



Phytoavailability, bioaccumulation, and human health risks of metal(loid) elements in an agroecosystem near a lead-zinc mine

Liqiang Luo¹ · Yating Shen¹ · Xiaofang Wang¹ · Binbin Chu¹ · Tao Xu¹ · Ying Liu¹ · Yuan Zeng¹ · Jian Liu¹

Received: 28 November 2017 / Accepted: 3 June 2018 / Published online: 11 June 2018
© Springer-Verlag GmbH Germany, part of Springer Nature 2018

Abstract

Soil near a Pb-Zn-Mn mine was polluted by mining, which may have an impact on human health via the food chain. To evaluate the pollution effects, arsenic (As), cadmium (Cd), chromium (Cr), copper (Cu), manganese (Mn), lead (Pb), and zinc (Zn) in vegetables were determined by inductively coupled plasma atomic emission and mass spectrometry. Lead species were analyzed by X-ray absorption near-edge structure (XANES). Phytoavailability of the elements was evaluated by bioaccumulation of the elements, the sequential extraction procedure, Pb species, and plant uptakes. The target health quotient (THQ) was calculated to evaluate the human health risks. It was found that (1) high concentrations of As, Cd, Cr, and Pb were detectable in vegetables, and bioaccumulation was in the order of Mn > Zn > Cr > Pb > Cu > As > Cd; (2) phytoavailability of the elements was controlled mainly by the soluble fraction, and a linear relationship observed between the soluble fraction and bioaccumulation; (3) a new Pb-fulvic acid complex (Pb-FA) was identified by XANES in rhizosphere soil, and high content of Pb organic matter (60%) and soluble Pb (18%) were found; (4) both Cd and Zn accumulated in both of the *Amaranthaceae* and the *Apiaceae* families, indicating that the plants in the same family have the same bioaccumulation trend for the elements in the same group; (5) agricultural activities and plant growing increased phytoavailability of As, Cd, Cu, Pb, and Zn by decreasing the residual and raising the soluble and extractable fractions; (6) arsenic is top of the high health risks, followed by Pb, Cd, and Mn. Coriander, celery, and spinach were the top three highest health risks in the area.

Keywords Phytoavailability · Bioaccumulation · Pb species · X-ray absorption near-edge structure · Vegetable · Soils · Health risks

Highlights

- The bioaccumulation of the elements by plants was proportional to the relative soluble and the reducible fractions, and inversely to the oxidizable fraction.
- Dressing procedures changed Pb species and resulted in a higher extractable fraction and may bring more soluble Pb into ecosystems.
- Plants in the same family have the same bioaccumulation trend for elements in the same group.
- Agricultural activities and plant growing increased phytoavailability of metal and metalloid elements by raising the soluble and extractable fractions.
- The rhizosphere soil increased the phytoavailability of Pb by providing Pb-FA complex and soluble Pb, and conducted to Pb uptake by plants.

Responsible editor: Elena Maestri

Electronic supplementary material The online version of this article (<https://doi.org/10.1007/s11356-018-2482-4>) contains supplementary material, which is available to authorized users.

✉ Liqiang Luo
luoliqiang@cags.ac.cn

Introduction

As, Cd, and Pb are toxic elements that are harmful to human health. Cu, Cr, and Mn are either the essential elements for human health or toxic elements. Zn is an essential element present in all human organs, tissues, fluids, and secretions, and intake and supplementation of Zn is thought to have a beneficial effect (Jomova and Valko 2011).

As, Cd, Cr, and Pb can enter the food chain via plants and vegetables. Food consumption has been identified as the major pathway of human exposure to pollution, and considered to account for more than 90% compared with inhalation and dermal contact (Loutfy et al. 2006). High accumulation and translocation of toxic metals in the edible parts of plants and vegetables were reported in spinach, radish, tomato, chili, and cabbage growing in agricultural fields, and their cultivation is unsafe due to possible transfer to the food chain and consequent health hazards (Tiwari et al. 2011). Transfer capability of the elements to the food chain via plants is determined by both phytoavailability of the elements in soil and their uptake

¹ National Research Center of Geoanalysis, 26 Baiwanzhuang Street, Beijing 100037, China

by plants. A correlation between As content in the vegetables and the bioavailable As in soil was observed (Kar et al. 2013). A linear relationship was found between Cd phytoavailability and the CaCl_2 extracted Cd/DOC (dissolved organic matter) level (Tang et al. 2017). An approach of assessing phytoavailability was the single extraction procedure (Meers et al. 2007; Pinto et al. 2015). The modified BCR approaches were applied to assessing phytoavailability (Ferri et al. 2015; Tang et al. 2017). BCR was thought as a useful approach to predict mobility of the trace elements (Pueyo et al. 2008). By the modified BCR, Cd, Mn, and Zn were extracted primarily in water and weak acid extraction fractions, but it was thought of as poor predictors of phytoavailability (Ferri et al. 2015). Indeed, the significant correlation between phytoavailability and the extractable fractions was not always observed (Tang et al. 2017). The correlation between soil extractable metal concentrations and plant metal concentrations was usually poor (Ferri et al. 2015; Oyeyiola et al. 2011). No extraction procedure proved to be able to accurately predict the phytoavailability (Fedotov et al. 2012).

The contrast findings imply that it is still a challenge to correlate the extractable fractions of the elements in soil with phytoavailability and uptake of plants. Firstly, not only are the extractable fractions of elements in soil but also the types and families of plants are needed to be considered in such correlations. Secondly, the species and transformation of the elements in soil and rhizosphere may play a key role in the phytoavailability of the elements and their uptake by plants, since speciation of elements in plants is important for understanding the mechanics of elemental uptake and biotransformation in plants (Shen 2014). Thirdly, agricultural activities should make impacts on the phytoavailability and bioaccumulation of the elements.

The phytoavailability of heavy metals for uptake by plants is associated with their sorption and desorption by soil components (Tahervand and Jalali 2016). Lead(II) binds to iron (hydr)oxides, such as ferrihydrite (Nyquist and Greger 2009), or organic matter, such as carboxylate groups (Wang et al. 2006). By forming such complexes with oxygen-containing ligands and singly coordinated OH groups of (hydr)oxides, Pb(II) is strongly adsorbed to soil organic matter (soil pH < 6) and iron (hydro)oxides (soil pH > 6), and will result in low mobility and plant availability of Pb^{2+} (Gustafsson et al. 2011). On the other hand, it was also thought that a strong relationship between dissolved Pb and DOC was suspected, yet only a weaker correlation was observed (Linde et al. 2007). The sorption and retention of Cd, Cu, and Pb are mainly controlled by cation exchange capability, pH, and Mn oxides's content (Tahervand and Jalali 2016). Formation of organometallic complexes in soil solution has a strong influence on metal phytoavailability by restricting Pb ions from playing their chemical roles (Shahid et al. 2011; Shen and Song 2017). Though Pb uptake decreased in the presence of

river fulvic acid with respect to noncomplexed Pb, total adsorbed Pb was higher than predicted from Pb^{2+} activities (Slaveykova et al. 2003). Some reports indicated that metal uptake was favored by humic substances because of the high presence of carboxylic acids (Salati et al. 2010), and humic acids contributed to the mobilization of Pb (Laborda et al. 2008). It was reported that humic acids increased the phytoavailability of Pb and Cd to wheat plants with increased extractable metals (Khan et al. 2008). Pb bio-uptake was higher in the presence of river fulvic acid or riverine organic matter (Slaveykova et al. 2003). Thus, the role of organic matter in the phytoavailability of heavy metals for uptake by plants is still needed to conduct a deeper investigation.

Uptake of toxic elements by vegetables poses the potential health risks via dietary consumption of foods. The toxic elements in minerals, such as Cd and Pb in pyrite, pyrrhotite, and chalcopyrite, have potential health risks (Zhuang et al. 2009). In city and industrial areas, Cr was the major pollutant with the highest health quotient (Liu et al. 2013; Zhao et al. 2018). On the basis of an indoor dust investigation, Pb posed the highest health risk (Kurt-Karakus 2012). In a Pb-Zn mine, Pb, As, and Cd were the major risks (Li et al. 2014). In a case of crops with wastewater irrigation, Mn, Cd, and Pb had a health risk index > 1 and indicated a possible human health risk via food crops (Khan et al. 2013). All of these results reveal that health risks exist in areas polluted by mining, industrial, and anthropogenic activities. Obviously, the potential health risks need to be assessed. The health risk index (Khan et al. 2013) or health risk quotient (THQ) (Bortey-Sam et al. 2015) were used to make a quantitative estimation of the risks. THQ is the ratio of the daily intake of metals to the oral reference dose. When the ratio is < 1, none of the exposed population would be likely to experience obvious adverse effects, and if the ratio is > 1, the inhabitants will suffer a relatively high health risk (Bortey-Sam et al. 2015; Kurt-Karakus 2012; Zhuang et al. 2009). High concentrations of Cd and Pb were reported in irrigation water and crops, and the health risk indexes of Cd and Pb were > 1, which poses a possible health risk (Khan et al. 2013). Therefore, the objective of this study is to quantitatively obtain information on the bioaccumulation of metal(loid) elements in the vegetables; to investigate phytoavailability of the elements in soil; to explore the effects of the elemental species, the families of vegetables, and agricultural activities on phytoavailability, bioaccumulation, and plant uptake; and to assess the health risks of the toxic elements in this area.

Materials and methods

Sampling and sample analysis

The investigation site is located in an area near a Pb-Zn-Mn mine (Fig. 1S in supplemental material), which has been in

operation for > 50 years. Silver (Ag), gold (Au), Mn, Pb, sulfur (S), and Zn are its major extracts. The residential houses and vegetable fields are around the mine. The mining activities have introduced pollution into agricultural soils and irrigation systems (Luo et al. 2014).

Vegetables, plants, rhizosphere soil, field soils, and irrigation water were sampled together. In total, 204 vegetable samples were taken from the agricultural fields and 205 soils samples were taken from the landscape, agricultural fields, residential yards, traffic sites, and industrial areas around the mine.

The plant samples were thoroughly washed using a brush and tap water, and the process was repeated three times with distilled water. The cleaned plants were wrapped in pieces of gauze and left to dry at room temperature. The plant samples were powdered to 76 μm . An average conversion factor was calculated for a ratio of fresh and dry plants on the basis of 34 fresh and dry vegetable samples.

For analysis of plant samples, a set of containers was used, in which an inner polytetrafluoroethylene container was within an outer steel container; 0.5000 \pm 0.0005 g of powdered sample was weighed into the inner polytetrafluoroethylene container, then 5.00 ml of HNO_3 and 1.00 ml of H_2O_2 were added, and the samples kept overnight. The containers were heated at 70–80 $^\circ\text{C}$ until yellow smoke containing nitrogen-oxygen components vanished and the solution was almost dry. Next, 5.00 ml of HNO_3 and 2.00 ml of H_2O_2 were added to the inner containers. The steel containers were moved into an oven and kept at 150 $^\circ\text{C}$ for 4 h. After the container was taken out and cooled to room temperature, 50 ml of the distilled water was added into the inner container quantitatively; 1 ml of the solution containing the dissolved plant sample was diluted to a volume of 5 ml with a 5% acid solution. The solution was analyzed by inductively coupled plasma atomic emission and mass spectrometry (ICP-AES, Thermo IRIS Advantage, and ICP-MS, Thermo X-series). For quality control, four certified reference materials, GBW10010 (Rice), GBW10015 (Spinach), GBW10015 (tea leaf), and GBW10020 (citrus leaf), were used, and 20% of the plant samples were analyzed in duplicate in addition to the analysis of blank samples. Pb isotopes were determined by Agilent-7500a ICP-MS. Certified reference material, NBS981, was used to monitor the analytical quality. It was found that the determination of Cd in the geochemical samples by ICP-MS was affected by zirconium (Zr) and molybdenum (Mo) oxides and hydroxides, and the application of membrane dissolution could possibly reduce the interference (WANG et al. 2017). In addition, another challenge of analyzing the polluted soils is the lack of soil certified reference materials with high concentrations of heavy metals. A certified reference material taken from the agricultural soil surrounding the mining districts was reported, in which the concentrations of As, Cd, and Pb was 297, 3.09, and 971 mg/kg, respectively (Tian et al. 2017).

XANES experiments were conducted in the 15 U1 and 14 W1 beamline of the Shanghai Synchrotron Radiation Facility.

A double crystal monochromator of Si (111) was applied to achieve an energy resolution of 2.0×10^{-4} , and a K-B mirror was used in a focusing optics system to obtain an ultimate beam size of $2 \times 2 \mu\text{m}^2$. Due to low Pb concentrations in the samples, a defocused beam size of $100 \times 100 \mu\text{m}^2$ was used for the XANES measurements. X-ray fluorescence spectra were collected using a Vortex-90EX Si drift detector in both fluorescence mode (samples) and combined fluorescence/transmission mode (standards) measurements.

Sequential extraction

On the basis of the modified BCR sequential extraction procedure (Sutherland 2010; Sutherland and Tack 2003), five fractions were used in the study using the sequential extraction procedure: (1) water soluble, 1.0 g soil sample was extracted with 20 ml distilled water for 16 h at 22 $^\circ\text{C}$; (2) weak acid extractable, 1.0 g soil sample was extracted with 40 ml acetic acid (0.11 M HOAc); (3) reducible, 40 ml of hydroxylamine hydrochloride was added to the washed sample; (4) oxidizable, the sample was dissolved in 10 ml of H_2O_2 in a sealed bottle; and (5) residual, 0.1000 g residual was weighted into a Teflon container and HCl, HNO_3 , HClO_4 , and HF acids (3, 2, 1, and 5 ml) were added to solve it.

The sum of the elemental concentrations in the five fractions were compared with the elemental concentrations in soil obtained by XRF, and the average relative errors were 3.0, 3.0, 10.2, 14.5, and 9.2% for As, Cd, Cu, Pb, and Zn, respectively. The recovery (the ratio of the sum and the concentration) ranged from 92 to 100, 91–102, 101–121, 107–127, and 100–108% for As, Cd, Cu, and Zn, respectively. The results by this study are comparable to the precision and accuracy of 10 and $\pm 15\%$ by other researchers (Anju and Banerjee 2011; Fleming et al. 2013; Marguá et al. 2004). For example, the recoveries by Tokahoglu and Kartal (2004) were 76–102%. The precision by professional laboratories was between 3.7 and 4.6% for the most precise, and 32.6 and 32.9% for the least precise, and the highest precision was associated with the acid extractable step for Cd (6.2%) and the reducible step for Pb (6.3%), while the lowest precision was associated with the oxidizable step for Pb (19.0%) and the acid extractable step for Cr (15.6%) (Sutherland 2010). The higher the concentrations, the greater the analytical precision.

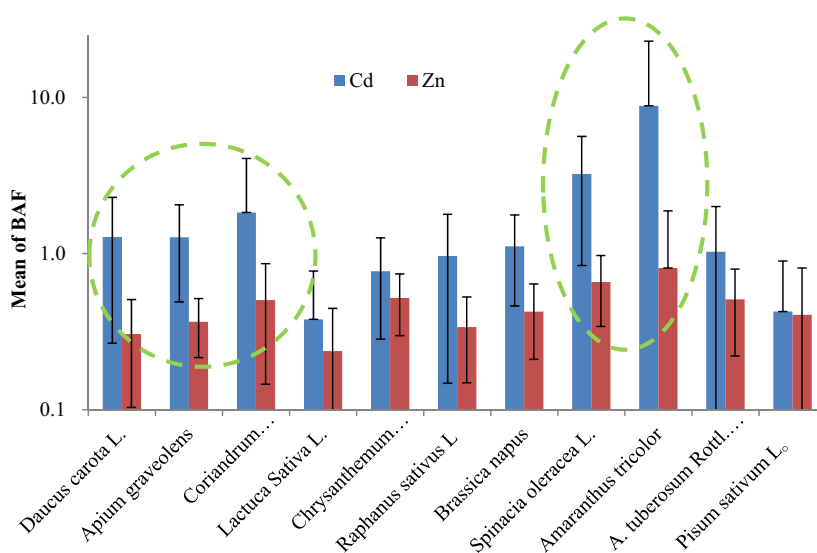
In the study, water and weak acid extractable fractions were included as the soluble fraction, and the sum of the water, weak acid, reducible, and oxidizable extractable fractions were included as the extractable fractions.

Data analysis

Bioaccumulation factors

Bioaccumulation factors (BAFs) were expressed either on a dry weight basis of plants (McAloon and Mason 2003) or a

Fig. 1 Means and SD of BAFs of Cd and Zn in various vegetables. *Spinacia oleracea L.* (Spinach) and *Amaranthus tricolor* (three-colored amaranth) are the plants of *Amaranthaceae* family, in which the mean of BAFs of Cd and Zn is over 3.0 and 0.6, respectively. *Daucus carota L.* (Carrot), *Apium graveolens* (celery), and *Coriandrum sativum L.* (coriander) belong to *Apiaceae* family, in which the mean of BAFs of Cd and Zn is over 1.2 and 0.3, respectively



fresh weight basis (Judy et al. 2012). In the present study, BAFs were calculated by the ratios of element concentrations in plants (fresh weights, FW) and soils. BAFs were calculated using the following equation:

$$BAF = \frac{C_{vegetable}}{C_{soil}} \tag{1}$$

where $C_{vegetable}$ represents the heavy metal concentrations in dry vegetables, and C_{soil} , the heavy metal concentrations in soils.

Statistics

Pearson’s product correlation coefficients were used in the study for statistics analysis, and a two-tailed test of significance was used with a confidence level 0.95. Linear combination and fitting algorithm, and principle component analysis were used to extract the information on the species of Pb in the investigated samples by XANES and Athena software (Ravel and Newville 2005).

Estimated daily intake

The estimated daily intake (EDI, $\mu\text{g kg}^{-1} \text{ person}^{-1} \text{ day}^{-1}$) was calculated using the following equation:

$$EDI = \frac{C_{FreshVegetable} M_{ingested}}{B_w} \tag{2}$$

where $C_{FreshVegetable}$ is the concentration of heavy metals in fresh vegetables ($\mu\text{g g}^{-1}$, fresh weight), $M_{ingested}$, the mass of daily vegetable ingested per person per day, or rate of vegetable ingestion ($301 \text{ g day}^{-1} \text{ person}^{-1}$, carbohydrate), and B_w , the average body weight (62.8 kg, a mean of male (66.2 kg

and female (57.3 kg), respectively). The mass of daily vegetable ingested and the average body weight were taken from the report on nutrition and chronic diseases of Chinese residents (2015).

Target hazard quotient

The target hazard quotient (THQ) is defined as follows:

$$THQ = \frac{F_{expfrq} D_{expdr} C_{FreshVegetable} M_{ingested}}{R_{fDs} B_w T} \times 10^{-3} \tag{3}$$

where F_{expfrq} is the exposed frequency (365 days per year), D_{expdr} exposure duration (70 years, average lifetime), R_{fDs} , the oral reference dose ($\text{mg kg}^{-1} \text{ day}^{-1}$), and T , the averaging exposure time for non-carcinogens ($365 \text{ days year}^{-1}$ multiplied by number of exposure years, 70 years in this study). When the same exposed frequency and exposure duration as the average exposure time for non-carcinogens are used in formula (4), i.e., $F_{expfrq} \times D_{expdr} = T$, the THQ formula is simplified as the following:

$$THQ = \frac{C_{FreshVegetable} M_{ingested}}{R_{fDs} B_w} \times 10^{-3} = \frac{EDI}{R_{fDs}} \times 10^{-3} \tag{4}$$

Results

Concentrations of metal and metalloid elements in vegetables

In the vegetables collected from the vegetable fields, the maximum concentrations ($Wt.$, mg/kg , fresh weight) were observed in celery for As (1.38) and Pb (8.94), three-color

amaranth for Cd (1.14), coriander for Cr (29.83), soybean stem for Cu (8.50), spinach for Mn (76.88), and radish root for Zn (81.68), respectively. The highest values of As, Cd, Cr, and Pb were 3, 4, 60, and 30 times higher than the maximum allowable concentrations (MACs) of contaminants in foods (GB2762-2012 2012), respectively. The Pb concentrations in all samples of coriander, celery, Chinese radish, and leek exceeded the MACs. Their means are shown in Table 1.

The concentrations of metal(loid) elements in vegetables followed the order: (1) for As, coriander > celery > *Chrysanthemum coronarium* (*C. coronarium*) > spinach and leek; (2) for Cd, spinach > coriander > celery > leek; (3) for Cr, coriander > soybean > leek > *C. coronarium*; and (4) for Pb, coriander > celery > *C. coronarium* > spinach. Generally, coriander, celery, and spinach contained high concentrations of As, Cd, and Pb. They are very popular vegetables in the area of the study.

Bioaccumulation of elements in vegetables

The bioaccumulation of elements by plants varied with plant species and the elemental properties. In the investigated plants, the maximum BAFs were observed in coriander for As (0.23), Cr (1.79), and Pb (0.42); three-color amaranth for Cd (25.10); leek for Cu (0.64); spinach for Mn (0.65); and radish root for Zn (14.69), respectively. The bioaccumulation of the elements in the popular vegetables is as follows: Cd > Zn > Cu > Mn > Cr > Pb > As. Among the investigation elements, BAF of As was lowest, ranging from 0.001 to 0.23.

On the basis of mean BAFs (Table 1) and the number of the collected samples (not less than five), in the current investigation, bioaccumulation of the elements by the vegetables in the present investigation followed the order: for As, *C. coronarium* > coriander > leek > spinach > celery and radish > carrot and *B. chinensis*; for Cd, spinach > coriander > carrot > celery > *B. chinensis* > leek > radish > *C. coronarium*; and for

Table 1 Means of concentrations of the elements in the vegetables (Wt, mg kg FW⁻¹) and bioaccumulation factor (BAF)

	n ³⁾		As		Cd		Cr		Cu		Mn		Pb		Zn	
			Wt	BAF	Wt	BAF	Wt	BAF	Wt	BAF	Wt	BAF	Wt	BAF	Wt	BAF
			Non-leafy vegetables													
Carrot (<i>Daucus carota</i> L.)	5	Mean	0.038	0.031	0.045	1.28	0.15	0.032	0.49	0.23	3.40	0.071	0.22	0.068	2.02	0.31
		SD	0.012	0.014	0.017	1.01	0.14	0.034	0.18	0.12	3.09	0.075	0.10	0.042	0.72	0.20
Celery (<i>Apium graveolens</i>)	26	Mean	0.17	0.051	0.14	1.27	0.34	0.041	0.90	0.24	8.94	0.083	1.11	0.085	5.93	0.37
		SD	0.27	0.024	0.12	0.78	0.57	0.064	0.26	0.086	8.92	0.057	1.77	0.039	3.48	0.15
Coriander (<i>Coriandrum sativum</i> L.)	9	Mean	0.34	0.079	0.23	1.83	6.98	0.43	2.46	0.35	25.05	0.15	1.58	0.12	11.08	0.50
		SD	0.38	0.072	0.26	2.23	10.65	0.64	0.86	0.11	20.24	0.10	1.71	0.12	9.71	0.36
<i>Asparagus lettuce</i> (<i>Lactuca sativa</i> L.)	2	Mean	0.20	0.029	0.08	0.38	0.21	0.029	1.10	0.29	6.61	0.040	1.72	0.044	6.02	0.24
		SD	0.22	0.021	0.072	0.39	0.054	0.017	0.35	0.21	2.56	0.031	2.14	0.043	4.21	0.21
Radish (<i>Raphanus sativus</i> L.)	26	Mean	0.077	0.053	0.058	0.96	0.49	0.093	0.39	0.14	5.30	0.082	0.73	0.10	3.34	0.34
		SD	0.055	0.044	0.042	0.82	1.03	0.18	0.17	0.09	3.92	0.068	0.79	0.079	1.87	0.19
Leafy vegetables																
Chinese Cabbage (<i>Brassica napus</i>)	49	Mean	0.026	0.030	0.032	1.11	0.10	0.046	0.21	0.16	2.02	0.065	0.22	0.055	2.18	0.42
		SD	0.021	0.019	0.020	0.653	0.46	0.22	0.061	0.075	1.48	0.059	0.25	0.039	1.72	0.21
<i>C. coronarium</i> L.	6	Mean	0.15	0.086	0.064	0.77	0.54	0.11	1.01	0.40	6.87	0.12	0.99	0.15	4.87	0.52
		SD	0.18	0.057	0.087	0.49	0.77	0.16	0.37	0.11	3.27	0.064	1.59	0.13	4.31	0.22
Spinach (<i>Spinacia oleracea</i> L.)	12	Mean	0.11	0.057	0.26	3.23	0.41	0.070	0.88	0.27	15.58	0.19	0.94	0.095	8.94	0.66
		SD	0.086	0.027	0.25	2.40	0.70	0.13	0.19	0.13	20.58	0.18	0.99	0.065	5.96	0.32
<i>Amaranthus tricolor</i>	3	Mean	0.28	0.024	0.51	8.84	0.41	0.043	1.65	0.20	12.94	0.10	1.58	0.018	16.19	0.81
		SD	0.059	0.010	0.55	14.09	0.37	0.039	0.26	0.065	8.94	0.13	0.86	0.007	8.74	1.07
Leek (<i>A. tuberosum</i> Rott)	11	Mean	0.11	0.078	0.10	1.03	0.59	0.062	1.22	0.37	12.01	0.15	0.77	0.13	5.67	0.51
		SD	0.04	0.040	0.15	0.97	1.16	0.10	0.33	0.14	12.25	0.14	0.46	0.066	1.34	0.29
Beans																
Pea (<i>Pisum sativum</i>)	2	Mean	0.29	0.021	0.07	0.43	0.26	0.054	1.52	0.21	13.65	0.075	3.58	0.048	14.82	0.41
		SD	0.32	0.018	0.038	0.47	0.020	0.045	0.40	0.13	2.14	0.089	4.43	0.044	7.23	0.40

Note: 1) FW: Fresh weight. 2) n: the number of the measured samples; when n > 1 in the table, the data indicate mean values; 3) MAC for As, Cd, Cr, and Pb is 0.5, 0.05, 0.5, and 0.1, respectively, in GB2762-2012. For Cd, MAC of leaf and celery was 0.2; MAC of beans, root, tuber, and stem was 0.1. For Cr, MAC of beans was 1.0. For Pb, MAC of leaf and brassica was 0.3. MAC of beans and potato was 0.2

Pb, *C. coronarium* > leek > coriander > radish > spinach > celery > carrot > *B. chinensis*. The means of BAFs of Cd were over 1.0 in 7 vegetables, accounting for 64%, and much higher than the others. Coriander showed high bioaccumulation of As, Cd, and Pb, being always in the top three of the investigation vegetables.

Bioaccumulation is decided by the plant species and the element properties. Spinach and three-colored amaranth belong to the *Amaranthaceae* family and their means and standard deviation (SD) of BAFs of Cd were over 3.0, the highest among all of the investigated vegetables, as shown in Fig. 1. Next were carrot, celery, and coriander, belonging to *Apiaceae* family, and their BAFs of Cd were over 1.0. Both the *Amaranthaceae* and *Apiaceae* families have high bioaccumulation of Cd. In the elemental periodic table, Zn is in the same group as Cd. The high BAFs were also observed in spinach and three-colored amaranth of the *Amaranthaceae* family, as well as in carrot, celery, and coriander of the *Apiaceae* family. This indicates that both Cd and Zn can accumulate in the plants belonging to both *Amaranthaceae* and *Apiaceae*

families. This evidence reveals the fact that the plants in the same family have the same bioaccumulation trend of the elements which are in the same group but are a different period.

Extractable fractions of elements in soils and bioaccumulation in plants

Extractable fractions of As

Phytoavailability of elements in soils was determined mainly by the chemical species. Most of As in the whole collected soil samples occurred in the residual fraction, accounting for 58.6–99.2%. In the non-vegetable soils, the concentrations of As in the water soluble fraction were only from 0.055 to 0.99 mg/kg, and As in the weak acid soluble fraction from 0.12 to 0.91 mg/kg, as shown in Table 2. In the vegetable soils, the concentrations of As in the water soluble fraction ranged from 0.55 to 1.46 mg/kg, and As in the weak acid fraction was from 2.02 to 6.19 mg/kg.

Table 2 Mean of elemental concentrations in sequential extraction fractions in soil (mg kg)

	<i>n</i> ¹⁾		Water soluble		Weak acid soluble		Reducible		Oxidizable		Residue		Recovery(%) ²⁾
As VegFarm ³⁾	7	Mean	0.98	0.36	3.77	1.56	18.85	8.42	1.92	0.76	67.01	32.10	97.08
		SD											
Hill ⁴⁾	3	Mean	0.63	0.31	0.31	0.16	39.95	30.33	10.82	3.86	1797	1196	91.06
		SD											
Refinery ⁵⁾	2	Mean	0.06	0.04	0.15	0.22	0.29	0.18	0.17	0.030	13.47	2.36	116.5
		SD											
Vent ⁶⁾	1		0.15		0.12		2.02		1.94		462.5		103.8
Sludge ⁷⁾	1		0.055		0.91		32.02		605.3		984		102
Cd VegFarm	7	Mean	0.028	0.016	2.37	1.90	1.74	1.02	0.34	0.30	0.45	0.22	97.13
		SD											
Hill	3	Mean	0.009	0.003	5.74	4.40	21.57	28.69	1.43	1.58	5.62	3.96	104.6
		SD											
Refinery	2	Mean	0.002	0.001	0.27	0.021	0.16	0.014	0.045	0.007	0.22	0.19	116.9
		SD											
Vent	1		0.002		3.79		12.80		0.34		0.77		99.4
Sludge	1		0.21		7.68		0.98		72.28		165.3		99.04
Cu VegFarm	7	Mean	0.86	0.29	4.75	5.32	30.85	16.31	12.32	8.87	41.18	4.04	110.8
		SD											
Hill	3	Mean	0.83	0.66	19.31	15.96	127.8	51.56	43.61	6.28	348.0	282.3	115.4
		SD											
Refinery	2	Mean	0.22	0.085	0.44	0.049	6.76	1.88	2.37	0.69	28.68	1.54	99.1
		SD											
Vent	1		0.15		0.64		11.52		3.18		44.18		108.9
Sludge	1		0.87		72.52		72.22		717.0		1120		112.4
Pb VegFarm	7	Mean	2.68	2.22	9.87	6.34	600.1	207.9	36.48	9.76	111.4	45.18	115.8
		SD											
Hill	3	Mean	2.68	2.34	583.4	722.5	4464	2174	411.3	249.6	4243	3401	116.2
		SD											
Refinery	2	Mean	0.032	0.021	0.14	0.035	29.07	8.34	3.35	1.22	14.91	1.86	108
		SD											
Vent	1		0.027		0.93		1363		62.92		107.1		113.5
Sludge	1		3.39		5940		3406		1295		18,075		121.7
Zn VegFarm	7	Mean	3.08	2.12	292.6	312.2	305.2	214.5	83.19	62.63	177.5	47.33	109.8
		SD											
Hill	3	Mean	0.65	0.35	314.3	280.3	2566	3286	254.8	283.7	1847	1762	112.2
		SD											
Refinery	2	Mean	0.21	0.042	27.65	1.77	53.62	16.69	15.71	5.66	68.10	0.88	91.7
		SD											
Vent	1		0.20		219.0		1382		83.71		1149		106.5
Sludge	1		11.00		2181		522.0		11,040		38,030		131.4

Note: 1) *n*: the number of the measured samples; when *n* > 1 in the table, the data indicate mean. 2) The ratio of sum of fractions and total elemental concentration. 3) VegFarm: vegetable farmland soils. 4) Hills, soils on the hills. 5) Refinery: soils from oil refinery and gas station. 6) Vent: soils around an air vent from the mine. 7) Sludge: sewage sludge from ore dressing plant

The concentrations of As in the vegetables did not correlate with any of the sequential extraction fractions nor with pH. None of the correlation coefficients was higher than 0.5. However, the concentration of As in *B. chinensis* and celery were moderately correlated with the soil As. The concentrations of As in *C. coronarium* was strongly correlated with soil As ($r = 0.81$, $p < 0.05$). Partly and moderately, As in the vegetables was correlated with Mn oxides, but not with Fe oxides.

Extractable fractions of Cd

In the whole collected soil samples, Cd was mainly in soluble and reducible fractions and accounted for 35.1 and 35.5%, respectively. In the non-vegetable soils, Cd in the two fractions accounted for 30.3 and 43.8%, respectively. In the vegetable soils, Cd in the soluble fraction increased and accounted for 46.3%, and the reducible Cd accounted for 36.8%. Cd in the extractive fractions accounted for 89.7% in total. However, Cd in a sewage sludge sample from an ore dressing plant contained a very low soluble fraction (3.20%).

In the investigation, correlations were observed between plant Cd and the extractable Cd ($r > 0.5$, $p < 0.05$). The plant Cd correlated with the Cd in soluble fraction ($r = 0.75$, $p < 0.05$). Cadmium in *C. coronarium* strongly correlated with soil Cd ($r = 0.99$, $p < 0.05$). Cd in *B. chinensis* and celery moderately correlated with soil Cd. High extractable fractions of Cd was also reported by other researchers. For example, the acid soluble (39.41%) and the reducible (30.44%) fractions were reported in soils around a Pb-Zn mine (Anju and Banerjee 2011). Cadmium in exchangeable and carbonate fractions accounted for 47.53% in soil (Wang et al. 2016a). Soil Cd is highly available (Sterckeman et al. 2009) and tends to be more readily available to plants than many other heavy metals (Shaheen 2009).

Extractable fractions of Cu, Pb, and Zn

In the soil samples, most of the Cu was in the residual fraction with a proportion of 57.7%. Pb was predominantly present in the reducible fraction, accounting for 64.6%. Zinc was mainly in reducible and residual fractions, accounting for 36.03 and 36.02%, respectively. The results are consistent with the reports by other studies. For example, the reducible fraction of Pb accounted for 34.24–77.77% in a Pb-Zn mine area (Anju and Banerjee 2011) and 60.65–64.97% in historically contaminated orchard soil (Fleming et al. 2013).

Typically, the exchangeable and weak acid soluble amount of Pb in soils was low, such as < 0.20% (Marguí et al. 2004), 4.7–5.4% (Fleming et al. 2013), or 0.4–36.02% (Anju and Banerjee 2011). In this study, the soluble fraction of Pb accounted for only 1.65%. In the non-vegetable soils, the Pb concentrations in the water soluble fraction ranged from 0.02 to 4.47 mg/kg. In the vegetable soils, however, the Pb

concentrations in the water soluble fraction increased and ranged from 0.36 to 6.87 mg/kg, and the reducible fraction of Pb increased to account for 78.5%.

In the sample taken from the sewage sludge in the drain outlet of an ore dressing plant, most of the Pb was found in the residual fraction, as well as in the soluble fraction, accounting for 62.9 and 20.7%, respectively. The dressing procedures changed species of Pb, and resulted in a much higher extractable fraction of the toxic element, which may bring more soluble Pb into ambient soils and stronger risks to ecosystems.

Discussion

Phytoavailability and bioaccumulation of elements

In this investigation, a linear relationship between the bioaccumulation factor of metal(loid)s and their soluble and extractable fractions was found. The relative ratio of the soluble and extractable fractions to the total fractions was first calculated. By comparing the means and SD of the element BAFs, as shown in Fig. 2, the bioaccumulation of As, Cd, Cu, Pb, and Zn was correlated with their relative soluble and extractable proportion in the total fractions based on the non-rhizosphere soil. A linear relationship and a linear multiple function were obtained among the means of BAFs of the five elements and the relative soluble and extractable proportions as follows:

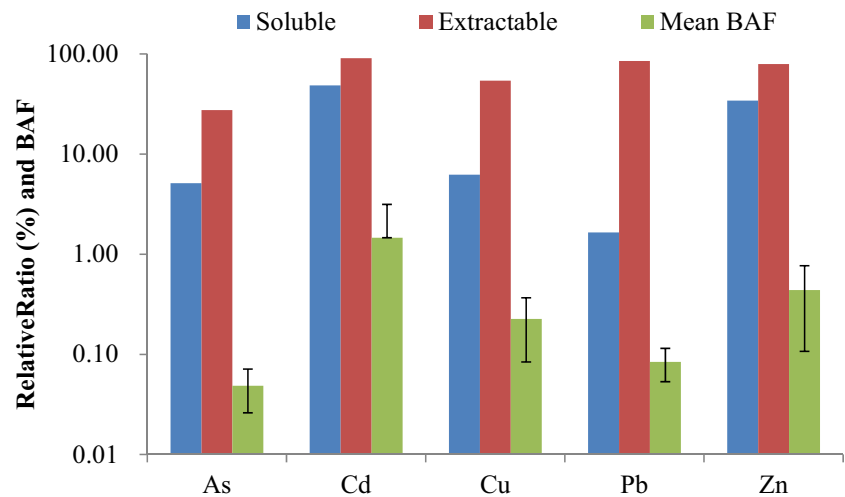
$$\text{BAF} = 0.02517f_{\text{soluble}} - 0.03132, r = 0.87 \quad (5)$$

$$\begin{aligned} \text{BAF} &= 0.02878f_{\text{soluble}} \\ &+ 0.00584f_{\text{reducible}} - 0.00732f_{\text{oxidizable}} - 0.1425, r \\ &= 0.97 \end{aligned} \quad (6)$$

Here, adjusted R-squares were used since the fitting was from a small sample. The linear correlation is shown in Fig. 2S in the supplemental material. The equations imply that the bioaccumulation of the elements by plants is proportional to the amount of the soluble and reducible fractions, and inversely proportional to the oxidizable fraction.

The relationship reveals that the bioaccumulation of the elements in plants and the phytoavailability of the elements in soils are linearly correlated with their relative soluble and extractable proportion, rather than their absolute concentrations. In addition, the soluble proportion of the elements is in the order $\text{Cd} > \text{Zn} > \text{Cu} > \text{As} > \text{Pb}$, the extractable order $\text{Cd} > \text{Pb} > \text{Zn} > \text{Cu} > \text{As}$, and the bioaccumulation $\text{Cd} > \text{Zn} > \text{Cu} > \text{Pb} > \text{As}$. Thus, the phytoavailability of the elements in soils follows the order $\text{Cd} > \text{Zn} > \text{Cu} > \text{Pb} > \text{As}$. The phytoavailability of the elements in soils was generally determined by the soluble fraction, and partly by the extractable fraction.

Fig. 2 Relative ratio (%) of the soluble and extractable fraction to the whole fractions in the vegetable soil, and the means and SD of BAFs of the elements



Effects of soil pH on Cd phytoavailability

Soil pH has effects on Cd phytoavailability and a dual effect can be observed. A negative correlation between plant Cd uptake and soil pH (pH 4.5–7.2) was reported (Delcastilho and Chardon 1995). However, it has also been reported that total Cd uptake at pH = 4 was about one fourth of the uptake at pH = 6 (Sterckeman et al. 2011). In the nettle, only Cu and Zn, not Cd, were negatively correlated with pH (Boshoff et al. 2014). In fact, different soils had various responses to acidification treatment and a different optimum pH may exist (Wang et al. 2006).

In the current investigation, Cd in non-leaf vegetables was not correlated with soil pH. Most of the Cd in the vegetables was not correlated with Fe and Mn oxides in soils, as shown in Table 3. However, Cd in the leafy vegetables increased with pH increment at pH 6.61–7.71, with a correlation of $r = 0.63$ ($p < 0.05$), as shown in Fig. 3S in the supplemental material. In the study area, pH in the irrigation water system ranged from 7.3 to 9.9, and the soils mainly consisted of clay and carbonate (Luo et al. 2014). Moreover, a complex of a metal with the dissolved organic matter (DOM) was identified (Luo et al. 2016).

Indeed, lowering the pH increased phytoavailable Cd and enhanced metal uptake (Wang et al. 2006) due to the increase in Cd solubility with proton concentration (Alloway 1995). However, the contrary evidence is that protons in solutions compete with Cd for the binding site on the cell wall and the plasma membrane (Sterckeman et al. 2011). Moreover, most of the sites in the apoplasm are weak acids with pK values similar to that of polygalacturonic acid (Alam et al. 2003). Therefore, the competition between proton and Cd always exists. The competition results in a dual effect of pH on Cd phytoavailability and plant uptake (Wang et al. 2011). Finally, the dual effects would result in a balance. In addition, Cd phytoavailability is affected by the contents of Ca, clay, and

DOM in soils. Cadmium is taken up through Ca channels, and both Cd and Ca ions compete for this absorption site (Lindberg et al. 2004).

Effects of Pb species in soils on the phytoavailability

In the current investigation, soil Pb is dominant in the reducible fraction, accounting for 74.75–84.34%. The concentrations of Fe and Mn oxides in the vegetable soils ranged from 3.28 to 4.35% and 0.08 to 1.26%, and the correlation coefficients of Pb-Fe and Pb-Mn oxides were 0.38 and 0.81 ($p < 0.05$), respectively. Pb in most of the vegetables was moderately correlated with Mn and Zn oxides in soils, but not with Fe oxides, as shown in Table 3. This suggests that Pb is mainly bound to Mn oxides, as well as Zn oxides. In the sequential extraction procedure, the reducible fraction is an implication of an element which is bound to Fe or Mn oxides (Fleming et al. 2013). Though the reducible fraction was the major species of Pb in the investigated soils, it is notable that Pb in plants was not correlated with the reducible fraction nor with any single fraction or pH. No significant effects of the extractable fraction were observed on the phytoavailability of Pb in soils. Pb in most of the vegetables was correlated with soil Pb. The correlation coefficients of five vegetables ranged from 0.51 to 0.86. When two soil outliers from the vegetable pad near busy roads were removed, a strong correlation ($r = 0.96$, $p < 0.05$) was observed between vegetable Pb and soil Pb, as shown in Fig. 3. The correlation between soil Pb and plant Pb was also confirmed by other researchers. For example, Pb content in rice is positively correlated with soil Pb (Wang et al. 2016b), and Pb uptake is significantly correlated with pseudo-total content based on aqua regia digestion, as well as with all aggressive extraction procedures (Meers et al. 2007).

The Pb isotope fractions of materials depend only on the sources of minerals or ores in samples, and have no correlation with any anthropogenic activities. Thus, four natural Pb

Table 3 Correlation coefficients of heavy elements ($p < 0.05$)

Correlation coefficients of the elements between the vegetables and soils									Correlations between plants and sequential extraction fraction/pH			
Plant	$n^{1)}$	As Soil	Cd Soil	Cr Soil	Cu Soil	Mn Soil	Pb Soil	Zn Soil	Fraction	As Plant	Cd Plant	Pb Plant
Radish	32	0.083	0.15	-0.15	-0.071	-0.20	0.26	0.017	Water/weak acid	0.43	0.75	-0.39
<i>B. chinensis</i>	49	0.72 ²⁾	0.57	-0.12	0.067	0.19	0.77	0.50	Reducible	0.13	0.52	-0.10
Celery	26	0.68	0.57	0.47	0.24	0.32	0.86	0.47	Oxidizable	0.06	0.68	-0.14
Spinach	12	0.45	0.30	-0.090	-0.22	0.18	0.62	0.50	Residue	-0.08	0.48	-0.12
Leek	11	0.090	0.00092	0.81	0.20	0.054	0.51	-0.18	Extractable	0.17	0.59	-0.14
Coriander	9	0.27	0.081	0.37	0.33	0.69	0.026	0.29	pH	-0.20	0.27	-0.20
<i>C. coronarium</i>	6	0.81	0.99	-0.16	0.62	0.018	0.67	0.92				

Correlation coefficients of the elements between the vegetables and Fe/Mn oxides in soil													
Plant	n^*	As-Fe	As-Mn	As-Zn	Cd-Fe	Cd-Mn	Cd-Zn	Pb-Fe	Pb-Mn	Pb-Zn	Cr-Fe	Cr-Mn	Cr-Zn
Radish	32	0.022	0.027	0.57	-0.062	0.030	0.19	-0.23	-0.11	0.65	0.22	-0.17	-0.077
<i>B. chinensis</i>	19	-0.12	0.54	0.49	-0.03	0.34	0.31	-0.093	0.46	0.56	-0.18	-0.076	-0.074
Celery	26	-0.13	0.47	0.46	-0.28	0.13	0.19	-0.13	0.40	0.50	0.28	-0.14	0.32
Spinach	12	-0.25	0.44	0.52	-0.39	0.04	0.018	-0.11	0.64	0.72	-0.24	-0.29	-0.31
Leek	11	-0.30	-0.13	0.13	-0.037	0.17	-0.083	0.51	0.67	0.11	0.24	-0.099	0.97
Coriander	9	-0.27	0.61	0.41	-0.62	-0.084	-0.24	-0.29	0.63	0.34	0.37	0.65	0.38
<i>C. coronarium</i>	6	-0.43	0.56	0.91	-0.33	0.55	0.94	-0.39	0.56	0.95	-0.64	-0.86	-0.48

Note: 1) n was the number of the measured samples; when $n > 1$ in the table, the data indicate mean values in the table

isotopes, ²⁰⁴Pb, ²⁰⁶Pb, ²⁰⁷Pb, and ²⁰⁸Pb, were used to trace the sources of Pb in the research. The ratios of Pb isotopes in the plants collected from the investigated area ranged from 1.126 to 1.170 (²⁰⁶Pb/²⁰⁷Pb) and 2.088 to 2.163 (²⁰⁸Pb/²⁰⁶Pb). The Pb data from the plants formed an ellipse in which one end was within the range of irrigation water and another connected with soil samples, which indicates a connection bridge between soil and water, as shown in Fig. 4. In that bridge, there was a mixing between aerosol and gasoline exhaust particles. Pb isotopes in the plants overlapped with Pb minerals. The results reveal that Pb in plants originate mainly from the vegetable soils correlated with Pb minerals and the irrigation water, partly from aerosols and vehicle exhaust particles.

The more the soluble components of Pb in soils, the more phytoavailability of it in soils. The oxidizable fraction of Pb in the collected vegetable soils, which was related with organic matter and sulfides, accounted for 4.90%. The average soluble fraction accounted for 1.64% in the total fractions. In a non-rhizosphere loose and dried powder sample from the LP region (M_5_LPSoils), two major components, Pb₃(PO₄)₂ and Pb₅(PO₄)₃Cl, were identified by XANES, which accounted for 51 and 49%, respectively, with an R-factor of 0.002932, as shown in Fig. 5. No soluble component was detectable. When the sample was scanned and measured in XRF mode, a significant XRF peak was detected in one spot. The spot (LPSoils_special) was then measured by XANES. In the

Fig. 3 Correlation of Pb in *B. chinensis* L. and in soil ($r = 0.77$, $p < 0.05$). When two outliers of the soil samples taken from the vegetable pad near traffic roads were removed, a strong correlation ($r = 0.96$, $p < 0.05$) was observed

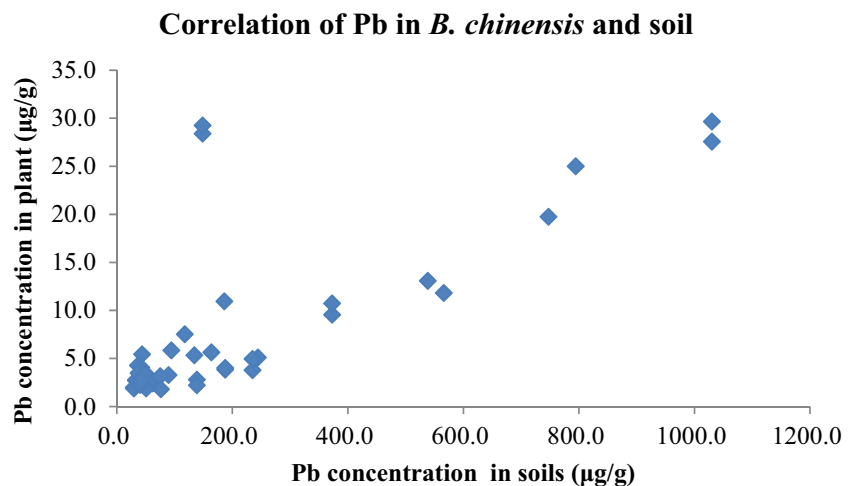
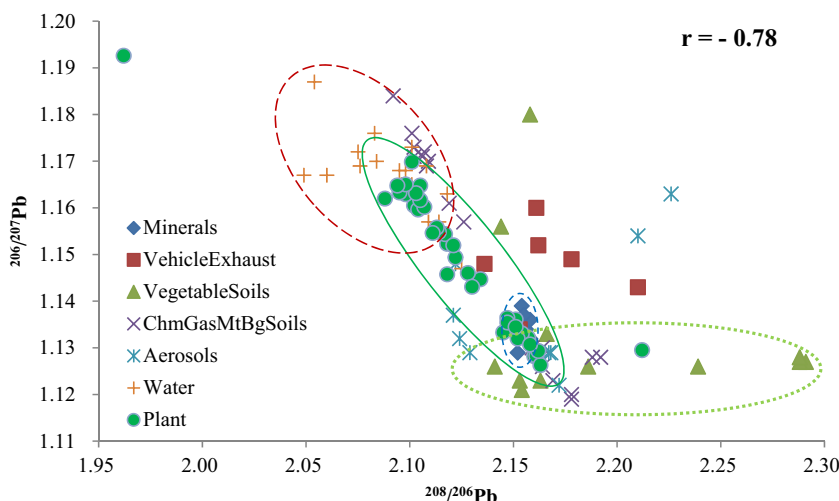


Fig. 4 Pb isotopes in the collected samples. Lead isotopes in the plants formed an ellipse, one end being within the range of water, another connected with soils. Pb isotopes in parts of plants overlapped with Pb minerals. In the figure, Minerals means Pb minerals, VehicleExhaust means gasoline and diesel vehicle exhaust particles, VegetableSoils means soils taken from the vegetable fields, Aerosols means Aerosols and dust particles, Water means water samples from water well and irrigation water system, Plant means plants and vegetables



micro area, hydrocerussite $Pb(CO_3)_2Pb(OH)_2$, $Pb_5(PO_4)_3Cl$, and $Pb(NO_3)_2$ were detectable, accounting for 53, 29, and 18%, respectively. The total insoluble components in the micro non-rhizosphere soils accounted for 82%. In a rhizosphere soil sample (M_2_NJSoils), a Pb-FA complex was found by XANES. Three components were identified as the Pb-FA complex, pyromorphite $Pb_5(PO_4)_3Cl$, and $Pb(NO_3)_2$, accounting for 60, 22, and 18%, respectively, with an R-factor of 0.0125. In the micro size of $100 \times 100 \mu m^2$, the amount of Pb-FA and the soluble Pb compound ($Pb(NO_3)_2$) were much larger than those found by the modified BCR with a large amount of soils. In the rhizosphere soil, Pb organic complex and soluble Pb accounted for 78%. Compared with non-rhizosphere soil and soluble fraction, the rhizosphere soil increased the phytoavailability of Pb by providing a large

quantity of Pb-FA complex and soluble Pb in soils, and favored Pb uptake by plants.

Effect of agricultural soils on elemental phytoavailability

Soil treatments with biosolids (Lavado et al. 2005) and biochar (Moreno-Jiménez et al. 2016) have effects on bioavailability of elements in soils. In the current investigation, it was observed that the agricultural activities changed the extractable properties and therefore phytoavailability of the elements in soils. In the soil samples collected from hills, industrial areas, and gas station sites (non-agricultural soils), the residual fraction of As accounted for 90.1–99.2% in the total five fractions. In the vegetable soils, the residual fraction of As decreased and only accounted for 58.6–77.3%. Moreover, the soluble fractions of As increased from 0.03–3.0% in the non-agricultural soils to 3.5–8.7% in the vegetable soils, as shown in Fig. 6. The extractable fractions of As in agricultural soils (22.7–41.4%) was much larger than those (0.84–9.86%) in the non-agricultural soils. Generally, the residual fraction of As decreased in agriculture soils, and the extractable and soluble fractions increased significantly.

The proportion of the residual fraction to sum fractions of Cd, Cu, and Zn in non-agricultural soils ranged from 4.4 to 42.5%, 52.4 to 79.1%, and 33.3 to 51.8%, respectively. The residual proportion of them in agricultural soils decreased to 7.4–15.0, 28.3–58.3, and 11.9–36.6%, respectively. The proportion of the soluble fraction of them in non-agricultural soils ranged from 13.9 to 51.8, 1.3 to 4.6, and 5.5 to 19.0%, respectively. In the agricultural soils, the soluble proportion increased to 41.5–54.5, 3.4–11.3, and 20.0–45.4%, respectively. The average proportion of the whole extractable fractions of them in agricultural soils was 89.7, 50.9, and 73.5%, respectively,

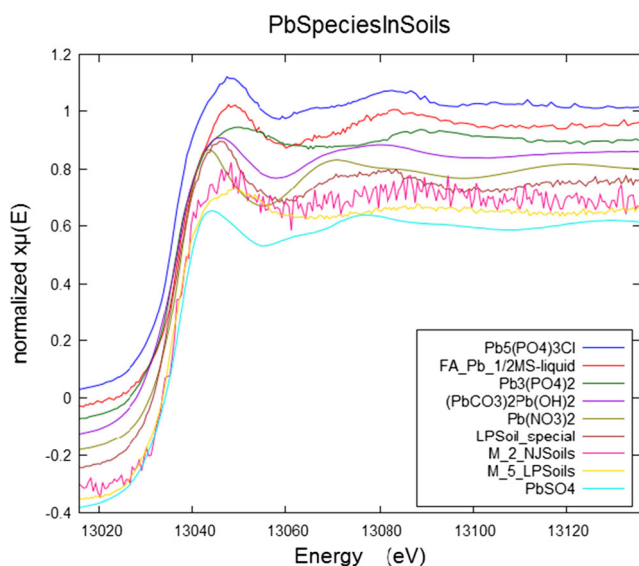
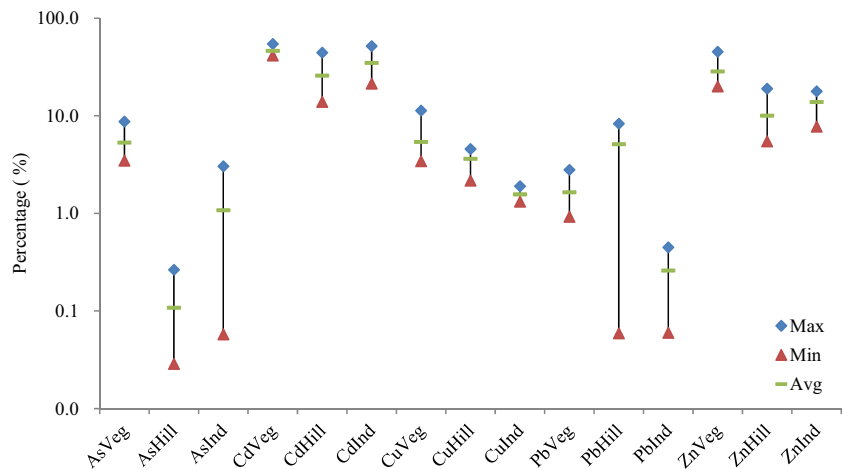


Fig. 5 XANES Spectra of Pb L3 edge in the reference compounds, the collected soils, and the plants taken from the fields

Fig. 6 Water and weak acid extractable fractions of elements in different soils. In the figure, -Veg means soils from vegetable fields, -Hill means soils from hill site, and -Ind means soils from industrial sites



Water and weak-acid extractable fraction in different soils

and those in non-agricultural soils was 78.7, 32.8, and 58.5%. Thus, the soluble and extractable fractions of Cd, Cu, and Zn in the agricultural soils were much higher than those in the non-agricultural soils.

The residual fraction of Pb in the non-agricultural soils accounted for 7.0–48.1% in the total fractions. Its residual proportion in the agricultural soils decreased to 7.6–18.8%. The average proportion of the reducible fraction of Pb was 59.7% in non-agricultural soils, and in the agricultural soils, it was 78.5%. From Eq. (6), the same fact can also be observed that the bioaccumulation of the elements in plants is proportional to the amount of the reducible fraction. Generally, the proportion of the extractable fractions of Pb increased from 68.0% in non-agricultural soils to 85.0% in agricultural soils. However, the average proportions of the soluble fractions in the agricultural and non-agricultural soils were 1.6 ± 0.6 and $2.7 \pm 3.9\%$, respectively, and there was no significant difference between them.

In general, the agricultural activities and plant growing increased the extractable fractions and phytoavailability of As, Cd, Cu, Pb, and Zn by decreasing their residual fraction in soils and raising the soluble or extractable fractions.

Assessment of human health risks

In the investigation area, the concentrations of As, Cd, Cr, and Pb in parts of the popular vegetables were over MACs, as described in the results section. They may enter the human body by a routine diet of the vegetables. An assessment on a potential health risk was made on the basis of EDI of the vegetables and THQ.

The estimated daily intake was calculated and compared, as shown in Table 1S in the supplemental materials. Coriander, three-colored amaranth, and celery were the top three vegetables of intakes of toxic elements.

When the THQ is over 1.0, the vegetable containing that element poses a potential risk to human health. The larger the THQ, the higher is the health risk. In this study, as shown in Table 4 and in Fig. 4S(a)–(g) in the supplemental materials, the maximum THQs of As in celery and coriander were over 20, and the maximum THQ of Pb in celery was over 10. The THQs of As, Cd, and Pb in parts of the vegetables were between 5.0 and 10.0. The maximum THQs of Mn were over 1.0 in four vegetables.

The average THQs of As and Pb in radish, spinach, celery, leek, coriander, *C. coronarium*, three-colored amaranth,

Table 4 Target hazard quotient (THQ) of elements in edible vegetables

THQ	Carrot <i>n</i> = 5	Radish <i>n</i> = 26	A. Lettuce <i>n</i> = 2	Celery <i>n</i> = 26	<i>B. Chinensis</i> <i>n</i> = 49	Spinach <i>n</i> = 12	Leek <i>n</i> = 11	Coriander <i>n</i> = 9	Coronarium <i>n</i> = 6	T. amaranth <i>n</i> = 3	Cabbage <i>n</i> = 3	Lettuce <i>n</i> = 2	Pea <i>n</i> = 2
As	0.61	1.24	3.16	2.72	0.16	1.78	1.84	5.46	2.45	4.48	0.79	0.90	4.59
Cd	0.22	0.28	0.38	0.69	0.03	1.27	0.49	1.11	0.31	2.46	0.27	0.31	0.35
Cr (*10 ⁻³)	0.49	1.56	0.67	1.08	0.0089	1.32	1.89	22.4	1.75	1.33	4.22	1.54	0.82
Cu	0.06	0.05	0.13	0.11	0.02	0.11	0.15	0.30	0.12	0.20	0.05	0.07	0.18
Mn	0.12	0.18	0.23	0.31	0.02	0.54	0.41	0.86	0.24	0.45	0.12	0.22	0.47
Pb	0.31	1.01	2.36	1.53	0.08	1.30	1.05	1.05	1.37	2.18	0.39	0.81	4.93
Zn	0.03	0.05	0.10	0.10	0.02	0.14	0.09	0.18	0.08	0.26	0.06	0.09	0.24

lettuce, and pea were between 1.0 and 5.0, accounting for 69% in 13 vegetables. The vegetables posed binary healthy risks. The average THQs of Cd in spinach, coriander, and three-colored amaranth were over 1.0 and below 3.0, accounting for 23%. Thus, spinach, coriander, and three-colored amaranth had a ternary blended health risks with As, Cd, and Pb. In the investigated agricultural fields near the Pb-Zn mine, therefore, celery, coriander, spinach, three-colored amaranth, *C. coronarium*, and leek presented the highest potential health risks. The health risks of the elements ranked in order of As > Pb > Cd > Mn > Cu > Zn > Cr.

In addition, a correlation between THQ and BAF was found in parts of the investigated elements. The correlation coefficients of Cd and Cr between THQ and BAF were 0.92 and 0.93 ($p < 0.05$), respectively. The medium correlations were found between THQ and BAF of Mn ($r = 0.64$, $p < 0.05$) and Zn ($r = 0.55$, $p < 0.05$). The correlation between THQ and BAF implied that elements in soils posed a direct effect and risk for human health by the biogeochemical chains.

Conclusions

The vegetable fields near the Pb-Zn mine have been polluted by over 50 years of mining activities, and the concentrations of As, Cd, Cr, and Pb in parts of the vegetables grown in the fields exceed the maximum allowable concentrations. The assessment by THQ reveals that the pollution of metal(loid) elements pose a serious risk to human health for the residents living in the area.

Both Cd and Zn can accumulate in plants of both the *Amaranthaceae* and *Apiaceae* families. This evidence reveals a new fact that the plants in the same family have the same trend of bioaccumulation of the elements in the same group in the periodic table of chemical elements but are in a different period.

The concentrations of As in the vegetables were not correlated with any of the sequential extraction fractions. The plant Cd was correlated with the Cd in the soluble fraction and extractable fractions in the soils. Pb in most of the vegetables was correlated with soil Pb. The results by XANES reveal that the phytoavailability of Pb increases in the rhizosphere soil with a large quantity of Pb-FA complex and soluble Pb by plant root activities.

The bioaccumulation of the elements in plants and the phytoavailability of the elements in soils were determined by their soluble fraction, as well as by the extractable fraction. A linear relationship was found between the means of BAFs of As, Cd, Cu, Pb, and Zn and their relative soluble proportions in soils. The bioaccumulation of the elements by plants was proportional to the amount of the soluble and reducible fractions, and inversely proportional to the oxidizable fraction.

The agricultural activities and plant growing increased the soluble and extractable fractions and phytoavailability of As,

Cd, Cu, Pb, and Zn by decreasing their residual fraction in soils and raising the soluble or extractable fractions.

Since the potential health risks in the area are very real, as shown by the study, the focus of research into the effects of heavy metals on human health from the food chain will be the next step in this investigation.

Acknowledgements We would like to thank Dr. Lesley Egden for her checks and suggestions on the manuscript. The Pb species analyses were conducted in Shanghai Synchrotron Radiation Facility (14U and 15W stations, SSRF) and Beijing Synchrotron Radiation Facility (BSRF).

Funding This work was supported by the National Key Technologies R&D Program of China (Grant No. 2016YFC0600603), the National Natural Science Foundation of China (Grant No. 20775018 & 41201527), the National High Tech R&D Program (Grant No. 2007AA06Z124), and the China Geological Survey (Grant No. DD20160340).

References

- Alam MGM, Snow ET, Tanaka A (2003) Arsenic and heavy metal contamination of vegetables grown in Samta village, Bangladesh. *Sci Total Environ* 308:83–96. [https://doi.org/10.1016/s0048-9697\(02\)00651-4](https://doi.org/10.1016/s0048-9697(02)00651-4)
- Alloway BJ (1995) Cadmium. In: Alloway, B.J. (Ed.), *Heavy metals in soils*. Blackie Academic & Professional, pp. 122–151, second ed. Glasgow
- Anju M, Banerjee DK (2011) Associations of cadmium, zinc, and lead in soils from a lead and zinc mining area as studied by single and sequential extractions. *Environ Monit Assess* 176:67–85. <https://doi.org/10.1007/s10661-010-1567-4>
- Bortey-Sam N, Nakayama SMM, Ikenaka Y, Akoto O, Baidoo E, Yohannes YB, Mizukawa H, Ishizuka M (2015) Human health risks from metals and metalloid via consumption of food animals near gold mines in Tarkwa, Ghana: estimation of the daily intakes and target hazard quotients (THQs). *Ecotoxicol Environ Saf* 111:160–167. <https://doi.org/10.1016/j.ecoenv.2014.09.008>
- Boshoff M, De Jonge M, Scheifler R, Bervoets L (2014) Predicting As, Cd, Cu, Pb and Zn levels in grasses (*Agrostis* sp. and *Poa* sp.) and stinging nettle (*Urtica dioica*) applying soil–plant transfer models. *Sci Total Environ* 493:862–871. <https://doi.org/10.1016/j.scitotenv.2014.06.076>
- Delcastilho P, Chardon WJ (1995) Uptake of soil cadmium by 3 field crops and its prediction by a PH-dependent FREUNDLICH sorption model. *Plant Soil* 171:263–266
- Fedotov PS, Kordel W, Miro M, Peijnenburg W, Wennrich R, Huang PM (2012) Extraction and fractionation methods for exposure assessment of trace metals, metalloids, and hazardous organic compounds in terrestrial environments. *Crit Rev Environ Sci Technol* 42:1117–1171. <https://doi.org/10.1080/10643389.2011.556544>
- Ferri R, Hashim D, Smith DR, Guazzetti S, Donna F, Ferretti E, Curatolo M, Moneta C, Beone GM, Lucchini RG (2015) Metal contamination of home garden soils and cultivated vegetables in the province of Brescia, Italy: implications for human exposure. *Sci Total Environ* 518:507–517. <https://doi.org/10.1016/j.scitotenv.2015.02.072>
- Fleming M, Tai Y, Zhuang P, McBride MB (2013) Extractability and bioavailability of Pb and As in historically contaminated orchard soil: effects of compost amendments. *Environ Pollut* 177:90–97. <https://doi.org/10.1016/j.envpol.2013.02.013>
- GB2762-2012 (2012) Maximum levels of contaminants in foods vol GB2762-2012

- Gustafsson JP, Tiberg C, Edkymish A, Kleja DB (2011) Modelling lead(II) sorption to ferrihydrite and soil organic matter. *Environ Chem* 8:485–492. <https://doi.org/10.1071/EN11025>
- Jomova K, Valko M (2011) Advances in metal-induced oxidative stress and human disease. *Toxicology* 283:65–87. <https://doi.org/10.1016/j.tox.2011.03.001>
- Judy JD, Unrine JM, Rao W, Bertsch PM (2012) Bioaccumulation of gold nanomaterials by *Manduca sexta* through dietary uptake of surface contaminated plant tissue. *Environ Sci Technol* 46:12672–12678. <https://doi.org/10.1021/es303333w>
- Kar S, Das S, Jean J-S, Chakraborty S, Liu C-C (2013) Arsenic in the water-soil-plant system and the potential health risks in the coastal part of Chianan Plain, southwestern Taiwan. *J Asian Earth Sci* 77:295–302. <https://doi.org/10.1016/j.jseaes.2013.03.003>
- Khan S, Cao Q, Zheng YM, Huang YZ, Zhu YG (2008) Health risks of heavy metals in contaminated soils and food crops irrigated with wastewater in Beijing, China. *Environ Pollut* 152:686–692. <https://doi.org/10.1016/j.envpol.2007.06.056>
- Khan MU, Malik RN, Muhammad S (2013) Human health risk from heavy metal via food crops consumption with wastewater irrigation practices in Pakistan. *Chemosphere* 93:2230–2238. <https://doi.org/10.1016/j.chemosphere.2013.07.067>
- Kurt-Karakus PB (2012) Determination of heavy metals in indoor dust from Istanbul, Turkey: estimation of the health risk. *Environ Int* 50:47–455. <https://doi.org/10.1016/j.envint.2012.09.011>
- Laborda F, Bolea E, Górriz MP, Martín-Ruiz MP, Ruiz-Beguería S, Castillo JR (2008) A speciation methodology to study the contributions of humic-like and fulvic-like acids to the mobilization of metals from compost using size exclusion chromatography–ultraviolet absorption–inductively coupled plasma mass spectrometry and deconvolution analysis. *Anal Chim Acta* 606(1):1–8. <https://doi.org/10.1016/j.aca.2007.10.048>
- Lavado RS, Rodríguez MB, Taboada MA (2005) Treatment with biosolids affects soil availability and plant uptake of potentially toxic elements. *Agric, Ecosyst Environ* 109:360–364. <https://doi.org/10.1016/j.agee.2005.03.010>
- Li ZY, Ma ZW, van der Kuijp TJ, Yuan ZW, Huang L (2014) A review of soil heavy metal pollution from mines in China: pollution and health risk assessment. *Sci Total Environ* 468:843–853. <https://doi.org/10.1016/j.scitotenv.2013.08.090>
- Lindberg S, Landberg T, Greger M (2004) A new method to detect cadmium uptake in protoplasts. *Planta* 219:526–532. <https://doi.org/10.1007/s00425-004-1256-z>
- Linde M, Öborn I, Gustafsson JP (2007) Effects of changed soil conditions on the mobility of trace metals in moderately contaminated urban soils. *Water Air Soil Pollut* 183:69–83. <https://doi.org/10.1007/s11270-007-9357-5>
- Liu XM, Song Q, Tang Y, Li W, Xu J, Wu J, Wang F, Brookes PC (2013) Human health risk assessment of heavy metals in soil-vegetable system: a multi-medium analysis. *Sci Total Environ* 463:530–540. <https://doi.org/10.1016/j.scitotenv.2013.06.064>
- Loutfy N, Fuerhacker M, Tundo P, Raccanelli S, El Dien AG, Ahmed MT (2006) Dietary intake of dioxins and dioxin-like PCBs, due to the consumption of dairy products, fish/seafood and meat from Ismailia city, Egypt. *Sci Total Environ* 370:1–8. <https://doi.org/10.1016/j.scitotenv.2006.05.012>
- Luo L, Chu B, Liu Y, Wang X, Xu T, Bo Y (2014) Distribution, origin, and transformation of metal and metalloid pollution in vegetable fields, irrigation water, and aerosols near a Pb-Zn mine. *Environ Sci Pollut Res* 21:8242–8260. <https://doi.org/10.1007/s11356-014-2744-8>
- Luo L, Shen Y, Liu J, Zeng Y (2016) Investigation of Pb species in soils, celery and duckweed by synchrotron radiation X-ray absorption near-edge structure spectrometry. *Spectrochim Acta Part B: At Spectrosc* 122:40–45. <https://doi.org/10.1016/j.sab.2016.05.017>
- Marguí E, Salvadó V, Queralt I, Hidalgo M (2004) Comparison of three-stage sequential extraction and toxicity characteristic leaching tests to evaluate metal mobility in mining wastes. *Anal Chim Acta* 524:151–159. <https://doi.org/10.1016/j.aca.2004.05.043>
- McAloon KM, Mason RP (2003) Investigations into the bioavailability and bioaccumulation of mercury and other trace metals to the sea cucumber, *Sclerodactyla briareus*, using in vitro solubilization. *Mar Pollut Bull* 46:1600–1608. [https://doi.org/10.1016/S0025-326X\(03\)00326-6](https://doi.org/10.1016/S0025-326X(03)00326-6)
- Meers E, Samson R, Tack FMG, Ruttens A, Vandegheuchte M, Vangronsveld J, Verloo MG (2007) Phytoavailability assessment of heavy metals in soils by single extractions and accumulation by *Phaseolus vulgaris*. *Environ Exp Bot* 60:385–396. <https://doi.org/10.1016/j.envexpbot.2006.12.010>
- Moreno-Jiménez E, Fernández JM, Puschenreiter M, Williams PN, Plaza C (2016) Availability and transfer to grain of As, Cd, Cu, Ni, Pb and Zn in a barley agri-system: impact of biochar, organic and mineral fertilizers. *Agric, Ecosyst Environ* 219:171–178. <https://doi.org/10.1016/j.agee.2015.12.001>
- Nyquist J, Greger M (2009) Response of two wetland plant species to Cd exposure at low and neutral pH. *Environ Exp Bot* 65:417–424. <https://doi.org/10.1016/j.envexpbot.2008.11.011>
- Oyeyiola AO, Olayinka KO, Alo BI (2011) Comparison of three sequential extraction protocols for the fractionation of potentially toxic metals in coastal sediments. *Environ Monit Assess* 172:319–327. <https://doi.org/10.1007/s10661-010-1336-4>
- Pinto E, Almeida AA, Ferreira IMPLVO (2015) Assessment of metal(-loid)s phytoavailability in intensive agricultural soils by the application of single extractions to rhizosphere soil. *Ecotoxicology and Environmental Safety* 113:418–424. <https://doi.org/10.1016/j.ecoenv.2014.12.026>
- Pueyo M, Mateu J, Rigol A, Vidal M, López-Sánchez JF, Rauret G (2008) Use of the modified BCR three-step sequential extraction procedure for the study of trace element dynamics in contaminated soils. *Environ Pollut* 152:330–341. <https://doi.org/10.1016/j.envpol.2007.06.020>
- Ravel B, Newville M (2005) ATHENA, ARTEMIS, HEPHAESTUS: data analysis for X-ray absorption spectroscopy using IFEFFIT. *J Synchrotron Radiat* 12:537–541. <https://doi.org/10.1107/S0909049505012719>
- Salati S, Quadri G, Tambone F, Adani F (2010) Fresh organic matter of municipal solid waste enhances phytoextraction of heavy metals from contaminated soil. *Environ Pollut* 158:1899–1906. <https://doi.org/10.1016/j.envpol.2009.10.039>
- Shaheen SM (2009) Sorption and lability of cadmium and lead in different soils from Egypt and Greece. *Geoderma* 153:61–68. <https://doi.org/10.1016/j.geoderma.2009.07.017>
- Shahid M, Pinelli E, Pourrut B, Silvestre J, Dumat C (2011) Lead-induced genotoxicity to *Vicia faba* L. roots in relation with metal cell uptake and initial speciation. *Ecotoxicol Environ Saf* 74:78–84. <https://doi.org/10.1016/j.ecoenv.2010.08.037>
- Shen Y (2014) Distribution and speciation of lead in model plant *Arabidopsis thaliana* by synchrotron radiation X-ray fluorescence and absorption near edge structure spectrometry. *X-Ray Spectrom* 43:146–151. <https://doi.org/10.1002/xrs.2531>
- Shen YT, Song YF (2017) Effects of organic ligands on Pb absorption and speciation changes in *Arabidopsis* as determined by micro X-ray fluorescence and X-ray absorption near-edge structure analysis. *J Synchrotron Radiat* 24:463–468. <https://doi.org/10.1107/s1600577517001941>
- Slaveykova VI, Wilkinson KJ, Ceresa A, Pretsch E (2003) Role of fulvic acid on lead bioaccumulation by *Chlorella kesslerii*. *Environ Sci Technol* 37:1114–1121. <https://doi.org/10.1021/es025993a>
- Sterckeman T, Carignan J, Srayeddin I, Baize D, Cloquet C (2009) Availability of soil cadmium using stable and radioactive isotope

- dilution. *Geoderma* 153:372–378. <https://doi.org/10.1016/j.geoderma.2009.08.026>
- Sterckeman T, Redjala T, Morel JL (2011) Influence of exposure solution composition and of plant cadmium content on root cadmium short-term uptake. *Environ Exp Bot* 74:131–139. <https://doi.org/10.1016/j.envexpbot.2011.05.010>
- Sutherland RA (2010) BCR@-701: a review of 10-years of sequential extraction analyses. *Anal Chim Acta* 680:10–20. <https://doi.org/10.1016/j.aca.2010.09.016>
- Sutherland RA, Tack FMG (2003) Fractionation of Cu, Pb and Zn in certified reference soils SRM 2710 and SRM 2711 using the optimized BCR sequential extraction procedure. *Adv Environ Res* 8: 37–50. [https://doi.org/10.1016/S1093-0191\(02\)00144-2](https://doi.org/10.1016/S1093-0191(02)00144-2)
- Tahervand S, Jalali M (2016) Sorption, desorption, and speciation of Cd, Ni, and Fe by four calcareous soils as affected by pH. *Environ Monit Assess* 188:322. <https://doi.org/10.1007/s10661-016-5313-4>
- Tang W, Zhong H, Xiao L, Tan Q, Zeng Q, Wei Z (2017) Inhibitory effects of rice residues amendment on Cd phytoavailability: a matter of Cd-organic matter interactions? *Chemosphere* 186:227–234. <https://doi.org/10.1016/j.chemosphere.2017.07.152>
- Tian K, Yang J, Sun ZJ, Zhou YM, Xing SC, Feng YP (2017) Preparation of soil certified reference materials for heavy metals in contaminated sites rock and mineral. *Analysis* 36:82–88
- Tiwari KK, Singh NK, Patel MP, Tiwari MR, Rai UN (2011) Metal contamination of soil and translocation in vegetables growing under industrial wastewater irrigated agricultural field of Vadodara, Gujarat, India. *Ecotoxicol Environ Saf* 74:1670–1677. <https://doi.org/10.1016/j.ecoenv.2011.04.029>
- Tokahoglu S, Kartal S (2004) Bioavailability of soil-extractable metals to tea plant by BCR sequential extraction procedure. *Instrum Sci Technol* 32:387–400. <https://doi.org/10.1081/ci-120037671>
- Wang AS, Angle JS, Chaney RL, Delorme TA, Reeves RD (2006) Soil pH effects on uptake of Cd and Zn by *Thlaspi caerulescens*. *Plant Soil* 281:325–337. <https://doi.org/10.1007/s11104-005-4642-9>
- Wang P, Kinraide TB, Zhou DM, Kopittke PM, Peijnenburg W (2011) Plasma membrane surface potential: dual effects upon ion uptake and toxicity. *Plant Physiol* 155:808–820. <https://doi.org/10.1104/pp.110.165985>
- Wang T-J, Pan J, Liu X-L (2016a) Speciation and translocation characteristics of soil heavy metals in the water level fluctuating zone of Pengxi River in three gorges reservoir area rock and mineral. *Analysis* 35:425–432. <https://doi.org/10.15898/j.cnki.11-2131/td.2016.04.015>
- Wang T-Y, Zhou G-h, Sun B-B, He L, Zeng D-M, Chen Y-D, Ye R (2016b) Soils and Rice in coastal areas, Fujian Province, including influencing factors rock and mineral. *Analysis* 35:295–301. <https://doi.org/10.15898/j.cnki.11-2131/td.2016.03.013>
- Wang L, Yang L-F, Tan X-Z, Wu Z-H (2017) Determination of cd in environmental geological samples by inductively coupled plasma-mass spectrometry with membrane desolvation rock and mineral. *Analysis* 36:574–580. <https://doi.org/10.15898/j.cnki.11-2131/td.201703130032>
- Zhao Q, An M, Chen H (2018) Research on geochemical characteristics of soil in a chemical industrial factory site in Jinan City[J]. *Rock Miner Anal Rock Miner Anal* 37:201–208. <https://doi.org/10.15898/j.cnki.11-2131/td.201708240135>
- Zhuang P, McBride MB, Xia HP, Li NY, Lia ZA (2009) Health risk from heavy metals via consumption of food crops in the vicinity of Dabaoshan mine, South China. *Sci Total Environ* 407:1551–1561. <https://doi.org/10.1016/j.scitotenv.2008.10.061>