Heavy metal contents and chemical speciations in sewage-irrigated soils from the eastern suburb of Beijing, China

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Abstract

Accumulation of heavy metals in agricultural sewage-irrigated soils has caused increasing concern. This study analyzed the total concentrations and chemical speciations of heavy metals including Cd, Cr, Cu, Zn and Ni in sewage–irrigated soils in the eastern suburb of Beijing, China. The results showed that there was remarkable buildup of Cd, Cr, Zn and Cu in sewage-irrigated topsoils compared to reference topsoils. Besides, the total Cd and a part of Ni were beyond Chinese agricultural soil environmental quality criteria. In sewage-irrigated soils, Cd, Cr, Ni, Zn and Cu were dominated by residual fractions and few were present in exchangeable and carbonate fractions as a result of higher soil pH. The mobility and bioavailability of the five metals declined in the following order: Zn, Cu, Ni, Cd and Cr. However, other than the four metals, Cd was more mobile and bioavailable in the sewage-irrigated topsoils than in the reference topsoils. This indicated higher Cd contents in sewage-irrigated soils may constitute a potential risk to food security and human health.

Key Words

Heavy metals, chemical speciation, sewage irrigation, agricultural soil, bioavailability.

Introduction

The rapid development of urbanization and industrialization, together with the shortage of availability of fresh water to be used for irrigation led to the rising use of sewage for agricultural land irrigation. While sewage provides water and valuable plant nutrients, it leads to the potential accumulation of heavy metals (HMs) in agricultural soils(Abdel-Sabour 2003; Zhang *et al.* 2008). When the contents of HMs exceed the permitted threshold, they will impact the normal growth of crops or even might enter food chain to threat human and animal health (Akoumianakis *et al.* 2009; Fu *et al.* 2009; Salvatore *et al.* 2009). In the study of S. Khan *et al.* (2008), it was suggested that there was a substantial buildup of HMs in plants grown in wastewater-irrigated soils of Beijing, in which the HMs concentrations were significantly higher than those in the reference soil, and exceeded the permissible limits set by SEPA in China and WHO.

The toxicity and the mobility of heavy metals in soils depend not only on the total concentration, but also on their specific chemical form and soil properties like pH, organic matter content etc. (Lu *et al.* 2003). The chemical fractionation of heavy metals must be taken into account in pollution studies since total contents in soils provide, in most cases, limited information on the mobility and bioavailability of heavy metals (Kartal *et al.* 2006) and can be misleading when assessing environmental effects due to a potential overestimation of exposure risk (Cuong and Obbard 2006). The objective of this study was to determine the total concentrations and geochemical speciation of Cd, Cr, Cu, Zn and Ni in Calcaric Cambisol under sewage irrigation in the eastern suburb of Beijing, China.

Materials and methods

Description of study area

The sewage-irrigated area studied is located in the connection region between the Tongzhou District of Beijing City and the Xianghe County of Hebei Province, where several rivers form a fan-shaped alluvial plain, characterized by continental monsoon climate. The predominant soil type in the area is Calcaric Cambisol. And the agricultural land has been mainly irrigated using sewage from the Beiyun River which runs through the urban area to rural agriculture land, and from the Fenggangjian River, or the Gaobeidian wastewater treatment plant. The Beiyun River and the Fenggangjian River are the main domestic and production effluent recipients and also are the main sources for irrigation in the southeast area of Beijing.

Collection of soil samples

Sewage-irrigated and reference soils were collected in the summer of 2007. Sewage-irrigated soil samples were collected in the area irrigated with sewage from the Beiyun River and the Fenggangjian River, including 20 samples of topsoil (0-20 cm) and 10 samples of subsoil (20-40 cm). Reference soils were

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collected in non-sewage-irrigated areas from the northeast area of the Chaobai River, including 6 topsoil samples. All soil samples were collected from farmlands far from the highways as shown in Fig. 1.

Analytical methods

Immediately after collection, all samples were air-dried at room temperature and ground in an agate mortar to allow passage through a 2-mm nylon sieve. A subsample of each soil sample was further ground to allow passage through a 0.149-mm nylon sieve. The sequential extraction scheme proposed by Tessier *et al.* was adopted to partition HMs into five fractions: exchangeable (exch.), bound to carbonates (carb.), bound to Fe-Mn oxides (Fe/Mn ox.), bound to organic matter (orga.) and residual (resi.) (Tessier *et al.* 1979). The defining and specific approach were performed according to our published literature (*Chen et al.* 2009). The total elemental contents of soil samples and residual fractions were digested 0.1000 g of dried soil samples with HNO_3-HF-$HClO_4$ mixture followed by instrumental analysis. The elemental concentrations of all solutions were determined using HR-ICP-MS (Element 2, Finnigan Co., USA). The soil pH was measured in a 1:2.5 (w/v) mixture of soil and water using a glass electrode, the $CaCO_3$ content was measured using the gas-volumetric method and the organic carbon content of the soil was determined by the $K_2Cr_2O_7$–H_2SO_4 digestion method (Liu *et al.* 2005).

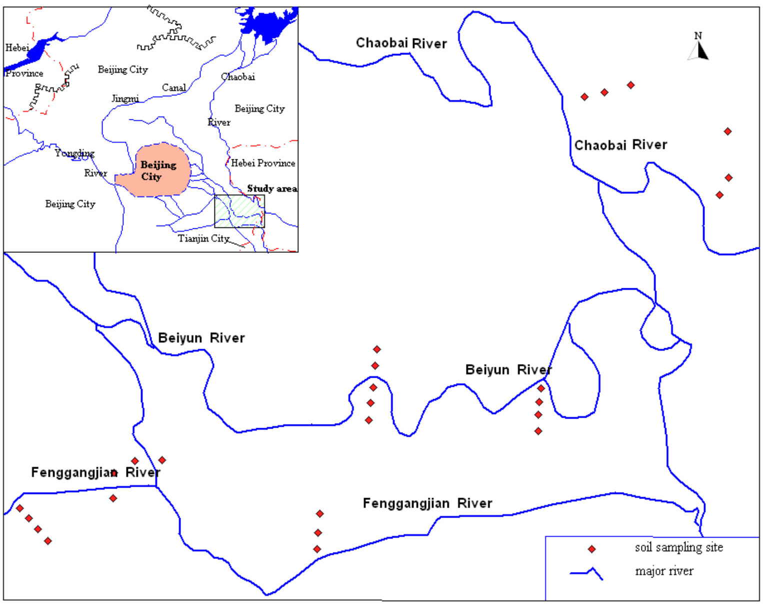

Figure 1 Soil sampling sites for heavy metal investigation in the east suburb of Beijing

Results

Total concentrations of heavy metals in the soils were shown in Table 1. The Cd, Cr, Ni, Zn and Cu fractions expressed as percentages of the sum of individual chemical forms in ST, SS and RT are presented in Table 2, respectively.

Table 1 Total content of heavy metals in the soils (unit: mg/kg)

			Cd	Cr	Ni	Zn	Cu
sewage-irrigated soils	0-20cm n=20	Mean, SD	0.81±0.16	78.3±20.2	31.8±17.4	71.5±14.0	25.5±4.3
		Range	0.62-1.19	55.7-124.4	14.7-85.1	52.1-91.1	17.2-32.8
	20-40cm n=10	Mean, SD	0.45±0.34	58.7±13.7	23.3±5.5	66.0±11.7	21.8±4.6
		Range	0.27-0.65	41.7-73.2	15.7-28.8	54.3-81.9	15.1-25.8
reference soils	0-20cm n=6	Mean, SD	0.36±0.25	53.8±8.1	18.7±3.0	51.9±4.4	16.0±3.7
		Range	0.12-0.68	47.4-65.7	14.9-22.0	45.4-53.6	12.2-21.1
Criteria of agricultural soil quality [a]			0.60	250	60	300	100
Background of soils in Beijing[b]			0.12	29.8	26.8	57.5	18.7

[a] National Standard of PR China (1995) (GB 15618-1995).

[b] Chen T B et al (2004).

Table 2 Chemical fractionation of heavy metals in the study area (unit: %)

			Exch.	Carb.	Fe/Mn ox.	Orga.	Resi.
Cd	ST	Mean, SD	6.98±10.16	n.d.	23.85±12.18	7.37±11.46	61.77±13.36
		Range	n.d.-32.97		n.d.-40.47	n.d.-45.92	0.34-0.69
	SS	Mean, SD	13.38±12.05	n.d.	n.d.	4.60±2.41	82.01±12.72
		Range	n.d.-24.37			1.95-7.80	67.83-95.72
	RT	Mean, SD	20.24±14.93	n.d.	4.30±8.61	n.d.	75.46±20.59
		Range	n.d.-31.37		n.d.-17.22		51.49-100.00
Cr	ST	Mean, SD	0.04±0.07	0.08±0.16	2.30±0.88	13.46±5.10	84.12±5.41
		Range	n.d.-0.17	n.d.-0.55	1.30-3.84	6.26-27.17	70.33-92.42
	SS	Mean, SD	0.04±0.02	0.55±0.22	2.00±0.44	22.72±5.57	74.71±6.16
		Range	0.01-0.06	0.29-0.79	1.56-2.58	17.65-28.94	67.69-80.04
	RT	Mean, SD	0.08±0.10	0.36±0.26	2.11±0.83	15.47±4.98	81.99±4.83
		Range	n.d.-0.20	n.d.-0.58	1.47-3.33	9.96-20.47	77.10-86.71
Ni	ST	Mean, SD	0.43±0.57	0.19±0.48	10.75±4.41	33.87±12.56	54.75±13.58
		Range	n.d.-1.92	n.d.-1.77	4.10-19.22	8.88-62.36	29.86-86.78
	SS	Mean, SD	0.70±0.84	2.21±0.52	6.26±1.25	55.37±11.31	35.47±10.81
		Range	0.12-1.93	1.65-2.86	4.84-7.39	44.21-67.53	25.45-47.98
	RT	Mean, SD	0.38±0.42	1.31±1.07	6.47±4.94	38.80±7.35	53.05±6.48
		Range	0.12-1.00	n.d.-2.44	3.44-13.85	32.11-49.17	43.89-57.98
Zn	ST	Mean, SD	1.76±3.67	1.55±1.67	14.92±6.78	32.55±5.75	49.23±8.73
		Range	n.d.-10.52	0.24-5.45	5.25-29.64	23.77-45.60	31.12-67.23
	SS	Mean, SD	9.93±2.05	1.95±1.21	7.19±1.07	45.20±6.27	35.73±9.54
		Range	7.96-12.61	1.01-3.70	6.16-8.63	37.05-50.82	26.49-46.20
	RT	Mean, SD	3.57±3.34	2.86±1.17	12.25±5.49	37.89±6.31	43.43±4.16
		Range	n.d.-7.84	2.00-4.54	7.94-20.29	29.80-44.78	39.18-48.29
Cu	ST	Mean, SD	0.37±0.27	0.12±0.26	17.50±9.98	30.25±6.57	51.76±11.19
		Range	0.17-1.24	n.d.-0.83	6.91-40.55	18.00-43.19	27.78-69.36
	SS	Mean, SD	0.41±0.30	1.31±0.48	20.73±3.65	39.32±5.44	38.24±9.10
		Range	0.22-0.86	0.85-1.79	17.23-25.13	34.66-45.23	30.12-46.24
	RT	Mean, SD	0.52±0.20	0.19±0.20	11.64±3.31	37.32±8.06	50.33±8.22
		Range	0.27-0.72	n.d.-0.38	8.24-15.09	25.51-43.64	40.43-60.44

n.d. means not detected.

Discussion and conclusion

In ST, an obvious accumulation of Cd, Cr, Zn and Cu was found compared with reference soils, and the concentrations of the HMs except Cd and Ni were below the Chinese agricultural soil environmental quality criteria. In sewage-irrigated soils, Cd, Cr, Ni, Zn and Cu were predominately present in the residual fraction. The order of Cu, Zn and Ni in sewage-irrigated topsoils in each fraction was residual > organic > Fe-Mn oxide > exchangeable > carbonate, for Cd in sewage-irrigated soils, the order was residual > Fe-Mn oxide > organic > exchangeable > carbonate, and for Cr in sewage-irrigated soils, the order was residual > organic > Fe-Mn oxide > carbonate > exchangeable. However, for Cu and Ni in sewage-irrigated subsoils, the order was organic > residual > Fe-Mn oxide > carbonate > exchangeable, for Zn the order was organic > residual > exchangeable > Fe-Mn oxide > carbonate, and for Cd the order was residual > exchangeable > organic > Fe-Mn oxide and carbonate. The contents of the exchangeable and carbonate fractions were very low, which may be related to higher soil pH. It was observed that the contents of residual speciation and the Fe-Mn oxygenation state in ST were higher than those in RT for all heavy metals except Cd, while the contents of the organic state and other states were relatively lower than those in RT. Likewise, the contents of the residual and Fe-Mn oxide fractions in ST were higher than those in SS for all the metals with the exception of Cu and Cd, while the contents of organic, carbonate and other states were relatively lower than those in SS. The relatively high percentage of heavy metal carbonated bound fraction in subsoils may be related to adsorption and consolidation of $CaCO_3$ in subsoils. The mobility and bioavailability of the five metals declined in the following order: Zn, Cu, Ni, Cd and Cr. Cd being different from other four heavy metals was more mobile and bioavailable in the sewage-irrigated topsoils than in the reference topsoils. Therefore, higher Cd contents in sewage-irrigated soils will have potential risk for human health.

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