

Lead/Cadmium Contamination and Lead Isotopic Ratios in Vegetables Grown in Peri-Urban and Mining/Smelting Contaminated Sites in Nanjing, China

Xin Hu · Zhuhong Ding

Received: 27 May 2008 / Accepted: 1 September 2008 / Published online: 16 September 2008
© Springer Science+Business Media, LLC 2008

Abstract Lead/cadmium contamination in vegetables grown in peri-urban area of Nanjing, China was assessed and the route for metals entering into plants was investigated through lead isotopic tracing. Results show that agricultural soils have been polluted with Cd. Contents of Pb (22.1–37.5 mg kg⁻¹ dw) and Cd (2.53–4.19 mg kg⁻¹ dw) in vegetables' edible parts nearby a lead/zinc mining/smelting plant were beyond their maximum allowable limit prescribed in the (EC) No 1881/2006. Pb isotope ratios in plants differed from those in the corresponding soils, suggesting that soils were not the only contamination source of Pb and Cd in plants.

Keywords Contamination · Lead isotope ratio · Vegetables · Peri-urban area

Industrialization and urbanization have promoted socio-economic development. However, they have also led to variety of environmental problems in peri-urban areas, such as agricultural soil contamination by heavy metals via various pathways. Commercial and residential vegetable growing areas are often located in the peri-urban areas for better market accessibility and higher prices (Smit 1996). Risk assessment of heavy metal contamination in vegetables in urban/peri-urban areas has been widely studied over

recent decades (Singh and Kumar 2006). Lead and cadmium are considered as the most significant heavy metals affecting crops, and pose a great risk to human health via the consumption of vegetables. For example, the maximum level (ML) of Cd and Pb allowable in vegetable crops was set by the Commission of the European Communities (2006).

However, most of this research has focused on the total metal contents in vegetables and/or the metal fraction in soils (Fernandez-Turiel et al. 2001; Sterckeman et al. 2002; Douay et al. 2007; Kachenkom and Singhm 2006; Lim et al. 2008; Yan et al. 2007; Zheng et al. 2007). Are soils the sole contamination source for metal accumulation in plants? In fact, it has been confirmed that plants' leaves can accumulate heavy metals from the atmosphere (Harrison and Chirgawi 1989; Temmerman and Hoenic 2004), thus the impacts of airborne heavy metals should not be neglected where atmospheric particles have high concentrations of heavy metals. The lead isotope ratio has been widely used to trace sources of metal pollution in the environment fields (Weiss et al. 1999; Hansmann and Koppel 2000; Ng et al. 2005; Cloquet et al. 2006; Erel et al. 2006; Komárek et al. 2008; Patrick and Farmer 2007). The lead isotope ratio in vegetables that originates from soils remains constant over time, and changes only if another source of lead with a different lead isotope ratio is introduced. In that case, the new lead isotopic content in vegetables will be a combination of the two lead sources, so it can indicate whether the surrounding soil was the sole source of contamination in the plants.

Nanjing, the capital of Jiangsu province, is a city with more than 2000 years of history, located in the lower reaches of the Yangtze River. Since the 1990s, Nanjing has been one of the fastest developing districts in industrialization and urbanization. Heavy metals contamination is a

X. Hu (✉)
Center of Material Analysis, Nanjing University,
Nanjing 210093, People's Republic of China
e-mail: huxin_china@yahoo.com

Z. Ding
College of Environmental Science and Engineering,
Nanjing University of Technology,
Nanjing 210098, People's Republic of China

very serious problem (Zhang et al. 2005). Urban atmospheric Pb concentrations in Nanjing in winter and summer were 317 ± 28 and 200 ± 113 ng m⁻³, respectively (Mukai et al. 2001). The Qixiashan Lead–Zinc Mining/Smelting Plant (QLZMSP), located in the peri-urban area of Nanjing, has the largest lead–zinc deposit in East China. Approximately 350,000 tons of ore are treated per year, producing 50,000 tons of Zn and Pb. The unprotected mining wastes dispersed by wind and water, and atmospheric deposits of mining and smelting dust are important sources of pollution in the surrounding areas. In the present work, we investigated five popular leafy vegetables, two wild plants and the corresponding rhizospheric soils near the QLZMSP. Four leafy vegetables and the corresponding rhizospheric soils were also collected as controls from an area more distant from Nanjing. We aimed to assess Cd and Pb contamination in plants and corresponding soils in peri-urban and mining/smelting contaminated sites, and to elucidate the Pb contamination route for metal accumulation in plants through analysis of Pb isotope ratios.

Materials and Methods

Five popular vegetable species were collected from farmland approximately 100–200 m away from the QLZMSP (SI). The vegetables included pakchoi (*Brassica chinensis* L.), malabar spinach (*Basella alba* L.), celery (*Apium graveolens* L.), amaranth (*Amaranthus spinosus* L.), and lettuce (*Lactuca sativa* L.). Two wild plants were collected from the lawn at the QLZMSP (SII): *Taraxacum mongolicum* Hand.-Mazz and *Rostellaria procumbens* (L.) Nees. Farmland in Tangshan, approximately 5 km away from the QLZMSP, was selected as a control site (SIII). Four vegetables were collected from the control site; spinach (*Spinacia oleracea* Linn.), amaranth (*Amaranthus spinosus* L.), cole (*Brassica campestris* L.), and lettuce (*Lactuca sativa* L.). We collected 3–5 samples of each plant from each of the sites. The powdery remnant soils on the roots of plants were collected as the corresponding rhizospheric soil. The fresh vegetable samples were transported in clean plastic bags to the laboratory for further treatment as soon as possible. After being washed with tap water and Milli-Q water, each vegetable was separated into two parts; underground (roots) and above-ground (shoots). Plant material was dried in an electric drying oven at approximately 75°C. Soil samples were air-dried, crushed, and passed through a 0.15 mm-mesh sieve, then stored in polythene zip-bags at ambient temperature until further analysis.

Using a pH meter, soil pH was measured in 10 mM CaCl₂ with a soil-to-solution ratio of 1:2.5 (w/v). Soil pH ranged from 6.7 to 7.4 for the studied rhizospheric soil. Triplicate soil samples were analyzed for metal content using *aqua*

regia digestion (ISO 11466 (1995)). Two replicates of dry plant samples were digested with a HNO₃–HClO₄ mixture. Blanks for digestion and analysis methods and internal reference samples were carried out in triplicate with each set of samples. Precision and accuracy were verified using standard reference materials from the National Research Center for Geoanalysis, China (GBW07605 tea leaf). The recoveries were 98.5% for Pb and 91.2% for Cd. Water used for dilution and dissolution was purified using a Millipore deionizing system at 18.2 MΩ HCl, HNO₃, and HClO₄ were Suprapur reagents (Merck). Solutions from digested soil and plant samples were stored in 25 mL high density polyethylene samples bottles at 4°C until analysis. Lead and Cd were measured using a Perkin-Elmer ICP-MS SCIEX Elan 9000. The limits of detection for Pb and Cd were 0.005 and 0.002 μg L⁻¹ in the present study. Lead isotopic analyses were conducted using a Perkin-Elmer ICP-MS SCIEX Elan 9000 as already described in the literature (Quétel et al. 1997; Bindler et al. 2004; Godoy et al. 2007). Precision and accuracy were verified using a standard reference material from the National Institute of Standards and Technology (SRM 981 common lead isotopic material). Repeated measurements of the SRM 981 Pb reference material over different analytical sessions showed uncertainties of <0.3% for ²⁰⁸Pb/²⁰⁶Pb and ²⁰⁶Pb/²⁰⁷Pb. Microsoft Excel (Ver. 2003) was used for data analysis in this study.

Results and Discussion

Concentrations of Cd and Pb in the studied rhizospheric soils are listed in Table 1. The order of concentrations of Pb and Cd in rhizospheric soil was SI > SII > SIII. Lead concentrations at the three sampling sites were all greater than background values in Nanjing district. Concentrations of Cd at SI and SII were greater than its background values. P_{Pb} was <1 at SII and SIII, but >1 at SI. However, P_i values for Cd all were >1 (Table 1). These results show that agricultural soils near the mining/smelting plant have been polluted with Pb and Cd. mining/smelting activities are the most important sources of heavy metals contaminating the environment. Fernandez-Turiel et al. (2001) found that metal concentrations were 31–8714 mg kg⁻¹ for Pb, 0.27–30.68 mg kg⁻¹ for Cd, 21–242 mg kg⁻¹ for Cu, and 44–4637 mg kg⁻¹ for Zn in soils located within the vicinity of a Pb smelter in Lastenia, Argentina. Sterckeman et al. (2002) reported that Cd, Pb, and Zn were the most abundant contaminants in the cultivated soils around two lead and zinc smelters. It was also reported that concentrations of heavy metals in soils decreased exponentially with distance from the mine source (Jung and Thornton 1996). Thus, heavy metals in soils at SI may be a combination of two or more sources. The lawn at the QLZMSP

Table 1 Total concentration of Cd and Pb in the rhizospheric soils (mg kg^{-1})

	Pb			Cd		
	Range	Median	Pi ^c	Range	Median	Pi ^c
SI	287–379	361	1.20	1.40–2.59	1.60	5.33
SII	155–159	157	0.52	1.13–1.40	1.27	4.22
SIII	57.5–77.8	65.9	0.22	0.52–0.86	0.69	2.31
Background ^a		25.9 ± 21.0			0.59 ± 0.47	
Standard ^b		300			0.3	

^a Background values of soil elements in Nanjing district (Xia et al. 1987)

^b Environmental quality standards for soils in China [grade 2 (pH 6.5–7.5)] (GB15612-1995)

^c $Pi = Ci/Si$ [Pi is an environmental quality pollution index for a special heavy metal i, Ci is the heavy metal content in a soil sample (mg kg^{-1}); and Si is the permitted standard of the same metal (mg kg^{-1})]

(SII) was sown approximately 5 years ago to beautify the plant, and the soil was taken from an area outside the plant. This may be one of the reasons why Pb and Cd concentrations at SII were lower than those at SI. The lowest concentrations of Pb and Cd were found in soils at SIII. Atmospheric deposition was the most important contamination source at the SIII sampling site. The background value of Cd in soils in the Nanjing district is above standards for soils environmental quality of People's Republic of China, thus the soil contamination at SIII was not serious.

The contents of heavy metals in the shoots and roots of vegetables are listed in Table 2. Contents of Cd and Pb varied greatly among the various vegetable species. The order of concentrations of Pb and Cd in shoots and roots was SII > SI > SIII. There were significant differences in Pb and Cd contents in plants among the three sampling sites. Pb and Cd contents in vegetables at SI and SII were much higher than those in vegetable collected from SIII. Maximum levels for Pb and Cd in brassicas and leaf vegetables are 0.30 and 0.20 mg kg^{-1} wet weight, respectively, in (EC) No 1881/2006. The conversion factor 0.085 was used to convert fresh green vegetable weight to dry weight, as described by Rattan et al. (2005). The maximum levels for Pb and Cd in this study were therefore approximately 3.53 and 2.35 mg kg^{-1} dry weight. Pb and Cd concentrations of the vegetables' edible parts (shoots) were all beyond their maximum levels at SI, and below maximum levels at SIII. This result indicated that vegetables around the plant were heavily polluted with Cd and Pb and posed a great risk to consumers. This result also suggests that heavy metals contamination in vegetables caused by mining/smelting activities is more serious than urban atmospheric depositions.

The shoot/root ratio of Cd and Pb contents showed that the tissue distribution of Cd and Pb varied greatly among various vegetable species (Table 2). The shoot/root ratio of Cd in lettuce was approximately twice that in celery at SI.

Table 2 Concentrations of Cd and Pb in shoots and roots of plants (mg kg^{-1} dw) and enrichment coefficients from root to shoot

	Pb			Cd		
	Shoot	Root	Shoot/ root	Shoot	Root	Shoot/ root
SI						
<i>B. alba</i> L.	26.7	17.2	1.55	3.39	2.01	1.69
<i>A. graveolens</i> L.	22.1	80.0	0.28	3.57	4.27	0.84
<i>A. spinosus</i> L.	45.7	40.8	1.12	3.85	2.87	1.34
<i>L. sativa</i> L.	37.5	168	0.22	4.19	2.28	1.84
<i>B. chinensis</i> L.	36.2	47.3	0.77	2.53	1.59	1.59
Median	36.2	47.3	0.77	3.57	2.28	1.59
SII						
<i>T. mongolicum</i>	187	98.4	1.90	7.87	5.65	1.39
<i>R. procumbens</i>	165	94.8	1.74	2.81	4.32	0.65
Median	176	96.6	1.82	5.34	4.985	1.02
SIII						
<i>S. oleracea</i> Linn	1.43	2.53	0.56	2.02	2.80	0.72
<i>A. spinosus</i> L.	2.66	3.87	0.69	0.81	2.16	0.37
<i>L. sativa</i> L.	1.14	10.1	0.11	1.49	1.88	0.79
<i>B. campestris</i> L.	0.63	12.7	0.05	0.26	0.90	0.29
Median	1.29	6.99	0.34	1.15	2.02	0.55

At SI the shoot/root ratio of Pb in lettuce was 0.22, whereas it was approximately seven times higher in malabar spinach (1.55). High values of shoot/root ratio indicated that more metal was accumulated in shoots. It is consistent with the findings of Zheng et al. (2007) and Lim et al. (2008). Generally, metal content in shoots were less than those roots of plants growing in an unpolluted-air area (Finster et al. 2004; Deng et al. 2004; Sharma and Dubey 2005). These observations suggest that the impact of airborne heavy metals should not be neglected where atmospheric particles have high concentrations of heavy metals.

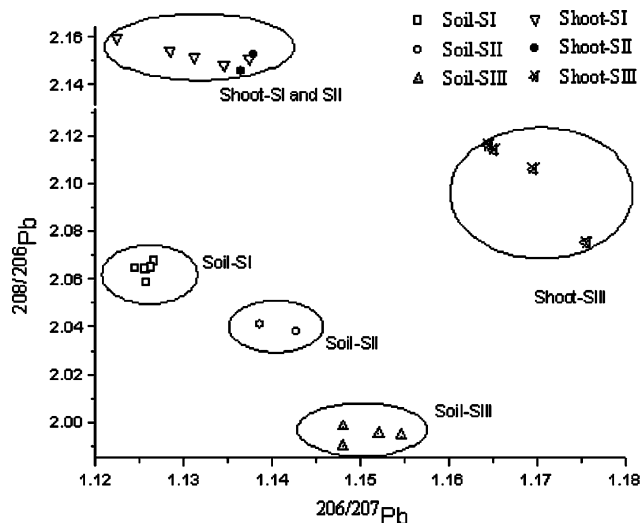


Fig. 1 Pb isotope ratios in shoots of plants and the corresponding soils at the three sampling sites

Figure 1 shows Pb isotope ratios in shoots of plants and soils at the three sampling sites. Pb isotope ratios in shoots of plants and soils at SI and SII were clearly different to those at SIII. This may be because SI and SII are exposed to metal contamination from both urban atmospheric transport and from mining/smelting dust deposition, whereas SII is only exposed to contamination from urban atmospheric transport. There was a clear distinction in Pb isotope ratios between soils and shoots of plants (Fig. 1). Pb isotope ratios in shoots of plants at SI and SII were similar. They had high $^{208/206}\text{Pb}$ values, compared to the corresponding soils. Values of $^{208/206}\text{Pb}$ and $^{206/207}\text{Pb}$ in shoots of vegetables at SIII were also higher than those in the corresponding soils. If no new sources of Pb with different Pb isotope ratios were introduced, the lead isotope ratios in plants should be similar to those in the corresponding soils. The Pb stable isotope ratios in vegetables indicated that there was a combination of two or more Pb sources. This result indicated that soils were not the sole contamination source for metal accumulation in plants. Airborne Pb may be the other source of contamination in plants in peri-urban and mining/smelting sites in the present study. It has been confirmed that plants' leaves can accumulate heavy metals from the atmosphere (Harrison and Chirgawi 1989; Voutsas et al. 1996; Temmerman and Hoenic 2004). Thus, the Pb isotopic content in plants is possibly a combination of soilborne Pb uptaken through the soil-to-root pathway, and airborne Pb assimilated via the atmosphere-to-leaf pathway.

Acknowledgment This study was supported by the Natural Science Foundation of China (NSFC) (Grant No.: 20607010).

References

- Bindler R, Renberg I, Klaminder J, Emteryd O (2004) Tree rings as Pb pollution archives? A comparison of $^{206}\text{Pb}/^{207}\text{Pb}$ isotope ratios in pine and other environmental media. *Sci Total Environ* 319:173–183
- Cloquet C, Carignan J, Libourel G (2006) Isotopic composition of Zn and Pb atmospheric depositions in an urban-periurban area of Northeastern France. *Environ Sci Technol* 40(21):6594–6600
- Commission European Communities (2006) Commission regulation (EC) No 1881/2006 of 19 December 2006 setting maximum levels for certain contaminants in foodstuffs, Off J Eur Commun L364:5–24 (http://www.fsai.ie/legislation/food/eu_docs/contam_foodstuffs/General%20Provisions/Reg1881_2006.pdf)
- Deng H, Ye ZH, Wong MH (2004) Accumulation of lead, zinc, copper and cadmium by 12 wetland plant species thriving in metal-contaminated sites in China. *Environ Pollut* 132:29–40
- Douay F, Roussel H, Fourrier H, Heyman C, Chateau G (2007) Investigation of heavy metal concentrations on urban soils, dust and vegetables nearby a former smelter site in Mortagne du Nord, Northern France. *J Soils Sediments* 7(3):143–146
- Erel Y, Dayan U, Rabi R, Rudich Y, Stein M (2006) Trans boundary transport of pollutants by atmospheric mineral dust. *Environ Sci Technol* 40(8):2525–2530
- Fernandez-Turiel JL, Ac enolaza P, Medina ME, Llorens JF, Sardi F (2001) Assessment of a smelter impact area using surface soils and plants. *Environ Geochem Health* 23:65–78
- Finster ME, Gray KA, Binns HJ (2004) Lead levels of edibles grown in contaminated residential soils: a field survey. *Sci Total Environ* 320:245–257
- Godoy JM, Godoya MLDP, Aronne CC (2007) Application of inductively coupled plasma quadrupole mass spectrometry for the determination of monazite ages by lead isotope ratios. *J Braz Chem Soc* 18(5):969–975
- Hansmann W, Koppel V (2000) Lead-isotopes as tracers of pollutants in soils. *Chem Geol* 171:123–144
- 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(1–2):13–34
- ISO (1995) Soil quality. Extraction of trace elements soluble in Aqua Regia, ISO 11466
- Jung MC, Thornton I (1996) Heavy metal contamination of soils and plants in the vicinity of a lead–zinc mine, Korea. *Appl Geochem* 11:53–59
- Kachenkom AG, Singhm B (2006) Heavy metals contamination in vegetables grown in urban and metal smelter contaminated sites in Australia. *Water Air and Soil Pollut* 169:101–123
- Kom arek M, Ettler V, Chrastny V, Mihaljevic M (2008) Lead isotopes in environmental sciences: a review. *Environ Int* 34:562–577
- Lim HS, Lee JS, Chon HT, Sager M (2008) Heavy metal contamination and health risk assessment in the vicinity of the abandoned Songcheon Au–Ag mine in Korea. *J Geochem Explor* 96(2–3):223–230
- Ministry of Environmental Protection of the People's Republic of China (MEP, China) (1995) Environmental quality standards for soils (GB15612-1995)
- Mukai H, Tanaka A, Fujii T, Zeng Y, Hong Y, Tang J, Guo S, Xue H, Sun Z, Zhou J, Xue D, Zhao J, Zhai G, Gu J, Zhai PY (2001) Regional characteristics of sulfur and lead isotope ratios in the atmosphere at several Chinese urban sites. *Environ Sci Technol* 35:1064–1071
- Ng OH, Tan BC, Obbard JP (2005) Lichens as bioindicators of atmospheric heavy metal pollution in Singapore. *Environ Monit Asses* 123:63–74

- Patrick GJ, Farmer JG (2007) A lead isotopic assessment of tree bark as a biomonitor of contemporary atmospheric. *Sci Total Environ* 388(1–3):343–356
- Quétel CR, Thomas B, Donard OFX, Grousset FE (1997) Factorial optimization of data acquisition factors for lead isotope ratio determination by inductively coupled plasma mass spectrometry. *Spectrochim Acta Part B* 52:177–187
- Rattan RK, Datta SP, Chhonkar PK, Suribabu K, Singh AK (2005) Long-term impact of irrigation with sewage effluents on heavy metal content in soils, crops and groundwater—a case study. *Agric Ecosyst Environ* 109:310–322
- Sharma P, Dubey RS (2005) Lead toxicity in plants. *Brazilian J Plant Physiol* 17(1):35–52
- Singh S, Kumar M (2006) Heavy metal load of soil, water and vegetables in peri-urban Delhi. *Environ Monit Assess* 120:79–91
- Smit J (1996) Urban agriculture, progress and prospect 1975–2005. Report 18, Cities Feeding People Series, March 1996, IDRC, Canada
- Sterckeman T, Douay F, Proix N, Fourrier H, Perdrix E (2002) Assessment of the contamination of cultivated soils by eighteen trace elements around smelters in the north of France. *Water Air Soil Pollut* 135:173–194
- Temmerman LD, Hoenic M (2004) Vegetable crops for biomonitoring lead and cadmium deposition. *J Atmos Chem* 49:121–135
- Voutsas D, Grimanis A, Samara C (1996) Trace elements in vegetables grown in an industrial area in relation to soil and air particulate matter. *Environ Pollut* 94(3):325–335
- Weiss D, Shotyk W, Appleby PG, Kramers JD, Cheburkin AK (1999) Atmospheric Pb deposition since the industrial revolution recorded by five Swiss peat profiles: enrichment factors, fluxes, isotopic composition, and sources. *Environ Sci Technol* 33:1340–1352
- Xia Z, Li S, Li Y (1987) Background values of soil elements and the study methods. Weather Press, Beijing, p 295
- Yan S, Ling QC, Bao ZY (2007) Metals contamination in soils and vegetables in metal smelter contaminated sites in Huangshi, China. *Bull Environ Contam Toxicol* 79:361–366
- Zhang G, Yang F, Zhao Y, Zhao W, Yang JL, Gong ZT (2005) Historical change of heavy metals in urban soils of Nanjing, China during the past 20 centuries. *Environ Int* 31:913–919
- Zheng N, Wang Q, Zheng D (2007) Health risk of Hg, Pb, Cd, Zn, and Cu to the inhabitants around Huludao Zinc Plant in China via consumption of vegetables. *Sci Total Environ* 383:81–89