Risk assessment of heavy metals in soil previously irrigated with industrial wastewater in Shenyang, China

Peijun Li [a], Xin Wang [a,*], Graeme Allinson [b], Xiaojun Li [a], Xianzhe Xiong [a]

[a] Institute of Applied Ecology, Chinese Academy of Sciences, PO Box 417, Shenyang 110016, China
[b] Environmental Health and Chemistry, Future Farming Systems Research, Department Primary Industries, PO Box 114, Queenscliff, Vic. 3225, Australia

ARTICLE INFO

ABSTRACT

The Zhangshi Irrigation Area (ZIA) in Shenyang, China has been irrigated by industrial wastewater since 1962. Since then, parts of the ZIA have been rezoned for industrial uses, but the remaining area, named Sluice Gate III (SLIII) and Lower Reaches (LR), still occupies 1825 ha. Although land irrigation with industrial wastewater ceased in 1992, a study on heavy metals in soils was carried out to assess the feasibility of agricultural crop cultivation in SLIII and LR. A detailed field investigation was conducted and both total heavy metal concentrations and bioavailable fraction in soil were determined.

The results have highlighted that Cd concentrations in soils still exceed the Environmental Quality Standard for Soil in China (GB15618-1995) grade C standard in SLIII region, and grade B standard in LR. In the SLIII, Zn and Pb concentrations in soil are higher than the grade A standard, although Cu is close the grade A standard. In SLIII the dominant chemical fractions were the exchangeable and carbonatic forms, which represent up to 43% and 35% of the Cd, respectively. The Cd in these two fractionations poses the highest risk for the plant absorption and accumulation. Therefore the SLIII should be abandoned for cultivated crops to prevent the Cd contamination of food chain and any associated hazards to human health.

1. Introduction

Land irrigation with wastewater has a long history in agricultural areas in China. In China, although the wastewater treatment capacity is 35.785×10^6 t/day, only 40% of total wastewater discharged is treated [1], and some of un-treated wastewater from industries and communities is used for land irrigation. Although wastewater irrigation may increase the agricultural production and farmers' incomes, many contaminants in municipal and industrial wastewater are sequestered in the soils and consequently pose environmental problems. Heavy metals in wastewater are one of the main causes of soil contamination in China [2,3]. Chen et al. reported that 45% of wastewater irrigation areas in China are contaminated with heavy metal at the most serious level [4]. Cadmium and lead are the elements most seriously contaminating Chinese soils, with up to 13,000 ha of arable land in 25 regions in 11 provinces polluted by Cd, and the quantity of Cd-contaminated rice reaching 50 million kg in 1999 [4,5].

Heavy metal contamination of soils through wastewater irrigation is a widespread and serious problem in many countries, for example, in Germany, France and India [6–8]. The contaminants may transfer into the food chain, in particularly if the contaminants are sequestered in bioavailable forms. Many crops accumulate heavy metals and result in an inexorable rise in the metal content of a farm's production [9,10]. Food chain translocation of heavy metals is one of the consequences of soils polluted with such elements, and excessive intake of heavy metals is associated with human health problems, e.g. itai–itai disease (caused by excess Cd) and Minamata disease (excess Hg).

The total amount of heavy metals in a soil can be used to quickly assess the condition of a soil through comparison with regulatory guideline values. However, increasingly the bioavailable fraction of heavy metals in soil is deemed essential for risk assessment purposes. Heavy metal mobility and availability in soils is frequently studied with sequential extraction procedures, which allow partitioning the total metal content into different fractionations. For instance, the Tessier method and Testing Programme of the European Commission (formally BCR method) are widely used for sequential extraction to assess metal partitioning in contaminated soils and to predict their environmental risks [11–15].

In Zhangshi Irrigation Area (hereafter abbreviated to ZIA), the wastewater originates from the industrial districts of Shenyang, and is produced from many industries, including the Shenyang Smelter that produces zinc, lead and a small amount of gold. Land irrigation with wastewater in ZIA commenced in 1962 [16]. At that time in China an emphasis was placed on increasing production of food

* Corresponding author. Tel.: +86 24 8397 0367; fax: +86 24 8397 0300.
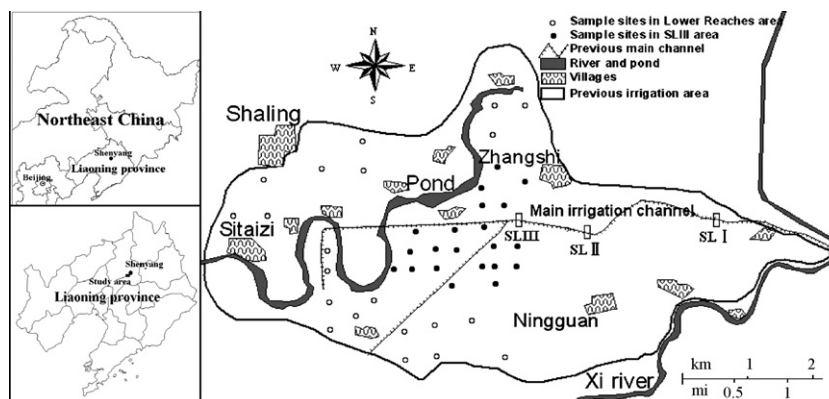E-mail address: wangxin@iae.ac.cn (X. Wang).

Fig. 1. Location of Zhangshi Irrigation Area and soil sampling sites. *Note*: SL I, SL II and SL III for Sluice Gate I, Sluice Gate II and Sluice Gate III, respectively.

crops, and consequently many dry-land agricultural regions were converted to paddy farms and wastewater used for irrigation. The wastewater discharged from factories, including the wastewater supplied to ZIA, was largely untreated and contained high levels of heavy metals and other pollutants.

Based on a number of previous studies related to ZIA [16,17] which narrated the historical perspective and temporal variation in heavy metals in soils across the whole ZIA. The local government decided parts of ZIA (Sluice Gate I and Sluice Gate II areas) were to be used for industrial construction, rather than agriculture. The remaining area, named Sluice Gate III (SLIII) and Lower Reaches (LR), still occupies 1825 ha, and although land irrigation with wastewater has not been practiced for 14 years (having ceased in 1992), the utilization of the land in SLIII and LR is still of concern to governmental authorities and local farmers. Consequently, as part of a National Basic Research Program of China (973 Project) entitled "Forming mechanism of environmental pollution and ecological remediation of contaminated environment in old industrial base in northeastern China" (2004–2009), the aim of the project is to study the consistency of temporal change of metal concentrations in soil and assess the feasibility of agricultural crop cultivation in the SLIII and LR areas. Following risk assessment incorporating aspects of remediation technology [18–22], the management and remediation options for the ZIA were suggested.

2. Materials and methods

2.1. Terrain investigation and sampling

The ZIR is located in the western suburbs of Shenyang (Long. 122°25′–123°48′E and Lat. 41°12′–42°17′N) shown in Fig. 1. Shenyang in northeastern China is the capital city of Liaoning

Province, and its boundaries encompass a total area of 8515 km², and a population of some 6 million. Shenyang is a major communication hub and trade centre in northeast China. It is also one of China's major steel, metal-fabricating and machinery-manufacturing centres.

The field sites of the study were established in the 1825 ha of the Sluice Gate III and Lower Reaches areas of the ZIA, and control area was established outside of ZIA for comparison. In total, 42 points were investigated, 21 sites in the SLIII area, and another 21 points in the LR area shown in Fig. 1. In addition, soil samples were collected at nine points in a control area that was located outside of ZIA. The control area was irrigated with fresh water and the soil type is the same as the soil in the ZIA.

The soils were sampled at two layers: 0–20 cm and 20–40 cm. Approximately, 10 kg of soil (thoroughly mixed) was collected from each layer at each point, and then air-dried for about 10 days in laboratory. The samples were then sieved. Clay aggregates were powdered to assist their passage through the nylon sieve. Soil materials that passed through a 2 mm (10-mesh/in.) sieve was used for chemical fraction analyses, and that which passed through 100-mesh/in. was digested to determine total amount concentration of heavy metals.

The type of soil in ZIA is a meadow brown soil [23] and its texture classification is loam. The characteristics in soil profile analyzed in the soil are shown in Table 1.

2.2. Method of chemical analyses

Sample pretreatment and basic chemical analyses were conducted according to the routine analytical methods of agricultural chemistry in soil [24]. In this study the concentration of Cd within six chemical fractions of the 0–20 cm depth soils was determined

Table 1
Soil characteristics in Zhangshi Irrigation Area (ZIA)

Depth (m)	Particle size (%)[a]				pH[b]	OC (%)[c]	CEC (cmol kg^{-1})[d]				
	CS	FS	Silt	Clay			Ca^{+2}	Mg^{+2}	Na^{+1}	K^{+1}	Total
0.0–0.1	21.6	33.2	36.0	9.2	6.00	1.84	11.9	3.7	0.3	0.6	16.5
0.1–0.2	27.3	31.3	27.6	13.8	6.19	1.52	11.0	3.5	0.3	0.7	15.5
0.2–0.3	32.0	30.4	21.2	16.4	6.26	1.07	10.5	3.2	0.3	0.5	14.5
0.3–0.4	27.8	29.7	25.4	17.1	6.31	1.11	9.1	3.1	0.4	0.3	12.9
0.4–0.5	36.8	31.2	15.6	16.4	6.28	0.92	8.7	3.5	0.2	0.5	12.9
0.5–0.6	38.9	26.4	17.9	16.8	6.35	0.89	8.1	3.9	0.2	0.4	12.6
0.6–0.7	37.6	25.6	18.8	18.0	6.38	0.71	6.9	5.3	0.2	0.3	12.7

[a] Hydrometer methods: CS, coarse sand (0.2–2.0 mm); FS, fine sand (0.02–0.2 mm); silt (0.002–0.02 mm); clay (<0.002 mm).

[b] Water:soil = 2.5:1.

[c] Organic carbon.

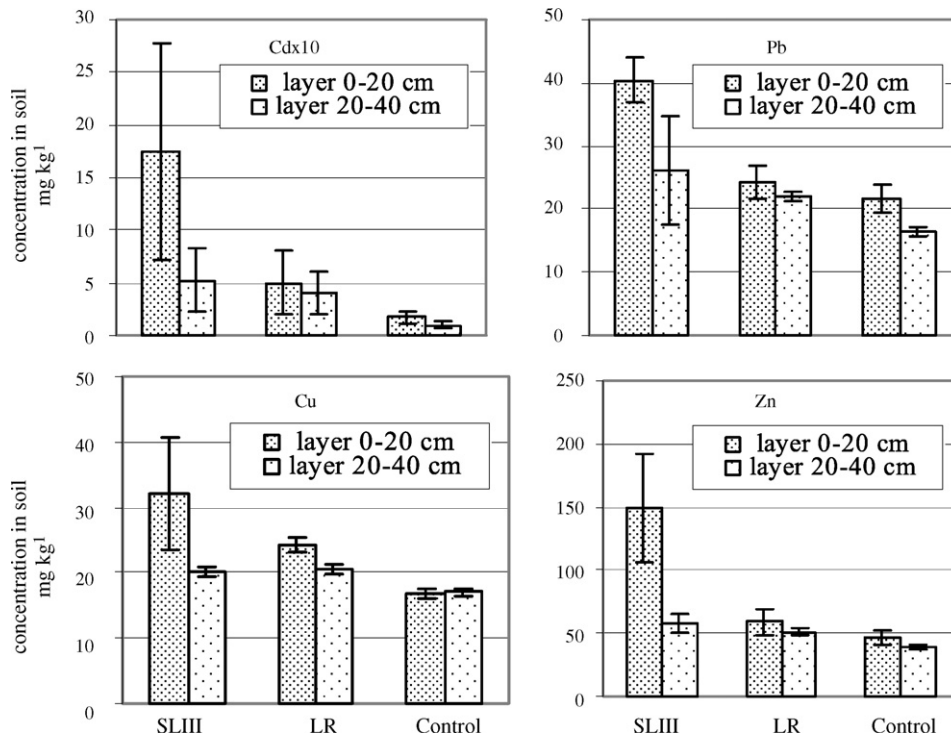[d] Method: 1 M NH$_4$ acetate extractable cations with prewash.

Fig. 2. The concentration of Cd, Pb, Cu and Zn in SLIII, LR and control area. *Note*: Cd concentration in Fig. 1 is multiplied by 10 in order it can be clearer appeared in the figure.

using a sequential extraction method firstly proposed by Tessier et al. [25], with some minor modifications. Specifically, the procedure to determine the six different fractions of Cd is (I) *Exchangeable fraction*: to 2 g soil, add 40 ml of 1 M ammonium acetate, shake for 2 h, then centrifuge. Determine metal concentration in supernatant liquid, and use the residue in the next step. (II) *Carbonatic fraction*: add 40 ml of 1 M sodium acetate to the residue from step (I), adjusted with acetic acid to pH 5. Shake for 5 h, then centrifuge, and determine metal concentration in supernatant liquid. Use the residue in the next step. (III) *Reducible fraction A* (*e.g. Mn-oxides*): add 50-ml of 0.1 M hydroxylamine hydrochloride, adjusted to pH 2 with nitric acid. Shake for 12 h, then centrifuge. Determine metal concentration in supernatant liquid; use the residue in the next step. (IV) *Reducible fraction B* (*e.g. Fe-oxides*): add 50-ml of 0.2 M ammonium oxalate, adjusted to pH 3 with oxalic acid. Shake for 24 h, then centrifuge. Determine metal concentration in supernatant solution; use the residue in the next step. (V) *Organic fraction and sulfides*: add 5 ml of 30% hydrogen peroxide firstly, adjusted to pH 2 with nitric acid, and heat the mixture in a water bath at 85 °C, then add hydrogen peroxide for another three times to complete the reaction (i.e. until no further bubbling). Then extract the mixture with 20 ml of 1 M ammonium acetate, shake for 2 h, then centrifuge. Determine metal concentration in supernatant liquid, use the residue in the last step. (VI) *Residual fraction*: digest with 14 ml of a mixture of 3:1 (HCl: HNO$_3$) in a glass vessel. After complete digestion, add 20 ml water, filter, and dilute the filtrate to 50 ml for analysis.

2.3. Equipment and analytical accuracy

Metal concentrations were determined using an Hitachi 180-80 atomic adsorption spectrophotometer (AAS). A Certified Reference Material (CRM) (Code GBW 08303 for contaminated arable soil, EPA, China) was used to check analytical accuracy and precision. Analyses of CRM digests found that elemental recoveries ranged from 88% to 107% (Table 2). The high recoveries are essential and prerequisite for this study.

3. Results and discussion

3.1. Heavy metal concentrations of soils in ZIA

Cd, Pb, Cu and Zn concentrations of soil in SLIII, LR and control area are shown in Fig. 2. The mean Cd concentration in the 0–20 cm soil layer in SLIII is 1.75 mg kg^{-1} (n = 21; range 0.42–3.93 mg kg^{-1}). The mean Pb, Cu and Zn concentrations in the 0–20 cm soil layer in SLIII are 40.46 mg kg^{-1}, 32.15 mg kg^{-1} and 150.10 mg kg^{-1}, respectively. The mean Cd, Pb, Cu and Zn concentrations in the 0–20 cm soil of control area are only 0.10 mg kg^{-1}, 21.60 mg kg^{-1}, 16.88 mg kg^{-1} and 46.46 mg kg^{-1}, respectively.

A comparison of these results with archival data suggests the Cd concentration in the 0–20 cm soil layer in SLIII has declined somewhat since cessation of land irrigation with wastewater. For instance, in the same area in 1990 (2 years before the irrigation with wastewater ceased in 1992), the Cd concentrations ranged from 0.75 mg kg^{-1} to 4.47 mg kg^{-1} [16], i.e. both the update lowest concentration (0.42 mg kg^{-1}) and highest concentration (3.93 mg kg^{-1}) are lower than those of corresponding 1990 data. This is broadly consistent with [26], who reported that half-life of Cd in the soil could be anything from 15 to 1100 years depending on soil characteristics and other related environmental conditions, i.e. Cd concentrations are expected to decline, but only very slowly.

Table 2
The results of Certified Reference Material (CRM) for checking the analytical accuracy (Code GBW 08303 for contaminated arable soil)[a]

Element	Certified value (mg kg^{-1})	Observed value (mg kg^{-1})	Recovery (%)
Cd	1.20 ± 0.07	1.08–1.26	90–105
Cu	120 ± 6	114–124.8	95–104
Pb	73 ± 2	64.2–77.4	88–106
Zn	187 ± 9	166.43–200.09	89–107

[a] The standard of "Certified Reference Material" was provided by EPA, China for checking the analytical accuracy.
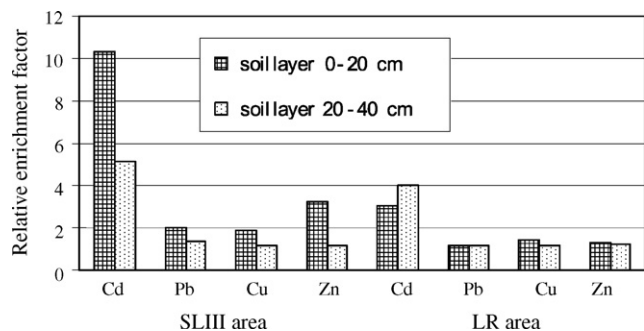
Fig. 3. Relative enrichment factors of Cd, Pb, Cu and Zn in SLIII and LR areas comparing with control area (background values of Cd, Pb, Cu and Zn were shown in Fig. 2).

The concentration of soil in control area was used as a background for comparison for the soils at SLIII and LR in ZIA. In general, the highest increase in concentration (wastewater irrigation area compared with control area) was seen for Cd, followed by Zn. For instance, the Cd concentration in the area of SLIII is some 10-fold higher than comparable background values, and 5-fold higher in the 20–40 cm, as shown in Fig. 3. Cd concentrations in the soils in LR area are some 3-fold higher than control soils in the 0–20 cm soils, and 4-fold higher in the 20–40 cm layer, respectively. Similar, but lower, enhancement of concentration was seen for Cu, Pb, and Zn in SLIII and LR areas, as shown in Fig. 3, i.e. for the most part the increase in elemental concentration was at or below 2-fold, with the exception of zinc in SLIII (∼3-fold).

3.2. Assessment of heavy metal concentrations in soil

The Environmental Quality Standard for Soil in China (GB15618-1995) is a national standard, which is divided into three grades (A, B and C) for different types of soil utilization, as shown in Table 3.

The average Cd concentration in the 0–20 cm soil layer in SLIII ($1.75\,\text{mg}\,\text{kg}^{-1}$) is higher than the grade C standard ($1.0\,\text{mg}\,\text{kg}^{-1}$), and in the 20–40 cm soil layer ($0.51\,\text{mg}\,\text{kg}^{-1}$) higher than the grade B standard ($0.3\,\text{mg}\,\text{kg}^{-1}$ in farmland, vegetable, tea, fruit and grazing lands, for the soil at pH < 6.5). The average Cd concentration in the 0–20 cm soil layer in LR area ($0.52\,\text{mg}\,\text{kg}^{-1}$) is higher than the grade B standard ($0.3\,\text{mg}\,\text{kg}^{-1}$, for the soil at pH < 6.5). Indeed, the Cd concentration in the 0–20 cm layer in the SLIII ($1.75\,\text{mg}\,\text{kg}^{-1}$) even exceeded the grade C standard ($1.0\,\text{mg}\,\text{kg}^{-1}$, in forestry land and the land with higher absorption capacity). Similarly, the Pb and Zn concentrations in the 0–20 cm soil layer at SLIII ($40.46\,\text{mg}\,\text{kg}^{-1}$ and $150.01\,\text{mg}\,\text{kg}^{-1}$, respectively) are higher than their corresponding grade A standards ($35\,\text{mg}\,\text{kg}^{-1}$ and $100\,\text{mg}\,\text{kg}^{-1}$, respectively).

The Cu concentration ($32.15\,\text{mg}\,\text{kg}^{-1}$) in soil layer 0–20 cm is close the grade A standard ($35\,\text{mg}\,\text{kg}^{-1}$). Given the 10- and 3-fold increase in Cd concentration in the SLIII and LR areas, respectively (cf. background levels of the soil in control area), it is thus clear that the limiting factor for agricultural uses in the irrigation areas previously using industrial wastewater is the Cd concentration in the soil. Consequently, the total area of SLIII and part of the LR area will have to be abandoned as farmland, grazing lands or vegetable, tea, fruit producing areas if the standard B (for the soil at pH < 6.5) shown in Table 3 is applied.

3.3. Vertical distribution and migration

The exogenous heavy metals in SLIII and LR areas and migration rates from layer 0–20 cm to 20–40 cm are shown in Table 4. In Table 4 the exogenous of heavy metal is calculated by subtracting the background concentrations in control area from that the heavy metal concentrations in SLIII and LR areas, respectively.

Since irrigation with wastewater began in 1962, the concentrations of exogenous heavy metals in soil layers 0–20 cm and 20–40 cm have increased. Most of exogenous heavy metals have accumulated in the upper 0–20 cm soil layer, although some exogenous metals have migrated to the lower 20–40 cm layer. The migration rates of the different metals for which data is available are quite different, and there are differences between the two zones discussed in this study, i.e. in general the migration rates in the LR area are higher than the SLIII area, although the total amount of exogenous material transported may be lower. For instance, the vertical migration rate of Cd from layer 0–20 cm to 20–40 cm in the LR region (46.15%) is higher than in SLIII (20.60%), although the exogenous concentration of Cd is higher in the SLIII soils ($0.41\,\text{mg}\,\text{kg}^{-1}$) than in the LR soils ($0.30\,\text{mg}\,\text{kg}^{-1}$).

3.4. Bioavailability of Cd in Sluice Gate III and Lower Reaches area

The proportions of Cd in the six chemical fractions at the 0–20 cm layer of SLIII and control soils are shown in Fig. 4. In SLIII the dominant fractions are the exchangeable (I) and carbonatic (II) fractions, which represent up to 43% and 35% of the total Cd in the soil, respectively. The residual fraction (VI) is very low (5%). In contrast, in control area fractions (I) and (II) are very low (5% and 10%, respectively), but the residual fractions (VI) and (IV) are very high (up to 49% and 21%, respectively).

Although the total amount of heavy metals in a soil is important, and can be used to quickly assess the condition of a soil through comparison with regulatory guideline values, increasingly the bioavailable fraction of heavy metals in soil is deemed essential for risk assessment purposes. Environmental conditions are important in determining in which fraction a metal will be found. The
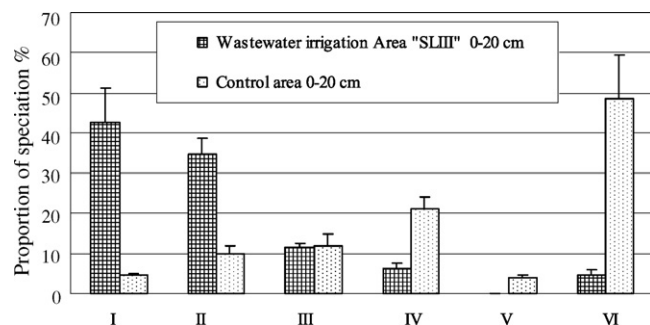
Table 3
Maximum metal concentrations prescribed by the Environmental Quality Standard for Soil in China (GB15618-1995) ($\text{mg}\,\text{kg}^{-1}$)

Metal	Soil grade				
	A[a]	B[b]			C[c]
		pH < 6.5	pH 6.5–7.5	pH > 7.5	
Cd	0.20	0.30	0.30	0.60	1.0
Cu farm	35	50	100	100	400
Cu Garden	–	150	200	200	400
Pb	35	250	300	350	500
Zn	100	200	250	300	500

[a] Grade A: natural conservation area, drinking water catchments, tea garden. Metals in soil at natural background value.

[b] Grade B: farmland, vegetable land, tea land, fruit land and grazing land.

[c] Grade C: forestry land and the land with higher absorption capacity.

Fig. 4. The proportions of Cd in the six chemical fractions in SLIII and control soil at layer 0–20 cm. *Note*: I–IV are the six species of fractionations of Cd, total concentration of Cd is $1.75\,\text{mg}\,\text{kg}^{-1}$.

Table 4
Exogenous heavy metals contributed by wastewater irrigation

Soil layer (cm)	Sluice Gate III area				LR area			
	Cd	Pb	Cu	Zn	Cd	Pb	Cu	Zn
Exogenous heavy metals in SLIII and LR areas (mg kg^{-1})[a]								
0–20 (I)	1.58	20.16	15.27	103.54	0.35	4.05	7.48	12.34
20–40 (II)	0.41	9.65	3.20	16.73	0.30	3.01	3.44	9.59
I + II	1.99	29.81	18.47	110.27	0.65	7.06	10.92	21.93
Migration rate from layer 0–20 cm to 20–40 cm in SLIII and LR areas (%)								
II/(I + II) %	20.60	32.37	17.32	15.17	46.15	42.64	31.50	43.73

[a] Exogenous of heavy metal is calculated by subtracting the background concentrations in control area from that the heavy metal concentrations in SLIII and LR areas, respectively.

most significant factors controlling metal fractionation at a particular point in space and time include pH, the composition and amount of organic matter in the soil, clay mineral content, the presence and form of Fe/Mn/Al oxides and hydroxides, redox potential, concentration of salts and complexing agents, and anion and cation content of soil [27,28]. In SLIII, the soil (layer 0–40 cm) pH ranges from 6.0 to 6.31, and is considered the most important factor to control the fraction of Cd in soil. The large differences in the proportion of the bioavailable Cd fraction between the SLIII and control areas, as shown in Fig. 4, have definitely been caused by long-term (30 years: 1962–1992) irrigation with wastewater. The exchangeable fraction of Cd is correlated significantly with plant available Cd ($r = 0.735$, $p = 0.01$) [29]. With more than 40% of the Cd in the exchangeable fraction at the SLIII soil, it is clear that in the area once treated with industrial wastewater there is an excess of Cd at levels high enough for absorption and accumulation from the soil matrix into plant tissues.

4. Conclusion

From an historical perspective ZIA provided a short-term agricultural and economic success in terms of increased product and farmers' income, but long-term land irrigation with untreated wastewater has now proven to be the cause of significant soil contamination. The Sluice Gate III and Lower Reaches are the only remaining areas of ZIA and although irrigation with wastewater ceased 14 years ago, the Cd concentration in soil at SLIII area is higher than prescribed by China's grade C standard, and higher than the grade B standard in the LR area. The Zn and Pb concentrations at SLIII area are higher than grade A standard; the Cu concentration in soil is close the grade A standard. In the SLIII the dominant fractions of Cd in six fractionations are the forms of exchangeable (I) and carbonatic fraction (II), which represent up to 43% and 35% of the total amount of Cd, respectively.

The study results reiterated that the persistence and intractability of metals are the most obvious and significant characteristics of soils contaminated by heavy metals. The study also clearly indicated that the SLIII area should be abandoned for cultivated crops to prevent the contamination of food chain and any associated hazards to human health. On the bases of risk assessment, other feasible land uses include hydroponic cultivation of vegetables in greenhouses and/or growing turf for lawns used city landscaping. Alternatively, bioremediation utilizing host super-accumulation plants in a symbiotic relationship with mycorrhizal fungi could also be trialed.

Acknowledgements

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