Bull Environ Contam Toxicol (2009) 83:920–925
DOI 10.1007/s00128-009-9853-y

Distribution of Mercury Pollution and Its Source in the Soils and Vegetables in Guilin Area, China

Jianping Qian · Li Zhang · Huazhen Chen · Ming Hou · Yunfei Niu · Zheping Xu · Huili Liu

Received: 20 December 2007 / Accepted: 9 July 2009 / Published online: 17 September 2009
© Springer Science+Business Media, LLC 2009

Abstract Soils and vegetables were sampled and analyzed from nine vegetable fields in Guilin area, China. The average mercury (Hg) concentrations varied from 0.099 to 0.546 mg/kg in soils and from 0.046 to 0.132 mg/kg in plants. The distribution of Hg pollution in plants was correlated with that in soils. Generally, the Hg concentration in the plants decreased with the increasing distance between sampling sites and the city center. The Hg existed mostly in leaves of the plants, and then in their roots and stems, which suggested that the Hg in the atmosphere might be an important source of Hg in plants.

Keywords Soil · Vegetable · Mercury (Hg) · Source

It is well known that Hg is a toxic heavy metal that may be concentrated by the food chain. In recent years, investigation into the sources of Hg pollution and its distribution in the environment are hot research focuses. Guedron et al. (2006) indicated that there were the two possible source of Hg in tropical soil, one being the lithogenic Hg from in situ weathering of soil parental material, and the other being exogenous Hg. Exogenous Hg mainly comes from the atmosphere and human activities. Hg concentration in tropical soil varies horizontal with atmospheric Hg concentration (Grimaldi et al. 2008). Gaseous Hg deposition on soil could be an important way for Hg to migrate into soil (Xin and Gustin 2007). The H_2O_2-oxidizable mercury fraction is the major solid-phase fraction in soils freshly contaminated with soluble mercury compounds, while the cinnabar fraction is the major solid phase fraction in soils contaminated with HgS (Han et al., 2006). Mauclair et al. (2008) created a set of surface samples using purified laboratory grade sand treated with 0.05 μg/g Hg as the $HgCl_2$ salt and various concentrations of purified humic and fulvic acids. Both humic and fulvic acids show an inhibitory effect on surface Hg emissions. Millán et al. (2006) studied the easily available forms of mercury in the Almadén area (Spain) and the mercury accumulation in different plant species. The Almadén area shows a great variability in mercury content in soil, but this mercury is mainly in a nonavailable form. The plant species show varying capability to absorb and translocate mercury. Plants from plots where mercury content in the soil is higher show a high capability to accumulate mercury in the aerial part.

The Guilin area has been contaminated by Hg(Qian et al. 2000). In the present work, the distribution of Hg in plants and soils from vegetable fields in Guilin were investigated in detail to determine the relationship between the soil Hg contamination and the plant Hg contamination.

Materials and Methods

Nine vegetable fields were selected in the research: northeast of Yushan Bridge, Pengjialing, east of Ludi Park, southeast of Yushan Bridge, northeast of Seven Star Park, northwest of Xishan Park, south of Chuanshan Hill, north of Chuanshan Hill and Zhimapu (Fig. 1) (Qian et al. 2003).

The collected soils were air-dried, passed through a 106 μm nylon screen, and then put in a polytetrafluoroethylene crucible for testing. The plant samples were soaked for 10 min in deionized water, divided into root,

J. Qian (✉) · L. Zhang · H. Chen · M. Hou · Y. Niu · Z. Xu · H. Liu
Department of Resources and Environmental Engineering, Guilin University of Technology, Guilin, China
e-mail: jpqian@163.com

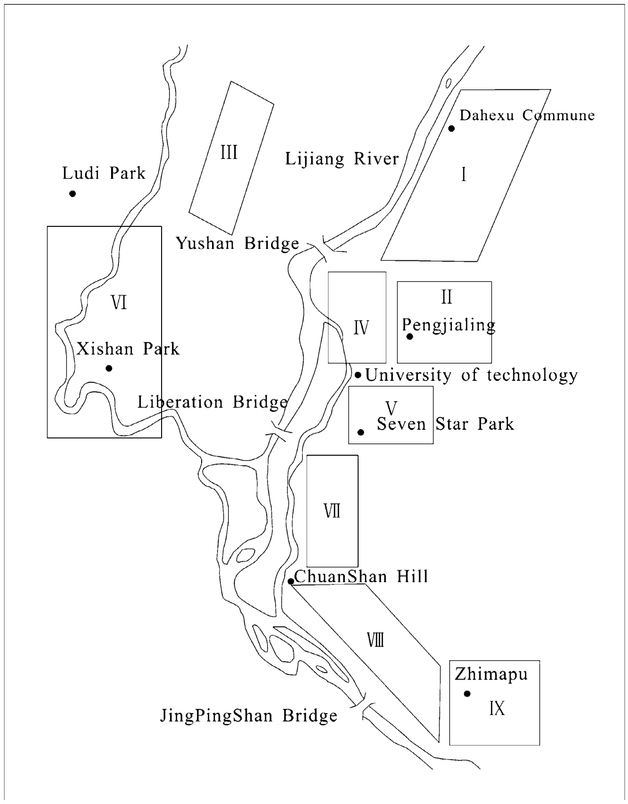

Fig. 1 Sampling location of soils and vegetables

stem and leaf and dried at a temperature of 38–42°C for 3–4 days. The dried plants were ground and passed through a 150 μm nylon screen, and then stored in an exsiccator.

The Hg concentrations in different fractions were investigated by the sequential extraction method according to the description of Pang et al. (1981), Feng et al. (1996), Sladek and Gustin (2003), Hou et al. (2005).

Soil and plant samples were digested by microwave system (MDS-2003F). Each 0.3000 g soil sample was put into the sample dissolution tin and 4 mL nitric acid was added. After 30 min soaking, 2 mL sulfuric acid was added slowly. After 10 min soaking, the sample was digested. Each 0.5000 g plant sample was put into the sample dissolution tin and 5 mL nitric acid was added. After 30 min soaking, 2 mL peroxide was added slowly. After 10 min soaking, each sample was digested using the microwave system. The samples were examined by FI-HG-CAAS (FI-AAS-700, PerkinElmer) after digestion. National standard materials (GBW07405 for soil, GBW07604 for plants) were used for quality control.

Results and Discussion

The total mercury content was determined and listed in Table 1. The average Hg content in the soils ranged from 0.099 to 0.546 mg/kg, and was 1.39–7.68 times the average Hg content (0.071 mg/kg) in standard soils of China. In general, the distribution of Hg content is geographically symmetrical. The Hg content is highest in the city center, lower in the south and in the north of Guilin. It is obvious that the Hg pollution is gradually intensified from suburb to the urban district.

Hg concentrations in the soils varied with different particle fractions. Fine grained soil had high enrichment capability for Hg. For instance, the soil Hg in the north of Chuanshan Hill increased from 0.127 to 0.447 mg/kg while the soil particle size decreased from 0.18 to 0.098 mm. Most of the Hg may be adsorbed in clay, which agreed with the result reported by Williams et al. (1999).

The correlation coefficients among the soil organic content, the conductivity, the pH value and the soil Hg content are calculated (Table 2): the correlation coefficient between the soil Hg content and the organic content is 0.279 (n = 32). A significant correlation coefficient test indicated that $r_{0.1,\ 30} = 0.296$. It shows that r is close to $r_{\alpha,\ n-2}$, therefore the soil Hg content is correlated to the organic content to some extent, but is not correlated to the pH value and the conductivity.

Table 1 Hg concentration in the soils from different sampling sites

	Site	n	Hg concentration (mg/kg)	Mean (mg/kg)	SD	CV
I	Northeast of Yushan Bridge	21	0.044–0.326	0.141	0.079	0.56
II	Peng Jialing	21	0.025–0.528	0.178	0.126	0.71
III	East of Ludi Park	5	0.139–0.523	0.380	0.146	0.38
IV	Southeast of Yushan Bridge	38	0.067–3.134	0.546	0.660	1.21
V	Northeast of Seven Star Park	12	0.126–0.941	0.332	0.282	0.85
VI	Northwest of Xishan Park	15	0.134–0.401	0.282	0.081	0.29
VII	North of Chuanshan Hill	17	0.037–0.407	0.213	0.124	0.58
VIII	South of Chuanshan Hill	38	0.033–0.218	0.099	0.049	0.50
IX	Zhi Mapu	19	0.043–0.267	0.153	0.078	0.51

SD standard deviation, *CV* coefficient of variation

Table 2 Correlation analyses between soil physical parameters and soil Hg contents

Physical parameters	Max	Min	Average value	SD	CC
pH	8.06	5.29	6.87	0.67	−0.057
Conductivity	54.90	6.71	21.27	9.22	0.087
Organic matter (%)	7.2820	1.1618	2.3149	1.06	0.279

SD standard deviation, *CC* correlation coefficients

The mean value of mercury content in the plants and standard deviation are shown in Table 3. The mean value of Hg content in the plants ranged from 0.046 to 0.132 mg/kg. The distribution of Hg contamination in these plants with respect to their field of origin is similar to the distribution of Hg pollution in the field.

The correlation between *B. chinensis* var. *oleifera* and soil Hg contents is shown in Fig. 2. The regression equation is as follows: $Y_{B.\ chinensis\ \mathrm{var.}\ oleifera} = 0.05964 + 0.1908X_{\mathrm{soil}}$. According to the results of mathematical statistics, the correlation coefficient is 0.6261 (n = 32), the significant correlation coefficient test: $r_{0.05,\,30} = 0.0345$, $r_{0.01,\,30} = 0.449$, $r > r_{\mathrm{a},\ n-2}$, therefore X_{soil} and $Y_{B.\ chinensis\ \mathrm{var.}\ oleifera}$ are significantly correlative.

Nine edible plants were collected. To study the Hg content of different parts of the plant, they were divided into four parts (root, leaf, stem and fruit), and the Hg concentration was measured (Table 4). Different plants accumulated Hg differently. The concentrations of Hg in plants followed the rules that (1) *Lycium chi-nense Mill.* > *B. pekinensis* > *Brassica chinensis* > *Apium graveolens* > *B. chinensis* var. *oleifera* > *Brassica oleracea* L.var. *capitata* L., (2) perennial plants > seasonal plants and (3) leaf plants > melon and fruit plants. Moreover, the accumulation capability of Hg in different tissues of the plants was different. Hg concentration follows the order that (1) leaf > root > stem in leaf plants, (2) root > stem and leaf > fruit in melon and fruit plants. It is indicated that atmospheric Hg may be one of the important sources in plants. Hg contamination and the enrichment capability of Hg in different parts have a very close relation with its growing period.

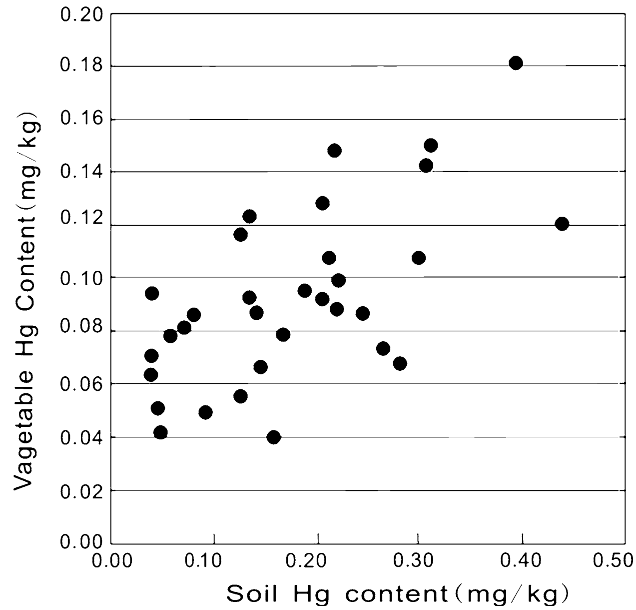

Fig. 2 Correlation between soil and vegetable Hg content

Seven Hg species from 23 soil samples were examined by the method of successive extraction-species analysis. The total values of seven Hg species were close to the values of Hg concentration digested by nitrohydro-chloric acid. By using simultaneous examination of International geochemical reference soil samples (GBW-07405) and our samples, it was determined that the relative error is under 10%; therefore the sample analysis result meets the requirements (Table 5).

The order of concentration of Hg species is as follows: the crystal lattice form > the combined humic acid form > the bio-refractory organic form > the easily biodegradable organic form > the carbonate and Fe/Mn oxide form > the soluble form > the exchangeable form. Among

Table 3 Distribution of Hg in *B. chinensis var. oleifera*

	Site	n	Hg concentration (mg/kg)	Mean (mg/kg)	SD	CV
I	Northeast of Yushan Bridge	12	0.028–0.071	0.046	0.013	0.29
II	Peng Jialing	12	0.039–0.085	0.060	0.017	0.29
III	East of Ludi Park	5	0.080–0.109	0.093	0.011	0.11
IV	Southeast of Yushan Bridge	28	0.057–0.200	0.090	0.028	0.31
V	Northeast of Seven Star Park	11	0.067–0.183	0.132	0.039	0.30
VI	Northwest of Xishan Park	9	0.066–0.123	0.093	0.019	0.21
VII	North of Chuanshan Hill	10	0.075–0.145	0.102	0.023	0.23
VIII	South of Chuanshan Hill	19	0.055–0.102	0.082	0.012	0.15
IX	Zhi Mapu	12	0.034–0.098	0.061	0.022	0.35

SD standard deviation, *CV* coefficient of variation

Table 4 Hg content in different parts of different plants (mg/kg)

Plants	Root	Stem	Leaf	Fruit	n
Lycium chi-nense Mill.	0.122	0.120	0.276		4
B. chinensis var. *oleifera*	0.061	0.050	0.106		44
Brassica chinensis	0.098	0.098	0.119		4
Apium graveolens	0.138	0.056	0.102		2
Brassica oleracea L.var. *capitata* L.	0.023	0.03	0.076		3
B. pekinensis	0.162	0.182 (stem and leaf)			2
Memordica charantia L.	0.069	0.064 (stem and leaf)		0.041	3
Cucumis sativus L.	0.094	0.076 (stem and leaf)		0.046	2
Phaseolus vulgaris	0.083	0.065 (stem and leaf)		0.054	2

Table 5 Distribution of soil Hg species (ng/g)

Sampling site	Sample no.	X_1	X_2	X_3	X_4	X_5	X_6	X_7	Sum	Total Hg	Error (%)
Northeast of Yushan Bridge	YN-1	7.6	13.1	11.1	27.8	20.5	44.3	58.1	182.5	162.5	−12.3
	YN-2	13.1	9.9	29.8	26.1	32.7	69.8	69.8	251.2	252.6	0.55
	YN-3	19.6	17.4	40.6	132.7	74.8	94.6	368.7	748.4	757.6	1.21
Peng Jialing	P-1	11.5	10.7	27.6	71.2	29.4	45.8	326.4	522.6	511.9	−2.09
	P-2	12.3	12.3	48.1	94.7	34.9	76.3	234.9	513.5	535.7	4.14
	P-3	10.7	14.6	19.5	54.5	30.5	96.0	169.4	395.2	398.5	0.82
Southeast of Yushan Bridge	YS-1	12.3	18.5	15.0	49.5	31.6	103.4	62.9	293	267	−9.74
	YS-2	51.0	16.9	213.8	507.3	236	119.0	804.9	1949.6	2137.4	8.79
	YS-3	53.0	26.9	50.5	123.5	48.1	453.2	1048.2	1803.4	1781.9	−1.20
Northeast of Seven Star Park	Q-1	9.9	14.6	34.2	77.9	51.3	58.9	296.4	543.2	561.8	3.31
	Q-2	0.55	10.7	6.8	51.2	36.0	62.2	294.6	462.0	492.0	6.09
Northwest of Xishan Park	X-1	45.0	11.9	39.4	149.8	67.6	87.2	345.3	746.2	771.1	3.23
	X-2	17.9	10.8	44.2	168.6	24.1	74.7	91.8	432.1	474.7	8.97
North of Chuanshan Hill	CN-1	5.2	14.6	7.0	31.7	22.9	38.7	49.6	169.7	156.7	−8.30
	CN-2	13.8	31.6	17.4	193.3	68.5	96.7	649.8	1070.3	1030.4	−3.87
South of Chuanshan Hill	CS-1	15.3	9.8	15.4	63.8	27.6	49.6	94.2	275.7	247.9	−11.2
	CS-2	20.9	12.9	32.5	98.8	24.1	65.8	98.0	353.0	348.7	−1.23
	CS-3	12.9	8.8	54.5	98.8	34.2	77.2	98.0	384.4	386.8	0.62
	CS-4	12.9	15.9	32.5	65.8	35.4	51.9	66.3	280.7	265.9	−5.57
Zhi Mapu	Z-1	13.9	10.8	26.8	82.9	24.1	59.5	241.4	459.4	470.0	2.26
	Z-2	11.4	8.8	22.3	52.8	29.4	27.5	76.8	229.0	214.2	−6.91
	Z-3	21.8	13.7	38.6	75.8	30.6	72.3	89.2	342.0	313.6	−9.06
	Z-4	24.9	12.9	69.6	119.2	51.9	79.8	141.6	499.9	473.9	−5.49
Mean		18.2	14.3	39.0	104.7	46.4	87.2	251.1	561	563.0	0.36
Percent of each Hg fraction		3.24	2.55	6.95	18.72	8.27	15.52	44.74	100		

X_1, water-soluble Hg; X_2, exchangeable Hg; X_3, carbonate and Fe/Mn oxide Hg; X_4, combined with humic acid Hg; X_5, easily biodegradable organic Hg; X_6, biorefractory organic Hg; X_7, crystal lattice Hg

the seven species, the concentration of Hg in the crystal lattice (residue) form was the highest (251.1 ng/g), accounting for 46.96% of the total Hg. In addition, the combined (complex compound) humic acid form content is 104.7 ng/g, accounting for 19.58%. Also the content of alkali soluble Hg is higher among the seven species, which indicates that Hg chelated by the organic matter is one of main states. This is very beneficial to soil mercury-fixation. But when the environment medium conditions are changed, the alkali-soluble Hg will be released more easily than the residue Hg. The four remaining species are less than 10% each. The content of the soluble Hg and the exchangeable

Hg in eight sampling areas are lower among the seven species (11 ng/g). Therefore the water-soluble and the exchangeable Hg can be absorbed directly by plants and the amount is not high.

The sources of soil and plant Hg contamination are complicated. Firstly, the soil parental material usually contains evident Hg in greatly different levels. According to the data of Qian et al. (2000), for different types of rock in Guilin, the Hg content follows the increasing order of carbonate rock < sandstone < carbonaceous shale. The result indicates that the Hg content of carbonaceous shale of the Yanguan group of Lower Carboniferous Series is very high and it can easily form soil. This is an important factor in the higher background soil Hg content of Guilin. Secondly, the rapid development of industrialization and transportation in Guilin are two sources of the soil Hg pollution. Hg pollution decreased from the city centre to the suburb. Hg content in the surface soil layer is higher than the lower soil layer. According to the study of Hg species, the crystal lattice (residue) form is the main species. This indicates that the Hg in soil is derived mainly from the process of urbanization. Furthermore, the agriculture production also brings about Hg pollution in a way, and the process of agriculture production may aggravate the degree of pollution. With contamination of irrigation water and fertilization, the use of pesticide containing Hg and garbage compost, Hg pollution of the soil could be increased. Although the government has been strengthening sewage management and has prohibited the use of pesticides containing Hg, the soil Hg pollution still exists due to the easy adsorption and difficult desorption by the soil.

As noted in the present work, the Hg pollution in plants is serious. Firstly, the degree of pollution gradually decreased from the centre of the city to the suburbs. In terms of Hg concentration, there is an obvious correlation between plants and soil. The Hg content of plants used in this research increased with the rise of soil Hg content, so it can be concluded that soil Hg results in plant Hg pollution. Secondly, little Hg is shown in soil by the analysis of Hg species. There is a more significant conclusion: that the Hg content in leaf is higher than that in stem and root, which indicates that, besides soil, atmospheric Hg is also an important pollution source for plant Hg.

It is well known that Hg can be taken up by plants in two ways: atmospheric Hg is absorbed by the respiration of the leaf surface. The other is that available Hg (water-soluble Hg and exchangeable Hg) can be exchanged by the ion-exchange action in plant roots. Thus Hg is accumulated gradually. From the perspective of ecology, this is a typical bioaccumulation process. For some plants, the result of this process may lead to more serious Hg pollution in the plant than in the corresponding soil. Because Hg is absorbed mainly from soil and accumulated in the plant root, it can not be easily transferred upward and thus the root plays a shielding effect (Lindqvist et al. 1991), which has been verified by pot experiments (Hou and Yin 2007).

In view of the higher Hg content in leaf than that in stem and root in Guilin, another important Hg pollution source is atmospheric Hg. The relative increment of atmospheric Hg is obviously related to the Hg released from the combustion of coal, fuel gas and fuel oil (Qian et al. 2007). In fact, the Hg pollution arising from fossil fuel combustion becomes atmospheric "Hg bar" in many cities, especially in industrial cities. This may indicate an obvious change in the structure of the sources of Hg pollution.

Acknowledgments The research is supported by the National Natural Science Foundation of China (40563001) and the Program of Small Highland Talents of Guangxi universities for geological resource and geological engineers (Guilin Teachers [2005]80).

References

Feng XB, Chen YC, Zhu WG (1996) The distribution of various mercury species in soils. Acta Mineralogica Sinica 16:218–222

Grimaldi C, Grimaldi M, Guedron S (2008) Mercury distribution in tropical soil profiles related to origin of mercury and soil processes. Sci Total Environ 401:121–129

Guedron S, Grimaldi C, Chauvel C, Spadini L, Grimaldi M (2006) Weathering versus atmospheric contributions to mercury concentrations in French Guiana soils. Appl Geochem 21:2010–2022

Han FX, Su Y, Monts DL, Waggoner CA, Plodinec MJ (2006) Binding, distribution, and plant uptake of mercury in a soil from Oak Ridge, Tennessee, USA. Sci Total Environ 368:753–768

Hou M, Yin HA (2007) Transformation of Hg forms in a soil-vegetable system. Soils 39:561–566

Hou M, Qian JP, Yin HA (2005) A study on mercury species in Guilin soil. Chinese J Soil Sci 36:398–401

Lindqvist O, Johansson K, Aastrup M, Anderson A, Bringmark L (1991) Mercury in the Swedish environment: recent research on causes, consequences and corrective methods. Water Air Soil Pollut 55:xi–261

Mauclair C, Layshock J, Carpi A (2008) Quantifying the effect of humic matter on the emission of mercury from artificial soil surfaces. Appl Geochem 23:594–601

Millán R, Gamarra R, Schmid T, Sierra MJ, Quejido AJ (2006) Mercury content in vegetation and soils of the Almadén mining area (Spain). Sci Total Environ 368:79–87

Pang SW, Qiu GK, Sun JF (1981) Discussion on Hg species of sediment determined by the sequential extraction method. Acta Sci Circumstantiae 1:234–241 (in Chinese with an English abstract)

Qian JP, Zhang L, Liu HL, Ye J (2000) Soil Hg distribution and pollution in urban and suburbs of Guilin. Geochimica 29:94–99 (in chinese with a English abstract)

Qian JP, Hou M, Xu ZP (2003) Pollution of Hg in soil-vegetable system in Guilin. In: academic abstract proceedings of 9th conference on mineral and rocks geochemistry 9 (in Chinese with an English abstract)

Qian JP, Zhang L, Chi ZD, Huang CX (2007) Investigation on atmospheric Hg pollution in Guilin. Bull miner rocks geochem 26(Suppl):571–572 (in Chinese with an English abstract)

Sladek C, Gustin MS (2003) Evaluation of sequential and selective extraction methods for determination of mercury speciation and mobility in mine waste. Appl Geochem 18:567–576

Williams TM, Weeks JM, Apostol AN Jr, Miranda CR (1999) Assessment of mercury contamination and human exposure associated with coastal disposal of waste from a cinnabar mining operation, Palawan, Philippines. Environ Geol (Berl.) 39:51–60

Xin M, Gustin MS (2007) Gaseous elemental mercury exchange with low mercury containing soils: Investigation of controlling factors. Appl Geochem 22:1451–1466