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Levels, Spatial Distribution and Possible Sources of Heavy Metals Contamination of Suburban Soils in Tianjin, China

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Abstract Representative soil samples (n = 86) of suburban areas in Tianjin (Xiqing, Dongli, Jinnan, Beichen) were evaluated for heavy metals. The results showed that the average concentration of Cr, Cu, Zn, As, Cd, Pb and Hg in soil of Tianjin suburban was 101.0, 67.0, 100.6, 9.5, 0.49, 52.5 and 0.97 mg/kg, respectively. Pollution of Cr and Zn were minimal compared to the other elements while concentrations of Cd and Hg were higher than their natural background values. Spatial variations of Cd, Hg, Pb and Cu in soil were illustrated; Pollution status and comparison in the four districts were also investigated. Higher concentrations of Hg and Cd were found in soils of Beichen than others indicating that Beichen was suffering from metal contamination. Principal Component Analysis in combination with local specific environment suggested that heavy metal contamination had different origination. Wastewater and sludge irrigation, air deposition might be the most important sources. These results, especially the spatial distribution of pollutants, would be helpful to develop proper management strategies and decrease source pollution by various remediation practices in Tianjin, China.

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Accumulation of heavy metals (HMs) by plants from contaminated soils may pose health risks. As China's third greatest metropolises, Tianjin (Fig. 1, N: 38°34′–40°15′; E: 116°43′–118°194′) has a population of more than 11 million and covers about 11 thousands km^2. Tianjin has been facing a range of environmental challenges associated with water scarcity which was mainly caused by its huge population and fast economy growth. Waste water from Beijing and Tianjin has been used for irrigation in agricultural area in Tianjin for decades (Wang and Zhang 2005). Waste water irrigation added the agricultural water supply, but large amount of toxic heavy metals in waste water polluted the soil and became a great risk to the health of local residents through the food chain. Rapid development of local industry including coking, chemistry, metallurgy, manufacture and electronic industry added the emission of heavy metals and further aggravated the pollution. Previous studies had proved that pollution did exist in the soil and food of Tianjin, especially in the wastewater irrigated area (Li et al. 2005; Wang et al. 2005).

But many studies before only focused on the levels, profiles of HMs in specific area in Tianjin city, for example, some wastewater irrigated fields. The sampling sites were not systematic and failed in detail; On the other hand, HMs in foods, especially in vegetables were emphasized while soils samples were often neglected in many studies. Finally, to our best of knowledge, samples in the latest study on HMs pollution in the soil were collected before 2005, and the pollution status had not been monitored and evaluated for many years, it is very necessary to survey the concentrations, contamination levels, spatial variation and possible sources of heavy metals in soils of Tianjin suburban.

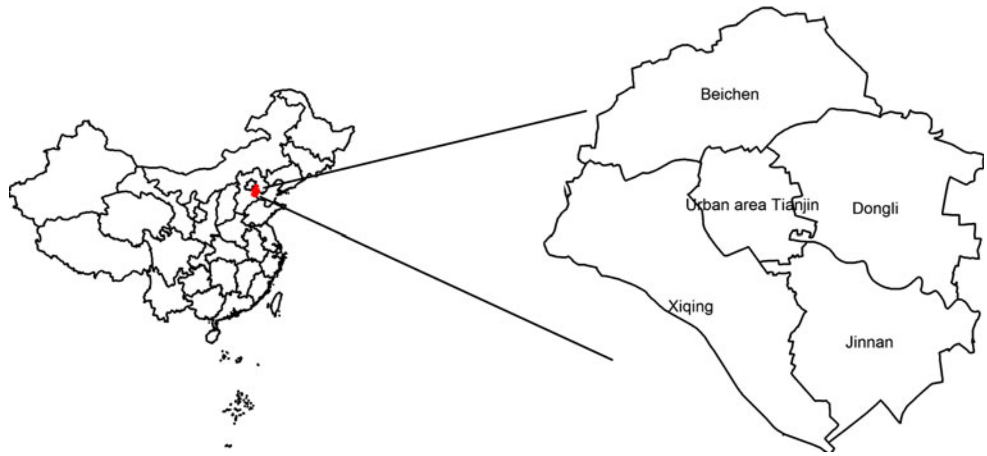

Fig. 1 Location of studying area

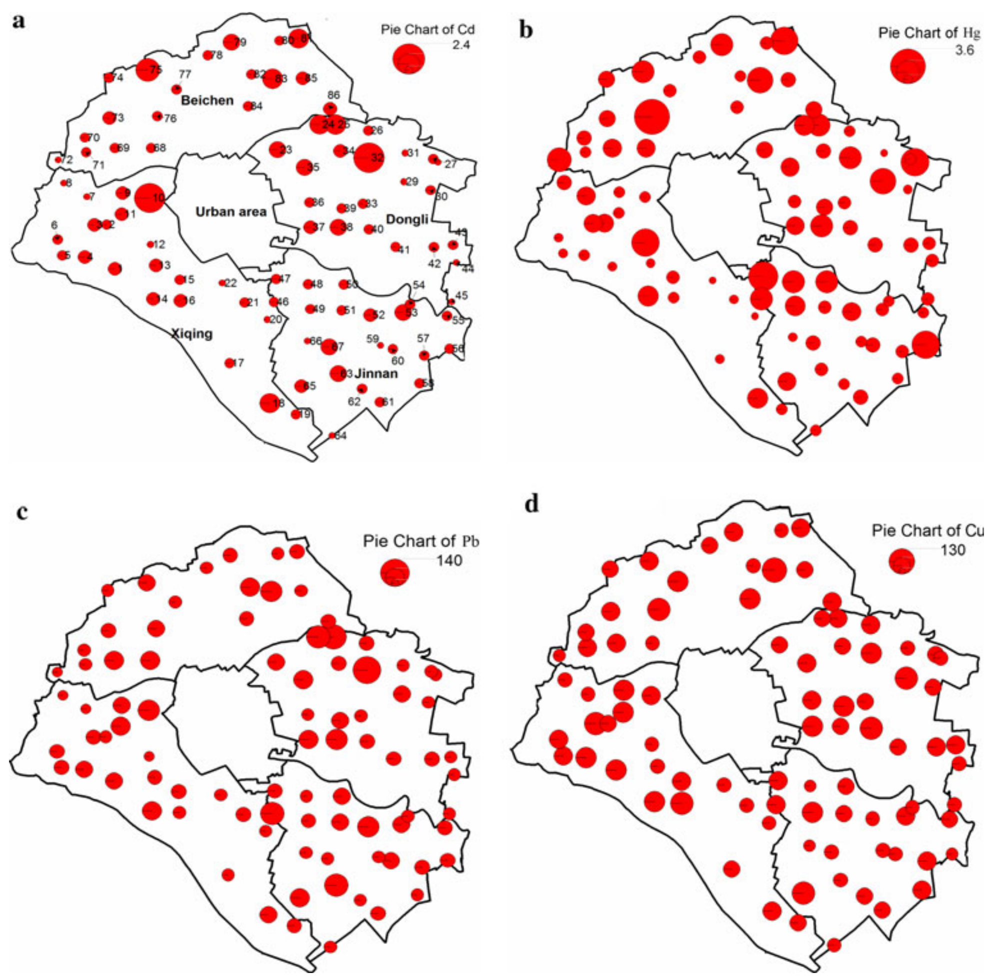

Fig. 2 Spatial distribution of Cd, Hg, Pb, Cu in suburban Tianjin (mg/kg)

Materials and Methods

The sampling sites in four suburban districts of Tianjin: Dongli, Xiqing, Jinnan, Beichen, were illustrated in Fig. 2. Samples were sampled in August 2008. 86 soil samples (0–10 cm soil layer, 1 kg each) were collected with stainless steel scoops and then stored in PE bags. Each sample was composed of 20 sub samples within $10 \times 10\ m^2$. Between sampling the scoop was rinsed by deionized water. Samples were placed in dark and transported to the laboratory as soon as possible. Soil samples were air dried, ground and sieved through a 50 mesh sieve. All samples were stored in −20°C before analysis.

Ultra pure water was used for dilution. All standard solution and internal standards were purchased from Agilent Technology Inc. Microwave-assisted digestion was carried out with a Mars Xpress (maximum power: 1200 W) laboratory microwave digestion system (CEM, Matthews, NC, USA). Agilent 7500a ICP-MS (Agilent, USA) was employed for element analysis. Briefly, 0.1 g samples were added into the PTFE pressure bomb and then 1 mL HNO_3, 1 mL HCl, 1 mL HF were added. The vessels were placed in microwave set at 150°C for 1 h. After cooling down to the room temperature, shake the vessels for 1 min and digest with the same time procedure again. The supernatant were poured out, drawn through 0.45 μm filter and diluted to 50 mL with water for ICP-MS analysis.

The concentrations of heavy metals were calculated by a five-point calibration curve (1, 5, 10, 50, 100 μg/L standard solution and 1 mg/L internal standard) with ICP-MS in which linearity of all target elements were higher than 0.99. Samples were measured for three times and the data were considered acceptable when RSD < 20%. Chinese Standard Reference Material-Coal Fly Ash (GBW08401) was employed to monitor the performance of the method. The recovery of Hg was 112.50%, Cr 77.91%, As 101.36%, Cd 81.25%, Pb 109.85%.

Results and Discussion

Grade classification of soil quality in Tianjin according to Chinese national standard GB 156-18-1995 and Wang's study (Wang and Zhang 2005) was shown in Table 1. Six grades were classified: background (I), not polluted (II), slightly polluted (III), median polluted (IV), seriously polluted (V), very seriously polluted (VI).

Table 2 showed the statistics results of the HMs in soils of Tianjin suburban. The average concentrations of Cr, Cu, Zn, As, Cd, Pb and Hg in soil of Tianjin were 101.0, 67.0, 100.6, 9.5, 0.49, 52.5 and 0.97 mg/kg, respectively. According to the average concentrations and the classification of Wang, the levels and pollution status in different districts were concluded. It indicated that pollution of Cr and Zn were minimal compared to the other elements while concentrations of Cd and Hg were higher than their natural background values. Pb and Cu pollution were also found to different extend.

Spatial variation of four metals with relatively higher concentrations in soil: Cd, Hg, Pb and Cu were illustrated in Fig. 2; The highest concentration of Cd, Hg, Pb, Cu appeared in Xiqing, Beichen, Dongli, Beichen respectively. From Fig. 2, pollution status and comparison in the four districts were also investigated. Cu and Pb pollution were found slightly and the concentrations of Cu and Pb varied not significantly in four districts (Fig. 2c–d). Higher concentrations of Hg and Cd found in soils of Beichen than others indicated that Beichen was suffering from metal contamination (Fig. 2a–b). Cd concentrations in Xiqing, Dongli and Beichen were higher than those in many cities in China, e.g. Shenyang (0.42 mg/kg) (Sun et al. 2010); Beijing (0.119 mg/kg) (Chen et al. 2004). Cd concentrations in all four districts exceeded 0.3 mg/kg, the grade II limit in Chinese national standards "Standard for Soil Environment Quality GB15618-1995". Hg concentrations in four districts also highly exceeded concentration allowed for soil in China (0.5 mg/kg, GB15618-1995). The results revealed that soil in suburban region in Tianjin suffered great contamination risk associated with Cd and Hg.

Table 1 Grade classification of soil quality in Tianjin (mg/kg^{-1})

Grade	Cd	Hg	As	Cu	Pb	Cr	Zn
I	≤0.09	≤0.05	≤11.07	≤28.35	≤20.32	≤98.38	≤76.27
II	>0.09	>0.05	>11.07	>28.35	>20.32	>98.38	>76.27
	≤0.159	≤0.258	≤16.67	≤43.71	≤32.83	≤107.0	≤115.3
III	>0.159	>0.258	>16.67	>43.71	>32.83	>107.0	>115.3
	≤0.380	≤0.6	≤18	≤70	≤190	≤228	≤190
IV	>0.380	>0.6	>18	>70	>190	>228	>190
	≤0.6	≤1.0	≤20	≤100	≤350	≤350	≤300
V	>0.6	>1.0	>20	>100	>350	>350	>300
	≤1.0	≤1.5	≤30	≤400	≤500	≤400	≤500
VI	>1.0	>1.5	>30	>400	>500	>400	>500

Principal Component Analysis (PCA) was a powerful tool to identify the possible sources of HMs in soil. Previous studies suggested that using sludge as fertilizer and wastewater irrigation contribute most to the HMs pollution in suburban Tianjin. PCA was employed in this study to further clarify the potential sources. As shown in Table 3, the first principle component (PC1) accounting for 33.7%, 57.1%, 46.7% and 35.9% of the total variance in Xiqing, Dongli, Jinnan, Beichen respectively. Loading of all HMs PC1 in Xiqing, Dongli and Jinnan were found all positive. According to Zheng et al. (2002), waste water irrigation would significantly increase the concentrations of Hg, Cd, Cr, As, Cu, Zn, Pb in soil. Anthony (1997) also reported that using sludge as fertilizer would increase the concentrations of Hg, Cd, Pb. In consideration of local specific environment, PC1 should be classified as the representative of the sources associated with wastewater and sludge fertilizer. Loadings of Hg, Cd, Pb in these three districts were higher and more characteristic indicating sludge application might account more for the pollution. For Beichen, high loading of As, Hg, Pb, Cd were found in PC1. Dry and wet deposition from air might be the possible sources. Sutherland (2003) and Nam and Lee (2006) suggested that Pb and Cd in soil or air might come from traffic, Manson et al. (1994) also reported the dry and wet deposition of Hg

Table 2 Heavy metal contents in soils and soil environmental grades in Tianjin (mg kg^{-1})

District	Statistics	Cu	Pb	Zn	Cr	Cd	As	Hg
Xiqing	Range	43.1–99.9	25.6–93.1	46.4–215.0	46.9–173.6	0.2–2.4	5.3–14.3	0.3–2.3
	Average	69.8	49.0	109.5	98.4	0.5	9.0	0.7
	Level	III	III	II	II	IV	I	IV
	Pollution status	Slightly polluted	Slightly polluted	Not polluted	Not polluted	Polluted	Background	Polluted
Dongli	Range	44.4–97.7	32.3–131.5	45.9–272.9	53.1–241.6	0.2–2.2	6.0–12.5	0.2–2.3
	Average	68.2	57.5	105.2	104.0	0.5	9.1	0.99
	Level	III	III	II	II	IV	I	IV
	Pollution status	Slightly polluted	Slightly polluted	Not polluted	Not polluted	Polluted	Background	Polluted
Jinnan	Range	38.2–96.0	31.9–107.4	31.8–337.7	43.9–178.0	0.2–0.9	5.0–16.7	0.4–2.5
	Average	58.8	52.2	104.0	92.6	0.4	8.7	1.00
	Level	IV	III	II	I	IV	I	IV
	Pollution status	Slightly polluted	Slightly polluted	Not polluted	Background	Polluted	Background	Polluted
Beichen	Range	40.2–127.3	30.9–84.1	38.4–128.6	45.0–152.5	0.2–1.4	4.1–23.8	0.5–3.5
	Average	70.5	50.3	80.6	110.3	0.5	11.2	1.2
	Level	IV	III	II	III	IV	II	V
	Pollution status	Polluted	Slightly polluted	Not polluted	Slightly polluted	Polluted	Not polluted	Seriously polluted

Table 3 PCA of heavy metals in soils in Tianjin

HMs	Xiqing		Dongli		Jinnan		Beichen	
	PC1	PC2	PC1	PC2	PC1	PC2	PC1	PC2
Loading	33.7%	17.1%	57.1%	13.7%	46.7%	18.4%	35.9%	19.7%
Cr	0.32	0.66	0.61	−0.63	0.82	−0.38	0.29	−0.72
Ni	0.61	−0.21	0.85	0.11	0.84	−0.30	−0.68	0.54
Cu	0.71	−0.35	0.50	0.76	0.71	0.57	0.49	0.47
Zn	0.45	0.49	0.94	−0.02	0.70	0.55	0.31	0.59
As	0.20	−0.38	0.48	0.17	0.84	−0.05	0.57	0.27
Cd	0.83	0.16	0.95	−0.19	0.75	−0.22	0.59	0.25
Pb	0.88	−0.05	0.94	−0.08	0.90	0.15	0.69	0.20
Hg	0.69	−0.12	0.67	0.17	0.73	0.11	0.84	−0.11

from air to soil. Considering the specific environment, coal combustion e.g., in the coal-fueled power plant and chemical plants, might be responsible for the higher concentration of Hg in the soil in Beichen while petrol combustion in traffic might be important source of Pb and Cd.

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