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Heavy Metal Accumulation of Edible Vegetables Cultivated in Agricultural Soil in the Suburb of Zhengzhou City, People's Republic of China

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Heavy metals are not biodegradable and can accumulate in human vital organs, producing progressive toxicity. Many researches have revealed the carcinogenic effects of several heavy metals such as cadmium (Cd), chromium (Cr), lead (Pb), mercury (Hg) and arsenic (As) (Trichopoulos 1997; Feig et al. 1994; Gibb and Chen 1989). High concentrations of metals (Co, Cd, Pb, Mn, Ni and Cu) in fruit and vegetables in Van region of Eastern Turkey were related to the high prevalence of upper gastrointerestinal (GI) cancer rates (Türkdoğan et al. 2002). For most people the main route of exposure to these toxic heavy metals is through the diet. Some regulations to restrict the emission of heavy metals and the tolerance limit in food have been set up in many countries or areas. Quality of the roadside vegetables had also established in terms of heavy metals in the light of recent dietary guidelines (Bahemuka et al. 1999). Heavy metal contamination of vegetables was studied owing to mining operation, mine spill and volcanic events (Queirolo et al. 2000; Miller et al. 2004; Liu et al. 2005). These studies primarily evaluated the bioaccumulation of a few selected elements in a single plant type or several plant types growing in high contaminated soils (Wong et al. 2002; Alam et al. 2003; Samsøe-Petersen et al. 2002). However, few emphases have been placed on accumulation of heavy metal of various vegetables in agriculture soils, determining differences in metals absorption by different vegetable species.

The soil and atmosphere affected the accumulation of heavy metals in vegetables in a dual growth cabinet (Harrison and Chirgawi 1989). Moreno et al. (2002; 2005) studied their accumulation in Chinese cabbage from agriculture soil under protected cultivation. In China, the cultivation of vegetables is mainly under natural open-field conditions. Accordingly, it is important to study heavy metals accumulation in vegetables in natural environment. Hence, we performed a comprehensive study of toxic heavy metals in 23 vegetable species from agricultural soil under natural condition. Then principal component analysis (PCA) was applied to identify the enrichment ability of various vegetables to these heavy metals.

MATERIALS AND METHODS

Twenty three vegetable species were collected from four sampling sites: MaoZhuang (MZ), LaoYaChen (LYC), YaoQiao (YQ) and HuaYuanKou (HYK).

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These sites locate in the suburb of Zhengzhou city, Henan Province, China (34°42' N; 113°45' E; altitude 110.4 m). The area has a warm spring continental weather with an annual average temperature and rainfall of 14.3 °C and 640.5 mm, respectively. These selected vegetables are broadly cultivated, and have a large abundance yields at MZ and LYC sites. YQ and HYK sites are bases to yield lotus root. Most of the vegetables cultivated at these sites enter the local markets for a population of approximately 2,000,000 inhabitants.

Vegetables were selected using a random sampling procedure (replicate) and identified by a horticulturist (Table 1). They were collected during vegetables maturity by hand using vinyl gloves in September–November 1999, carefully packed into polyethylene bags. In addition, the corresponding soil (at 0-20 cm in depth) was collected. In the laboratory, different parts of vegetables were separated manually. The edible portions were washed three times with distilled water and finally rinsed with deionized water and dried in an oven at 65 °C, ground using a ceramic-coated grinder and used for metal analysis. The soil samples were air-dried at room temperature, finely powdered and sieved through 2 mm nylon mesh to remove large debris, stones and pebbles. Soil samples (500g) were dried at 105 °C for 2 h and ground to pass through 60 mesh sieve and homogenized for analysis.

Metals As, Hg, Cd, Pb, Cu and Cr were determined according to previously described methods (Schuhmacher et al. 1993). A microwave assisted digestion procedure was used. About 0.5 - 3 g of homogenized samples was digested under pressure in Teflon vessels with 4 mL of nitric acid and 1.5 mL of hydrogen peroxide. Samples with a low aqueous content were ashed at 450 °C in a furnace. On completion of the digestion and after adequate cooling, solutions were filtered and made up to 50 mL with 1 % nitric acid.

Metals Cr, Cd, Pb and Cu contents were analyzed by flame atomic absorption spectrometry (FAAS, Hitachi Z-8000, Hitachi Ltd., Tokyo, Japan), whereas concentrations of Hg and As were determined using cold-vapor atomic absorption spectrometry (CV-AAS) with a hydride generation VA-90 model (TongJi University, China) and sodium borohydride as the reductant. All reagents were supra-pure and high-purity water was employed throughout. A sample of standard reference material (NIST SRM 2709), a blank, and a determination in duplicate were included for assurance of analytical accuracy. The analytical results showed no signs of contamination and that the precision and bias of the analysis were generally < 10 % for metals. The recovery rates for heavy metals in SMR were around 85-105%.

RESULTS AND DISCUSSION

The results of heavy metals in the soils are presented in Table 2. The concentrations of Cd, Pb, Cr, As and Cu at all four sites were below the threshold levels in natural background soil as defined by China. The mean concentrations of Cd, Pb, Cr and Cu were lower in these soils compared with crop soils of the Pearl River Delta, South China (Wong et al. 2002). Average Cd and Pb levels were

Table 1. Average concentrations of heavy metals in vegetables (mg kg^{-1}dw).

Sample number	Vegetable species	Latin	Sampling site	Cd	Pb	As	Cr	Hg	Cu
S1	Leek	*Allium porrum* L.	MZ	0.055	0.92	0.62	15.38	0.19	22.13
S2	*Yubaicai pakchoi*	*Brassica campestris* L. spp. *chinensis* L	MZ, LYC	0.094	0.59	2.54	8.58	0.39	23.18
S3	*Pak choi*	*Brassica chinensis*	MZ, LYC	0.11	2.02	3.00	5.69	0.41	28.05
S4	Swamp cabbage	*Ipomoea aquatica* Forsk.	MZ, LYC	0.094	2.73	1.00	2.83	0.43	47.81
S5	Edible amaranth	*Amarantus mangostanus* L.	MZ, LYC	0.16	1.91	0.67	1.85	0.27	42.82
S6	Cabbage	*Brassica oleracea var. capitata*	MZ, LYC	0.076	1.00	0.81	0.66	0.21	37.62
S7	Chinese cabbage	*Brassica campestris* L. spp. *Pekinensis* (Lour) Olsson	MZ, LYC	0.20	2.05	0.45	0.44	0.15	35.06
S8	Leafy cabbage	*Brassica rape*	MZ, LYC	0.12	1.55	1.12	0.28	0.15	28.39
S9	Celery	*Apium graveolens* L.	MZ, LYC	0.10	1.76	0.49	0.08	0.31	109.89
S10	Chinese chive	*Allium tuberosum* Rottl. ex Spr.	MZ, LYC	0.12	2.53	0.57	1.82	0.32	41.68
S11	Jingjie	*Nepeta japonica*	LYC	0.075	1.36	1.09	0.54	0.13	68.98
S12	Asparagus bean	*Vigna unguiculata* w. ssp. *Sesquipedalis* (L.) verd	MZ	0.12	7.75	0.88	1.53	0.22	317.71
S13	Kidney bean	*Phaseolus vulgaris L.*	MZ, LYC	0.036	0.91	2.98	1.13	0.27	26.51
S14	Egg-plant	*Solanum melongena* L.	MZ, LYC	0.16	1.30	0.98	1.15	0.26	41.37
S15	Broccoli	*Brassica oleracea* L. var. *italica* P.	MZ	0.048	0.34	0.59	0.64	0.12	9.52
S16	Pepper	*Capsicum frutescens* L.	MZ, LYC	0.15	4.25	0.39	1.00	0.14	156.75
S17	Cucumber	*Cucumis sativus* L.	MZ, LYC	0.059	1.39	0.53	0.35	0.15	49.12
S18	Tomato	*Lycopersicon esculentum* Miller	LYC	0.11	5.23	0.46	0.34	0.13	201.75
S19	Lotus root	*Nelumbo nucifera* Gaertn.	YQ, HYK	0.017	0.18	0.49	0.32	0.16	9.95
S20	Radish	*Raphanus sativus* L.	MZ, LYC	0.083	0.47	0.22	0.38	0.21	8.65
S21	Radish leaves	*Raphanus sativus* L.	MZ, LYC	0.18	4.06	0.37	1.21	1.06	60.32
S22	Carrot	*Daucus carota* L.	MZ	0.085	0.92	0.15	0.38	0.24	27.12
S23	Carrot leaves	*Daucus carota* L.	MZ	0.13	2.86	1.72	0.89	0.35	13.22
Average value				0.10	2.09	0.96	2.06	0.27	61.20
Range				0.036-0.18	0.18-7.75	0.15-3.00	0.08-15.38	0.12-1.06	8.65-317.71
Tolerance limit (Food Sanitary Regulation of China, 1994)				0.05	0.2	0.5	0.5	0.01	10

Table 2. Average concentrations of heavy metals in the soils (mg kg^{-1}dw).

Element	MAC of elements in agricultural soil in China[a]	Threshold of elements in natural background soil in China[a]	Sampling Site			
			MZ	LYC	HYK	YQ
Cd	0.6	0.2	0.17	0.15	0.18	0.13
Pb	300	35	14.49	14.47	9.83	5.23
Cr	200	90	13.45	6.61	4.53	2.48
As	30	15	5.54	6.48	5.57	3.49
Hg	1.0	0.15	5.50	4.03	6.55	6.57
Cu	100	35	12.41	10.72	9.24	4.43

[a] National Environmental Protection Agency of China, GB15618,1995.

significantly lower than that in the endemic upper gastrointestinal cancer region of Turkey, where mean Cd and Pb levels were 5.9 and 80 mg kg^{-1}, respectively (Türkdoğan et al. 2002). The range of Hg concentration in the four soils was narrow, whereas these values exceed the maximum allowable concentration (MAC) level in agricultural soil in China. This showed that the soil was contaminated by mercury.

Table 1 summarized the concentrations of heavy metals in the vegetables. 87% vegetable species for Cu, 87% for Cd, 96% for Pb, 65% for As, 65% for Cr and 100% for Hg exceeded tolerance limit of Food Sanitary Regulation of China. The mean Cd, Pb, As, Cr, Hg and Cu concentrations of these vegetables were elevated compared with the corresponding tolerance limit. The maximum concentration of Hg was found in radish leaves, followed by swamp cabbage. High Hg levels of vegetables could be related to their high concentration in the soils. The highest Cr concentration was 15.38 mg kg^{-1} (leek) and 8.58 mg kg^{-1} (*yubaicai pakchoi*). The concentration of Cu was the highest in asparagus bean (317.71 mg kg^{-1}) and tomato (201.75 mg kg^{-1}), which exceeded tolerance limit for Cu by approximately 31 and 19 times, respectively. The range of copper was higher than these values (from 2.5 to 16 mg kg^{-1}) reported by Bahemuka and Mubofu (1999). In addition, the average value of Cu was higher than these values for Msimbazi (9.1 mg kg^{-1}) and Sinza (6.8 mg kg^{-1}) green vegetables, and also higher than that of vegetable from Samta village, Bangladesh (Alam et al. 2003).

The concentration of Pb was the highest in asparagus bean (7.75 mg kg^{-1}), followed by tomato (5.23 mg kg^{-1}), which exceed the tolerance limit level of China for Pb by approximately 38 and 25 times, respectively. The concentration of Pb was higher than Cd in all the vegetables. The concentration of Cd was the highest in Chinese cabbage (0.2 mg kg^{-1}), followed by radish leaves (0.18 mg kg^{-1}). However, the concentration of Cd was lower than the range (from 0.1 to 0.6 mg kg^{-1}) for vegetable reported by Bahemuka and Mubofu (1999). Mean Cd and Pb levels of vegetables were significantly lower than that in the endemic upper gastrointestinal cancer region of Turkey, where mean Cd and Pb levels of the fruit and vegetables were 25 and 409 mg kg^{-1}, respectively (Türkdoğan et al. 2002).

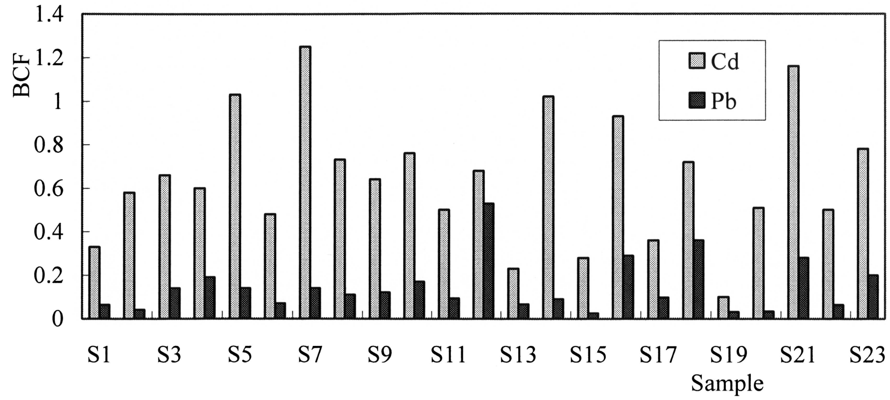

Figure 1. BCF values of Cd and Pb of 23 vegetable species from the suburb of Zhengzhou, China.

It is worth noticing that the contents of heavy metals in leaves part of radish and carrot were higher than the corresponding stem. Radish and carrot leaves were efficient bioaccumulation of these heavy metals, and the edible parts of radish and carrot were generally less contaminated than leaves.

To appraise the bio-accumulation effects of vegetables that uptake metals from the soils, bioconcentration factors (BCF) values were calculated as the ratio between the concentration of heavy metals in the vegetable and that in the corresponding soil (all based on dry weight) for each vegetable at each site separately. The BCF value ranges were: Cu 0.73-25.6, Cd 0.1-1.25, Pb 0.03-0.53, Cr 0.006-1.14, As 0.028-0.53 and Hg 0.031-0.26. The average BCF values were 5.31 for Cu, 0.65 for Cd, 0.45 for Pb, 0.20 for Cr, 0.16 for As and 0.062 for Hg. This indicated that mercury had the lowest bioavailability in our studied soil-vegetable system.

The BCF values for Cu of each vegetable species were the highest among all considered heavy metals. The highest value was found in asparagus bean (25.6), followed by tomato (18.82). Since a visual check of the BCF value of Cu was exceedingly high, Cu BCF value was considered as an outlier. Cu concentrations in these soils were below the threshold levels of national natural background (Table 2). Moreover, the exchangeable and carbonated-bound Cu, which were considered readily and potentially bioavailability, accounted < 10% of the total Cu in crop soils in general (Wong et al. 2002). Therefore, enrichment of vegetable for Cu had other pathway except absorption from soils. Based on the field investigation, during vegetation process of crop the pesticide containing $Cu(OH)_2$ was sprayed on the vegetables, so the copper residue was high and could accumulate in the vegetables through foliage absorption.

The highest BCF value of Cd was 1.25 (Chinese cabbage), the second one was 1.16 (radish leaves). The highest BCF value of Pb occurred in asparagus bean (0.53),

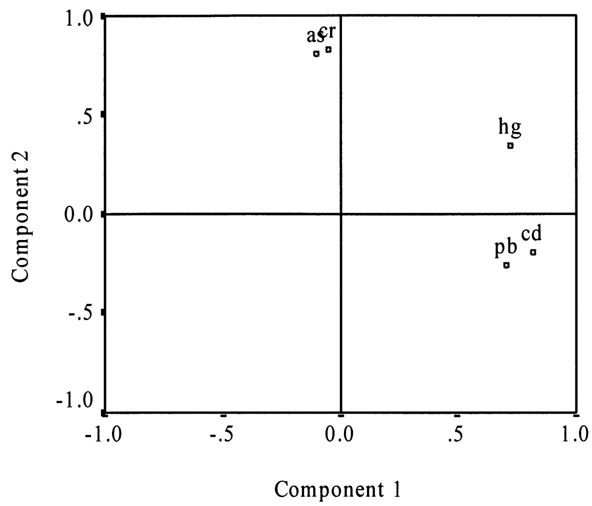

Figure 2. Component plot in rotated space (A rotation converged in 3 iterations)

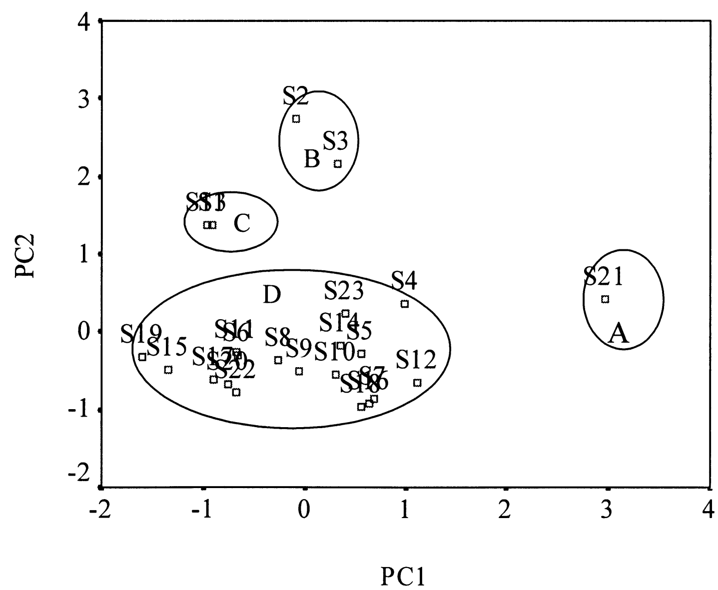

Figure 3. PC1-PC2 sample score subspaces, rotated components, Rotation Method: Varimax with Kaiser Normalization.

followed by tomato (0.36). BCF values of Cd were higher than Pb, while the concentrations of Cd were lower than Pb in all the vegetables (Figure 1). Lead in the crop soils was largely associated with the Fe-Mn oxide phase, followed by the organic/sulphide and residual fractions, so that Pb bioavailability was not high (Wong et al. 2002). Cadmium was more easily taken up and accumulated than Pb by vegetables through the root systems from soil.

Further, to study the relationships among these heavy metals, principal component analysis (PCA) was performed using SPSS 10.0 for windows. In the PCA, Varimax with Kaiser Normalization was used as the rotation method in the analysis. Two PCs were chosen as the most significant ones since they explained up to 65 % of the total initial variance. The first PC, which showed high positive loading of elements Hg, Cd and Pb, accounted for 37 % of the initial information (Figure 2). The second PC (28 % of the variance) showed a definite relation with Cr and As. These edible vegetables were divided into four main groups. It could be observed that the first PC distinguished two essential blocks of samples (Figure 3). Using sample scores, those samples (group A), such as radish leaves, on the right sideshowed values higher than 2 on the first PC characterize. It had the maximum BCF values for Cd, Pb and Hg (1.16, 0.28 and 0.26, respectively) and medium values for As and Cr (0.062 and 0.18, respectively). PC2-scores > 2 discriminated one set of samples (group B, *Yubaicai pakchoi* and *Pak choi*). They had the highest BCF values for As and Cr (average 0.45 and 0.89, respectively). Group C could be seen when PC2 scores range from +1 to +2. This group was formed by leek and kidney bean, showing medium-high values for As and Cr (average 0.32 and 0.64, respectively) along with low BCF values in Cd (average 0.28), Pb (average 0.065) and Hg (average 0.046). Group D, containing 18 samples with PC1-scores form -2 to +1.5 and PC2- scores from -1 to +1, had low BCF values for heavy metals. The results showed that *Yubaicai pakchoi* and *pak choi* had the highest enrichment ability of As and Cr, and radish leaves had the highest enrichment ability of Pb, Cd and Hg among all considering vegetable species.

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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

Bahemuka TE, Mubofu EB (1999) Heavy metals in edible green vegetables grown along the sites of the Sinza and Msimbazi rivers in Dar es Salaam, Tanzania. Food Chem 66:63-66

Bosque MA, Schuhmacher M, Domingo JL, Llobet JM (1990) Concentrations of lead and cadmium in edible vegetables from Tarragona province, Spain. Sci Total Environ 95:61-67

Gibb H, Chen C (1989) Evaluation of issues relating to the carcinogen risk assessment of chromium. Sci Total Environ 86:181-186

Liu H, Probst A, Liao B (2005). Metal contamination of soils and crops affected by the Chenzhou lead/zinc mine spill (Hunan, China). Sci Total Environ 339:153-166

Miller JR, Hudson-Edwards KA, Lechler PJ, Preston D, Macklin MG (2004) Heavy metal contamination of water, soil and produce within riverine communities of the Río Pilcomayo basin, Bolivia. Sci Total Environ 320:189-209

Moreno DA, Víllora G, Hernάndez J, Castilla N, Romero L (2002) Accumulation of Zn, Cd, Cu and Pb in Chinese cabbage as influenced by climatic conditions under protected cultivation. J Agric Food Chem 50:1964-1969

Moreno DA, Víllora G, Soriano MT, Castilla N, Romero L (2005) Sulfur, chromium, and selenium accumulated in Chinese cabbage under direct covers. J Environ Manage 74:89-96

Queirolo F, Stegen S, Restovic M, Paz M, Ostapczuk P, Schwuger MJ, Muñoz L (2000) Total arsenic, lead and cadmium levels in vegetables cultivated at the Andean villages of northern Chile. Sci Total Environ 255:75-84

Harrison RM, Chirgawi MB (1989) The assessment of air and soil as contributors of some trace metals to vegetable plants I. Use of a filtered air growth cabinet. Sci Total Environ 83:13-34

Samsøe-Petersen L, Larsen EH, Larsen PB, Bruun P (2002) Uptake of trace elements and PAHs by fruit and vegetables from contaminated soils. Environ Sci Technol 36:3057-3063

Schuhmacher M, Domingo J L, Llobet J, Corbella J (1993) Dietary intake of copper, chromium and zinc in Tarragona Province, Spain. Sci Total Environ 132:3-10

Türkdoğan MK, Kilicel F, Kara K, Tuncer I, Uygan I (2002) Heavy metals in soil, vegetables and fruits in the endemic upper gastrointestinal cancer region of Turkey. Environ Toxicol Pharmacol 13:175-179

Trichopoulos D (1997) Epidemiology of cancer. In: DeVita, VT (ed) Cancer, Principles and Practice of Oncology. Lippincott Company, Philadelphia, p 231

Feig DI, Reid TM, Loeb, LA (1994) Reactive oxygen species in tumorigenesis. Cancer Res 54:1890-1894

Wong SC, Li XD, Zhang G, Qi SH, Min YS (2002) Heavy metals in agricultural soils of the Pearl River Delta, South China. Environ Pollut 119:33-44