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Bioavailability and soil-to-crop transfer of heavy metals in farmland soils: A case study in the Pearl River Delta, South China

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ABSTRACT

Soil-bound heavy metals are of great concern for human health due to the potential exposure via food chain transfer. In the present study, the occurrence, the bioavailability and the soil-to-crop transfer of heavy metals in farmland soils were investigated based on data from two agricultural areas, i.e. Sihui and Shunde in South China. Six heavy metals (As, Cu, Hg, Mn, Ni and Pb) were quantified in the farmland soils. The mean single pollution level indices (*PI*) were all lower than 1 except for Hg in soils from Shunde ($PI = 1.51 \pm 0.46$), suggesting the farmland soils were within clean and slightly polluted by heavy metals. As, Cu, Ni and Pb were found to be mostly present in the non-bioavailable form. The majority of Hg was considered potentially bioavailable, and Mn was found to be largely bioavailable. Soil pH was an important factor influencing bioavailability of soil-bound heavy metals. The concentrations of heavy metals in vegetables from Sihui and Shunde were within the food hygiene standards, while the rice grain from Sihui was polluted by Pb ($PI = 10.3 \pm 23.4$). Total soil concentrations of heavy metals were not correlated to their corresponding crop concentrations, instead, significant correlations were observed for bioavailable concentrations in soil. The results supported the notion that the bioavailability of the investigated heavy metals in the soil was largely responsible for their crop uptake. The soil-to-crop transfer factors based on bioavailable concentrations suggested that Cu, As and Hg in soils of the study area had greater tendency to be accumulated in the vegetables than other heavy metals, calling for further human health assessment by consuming the contaminated crops.

1. Introduction

Soil serves as a critical landscape for ecosystem and is the basic resource for food production, while soil is threatened by a large number of toxicants among which heavy metals are of great concern (Chen et al., 2015; Nannoni et al., 2011; O'Connell et al., 2008). Heavy metals in arable lands partially originated from natural sources, but in many cases they are from anthropogenic activities, such as fossil fuel combustion, mining, smelting, traffic, waste water irrigation and sewage sludge reuse, and the excessive application of pesticides and fertilizers (Lu et al., 2012; Temmerman et al., 2003). Soil-bound heavy metals in farmlands are likely to accumulate in agricultural products, e.g. vegetables and grains, which pose risks to human population which consume the polluted agricultural food or indirectly consume animals feeding on the agricultural products via the food chain (Chen et al., 2015; Liu et al., 2013; Nannoni et al., 2011; Sungur et al., 2014). Therefore, the transfer process of soil-bound heavy metals in soil-crop system has attracted increasing attention in recent years (Adamoa et al., 2014; Luo et al., 2011).

Accumulation of heavy metals from soil to plants mainly depends on the uptake mechanisms, the physicochemical properties of the soil and the chemical speciation of the metals and metalloids in soils (Kalembkiewicz and Palczak, 2005; Peijnenburg et al., 2007). Conventional risk assessment of soil-bound heavy metals is performed based on total metal concentrations in soils which

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may overestimate the risk (Hu et al., 2013; Li et al., 2004, 2014) and further result in the unnecessary and expensive soil remediation (Alexander, 2000; Kim et al., 2015; NRC, 2003). Conversely, the accumulation of heavy metals from soil to plants has been found to be better correlated with their bioavailable concentrations in soils (Adamoa et al., 2014; Kim et al., 2007). To date, studies on the bioavailability and transfer of heavy metals in soil-plant system mainly focused on the phytoremediation of soil in urban, mining and waste disposal sites using pot or field-plot experiments with limited sampling sites (Blanco et al., 2016; Vazquez et al., 2016). Several studies have assessed the bioavailability and transfer of heavy metals in soil-crop system in agricultural areas with specific pollution sources, e.g. mining and e-waste recycling sites, where the accumulation of heavy metals from soil to crops directly threatened human health via food consumption (Adamoa et al., 2014; Luo et al., 2011; Wang et al., 2012). However, limited information about the soil to crop transfer of potentially toxic metals and metalloids is available in the areas where residents are unaware of the potential metal pollution in farmland soils and consume local planting crops, which may cause broader exposure risk than those in the well-known severely polluted areas due to the unawareness.

The Pearl River Delta (PRD) is one of the most industrialized, urbanized and populous areas in China, and soil heavy metal pollution is one of the most concerning environmental issues in this region (Hu et al., 2013). A large number of studies have assessed the occurrence, distribution, fractionation and potential risk of heavy metals in soils in the PRD, with a focus on highly polluted areas, like mining sites (e.g. Zhuang et al., 2009) and e-waste recycling sites (e.g. Luo et al., 2011). However, attention has been scarcely paid on the bioavailability and soil-to-crop transfer of heavy metals in farmlands in remote areas, which was the main aim of the current study. Sihui and Shunde in the PRD were chosen as representative sites to fulfill the aim using the following steps: (1) to determine the concentrations of heavy metals in the farmland soils; (2) to determine the bioavailability of heavy metals in the soils and evaluate the influence of soil properties on the bioavailability; (3) to investigate the transfer of heavy metals in the soil-crop system based on their total and bioavailable concentrations in the soils. Sihui is located in the mid-west of Guangdong Province with agriculture, forestry and fishery as the primary industry. Shunde has experienced rapid transition from an agriculture-based economy to an industry-based economy during the last three decades (Li et al., 2009). Heavy metals have been detected in soils from Shunde (Cai et al., 2015, 2016), yet the bioavailability and soil-to-crop transfer of heavy metals in farmland soils are unknown. Therefore, Sihui and Shunde served as good representatives and comparisons to study the heavy metal pollution in farmland soils.

2. Materials and methods

2.1. Study area, sample collection and sample preparation

Soil samples were collected from agricultural areas of Sihui and Shunde in the PRD, South China, with a sampling area of about 77 km^2 and 50 km^2, respectively (Fig. 1). The study area is located in a subtropical climate zone with an average annual temperature and rainfall of 22.3 °C and 1832 mm, respectively and 83% of the rainfall is in the rainy season (from April to September) (SLRO, 2012). River alluvial deposits from the West River and North River are the main source of soil matters in the study area, resulting in extensive agricultural activities in the land (Cai et al., 2015). The river alluvial deposits are formed by the weathering of limestone, granite, quartz, shale and sandstone, and mainly consist of sand, clay and sandy clay. Soils in the study area are classified as paddy soil, stacked soil and lateritic red soil according to the classification and codes for Standardization Adminitration of the People's Republic of China (SAPRC, 2009). Rice, lettuce, pakchoi, lettuce, Chinese cabbage and flowering cabbage are the main crops cultivated in the study area. Comparatively, Shunde is more industrialized than Sihui.

A total of 68 surface soil samples (0–20 cm) together with 35 lettuce samples (the edible parts) and 31 rice grain samples were collected from agricultural fields in Sihui. In addition, 29 surface soil samples with 50 vegetable samples (Chinese cabbage, lettuce, rape, leaf lettuce, flowering cabbage and Chinese kale) were collected from the fields in Shunde (Fig. 1). Five sub-samples (soil, vegetable and rice grain) were collected within an area of 20 m^2 from each sampling site and mixed together to obtain a single composite sample. The samples (about 0.5 kg each) were placed in the plastic bags, transported back to the laboratory on ice and stored at −20 °C prior to analysis. The details of each site sample are presented in Tables S1 and S2 in the Supplementary Data.

The soil samples were dried at 60 °C for 72 h, sieved through a 2-mm nylon sieve (Jingxin Industrial Development Co., LTD, Shanghai, China) to remove sand, gravel and plant debris, and used for analyzing the soil pH and soil organic matter (OM). The pre-sieved soil was finely powdered by an agate ball-grinder (Jingxin Industrial Development Co., LTD) for 1 h using 10-mm agate balls, further sieved using a 74-μm nylon sieve and used for measuring the soil heavy metal contents (Hu et al., 2013).

The crop samples (vegetables and rice grain) were sequentially washed with tap water and de-ionized water, cut into small pieces with a stainless steel knife after drying at room temperature, and weighed and recorded as fresh weight. The plant samples were oven-dried at 85 °C for 30 min, kept in the oven at 60 °C for about two days until reaching a constant weight, weighed and recorded as dry weight (Wang et al., 2006). The plant moisture content was determined from the fresh and dry weights. Finally, the plant samples were grounded to fine powder using an agate ball-grinder, sieved through a 74-μm nylon mesh sieve, and stored in sealed plastic bags at room temperature prior to heavy metal analysis.

2.2. Chemical analysis

Total concentrations of heavy metals (As, Cu, Hg, Mn, Ni and Pb) in the soil and crop samples were analyzed after microwave digestion. Accurately weighed soil or crop sample (0.5 g) was digested with a mixture of concentrated nitric acid (15 mL) and hydrofluoric acid (5 mL) using a MARS microwave digestion system (CEM, USA) according to EPA method 3052 (USEPA, 1996). After evaporating the digested solution to near dryness, the residues were re-diluted to 50 mL with 1 M HNO_3.

Fractionation of the metals/metalloids of interest was obtained by a sequential extraction method (CGS, 2005). Heavy metals in the soil samples were successively extracted as the following seven fractions: water soluble fraction (F_1), ion-exchangeable fraction (F_2), fraction bound to carbonates (F_3), fraction bound to humic acid (F_4), fraction bound to Fe–Mn oxides (F_5), fraction bound to OM (F_6) and residual fraction (F_7). The detailed procedures of chemical fractionation are presented in the Supplementary Data.

The concentrations of heavy metals in the samples were analyzed by inductively coupled plasma-optical emission spectrometry (ICP-OES; Optima 2000DV, Perkin Elemer, USA), except for As and Hg, which were analyzed by atomic fluorescence spectrophotometry (AFS-230, Beijing Haiguang Instrument Co., Ltd, Beijing, China) at a wavelength of 253.7 nm. The reporting limits of As and Hg in the soil and crop samples were 0.001 and 0.0001 mg/kg dry wt., respectively.

The pH of soil samples was determined by soaking a pH probe in

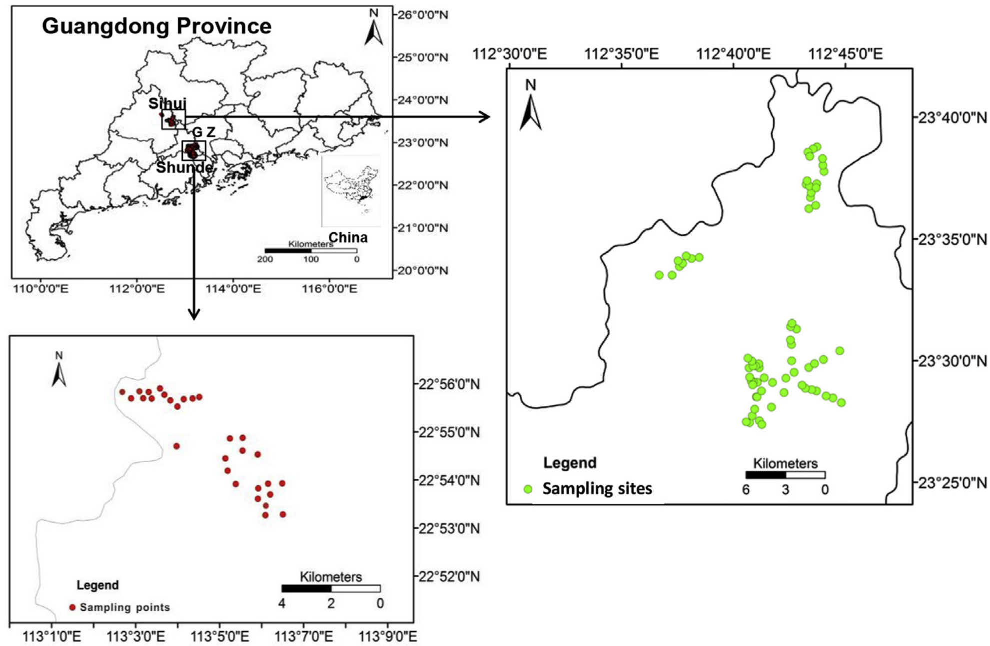

Fig. 1. Map of the sampling sites in Sihui and Shunde in the Pearl River Delta, South China.

the soil suspension (soil: water, 1: 2.5, w/v) (Grewelling and Peech, 1960). The OM content of soil samples was analyzed through the oxidation of OM using $K_2Cr_2O_7$ in an acid medium (Lu, 2000).

2.3. Quality control

All the chemicals used in the current study were guaranteed reagent grade (Merck, Germany). De-ionized water (TKA GenPure, Germany) was used in the experiments. All the plastic materials and glassware were kept in 20% HNO_3 overnight and subsequently cleaned with 1% HNO_3 at room temperature. Blanks, standard reference materials (Chinese standard reference GSS-1 (dark brown soil), GSS-2 (chestnut soil), GSS-3 (yellow brown soil) and GSS-8 (yellow soil) for soils, and GSB-5 (cabbage), GSB-6 (spinach) and GSB-7 (tea) for plants) and duplicate samples were used for quality control during the analytical process. The recoveries of the target heavy metals in the standard references ranged from 85% to 119%.

2.4. Data analysis

Distribution of heavy metal concentrations in the soils and plants was evaluated with Kolmogorov-Smirnov (K-S) test. Spearman's correlation analysis was applied to evaluate the relationship between soil properties and heavy metal fractionation, and the correlation between metal concentrations in soils and plants. In addition, hierarchical cluster analysis (HCA) was used to determine the similarities of the heavy metal fractionation in soil and their concentrations in plants. The correlation between variables and a single linkage algorithm was used to link a cluster of variables with similar distances. The SPSS 19.0 program was used for statistical analysis.

Soil-to-crop transfer factors of heavy metals in soil-crop system were calculated using the following equations (Adamoa et al., 2014):

$$TF_{total} = C_{crop} \ / \ C_{total} \tag{1}$$

$$TF_{avail} = C_{crop} \ / \ C_{avail} \tag{2}$$

Where TF_{total} and TF_{avail} are soil-to-crop transfer factors based on total (C_{total}) and bioavailable (C_{avail}) concentrations of heavy metals in the soils, respectively, and C_{crop} is the concentration of heavy metals in the crops (rice and vegetable).The single pollution index (PI_i) has been commonly used to indicate pollution level of heavy metals in ecological risk assessment, and it was calculated using the following equation:

$$PI_i = C_i \ / \ S_i \tag{3}$$

Where C_i is the concentration of a given heavy metal (i) in the soil or crop and S_i is the reference value of the metal in the soil or crop. The S_i values of the heavy metals in soil were based on the second grade of environmental quality standard of heavy metals for farmland soil in China (MEPPRC, 1995a) except for Pb which was based on the soil of green food quality standards (NY/T391-2000) (CGFDC, 1994). The S_i values of the heavy metals in crop were based on the standards of food hygiene for heavy metals established by the Ministry of Health of the People's Republic of China (MHPRC, 2005).

3. Results and discussion

3.1. Soil properties and heavy metal concentrations in soils

Descriptive statistics of soil properties (pH and OM content) and the concentrations of heavy metals in farmland soils in Sihui and Shunde, South China are presented as mean values in Table 1 and individual data in Tables S3 and S4. The mean values of pH were 5.87 (3.35–8.83) and 5.70 (4.07–8.12) for soils from Sihui and Shunde, respectively. Furthermore, pH values for 90% and 93% of the soils were below 7, respectively, suggesting that the soil was commonly acidic in the study area. On average, the contents of OM in soils from Sihui were 1.31% (0.12%–3.54%), which were significantly lower than that in soils from Shunde (3.91% on average, 1.89%–7.33%). The concentration of metals and soil properties were log-normally distributed except for Cu, which was normally distributed.

Table 1
Descriptive statistics of selected physicochemical properties and heavy metal contents in the soils (mg/kg dry wt.).

Soil characteristics/ Heavy metals	Minimum value	Maximum value	Mean value	Geometric mean value	Standard deviation	Background of Guangdong[a]	Percent of exceeding the background (%)	Threshold[b]	*PI*[c]	Percent of *PI* > 1 (%)
Sihui ($n = 68$)										
pH	3.35	8.83	5.87	5.81	0.89	/[e]	/	/	/	/
OM (%)[d]	0.12	3.54	1.31	1.13	0.67	/	/	/	/	/
As	3.31	83.1	12.0	9.94	10.6	8.90	52.9	40.0	0.30 ± 0.27	1.50
Cu	4.60	62.3	16.6	15.1	8.52	17.0	41.2	50.0	0.33 ± 0.17	1.50
Hg	0.03	0.35	0.13	0.11	0.07	0.08	66.2	0.30	0.44 ± 0.23	1.50
Mn	148	825	386	361	141	279	79.4	/	/	/
Ni	4.81	61.7	14.7	13.2	7.96	14.4	44.1	40.0	0.37 ± 0.20	1.50
Pb	13.3	71.3	31.2	29.4	10.8	36.0	30.9	50.0	0.62 ± 0.22	4.41
Shunde ($n = 29$) (Liu et al., 2013)										
pH	4.07	8.12	5.70	5.62	0.93	/	/	/	/	/
OM (%)	1.89	7.33	3.91	3.70	1.34	/	/	/	/	/
As	14.7	33.4	21.6	21.0	5.50	8.90	100	40.0	0.54 ± 0.14	0
Cu	24.7	58.5	44.2	43.6	6.90	17.0	100	50.0	0.88 ± 0.14	17.2
Hg	0.17	0.75	0.45	0.43	0.14	0.08	100	0.30	1.51 ± 0.46	86.2
Mn	373	1054	636	618	161	279	100	/	/	/
Ni	24.0	49.2	35.4	34.8	6.37	14.4	100	40.0	0.89 ± 0.16	17.2
Pb	30.6	67.0	48.3	47.4	9.36	36.0	93.1	50.0	0.97 ± 0.19	48.3

[a] Background of Guangdong province (NEMC, 1990).
[b] The second grade of environmental quality standard of heavy metals except for Pb for farmland soil in China (MEPPRC, 1995b); Soil of green food quality standards (NY/T391-2000) for Pb (CGFDC, 1994).
[c] Single pollution index.
[d] Organic matter.
[e] Data not available.

As shown in Table 1, Mn was the dominant metal detected in the farmland soils in Sihui and Shunde among the target metals analyzed in the current study, which was consistent with the reference background of Guangdong Province (NEMC, 1990). On average, Mn accounted for more than 80% of the sum concentrations of metals in the soils, followed by Pb, Cu, Ni, As and Hg. In comparison, the concentrations of all the metals in soils from Shunde were significantly higher than those from Sihui ($p < .01$) (Table S5). Specifically, 52.9%, 41.2%, 66.2%, 79.4%, 44.1%, and 30.9% of the soil samples from Sihui exceeded the background values of As, Cu, Hg, Mn, Ni and Pb, respectively (Table 1 and Fig. S1). All the soil samples from Shunde contained metals exceeding the background values of As, Cu, Hg, Mn and Ni, and 93.1% of the soil samples contained Pb exceeding its background, suggesting the surface soil in Shunde has been polluted by heavy metals from anthropogenic sources. Shunde has a longer industrial history than Sihui, and the industrial activities, including appliances, furniture, coatings and electronics were important sources of heavy metal contamination in Shunde (Yang et al., 2007). Concentrations of heavy metals in the farmland soils from Sihui and Shunde were also compared to those from other regions in China (Table S6). Individually, concentrations of As and Hg in farmland soils from Shunde were higher than those in agricultural soils from most of the areas listed in Table S6, like Guangzhou (Li et al., 2009) and Taihang (Yang et al., 2009). Soil concentrations of Pb in Shunde were higher than those in agricultural soils from Taihang, Beijing and Gansu. On the contrary, soil concentrations of Cu and Ni in Shunde were comparable to those in agricultural soils from most of the areas (Table S6). The comparison indicated that heavy metal pollution has become an issue worthy of significant attention in Shunde. Rapid economic development has occurred in Shunde during the last thirty years, and different types of industry are booming in this area, like furniture and electronic factories (Wu et al., 2015). Factory discharges may contribute substantially to the heavy metal contamination in the surrounding soil. In addition, pesticide and fertilizer application in agricultural lands may enhance the accumulation of heavy metals in soil (Ignatowicz, 2008). Geographically, Shunde locates in the down-stream of Beijiang River, which originates from the Nanling metal ore belt and flows through a variety of metal mines in the upstream. Heavy metal pollution in water and sediment from Beijiang River has been reported in previous studies (He et al., 2014). Therefore, input of heavy metals from Beijiang River was another likely source of heavy metals in Shunde (Wu et al., 2015).

To quantitatively assess the pollution status of heavy metals in soils from Sihui and Shunde, their *PI* values were calculated using Eqn. (3) and the results are presented in Table 1. In total, only 1.5% of the soil samples from Sihui contained As, Cu, Hg and Ni and 4.41% of the soil samples contained Pb exceeding their thresholds. The mean *PI* values of the six metals in soils from Sihui were all below 1 (Table 1), suggesting that agricultural soil in Sihui was relatively clean (Table S7). On the contrary, 17.2%, 86.2%, 17.2% and 48.3% of the soil samples from Shunde contained Cu, Hg, Ni and Pb exceeding their thresholds (Table 1), respectively. The mean *PI* values of As, Cu, Ni and Pb were all below 1, while the *PI* of Hg was 1.51 (Table 1), indicating a slight pollution of Hg in agricultural soil in Shunde (Table S7). To date, most studies assessed the pollution status of soil-bound heavy metals based on total concentrations, which may overestimate their risk due to neglecting bioavailability.

3.2. Bioavailability of heavy metals in soil

Chemical fractionation analysis provides information on the origin, occurrence and biological availability of heavy metals (Adamoa et al., 2014). The first three fractions (F_1, F_2 and F_3) were considered as bioavailable fraction which was likely ready to be absorbed by plants (Zhao et al., 2011). The F_4, F_5 and F_6 were considered as potentially available fraction and could be absorbed by plants in strong acid medium. The F_7 was considered not available due to the entrapment by the crystal lattice of minerals (Zhao et al., 2011). In the current study, the F_1 and F_2 were combined as one fraction named exchangeable fraction ($F_{1,2}$) since the concentrations of heavy metals in F_1 were very low.

The fractionation of heavy metals in farmland soils from Sihui and Shunde are presented in Figs. 2 and S2 and Tables S8 and S9. In soils from Sihui, As, Cu, Ni and Pb were mostly in the residual

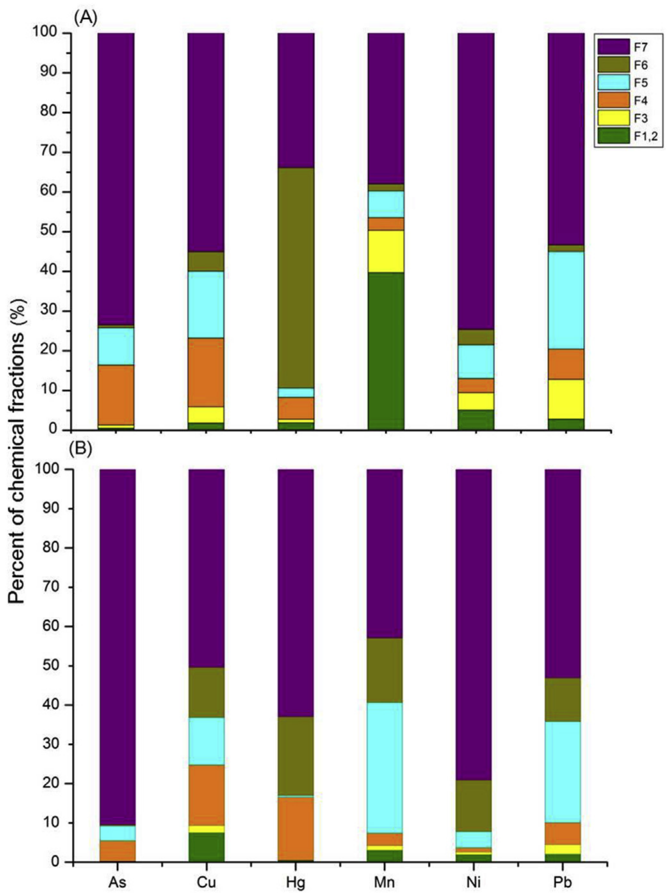

Fig. 2. Percent of heavy metals in each fraction of the soils from Sihui (A) and Shunde (B), South China. $F_{1,\ 2}$: exchangeable fraction; F_3: fraction bound to carbonate; F_4: fraction bound to humic acid; F_5: fraction bound to Fe-Mn oxides; F_6: fraction bound to organic matter; F_7: residual fraction.

fraction (F_7), accounting for 74.0% ± 50.2%, 54.8% ± 28.4%, 74.2% ± 56.4% and 53.4% ± 22.5% of the total heavy metal amounts, respectively, which were considered not bioavailable. The potentially bioavailable fractions (F_4, F_5 and F_6) of the four heavy metals accounted for 24.8% ± 22.0%, 39.3% ± 77.0%, 15.0% ± 9.19% and 33.3% ± 16.3%, respectively, and the percentages of bioavailable fraction ($F_{1,\ 2}$ and F_3) were less than 10% except for Pb (13.3% ± 13.4%). Most of Hg (62.3% ± 45.0%) in Sihui soils were considered potentially bioavailable (F_4, F_5 and F_6), and only 1.66% ± 0.28% was in bioavailable fraction. On the contrary, 48.9% ± 27.1% of Mn was in bioavailable fraction ($F_{1,\ 2}$ and F_3), followed by residual fraction (38.5% ± 23.8%) and potentially bioavailable fraction (12.6% ± 11.7%). In soils from Shunde, As, Cu, Hg, Ni and Pb were mainly found in the residual fraction (>50% on average), followed by potential bioavailable fraction, suggesting low bioavailability of the heavy metals in the soils. Regarding Mn, 54.6% ± 23.2% of the element was present in the potentially bioavailable fraction, and 41.1% ± 9.34% remained in the residual fraction.

The order of comparative mobility (%) for the heavy metals based on the sum of the bioavailable and potential bioavailable fraction was as follows: Hg > Mn > Cu > Pb > As > Ni in Sihui soils and Mn > Cu > Pb > Hg > Ni > As in Shunde soils. Specifically, high potential bioavailability and high total concentration of Mn in the soils (i.e. reaching 1054 mg/kg dry wt. in Shunde, Table 1) implied possible high uptake of this metal by crops. Although high percentage (63.3% on average) of Hg was detected in the potentially bioavailable fraction in soils from Sihui, it was unlikely to cause high risk because its total concentrations were low (Table 1). Therefore, both bioavailability and total concentration should be considered in risk assessment of heavy metals in soil (Liu and Sun, 2013; Zhang et al., 2010).

Spearman's correlation was applied to evaluate the influence of soil pH and OM on the chemical fractionation of heavy metals in soils (Table S10). Because the impact mechanism of soil properties on bioavailability of heavy metals varied among elements (Sungur et al., 2014), the correlations between soil properties and chemical fractionation were discussed separately for individual metals.

As: Arsenic in the F_6 (fraction bound to OM) in Sihui soil and F_4 (fraction bound to humic acid) in Shunde soil was positively ($r = 0.36$; $p < .05$) and negatively ($r = -0.41$; $p < .05$) correlated with soil pH, respectively (Table S10). No significant correlation was observed for other fractions. Soil pH was one of the most important factors affecting bioavailability of soil-bound As (Wei et al., 1999). Arsenic exists in the form of anions in soils with As (V) (e.g. $H_2AsO_4^-$ and $HAsO_4^{2-}$) being the dominated form and a small percentage of As (III) (e.g. $H_2AsO_3^-$ and $HAsO_3^{2-}$) (Wei et al., 1999). The arsenic anions are likely to be adsorbed by positively charged adsorbents, like amorphous iron and aluminum oxide. The adsorption of As (V) by positively charged adsorbents in soils decreases with increasing soil pH due to the increasing competition for positively charged adsorbent between OH^- and metal anions, and the adsorption of As (III) by positively charged adsorbents in soils increases with increasing soil pH (range: 4–9) (Wei et al., 1999). Therefore, increase of soil pH beyond 7.0 increases the mobility of As (V) in soils and subsequently enhances their toxicity and decrease the mobility of As (III), which is more toxic than As (V) (Cai et al., 2004). The narrow range of pH values in soils from Sihui and Shunde (Table 1) may be one reason for the insignificant correlation between soil pH and (potential) bioavailable fractions of As. Soil OM was not significantly correlated to the chemical fractionation of As in the soils from Sihui and Shunde.

Cu: A significantly negative correlation was observed between soil pH and concentrations of Cu in the $F_{1,\ 2}$ ($r = -0.42$; $p < .01$) in Sihui soils and F_3 in both Sihui ($r = -0.41$; $p < .05$) and Shunde soils ($r = -0.57$; $p < .01$), which was consistent with previous research that a significantly negative correlation was detected between soil pH and Cu in the bioavailable fractions (Cerqueira et al., 2011; Sungur et al., 2014). Decrease of soil pH decreases adsorption of dissolved Cu^{2+} by negative surfaces (e.g. clay minerals) and subsequently increased the mobility (Sungur et al., 2014). Cerqueira et al. (2011) found pH and Mn oxide contents were main soil properties influencing Cu^{2+} sorption, which was consistent with the current study. Therefore, soil acidification may increase mobility, bioavailability and potential toxicity of Cu in soils. In addition, significantly positive correlations were observed between the contents of OM and concentrations of Cu in the potentially bioavailable fraction, i.e. F_4 ($r = 0.40$; $p < .05$), F_5 ($r = 0.46$; $p < .01$) and F_6 ($r = 0.52$; $p < .05$) of Sihui soils, and F_5 ($r = 0.39$; $p < .05$) and F_6 ($r = 0.42$; $p < .05$) of Shunde soils.

Hg: A significantly negative correlation was observed between the soil pH and $F_{1,\ 2}$ ($r = -0.50$; $p < .01$) and F_6 ($r = -0.49$; $p < .01$) of Shunde soils. Soil OM content was negatively correlated with $F_{1,\ 2}$ ($r = -0.43$; $p < .05$) of Shunde soils, while was positively correlated with F_4 ($r = 0.58$; $p < .05$) and F_6 ($r = 0.37$; $p < .05$) of Sihui soils. The results showed that Hg had a tendency to accumulate in ion-exchangeable fraction ($F_{1,\ 2}$) in acidified soil with low OM content. In recent years, agricultural soil acidification has become a more and more serious issue in the PRD, which sped up the transformation of OM form of Hg to exchangeable form (Zhou et al., 2004).

Mn: A negative correlation was found between the soil pH and

$F_{1,2}$ of Mn in soils from Sihui ($r = -0.33$, $p < .05$) and Shunde ($r = -0.37$, $p < .05$). On the other hand, soil pH was positively correlated with F_3 ($r = 0.45$, $p < .01$) of Sihui soils and F_3 ($r = 0.59$, $p < .01$), F_4 ($r = 0.60$; $p < .01$) and F_5 ($r = 0.51$; $p < .01$) of Shunde soils. It has been reported that solubility of Mn in soil increased with decreasing pH values (Adriano, 2001), suggesting that the amount of Mn in the fractions of carbonate, humic acid and Fe-Mn oxides may decrease with decreasing soil pH and subsequently its bioavailability, i.e. the amount in the ion-exchangeable fraction may increase (Sungur et al., 2014). No significant correlation was found between Mn fractionation and OM contents in soil.

Ni: Significantly negative correlations were observed between soil pH values and $F_{1,2}$ of Ni in soils from Sihui ($r = -0.59$, $p < .01$) and Shunde ($r = -0.59$, $p < .01$). On the contrary, a significantly positive correlation was observed between pH and F_5 ($r = 0.77$; $p < .05$) of Ni in Shunde soils. Sungur et al. (2014) found that decrease of soil pH enhanced the desorption of Ni from soils and subsequently increased its bioavailability, which supported the negative correlations between pH and $F_{1,2}$ in the current study. Soil OM contents was not correlated with Ni fractionation in the soils.

Pb: Significantly negative correlations were observed between pH and $F_{1,2}$ of Pb in soils from Sihui ($r = -0.37$, $p < .05$) and Shunde ($r = -0.51$; $p < .01$). A significantly negative correlation was observed between pH and F_3 of Pb in soils from Shunde ($r = -0.49$; $p < .05$). The results were consistent with previous study that sorption of Pb^{2+} was significantly influenced by soil pH (Cerqueira et al., 2011). Lead fractionation in soils was not significantly correlated with OM contents in soil.

Overall, soil pH played an important role in influencing the chemical fractionation of heavy metals in farmland soils. In general, high pH values (pH > 8.0) promoted adsorption and precipitation while low pH (pH < 5.0) weakened the association of heavy metals to soil, and further changed their mobility in soil (Zhang et al., 2014). Soil properties influenced mobility and bioavailability of heavy metals in farmland soils and subsequently influenced their accumulation in crops from soil.

3.3. Accumulation of heavy metals from soil to crops

The concentrations of heavy metals in the edible part of vegetables and rice from Sihui and Shunde are reported in Table 2. The concentrations of As, Cu, Hg, Mn, Ni and Pb in lettuces from Sihui were 0.04 ± 0.05, 0.52 ± 0.18, 0.00094 ± 0.00027, 5.03 ± 5.97, 0.12 ± 0.04 and 0.20 ± 0.08 mg/kg dry wt., and were 0.09 ± 0.04, 2.53 ± 0.05, 0.0033 ± 0.0034, 10.1 ± 3.36, 0.26 ± 0.21, 2.05 ± 4.67 mg/kg dry wt. in rice from Sihui, respectively. Concentrations of the six heavy metals in rice were significantly higher than those in vegetables from Sihui (Table S11), suggesting higher accumulation potential of heavy metals in rice than lettuce. The six heavy metals were also detected in vegetables (Chinese cabbage, lettuce, rape, flowering cabbage and Chinese kale) from Shunde with respective concentrations at 0.03 ± 0.06, 0.35 ± 0.13, 0.006 ± 0.01, 3.81 ± 2.0, 0.18 ± 0.12, 0.07 ± 0.03 mg/kg dry wt. (Table 2). Concentrations of Cu and Pb in vegetables from Sihui were significantly higher than that from Shunde, and vice versa for Hg and Ni (Table S12). Overall, Mn was the dominant metal detected in the crops from Sihui and Shunde, followed by Cu. The two elements are essential elements for plants which may explain their easier uptake by crops than other elements (Adamoa et al., 2014; Sungur et al., 2014).

The concentrations of heavy metals in rice and vegetables from Sihui and Shunde were compared with those from other places in China and other countries (Table S13). In general, heavy metal concentrations in leaf-vegetables from Sihui and Shunde were similar to those from other places with the exception that Cu and Pb in vegetables from the current study area were significantly lower than that from Longtang, an e-waste recycling area in northern Guangdong province, China (Luo et al., 2011) and Turkey (Demirezen and Aksoy, 2006). Regarding heavy metal contamination in rice, concentrations of Cu in rice from Sihui were lower than that from Dabaoshan, a famous mining area in China (Zhuang et al., 2009), while Pb concentrations in rice from Sihui were significantly higher than that from Dabaoshan and Jiangsu in China (Cao et al., 2010; Zhuang et al., 2009).

The concentrations of heavy metals in rice and vegetables from Sihui and Shunde were compared to the food hygiene standards for vegetables and rice established by the Ministry of Health of the People's Republic of China (MHPRC, 2005). As shown in Table 2, the mean concentration of Pb (2.05 mg/kg) in rice from Sihui was 10 times higher than the acceptable limit for rice (0.2 mg/kg), and 75% of the rice samples exceeded this acceptable limit (MHPRC, 2005). The single pollution index (*PI*) of Pb in rice from Sihui was 10.3 ± 23.4, indicating serious pollution based on the pollution classification (Table S7). On the contrary, the mean *PI* values of other heavy metals in rice and vegetables were all below 1, with less than 20% of *PI* values being higher than 1. Therefore, heavy metals in rice and vegetables from Sihui and Shunde were within "clean" level, except for Pb in rice from Sihui. It is worthy of attention for human health due to long-term consumption of Pb contaminated rice in Sihui.

The Spearman's correlation between the concentrations of heavy metals in soil and crops are presented in Table S14. No significant correlation was observed between the total concentrations of heavy metals in soil and those in crops, suggesting that total soil concentration poorly predicted the accumulation potential of soil-bound heavy metals to crops (Sungur et al., 2014; Zhao et al., 2011). The correlation was further evaluated based on the chemical fractionation of heavy metals in soils. Significant correlations between bioavailable and/or potentially bioavailable fractions in soils and concentrations in crops were observed for As, Mn, Ni and Pb (Table S14). On the contrary, no significant correlation was observed for all the heavy metals in crops and OM fraction (F_6) or residual fraction (F_7) in soil. Furthermore, dendrograms were established by hierarchical cluster analysis (HCA) to determine the similarities between the concentrations of heavy metals in soils and those in crops (Fig. 3). The highest similarity was found between the bioavailable fraction ($F_{1,2,3}$) of As, Cu, Hg, Mn, Ni and Pb in soils and their concentrations in crops from Sihui and Shunde. Secondary similarity was observed between the potentially bioavailable fraction ($F_{4,5,6}$) of As, Ni, Pb and Hg in soils and their concentrations in crops. However, no remarkable similarity was found between the residual fraction (F_7) of heavy metals in soils and their concentrations in crops. Therefore, we concluded that bioavailable fraction ($F_{1,2,3}$) of heavy metals in soils were readily absorbed by crops, and potentially bioavailable fraction ($F_{4,5,6}$) could possibly be available for crops under certain circumstances (e.g. acid conditions) in a certain time period, while the residual fraction of heavy metals was hardly absorbed by crops due to the strong binding to crystal lattice of minerals. The conclusion was supported by previous studies (Zhong et al., 2008), which indicated that it is indispensable to incorporate bioavailability of heavy metals to more accurately assess their risk.

Soil-to-crop transfer factor (*TF*) is a key index to evaluate the human exposure to soil-bound heavy metals through the food chain (Adamoa et al., 2014). The *TF*s based on total concentration (TF_{total}) and bioavailable fractions (TF_{avail}) of the six heavy metals in soil from Sihui and Shunde are presented in Fig. 4. The higher the *TF* value is, the easier for a heavy metal to transfer from soil to crop. The order of TF_{total} values was Cu $(0.042 \pm 0.19) >$ Mn $(0.014 \pm 0.016) \approx$ Hg $(0.011 \pm 0.008) \approx$ Ni $(0.011 \pm 0.005) \geq$ Pb

Table 2
Heavy metal contents (mg/kg dry wt.) in crops from Sihui and Shunde, South China.

Metals	Minimum value	Maximum value	Mean value	Geometric mean value	Standard deviation	Food hygiene standards[a]	*PI*[b]	Percent of *PI* > 1 (%)
Vegetable from Sihui ($n = 35$)[c]								
As	0.01	0.19	0.04	0.03	0.05	0.05	0.88 ± 0.92	16.7
Cu	0.29	1.28	0.52	0.50	0.18	10.0	0.05 ± 0.02	0
Hg	0.0004	0.0018	0.00094	0.0009	0.00027	0.01	0.09 ± 0.03	0
Mn	0.84	27.17	5.03	3.41	5.97	/[e]	/	/
Ni	0.06	0.27	0.12	0.12	0.04	0.30	0.41 ± 0.15	0
Pb	0.09	0.43	0.20	0.18	0.08	0.30	0.65 ± 0.27	9.50
Rice from Sihui ($n = 31$)								
As	0.05	0.20	0.09	0.08	0.04	0.15	0.60 ± 0.24	3.60
Cu	1.71	3.60	2.53	2.49	0.50	10.0	0.25 ± 0.05	0
Hg	0.0013	0.018	0.0033	0.0025	0.0034	0.02	0.17 ± 0.17	0
Mn	5.59	24.4	10.0	9.63	3.36	/	/	/
Ni	0.08	0.77	0.26	0.20	0.21	0.30	0.86 ± 0.70	7.10
Pb	0.03	26.1	2.05	0.52	4.67	0.20	10.3 ± 23.4	75.0
Vegetable from Shunde ($n = 50$)[d]								
As	0.01	0.37	0.03	0.02	0.06	0.05	0.56 ± 1.15	5.77
Cu	0.14	0.64	0.35	0.32	0.13	10.0	0.04 ± 0.01	0
Hg	0.001	0.024	0.0057	0.0040	0.01	0.01	0.57 ± 0.61	13.5
Mn	0.96	8.09	3.81	3.31	2.00	/	/	/
Ni	0.04	0.59	0.18	0.14	0.12	0.30	0.59 ± 0.41	11.5
Pb	0.02	0.13	0.07	0.07	0.03	0.30	0.23 ± 0.09	0

[a] Standards of food hygiene for heavy metals were established by the Ministry of Health of the People's Republic of China (MHPRC, 2005).
[b] Single pollution index.
[c] The vegetables were leaf-lettuce.
[d] The vegetables included Chinese cabbage, lettuce, rape, leaf lettuce, flowering cabbage and Chinese kale.
[e] Data not available.

$(0.008 \pm 0.003) >$ As (0.005 ± 0.04) in Sihui, and the order in Shunde was Hg $(0.013 \pm 0.01) >$ Cu $(0.008 \pm 0.002) >$ Mn $(0.006 \pm 0.004) \geq$ Ni $(0.005 \pm 0.003) >$ Pb $(0.002 \pm 0.0006) \geq$ As (0.001 ± 0.002). As shown in Table S15, the TF_{total} values of As, Cu, Ni, Pb in Sihui was significantly higher than that in Shunde ($p < .01$), suggesting these heavy metals in Sihui soils were easier transferred to crops. Individually, Cu had significantly higher TF_{total} than Pb in both Sihui and Shunde (Table S16), which was consistent with previous studies (Cui et al., 2004; Luo et al., 2011) (Table S17). As discussed above, concentrations of heavy metals in crops were significantly correlated to their bioavailable, but not total concentrations in soils, suggesting that the *TF* values based on bioavailable concentrations may be better indicators to the transfer of soil-bound heavy metals in soil-crop system than that based on total concentrations (Wang et al., 2006).

In the current study, the bioavailable fraction ($F_{1, 2, 3}$) was used as the bioavailable concentration to calculate bioavailable *TF* values. The orders of TF_{avail} values were Cu ≥ As ≥ Hg > Ni ≥ Pb ≥ Mn in Sihui and Hg > As > Ni ≥ Mn ≥ Cu ≥ Pb in Shunde (Fig. 4), suggesting that the vegetables are high Cu/As/Hg–accumulator in Sihui and high Hg/As–accumulator in Shunde. The order of TF_{avail} and TF_{total} for some heavy metals was different due to various bioavailable fractions for different heavy metals. For example, soil-bound As in Sihui and Shunde was the least accumulative metal based on TF_{Total}, while it became the second most accumulative metal when bioavailable concentrations were used to calculate TF_{avail} (Fig. 4). Low bioavailability of As, i.e. $F_{1, 2, 3}$ was 1.16% in Sihui and 0.28% in Shunde, was the reason for the variation. Individually, the *TF* values for Cu, Hg and Pb differed significantly between Sihui and Shunde (Fig. 4), which possibly related to soil nutrient management and soil properties (Cui et al., 2004).

As shown in Figs. S3 and S4, TF_{total} and TF_{avail} values of the heavy metals decreased with increasing soil concentrations, which was consistent with the commonly applied exponential equation ($y = a \cdot x^b$) describing the correlation between *TF* values and the corresponding soil concentrations (Wang et al., 2006; Zhao et al., 2011). The correlation suggested that heavy metal uptake by vegetables was not solely controlled by their soil concentrations, and plant resistance mechanism may be an important reason for protecting vegetables from high accumulation of heavy metals in food chain transfer (Mullera et al., 2000; Zhao et al., 2011).

4. Conclusions

The current study provided new data concerning heavy metal pollution and bioavailability in soil-crop system in regional farmlands from Sihui and Shunde, South China. The farmland soils were within clean to slightly polluted by Hg in the study area. The vegetables from Sihui and Shunde were considered "clean" with heavy metal concentrations lower than the food hygiene standards, however, the rice grain from Sihui was heavily polluted by Pb. Soil-to-crop transfer factors indicated that Cu, As and Hg in the soils were easier accumulated in the vegetables than other heavy metals, calling for further study on their human health exposure via the food chain.

Bioavailability of heavy metals in the soils was evaluated by measuring their fractionation. Soil pH was a critical factor influencing the bioavailability of soil-bound heavy metals, i.e. bioavailable fractions of Cu, Hg, Ni, Mn and Pb increased with decreasing pH. Bioavailable instead of total concentrations of heavy metals in soils were significantly correlated to the accumulated metals in the crops, suggesting that bioavailable fractions were the fractions ready to be absorbed by crops and bioavailability should be incorporated in risk assessment of soil-bound heavy metals. Based on bioavailable soil-to-crop *TF*s, Cu, As and Hg in soils were easier transported to the vegetables, calling for further human health assessment by consuming the contaminated crops. Individually, the *TF*s for Cu, Hg and Pb were significantly differed between Sihui and Shunde probably due to difference in soil nutrient and properties. Furthermore, the *TF*s values decreased with increasing heavy metal concentrations in the soils, indicating that soil-to-crop transfer process was not solely controlled by soil concentrations, but plant resistance mechanism protected plants from dramatically accumulating heavy metals from soils. To better regulate crop planting

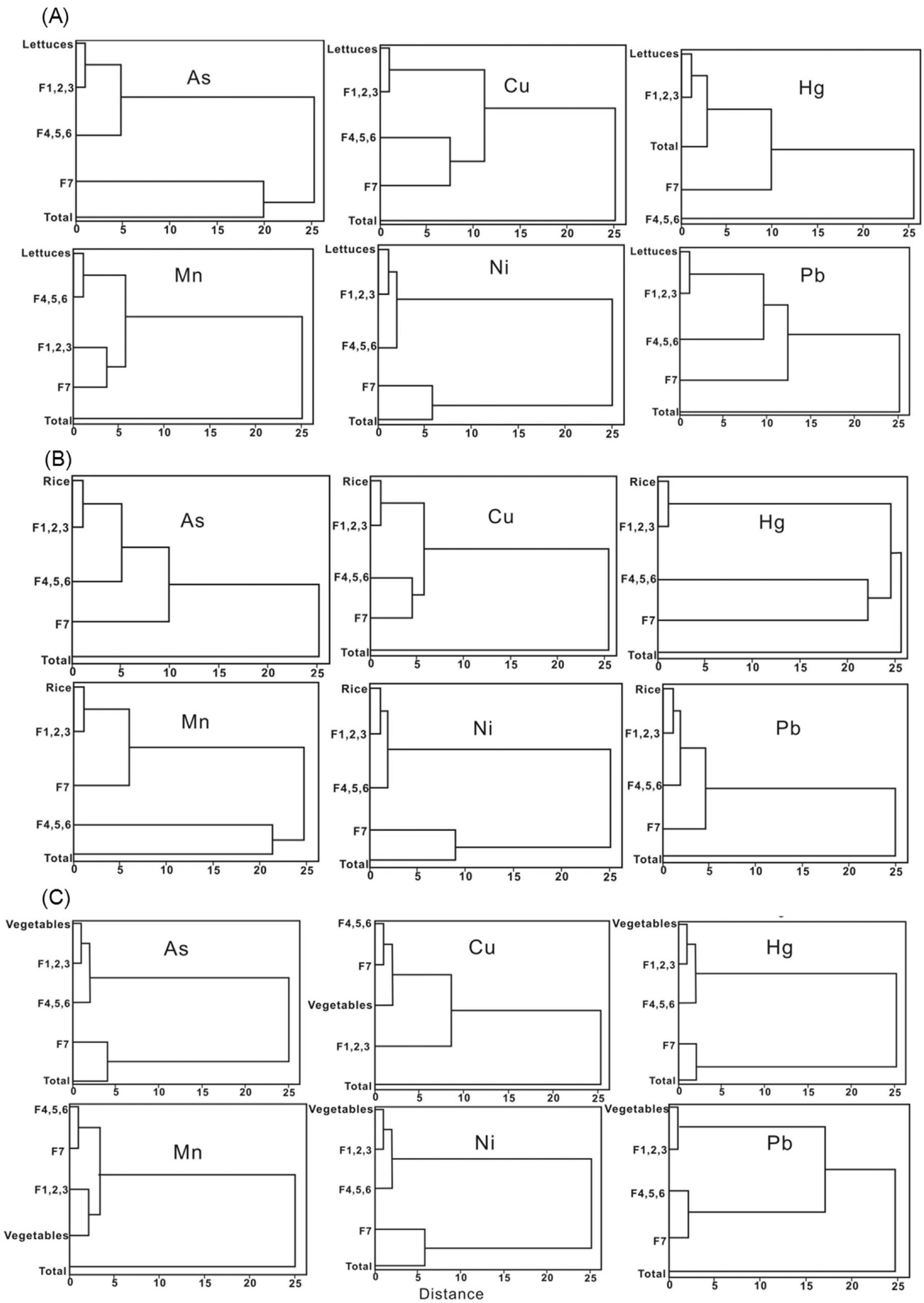

Fig. 3. Dendrograms of heavy metals in the soils and the crops, i.e. leaf lettuces from Sihui (A), rice from Sihui (B) and vegetables from Shunde (C).

and consumption, more research is required to investigate the influence mechanisms of bioavailability and plant resistance on the soil-to-crop transfer process and establish reliable correlations between soil concentrations and *TF*s.

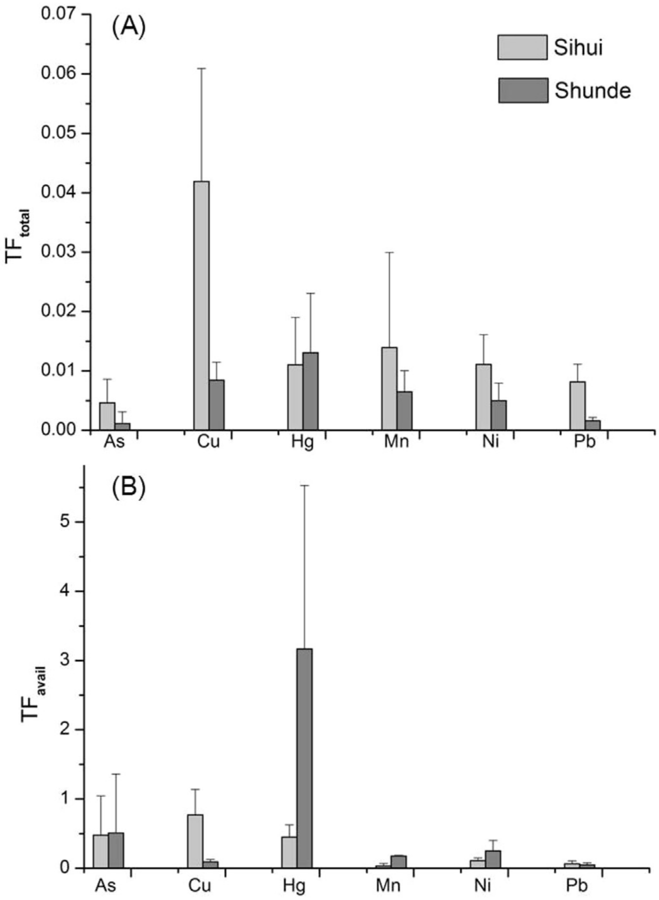

Fig. 4. Soil-to-plant transfer factors (*TF*) based on total (A) and bioavailable (B) concentrations of heavy metals in soils from Sihui and Shunde, South China.

Conflicts of interest

There are no conflicts of interest to declare.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at https://doi.org/10.1016/j.envpol.2017.12.106.

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