dominant food source of arsenic exposure to half of the world's population. Therefore, an *in situ* effective method for As risk evaluation in paddy soil is strongly needed to avoid As exposure through rice ingestion. Herein, we developed a rapid analytical methodology for determination of As in plant tissues using field portable X-ray fluorescence spectrometry (FP-XRF). This method was applied to rice roots in order to evaluate the As contamination in paddy soils. The results showed that rice roots with iron plaques were superior to rhizosphere soils for generating FP-XRF signals, especially for field sites with As concentrations lower than the soil detection limit of FP-XRF (30.0 mg/kg). Moreover, the strong linear relationships of As concentrations between the rice roots and corresponding leaves and grains proved that the rice root, rather than the soil, is a better predictor of As concentrations in rice grains. The research provides an efficient As monitoring method for As contaminated paddy fields by using wetland plant roots with iron plaques and XRF-based analytical techniques.

Introduction

Arsenic (As) contamination of paddy soils is a crucial global environmental issue (Williams et al., 2009, 2011, 2014; Newbigging et al., 2015; Xiao et al., 2016). As a known carcinogen (Cohen et al., 2016), arsenic is transported from soils to plants and is accumulated in rice grains (Ma et al., 2008; Zhao et al., 2009). Rice is the dominant staple food source of As exposure to half of the world's population, especially Southern and Southeast Asia (Khan et al., 2014; Zhang et al., 2014; FAOSTAT, 2015; Ahmed et al., 2016). The mitigation of human As exposure through rice consumption should be based on the data of As concentrations in rice and soils, however this data is hindered by the current measurement techniques of As in soils and plant tissues.

Traditionally, the soil As has been measured by laboratory-based analytical methods such as atomic absorption

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spectrometry (AAS) and inductively coupled plasma-mass spectrometry (ICP-MS) (Plantz et al., 1989; Li et al., 2014). Although lab-based methods may give highly accurate, the sample pretreatment process is complex and time-consuming. Additionally, arsenic has various species in environments. These species have very different toxicities and motilities (Moe et al., 2016). Thus, the total soil As concentrations cannot sufficiently illustrate the As accumulation and toxicity in rice (Khan et al., 2009). Therefore, an efficient method to rapidly evaluate available As in paddy soil is strongly needed.

Field portable X-ray fluorescence spectrometry (FP-XRF) has been widely used to determine the concentrations of heavy metals in soils and sediments (Kilbride et al., 2006; Hürkamp et al., 2009; Parsons et al., 2013; Radu et al., 2013). The advantages of detecting and monitoring soil contamination using FP-XRF include time saving, simultaneous analysis of multiple elements and non-destructive measurements (Radu et al., 2013). Recently, *in situ* pre-accumulation of metals by diffusive gradients in thin film (DGT) devices has extended the application of FP-XRF to aqueous environments (Chen et al., 2013). The biological tissues, *e.g.*, toxic metals accumulating oyster shells, have been tested using FP-XRF (Kramer et al., 1997; Chou et al., 2010).

The detection limits of FP-XRF for detection of As in soils is around 30 mg/kg, which restricts its application in analysis of environmental samples (Parsons et al., 2013). Nevertheless, As translocation from the rhizosphere to plants is particularly controlled by the iron (Fe) plaque covering on rice roots in paddy fields (Chen et al., 2005; Pan et al., 2014). The Fe plaque on the root surface is considered to be a barrier that accumulates high amounts of As (Liu et al., 2006). In this study, a rapid simultaneous analytical methodology of As in plant tissues was developed using FP-XRF. The results could be used for rapid evaluation of As contamination in paddy soils. The major objectives of this study were to: (1) investigate the factors influencing As detection in rice roots using FP-XRF, (2) identify the methodology detecting rice roots with iron plaque by FP-XRF to evaluate As contamination in paddy soil.

1. Materials and methods

1.1. Samples collection

The provinces, Hunan and Jiangxi, are the most important rice growing and metal mining areas in China (Zhao et al., 2015). Forty-two rice tissues (grains, straws, roots) and corresponding rhizosphere soils were collected from 14 field sites in these areas during harvest time. The exact sampling locations are showed in Appendix A Table S1.

1.2. FP-XRF analysis

The As levels in roots and soils were analyzed using the XL3t model FP-XRF (NITON Company, USA). Soil As levels were measured by FP-XRF according to the US-EPA Method 6200. The soil samples were lyophilized, then ground and sieved though a nylon screen mesh (38 μm) for FP-XRF analysis. More details of instrument operation parameters were reported in our previous publication (Chen et al., 2013).

The influences of sample pretreatment and measurement times on the performance of FP-XRF measurements of As in rice roots were investigated. FP-XRF in "soil-mode" was used in the measurements of all rice root samples. Four root samples were randomly selected to investigate the effect of pretreatment methods. Generally, air-dried roots can be collected in the field sites after harvest. The samples were air dried in a greenhouse at 20°C for 96 hr, then rinsed with water (tap water and DI water) up to three times to remove the rhizosphere soil. Finally, the samples were oven dried in a drying oven at 105°C for 96 hr. Thus, after each treatment, three types of drying processes (air dried, soil removal, oven dried) were tested three times using FP-XRF with the "soil-mode".

When measuring using FP-XRF, the roots were flattened and positioned in the path of the X-rays. Unlike the dense and solid soils, root samples can be easily penetrated by X-ray photons. To determine the critical FP-XRF penetration depth for As analysis in root samples using FP-XRF, oven-dried rice roots (<2 mm in length, 0.2 g–1.8 g in weight) were placed in a plastic cup (PTFE, diameter, 27.1 mm) and then compressed by hand and analyzed using FP-XRF. The thickness of the samples under the detection window was difficult to measure because the thickness changed with pressure on the samples. Thus, the thickness and weight of 3 samples were carefully measured using a caliper and an electronic balance, respectively. The data was used to develop a calibration curve which described the relationship between sample thickness and sample weight. The thickness of other samples was used to calculate the corresponding weights *via* the calibration curve. A counting time of 60 sec was used for each sample measurement. Each measurement was replicated 3 times.

Finally, one rice root sample was randomly selected from the 14 samples in order to investigate the influence of counting time on FP-XRF measurements. A plastic cup was filled with approximately 2.0 g roots, and FP-XRF measurements were performed for 10, 20, 30, 40, 50 and 60 sec, respectively. Three replicate measurements were performed for each discrete counting time investigated.

1.3. Dithionite-citrate-bicarbonate (DCB) extraction of iron plaque

Portions of the fresh rice root samples were extracted using DCB to dissolve the iron plaques located on the root surfaces. The extraction procedure thereafter was performed according to a previous study (Liu et al., 2004). The DCB-extracts were filtered with a membrane filter (0.45 μm, MFS, USA) and stored at 4°C for As analysis by ICP-MS (Agilent-7500, Agilent Technologies Co. Ltd., Palo Alto, CA, USA).

1.4. Plant tissues, rhizosphere digestion and ICP-MS analysis

Rice grains, flag leaves, intact roots, and roots without iron plaques (*i.e.*, subsequent to DCB extraction) were digested by concentrated nitric acid (HNO_3), and the levels of As in the digests were analyzed by ICP-MS. Because the As levels in flag leaves are the highest among all parts of rice straws (Zhao et al., 2013), the As levels in flag leaves were examined as the As transported from the roots to the shoots. Before digestion, air-dried grains, intact roots, extracted roots and flag leaves