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Metal Contamination of Soils in the Shenyang Zhangshi Irrigation Area

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Land disposal of urban waste water was not formally implemented by cities until about one hundred years ago. Essentially, land disposal involves channeling the waste water to open fields, over which it is then dispersed. The method offers opportunities for water quality maintenance, and also for crop and pasture irrigation. The oldest sites, together with younger but more intensively used sites, have accumulated measurable amounts of heavy metals since waste water distribution began, and this is reflected in the content of crops and animals raised on the land-disposal farm soils. Ideally, land disposal works best if the fields do not have a dormant growth season, but this is evidently not a severe constraint because in one of the most long-standing land-disposal sewerage farms in China, the Shenyang-Zhangshi in Liaoning Province, plants are dormant during the winter months. In the dormant season, the waste water is discharged directly into the Xi River, thus the heavy metals in soil of Shenyang Zhangshi Irrigation Area (SZIA) and in sediments of Xi River are derived from the same source.

The human health impacts of pollution of soils by metals are primarily related to bioaccumulation of the metals into food items. A number of diseases are caused by metals, including *itai-itai* disease resulting from over-consumption of Cd. In 1974, the Institute of Applied Ecology, Chinese Academy of Sciences, began monitoring the Cd content of the rice in the SZIA, and found Cd concentrations of rice up to 2.6 mg kg^{-1}. Sequential extraction of heavy metals in the SZIA soils was used to assess metal bioavailability. In the arable soils of western Shenyang, where the SZIA is located, the ratio of available (0.1 M HCl extractable) to total Cd is 68.57 % , Cu 31.48%, and Pb 29.73%. This is higher than southern and eastern areas of Shenyang (Yanai J. et al. 1998), and other wastewater irrigation areas in China (Wu, et al.1986).

Public health and environmental concerns have emerged concurrently with improvement in techniques for measurement and monitoring contamination. In this context, the time is now appropriate for managers of the SZIA to draw up maps of soil metal contamination to facilitate best-practice management of the irrigation

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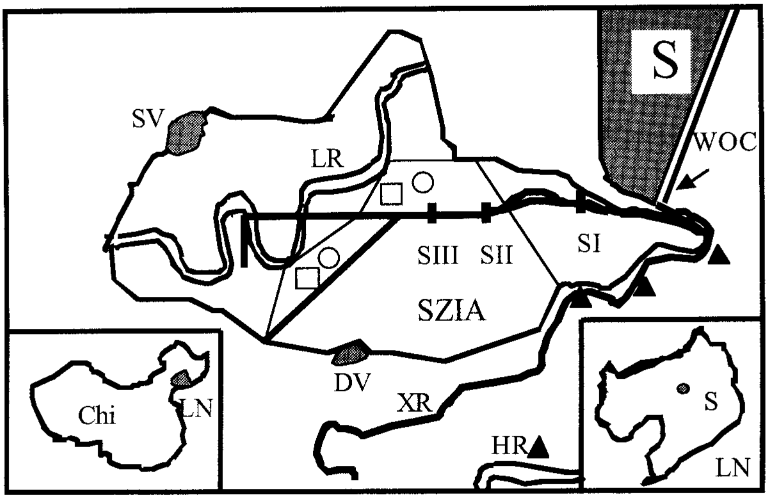

Figure 1. The location of Shenyang Zhangshi Irrigation Area (SZIA), Liaoning province, China. Figure legend: LN, Lioaning Province; S, Shenyang city; XR, Xi River; HR, Hun River. Sample locations: rice paddy O ; dryland □; sediments ▲; SI, Sluice gate I; S II, Sluice gate II; S III, Sluice gate III; LR,the area of lower reaches; SV, Sha Ling village; DV, De Sheng village.

zones. Herein, we report the results of further sequential extraction of SZIA soils designed to explore the characteristics of pollution in SZIA that may affect the transfer and accumulation of metals from soil into rice grain. It is with the search for the patterns of soil contamination that may be used for land use scenario modeling in other cities that this study is involved, and to that end, we compare metal bioavailability in SZIA soils with that of contaminated and clean river sediments.

MATERIALS AND METHODS

Shenyang, the capital city of Liaoning province ((Figure 1; pop. 5,650,000), is situated in the transition area from the Changbai Mountains to the alluvial plain of the Liao River. Shenyang is one of China s principal metal-fabricating and machinery centres. As part of the city s waste water disposal strategy, the 2720 ha Shenyang Zhangshi Irrigation Area (SZIA) was set established in 1962. The upper reaches of the SZIA (330 ha) are irrigated through sluice gate **I** (SL1) with water heavily polluted with Cd (mean Cd, 8.8 $\mu g\ L^{-1}$ (1990)). SL2 and SL3 water 1130 ha with somewhat less Cd contaminated water (mean Cd, 5.5 and 4.9 $\mu g\ L^{-1}$, respectively). Contamination by Cd is comparatively light in the lower reaches of the SZIA, eg around De Sheng village and Sha Ling village. The 1260 ha of this zone, receive water with total Cd in the range1-2 $\mu g\ L^{-1}$.

Two samples were collected from rice paddies, and two from dryland soils irrigated with water from SIII (RP1&2), and a further pair of soil samples from dryland (DL1 & 2). Three sediment samples were collected from Yu Tai Village, Fu Guan Bridge, Gan Guan Bridge on the Xi River (Xi 1-3), and one from Hou Mo Village on the Hun River (Hun 1). The Hun River is considered "clean" and was used as a reference water body. Elemental concentrations were detemined using an Hitach 180-80 Atomic Absorption Spectrophotometer. A certified reference material, GBW 08303 Contaminated Arable Soil (Monitoring Center of Environmental Protection, Beijing, China) was used to check method recoveries and analytical acuracy. Cd, Cu and Pb fractions were extracted using the procedure of Tessier et al (1979) in the following manner:

I. Exchangeable fraction: to 2 g soil or sediment, add 40 ml of 1 M ammonium acetate, shake for 2 hours, then centrifuge. Determine concentrations of Cd, Cu and Pb in supernatent liquid, use the residue in the next step.

II. Carbonatic fraction: add 40 ml of 1 M sodium acetate, adjusted with acetic acid to pH 5. Shake for 5 hours, then centrifuge, and determine concentrations of Cd, Cu and Pb in supernatent 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 hours, then centrifuge. Determine concentrations of Cd, Cu and Pb in supernatent 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 hours, then centrifuge. Determine concentrations of Cd, Cu and Pb in supernatent solution, use the residue in the next step.

V. Organic fraction and sulfides: add 5 ml of 30% hydrogen peroxide, adjusted to pH 2 with nitric acid, and heat the mixture in a waterbath at 85^0 C until the reaction stops (no more bubbles will produced). Add more H_2O_2 until no further reaction is observed. Then extract the mixture with 20 ml of 1 M ammonium acetate, shake for 2 hours, then centrifuge. Determine concentrations of Cd, Cu and Pb in supernatent solution, use the residue in the last step.

VI. Residual fraction: digestion with 14 ml of a mixture of 3:1 HCl : HNO_3 in glass vessel. After complete digestion, add 20 ml water, filter, and dilute the filtrate to 50 ml for analysis.

RESULTS AND DISCUSSION

Analysis of the certified reference material found the certified elements to be within 12 % of expected values (88-106% recovery, Table 1).

Table 1. Summary of concentrations of CRM, and concentrations determined Values quoted on a dry weight basis.

Element	CRM (Contaminated Arable Soil) Certified value	Observed value	Recovery (%)
	(mg kg^{-1})		
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

Table 2. Summary of soil characteristics

Depth (cm)	pH	Org C (%)	CEC cmol kg^{-1} Ca^{2+}	Mg^{2+}	H^+	Total
4-9	6.00	1.84	11.90	3.65	0.012	15.55
20-30	6.26	1.07	10.47	3.23	0.012	13.70
40-50	6.28	0.92	8.69	3.54	0.012	12.23
60-70	6.38		6.89	5.28	0.012	12.17

Table 3. Summary of sediment characteristics

Sample No.	Organic matter (%)	pH (1:10 water)	Cd (mg kg^{-1})	Total reduced S (mg g^{-1})
Xi 1	14.13	7.44	52.32	7.35
Xi 2	12.24	7.76	29.57	6.49
Xi 3	9.27	7.64	35.79	6.52
Hun 4	1.59	5.70	2.41	<0.04

The basic physical and chemical properties of the soil and sediments are shown in Tables 2 and 3. The soil is classified as meadow burozem. The concentration and proportion of Cd, Cu, and Pb in the six fractions are presented in Tables 4 and 5. Values quoted are the mean of three determinations. The Cd, Cu, and Pb concentration in most of the soils collected were higher than the Chinese Standard (Grade B in GB15618-1995, Table 5). Most of Cd in the soils was found in the exchangeable (I) and carbanotic metal (II) fractions (rice paddy, 48% and 40%; dryland soil, 44% and 40%, respectively). For Cu, the dominant fractions were the carbanotic (II) and Reducible b (IV) fractions (rice paddy 42% and 41%; dryland 36% and 46%, respectively). For Pb, fractions II and IV were again the dominant fraction (rice paddy 59% and 23%; dryland 51% and 26%). Krishnamrti and Naidu (2000) have shown that exchangeable forms of Cd are significantly correlated with plant available Cd. That the exchangeable forms of Cd are found in the SZIA soils in much higher proportions than Cu and Pb, suggests that Cd will be the more mobile of these elements in these soils, with greater risk of leaching, and more available to crops (McLaughlin et al 2000).

Table 4 Summary of Cd, Cu and Pb concentrations in SZAI soils (mg.kg^{-1} in each fraction).

Sample	Metal Fraction						
	I	II	III	IV	V	VI	sum
				Cd			
RP 1	1.11	0.73	0.19	0.05	0.00	0.02	2.00
RP 2	0.86	0.81	0.14	0.04	0.00	0.02	1.87
UL 1	0.52	0.42	0.11	0.06	0.00	0.03	1.14
UL 2	0.38	0.37	0.08	0.04	0.00	0.03	0.89
				Cu			
RP 1	10.42	74.30	7.10	89.78	4.15	15.48	201.21
RP 2	17.18	93.26	3.83	72.15	3.19	9.25	198.86
UL 1	5.52	42.36	2.48	60.03	2.35	13.45	126.18
UL 2	4.48	40.24	1.88	45.23	1.88	11.23	104.93
				Pb			
RP 1	68	303	23.0	126	0.08	23.0	543
RP 2	47	369	20.0	134	0.36	31.0	601
UL 1	76	258	12.0	105	0.00	26.0	477
UL 2	28	117	8.0	73	0.00	22.0	249

Table 5. Environmental quality standard for soil in China (GB15618-1995; metal concentrations, mg kg^{-1})

Metal	Soil Grade				
	A	B			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
Garden	-	150	200	200	400
Pb	35	250	300	350	500

Grade A: natural conservation area, drinking water catchment, tea garden. Metals in soil at natural background value.

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

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

The Xi River sediments contained high levels of Cd, Cu and Pb, suggesting that the river was polluted by sewage discharged from western part of Shenyang to such an extent that the control criterion for pollutants in agricultural sludges must have been exceeded (UDC 628.191:628.336 GB4284-84; Chen and Xiong 2000).

Table 6. Summary of Cd, Cu and Pb concentrations in Xi and Hun river sediments (mg kg^{-1}).

Sample	Metal Fraction						
	I	II	III	IV	V	VI	sum
				Cd			
Xi 1	0.12	0.35	0.19	0.06	22.76	18.85	42.33
Xi 2	0.62	10.06	4.78	2.20	4.75	10.90	33.31
Xi 3	0.12	7.96	3.23	1.55	4.94	17.98	35.78
Hun 1	0.07	0.37	0.09	0.05	0.03	0.11	0.72
				Cu			
Xi 1	0.24	0.05	0.63	0.15	420.49	121.58	543.13
Xi 2	0.47	3.86	0.12	82.78	343.81	109.23	540.26
Xi 3	0.21	0.19	0.41	66.73	347.50	64.28	479.32
Hun 1	0.00	1.59	0.00	7.00	5.13	5.93	19.64
				Pb			
Xi 1	5.56	110	4.0	30	21	169	340
Xi 2	21.0	682	23.0	67	59	391	1243
Xi 3	41.0	1628	56.0	108	299	1403	3536
Hun 1	0.28	11.0	0.0	7.0	0.00	5.0	24

The sediment of Hun River was not contaminated. Because the physico-chemical charateristics of the sediments are different to those of the soils, most of the Cd and Cu in the Xi river sediments was found in stable, strongly adsorbed forms (sum fractions IV, V, VI >70%), although the Pb was divided equally between the carbanotic and residual fractions (~40% each fraction). However, the sediment in Xi river should not be used for agricultural purposes, because the total metal content is too high, and weathering may cause these metals to become more available to crops.

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REFERENCES

Tao C, Xiong X (2000) Sludge disposal of wastewater treatment plant is an important subject in environmental science. Chinese J Ecol 19:54-57.

Krishnamrti GSR, Naidu R (2000) Speciation and phytoavailability of cadmium in selected surfice soils of South Australia. Australian J Soil Res 38:991-1004.

McLaughlin MJ, Hamon RE, McLaren RG, Speir TW, Rogers SL (2000) Review: A bioavailability-based rationale for controlling metal and metalloid

contamination of agricultural land in Australia and New Zealand. Australian J Soil Res 38:1037-86.
Oliver MA (1997) Soil and human health - A review. European J Soil Res 48: 573-592.
Tessier A., Campbell WG, Baisson M (1979) Sequential extraction procedure for the speciation of particulate trace metals. Anal Chem 51:844-850.
Wu Y, Chen T, Zhang X (1986) Pollution ecology of Cd in the Zhangshi Irrigation Area of Shenyang. edited by Gao Zhenmin Studies on Pollution of soil-plant systems China Science and Technology Press, Beijing, China.
Yanai J, Yabutani M, Kang YM, Huang B, Luo GB, Kosaki T (1998) Heavy metal pollution of agricultural soils and sediments in Liaoning Province, China. Soil Sci Plant Nut 44:367-375.