Environmental Science Processes & Impacts

Accepted Manuscript

ROYAL SOCIETY OF CHEMISTRY

rsc.li/process-impacts

Environmental Impact

Concerns have been raised over increasing potential human health risks owing to food safety along with rapid industrialization and urbanization in the Pearl River Delta (PRD) region. However, it is highly difficult to remediate low-pollution agricultural soils at a large scale using engineering methods. Our idea is that geochemical methodology may provide an effective way to decrease agricultural pollution and improve food safety. Therefore, the factors involved in heavy metal accumulation under field conditions need to be deeply understood in order to determine critical geochemistry factors, and find effective ways to inhibit the entry of heavy metals into food chains. On the view of geochemistry, increased extractable Fe contents and decreased clay contents help to alleviate metal pollution in balsam pear and cowpea. Thus, it is possible to reduce metal contents and the potential risks of consuming vegetables using geochemical methodology under field conditions at a large scale. The findings of this research will provide important guidelines for agricultural environmental administration in the PRD region.

Heavy metal accumulation in balsam pear and cowpea related to the geochemical factors of variable-charge soils in the Pearl River Delta, South China

Chun-Ying Chang[a,b,d] · Xiang-Hua Xu[b] · Chuan-Ping Liu[b] · Shu-Yi Li[b] · Xin-Rong Liao[b] ·Jun Dong[c] and Fang-Bai Li [b,*]

[a] *Guangdong Public Laboratory of Environmental Science and Technology, Guangdong Institute of Eco-Environmental and Soil Sciences, Guangzhou 510650, China*

[b] *Guangzhou Institute of Geochemistry, Chinese Academy of Sciences, Guangzhou 510640, China*

[c] *Zhongshan Institute, Univeristy of Electronic Science and Technology of China, Zhongshan, 528403, China*

[d] *Graduate University of Chinese Academy of Sciences, Beijing 100049, China*

*Corresponding author:

Fangbai Li (Guangdong Institute of Eco-Environmental and Soil Sciences)

Address: 808 Tianyuan Road, Guangzhou 510650, P. R. China

Tel: +86 20 87024721; fax: +86 20 87024123

E-mail: cefbli@soil.gd.cn

Abstract

Variable-charge (v-c) soils in subtropical areas contain considerable amounts of iron/aluminum (Fe/Al) oxides that can strongly influence the fate of heavy metals in agricultural ecosystems. However, the relationship between heavy metal accumulation in vegetables and the geochemical factors associated with v-c soils in subtropical region remains unknown. The present study investigated heavy metal accumulation under field conditions in the Pearl River Delta (PRD) by measuring the contents of 8 heavy metals (zinc (Zn), arsenic (As), copper (Cu), mercury (Hg), lead (Pb), chromium (Cr), nickel (Ni) and cadmium (Cd)) in 43 pairs of v-c soil and vegetable (balsam pear and cowpea) samples. Soil physicochemical properties including pH, texture, organic matter and oxide minerals (Fe_2O_3, SiO_2, Al_2O_3, CaO, MgO, K_2O and Na_2O) were also analyzed. Heavy metal accumulation from soil to vegetables was assessed based on the bioconcentration factors (BCFs). The results showed that soil extractable Fe, oxide minerals and chemical weathering indices of v-c soils strongly affected heavy metal accumulation, whereas the contents of Zn, Cu, Cr and Ni in vegetables were strongly affected by soil clay content. Significant correlations were found between the BCFs of heavy metals and oxide minerals. However, no significant relationship was found between pH and heavy metal accumulation (except for Cu) in balsam pear and cowpea. Correlation analyses showed that a lower oxalate/DCB-extractable Fe content might indicate greater heavy metal (Zn, Cu, Hg, Cr and Ni) accumulation in vegetables. Therefore, it can be deduced that oxalate/DCB-extractable Fe content is a critical geochemical factor that determines the bioavailability of heavy metals and that iron biogeochemical cycles play vital roles in the fate of heavy metals in vegetable fields in this area. These findings provide new insights into the behaviors and fate of heavy metals in subtropical v-c soils and can be used to develop possible guidelines for vegetable safety management.

Keywords Variable-charge soil · Vegetable · Heavy metal · Iron species · Food safety

Abbreviations:

PRD, Pearl River Delta; BCFs, Bioconcentration factors; p-c soil, permanent-charge soil; v-c soil, variable-charge soil; Fe_{ox}, oxalic acid-ammonium oxalate extractable Fe; Fe_p, pyrophosphate extractable Fe; Fe_d, citrate - bicarbonate - dithionite extractable Fe.

1. Introduction

Great attention has been paid to decreases in agricultural products safety,[1, 2] and increases in the incidence of chronic diseases such as deformity and cancer arising from soil contaminants entering the food chain.[3, 4] Therefore, it is of significant importance to assess the extent of heavy metal accumulation from soil into plants such as fruits and vegetables and the factors that are critical for this process. Some studies have examined heavy metal accumulation in rice or vegetables, as affected by a variety of soil physicochemical properties including pH, soil organic matter (SOM) content, oxidation-reduction status (Eh), cation exchange capacity (CEC) and oxide mineral contents.[5-8] It was consistently concluded that higher soil pH and SOM content, lower salinity and the presence of clay–rich soils often enhance soil ability to retain cationic metals and hence reduce the uptake of metals by plants.[9]

As far as we know, previous studies have mainly examined heavy metal accumulation in permanent-charge (p-c) soils, in which permanent charges result from isomorphous substitution of the clay mineral crystal layer; however, heavy metal accumulation in variable-charge (v-c) soils has been rarely studied.[10, 11] Soils in the Pearl River Delta (PRD) region, located in a subtropical zone, are characteristic of variable charge soils.[10] Compared to p-c soils, v-c soils have higher variable surface charge and abundant Fe/Al oxides. Studies of heavy metal accumulation in v-c soils mainly focused on their electrochemical characteristics, surface chemistry and metal adsorption behaviors.[12, 13] In v-c soils, surface charge and aging are closely associated with the levels of clay minerals, extractable Fe fractions and soil weathering indices.[13-15] As the minerals in parent material rocks are exposed to the atmosphere and water, chemical weathering occurs, and elements contained within can migrate from the minerals to plants.[16] Weathering controls the fate of mineral components in subtropical areas, and can affect soil chemical composition and elements that are involved in numerous reactions in soil solution and in plant tissues.[17, 18] Weathering indices are closely associated with soil physicochemical properties, which can further affect the concentration and activity of adsorbed Fe.[19, 20] Under enhanced weathering conditions, alkaline-earth elements (calcium (Ca), magnesium (Mg), potassium (K) and sodium (Na)) can easily be leached by water in the form of soluble carbonates and sulfates, whereas weakly migrating elements (silicon (Si), Al, Fe and heavy metals) can either be removed from the reaction site in soil solutions or incorporated through conversion into water-insoluble (hydr)oxides.[16, 18, 21] Therefore, weathering processes can regulate the bioavailability of elements, including heavy metals, in the soil. In addition, as indicated by previous studies,[20, 22] highly abundant iron oxides are the most important and active components controlling soil physicochemical and biological processes in subtropical regions. Based above, it is hypothesized that the accumulation of heavy metals in vegetables might be closely related to soil physicochemical properties, extractable Fe oxide contents and chemical weathering indices of v-c soils.

To verify the above hypothesis, the objectives of our study are as follows: (1) to assess the accumulation of 8 heavy metals (Zn, As, Cu, Hg, Pb, Cr, Ni and Cd) from soil into two representative subtropical fruiting vegetables (balsam pear and cowpea) in the PRD agricultural region; (2) to determine the major geochemical factors that influence metal enrichment in vegetables; and (3) to identify the major metal sources in this area using Pearson correlation analysis and principal component analysis (PCA). The results will offer guidelines for regional environmental management and sustainable agricultural production.

2. Materials and methods

2.1. Study area and sampling strategy

The PRD region covers an area of 54,733 km^2 in South China, including 13,357 km^2 of agricultural land and 4,829 km^2 of vegetable production.[23] The PRD region is located in a subtropical area in which the soils (classified as v-c soils) contain less Si and abundant Fe/Al due to active desilicification and allitization.[24, 25]

During September - November in 2011, 43 pairs of soil and vegetable samples were collected from agricultural lands and large vegetable farms in the PRD region (Fig. 1). Two kinds of vegetables, balsam pear (*Momordica charantia* L.) and cowpea (*Vigna unguiculata* (Linn.) Walp), were collected during the harvest period. Soil samples were taken from the 0–20 cm surface layer using a bamboo shovel and thoroughly mixed separately. All samples were sealed in polyethylene bags and immediately transported to the laboratory within 6 h of collection.

2.2 Chemical analyses

After large plant debris and impurities were manually removed, the soil samples were air dried at room temperature, ground using an agate mortar, and sieved to 80 mesh (0.2 mm). For the vegetable samples, decayed and withered tissues were manually removed; the edible parts were washed with tap water to remove surface dirt, repeatedly rinsed in deionized water and dried at 60°C to a constant weight. Dry vegetable samples were crushed using a wooden hammer in a carnelian mortar and then passed through an 80-mesh sieve.

Soil pH was measured in soil slurries at a soil-to-water ratio of 1:2.5 using a calibrated PHS-3C pH meter (Sartorius, China). Soil organic matter (SOM) content was determined using the $K_2Cr_2O_7$–H_2SO_4 oxidation method,[26] and soil texture (clay <0.002 mm, silt 0.05–0.002 mm and sand 2.00–0.05 mm) was assessed using the pipette method.[27]

Different fractions of Fe (oxalate-extractable, Fe_{ox}; pyrophosphate-extractable, Fe_p; and citrate - bicarbonate - dithionite-extractable, Fe_d) were extracted using oxalic acid-ammonium oxalate (pH 3.2), sodium pyrophosphate (pH 8.5), and citrate-bicarbonate-dithionite buffer solutions, respectively.[28] The Fe content of the extract solutions was determined using a WFX-130 flame atomic absorption spectrophotometer (Braic, China).

Total Fe, Al, Ca, Mg, K and Na contents were measured by Inductively Coupled Plasma-Atomic Emission Spectrometry (Optima 3300DV, Perkin Elmer, USA) after digestion with HNO_3-$HClO_4$-HF.[26] Total Si content was determined using the silicon-molybdenum blue colorimetric method and an UV spectrophotometer (TU-800, Beijing). Total Fe, Si, Al, Ca, Mg, K and Na contents of the soils were recalculated and are reported as the equivalent oxide contents of Fe_2O_3, SiO_2, Al_2O_3, CaO, MgO, K_2O and Na_2O, respectively. Soil weathering indices are presented as the molecular ratios SiO_2/Al_2O_3 (WI-1), Al_2O_3/Fe_2O_3 (WI-2), (Al_2O_3+ Fe_2O_3)/ SiO_2 (WI-3), (K_2O+Na_2O)/Al_2O_3 (WI-4) and (K_2O+Na_2O+CaO+MgO)/Al_2O_3 (WI-5); these ratios were derived from the data obtained regarding the total Fe, Si, Al, Ca, Mg, K and Na contents.[17, 29]

The contents of heavy metals in the soil and vegetable samples were determined according to the methods of Rasmussen et al. (2001).[30] Briefly, 600 mg of air-dried soil was mixed with 6 ml of concentrated HNO_3-$HClO_4$ (87:13, v/v) and 6 ml of concentrated HF (mass fraction>40%). The mixture was digested and then dissolved in 2% HCl. Vegetable samples were digested in a mixture of HNO_3-$HClO_4$-H_2O_2 (87:13:10, v/v/v). The Hg and As contents in the digest solutions were determined using an atomic fluorescence morphological analyzer (SA-10, Titan, Beijing). Pb, Zn, Cu, Ni and Cr contents were determined using a flame atomic adsorption spectrophotometer (WFX-130, Braic, China), and Cd contents were determined using a graphite furnace atomic absorption spectrophotometer (Z-2700, Hitachi, Japan). Standard reference materials for soil (GBW07428 (GSS-14) and GBW07429 (GSS-15)) and citrus leaves (GBW10020 (GSB-11)) were assayed during sample analysis for quality control. Each batch of samples was run after ten determinations to calibrate the instrument and monitor the potential sample contamination during analysis. The results for GSS-14, GSS-15 and GSB-11 were found to be 91%, 92% and 88% of the certified value, respectively, and with the data indication a low error of typically less than 15%. Reagent blanks were included to ensure precise detection

(<5% precision).

2.3 Data analyses

The bioconcentration factor (BCF) is an important quantitative indicator for crop contamination and has commonly been used to estimate metal transfer from soils to plants.[31, 32] BCF can be calculated as follows:

$$BCF = \frac{C_{vegetable}}{C_{soil}}$$

where $C_{vegetable}$ is the total metal content in the vegetable (mg kg^{-1} dw) and C_{soil} is the corresponding metal content in the soil where the vegetable was grown (mg kg^{-1}).

Statistical analyses were performed using SPSS 13.0. Charts and graphs were prepared using Microsoft Excel 2011 and Origin V8.1. An attempt was made to investigate the main geochemical factors that influence metal enrichment in vegetables and to identify potential metal sources using two-tailed Pearson correlation analyses (significance level: $p<0.05$) and PCA. PCA was performed using a Varimax rotation method with Kaiser normalization, and the heavy metal contents of soils and vegetables, soil physicochemical properties, and soil major element contents were used as input data.

3 Results

3.1 Heavy metal distribution of soils and vegetables

The soils examined were typical v-c soils, as indicated by their low pH, high clay contents and relatively high Fe and Al contents (Table 1). Specifically, soil pH was acidic to slightly alkaline (5.05–7.38 for balsam pear soils and 4.70–7.12 for cowpea soils). The SOM contents of the balsam pear and cowpea soils largely varied between 14.1–48.6 g kg^{-1} and 6.67–42.7 g kg^{-1}, respectively. The surface soils were loam or loamy clay. The Fe_2O_3 and Al_2O_3 contents averaged approximately 4% and 15%, respectively. The F_{ox}, F_p and F_d contents clearly differed between the balsam pear and cowpea soils.

The content ranges of Zn, As, Cu, Hg, Pb, Cr, Ni and Cd in the balsam pear soils were 29.3–146, 5.29–45.9, 8.25–45.6, 0.12–1.66, 9.78–56.0, 12.1–73.2, 1.65–35.1 and 0.06–1.73 mg kg^{-1}, respectively (Table 2). The corresponding mean metal contents in the balsam pear soils descended in the order Zn>Cu>Pb>Ni>Cr>As>Cd>Hg. Compared to balsam pear soils, cowpea soils exhibited relatively low contents of heavy metals except for Cr and Ni, and the order of metal contents descended in the order Zn>Cu>Pb>Ni>Cr>Hg>Cd>As.

The metal contents found in the vegetables were very low relative to those found in the soils (Table 2). The metal contents of balsam pear and cowpea tissues generally descended in the order Zn>Cu>Ni>Cr>Pb>As>Cd>Hg. This trend was similar to that observed in soils, except that Pb occupied a higher position in soils compared with that in vegetables. The content ranges of Zn, As, Cu, Hg, Pb, Cr, Ni and Cd in balsam pear were 18.4–74.0, 0–0.55, 4.64–11.3, 0–0.06, 0.112–0.837, 0–3.48, 0.470–6.32 and 0-0.23 mg kg^{-1}, respectively, and those of cowpea were 28.4–59.4, 0–0.08, 6.22–21.7, 0–0.03, 0.047–0.882, 0–2.64, 0.99–3.91 and 0–0.08 mg kg^{-1}, respectively.

3.2 Bioconcentration factors

The mean BCFs of eight metals were comparable between the two vegetables (without significant differences). The BCFs of Zn, As, Cu, Hg, Pb, Cr, Ni and Cd ranged between 0.182–2.21, 0–0.019, 0.150–0.866, 0.002–0.253, 0.004–0.050, 0–0.172, 0.023–0.887 and 0.002–0.418 for balsam pear, respectively, and between 0.299–2.564, 0–0.011, 0.169–2.59, 0.003–1.32, 0.002–0.036, 0.0001–0.160, 0.063–0.886 and 0–0.374 for cowpea, respectively (the BCFs of cowpea were relatively high for Zn and Cu and low for As) (Fig. 2). The mean BCFs of Zn, As, Cu, Hg, Pb, Cr, Ni and Cd in balsam pear were 0.584, 0.004, 0.495, 0.061, 0.020, 0.041, 0.191 and 0.139, respectively, and those for cowpea were 0.843, 0.002, 0.737, 0.139, 0.019, 0.038, 0.227 and 0.081, respectively. The BCFs for eight metals descended in the order Zn>Cu>Ni>Cd and Hg>Cr>Pb>As (Cd>Hg for balsam pear; Hg>Cd for cowpea). In general, Zn, Cu, Hg and Ni were more easily transferred from soil to cowpeas than from soil to balsam pears, whereas Cd was more easily accumulated in balsam pear than in cowpeas.

3.3 The relationship between metal BCFs and soil geochemical factors

Table 3 shows that the BCF of Cu was significantly positively correlated with soil pH (r=0.311) (p<0.01), and the SOM content was significantly negatively correlated with the BCFs of Zn, Cu and Ni (r=-0.501, -0.344 and -0.428, respectively) (p<0.01). The BCFs of Zn, Cu, Cr and Ni were negatively correlated with clay content (p<0.05) while positively correlated with sand content (p<0.05). These results confirmed that heavy metals such as Zn, Cu, Cr and Ni were more easily absorbed onto the finer particles, due to strong interactions between the heavy metal ions and clay minerals via hydroxylation and hydration.[33, 34]

The BCFs of Zn, Cu, Cr and Ni were significantly negatively correlated with Fe_d content (r=-0.321 to -0.518), and the Zn and Cr BCFs were significantly negatively correlations with Fe_{ox} content (r=-0.395 and -0.503). The BCF of Hg was the only BCF to be significantly associated with Fe_p content (r=-0.330) ($p<0.05$).

The BCFs of heavy metals generally exhibited significant correlations with the contents of mineral oxides (except Na_2O); negative correlations existed with Fe_2O_3, Al_2O_3, CaO and MgO contents ($p<0.05$), and positive correlations existed with SiO_2 and K_2O contents ($p<0.05$). The BCF of Zn was significantly negatively correlated with Fe_2O_3, Al_2O_3, CaO and MgO contents (r=-0.468，-0.550，-0.420, and -0.447, respectively) and positively correlated with SiO_2 and K_2O contents (r=0.605 and 0.427, respectively) ($p<0.01$). The BCF of Cu was significantly correlated with Fe_2O_3, SiO_2 and K_2O contents (r=-0.313, 0.345 and 0.407, respectively). The BCFs of Cr and Ni were negatively correlated with Fe_2O_3 and MgO contents and positively correlated with SiO_2 and K_2O contents (Table 3). The BCFs of Pb and Cd were significantly negatively correlated with CaO (r=-0.413 and -0.410, respectively) ($p<0.01$). Arsenic and Hg enrichment were not correlated with any oxides tested in this study.

Of the five common weathering indices, WI-1 to WI-3 reflected the degree of desilicification and allitization, and WI-4 to WI-5 reflected the degree of salt leaching. As chemical weathering became more intense, the values of weathering indices decreased. The results of the correlation analysis (Table 3) show that WI-1 was positively correlated with the BCFs of Zn (r=0.615) and Ni (r=0.345); WI-2 was positively correlated with the BCF of Cr (r=0.510); WI-4 was positively correlated with the BCFs of Zn (*r*=0.526), Cu (*r*=0.442), Cr (*r*=0.365) and Ni (*r*=0.368); the BCFs of Zn were positively correlated with WI-5 (0.339); the BCFs of Zn (-0.624) and Ni (-0.336) were negatively correlated with WI-3. The BCFs of As, Hg, Pb and Cd exhibited no significant relationships with any of the 5 soil weathering indices examined.

3.4 Major source identification of metals

Pearson correlation analysis (Table 4) showed that the contents of heavy metals (Zn, Cu, Cr, Ni and Cd) and major elements (Fe_2O_3, SiO_2, MgO and CaO) were significantly correlated (p<0.01). Hg and Pb contents exhibited positive correlation (*r*=0.465), and both of these contents were correlated with Zn, Cd and CaO contents (*r*=0.405–0.671). The content of Al was significantly correlated with those of Zn, Cr and Ni (p<0.01). K_2O and Na_2O contents were both correlated only with Hg content (p<0.05). In general, 3 clusters of relationships were present between trace heavy metals and major elements in the vegetable soils tested. The first group contains the metals Zn, Cu, Cr, Ni and Cd; the second group includes Hg and Pb; the third group contains only As.

PCA of heavy metals for soil elements yielded three principal components (PCs) with eigenvalues >1. These three components described 86.1% of the total variance. The elements assembled around each factor with significant loadings and formed 4 main element groups indicative of 4 diverse sources (Table 5). The first principal component (PC1) explains 52.1% of the total variance. PC1 loaded heavily on Zn (0.897), Cu (0.834), Pb (0.621), Cr (0.813), Ni (0.824) and Cd (0.728), and loaded moderately on As (0.392) and Hg (0.322). The second principal component (PC2) was dominated by Hg (0.652), Pb (0.663) and As (0.404), accounting for 21.2% of the total variance. The third principal component (PC3) represented 12.9% of the total variance and was dominated by As (0.783) and associated negatively by Hg (-0.600).

4 Discussion

4.1 Current metals enrichment in studied vegetables in the PRD

In this study, the mean contents of Zn, As, Cu, Hg, Pb, Cr, Ni and Cd measured in soil samples were all greater than their background values in Guangdong province.[35] However, only the mean Cd content exceeded the Grade II national standard in China (GB 15618-1995, Chinese Environmental Quality Standard for soils). Individually, 6 samples (14.0%) exceeded the levels of Grade II of GB 15618-1995 for As, 11 samples (25.6%) exceeded levels for Hg, 1 sample (2.33%) exceeded acceptable levels for Ni and 21 samples (48.8%) exceeded levels for Cd (Table 2). These results demonstrated that Cd, Hg and As are the dominant metal pollutants, and the levels of these heavy metals are primarily due to increasing discharges to soils in the PRD arising from the recent rapid industrialization, agricultural intensification and urbanization.[34, 36]

The mean soil metal contents (except for Pb) reported here all exceeded the results reported by Cai et al. (2012)[37] in Huizhou, Guangdong Province but were lower than the average contents of Zn (84.7 mg kg^{-1}), Cu (33.0 mg kg^{-1}), Pb (40.0 mg kg^{-1}), Cr (71.4 mg kg^{-1}), Ni (21.2 mg kg^{-1}) and Cd (0.58 mg kg^{-1}) reported by Wong et al. (2002)[38] in crop soils in the PRD region. Such differences might be attributable to variation in the extent of metal pollution at the sampling sites: Cai et al. (2012)[37] and Wong et al. (2002)[38] obtained samples from less polluted soil in large-scale vegetable farm and heavily polluted areas in the PRD region, respectively.

For correction of water content (ranged between 79.8% to 92.3%), the mean contents of Cu (9.73 mg kg^{-1}), Pb (0.453 mg kg^{-1}) and Zn (42.2 mg kg^{-1}) measured in cowpea were expressed on a fresh weight basis, i.e., 1.19, 0.068 and 6.33 mg kg^{-1} fw, respectively. These values were similar to those reported by Hu et al. (2013)[39] from agricultural farms in Guangzhou, Guangdong Province. On the other hand, the mean contents of Cd (1.18), Cu (10.9), Pb (1.95) and Zn (49.6) in lettuce (*Lactuca sativa* L.) from Dongguan and Guangzhou (reported by Luo et al., 2012)[40] were much higher than those observed in this study (Table 2). It is possible that the rapid growth and high transpiration rates of leafy vegetables favor the root uptake of metals and that the broad leaves of leafy vegetables increase plant susceptibility to physical contamination by dust from the soil and the splashing of rainwater.[41]

In the balsam pear and cowpea samples measured here, the BCFs for Pb and Cd were lower and the BCFs for Cu and Zn were higher than those reported in cabbage and lettuce by Luo et al. (2012) in East River areas of Guangdong Province.[42] This is consistent with previously reported BCFs for Pb and Cd in the sense that the extent of metal enrichment in vegetables is higher in leaf vegetables than in tubers and fruit vegetables.[43] The BCFs of Cu and Zn were higher in balsam pear and cowpea than in leaf vegetables (cabbage and lettuce) studied by Luo et al. (2012), [42] possibly because

Cu and Zn are plant essential elements and can easily accumulate in plant tissues.[44-48]

4.2 Critical geochemical factors controlling metal enrichment in fruiting vegetables

Pearson correlation analysis showed that there was a positive correlation between the BCF of Cu and soil pH (Table 3). This trend was opposite to a previous finding by Zeng et al. (2011)[49] that Cu bioavailability was negatively correlated with soil pH in rice, which was likely due to competitive adsorption between H^+ and metal ions. Presently, the effect of pH on the bioavailability of heavy metals in soil and their accumulation in vegetables remains controversial and needs further examination.[50]

The significant correlation observed between Fe_d content and the BCFs of Zn, Cu, Cr and Ni (Table 3) indicates that Fe_d plays a role in immobilizing these metals in soils and then reducing their bioavailability in the PRD area. Fe_d mainly consists of amorphous iron oxides and crystalline iron oxides other than those that constitute layered-silicate, including active Fe (hydr)oxides. Fe_d might influence the bioavailability of heavy metals by mediating the reduction of Fe(III) to Fe(II) and the adsorption of Fe oxides, thereby stabilizing the metals in soils and consequently reducing plant uptake. In addition, iron oxides and extractable Fe fractions are important soil colloids that are involved in heavy metal immobilization and solid-liquid distribution.[51-53] Overall, extractable Fe (Fe_{ox}, Fe_p and Fe_d) had clear effects on the bioavailability of heavy metals; the redox and solid-liquid distribution varied depending on metal species, although similar trends were seen among them.

Absorption-desorption and oxidation-reduction often occur on the surface of soil oxides (e.g., Al_2O_3), and these processes are considered important mechanisms for heavy metal transformation and migration in soil environments. Soil oxides (e.g., Fe_2O_3, Al_2O_3, and SiO_2) are good adsorbents for heavy metals, and their redox cycle can lead to changes in heavy metal valence and bioavailability.[53] In general, the BCFs of heavy metals were significantly correlated with six soil oxides (except Na_2O); among these, Fe_2O_3, Al_2O_3, CaO and MgO exhibited negative correlations with BCFs and positive correlations with SiO_2 and K_2O. These findings show that the BCFs decreased with increased Fe, Al, Ca and Mg contents. With higher contents of Fe, Al, Ca and Mg in soils, less heavy metal is transferred into vegetables. Conversely, the BCFs of heavy metals increased with increasing soil Si and K contents. That is, at higher Si and K contents, more heavy metals are absorbed by vegetables. A possible reason is that Fe and Al oxides are the sorption center of heavy metals in soil. Sorption by the oxides or redox reactions may reduce the motility of metals and thus reduce their bioavailability, further reducing plant uptake. The effect of Si and K on metal uptake by vegetables is an apparent characteristic caused by Si depletion and Al enrichment in v-c soils and may indirectly reflect the interaction between metals and Fe/Al.[54]

Soil chemical weathering is essentially the interaction of water and rock. Therefore, the properties of soil pore water (e.g., pH, redox potential, and inorganic or organic anion contents) greatly affect the activity of heavy metals during weathering.[55, 56] CO_3^{2-}, HCO_3^-, HPO_4^{2-}, PO_4^{3-}, SO_4^{2-} and other inorganic anions present in soil solutions can easily bind heavy metals to form hydrates, thereby affecting the fate of heavy metals.[53] The significant correlation observed between Zn, Cr, and Ni with WI-1 and WI-2 in this study indicates that the metal bioavailability decreased with decreasing chemical weathering extent, as reflected by the decreasing WI-1 and WI-2 values, and that chemical weathering affects the reduction of Fe and Al in soils.[54, 57] The lack of significant correlation between the As, Hg, Pb and Cd with 5 soil weathering indices might be because anthropogenic discharge masks their associations with soil chemical weathering.

4.3 Metal source identification

The PCA results could be used to group the heavy metals in the soil into three classes. Zn, Cu, Pb, Cr, Ni and Cd constituted a highly related group (PC1); Hg, Pb and As constituted the second related group (PC2), and the third group included only As (PC3). These groups indicated the origins or controlling factors of the different heavy metals in soils. In general, soils contain certain contents of most heavy metals, and these metals are usually derived from the chemical weathering of parent rocks. Thus, PC1 can be termed a “natural factor”. Lead was a typical and more heavily loaded element in PC2. Wong et al (2002)[38] concluded that soil Pb in PRD regions mainly arises from vehicle exhaust emissions based on Pb isotope analysis. In addition, the emission of Hg from vehicles remains a largely ignored source of Hg, and no specific device is installed in automobiles to control Hg emissions. [58] Therefore, PC2 may be termed “anthropogenic sources”. As the dominant element of PC3, unlike other metals, arsenic generally exhibits negative valences, which inevitably affects its sources and fates in soil. Moreover, in view of the diversity of As inputs (e.g., from the atmosphere, irrigation, fertilizers and pesticides), the determined sources of As (PC3) needs further investigation.

4.4 Environmental application

In recent decades, rapid economic development, industrialization and urbanization in the PRD region have caused excessive releases of waste into the air, water and soil environments.[34, 59] Great attention has been paid to the increased potential for human health risk from the consumption of unsafe food. However, it is very difficult to remediate agricultural soils at a large-scale at lower pollution levels using engineering methods. Our idea is that geochemical methodology might be an effective way to decrease agricultural pollution and improve food safety. Therefore, the factors involved in heavy metal accumulation under field conditions need to be deeply understood in order to determine critical soil geochemistry factors and find effective ways to inhibit the entry of heavy metals into food chains.[60, 61] According to results of this study, higher fine-clay and lower extractable Fe contents imply greater metal (Zn, Cu, Hg, Cr and Ni) accumulation in balsam pear and cowpea. Increased extractable Fe contents and decreased clay contents will be helpful to alleviating metal absorption in balsam pear and cowpea. That is, it is possible to reduce metal contents and the potential risks of consuming vegetables using rational agricultural administration under field conditions at a large scale. Further investigation is ongoing to verify the effects of soil geochemical factors (e.g., extractable Fe/Al/Si and soil weathering indices) on the bioavailability of heavy metals in vegetables.

5 Conclusions

The BCFs of 8 metals in fruiting vegetables decreased in the order Zn>Cu>Ni>Cd and Hg>Cr>Pb>As (Cd>Hg for balsam pear; Hg>Cd for cowpea). The enrichment levels of Zn, Cu, Cr and Ni were strongly influenced by clay content. Extractable Fe levels significantly affected the accumulation of Zn, Cu, Hg, Cr and Ni in balsam pear and cowpea, although no significant relationship was observed between extractable Fe levels in soil and the BCFs of As, Pb, and Cd. Correlation analysis showed that higher extractable Fe contents might indicate lower metal accumulation (Zn, Cu, Hg, Cr and Ni) in vegetables. The BCFs of heavy metals exhibited significant correlations with the oxide mineral contents tested. Soil chemical weathering indices strongly affected the accumulation of Zn, Cu, Cr and Ni, and the extent of influence differed depending on metal species. These findings suggest that the level of soil weathering affects the bioavailability of heavy metals in subtropical v-c soils.

Acknowledgments

The research was financially supported by the National Natural Science Foundation of China (no. 41001135), the Natural Science Foundation of Guangdong Province (nos. S2012010010132, S2011010006107 and S201103000282), the Guangzhou Municipal Technology Support Program (no. 2012J2200004), the Guangdong Provincial Research & Development Project (no. 2011B030900004) and the “863” Program (no. 2013AA06A209).

References

1. W. H. Liu, J. Z. Zhao, Z. Y. Ouyang, L. Söderlund and G. H. Liu, *Environ Int*, 2005, **31**, 805-812.
2. M. Muchuweti, J. W. Birkett, E. Chinyanga, R. Zvauya, M. D. Scrimshaw and J. N. Lester, *Agriculture, Ecosystems & Environment*, 2006, **112**, 41-48.
3. M. Müller and M. Anke, *Sci Total Environ*, 1994, **156**, 151-158.
4. M. A. E. Ramadan and E. A. Al-Ashkar, *Australian Journal of Basic and Applied Science*, 2007, **1**, 300-306.
5. F. R. Zeng, S. Ali, H. T. Zhang, Y. N. Ouyang, B. Y. Qiu, F. B. Wu and G. P. Zhang, *Environ Pollut*, 2011, **159**, 84-91.
6. V. Antoniadis, J. S. Robinson and B. J. Alloway, *Chemosphere*, 2008, **71**, 759-764.
7. M. A. Kashem and B. R. Singh, *Nutr Cycl Agroecosys*, 2001, **61**, 247-255.
8. G. Nabulo, C. R. Black and S. D. Young, *Environ Pollut*, 2011, **159**, 368-376.
9. M. J. McLaughlin, *Dealing with Contaminated Sites* (ed. F. A. Swartjes), 2011, pp. 325-367.
10. M. J. Wilson, Z. L. He and X. E. Yang, *The Red Soils of China*, Springer Netherlands, 2004.
11. P. Sollins, G. P. Robertson and G. Uehara, *Biogeochemistry*, 1988, **6**, 181-199.
12. R. Naidu, M. E. Sumner and R. D. Harter, *Environ Geochem Hlth*, 1998, **20**, 5-9.
13. T. R. Yu, G. L. Ji and C. P. Ding, *Electrochemistry variable charge soils*, Science Press, Beijing, 1996.
14. A. M. Heimsath and B. C. Burke, *Geomorphology*, 2013, **200**, 75-88.
15. P. Sollins, G. P. Robertson and G. Uehara, *Biogeochemistry*, 1988, **6**, 181-199.
16. A. D. Harley and R. J. Gilkes, *Nutr Cycl Agroecosys*, 2000, **56**, 11-36.
17. C. Rasmussen, R. A. Dahlgren and R. J. Southard, *Geoderma*, 2010, **154**, 473-485.
18. P. Guan, C. W. W. Ng, M. Sun and W. Tang, *Eng Geol*, 2001, **59**, 147-159.
19. L. Tao, W. Zhang, H. Li, F. B. Li, W. M. Yu and M. J. Chen, *Soil Sci. Soc. Am. J.*, 2012, **76**, 1579-1591.
20. F. B. Li, X. G. Wang, C. S. Liu, Y. T. Li, F. Zeng and L. Liu, *Geoderma*, 2008, **148**, 70-78.
21. B. Alloway, in *Heavy Metals in Soils*, Springer Netherlands, Editon edn., 2013, pp. 11-50.
22. B. A. Osei and B. Singh, *Geoderma*, 1999, **93**, 325-334.
23. X. W. Xing, J. F. Ye, W. D. Ou, Q. P. Peng, S. W. Zhu, Z. H. Liu and J. S. Gao, *Guangdong Statistical Yearbook - 2012*, China Statistical Press, Statistics Bureau Of Guangdong Province, Guangzhou, 2012.
24. F. L. Tao and Z. W. Feng, *Water, Air, and Soil Pollution*, 2000, **118**, 231-243.
25. L. Huang, F. Liu, W. F. Tan, H. Q. Hu and M. K. Wang, *J Geochem Explor*, 2009, **103**, 30-36.
26. M. Pansu and J. Gautheyrou, Springer-Verlag, Dordrecht, the Netherlands., Editon edn., 2006.
27. , Editon edn., 2004.
28. O. P. Mehra and M. L. Jackson, *Clay Clay Miner*, 1958, **7**, 317-327.
29. N. S. Duzgoren-Aydin, A. Aydin and J. Malpas, *Eng Geol*, 2002, **63**, 99-119.
30. P. E. Rasmussen, G. Mierle and J. O. Nriagu, *Water Air & Soil Pollut*, 1991, **56**, 379-390.

31. M. Á. García, J. Alonso and M. J. Melgar, *J Hazard Mater*, 2009, **167**, 777-783.

32. M. J. Melgar, J. Alonso and M. A. García, *Sci Total Environ*, 2009, **407**, 5328-5334.

33. Q. Shi, T. Leipe, P. Rueckert, D. Zhou and J. Harff, *J Marine Syst*, 2010, **82, Supplement**, S28-S42.

34. X. D. Li, O. W. H. Wai, Y. S. Li, B. J. Coles, M. H. Ramsey and I. Thornton, *Appl Geochem*, 2000, **15**, 567-581.

35. Soil Survey Office of Guangdong Province. Guangdong soils, 1993, **121**, 621-622.Beijing: Science Press

36. W. X. Liu, X. D. Li, Z. G. Shen, D. C. Wang, O. W. H. Wai and Y. S. Li, *Environ Pollut*, 2003, **121**, 377-388.

37. L. M. Cai, Z. C. Xu, M. Z. Ren, Q. W. Guo, X. B. Hu, G. C. Hu, H. F. Wan and P. G. Peng, *Ecotox Environ Safe*, 2012, **78**, 2-8.

38. S. C. Wong, X. D. Li, G. Zhang, S. H. Qi and Y. S. Min, *Environ Pollut*, 2002, **119**, 33-44.

39. J. L. Hu, F. Y. Wu, S. C. Wu, X. L. Sun, X. G. Lin and M. H. Wong, *Ecotox Environ Safe*, 2013, **91**, 18-24.

40. C. L. Luo, R. X. Yang, Y. Wang, J. Li, G. Zhang and X. D. Li, *Sci Total Environ*, 2012, **431**, 26-32.

41. C. L. Luo, C. P. Liu, Y. Wang, X. Liu, F. B. Li, G. Zhang and X. D. Li, *J Hazard Mater*, 2011, **186**, 481-490.

42. S. Khan, S. Rehman, A. Zeb Khan, M. Amjad Khan and M. Tahir Shah, *Ecotox Environ Safe*, 2010, **73**, 1820-1827.

43. J. Pandey and U. Pandey, *Environ Monit Assess*, 2009, **148**, 61-74.

44. V. Raguž, J. Jarsjö, S. Grolander, R. Lindborg and R. Avila, *J Environ Manage*, 2013, **126**, 147-156.

45. P. Mantovi, G. Bonazzi, E. Maestri and N. Marmiroli, 2003, **250**, 249-257.

46. Q. Zhu, M. Zhang and Q. Ma, *Sci Hortic-Amsterdam*, 2012, **143**, 109-114.

47. L. Shen, B. C. Xia and X. K. Dai, *Chemosphere*, 2013, **93**, 2254-2263.

48. F. R. Zeng, S. Ali, H. T. Zhang, Y. N. Ouyang, B. Y. Qiu, F. B. Wu and G. P. Zhang, *Environ Pollut*, 2011, **159**, 84-91.

49. E. A. Dayton, N. T. Basta, M. E. Payton, K. D. Bradham, J. L. Schroder and R. P. Lamno, *Environ Toxicol Chem*, 2006, **25**, 719-725.

50. C. Carlon, M. Dalla Valle and A. Marcomini, *Environ Pollut*, 2004, **127**, 109-115.

51. M. J. McLaughlin, D. R. Parker and J. M. Clarke, *Field Crop Res*, 1999, **60**, 143-163.

52. B. Alloway, Springer Netherlands, Editon edn., 2013, pp. 351-373.

53. L. Tao, W. Zhang, H. Li, F. B. Li, W. M. Yu and M. J. Chen, *Soil Sci. Soc. Am. J.*, 2012, **76**, 1579-1591.

54. J. Viers, B. Dupré, J. Braun, S. Deberdt, B. Angeletti, J. N. Ngoupayou and A. Michard, *Chem Geol*, 2000, **169**, 211-241.

55. D. Carroll, Springer US, Editon edn., 1970, pp. 89-115.

56. A. F. White, Springer New York, Editon edn., 2008, pp. 469-543.

57. J. H. Won, J. Y. Park and T. G. Lee, *Atmos Environ*, 2007, **41**, 7547-7552.

58. W. Y. Wen and Y. Q. He, *Trop Oceanol*, 1985, **4**, 53-58. (in Chinese)

59. X. P. Huang, *Trop Oceanol*, 1995, **14**, 1-6. (in Chinese)

60. C. Y. Chang, H. Y. Yu, J. J. Chen, F. B. Li, H. H. Zhang and C. P. Liu, *Environ Monit Assess*,

2013, **DOI 10.1007/s10661-013-3472-0**

61. J. H. Won, J. Y. Park and T. G. Lee, *Atmos Environ*, 2007, **41**, 7547-7552.

Figure legends

Fig. 1 Agricultural soil and vegetable sampling locations in the Pearl River Delta region, South China (◇Balsam pear and ● Cowpea).

Fig. 2 Bioconcentration Factors (BCFs) of target heavy metals in balsam pear (n=25) and cowpea (n=18). BCFs (dimensionless) represent the ratio of total metal contents in vegetables (mg kg^{-1} dw) to those in the corresponding soils (mg kg^{-1} dw).

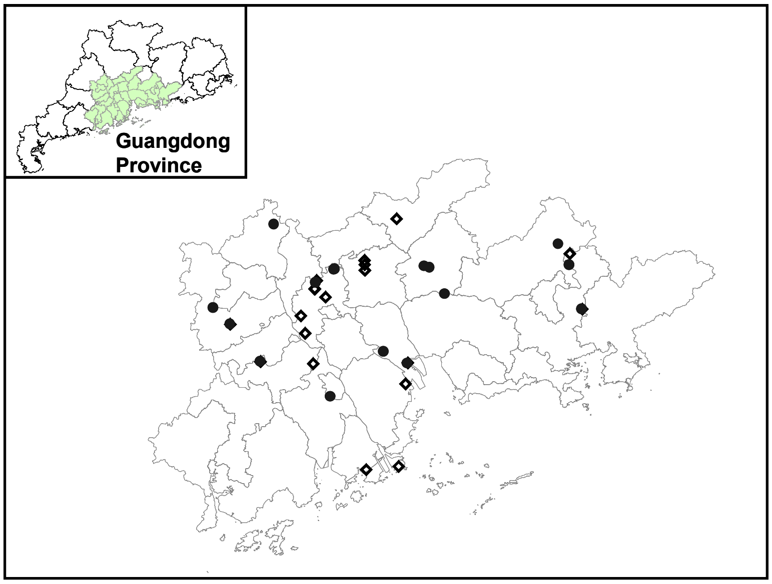

Fig. 1

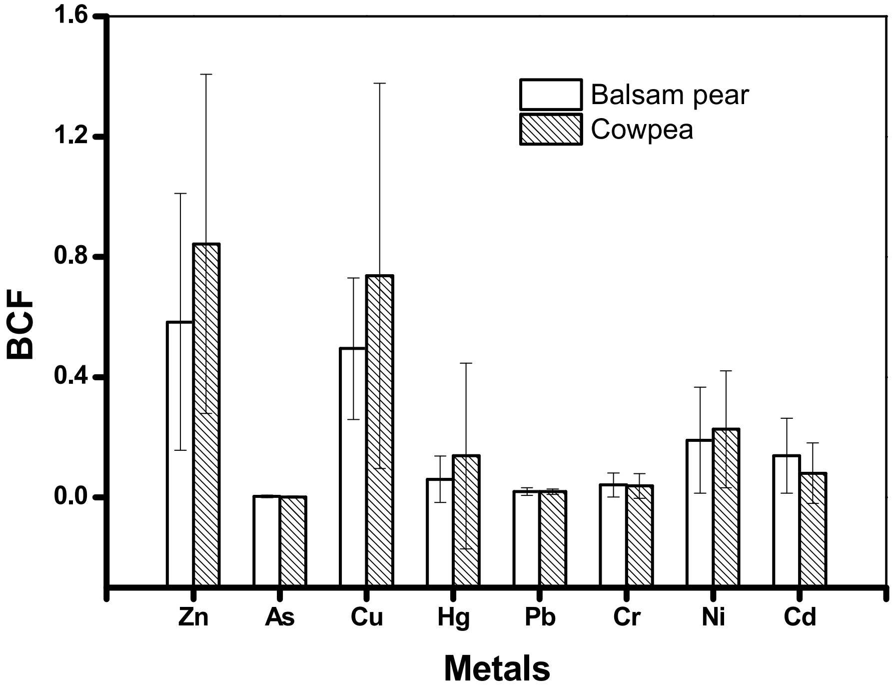
1.6
1.2
0.8
0.4
0.0
BCF
Balsam pear
Cowpea
Zn
As
Cu
Hg
Pb
Cr
Ni
Cd
Metals

Fig. 2

Tables

Table 1 Descriptive statistics of soil properties (mean ± standard deviation) in PRD regions

	Balsam pear	Cowpea
pH(H_2O)	5.98±0.61	5.91±0.79
SOM(g/kg)	26.9±7.65	23.9±9.8
Clay%	28.0±7.68	25.9±10.7
Silt%	30.7±12.6	28.5±13.7
Sand%	41.3±16.5	45.6±22.4
Fe_{ox}[a](g/kg)	4.68±2.53	3.59±2.16
Fe_p[a] (g/kg)	1.13±0.39	0.95±0.66
Fe_d[a] (g/kg)	19.6±9.7	19.7±9.9
Fe_2O_3(g/kg)	40.1±19.3	39.6±18.0
SiO_2(g/kg)	667±80	693.5±85.3
Al_2O_3(g/kg)	153±54	141.2±41.5
CaO(g/kg)	2.80±1.11	2.20±0.73
MgO(g/kg)	3.91±2.67	3.32±2.01
Na_2O(g/kg)	0.420±0.47	0.47±0.53
K_2O(g/kg)	5.53±4.27	6.25±5.70

[a] Soil extractable iron contents contain amorphous Fe (Fe_{ox}), complexed Fe (Fe_p) and dithionite-citrate-bicarbonate Fe (Fe_d).

Table 2 Contents (mg kg^{-1} dw, mean ± standard deviation) of heavy metals in soils and vegetables in the Pearl River Delta region, South China

		Zn	As	Cu	Hg	Pb	Cr	Ni	Cd
Soil	Balsam pear (n=25)	76.7±31.4	25.1±12.6	22.9±11.2	0.49±0.50	28.7±9.98	35.3±14.5	15.6±9.05	0.46±0.37
	Cowpea (n=43)	64.9±28.4	19.9±12.5	21.6±12.6	0.3±0.3	24.5±6.13	38.6±21.8	16.7±11.1	0.38±0.29
	Background in Guangdong	49.71	13.52	17.65	0.085	35.87	56.53	17.8	0.094
	National Environmental Quality Standard for Soils	250	30	100	0.5	300	200	50	0.3
Vegetable	Balsam pear (n=25)	35.8±13.7	0.08±0.12	8.79±2.02	0.017±0.018	0.476±0.171	1.20±0.867	2.32±1.58	0.045±0.047
	Cowpea (n=43)	42.2±9.61	0.019±0.026	9.73±3.78	0.014±0.008	0.453±0.207	1.02±0.658	2.60±0.905	0.018±0.022

Table 3 Pearson correlation coefficients of Bioconcentration factor (BCF)[a] values with soil properties, extractable iron contents[b] and soil weathering coefficients[c].

	Zn	As	Cu	Hg	Pb	Cr	Ni	Cd
pH(H_2O)	0.125	-0.159	0.311(*)	0.198	-0.127	0.277	0.148	-0.18
SOM	-0.501(**)	-0.092	-0.344(*)	-0.222	-0.272	-0.146	-0.428(**)	-0.218
Clay	-0.513(**)	0.069	-0.409(**)	-0.027	-0.101	-0.382(*)	-0.441(**)	-0.134
Silt	-0.326(*)	-0.078	-0.229	0.04	0.079	-0.257	-0.147	-0.173
Sand	0.466(**)	0.021	0.350(*)	-0.015	-0.006	0.356(*)	0.309(*)	0.181
Fe_{ox}	-0.395(**)	0.114	-0.283	0.093	-0.108	-0.503(**)	-0.214	-0.096
Fe_p	-0.042	0.041	-0.26	-0.330(*)	0.012	-0.200	0.258	0.067
Fe_d	-0.439(**)	0.021	-0.337(*)	0.027	-0.234	-0.518(**)	-0.321(*)	-0.248
Fe_2O_3	-0.468(**)	0.046	-0.313(*)	0.066	-0.222	-0.519(**)	-0.319(*)	-0.243
SiO_2	0.605(**)	-0.069	0.345(*)	-0.014	0.173	0.468(**)	0.387(*)	0.152
Al_2O_3	-0.550(**)	-0.103	-0.207	-0.006	-0.062	-0.087	-0.260	-0.086
CaO	-0.420(**)	-0.015	-0.176	0.045	-0.413(**)	-0.268	-0.244	-0.410(**)
MgO	-0.447(**)	0.146	-0.286	0.173	-0.207	-0.492(**)	-0.355(*)	-0.201
K_2O	0.427(**)	-0.024	0.407(**)	0.059	-0.095	0.329(*)	0.307(*)	-0.003
Na_2O	0.135	-0.014	0.195	0.045	-0.107	0.111	0.128	-0.092
WI-1	0.615(**)	-0.024	0.272	0.006	0.197	0.249	0.345(*)	0.177
WI-2	0.021	-0.104	0.158	-0.059	0.250	0.510(**)	0.054	0.207
WI-3	-0.624(**)	-0.075	-0.287	0.028	-0.149	-0.293	-0.336(*)	-0.167
WI-4	0.526(**)	-0.068	0.442(**)	0.113	-0.029	0.365(*)	0.368(*)	0.028
WI-5	0.339(**)	-0.024	0.269	0.140	-0.114	0.116	0.204	-0.061

** Correlation is significant at the 0.01 level (2-tailed).

* Correlation is significant at the 0.05 level (2-tailed).

[a] Bioconcentration Factors (BCFs, dimensionless) represent the ratios of total metal contents in vegetables (mg kg^{-1} dw) to those in the corresponding soils (mg kg^{-1} dw).

[b] Soil extractable iron contents contain amorphous Fe (Fe_{ox}), dithionite-citrate-bicarbonate Fe (Fe_d) and complexed Fe (Fe_p).

[c] Soil indices of chemical weathering include Si/Al ratio (WI-1, SiO2/Al2O3), Al/Fe ratio (WI-2, Al_2O_3/Fe_2O_3), Si-Fe-Al ratio (WI-3, $(Al_2O_3+Fe_2O_3)/SiO_2$), alkali metal leaching factor (WI-4, $(K_2O+Na_2O)/Al_2O_3$) and total base leaching factor (WI-5, $(K_2O+Na_2O+CaO+MgO)/Al_2O_3$).

Table 4 Pearson's correlations matrix for elemental contents in soils.

	Zn	As	Cu	Hg	Pb	Cr	Ni	Cd
Zn	1							
As	0.270	1						
Cu	0.703(**)	0.113	1					
Hg	0.417(**)	0	0.036	1				
Pb	0.671(**)	0.550(**)	0.268	0.465(**)	1			
Cr	0.597(**)	0.2	0.776(**)	0.031	0.180	1		
Ni	0.641(**)	0.136	0.831(**)	-0.039	0.210	0.888(**)	1	
Cd	0.705(**)	0.349(*)	0.572(**)	0.405(**)	0.553(**)	0.557(**)	0.545(**)	1
Fe_2O_3	0.633(**)	0.231	0.822(**)	-0.058	0.267	0.835(**)	0.862(**)	0.528(**)
SiO_2	-0.775(**)	-0.239	-0.683(**)	-0.186	-0.384(*)	-0.756(**)	-0.811(**)	-0.598(**)
Al_2O_3	0.438(**)	0.083	0.252	0.009	0.016	0.318(*)	0.436(**)	0.172
CaO	0.683(**)	0.195	0.508(**)	0.457(**)	0.571(**)	0.397(**)	0.397(**)	0.636(**)
MgO	0.604(**)	0.212	0.771(**)	-0.148	0.23	0.783(**)	0.885(**)	0.532(**)
K_2O	-0.258	0.134	-0.256	-0.307(*)	0.056	-0.267	-0.230	-0.235
Na_2O	0.132	0.132	0.168	-0.386(*)	0.139	0.165	0.250	0.035

** Correlation is significant at the 0.01 level (2-tailed).

* Correlation is significant at the 0.05 level (2-tailed).

Table 5 Matrix of the principal component analysis (PCA) of elemental contents in soils

Elements	PC1	PC2	PC3
Zn	0.897	0.162	-0.146
As	0.392	0.404	0.783
Cu	0.834	-0.396	-0.067
Hg	0.322	0.652	-0.600
Pb	0.621	0.663	0.158
Cr	0.813	-0.447	0.027
Ni	0.824	-0.490	0.013
Cd	0.728	0.208	-0.069
Eigenvalue	4.17	1.69	1.03
Variation %	52.1	21.2	12.9
Cumulative of variation %	52.1	73.3	86.1