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Mercury and Cadmium Contamination of Irrigation Water, Sediment, Soil and Shallow Groundwater in a Wastewater-Irrigated Field in Tianjin, China

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Abstract We investigated the concentrations of Hg, Cd, Pb and As in samples of irrigation water, sediment, soil and groundwater from a field in Tianjin that was irrigated with wastewater. The results showed that the concentrations (Hg, 0.82 μg/L; Cd, 0.18 μg/L; Pb, 1.5 μg/L; As, 8.02 μg/L) in the irrigation water did not exceed the China Surface Water Quality Standard or the maximum concentrations in irrigation water recommended by the FAO. The concentrations of metals in the groundwater of wells (Hg, 0.016 μg/L; Cd, 0.128 μg/L; Pb, 0.25 μg/L; As, 4.65 μg/L) were lower than China Groundwater Quality Standard and the WHO guideline values for drinking water. The groundwater had not yet been contaminated through vertical infiltration-induced leaching. However, a substantial buildup of Hg and Cd in river sediments (I_{geo} for Hg and Cd; 5.24 and 3.04, respectively) and wastewater-irrigated soils (I_{geo} for Hg and Cd; 2.50 and 3.09, respectively) was observed. Taken together, these results indicated that irrigation with wastewater damaged the soil quality over the long term and that metals more easily accumulated in vegetable fields than rice fields.

Keywords Wastewater irrigation · Metals · Soil · Groundwater

At present, water and soil are commonly contaminated by metals, which has aroused a great deal of concern among individuals due to the non-biodegradable nature and persistence of metals (Raghunath et al. 1999). The contamination of agricultural soils with metals has received a great deal of attention because contaminated soils can enhance the release and uptake of contaminant metals by plants and pose a risk to human health through trophic transfer into the food chain (Wang et al. 2005). There is a great deal of evidence that wastewater irrigation is one of the most important sources for metal contamination of local soils and agricultural products (Gupta et al. 2008). Long-term irrigation with sewage effluent has been shown to increase the amount and availability of metals in agricultural soils (Bhattacharyya et al. 2008). Indeed, the estimated metal loads from wastewater or wastewater mixed with river water over a 50-year period suggest that irrigation may account for up to 31% of the surface metals (Assadian et al. 1998). Consequently, predicting the mobility, bioavailability and health risks of trace elements in wastewater-irrigated soil has been of increasing concern for many decades (Chaudri et al. 2007; Khan et al. 2008). However, soil is not only a medium for plants to grow or a repository of waste materials, but also a source of emission of many contaminants to the atmosphere and plants. Specifically, recent studies have suggested that metals in wastewater may also contaminate shallow groundwater systems through vertical infiltration-induced leaching (Mohammed et al. 2003). As a result, the assessment of metal contamination of shallow groundwater underlying wastewater-irrigated fields is of vital importance (Tijani 2008), However, few studies on this subject have been conducted to date.

Tianjin is located in northern China, in the lower reaches of the Haihe River System. Nearly all of the rivers in this area have been contaminated by wastewater from the combined urban areas of Tianjin, Beijing and Hebei Province (Liu et al. 2007). Due to the shortage of freshwater in semiarid and arid zones, treated wastewater is becoming an important source of irrigation water for

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agriculture in Tianjin and has been used as such for at least 45 years. With the rapid development of agriculture and industry, metals are being emitted into the environment in large quantities. As a result, the suburban and urban areas of Tianjin have been polluted by metals (Shi et al. 2005; Wang et al. 2005). The main objective of this study was to estimate the levels of pollutants (Cd, Hg, Pb and As) in irrigation water, sediments, soils and shallow groundwater collected from an agricultural area receiving wastewater from the Beitang Drainage River near Tianjin City, Northern China.

Materials and Methods

The field evaluated in this study is approximately 125 km^2 and located in one of three major wastewater-irrigated areas in Tianjin. The field is irrigated with wastewater from the Beitang Wastewater Drainage River (34 km full-length). Six sediments and six superficial water samples were collected along the river. In addition, 10 superficial soil samples (five from rice fields and five from vegetable fields) and 10 groundwater samples from wells in the wastewater-irrigated field were collected. A map of the studied area and the locations of the sampling sites is shown in Fig. 1. The surface sediment and soil layer was sampled to a depth of 0–25 cm, and the plough layer in the study area is always 25 cm. At each sampling point, 3–5 sub-samples from approximately 9 m^2 were taken and then mixed to obtain a bulk sample, after which they were placed into polyethylene plastic bags. River water and shallow groundwater samples at each site or well were also taken twice in two days. The water samples were collected into polyethylene bottles and acidified with HNO_3 to keep the dissolved metals in solution.

To avoid possible contamination, all glassware and plastic containers were previously soaked overnight in 25% nitric acid and then rinsed three times with Milli-Q water. All extraction solutions were prepared using guarantee reagents. Sediment and soil samples were air-dried at room temperature in the laboratory, passed through a 100-mesh nylon sieve, and then thoroughly homogenized and kept in a silica gel desiccator until analysis. Upon analysis, approximately 0.25 g samples were weighed and digested with 9 mL HNO_3 and 4 mL HF using a suitable laboratory microwave unit (MARS 5, CEM) and the temperature and pressure conditions described in the USEPA Method 3052. After cooling, the vessel contents were filtered, centrifuged or allowed to settle and then diluted to 50 mL with Milli-Q water and then determined by the appropriate SW-846 method. Determinations of Cd and Pb in the dissolved soils and sediments were performed using an inductively coupled plasma mass spectrometer (ICP-MS, Perkin-Elmer/Sciex Elan 9000, USA). The Hg and As were determined

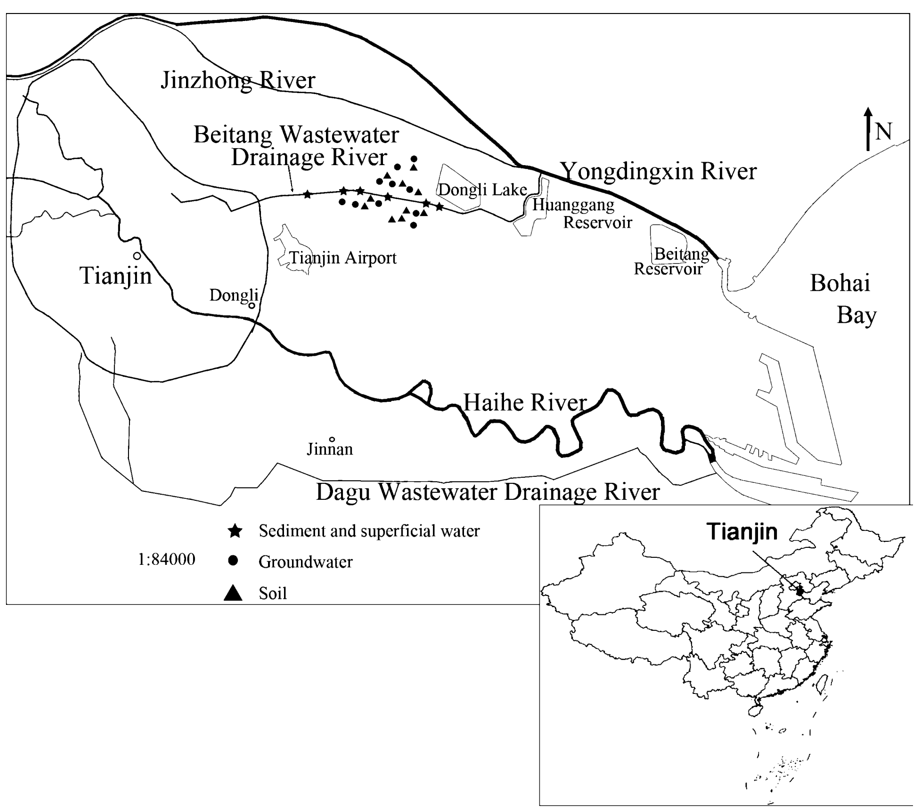

Fig. 1 The map of studied area and the locations of sampling sites

directly by atomic fluorescence spectrometry (AFS, Jitian Company, China) while the solution was clear. The concentrations of Pb and Cd in the aqueous samples were analyzed by ICP-MS, while AFS was used to determine the concentrations of As and Hg in the aqueous samples. A relative standard deviation between 4.5% and 9.3% was obtained for all analyses. The detection limits were estimated as 0.009 (μg/L) for Hg, 0.003 for Cd, 0.036 for Pb and 0.3 for As, which were calculated at 3σ. Our method was acceptable since satisfactory recoveries (86.2%–103.8%) for Hg, Cd, Pb and As were obtained.

Results and Discussion

As shown in Table 1, the concentrations (μg/L) of the analyzed metals in irrigation water collected from Beitang Wastewater Drainage River were relatively low and did not exceed the levels specified by the China Environmental Quality Standard for Surface Water or the maximum concentrations of trace elements in irrigation water recommended by the Food and Agriculture Organization (FAO). In the last 10 years, Tianjin has established a complete sewage treatment system in the city. As of 2008, the daily wastewater treatment capacity was 1.8×10^6 tons, which accounts for more than 81% of the sewage or wastewater in the urban area. Because industrial pollution abatement by key enterprises in Tianjin is a profitable industry, the water quality of the drainage river has improved somewhat. However, the metal present in the greatest concentration was Hg (0.82 μg/L), which indicates that the amount of Hg discharged from Tianjin industrial effluents or atmospheric emissions is still enormous (Table 1). Although large point-source discharges of wastewater containing Hg have been detected and emissions have been eliminated by process changes or plant closures, Hg pollution still persists in this area due to high Hg emissions from other Hg-releasing activities. For example, large quantities of coal are burned in Tianjin, which resulted in the emission of more than 3.33t Hg in 1999 (Streets et al. 2005).

Table 1 Metal concentrations in irrigation water collected from Beitang Wastewater Drainage River (μg/L)

	pH	Cd	Pb	As	Hg
Minimum	7.26	0.10	1.1	4.72	0.08
Maximum	7.70	0.245	2.0	12.3	2.05
Mean	7.39	0.18	1.5	8.02	0.82
Limited value (V)[a]	6–9	10	100	100	1
Guideline value[b]	6.5–8.4	10	5000	100	N/V[c]

[a] China Environmental Quality Standard for Surface Water (GB3838-2002); [b] Maximum concentrations of trace elements in irrigation water recommended FAO; [c] The abbreviation "N/V" means "no value"

Table 2 Metal concentrations of sediments in Beitang Wastewater Drainage River (mg/kg)

	Hg	Cd	Pb	As
Minimum	2.72	1.69	272.4	17.4
Maximum	2.96	1.77	305.8	18.2
Mean	2.84	1.73	289.1	17.8
Background value[a]	0.05	0.14	16.6	13
Limited value(I)[b]	N/V	0.50	60	20
Guideline value[c]	0.2	0.6	31	6

[a] Bohai Bay sediment background value (Meng et al. 2008); [b] China Marine Sediment Standards (GB18668-2002); [c] Soil, Ground Water and Sediment Standards (Ontario's Ministry of the Environment 2004)

The concentrations of the analyzed metals (Hg, Cd, Pb and As) in sediments from the Beitang Wastewater Drainage River are shown in Table 2. The mean levels of Hg, Cd and Pb far exceed the Tianjin Bayhai Bay sediment background values (Meng et al. 2008), the sediment quality limit values for marine fisheries set by the China Marine Sediment Standards and the guideline values for all types of property uses of Soil, Ground Water and Sediment Standards. However, the As concentration was relatively low.

The assessment of metals pollution and enrichment in soil and sediment can be conducted using several methods, the most common of which are the contamination factor (CF) and the index of geoaccumulation (I_{geo}). The CF is used by Håkanson to assess sediment contamination through comparison of the concentrations in the surface layer to background values. The CF is given by $CF = C^i_{0-1}/C^i_n$, where, C^i_{0-1} is the mean content of metals from the sampling sites and C^i_n is the pre-industrial concentration of individual metals or the background value. Four contamination categories are recognized based on the CF: $CF < 1$, low contamination factor; $1 \le CF < 3$, moderate contamination factor; $3 \le CF < 6$, considerable contamination factor; $6 \le CF$, very high contamination factor.

I_{geo}, which is used to study the degree of metal contamination in soils and sediments (Singh et al. 2002), is determined by the following equation: $I_{geo} = \log_2[C_n/(1.5 \times B_n)]$, where, C_n is the concentration of the element in the sample, B_n is the background value and 1.5 is the amend index. The I_{geo} value is divided into seven categories: $I_{geo} < 0$, practically uncontaminated; $0 \le I_{geo} < 1$, uncontaminated to moderately contaminated; $1 \le I_{geo} < 2$, moderately contaminated; $2 \le I_{geo} < 3$, moderately to heavily contaminated; $3 \le I_{geo} < 4$, heavily contaminated; $4 \le I_{geo} < 5$, heavily to very heavily contaminated; $I_{geo} \ge 5$, very heavily contaminated. The respective metal factors calculated are listed in Fig. 2.

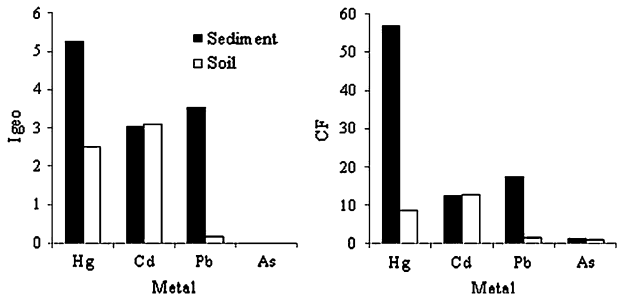

Fig. 2 CF and I_{geo} of metals in sediments and wastewater-irrigated soils

For metal contents in the sediment, the CF of Hg, Cd and Pb were greater than 6, indicating a "very high contamination". The I_{geo} of Hg was greater than 5, indicating "very heavily contaminated". The I_{geo} of Cd and Pb were slightly larger than 3, indicating "heavily contaminated". The I_{geo} of As was −0.13, indicating "practically uncontaminated". Therefore, Hg, Cd and Pb contamination in sediments is very serious, which indicates that a large quantity of municipal sewerage and industry wastewater have entered the Beitang Wastewater Drainage River in the past. Most pollutants (including metals) are prone to adhere to finer grains and accumulate in sediments. Several previous studies have shown that Hg and Cd pollution in Tianjin is very common, and comparable concentrations of Hg concentrations have been found, with the highest value of 8.7791 mg/kg (dry weight) being observed in sediments collected from Dagu Wastewater Drainage River, another important wastewater drainage river in Tianjin (Shi et al. 2005). Cd pollution has also been reported in the Haihe River at concentrations as high as 0.44–2.17 mg/kg (Liu et al. 2006).

The ranges and average metal concentrations in the wastewater-irrigated soils are summarized in Table 3. The results revealed that the concentrations of Hg, Cd and Pb are higher than the Tianjin soil environment background value (Tianjin Environmental Protection Bureau 1996). However, with the exception of Cd, the concentrations of the metals do not exceed the limit value (soil quality for agriculture use) specified in the China Environmental Quality Standard for Soils (GB 15618-1995). Additionally, only the Hg concentration exceeds the guideline value set for agricultural use specified in the Soil, Ground Water and Sediment Standards set by the Ontario Ministry of the Environment (2004), while the Cd concentration is similar to the guideline value and the Pb and As concentrations are lower than this value. With the exception of Pb and As, the metal concentrations were higher than those reported in 1995 (Tianjin Environmental Protection Bureau 1996), which demonstrates that Hg and Cd pollution in the soils has increased in the past 12 years. Additionally, Wang et al. (2005) reported that the Hg concentrations in agricultural soils in the Dongli and Jinnan Districts of Tianjin were 1.3 and 3.04 mg/kg, respectively, while the Cd levels were 1.12 and 0.34 mg/kg, respectively. Comparable concentrations have been found in soils irrigated with wastewater in Mexico City (Pb 18.1–131.7 mg/kg; Cd 0.86–5.07 mg/kg; Flores et al. 1997) and Titagarh, India (Pb 99.3–168.3 mg/kg; Cd 22.2–51 mg/kg; Gupta et al. 2008). The Pb and Cd concentrations in this study were similar to those in Mexico City, but lower than those in Titagarh, India.

Table 3 Metal concentrations of soils in wastewater-irrigated field (mg/kg)

	Hg	Cd	Pb	As	pH
Minimum	0.042	0.101	22.0	7.14	8.04
Maximum	1.883	3.625	52.0	16.53	8.42
Mean	0.4235	1.152	34.25	9.82	8.26
Background value[a]	0.05	0.09	20.32	9.32	N/V
Data in 1995[b]	0.379	0.779	75.33	10.463	N/V
Limited value(III)[c]	1.0	0.60	350	25 (20)	>7.5
Guideline value[d]	0.16	1.0	55	14	N/V

[a] Tianjin soil environment background value (Tianjin Environmental Protection Bureau 1996); [b] Data investigated in 1995 (Tianjin Environmental Protection Bureau 1996); [c] China environmental quality standard for soils (GB15618-1995); [d] Soil, Ground Water and Sediment Standards (Ontario's Ministry of the Environment 2004)

Evaluation of CF and I_{geo} in wastewater-irrigated soils (Fig. 2) revealed that the highest values were obtained for Cd (12.8, 3.1), indicating a "very high contamination factor" and "heavily contaminated", respectively. Overall, the CF and I_{geo} values decreased in the following order: Cd > Hg > Pb > As. Metals in agricultural soils have accumulated due to wastewater irrigation and they show similar pollution characteristics to the sediments. The CF and I_{geo} values revealed that increasing accumulation of metals (Cd, Hg) occurred during the period of wastewater irrigation, which is in accordance with the results of a previous study conducted in Tianjin in different agricultural soils (Wang et al. 2005). However, Pb and As were not found to be significantly enriched in the present study.

As shown in Fig. 3, the metal contents in vegetable field (VF) soils were higher than those in the rice field (RF) soil, which was likely due to differences in their physical interactions, hydrodynamics and dilution conditions between the soils. Acidic pH and high organic matter in vegetable field soils maximizes the effect of the metals load. Additionally, in rice fields, Hg and Cd can easily combine with Cl^- ions to form $HgCl_4^{2-}$ and $CdCl_2$; hence, the mobility is likely to increase (Usman et al. 2005), resulting in the metals finally being lost through rain-induced leaching.

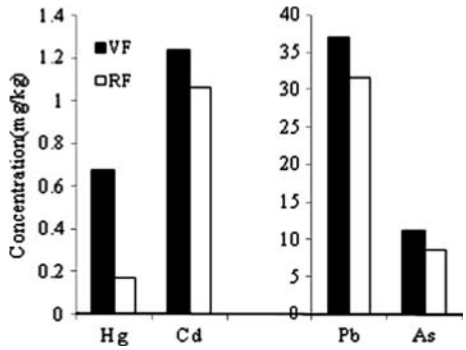

Fig. 3 Metal concentrations in rice (*RF*) and vegetable (*VF*) field soils

Table 4 Metal concentrations in groundwater of wells in wastewater-irrigated field (μg/L)

	Hg	Cd	Pb	As	TOC	TP	pH
Minimum	0.010	0.103	0.047	1.88	0.59	0.036	8.42
Maximum	0.047	0.135	0.68	7.6	1.39	0.179	8.67
Mean	0.016	0.128	0.25	4.65	0.86	0.104	8.52
Limited value(I)[a]	0.05	1	5	5	N/V	N/V	6.5–8.5
Guideline value[b]	1	3	10	10	N/V	N/V	N/V
Standards value[c]	0.02	0.5	1	25	N/V	N/V	N/V

[a] China Quality Standard for Ground Water (GB/T14848-9); [b] WHO guideline values for chemicals that are of health significance in drinking water; [c] Soil, Ground Water and Sediment Standards(Ontario's Ministry of the Environment 2004)

The metal concentrations in groundwater from wells situated in the wastewater-irrigated field are shown in Table 4. The average contents of Hg, Cd, Pb and As were generally lower than the limit values (I) set by the China Quality Standard for Ground Water and the WHO (World Health Organization) guideline values for chemicals that are of health significance in drinking water. When compared to the Soil, Ground Water and Sediment Standards, the mean Hg and Cd concentrations are relatively high. However, it should be noted that there are marked differences among the limit values set by these three standards, with the strictest guideline values for Hg, Cd and Pb being present in the Soil, Ground Water and Sediment Standards. In general, the groundwater from wells in this area has not been reported to be contaminated by leaching of these metals from wastewater-irrigated soil until now. Metals entering agriculture soil may have accumulated in the plough layer, but they have not yet contaminated groundwater through vertical infiltration-induced leaching. The soils in the area have pH values of 8.04–8.42,which would reduce metal mobility. Additionally, there were low total organic carbon (TOC) and total phosphorus (TP) levels observed, which further supports the absence of anthropogenic contamination in the groundwater.

When compared with the Hg, Cd, Pb and As concentrations in groundwater from wells, the contents in the irrigation water were relatively higher. Specifically, the Hg, Pb, As and Cd concentrations of river water used for irrigation were about 51, 6.0, 1.7 and 1.4 fold greater than their contents in groundwater. Such depletion of metals in groundwater may be attributed to natural attenuation, uptake by the plants through soil solution, as well as chelation and complexation as the irrigation water percolates through the soil column (Tijani 2008). Flores et al. (1997) analyzed the total metal concentrations in wastewater irrigated soil profiles and found that accumulation of metals occurred in the surface layers of soils. Similarly, Shomar et al. (2005) found that the upper 40 cm of soil comprised the zone affected by wastewater and sludge.

Assessment of pollution with and accumulation of metals (Hg, Cd, Pb and As) in irrigation water, sediment, soil and groundwater from wells in a wastewater-irrigated field in Tianjin were conducted. The irrigation water pumped from the Beitang Wastewater Drainage River is not polluted with metals (Hg, Cd, Pb and As) and does not contain metals in levels that exceed the limit values (I) set by the China Environmental Quality Standard for Surface Water or the maximum concentrations in irrigation water recommended by the FAO. However, the analyzed metal concentrations in sediments collected from Beitang Wastewater Drainage River are extraordinarily high. Specifically, Hg, Cd and Pb showed significant accumulation (CF = 56.8 for Hg, 12.3 for Cd, 17.4 for Pb), which suggests that there has been a great anthropogenic contribution due to the sewage and industrial effluents discharged into the system over the long term. The metal contents in agricultural soil are also influenced by wastewater irrigation. The metal pollution characteristics in soils were found to be similar to those in sediments, with the CF of Hg, Cd and Pb reaching 8.47, 12.8 and 1.68, respectively. Finally, the analyzed metals more easily accumulated in vegetable field soils than in rice field soils.

According to the geoaccumulation index, Hg and Cd contamination are serious problems in the Tianjin wastewater-irrigated field evaluated in this study and may pose major risks to human health through trophic transfer into the food chain. The Hg and Cd concentrations increased slightly in contaminated soil from the sampling sites when compared with previous monitoring data collected in 1995. This increase in metal levels indicates a need for constant monitoring. Additionally, appropriate remediation goals or restrictions must be imposed to control human exposure to metal contamination. Although the agricultural soils irrigated with wastewater have become highly enriched with Hg and Cd over the long term, those metals have not yet entered the shallow groundwater system. Indeed, the levels of metals in the well groundwater do not exceed the permissible limits specified by the China Quality Standard for Ground Water and the WHO guideline values for drinking water.

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References

Assadian NW, Esparza LC, Fenn LB, Ali AS, Miyamoto S, Figueroa UV, Warrick AW (1998) Spatial variability of heavy metals in irrigated alfalfa fields in the upper Rio Grande River basin. Agric Water Manage 36(2):141–156

Bhattacharyya P, Tripathy S, Chakrabarti K, Chakraborty A, Banik P (2008) Fractionation and bioavailability of metals and their impacts on microbial properties in sewage irrigated soil. Chemosphere 72:543–550

Chaudri A, McGrath S, Gibbs P (2007) Cadmium availability to wheat grain in soils treated with sewage sludge or metal salts. Chemosphere 66:1415–1423

Flores L, Blas G, Hernández G, Alcalá R (1997) Distribution and sequential extraction of some heavy metals from soils irrigated with wastewater from Mexico City. Water Air Soil Pollut 98(1–2):105–117

Gupta N, Khan DK, Santra SC (2008) An assessment of heavy metal contamination in vegetables grown in wastewater-irrigated areas of Titagarh, West Bengal, India. Bull Environ Contam Toxicol 80:115–118

Khan S, Zheng YM, Huang YZ (2008) Health risks of heavy metals in contaminated soils and food crops irrigated with wastewater in Beijing, China. Environ Pollut 152:686–692

Liu L, Li FS, Xiong DQ, Song CY (2006) Heavy metal contamination and their distribution in different size fractions of the surficial sediment of Haihe River, China. Environ Geol 50:431–438

Liu C, Wang ZY, He Y, Cheng DS (2007) Evaluation of water and sediment qualities at river mouths in the Haihe river system. Int J Sediment Res 22(4):318–326

Meng W, Qin Y, Zheng BH, Zhang L (2008) Heavy metal pollution in Tianjin Bohai Bay, China. J Environ Sci-China 20:814–819

Mohammed MAS, Marwan H, Numan M, Inaya M (2003) Impacts of irrigation with water containing heavy metals on soil and groundwater-a simulation study. Water Air Soil Pollut 146:141–152

Ontario's Ministry of the Environment (2004) Soil, Ground Water and Sediment Standards. Queen's Printer for Ontario

Raghunath R, Tripathi RM, Kumar AV, Sathe AP, Khandekar RN, Nambi KSV (1999) Assessment of Pb, Cd, Cu, and Zn exposures of 6 to 10-year-old children in Mumbai. Environ Res 80:215–221

Shi JB, Liang LN, Jiang GB, Jin XL (2005) The speciation and bioavailability of mercury in sediments of Haihe River, China. Environ Int 31:357–365

Shomar BH, Muller G, Yahya A (2005) Geochemical characterization of soil and water from a wastewater treatment plant in Gaza. Soil Sediment Contam 14(4):309–327

Singh M, Müller G, Singh IB (2002) Heavy metals in freshly deposited stream sediments of rivers associated with urbanisation of the Ganga Plain, India. Water Air Soil Pollut 141:35–54

Streets DG, Hao JM, Wu Y, Jiang JK, Chan M, Tian HZ, Feng XB (2005) Anthropogenic mercury emissions in China. Atmos Environ 39:7789–7806

Tianjin Environmental Protection Bureau (1996) Environmental quality report of Tianjin. Tianjin Environmental Protection Bureau, Tianjin, China

Tijani MN (2008) Contamination of shallow groundwater system and soil-plant transfer of trace metals under amended irrigated fields. Agric Water Manage 96(3):437–444

Usman ARA, Kuzyakov Y, Stahr K (2005) Effect of immobilizing substances and salinity on heavy metals availability to wheat grown on sewage sludge-contaminated soil. Soil Sediment Contam 14(4):329–344

Wang XL, Sato T, Xing BS, Tao S (2005) Health risks of heavy metals to the general public in Tianjin, China via consumption of vegetables and fish. Sci Total Environ 350:28–37