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RESEARCH ARTICLE

The accumulation and health risk of heavy metals in vegetables around a zinc smelter in northeastern China

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Abstract Mining and smelting activities engender soil contamination by metals severely. A field survey was conducted to investigate the present situation and health risk of heavy metals (Cd, Pb, Zn, Cu, Cr, As, and Hg) in soils and vegetables in the surrounding area of an 80-year-old zinc smelter in northeastern China. Soil pH, organic matter (SOM), and cation exchange capacity (CEC) were determined, and their relations with heavy metal contents in edible parts of vegetables were analyzed. Results showed that the smelting had led to the significant contamination of the local soils by Cd and Zn, with average concentrations of 3.88 and 403.89 mg kg^{-1}, respectively. Concentrations of Cd and Zn in greenhouse soils were much lower than those in open farmland soils. Cd concentrations in vegetable edible parts exceeded the permissible limits severely, while other metal concentrations were much lower than the corresponding standards. Leaf and root vegetables had higher concentrations and bioaccumulation factors (BCFs) of Cd than fruit vegetables. Hazard quotient and hazard index showed that cadmium is imposing a health risk to local residents via vegetable consumption. Cd uptake of some vegetables can be predicted by empirical models with the following parameters: soil pH, SOM, CEC, Zn concentrations, and Cd concentrations. Vegetables such as cabbage, Chinese cabbage, tomato, cucumber, and green bean were screened out as being suitable to grow in the studied area.

Keywords Cadmium · Zinc smelter · Bioaccumulaiton factor (BCF) · Risk assessment · Empirical model · Hazard quotient (HQ)

Introduction

Soil contamination by metals and metalloids from anthropogenic activities is of great concern worldwide (Su et al. 2014). Heavy metals are mainly introduced into plants grown in contaminated soil through roots and translocated to foliage and edible parts (Fytianos et al. 2001). When heavy metal-laden plants and their foodstuffs are consumed, they pose a serious health hazard to humans through food-chain biomagnifications (Nabulo et al. 2010; Zhuang et al. 2009). Cadmium, lead, arsenic, and mercury have the potential of accumulating in the different body organs with long biological half-lives, which leads to toxic effects (Steenland and Boffetta 2000; Jarup 2003; Smith and Steinmaus 2009). Although zinc, copper, and chromium are essential elements for maintaining human health, they can be toxic when taken in excess (Shi et al. 2013; Liao et al. 2011; Cohen et al. 1993).

Food safety is a burning issue regarding human health in recent decades. A number of research works have been conducted to work on health risk of heavy metal with consumption of food crops cultivated in soils contaminated by water irrigation, solid waste disposal, sludge application, mining and smelting processes, and agricultural activities (Massaquoi et al. 2015; Li et al. 2014; Yang et al. 2014; Smith 2009).

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Vegetables are one of the important parts of our dietary intake, and they play a significant role in terms of human exposure to heavy metal, which contribute about 90 % of the total metal intake (Martorell et al. 2011). Therefore, there is an urgent need to develop reasonable farming strategies and adopt the best suitable agriculture practices for producing vegetables with low heavy metals in contaminated areas.

Mining and smelting activities are the main sources of heavy metals in the environment (Luo et al. 2014; Xu et al. 2013; Sterckeman et al. 2002; Dudka and Adriano 1997). China is one of the largest producers and consumers of zinc and lead in the world (Zhang et al. 2012), and lead/zinc mining and smelting activities have resulted in heavy metal contamination in soils and vegetables (Li et al. 2005, 2009, 2014; Yang et al., 2014). Huludao Zinc Plant, situated in Liaoning Province of China, is the largest zinc smelter in Asia. For more than 70 years up to 2010, the smelter generated significant quantities of dust. The emissions generated by this smelter have led to substantial contamination of the surrounding soils by heavy metals, including Zn, Pb, Cd, Cu, As, and Hg (Zhang et al. 2010; Li et al. 2006). Liu et al. (2003) reported that the soils in the range of 10 km at the north of Huludao Zinc Plant were contaminated seriously by cadmium, and the range of exceeding times of Cd in soils were 4–12 according to the permissible limit of Cd in arable soil of China (0.3 mg kg^{-1}). Vegetables in open field closed to the smelter (<2.0 km) were primarily contaminated by Cd, Pb, Zn, and Hg and posed health risk to the inhabitants via consumption (Zheng et al. 2007).

Due to the environmental protection policies and economic transformation in China, the smelting process was promoted greatly in 2010, and the metalliferous dust emission significantly decreased but soil in a large area will stay contaminated for years. In recent years, all the farmlands closed to the smelter (<3–5 km) were used to build an industry zone with the rapid development of local economy. In the meantime, more and more farmlands in long distance (>3–5 km) from the smelter were transformed to cultivate vegetables, and a large number of greenhouses were also built to increase profitability. The vegetables produced in this area are generally consumed by local communities and play a significant role in the daily diet of people in Huludao City. Up to now, there was no any information about the accumulation and health risk of heavy metals in the vegetables near the smelter after the dust emission decreased. Compared with open-field cultivation, greenhouse farming maintains higher productivity through chronic intensive agriculture, a high multi-cropping index, and excessive use of fertilizer, which can lead to a series of environmental problems, such as soil acidification and heavy metal accumulation (Yang et al. 2014). However, the effect of greenhouse farming on heavy metal accumulation in soils contaminated by smelting activities still needs further investigation. Information was very important to develop reasonable farming strategies and manage the contaminated farmlands.

The objectives of this study were to (i) investigate the present accumulation status of Cd, Zn, Cu, Pb, Cr, As, and Hg in soils and vegetables in the study area, (ii) compare the difference of heavy metal accumulation in soils and vegetables between open-field and greenhouse farming, (iii) evaluate the health risks of heavy metals by the consumption of vegetables, and (iv) screen out the low-Cd uptake vegetable species suitable to grow in studied area.

Materials and methods

Study area

The study area is situated at the north of Huludao Zinc Plant (40° 43′ 01″ N, 125° 55′ 58″ E) in Liaoning Province of China, and the straight-line distance from smelter is about 4.0–7.0 km (Fig. 1). The climate of Huludao is typically continental monsoon with a long-term average annual temperature of 9.0 °C and an annual precipitation of 590 mm. The primary wind is northeastern in winter and southwestern in summer. The soils in this study area belong to the zonal brown soil and are classified as a sandy soil (23 % clay, 18 % silt, and 59 % sand). Corn is the traditional crop cultivated in the area. In recent years, more and more farmlands near the smelter were used to cultivate vegetables, and a large number of greenhouses were also established to increase vegetable rotation for more economic income.

Sampling and sample pretreatment

Sampling was conducted from July 2014 to November 2015. A total of 271 vegetable samples (edible parts) with their corresponding soil samples around the roots (0–20 cm) of crops were collected in six sampling plots (Fig. 1). A total of 125 samples from greenhouse and 146 samples from open field, including 18 usual vegetable species were collected (Table 1). All fresh vegetable samples were thoroughly cleaned with tap water by hand and then washed three times with deionized water. Water on the surface of the vegetable samples was absorbed by filter papers. Each sample was ground with a blender, the mixture was subdivided into three plastic bowels, of which one was stored in a refrigerator at 4 °C for analysis of heavy metals and the other two were stored at −18 °C for re-analysis if necessary.

Soil samples were air-dried at room temperature and mixed thoroughly. Portions (approximately 100 g) of the soil samples were ground into powder with a mill, sieved through a 0.2-

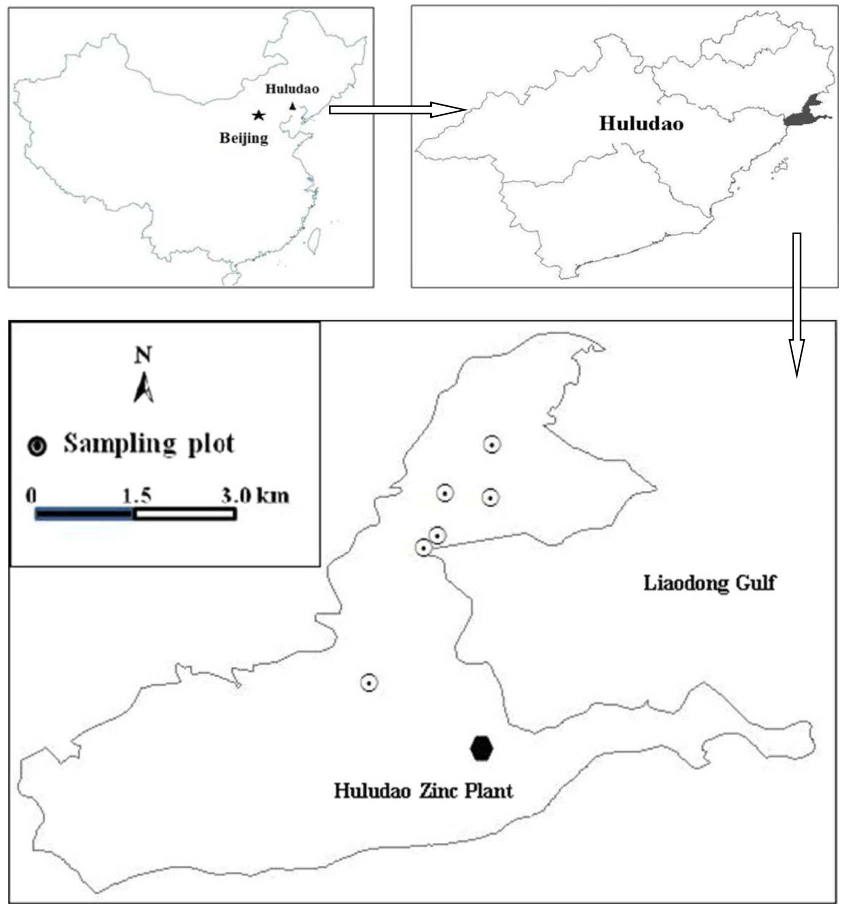

Fig. 1 Locations in the contaminated area by Huludao Zinc Plant, China, from which vegetable samples were collected

mm sieve, and stored in polyethylene bags for chemical analysis.

Sample analysis

Based on the national standard methods, soil pH was determined in a 1:2.5 soil/water suspension in triplicate by potentiometric pH meter (PB-10, Sartorius, China); soil organic matter (SOM) concentration was determined by the K_2CrO_7–H_2SO_4 oxidation method, and cation exchange capacity (CEC) was analyzed by ammonium acetate method. The total metal analysis of soil was conducted as follows: soils (0.300 g) were subsequently digested in Teflon vessels with 4 mL HNO_3 (65 %, *v*/*v*), 1 mL $HCLO_4$ (70 %, *v*/*v*), and 5 mL HF (40 %, *v*/*v*) according to national standard methods. The digestion was then transferred to a 25-mL volumetric flask and diluted to the required volume with deionized water. Determination of Cd, Zn, Pb, Cu, and Cr were conducted by atomic absorption spectroscopy (AAnalyst 800, Perkin-Elmer, USA) with graphite furnace and flame. For the determination of As and Hg, soil samples (0.200 g) were digested in glassware with 5 mL of 50 % aqua regia (HNO_3/HCL, 1:9) in boiling water for 2 h. The digestion solution was transferred to a volumetric flask and diluted to 25 mL with deionized water after adding 5 mL thiourea (50 g L^{-1}). The mixture was mixed and placed for 30 min in room temperature for the detection of As and Hg by a hydrogen-generation atomic fluorescence spectrometer (HG-AFS, AFS-9700A, Beijing Haiguang Instrument Co., Ltd., China).

Vegetable samples (3.00 g) were digested with 5 mL HNO_3 (65 %, *v*/*v*) and 2 mL H_2O_2 (30 %, *v*/*v*) with microwave ovens (MARS^{X}press, CEM, USA). Digested samples were diluted to a final volume of 50 mL with deionized water. The solution was used to measure the concentrations of Cd, Pb, Zn, Cu, Cr, As, and Hg by inductively coupled plasma mass spectrometer (ICP-MS; NexION™300X, Perkin-Elmer, USA). The detection limit of the method was 0.001 mg kg^{-1} for Cu, Cd, As, and Hg, 0.005 mg kg^{-1} for Pb, and 0.01 mg kg^{-1} for zinc and Cr. To correct the potential signal drift, internal standardization based on Indium recovery (20 μL L^{-1}) was performed.

Data quality was checked by analysis of the recovery rate using standard reference materials of soil (GBW 07425) and celery (GBW 10048), which were analyzed for corresponding elements. The samples of every batch were analyzed in triplicate, and reagent blanks and certified reference materials were carried out in the same way. The recoveries calculated for Cu, Pb, Cd, Zn, Cr, As, and Hg were 90–96, 90–102, 91–105, 88–93, 89–96, 96–99, and 105–110 %, respectively.

Table 1 Different vegetable species in greenhouse and open field in studied area of Huludao

Vegetable group	English name	Latin name	Family	No. of VG[a]	No. of VOF[b]
Leaf vegetables	Spinach	*Spinacia oleracea*	Convolvulaceae	6	4
	Endive	*Cichorium endivia*	Asteraceae	11	2
	Lettuce	*Lactuca sativa*	Asteraceae	9	3
	Garland chrysanthemum	*Chrysanthemum coronarium* Schousb	Asteraceae	2	–
	Pakchoi	*Brassica campestris* Makino var. *communis*	Cruciferae	12	3
	Celery	*Apium graveolens*	Umbelliferae	11	4
	Cabbage	*Brassica oleracea* var.*capitata*	Cruciferae	16	42
	Chinese cabbage	*Brassica campestris pekinensis* Olsson	Cruciferae	–	10
Fruit vegetables	Eggplant	*Solanum melongena*	Solanaceae	3	9
	Green bean	*Phaseolus vulgaris*	Leguminosae	6	–
	Cucumber	*Cucumis sativus*	Cucurbitaceae	14	3
	Green pepper	*Capsicum annuum*	Solanaceae	6	9
	Tomato	*Lycopersicon esculentum*	Solanaceae	29	4
	Cauliflower	*Brassica oleracea* var. *botrytis*	Cruciferae	–	26
Root vegetables	Carrot	*Daucuscarota* var. *sativa*	Umbelliferae	–	5
	Potato	*Solanum tuberosum*	Solanaceae	–	5
	Radish	*Raphanus sativus*	Cruciferae	–	12
	Onion	*Allium cepa*	Liliaceae	–	5

[a] The number of vegetables in greenhouse (VG)

[b] The number of vegetables in open field (VOF)

Data analysis

All statistical analyses were processed using SPSS16.0 software (SPSS, USA). The tests of normality of soil parameters and metal contents in vegetables were carried out by Kolmogorov-Smirnov program. Since the statistical distribution of most variable was not normal, the differences on the average values of data sets of soil parameters and vegetable metals between greenhouse and open field were tested using Mann-Whitney *U*, which is a non-parametric alternative to the *t* test for independent samples. Pearson correlation was used to relate total heavy metal concentrations in soils and vegetables. In case the heavy metal concentrations in vegetable were lower than the method detection limit (LOD), the LOD was used for statistical analysis. Figures were drawn by Microsoft Excel software (Excel 2010).

To assess the long-term potential health risks associated with heavy metal intakes from consumption of vegetables, hazard quotients (HQ) were calculated to evaluate the non-carcinogenic health risk. HQ values is described by USEPA (2007) as the ratio of the dose resulting from exposure to site media compared with a dose that is believed to be without risk of effects. If the HQ is higher than 1, it is believed that there is a potential health risk. The HQ of metals was based on the following equations:

$$HQ = \frac{EF \times ED \times VI \times MC}{RfD_0 \times BW \times AT}$$

where EF is the exposure frequency (365 day year^{-1}), ED is the exposure duration (70 years for adult), VI is the vegetable ingestion, considered to be 0.139, 0.160, and 0.072 kg person^{-1} day^{-1} for leaf, fruit, and root vegetables for adults in China, respectively (WHO/GEMS/FOOD 2012), MC is the average metal concentration in the edible part of the vegetable (mg kg^{-1} fresh weight (FW)), RfD_0 is the oral reference dose (mg kg^{-1}d^{-1}), BW is the average adult body weight (60.0 kg person^{-1}), and AT is the average time for non-carcinogens (ED × 365 day year^{-1}). Since the values of the maximum tolerable intakes per day for As and Pb have been withdrawn by the Joint FAO/WHO Expert Committee on Food Additives in 2011, here only the containments of Cd, Zn, Cr, Cu, and Hg were selected for hazard risk assessment. The RfD_0 values for Cd, Zn, Cr, and Cu were 0.001, 0.3, 1.5, and 0.5 mg kg^{-1} bw, respectively (USEPA 1989, 1998, 2005; JECFA 1982). The provisional tolerable weekly intake (PTWI) of Hg was 0.004 mg kg^{-1} bw (JECFA 2010).

The hazard index (HI) can be expressed as the sum of the hazard quotients (HQ) for all metals (Zheng et al. 2007). The HI was calculated as follows:

$$HI = \sum_{1}^{5} HQ$$

Results

Soil pH, CEC, SOM and heavy metal contents

The main physico-chemical parameters determined for soils from the studied area were as follows (Table 2). The soils were mainly acidic to neutral, with the average pH value of 6.21. The average value of CEC and SOM was 17.12 cmol kg^{-1} and 22.21 g kg^{-1}, respectively. Compared with background values of Liaoning Province farmland (Wu et al. 1994), the average value of soil pH was much lower, while SOM and CEC in greenhouse soil were much higher. The average concentration of Cu, Pb, Cd, Zn, Cr, As, and Hg in soils was 42.61 43.67, 3.88, 403.89, Cr, As, and 0.21 mg kg^{-1}, respectively. The CV % of Pb, Cd, Zn, Cr, and Hg was higher than that of Cu and As, even 97.6 % for Hg and 62.3 % for Cd. It suggested that the distribution of Pb, Cd, Zn, Cr, and Hg was not as homogenous as that of Cu and As.

Overall, soil pH, CEC, SOM, and total Cr concentrations were significantly lower while Cd, Pb, Zn and As concentrations were evidently higher in open-field soils than greenhouse soils (Table 2). The Cu, Pb, Cd, Zn, Cr, As, and Hg concentrations in both open-field and greenhouse soils were found significantly higher than background values of Liaoning Province farmland (Wu et al. 1994). Based on the environmental quality evaluation standard for greenhouse vegetable production (SEPAC 2007), the mean concentration of Cd and zinc in greenhouse soils exceeded the permissible limit seriously, with the average values of 2.89 and 324.22 mg kg^{-1} for Cd and zinc, respectively.

The simple correlations between heavy metal and soil parameter concentrations in soils are shown in Table 3. In open field, there were significant positive correlations ($P < 0.01$) between Cu, Pb, Cd, Zn, and Cr, except for the relationship between Zn and Cr; there were significant negative correlations ($P < 0.01$) of As with Cu, Pb, Cr, and CEC and significant positive correlations ($P < 0.01$) of As with Zn and SOM; similarly, the significant positive correlations of Hg with Cu, Pb, Cd, and Zn were also observed. Compared with open field, there were no significant correlations of Zn with other metals. Not like the negative correlations of pH with Cu, Pb, Zn, Cr, and Hg in open-field soils,

Table 2 Statistical summaries of physical-chemical properties (cmol kg^{-1} for CEC, g kg^{-1} for SOM) and heavy metals (mg kg^{-1}) in open-field soils (n = 146) and greenhouse soils (n = 125)

Soil	Parameters	pH	CEC	SOM	Cu	Pb	Cd	Zn	Cr	As	Hg
All samples	Mean	6.21	17.12	22.21	42.61	43.67	3.88	403.89	71.12	12.32	0.21
	CV %	12.01	28.01	48.12	37.40	48.89	62.31	53.67	57.04	23.03	97.61
	Percentiles										
	25 %	5.62	14.42	14.41	30.71	30.22	2.38	287.12	43.89	10.21	0.09
	50 %	6.31	16.31	19.92	38.89	40.23	3.45	382.23	63.14	12.11	0.13
	75 %	6.83	19.53	28.71	52.78	49.89	4.87	469.03	78.44	13.94	0.21
	95 %	7.31	24.82	40.62	67.67	81.23	7.55	892.06	158.46	16.63	0.72
	Skewness	−0.26	1.04	0.83	1.22	1.77	1.81	1.51	2.57	0.98	2.23
	Kurtosis	−0.91	2.45	0.76	2.49	4.66	5.79	4.13	8.90	1.93	4.65
Open field	Mean	6.11a	14.21a	21.01a	41.21a	44.67a	4.73a	472.12a	64.45 a	13.22a	0.17a
	Min	4.82	7.42	10.82	14.13	19.33	0.80	70.23	23.04	6.53	0.03
	Max	8.12	21.12	46.21	115.41	142.02	15.90	1534.34	292.02	23.29	0.88
	CV	13.10	19.71	34.31	39.78	52.80	56.01	48.73	46.41	22.71	88.22
Greenhouse	Mean	6.41b	20.42b	23.51b	44.33a	42.58b	2.89b	324.22b	78.78b	11.12b	0.25a
	Min	4.72	12.71	2.51	23.12	12.54	0.08	67.34	20.78	7.87	0.01
	Max	7.53	39.72	61.82	98.04	92.44	10.33	855.44	292.05	16.73	1.11
	CV	9.40	21.60	57.40	34.31	43.41	56.40	51.78	62.32	18.84	96.01
Background		7.08	14.67	20.51	19.80	21.10	0.11	63.50	57.91	8.82	0.04
Standard					50	50	0.3	200	150	30	0.25

Different letters in the same column indicate a significant difference at $P < 0.05$. Background values were from the "Background Values of Elements in Soils of China, 1990." Standard values were from the "Environmental Quality Evaluation Standard for Farmland of Greenhouse Vegetables Production" (HJ 333-2006), pH <6.5, (SEPAC 2007)

Min minimum, *Max* maximum, *CV* coefficient of variation, *DW* dry weight, *CEC* cation exchange capacity, *SOM* soil organic matter

Table 3 Correlation coefficients among the contents of heavy metals and soil physical-chemical properties in open-field soils (n = 146) and greenhouse soils (n = 125)

Soil	Item	pH	CEC	SOM	Cu	Pb	Cd	Zn	Cr	As	Hg
Greenhouse	pH	1									
	CEC	0.407**	1								
	SOM	0.471**	0.472**	1							
	Cu	0.121	−0.035	0.474**	1						
	Pb	0.373**	0.229**	0.475**	0.583**	1					
	Cd	0.287**	0.141	0.291**	0.175*	0.499**	1				
	Zn	0.198*	−0.069	−0.066	−0.011	0.013	0.139	1			
	Cr	0.221*	−0.072	0.152	0.347**	0.258**	0.063	0.098	1		
	As	0.305**	−0.149	−0.205*	−0.277**	−0.317**	−0.109	0.176**	−0.193*	1	
	Hg	0.118	0.054	0.220**	0.399**	0.222**	0.030	0.172	0.155	0.141	1
Open field	pH	1									
	CEC	−0.030	1								
	SOM	0.136	−0.337**	1							
	Cu	−0.157	0.376**	−0.112	1						
	Pb	−0.020	0.331**	−0.194*	0.512**	1					
	Cd	0.056	0.140	0.183*	0.340**	0.528**	1				
	Zn	−0.190*	−0.135	0.203*	0.259**	0.402**	0.546**	1			
	Cr	−0.229*	0.536**	0.242**	0.369**	0.325**	0.412**	−0.056	1		
	As	0.058	−0.399**	0.378**	−0.419**	−0.395**	−0.115	0.340**	−0.376**	1	
	Hg	−0.054	0.093	0.021	0.211*	0.178*	0.289**	0.205*	0.030	0.121	1

*Correlation is significant at the 0.05 level; **correlation is significant at the 0.01 level

significant and non-significant positive correlations of pH with all the metals in greenhouse soils were observed.

Heavy metal concentration in the edible part of vegetable

Heavy metal concentrations in the edible parts of vegetables varied greatly and decreased in the order of Zn > Cu > Cd > Cr, Pb, and As >> Hg (Table 4). The mean concentrations of Zn ranged from 1.54 to 21.8 mg kg^{-1}. The highest Zn concentration was found in onion, while the lowest was in tomato. The mean concentrations of Cu ranged from 0.163 to 2.262 mg kg^{-1}, and the highest Cu concentration was found in green pepper. The highest average concentration of Cd was detected in endive (0.643 mg kg^{-1}) and the lowest one was in green bean (0.009 mg kg^{-1}), respectively. The concentrations of Cu, Cr, As, and Hg in all vegetables were detected to be far less than the permissible limits of China; the Pb concentrations in some eggplant and green pepper samples exceeded the permissible limit (0.1 mg kg^{-1}). Similarly, Zn concentrations in some onion and spinach samples exceeded the allowable values. However, the mean concentrations of Cd in 60 % of vegetable species exceeded the permissible limits. Overall, the leaf and root vegetables had much higher concentrations of Cd than fruit vegetables. The relatively low-Cd concentrations were found in the species of Chinese cabbage, cabbage, cucumber, tomato and green bean, which were within the permissible limits of Cd in food.

The accumulation levels of Cd in ten main vegetable species between greenhouse and open field were compared (Fig. 2). Overall, the mean value of Cd in vegetable grown in greenhouse was low, although significant difference in Cd accumulation between open field and greenhouse was not observed, except for cabbage (Fig. 2).

Bioaccumulation factor

Bioaccumulation factor (BCF) is defined as the ratio of heavy metal concentration in edible part of plant (mg kg^{-1} FW) to the total metal concentration in soil (mg kg^{-1}). The results showed that the BCF values varied among different vegetables and heavy metals (Table 5). Overall, the BCF values decreased in the order of Cd > Zn > Cu > Pb, Cr, and As. The average BCF value for Cd was 0.075 and was three times that of Zn and four times of Cu. The highest BCF values of Cd, Cu, Zn, and Pb were observed in lettuce, green pepper, onion, and eggplant, respectively. Depending on vegetable type, the average BCF values of Cd decreased in order of leaf vegetables > root vegetables > fruit vegetables; the zinc BCF values followed the sequence of root vegetables > leaf vegetables > fruit vegetables; yet the

Table 4 Heavy metal concentrations (means and standard deviations, mg kg^{-1} FW) in the edible parts of vegetables and permissible limits set by China

Vegetable group	English name	Cu	Pb	Cd	Zn	Cr	As	Hg
Leaf vegetables	Endive	0.626 ± 0.236	0.097 ± 0.094	0.643 ± 0.209	13.121 ± 7.791	0.030 ± 0.006	0.094 ± 0.101	0.003 ± 0.002
	Spinach	0.695 ± 0.134	0.096 ± 0.029	0.485 ± 0.342	17.632 ± 9.960	0.046 ± 0.008	0.094 ± 0.100	0.004 ± 0.001
	Lettuce	0.727 ± 0.511	0.076 ± 0.053	0.314 ± 0.235	7.864 ± 5.883	0.042 ± 0.016	0.094 ± 0.069	0.004 ± 0.004
	Celery	1.039 ± 0.510	0.055 ± 0.051	0.209 ± 0.150	15.682 ± 4.951	0.127 ± 0.099	0.048 ± 0.027	nd
	Pakchoi	0.485 ± 0.265	0.107 ± 0.168	0.192 ± 0.115	10.112 ± 5.880	0.063 ± 0.021	0.079 ± 0.085	0.008 ± 0.011
	Cabbage	0.287 ± 0.115	0.015 ± 0.027	0.095 ± 0.053	7.967 ± 3.972	0.079 ± 0.046	0.008 ± 0.015	0.003 ± 0.002
	Garland chrysanthemum	1.073 ± 0.073	0.059 ± 0.004	0.078 ± 0.026	7.341 ± 1.533	0.063 ± 0.020	0.066 ± 0.008	nd
	Chinese cabbage	0.163 ± 0.072	0.015 ± 0.012	0.064 ± 0.025	4.389 ± 0.978	0.172 ± 0.170	0.110 ± 0.043	0.002 ± 0.002
	Mean	0.499	0.045	0.213	9.654	0.076	0.050	0.002
Fruit vegetables	Eggplant	1.378 ± 0.803	0.199 ± 0.187	0.216 ± 0.108	2.467 ± 1.643	0.302 ± 0.083	0.031 ± 0.014	nd
	Green pepper	2.262 ± 1.259	0.082 ± 0.107	0.079 ± 0.058	2.411 ± 0.842	0.073 ± 0.040	0.027 ± 0.026	nd
	Cauliflower	0.337 ± 0.183	0.053 ± 0.040	0.071 ± 0.044	7.722 ± 1.823	0.213 ± 0.106	0.005 ± 0.008	nd
	Cucumber	0.636 ± 0.351	0.007 ± 0.006	0.016 ± 0.017	2.656 ± 1.463	0.071 ± 0.068	0.029 ± 0.032	nd
	Tomato	0.822 ± 0.366	0.043 ± 0.014	0.016 ± 0.029	1.544 ± 0.701	0.120 ± 0.093	0.016 ± 0.029	nd
	Green bean	0.975 ± 0.126	0.018 ± 0.027	0.009 ± 0.007	4.053 ± 0.702	0.259 ± 0.151	0.079 ± 0.071	nd
	Mean	0.969	0.057	0.064	3.553	0.147	0.022	nd
Root vegetables	Carrot	1.038 ± 0.244	0.071 ± 0.022	0.403 ± 0.084	9.447 ± 1.162	0.247 ± 0.017	0.014 ± 0.001	0.003 ± 0.001
	Onion	0.537 ± 0.272	0.020 ± 0.019	0.428 ± 0.267	21.801 ± 5.562	0.018 ± 0.002	0.016 ± 0.005	0.001 ± 0.000
	Potato	1.405 ± 0.174	0.011 ± 0.012	0.230 ± 0.050	10.767 ± 2.081	0.129 ± 0.012	0.009 ± 0.002	nd
	Radish	0.333 ± 0.076	0.015 ± 0.019	0.089 ± 0.044	8.553 ± 4.032	0.138 ± 0.028	0.003 ± 0.005	nd
	Mean	0.700	0.026	0.236	11.583	0.134	0.009	0.001
Mean		0.708	0.048	0.156	7.393	0.111	0.034	0.002
Permissible limits		10	0.3[a], 0.1[bc]	0.2[a], 0.05[b], 0.1[c]	20	0.5	0.5	0.01

Permissible limits of Pb, Cd, Cr, As, and Hg were from "Permissible limit of contaminants in foods" (GB2762-2012, China). Permissible limits of Cu and Zn were from GB 15199-1994 and GB 13106-1991, respectively

FW fresh weight, *nd* the value was below the detection limit of method

[a] Permissible limit for leaf vegetables

[b] Permissible limit for fruit vegetables

[c] Permissible limit for root vegetables

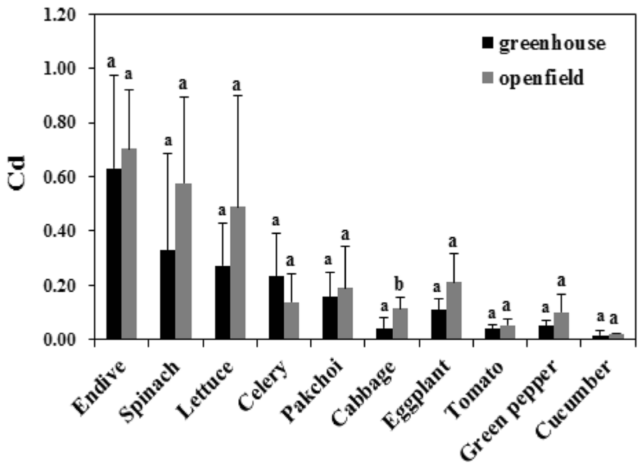

Fig. 2 Comparison of Cd concentration (mg kg^{-1} FW) in the edible part of ten vegetables grown in greenhouse and open field (means and standard deviations). Statistically significant differences ($P < 0.05$) are indicated by *different letters above the bars* for the same vegetable

BCF values of Cu were presented as root vegetables > fruit vegetables > leaf vegetables. It was also found that Chinese cabbage, tomato, cucumber, and green bean had the relatively weak bioaccumulation of Cd. Because mercury concentrations in most of the vegetables were lower than the detection limit, the BCF of mercury was not calculated in the present study.

Regression analysis of Cd uptake by vegetables and soil parameters

Single linear correlation coefficients showed the relationships between Cd concentrations in the edible parts of vegetables and soil parameters (pH, SOM, CEC, Zn, and Cd concentrations) were dependent on vegetables (Table 6). As for lettuce, Chinese cabbage, eggplant, green bean, green pepper, carrot, and onion, no significant correlations existed between Cd concentrations in the edible parts and soil parameters. In order to predict the risk of Cd in the edible parts of vegetables grown in the studied area, stepwise regression analyses were conducted between Cd concentrations in the edible parts of vegetables and soil parameters (pH, SOM, CEC, Zn, and Cd concentrations) (Table 6). The results showed that the effectiveness of the equations varied greatly with vegetable species, although the Cd contents in edible parts of vegetables could be described by the established equations. The R adj^2 values of equations of spinach, potato, radish, cabbage, and pakchoi were higher than 0.5, suggesting that above 50 % of the variability of Cd uptake of these vegetables could be explained by these soil parameters. However, the effectiveness of the models for endive, celery, cauliflower, cucumber, and tomato were not so good because of the relatively low R^2 values.

Table 5 Bioaccumulation factors of heavy metals in vegetable samples (means and standard deviations)

Vegetable group	English name	Cu	Pb	Cd	Zn	Cr	As
Leaf vegetables	Endive	0.022 ± 0.010	0.005 ± 0.005	0.310 ± 0.198	0.040 ± 0.028	0.001 ± 0.001	0.002 ± 0.002
	Spinach	0.023 ± 0.004	0.004 ± 0.001	0.122 ± 0.061	0.049 ± 0.028	0.001 ± 0.000	0.005 ± 0.004
	Lettuce	0.025 ± 0.019	0.003 ± 0.001	0.346 ± 0.424	0.050 ± 0.032	0.001 ± 0.000	0.007 ± 0.005
	Celery	0.022 ± 0.011	0.001 ± 0.002	0.087 ± 0.102	0.050 ± 0.022	0.002 ± 0.001	0.005 ± 0.003
	Pakchoi	0.015 ± 0.008	0.002 ± 0.002	0.303 ± 0.518	0.030 ± 0.011	0.001 ± 0.000	0.006 ± 0.006
	Cabbage	0.008 ± 0.004	<0.001	0.024 ± 0.013	0.018 ± 0.009	0.001 ± 0.001	0.001 ± 0.001
	Garland chrysanthemum	0.027 ± 0.001	0.001 ± 0.000	0.030 ± 0.011	0.021 ± 0.001	0.001 ± 0.000	0.008 ± 0.002
	Chinese cabbage	0.003 ± 0.002	<0.001	0.010 ± 0.009	0.011 ± 0.004	0.002 ± 0.002	0.013 ± 0.006
	Mean	0.014	0.002	0.125	0.030	0.001	0.004
Fruit vegetables	Eggplant	0.038 ± 0.029	0.006 ± 0.005	0.039 ± 0.023	0.008 ± 0.007	0.007 ± 0.002	0.003 ± 0.001
	Green pepper	0.059 ± 0.048	0.002 ± 0.002	0.018 ± 0.013	0.007 ± 0.003	0.002 ± 0.001	0.003 ± 0.003
	Cauliflower	0.009 ± 0.005	0.002 ± 0.001	0.030 ± 0.017	0.027 ± 0.022	0.003 ± 0.002	<0.001
	Cucumber	0.014 ± 0.009	<0.001	0.005 ± 0.006	0.014 ± 0.018	0.001 ± 0.000	0.002 ± 0.003
	Tomato	0.017 ± 0.008	<0.001	0.012 ± 0.005	0.005 ± 0.004	0.001 ± 0.000	0.002 ± 0.003
	Green bean	0.022 ± 0.006	<0.001	0.004 ± 0.003	0.018 ± 0.003	0.002 ± 0.002	0.008 ± 0.007
	Mean	0.023	0.001	0.019	0.013	0.002	0.002
Root vegetables	Carrot	0.039 ± 0.008	0.002 ± 0.001	0.114 ± 0.015	0.010 ± 0.001	0.005 ± 0.001	0.001 ± 0.000
	Onion	0.024 ± 0.020	<0.001	0.075 ± 0.034	0.173 ± 0.119	0.001 ± 0.000	0.001 ± 0.000
	Potato	0.044 ± 0.011	<0.001	0.033 ± 0.009	0.015 ± 0.009	0.001 ± 0.000	0.001 ± 0.000
	Radish	0.012 ± 0.005	0.001 ± 0.001	0.019 ± 0.006	0.021 ± 0.010	0.003 ± 0.000	<0.001
	Mean	0.025	0.001	0.049	0.046	0.002	0.001

Table 6 Multiple regression analysis models and single linear correlation coefficients between Cd concentrations in edible parts of vegetables and related soil physico-chemical properties

Vegetable group	Species	Stepwise multiple regression analysis		Single linear correlation coefficients				
		Equation	R adj^2	pH	CEC	SOM	Cd	Zn
Leaf vegetables	Endive (n = 13)	Cd[a] = 3.322 − 0.400 pH	0.445**	−0.701**	−0.183	−0.273	0.223	0.125
	Spinach (n = 10)	Cd = −2.660 + 0.084 Cd + 0.002 Zn + 0.173 CEC − 0.032 SOM	0.959**	−0.496	−0.048	0.113	0.536	0.715*
	Celery (n = 15)	Cd = 0.827 − 0.016 SOM − 0.016 CEC	0.469**	−0.559*	−0.007	−0.589*	−0.461	−0.102
	Pakchoi (n = 15)	Cd = 0.026 + 0.0005 Zn	0.599**	−0.107	−0.433	−0.165	0.502	0.792**
	Cabbage (n = 58)	Cd = 0.179 − 0.008 CEC + 0.009 Cd	0.527**	−0.519**	−0.691**	−0.572**	−0.522**	0.293*
Fruit vegetables	Cauliflower (n = 26)	Cd = 0.119 + 0.022 Cd − 0.0003 Zn	0.462**	−0.161	0.084	−0.385	0.556**	−0.398*
	Cucumber (n = 17)	Cd = 0.081 − 0.003 CEC	0.364**	0.391	−0.635**	0.278	0.188	−0.125
	Tomato (n = 33)	Cd = 0.037 + 0.0004 SOM	0.098*	0.278	−0.176	0.355**	0.090	0.203
Root vegetables	Potato (n = 5)	Cd = 1.135 − 0.047 OM	0.823*	−0.299	−0.808	−0.931*	−0.920*	0.822
	Radish (n = 12)	Cd = −0.0001 + 0.018 Cd	0.558**	−0.617**	0.271	−0.281	0.773**	0.086

[a] Metal concentrations in the edible parts of vegetables

*$P < 0.05$; **$P = 0.01$—correlation is significant at these levels (two-tailed)

Health risk of heavy metals via vegetable consumption

Figure 3 displays the HQ and HI values of heavy metals in vegetables for adults via consumption. The HQ values of Cu, Cr, and Hg in most of the vegetable samples were below 0.010, and the HQ values of Zn were in the range of 0.010 to 0.120. However, the HQ values of Cd were much higher than those of the above metals and accounted for 81.4 to 86.1 % of the HI values. The average HQ values of heavy metals decreased in the order of leaf vegetable > root vegetable > fruit vegetable. The total HI value was higher than the threshold of 1, indicating that there was a certain health risk of heavy metals for local residents via daily intake of vegetables.

Discussion

Soil properties and heavy metal accumulation

There are rather few data sets of soil properties that can be used for comparison near the Huludao Zin Plant. The soils in the studied area were acidified seriously, which was in accordance with previous studies (Liu et al. 2003; Zhu et al. 2001). The SOM contents (10.82–61.82 g kg^{-1}) detected in this study were higher than the values (10.40–16.10 g kg^{-1}) reported by Zhu et al. (2001) and were comparable with the contents (9.10–145.0 g kg^{-1}) reported by Zheng et al. (2007). The average content of CEC (17.12 cmol kg^{-1}) determined in this survey was higher than the value (13.32 cmol kg^{-1}) reported by Zhu et al. (2001).

Compared with the previous research (Zheng et al. 2007, 2008, 2010), the concentrations of heavy metals (Zn, Cd, Cu, Pb, Cr, As, and Hg) in both open-field and greenhouse soils in this studied area were much lower. It confirmed that the atmospheric deposition decreased with the increasing distance from the Huludao Zinc Plant (Zhang et al. 2008; Liu et al. 2003). The soil samples in this study were collected mostly in the site with a straight-line distance of 4.0–7.0 km from the smelter, while the sampling plots in previous investigations were mainly distributed within 3.0 km from the smelter. For example, the average content of Cd, Zn, Pb, and Cu in soils within 2.0 km from the Huludao Zinc Plant (Zheng et al. 2007) was more than 9.1, 5.2, 6.3, and 2.8 times the relevant value determined in this study, respectively. Although the contamination levels of soils decreased significantly, the soils in the studied area were still contaminated seriously by Cd, and more attention should be paid to develop reasonable farming strategies and manage the farmlands contaminated by Cd.

Significant positive relationships between metals (except for As) in open-field soils indicated that those metals might originate from the same source. However, relationships between metals in greenhouse soils were not as good as those

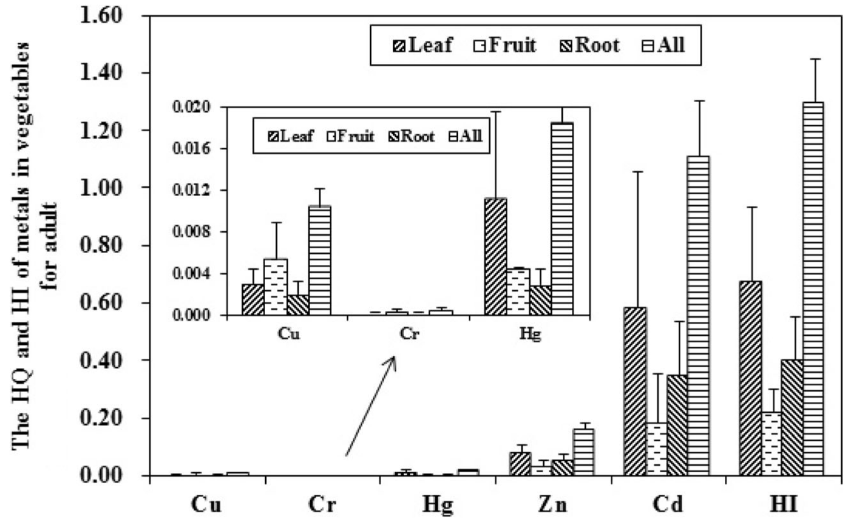

Fig. 3 Hazard quotient (*HQ*) and hazard index (*HI*) of metals in the edible parts of different vegetables for adults in the studied area contaminated with heavy metals from Huludao Zinc Plant. The *error bars* indicate the standard deviations

in open-field soils (especially Zn). In addition, compared with open field, concentrations of Cd and Zn in greenhouse soils decreased significantly. It could be induced that greenhouse soils were disturbed by agricultural practices significantly. It is well known that large amounts of organic fertilizer or poultry dung are applied to maintain high productivity of vegetables in greenhouse (Hu et al. 2014; Chen et al. 2013), and some other agricultural materials (e.g., lime and foreign soil) are used to improve soil physical-chemical properties (Chen et al. 2014). In general, greenhouse cultivation with high-intensity use of agricultural materials will result in accumulation of heavy metals in soils (Xu et al. 2015; Chen et al. 2014; Yang et al. 2015). Fan et al. (2013) reported that horse manure application could increase Cr concentration in bulk soils compared with controls. Moreno-Caselles et al. (2005) claimed that repeated application of pig manure would lead to the accumulation of Zn and Cu. However, with regard to the soils contaminated by Cd and Zn seriously, the concentrations of Cd and Zn in greenhouse soils would be diluted by large amount of agricultural materials, since the concentrations of Cd and Zn in those materials were significantly lower than those in the contaminated soils.

Heavy metal contamination in vegetables

As it is well known, plants accumulate heavy meals by absorbing them from soil or from deposits on the surface of the plants exposed to polluted air (Bigdeli and Seilsepour 2008; Krishna and Govil 2007; Khairiah et al. 2004). Results from previous studies demonstrated that vegetables grown in the area affected by mining and smelting were contaminated severely by heavy metals (Li et al. 2014; Křibek et al. 2014). However, the present study showed that the concentration levels of heavy metals in vegetables were much lower compared with the results from previous studies. Zheng et al. (2007) reported that the average content of Cd, Zn, Pb, and Cu in the edible part of vegetables around the Huludao Zinc Plant was respectively 6.4, 2.3, 33.3, and 1.4 times as high as the relevant value determined in this study (Fig. 4). It was mainly attributed to the lower concentrations of heavy metals in soils and the significant decrease of atmospheric deposition in the studied area as mentioned previously. The low concentrations of heavy metals in soils would result in the low accumulation of heavy metals in vegetables through root uptake (Massas et al. 2013; Zeng et al. 2011; Sharma et al. 2008). Zheng et al. (2007) reported that Hg and Pb in vegetables near the Huludao Zinc Plant are mainly derived from the atmosphere and the high atmospheric deposition in dust particles. In addition, the vegetable samples, collected in the present study, were not exactly the same species as those collected by Zheng et al. (2007). Different vegetable species had different abilities and capacities to take up and accumulate metals (Singh et al. 2010; Peris et al. 2007). Although the contamination levels of heavy metals in vegetables decreased significantly, the vegetables in the studied area were still

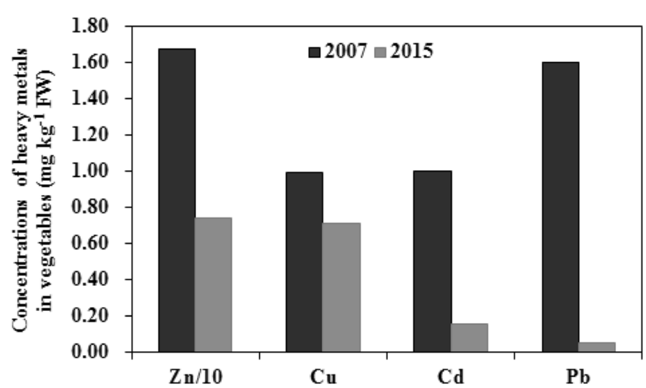

Fig. 4 Comparisons of average concentration of heavy metals in the edible part of vegetables growing near the Huludao Zinc Plant between the years of 2007 and 2015. The Zn concentration was reduced to one tenth and was expressed as Zn/10

contaminated by Cd, and reasonable strategies should be developed to assure the quality safety of vegetables.

In ten vegetable species, only cabbage in open field had higher Cd concentration than in greenhouse, and there were no significant differences in Cd concentration between open field and greenhouse for other nine vegetable species. Overall, the mean value of Cd in vegetable species grown in greenhouse was low, which was consistent with the lower-Cd content in greenhouse soil. In addition, high standard deviation of Cd concentration in those vegetables indicated that Cd accumulation in vegetable was influenced by various factors, such as soil properties and vegetable cultivars. For example, cabbage-accumulated Cd from soil was influenced significantly by soil pH, SOM, CEC, Cd, and Zn content (Table 6). In the present study, soil properties only may not be sufficient to explain the observed results.

In this study, the low concentration levels of Cd in cabbage, Chinese cabbage, tomato, cucumber, and green bean were found, indicating the weak accumulation ability of Cd for these vegetables. It is consistent with the previous researches (Chang et al. 2014; Li et al. 2014; Gebrekidan et al. 2013).

Heavy metal uptake in vegetables

Generally, heavy metals have the capability to migrate from soil to plant tissues (Stasinos and Zabetakis 2013). The present results showed that the average BCF value of Cd was much higher than that of other metals, which was in agreement with other research (Yang et al. 2014; Li et al. 2014). It is easier for Cd to transfer from soil to plant, and the high transfer ability might be attributed to that Cd is generally more available in soil (especially in contaminated soil) (Li et al. 2014; Waterlot et al. 2011) and can use various pathways of entering plant root as well as efficient transfer pattern from root to other parts of plant (DalCorso et al. 2013; Lux et al. 2011). Compared with the heavy metal BCF values obtained in the previous research (Li et al. 2014, 2015; Yang et al. 2014; Hu et al. 2014; Gebrekidan et al. 2013), great variations of BCF values were found. It might result from the differences in heavy metal concentrations in soils and the differences in heavy metal uptake among vegetable species and cultivars (Zheng et al. 2007).

The heavy metal uptake and accumulation of plants are influenced by various factors, including metal speciation and environmental conditions such as soil pH, CEC, SOM, and soil texture (Massas et al. 2013; Waterlot et al. 2013; Zeng et al. 2011; Sharma et al. 2008; Jung 2008). Therefore, empirical models derived from multiple linear regression analysis by soil properties and heavy metal concentrations in vegetables might be able to investigate the major factors influencing the heavy metal uptake in vegetables, and thus to regulate heavy metal movement from soil to vegetables. The present results showed that excellent multiple correlations between Cd concentration in edible parts of vegetables and soil parameters were found in spinach and potato, and the R^2 values of their regression equations were 0.959 and 0.823, respectively. As the major vegetables for local residents, cabbage, radish, and pakchoi had R^2 values of 0.5 above, thus the models of those vegetables might be applied to regulate the usability of Cd-polluted soil to ensure the safety of the vegetable production in the studied area. For example, based on the model of Cd accumulation in radish, the radish is not feasible to be cultivated in the soil with the Cd concentration being higher than 5.5 mg kg^{-1} lest the Cd concentration in radish exceeded the permissible limit (0.1 mg kg^{-1} FW).

Potential health risk of heavy metals via vegetable consumption

Being an important nutrient source, vegetables are the essential foods in Chinese daily life with large consumption. Heavy metal contamination in vegetables imposes a threat on food safety and human health. In this study, Cd was the major element contributing to the contaminants in vegetables. Leaf and root vegetables presented much higher risk of Cd than fruit vegetables, which was consistent with the results reported in other literatures (Li et al. 2015). It indicated that the health risk of vegetable consumption might be altered as a result of the changes in consuming different vegetables. Therefore, it was strongly suggested that in the study area, one should avoid eating the vegetables with large amount including endive, spinach, lettuce, eggplant, carrot, and onion in order to reduce health risks.

Conclusions

The present study demonstrated that heavy metals (Cd, Zn, Hg, Cu, Pb, As, and Cr) have been accumulated in the farmland soils surrounding the Huludao Zinc Plant, and Cd and Zn were contaminated severely. Greenhouse cultivation improved the soil parameters of the soil pH, CEC, and SOM and decreased the concentrations of heavy metals (especially Cd and Zn) in soils and the concentrations of Cd in the vegetables grown in those contaminated soils. This investigation showed that Cd in vegetables grown in the studied area posed a potential health risk for the local population via vegetable ingestion. More attention should be paid to develop reasonable farming strategies and manage the farmlands contaminated by Cd. The vegetable species with low-Cd uptake should be recommended, such as Chinese cabbage, cabbage, cucumber, tomato, and green bean. This study provided some basis and valuable information for the safety guideline of vegetable production in the studied area.

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