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Occurrence of arsenic in fruit of mango plant (*Mangifera indica* L.) and its relationship to soil properties

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ABSTRACT

Arsenic is a highly toxic element and its presence in foodstuffs will do harm to human health. In this study, the levels of arsenic in the fruits of three mango cultivars (*Mangifera indica* L.) from Hainan Island, China were investigated and their relationships to soil properties were discussed. The concentrations of arsenic in the mango fruits ranged from 0.6 to 50 μg kg^{-1} (FW) with a mean value of 8.6 μg kg^{-1}. The transfer factors (TFs) of arsenic from soil to fruit varied between 0.0001 and 0.055 with a mean value of 0.0059. Both arsenic concentrations in the mango fruits and TFs were negatively correlated with soil Al_2O_3, Fe_2O_3, and MnO concentrations that could be described by a power model ($y = ax^b$), suggesting that soil Al–Fe–Mn oxides may play an important role in limiting the bioavailability and bioaccumulation of arsenic in the mango fruits. In addition, arsenic accumulations in the mango fruits were influenced by the soil pH. Mango fruits from the soils with pH between 4.8 and 5.5 had relatively high arsenic concentrations and TF values.

1. Introduction

Soil to crop transfer of toxic metals/metalloids is an important pathway of human exposure to soil pollutants. Arsenic accumulation in the soil–crop system has received increasing attention due to its high toxicity to human health (IARC, 2004; McLaughlin et al., 1999; Williams et al., 2009). Arsenic occurs in soil primarily in inorganic forms (As(III) and As(V)) as well as in dimethylarsinic acid (DMA) and monomethylarsonic acid (MMA) (Caussy, 2003; Pantsar-Kallio and Manninen, 1997). The toxicities of different arsenic species vary greatly with inorganic forms much higher than organic compounds (Signes et al., 2008). Of the inorganic arsenic species, As(III) is more mobile and thus more toxic than As(V) because As(V) can be adsorbed more strongly to particle surfaces than As(III) (Korte and Fernando, 1991). Therefore, the study of arsenic adsorption by soil particles is critical to the evaluation of arsenic mobility and toxicity in the soil–plant system.

Once entering soil, arsenite and arsenate may form surface complexes with a number of different oxides, especially Fe, Mn, and Al oxides (Gustafsson and Bhattacharya, 2007; Wang and Mulligan, 2008), which could significantly lower their mobility and bioavailability. Hartley and Lepp (2008) demonstrated that goethite in soils could effectively reduce the arsenic bioavailability for spinach and tomato. Application of iron oxides to contaminated soils led to a significant decrease in arsenic concentrations in soil leachates (Hartley et al., 2004). Soil applied with 0.5% iron oxides resulted in a reduction of 32% of arsenic in the vegetables (Warren et al., 2003). The adsorption of arsenic by Al oxides is similar to those of the hydrous Fe oxides. Many studies have revealed that arsenic in soil is mainly associated with amorphous and/or crystalline Al and Fe oxides (Caille et al., 2004; Sarkar et al., 2007; Smith et al., 2006; Wang and Mulligan, 2008). Mn-oxides have also proved to be efficient arsenic adsorbents, since they are able to oxidize As(III) to As(V) and adsorb As(V) (Foster et al., 2003; Manning et al., 2002; Ouvrard et al., 2005; Wang and Mulligan, 2008). Arsenic adsorption on oxide surfaces is mainly pH dependent. As(V) is preferentially adsorbed on hydrous oxides for pH values ranging from 4 to 7, whereas As(III) is preferentially adsorbed at pH 7 to 10 (Pierce and Moore, 1980, 1982). Arsenic (V) sorption on activated alumina occurs best between pH 6.0 and 8.0 (Mohan and Pittman, 2007). Jeong et al. (2007) found that the adsorption of As(V) on Fe_2O_3 and Al_2O_3 followed the Langmuir isotherm between the pH values of 5 and 9 and the maximum As(V) uptake occurred at pH 6. These recognitions about interactions between arsenic and oxides were based mainly on external oxides/arsenic and chemical extraction studies and some greenhouse bioassays (Carbonell-Barrachina et al., 1997; Hartley and Lepp, 2008; Hartley et al., 2004; Merwin et al., 1994; Pendergrass and Butcher, 2006; Warren et al., 2003), but seldom on internal oxides/arsenic and field conditions (Warren et al., 2003).

In China, arsenic contamination in the soil–crop system is a growing environmental problem and has been frequently reported (e.g. Chen et al., 2006; Fu et al., 2011; Huang et al., 2006; Liu et al., 2010; Williams et al., 2009). In order to better protect human health against being poisoned by arsenic, the maximum allowable levels of arsenic in foods have been significantly lowered by the Chinese government

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since 2005. For example, the upper limit for inorganic arsenic in fruits was lowered to 50 ng/g (FW) (CFSA, Chinese Food Standards Agency, 2005). This means that the Chinese government has realized the gravity of the arsenic toxicity. However most of the recent works in China focused on arsenic accumulation in rice or vegetables (Chen et al., 2006; Fu et al., 2011; Huang et al., 2006; Liu et al., 2010; Williams et al., 2009), and the data about fruits were limited (Li et al., 2006; Yang et al., 2008). Mango is one of the most popular tropical fruit in the world which can grow well in various soil conditions. In this study, three cultivars of mango plants (*Mangifera indica* L.) were collected from an uncontaminated area, Hainan Island, China for the purpose of determining the levels of arsenic concentrations in the mango fruits and trying to find out the possible relationships between the internal soil properties and the accumulation of arsenic in the mango fruits.

2. Materials and methods

2.1. Study area

The study area, Hainan Island, is located in southern China (18°10′–20°10′N, 108°37′–111°03′E) and covers 33,920 km^2 of land area. The central Five Finger Mountain is the highest mountain in the island with an altitude of 1867 m above sea level. Climate in this area is tropical monsoon with average annual rainfall of 1600–2500 mm and average annual temperature of 23–25 °C.

The main soil types in Hainan are cambisols and ferrosols on the parent materials of acid igneous rocks, cambisols on clastic sediments, ferralosols on basic igneous rocks, and primosols and cambosola on marine sediments. In the study area, mango, banana, and pineapple are the main fruit crops with average annual productions of 0.26, 1.08, and 0.21 million tons, respectively.

2.2. Sampling and preparation

The sampling locations and sampling procedure have been described in previous study (Bi et al., 2010). Briefly, sixty-seven orchard soil and mango fruit (*M. indica* L.) (belong to three native cultivars: Ji-Dan, Tai-Nong and Xiang-Ya) samples were randomly collected from fourteen orchards. In this study, one sample was lost during processing and thus only 66 were left to discuss. After sampling, soil samples were air-dried at room temperature (25 °C), and ground to <0.1 mm with an agate mortar. Plant samples were thoroughly cleaned with tap water and Milli-Q water to remove adhering particles, and then the edible parts were separated and dried in oven at 60 °C. The dried samples were weighed for calculation of moisture content and ground with stainless mill to fine powder for the chemical analysis.

2.3. Analytical methods

Soil organic matter (SOM) contents and pH values of these experimental soils have been previously published (Bi et al., 2010). Briefly, soil pH was determined in a 2.5:1 water/soil suspension using a pH meter (LY/T, 1237-1999, 1999). Soil organic matter (SOM) content was determined by potassium dichromate method (LY/T, 1239-1999, 1999). For arsenic determination of the soil, 0.5 g thoroughly homogenized samples were weighed into 50 ml Teflon vessels, then added 10 ml of aqua regia (3:1, HCl:HNO_3) and heated on a hot plate until near dryness. After cooling, the residue was redissolved in 2 ml of 65% HNO_3 and diluted to 50 ml with Milli-Q water (modified from Huang et al., 2007). For fruit analysis, 1.0 g homogenized samples was weighed into 50 ml pyrex beakers and decomposed with 10 ml of 65% HNO_3 and 4 ml of 30% H_2O_2. After cooling, the residual suspension was filtered in a 50-ml volumetric flask and diluted to the mark (Du Laing et al., 2003). Extractable arsenic concentrations were determined by shaking 10 g of soil with 50 ml of 0.1 mol L^{-1} hydrochloric acid.

Arsenic concentrations in all the prepared solutions were determined by hydride generation atomic fluorescence spectrometry (HG-AFS). The detection limit for As in fruit was less than 0.1 μg kg^{-1} (fresh weight). The concentrations of Al_2O_3, Fe_2O_3, and MnO were determined by an X-ray fluorescence (XRF) spectrometer after the sample being further ground to ~75 μm (200 mesh). For quality assurance and quality control (QA/QC), the duplicates, method blanks and standard reference materials (limestone soil GSS-4 and shrub leaf GSV-1) were analyzed. Mean recoveries for soil were within 100 ± 10%, and for plants were within 100 ± 20%. Method blanks in each batch of samples were negligible.

The soil-to-fruit transfer factors (TFs) of arsenic were calculated using the following equation:

$$TF = \text{As in fruit (fresh weight, FW)} / \text{As in soil (dry weight, DW)}.$$

All the correlations and the regressions were carried out using SPSS 11.0 for Windows (SPSS Inc. USA). Statistical significances of differences were computed using one-way analysis variance (ANOVA).

3. Results

3.1. Soil properties

In this study we classified the soils into three kinds based on the three cultivar species and their corresponding properties are listed in Table 1. The soils were slightly acid, with pH value of 4.8–7.3 (mean 6.0). The organic matter (OM) content of the soils ranged from 0.4 to 2.9% (mean 1.4%). Al_2O_3, Fe_2O_3, and MnO concentrations ranged from 29 to 240 g kg^{-1} (mean 110 g kg^{-1}), 3.2 to 90 g kg^{-1} (mean 18 g kg^{-1}), and 0.1 to 1.1 g kg^{-1} (mean 0.57 g kg^{-1}), respectively. There were no significant differences of the above properties among the three kinds of soils.

Soil arsenic concentrations varied greatly, from 0.42 to 53 mg kg^{-1} with a mean value of 8.0 mg kg^{-1}, similar to the background values (mean 11 mg kg^{-1}) in China (EMC, Environmental Monitoring of China, 1990). However, some soil samples (9%) contained arsenic exceeding the Chinese national standard limit for dry land (40 mg kg^{-1} with pH < 6.5, CEPA, Chinese Environmental Protection Agency, 1995). The high arsenic in these soils might be derived from the parent materials since the bed rocks also contained high levels of arsenic (42–54 mg kg^{-1}, unpublished data). Depending on the parent materials, the soils of Ji-Dan cultivar have significantly higher arsenic (mean 15 mg kg^{-1}) than the others (mean 4.4 and 5.7 mg kg^{-1}, respectively) (Table 1).

The labile fraction of arsenic in soil is generally low because arsenic in soil is mainly presented in insoluble arsenate. In this study, the labile arsenic extracted by dilute HCl was evenly distributed among the three kinds of soils and only 0.02–2.2% (0.01–0.05 mg kg^{-1}) of the total arsenic was readily labile (Table 1). This result is comparable to previous findings extracted by other reagents of water (Camm et al., 2004), NH_4-OAc-EDTA (Bech et al., 1997), and acetic acid (Baroni et al., 2004; Williams et al., 2009). There were no obvious relationships between the labile arsenic and the total arsenic, suggesting that the amount of labile arsenic is independent of the total arsenic.

3.2. Arsenic in mango fruits and TFs

The concentrations of arsenic in mango fruits ranged from 0.6 to 50 μg kg^{-1} (FW) with a mean value of 8.6 μg kg^{-1} (Table 2). Except one, most fruits had arsenic concentrations lower than the Chinese maximum allowable value of 50 μg kg^{-1} (CFSA, Chinese Food Standards Agency, 2005). This means that mango fruits from Hainan Island were generally safe for consumption in terms of arsenic contamination. The TFs of arsenic in this study varied from 0.0001 to 0.055 with a mean value of 0.0059. The Ji-Dan cultivar had lower levels of