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Lead, Zinc, and Cadmium in Vegetable/Crops in a Zinc Smelting Region and its Potential Human Toxicity

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Abstract Lead, Zn, and Cd in vegetables/crops were investigated in a zinc smelting region in China, and their daily dietary intake by local residents was estimated. It is observed that Pb, Zn, and Cd were in 34.7–91.1, 242–575, and 0.199–2.23 μg g^{-1} dry weight in vegetables/crops with their greatest concentrations in leafy vegetable. The daily dietary intake of Pb, Zn, and Cd by adult residents reached 3, 646, 59,295, and 186 μg day, respectively, and lettuce and cabbage together contributed 75% of the Pb, 50% of the Zn, and 70% of the Cd.

Keywords Heavy metals · Daily dietary intake · Dietary habit

Worldwide metal mining/smelting activities result in a great release of heavy metals Pb, Zn, and Cd into surrounding soils and water bodies. Extreme accumulations of these metals in crops due to plant uptake or atmospheric deposition were reported (Uzu et al. 2010); therefore, a potential threat to human health is a big concern when these polluted crops are consumed (Lee et al. 2006). Toxicity of Pb, Zn, and Cd to human beings is well documented (WHO 250, WHO 659, WHO 553, 2009a, c, b). Recent studies demonstrate that intake of vegetables is one of the important sources of environmental cadmium exposure (Zheng et al. 2007).

Daily dietary exposure to these heavy metals poses a potential health risk to humans. In the metal polluted region, blood and hair samples, especially those from children, contained high concentrations of Pb, Zn, and Cd (Yasar and Ozyigit 2009). Zinc smelting activities in northwestern Guizhou, China resulted in extremely high concentrations of Pb, Zn, and Cd in soils, stream water, and plants, especially in crops (Bi et al. 2009), which could be a potential health threat to local residents due to daily dietary exposure. Previous studies revealed high Cd levels in the urine (~57 μg L^{-1}) and hair (~6.80 μg g^{-1}) of local children (Li and Ke 1985) as well as high blood Pb (Wu 2001), which was attributed to the respiration inhalation of smelting dust. However, the risk from dietary exposure was a neglected aspect and has been a long term issue, since vegetables/crops growing in the heavy metal polluted soils are mainly self-consumed and are harvested year by year. Therefore, the authors hypothesized that the accumulation of heavy metals in arable soils could pose a health risk to local residents through the food chain. The objectives of this study were to survey the accumulated levels of Pb, Zn, and Cd in vegetables/crops in the smelting region, and to estimate the dietary exposure risk to local residents.

Materials and Methods

Sampling was carried out in three regions. One is a former zinc smelting region (large scale smelting activities ceased in 2001) in northwestern Guizhou, China (longitude/latitude: 104°41′/27°07′). The second one is a green agricultural vegetable/crop production base in Malin Township, central Guizhou, China (longitude/latitude: 106°37′/26°17′). It is a mountainous region with mild climate and friendly ecological conditions, and is supposed to be free of industrial pollution. The third one is a farmers' market in Magu Township in the zinc smelting region, northwestern Guizhou, China (longitude/latitude: 104°33′/26°58′).

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In the former zinc smelting region, plants (maize, bean, and potato) were randomly collected. Each plant sample was a composite of 3 random samplings in 1 m^2 area. Soils were sampled in the respective root zone (0–30 cm) of each plant; therefore, each soil sample is a thorough mixing of 3 random root soils containing about 1 kg of soil. Sampling was accomplished in an area of about 4.5 km^2, which had distances from 5 m up to 500 m away from the Zn smelting furnaces (or slag piles). In total, 41 of plant samples (27 of maize, 8 of beans, and 6 of potatoes), together with 41 root soils were taken. For comparison, ten maize samples and their root soils were collected in the same way from the green agricultural vegetable/crop production base in Malin Township in an area of about 2 km^2. In the farmers' market in Magu Township, procured vegetable/crop samples were randomly collected, each containing a fresh weight of about 0.5 kg. Totally 84 samples were collected, which were composed of 3 maize corn (Zea mays L.), 29 of stem vegetables, 27 of leafy vegetables, 13 of fruity vegetables, and 12 of root vegetables.

After air-dried, soils were subjected to measurements of pH and total organic carbon. Soil pH was measured using a pH meter following EPA method 150.1 in the slurry of soil: deionized water ratio of 1:1 (w/w). Loss on ignition (LOI) was determined by heating soils in a muffle oven for 12 h at 900°C, soil total organic carbon (TOC) was then calculated from the LOI using a conversion equation of TOC = 0.476 LOI −1.87.

In laboratory, plants were divided into root, shoot, and fruit (if any). After washing using tap water and rinsing using DI water, plant tissues were oven-dried at 70°C for 48 h. The moisture of plant tissues was then calculated based on the weight differences before and after drying. A microwave digestion system was adopted to digest the plant tissue samples (Bi et al. 2009). After being air-dried, soil samples were subjected to digestion using the microwave digestion system (Bi et al. 2009). The concentrations of Pb, Zn, and Cd in the digestion solution were determined using a flame or graphite furnace atomic absorption spectroscopy (GFAAS, Model 5100PC, Perkin-Elmer, USA). For quality assurance and quality control (QA/QC), sample duplicates, method blanks, and standard reference materials of soil and plant tissues (SRM 2710, GBW 07404 and GBW 07602) were used during analyses; recoveries for SRM and GBWs were in 87%–114% (Bi et al. 2009). The detection limits for Pb, Zn, and Cd on GFAAS were 0.50, 0.01, 0.03 $\mu g\ L^{-1}$, respectively.

Daily dietary intake (DDI) of Pb, Zn, and Cd was applied to estimate the health risk to local residents from dietary exposure. The daily quantity of foodstuffs consumed by adults was adopted from the investigation of Li and Ke (1985). Concentrations of Pb, Zn, and Cd in the edible parts of vegetables/crops from the farmers' market in Magu Township were used for the estimates. DDI of Pb, Zn, and Cd was calculated using the formula:

$$\begin{aligned} &\mathrm{DDI}\,(\mu\mathrm{g\ metal\ day}) = \mathrm{Metal\ concentration}\,(\mu\mathrm{g\,g^{-1}}) \\ &\mathrm{in\ the\ edible\ part\ of\ vegetables/crops} \\ &\times \mathrm{Quantity\ of\ daily\ consumption} \times (\mathrm{g\,day}) \times \mathrm{TC}. \end{aligned}$$

where TC is a moisture transfer coefficient from dried plants to fresh plants; quantity of daily consumption is the average amount of fresh vegetables/crops consumed by a 60 kg adult in 1 day (Li and Ke 1985). It is assumed that 100% of the metals retains in body.

Analysis data were graphed using SigmaPlot 10.0 (SPSS Inc., Richmond, CA, USA). One way-ANOVA was applied to compare means among varying sample groups using SPSS 10.0 software (SPSS Inc., Richmond, CA, USA). An equal variance assumed method (Duncan) was chosen for post-hoc multiple comparison procedure (MCP). Significance level was set at an alpha level of 0.05. No significant statistic difference in Pb, Zn, and Cd concentrations was observed among varying species of herb plants, therefore, they were pooled together as one group to perform MCP analysis with other plants.

Results and Discussion

Soil chemical properties in the studied region were listed in Table 1. Except for total organic carbon, studied soils were

Table 1 Total organic carbon, pH, and total metal contents in soils from the studied regions

Location	Land use	No. of samples	Total organic carbon (g kg^{-1})	pH (H_2O)	Pb (mg kg^{-1})	Zn (mg kg^{-1})	Cd (mg kg^{-1})
Malin township	Maize	10	41.9 ± 13.7a	6.31 ± 0.463ab	44.0 ± 3.81c	395 ± 75.7c	0.250 ± 0.037b
Zinc smelting region	Maize	27	42.7 ± 21.6a	6.17 ± 0.958ab	5,116 ± 5443b	6,028 ± 6885b	41.4 ± 32.8a
	Bean	8	36.9 ± 35.5a	5.64 ± 0.706b	481 ± 431b	585 ± 261c	36.5 ± 32.2a
	Potato	6	60.3 ± 4.40a	6.62 ± 0.319a	24,810 ± 9521a	12,181 ± 2521a	59.5 ± 25.2a

Data are presented as mean ± 1 standard deviation

Columns with different letters represent a difference at significance level of $p < 0.05$

Table 2 Concentrations of Pb, Zn, and Cd in the plants from the studied regions

Sampling location	Plant/tissue	No. of samples	Pb (μg g^{-1} dry weight)	Zn (μg g^{-1} dry weight)	Cd (μg g^{-1} dry weight)
Malin township	Maize shoot	10	1.76 ± 0.223b	27.6 ± 7.49a	0.124 ± 0.036b
	Maize root	10	4.48 ± 3.30a	45.0 ± 30.4a	0.407 ± 0.244a
Zinc smelting region	Maize corn	22	63.7 ± 40.0b	289 ± 242a	0.629 ± 0.834b
	Maize shoot	34	104 ± 85a	625 ± 408a	4.08 ± 5.54a
	Maize root	27	319 ± 267a	1,132 ± 547a	7.42 ± 4.31a
	Bean pod	10	34.7 ± 15.7b	242 ± 162b	0.199 ± 0.419c
	Bean shoot	10	48.6 ± 29.5b	293 ± 150b	3.68 ± 2.32b
	Bean root	8	119 ± 17.7a	1,096 ± 424a	8.64 ± 5.08a
	Potato Tuber	6	91.1 ± 9.34b	575 ± 123b	2.23 ± 1.49b
	Potato shoot	6	518 ± 187a	1,411 ± 316a	10.7 ± 1.49a
	Potato root	6	622 ± 307a	1,534 ± 597a	10.3 ± 3.41a
Farmers' market	Maize corn	3	0.640 ± 0.640b	27.6 ± 8.71b	0.007 ± 0.006b
	Fruity vegetable	13	1.20 ± 0.913b	24.0 ± 14.0b	0.035 ± 0.046b
	Leafy vegetable	27	16.0 ± 16.6a	153 ± 141a	0.886 ± 0.649a
	Root vegetable	12	4.84 ± 5.97b	47.9 ± 50.7b	0.304 ± 0.383b
	Stem vegetable	29	2.87 ± 7.07b	31.3 ± 17.8b	0.202 ± 0.215b

Data are presented as mean ± 1 standard deviation

Columns with different letters in the same plant specie/same sampling location refer to differences at a significance level of $p < 0.05$

different in pH and contents of Pb, Zn, and Cd with varying land uses. Such differences may be the dominate factor resulting in variety of Pb, Zn, and Cd in varying vegetable/crops (Table 2). Concentrations of Pb, Zn, and Cd in maize plant from the zinc smelting region were 10 times more than those from Malin Township (Table 2). Concentrations of Pb and Cd were greater in maize root and shoot than in maize corn, whereas, Zn was not the case (Table 2). In bean plant, the highest concentrations of Pb, Zn, and Cd were measured in its root, and concentrations of Pb and Zn were similar in its shoot and pod, whereas, Cd was lowest in its pod (Table 2). Concentrations of Pb, Zn, and Cd in bean pods were 175, 12, and 4 times over their respective national maximum levels (NMLs) for vegetables in China (0.200, 20, and 0.050 μg g^{-1} for Pb, Zn, and Cd, respectively) (MHC 1991, 2005). In potato plant, concentrations of Pb, Zn, and Cd in roots and shoots were similar, but they were much higher than in the potato tuber (Table 2), even though the latter had Pb, Zn, and Cd concentrations of ~450, ~30, and ~45 times over their respective NMLs for vegetables in China (Table 2). Of the three vegetable/crop species in the Zn smelting region, potato had the greatest accumulation of Pb, Zn, and Cd (Table 2). Of the procured vegetables/crops from the farmers' market in Magu Township, leafy vegetable had the highest average concentrations of Pb, Zn, and Cd, whereas, others (maize corn ear, fruity vegetable, root vegetable, and stem vegetable) were different in the concentrations of these metals (Table 2). In the edible parts of the procured vegetables/crops, the highest concentrations of Pb (18.9 μg g^{-1}), Zn (187 μg g^{-1}), and Cd (0.997 μg g^{-1}) were measured in leafy vegetable, about 95, 9, and 20 times over their respective NMLs in China. The highest concentrations of Pb (67.3 μg g^{-1}) and Cd (2.16 μg g^{-1}) were detected in lettuce and Zn (587 μg g^{-1}) was in bok choy. Except for the maize corn ear and fruity vegetable (Cd < NML), the edible parts of other vegetables had much higher Cd concentrations (0.185–0.997 μg g^{-1}) than its NML in China (3.7–20 times). Only the maize corn ear had Zn < NML, the others contained Zn over its NML. Furthermore, Pb in the edible parts of all the procured vegetables/crops (0.64–18.9 μg g^{-1}) was above its NML.

DDI of Pb from varying vegetables/crops was in the range of 4.78–1843 μg day with its highest value in lettuce (1843 μg day), followed by cabbage (937 μg day), then maize corn (276 μg day), bean (203 μg day), and potato (182 μg day). The greatest DDI of Zn was from lettuce (14,822 μg day) and cabbage (14,781 μg day), followed by maize corn (11,906 μg day), bean (7,110 μg day), and potato (6,244 μg day), whereas, the greatest DDI of Cd was from lettuce (82.5 μg day), followed by cabbage (45.7 μg day), then potato (28.8 μg day), and bean (10.7 μg day). The total DDI of Pb (3,646 μg day), Zn (59,295 μg day), and Cd (186 μg day) were ~8.5, ~4, ~3.0 times over their respective WHO daily limits for adults (429 μg day for Pb, 15,000 μg day for Zn, 57.4–71.1 μg day for Cd, respectively, WHO. 250, WHO. 659, and WHO. 553, 2009a, c, b), which suggested a very

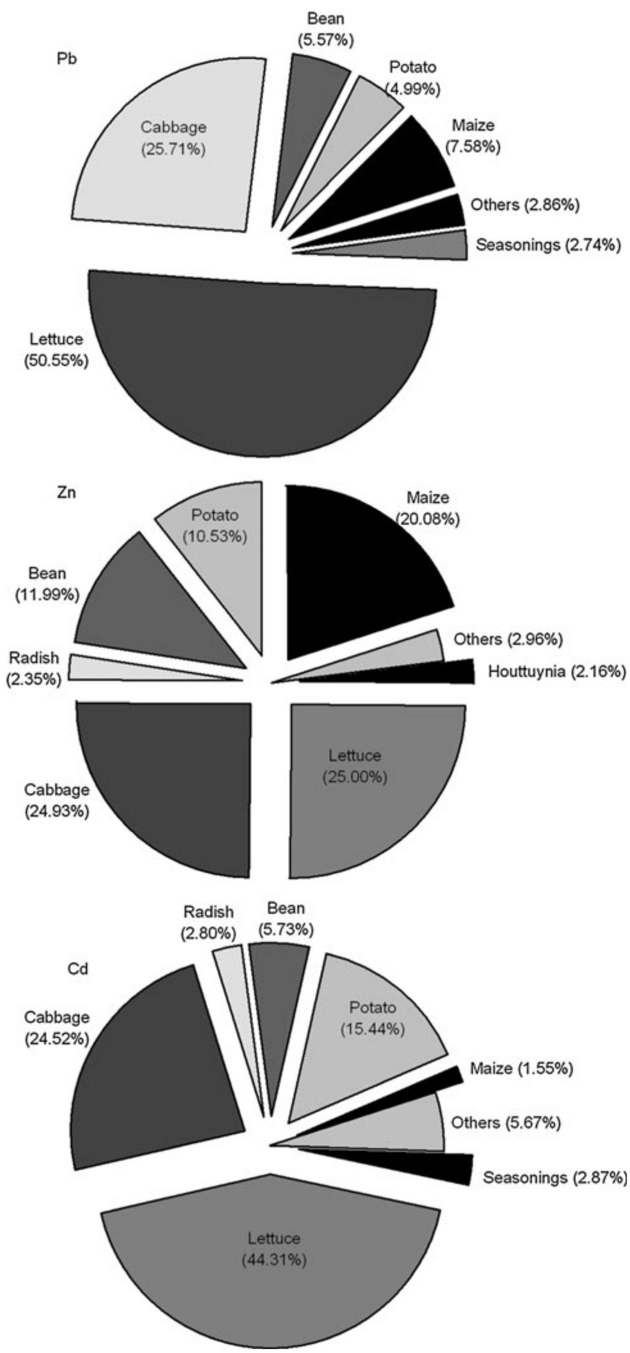

Fig. 1 Contribution (%) of different vegetables/crops (edible parts) to the daily dietary intake estimate

high potential exposure risk to Pb, Zn, and Cd in local residents. Noticeably, lettuce potentially contributed the largest portion in the daily intake of Pb (>50%), followed by cabbage (>25%), then maize, bean and potato (~5%). Seasonings (garlic, green onion, ginger, and cilantro) had a significant contribution as well (Fig. 1). Lettuce and cabbage also contributed the largest portion in the daily intake of Zn (50% in total), followed by maize, bean, and potato (~42% in total) (Fig. 1). A similar situation was observed for Cd, which lettuce and cabbage were the predominate contributors (~70% in total), however, potato increased its contribution up to ~15% and seasonings up to ~3%, whereas, maize was down to ~2% (Fig. 1). In total, leafy vegetable (lettuce and cabbage) contributed the most Pb (75%), Zn (50%), and Cd (70%) to their dietary intake by local residents, followed by potato.

Previous studies reported excessive amounts of heavy metals in the edible parts of vegetables/crops over their respective national or FAO/WHO limits in different regions (Demirezen and Aksoy 2006). In the zinc smelting region, Pb, Zn, and Cd in maize corn ear, bean pod, and potato tuber (Table 2) were much higher than their peers in previous reports (Santos et al. 2004; Demirezen and Aksoy 2006; Lee et al. 2006). Lead, Zn, and Cd in leafy vegetable procured from the farmers' market surpassed those from previous reports as well (Santos et al. 2004).

Upon consuming these metal-contaminated vegetables/crops, dietary intake exposure in humans is a big concern. Excessive dietary exposure to heavy metals in humans has been reported (Lee et al. 2006). In the studied region, potato (780 g day), maize corn (540 g day), and bean (276 g day) are staple daily food for local residents, and leafy vegetable (1,005 g day in total) as primary subsidiary foodstuffs (Li and Ke 1985). Such dietary structure was long-standing inhabited and discriminated to others, especially, leafy vegetable consumption as foodstuff was far more than in other regions (Sipter et al. 2008). As estimated, DDI of Pb (3,646 g day), Zn (59,295 g day), and Cd (186 g day) in local residents were 8.5, 4, and 3.0 times over their respective WHO daily limits for adults, suggesting that Pb was the greatest potentially hazardous metal (Sipter et al. 2008). In this case, dietary intake Pb could be the key factor resulting in high blood Pb level in local residents. By comparison, the DDI of Pb or Cd was also much greater than those from other countries such as Spain (Cuadrado et al. 1995), USA (MacIntosh et al. 1996), or UK (Ysart et al. 1999). Consuming too much leaf vegetable (especially 200 g day of lettuce and 300 g day of cabbage), and potato (780 g day) and maize corn (540 g day), which were abundant in Pb, Zn, and Cd, could be the key factor resulting in great DDI in local residents. A change in the long-standing dietary habit could be an imperative measure to ameliorate the present dietary exposure risk. For example, peeling a potato before consuming it could be an effective way to reduce dietary intake of heavy metals from potato, since more Pb, Zn, and Cd accumulated in potato peel (5.81, 36.5, and 0.234 μg g^{-1}) than in potato flesh (0.778, 26.7, and 0.123 μg g^{-1}). Reducing quantities of leafy vegetable in diet could be another possible way, since heavy metals were prone to accumulating in the leaves.

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