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

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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 regions remains unknown. The present study investigated heavy metal accumulation under field conditions in the Pearl River Delta (PRD) by measuring the content 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 (Fe₂O₃, SiO₂, Al₂O₃, CaO, MgO, K₂O and Na₂O) were also analyzed. Heavy metal accumulation from soil to vegetables was assessed based on 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 content of Zn, Cu, Cr and Ni in vegetables was strongly affected by the 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.

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Environmental impact

Concerns have been raised over increasing potential human health risks from food along with the rapid industrialization and urbanization in the Pearl River Delta (PRD) region. However, it is very difficult to remediate low-pollution agricultural soils at a large scale using engineering methods. Our idea is that a 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 well understood in order to determine critical geochemical factors and find effective ways to inhibit the entry of heavy metals into food chains. From a geochemical viewpoint, increased extractable Fe content and decreased clay content in soil help to alleviate metal pollution in balsam pear and cowpea. Thus, it is possible to reduce the metal contents and potential risks of consuming vegetables using a 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.

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1. Introduction

Much attention has been paid to decreases in the safety of agricultural products,^{1,2} and increases in the incidence of chronic diseases such as deformities 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 content.^{5–8} It has been consistently concluded that higher soil pH and SOM content, lower salinity and the presence of clay-rich soils often enhance the ability of soils 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 rarely been 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 have 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.^{11,13,14} 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.¹⁵ 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.^{16,17} Weathering indices are closely associated with soil physicochemical properties, which can further affect the concentration and activity of adsorbed Fe.^{18,19} 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 solution or incorporated through conversion into water-insoluble (hydr)oxides.^{15,17,20} Therefore, weathering processes can regulate the bioavailability of elements, including heavy metals, in the soil. In addition, as indicated by previous studies,^{19,21} 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 the soil physicochemical properties, extractable Fe oxide content 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 km² in South China, including 13 357 km² of agricultural land and 4829 km² of vegetable production.²² 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.^{23,24}

During September–November 2011, 43 pairs of soil and vegetable samples were collected from agricultural land 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 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



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

$K_2Cr_2O_7-H_2SO_4$ oxidation method,²⁵ 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.²⁶

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.²⁷ 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 .²⁵ 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.^{16,28}

The heavy metals content in the soil and vegetable samples was determined according to the method of Rasmussen *et al.* (2001).²⁹ 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 digested 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 the Cd content was 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 indicated a low error for the data, 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.^{30,31} 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 content 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, the 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 Fe_{ox} , Fe_p and Fe_d contents clearly differed between the balsam pear and cowpea soils.

The contents of Zn, As, Cu, Hg, Pb, Cr, Ni and Cd in the balsam pear soils were in the ranges 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 content 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 heavy metal content except for Cr and Ni, and the metal content descended in the order Zn > Cu > Pb > Ni > Cr > Hg > Cd > As.

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

	Balsam pear	Cowpea
pH (H_2O)	5.98 \pm 0.61	5.91 \pm 0.79
SOM ($g\ kg^{-1}$)	26.9 \pm 7.65	23.9 \pm 9.8
Clay%	28.0 \pm 7.68	25.9 \pm 10.7
Silt%	30.7 \pm 12.6	28.5 \pm 13.7
Sand%	41.3 \pm 16.5	45.6 \pm 22.4
Fe_{ox}^a ($g\ kg^{-1}$)	4.68 \pm 2.53	3.59 \pm 2.16
Fe_p^a ($g\ kg^{-1}$)	1.13 \pm 0.39	0.95 \pm 0.66
Fe_d^a ($g\ kg^{-1}$)	19.6 \pm 9.7	19.7 \pm 9.9
Fe_2O_3 ($g\ kg^{-1}$)	40.1 \pm 19.3	39.6 \pm 18.0
SiO_2 ($g\ kg^{-1}$)	667 \pm 80	693.5 \pm 85.3
Al_2O_3 ($g\ kg^{-1}$)	153 \pm 54	141.2 \pm 41.5
CaO ($g\ kg^{-1}$)	2.80 \pm 1.11	2.20 \pm 0.73
MgO ($g\ kg^{-1}$)	3.91 \pm 2.67	3.32 \pm 2.01
Na_2O ($g\ kg^{-1}$)	0.420 \pm 0.47	0.47 \pm 0.53
K_2O ($g\ kg^{-1}$)	5.53 \pm 4.27	6.25 \pm 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 Content (mg kg^{-1} dw, mean \pm 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 Environ- mental 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

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 $\text{Zn} > \text{Cu} > \text{Ni} > \text{Cr} > \text{Pb} > \text{As} > \text{Cd} > \text{Hg}$. This trend was similar to that observed in soils, except that Pb occupied a higher position in soils compared with that in vegetables. The contents of Zn, As, Cu, Hg, Pb, Cr, Ni and Cd in balsam pear were in the ranges 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 the 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 the eight metals descended in the order $\text{Zn} > \text{Cu} > \text{Ni} > \text{Cd}$ and $\text{Hg} > \text{Cr} > \text{Pb} > \text{As}$ ($\text{Cd} > \text{Hg}$ for balsam pear; $\text{Hg} > \text{Cd}$ 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 cowpea.

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.^{32,33}

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 correlated 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 mineral oxides content (except Na_2O); negative correlations existed with the 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

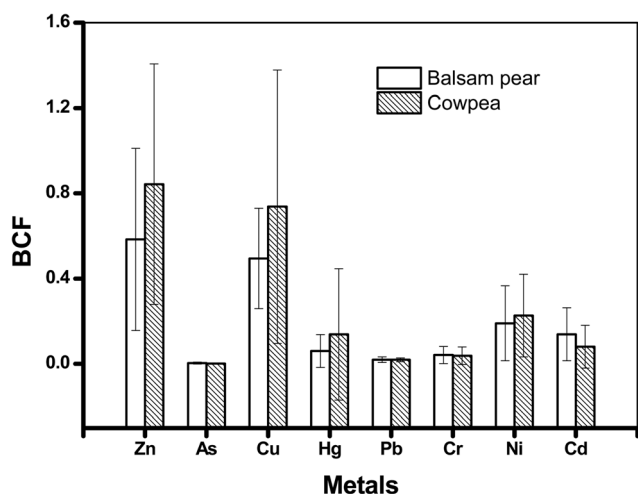


Fig. 2 Bioconcentration factors (BCFs) of target heavy metals in balsam pear ($n = 25$) and cowpea ($n = 18$). BCFs (dimensionless) represent the ratio of total metal contents in vegetables (mg kg^{-1} dw) to those in the corresponding soils (mg kg^{-1} dw).

Table 3 Pearson correlation coefficients of bioconcentration factor (BCF)^a values with soil properties, extractable iron contents^b and soil weathering coefficients^{cd}

	Zn	As	Cu	Hg	Pb	Cr	Ni	Cd
pH (H ₂ O)	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 ₂ O 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 ₂ O 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 ₂ O	0.427(**)	-0.024	0.407(**)	0.059	-0.095	0.329(*)	0.307(*)	-0.003
Na ₂ O	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

^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 the Si/Al ratio (WI-1, SiO₂/Al₂O₃), Al/Fe ratio (WI-2, Al₂O₃/Fe₂O₃), Si-Fe-Al ratio (WI-3, (Al₂O₃ + Fe₂O₃)/SiO₂), alkali metal leaching factor (WI-4, (K₂O + Na₂O)/Al₂O₃) and total base leaching factor (WI-5, (K₂O + Na₂O + CaO + MgO)/Al₂O₃). ^d ** Correlation is significant at the 0.01 level (2-tailed). * Correlation is significant at the 0.05 level (2-tailed).

significantly negatively correlated with the Fe₂O₃, Al₂O₃, CaO and MgO contents ($r = -0.468$, -0.550 , -0.420 , and -0.447 , respectively) and positively correlated with the SiO₂ and K₂O contents ($r = 0.605$ and 0.427 , respectively) ($p < 0.01$). The BCF of Cu was significantly correlated with the Fe₂O₃, SiO₂ and K₂O contents ($r = -0.313$, 0.345 and 0.407 , respectively). The BCFs of Cr and Ni were negatively correlated with the Fe₂O₃ and MgO contents and positively correlated with the SiO₂ and K₂O 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 BCF of Zn was positively correlated with WI-5 (0.339); and 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 (Fe₂O₃, SiO₂, MgO and CaO) were significantly correlated ($p < 0.01$). The Hg and Pb contents exhibited a positive correlation ($r = 0.465$), and both of these 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 ($p < 0.01$). K₂O and Na₂O contents were both correlated with the Hg content only ($p < 0.05$). 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 with Hg (-0.600).

Table 4 Pearson's correlations matrix for elemental contents of soils^a

	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 ₂ O 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 ₂ O 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 ₂ O	-0.258	0.134	-0.256	-0.307(*)	0.056	-0.267	-0.230	-0.235
Na ₂ O	0.132	0.132	0.168	-0.386(*)	0.139	0.165	0.250	0.035

^a ** 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 the elemental contents of 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 variation %	52.1	73.3	86.1

4. Discussion

4.1 Current metal 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.³⁴ 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 the acceptable level 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.^{33,35}

The mean soil metal contents (except for Pb) reported here all exceeded the results reported by Cai *et al.* (2012)³⁶ 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)³⁷ 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)³⁶ and Wong *et al.* (2002)³⁷ obtained samples from less polluted soils in large-scale vegetable farms and heavily polluted areas in the PRD region, respectively.

For correction of the water content (which ranged between 79.8% and 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)³⁸ 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)³⁹ 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.⁴⁰

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.³⁹ 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.^{41,42} 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),³⁹ possibly because Cu and Zn are plant essential elements and can easily accumulate in plant tissues.⁴³⁻⁴⁷

4.2 Critical geochemical factors controlling metal enrichment in fruiting vegetables

The Pearson correlation analysis showed that there was a positive correlation between the BCF of Cu and soil pH (Table 3). This trend is contrary to a previous finding by Zeng *et al.* (2011)⁵ 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.⁴⁸

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.^{19,49,50} 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.*, Al₂O₃), and these processes are considered important mechanisms for heavy metal transformation and migration in soil environments. Soil oxides (*e.g.*, Fe₂O₃, Al₂O₃, and SiO₂) are good adsorbents for heavy metals, and their redox cycles can lead to changes in heavy metal valence and bioavailability.¹⁹ In general, the BCFs of heavy metals were significantly correlated with six soil oxides (but not Na₂O); among these, Fe₂O₃, Al₂O₃, CaO and MgO exhibited negative correlations with the BCFs and SiO₂ and K₂O had positive correlations with the BCFs. 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 metals are 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 important for the sorption of heavy metals in soil. Sorption by these oxides or redox reactions may reduce the mobility of metals and thus reduce their bioavailability, further reducing plant uptake. Silicon and K do not directly affect the transfer of metals in soil-plant system, and they will influence the state and redox of Fe- and Al-oxides in soil, thus affecting the metal bioavailability indirectly.⁵¹

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 content) greatly affect the activity of heavy metals during weathering.^{52,53} CO₃²⁻, HCO₃⁻, HPO₄²⁻, PO₄³⁻, SO₄²⁻ and other inorganic anions

present in soil solutions can easily bind heavy metals to form hydrates, thereby affecting the fate of heavy metals.¹⁹ 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, as reflected by the decreasing WI-1 and WI-2 values, and that chemical weathering affects the reduction of Fe and Al in soils.^{51,54} The lack of significant correlation between the As, Hg, Pb and Cd with the 5 soil weathering indices might be because anthropogenic discharges mask 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)³⁷ 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.⁵⁵ 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 sources of As (PC3) need 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.^{33,56} Much attention has been paid to the increased potential for human health risks 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 a 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 well understood in order to determine critical soil geochemistry factors and find effective ways to inhibit the entry of heavy metals into food chains.^{57,58} According to the 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 content and decreased clay content will be helpful to alleviate 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 the 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 their 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.

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

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