



Characterization of the particle size fraction associated heavy metals in tropical arable soils from Hainan Island, China

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ABSTRACT

Tropical arable soils were sampled from Hainan Island. The particle size fractions associated Cr, As, Cd and Pb were characterized and their leachability was analyzed as well. The pollution of heavy metals in the arable soils was not severe except Cr (204 mg kg⁻¹) in Haikou. The distribution of heavy metals increased with decrease of particle size. Although the smallest fractions (<53 μm) occupied only 5.08–9.57%, they had the highest distribution factor (DF) of 3.50 for Cd, 2.11 for Pb, 1.73 for Cr and 1.09 for As, respectively. The contributions of micro-aggregates (<250 μm) to the total amount of heavy metals was 41.9% for Cr, 44.6% for As, 61.6% for Cd and 48.6% for Pb, respectively, and the second mass loading came from the particles of 250–1000 μm. The residues of Cr, Cd and Pb were correlated positively with the contents of organic carbon as well as Fe in fractions, while a large variation distribution of As was found in particles, indicating its high activity in soil microenvironment. The lowest leachability was found in the easily migratory micro-aggregates, which should be taken into account in the future environmental risk assessment and soil remediation.

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1. Introduction

Heavy metals in soil have attracted extensive attention worldwide since most of them are harmful to the crop quality and pose a potential threat to human health through the food chain (Huang and Jin, 2008; Quinton and Catt, 2007). In China, the harsh fact is that soil pollution by heavy metal is getting worse with the rapid urbanization for decades (Wei and Yang, 2010). Understanding the distribution characters of heavy metals in soil is the premise of risk assessment and soil remediation. Numerous studies have been conducted to determine heavy metals in both bulk soils and different particle size fractions. However, most previous studies are focused on urban soil, garden soil, dust and sediment (Acosta et al., 2009, 2011; Ajmone-Marsan et al., 2008; Beamer et al., 2012; Sutherland, 2003) and only few data are available about the distribution of heavy metals in various particle size fractions from arable soil (Qian et al., 1996; Quenea et al., 2009; Zhang et al., 2003).

The mobility and biological effectiveness of soil heavy metals have a strong correlation with the size and composition of particle fractions (Zhang et al., 2003). Various size fractions have different

composition and properties, which affected the behavior of pollutants in the soil microenvironment (Acosta et al., 2011). Generally, fine particles have a higher ability to carry the heavy metals due to the increase of specific surface area, the presence of clay minerals, organic matter, and Fe/Mn/Al oxides in the micro-aggregate (Cai et al., 2002; Ljung et al., 2006; Semlali et al., 2001; Sutherland, 2003; Wang et al., 2006), which would protect the heavy metals from remedial attempts. Moreover, since the fine soil fractions are often preferentially transported to deep soil, surface/ground water and air, they are more harmful to the environments (Farenhorst and Bryan, 1995; Uusitalo et al., 2001). Therefore, exploring the partition in soil particle sizes was very important for the assessment of mobility and bioavailability of heavy metals in soil (Wang et al., 2006).

Hainan Island is located in the South China Sea and it is becoming an international travel insight according to the national developing plan. The industrialization caused heavy metal accumulation in arable soil (Hao et al., 2009; Li et al., 2009). The concentration of Cr in the suburban soil in Haikou was up to 586.70 mg kg⁻¹ (Li et al., 2009). The rich precipitation and strong biological action in the study area could result in a rapid cycle of organic carbons in soil. The distribution character of heavy metals in particle size fractions is still unknown in arable soils in Hainan Island. Moreover, in order to predict both potential mobility and their bioavailability to plants, it is necessary

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to assess the leachability of heavy metals in different particles. Up to now, only few data about water-leaching risk of heavy metals in different particle size fractions have been reported (Magnuson et al., 2002; Zhang et al., 2003).

In order to assess the environmental risk and take applicable measures in the future, it is important to know in which scale particles the heavy metals are preferred to distribute. The objectives of this study are to: (1) assess the contamination levels of toxic Cr, Pb, As and Cd in arable soils in Hainan Island; (2) investigate the distribution patterns and leachability of heavy metals in different particle size fractions; and (3) discuss the factors effecting the residues of heavy metals in different particle size fractions.

2. Material and methods

2.1. Study site and sampling

Hainan Island ($18^{\circ}10'–20^{\circ}10'N$, $108^{\circ}37'–111^{\circ}03'E$) is separated from the mainland by a narrow strait. It features a typical tropical marine climate with an annual temperature of $23–26^{\circ}C$ and precipitation of 1500 mm. The island occupies an area of 33,920 km² and the major soil type is latosol (pH ≈ 5.00) with a complex terrain of plains and hills staggered.

Three composite surface arable soils (0–20 cm) were collected in 2011 from Haikou ($19^{\circ}44'N$, $110^{\circ}34'E$), Qionghai ($19^{\circ}22'N$, $110^{\circ}36'E$) and Tunchang ($19^{\circ}23'N$, $110^{\circ}09'E$), respectively, and the sites are shown in Fig. 1. Haikou is the northern island with a rapid urbanization. Qionghai and Tunchang are located in the eastern and central island, respectively. Vegetables were planted in the studied field and the uncultivated soils were collected as well.

Multiple cores were collected to get one sub-sample firstly and a few sub-samples were mixed gently to obtain a composite sample. The bulk soil was kept in plastic boxes. The samples were air-dried at room temperature and the coarse debris was removed before further processing. The water content in the soil was determined gravimetrically after drying individual sub-sample at $105^{\circ}C$ overnight until the weight was constant. All the results were reported as dried weight.

2.2. Analytical methods

Soil particle size fractions were separated by using standard dry-sieving procedure. 100 g of bulk soil was subjected to 3×10 min automatic shaking episodes into six particle size fractions moved with a stack of sieves of 4000, 2000, 1000, 250 and $53 \mu m$. The distribution of each particle size fraction was calculated by determining the weight of each size fraction.

Concentrations of total organic carbon (TOC) were analyzed for both bulk and each size fraction by the dichromate method (Wang, 2009). The sample was ground in a mortar and passed through a $20 \mu m$ sieve for analysis. 0.50 g of soil was weighed into volumetric flask and 10 mL $1.00 \text{ mol L}^{-1} \text{ K}_2\text{Cr}_2\text{O}_7$ and 20 mL concentrated H_2SO_4 were added to the reaction for 30 min, and then the mixtures were titrated using $0.5 \text{ mol L}^{-1} \text{ Fe}_2\text{SO}_4$ with phenanthroline as indicator. Finally the TOC were calculated according to the consumption volume of Fe_2SO_4 . The detection limit of TOC was 0.2%.

For each particle size fraction and bulk soil, about 0.100 g of well ground sample was digested using 5.00 mL HNO_3 , 2.00 mL HClO_4 and 1.50 mL HF in PTFE reactor at $160^{\circ}C$ for 6 h according to the reference (Li et al., 2008b). The total amounts of Cr, Cd, Pb and As were determined by inductively coupled plasma mass spectrometry (ICP-MS, Thermo-X7, Agilent). The detection limits obtain were 0.01, 0.036, 0.012 and 0.023 mg kg^{-1} for Cr, As, Cd and Pb, respectively. Reference standard soil from Tibet (GBW 08302, National Institute of Metrology P.R. China) and reagent blanks were used as the quality control sample during the analysis procedures. The recoveries were 86–96% for Cr, 102–110% for As, 90–123% for Cd and 99–103% for Pb, respectively. The relative standard deviations ($n=3$) of duplicate samples and blank samples were less than 10% and 5%, respectively. The concentration in samples was verified by the blank in this study.

For each particle size fraction, the leaching test of heavy metals was performed by dispersing 10 g soil in 100 mL high purity water (Wang, 2009). The mixture was stirred for 8 h by using a magnetic stirring apparatus (HJ-6A, Changzhou Guohua Electric Appliance Ltd. Co., China), then rested for 16 h. The pH was adjusted to 5.00 ± 0.20 by HCl (0.10 mol L^{-1}). Finally, the mixture was centrifuged and the

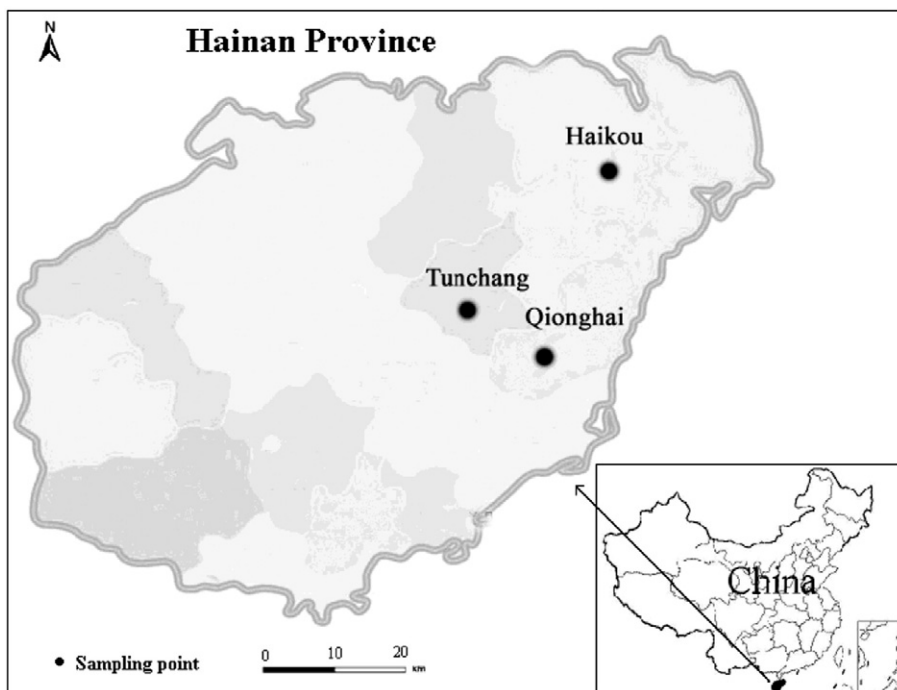


Fig. 1. Map of sampling sites in Hainan Island, China.

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