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Cadmium Contamination of Soils of the Shenyang Zhangshi Irrigation Area, China: An Historical Perspective

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Land disposal of sewage is implemented by dispersing liquid wastes over fields. The method reduces pathogens and other non-conservative contaminants in the waste water by micro-biological processing in the soils. The degree to which water quality is improved depends on the suitability of the soils and on their management. However, many contaminants of municipal and industrial waste water are sequestered in the soils of such land disposal "sewerage farms." From the soil, metal contaminants may find their way, directly or indirectly, into the human food chain. For instance, if metals are sequestered in the soil in bio-available form, phyto-accumulation by crops will see an inexorable rise in metal contents of farm produce. The soils of many land disposal sites have accumulated disturbing 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 (Xiong et al 2001). Concurrently, surrounding land has often become industrialised or urbanized, and public health and environmental concerns have emerged as techniques for measurement and monitoring contamination have improved and become more widely available, thereby constraining the scope for deploying "pollute and move on" tactics. In this context, managers of land disposal sewerage farms are increasingly having to draw up maps of soil metal contamination to facilitate best-practice management of the irrigation zones. From this perspective, herein we discuss the historical patterns of cadmium contamination of soils in the Shenyang Zhangshi Irrigation Area in Liaoning Province of China.

MATERIALS AND METHODS

The Shenyang Zhangshi Irrigation Area (SZIA, Figure 1) is located in the western suburbs of Shenyang (122°25′ - 123°48′ E, 41°12′ - 42°17′ N). High concentrations of Cd in rice grains (2.6 mg/kg) were first discovered in the SZIA in the autumn of 1974. Since that time, there have been several further investigations into the Cd concentrations of soil and rice, and some human health surveys. However, the information and data produced by these studies is very scattered. Therefore, the data set used herein was assembled using (a) archival data from the period 1975-1996, and (b) terrain investigation, sampling and sample analyses. In 2000, soils in the SLIII and Lower Reaches zones of the SZIA were collected at two depths: layer A, 0-20cm; layer B, 20-40 cm, respectively. The concentrations of Cd, Pb, Cu and Zn were determined using an Hitach 180-80 Atomic Absorption Spectrophotometer. A certified reference material (GBW 08303 Contaminated Arable Soil, Bureau of Chinese Standardization, Beijing, China) was used to check method recoveries and analytical accuracy.

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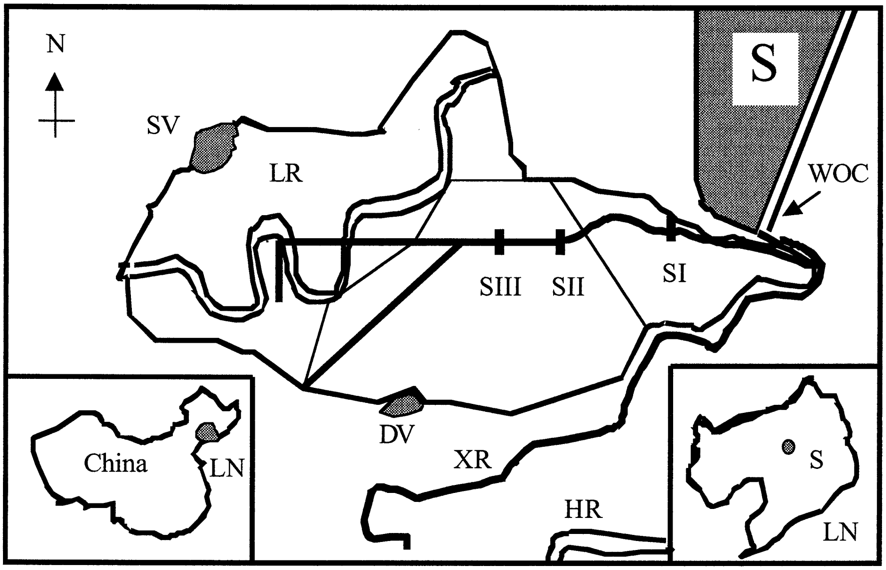

Figure 1. The location of Shenyang Zhangshi Irrigation Area (SZIA), in Liaoning province, China. Figure legend: LN, Lioaning Province; S, Shenyang city; XR, Xi River; HR, Hun River. SI, S II, S III, area served by Sluice gates I, II and III, respectively; LR,the Lower Reaches of the irrigation district; SV, Sha Ling village; DV, De Sheng village.

RESULTS AND DISCUSSION

The Zhangshi Irrigation channel receives sewerage flows from the Weigong Open Channel, with some dilution by Xi River water. The irrigation effluent flows through the head of channel, then through three sluice gates (SL I, SL II, SL III) and then the Lower Reaches (LR) in succession (Figure 1). The soils in SZIA can be classified as meadow burozems. These loamy soils are acidic and typically low in organic matter. For instance, topsoil (4-9 cm) is pH 6, with 1.8% organic carbon, and a CEC of 15.55 cmol/kg (Ca^{2+}, 11.9, Mg^{2+}, 3.65, H^{+}, 0.012 cmol/kg, respectively).

In 1975, the average Cd concentration in the Weigong Open Channel was 235 µg/L. The Shenyang Smelter was the main Cd source, contributing up to 84 kg/d of Cd. Since 1979, technological improvements to the Shenyang Smelter have seen the Cd concentration reduced to less than 10 µg/L. This latter concentration still exceeds Chinese water quality standards for irrigation water (5 µg/L Cd. GB 5084-92, enacted 1992). Analysis of the Cd concentration in channels providing irrigation water for SL I, SL II and SL III between 1986 and 1990 (Table 1). suggests that more of the irrigation waters exceeded the water quality standard in 1990 than 1986. This is not the result of tighter standards in China, because the 1990 and 1986 standards are same, 5 µg/L Cd in irrigation water (GB 5084-85, 1984-1991; GB 5084-92 from 1992).

Table 1. Mean Cd concentration in irrigation water (μg/L) in different zones of SZIA. Figures in parentheses indicate percentage (%) exceeding standard for Cd concentration in irrigation water in China (5 μg/ L Cd. GB 5084-85, 1984 – 1991, and GB 5084-92, post-1992).

Year	Head of Channel	SL I	SL II	SL III
1986	3.99 (27)	3.54 (20)	3.50 (20)	4.29 (27)
1987	8.31 (47)	10.96 (60)	9.70 (40)	4.92 (33)
1988	16.90 (73)	12.30 (73)	14.03 (80)	9.32 (70)
1989	10.27 (73)	11.93 (87)	8.13 (60)	7.00 (40)
1990	8.47 (53)	8.80 (80)	5.47 (53)	4.93 (47)

Cadmium concentrations in paddy soil in the SZIA have been monitored since 1975 (Table 2). Historically, the highest Cd concentrations were found in paddy soils and rice in the area irrigated through SLI, with concentrations decreasing through SLII, SLIII to the Lower Reaches. That said, the fields of the lower reaches have had Cd contents higher than those found in the control area, where irrigation water is not drawn from the sewerage system. Because of the heavy Cd pollution, the area served by SLI was re-zoned from agriculture to industry in 1986. From 1986 to 1990, Cd concentrations in paddy soil and rice grain (Table 3) were higher in the areas irrigated through SLII than those irrigated through SLIII. In that period (Yu 1991) the proportion of samples contaminated with less than 1 mg/kg Cd in paddy soil at SL II is lower than at SL III for every year of monitoring. In addition, the proportion of rice contaminated with more than 1 mg/kg Cd at SL II is higher, and the proportion contaminated with less than 0.4 mg/kg Cd is also lower than at SL III, for every year monitored. This confirms a prediction based on water quality data that the zone irrigated through SL II was more heavily contaminated with Cd than the area of SL III. Ultimately, the consequence of this was a decision to cease irrigation of wastewater on this zone in 1992.

The SZIA is located in Yu Hong District. A comparison with non-irrigated zones in the same district highlights the more than ten-fold increase in Cd contamination in the area served by SL III. For instance, in the Su Jia Tun, Dong Ling and Xin Cheng Zi boroughs of Yu Hong District, background concentrations of Cd are 0.155, 0.155, and 0.157 mg/kg, respectively (Wu 1994) *cf.* 1.12-2.75 mg/kg in SLIII soils. The Environmental Quality Standard for Soil in China for farmland, horticultural land, tea plantation soil, orchards and grazing land stipulates maximum concentrations of 0.3 and 0.6 mg/kg Cd at soil pH<7.5, and soil pH > 7.5, respectively (GB15618-1995). The Cd concentration at SLIII exceeds these soil standards, even though no sewage has been irrigated onto this land for 8 years. The current status is that the soils are not suitable for cultivation of crops. Cd pollution may still persist in the soil, but the current concentration of three other priority metals, Pb, Cu and Zn, meet the standard in the areas of SL III and LR (Table 4).

During the period 1977-1985, rice grown in Sha Ling Village (Lower Reaches) contained an average of 0.08 mg/kg Cd, equating to a daily intake of 33 μg of Cd for local people, or about 47% of the maximum tolerable intake recommended by WHO (1973) of 70 μg Cd per day (He 1999). Rice grown in the zones served by SLI, SLII, and SLIII contained approximately 17, 5 and 3 times the amount of Cd as Sha Ling village rice, and consumption of this grain would have provided

Table 2. Cd concentrations in paddy soils of the SZIA and control areas in the period of 1975-2000 (mg/kg) [The area served by SLI was re-zoned from agriculture to industry in 1986. Therefore, in 1986-1990 the samples were collected only in SLII and SLIII. In 1992, irrigation with sewage waste water ceased in SLII. Therefore, in 1996 samples were taken only in SL III, LR and outside the SZIA; and soil samples in 2000 at SLIII and LR].

Year	SZIA Area				Control Area	Ref.
	SL I	SL II	SL III	LR		
1975	0.75 - 9.25	1.04 - 3.08		0.70 - 1.20	0.13-1.00	Wu 1986
1977-1985	4.52 - 7.75	3.17 - 7.06	2.2 - 6.09	0.49 - 3.33 [d] 0.80 - 2.32 [s]		Wu 1986
1986		0.17 - 5.27	0.05 - 6.60			Yu 1991
1987		0.85 - 6.50	0.20 - 5.55			Yu 1991
1988		1.05 - 5.35	0.50 - 5.15			Yu 1991
1989		1.38 - 7.58	0.65 - 9.00			Yu 1991
1990		0.70 - 6.24	0.75 - 4.47			Yu 1991
1996			2.10 - 4.35	0.25 - 2.43	0.28-0.30	[e]
2000			1.12 - 2.75 [a] 0.14 - 0.80 [b]	0.47-0.66 [a] 0.41-0.53 [b]		This study

a = top-soil, 0-20 cm depth; b= sub-soil, 20-40 cm depth; d = at De Sheng village; s = at Sha Ling village; e = data found by X.X. in an internal report at the Shenyang Central Station of Environmental Monitoring; Zhu YF, Report on Cadmium pollution in soils at Sluice Gate III of Shenyang Zhangshi Irrigation Area (written 8th April 1996, in Chinese, internal publication only).

Table 3. Cd concentrations in rice grain from the SZIA and control areas in the period of 1975-1990 (mg/kg) [The area served by SLI was re-zoned from agriculture to industry in 1986. Therefore, in 1986-1990 the samples were collected in SLII and SLIII only].

Year	SZIA Area				Control Area	Ref.
	SL I	SL II	SL III	LR		
1975	0.79– 2.2	0.20 - 0.76		0.01-0.35	0.01-0.27	Wu 1986
1977-1985	0.53 - 2.34	0.20 - 0.52	0.06 - 0.36	0.04 - 0.42 [d] 0.04 - 0.20 [s]		Wu 1986
1986		0.04 - 1.65	0.08 - 1.26			Yu 1991
1987		0.22 - 2.49	0.02 - 1.82			Yu 1991
1988		0.42 - 3.56	0.22 - 2.54			Yu 1991
1989		0.17 - 2.96	0.06 - 2.67			Yu 1991
1990		0.44 - 3.87	0.03 - 2.46			Yu 1991

d = at De Sheng village; s = at Sha Ling village.

Table 4. Cu, Pb and Zn concentrations (mg/kg) in SL III and LR soils in 2000.

Location	Metal	Soil Depth			
		0 - 20 cm		20 — 40 cm	
		Mean	Range	Mean	Range
SLIII	Cu	34.73	24.81-45.56	23.71	23.16-24.62
	Pb	45.46	28.89 - 55.18	25.05	13.66 - 31.88
	Zn	147.25	60.49 - 244.53	58.87	49.14 - 63.42
LR	Cu	21.01	20.04 - 22.15	19.42	18.68 - 20.00
	Pb	26.35	24.43 - 29.37	24.04	23.49 - 24.92
	Zn	58.81	57.47 - 59.68	52.84	50.97 - 55.88

proportionately more of consumers daily Cd intake. Wu et al (1986) reported that the urine of humans living in the SZIA contained Cd concentrations in the range 0.07 - 89.54 μg/L in 1978, and 0.05 - 32.0 μg/L in 1978 and 1979. These were statistically significantly different to those of a reference site population (urine Cd concentrations in range 0 - 2.05 μg/L in 1978, and 0.01 - 2.6 μg/L in 1979, respectively). These concentrations are also higher than those found in many other countries (0.5-1.0 μg/L; He, 1999). Wu et al (1986) reported that in 1980 the Cd concentration in human blood was 1.06 μg/L in SZIA, compared with 0.42 μg/L in a reference area. In 1980, Cd concentrations in hair were 0.14 and 0.07 mg/kg for SZIA and reference area, respectively (Wu et al 1986). These concentrations were not as high as in threee contaminated villages of Hubei Province (0.18 - 0.34 mg/kg, respectively. Lin et al, 1999). However, Cd concentrations in hair may not a reliable biomarker of either exposure or body burden, since external contamination of the hair can not be distinguished from the endogenous Cd.

Wu et al (1986) reported that pigs in the ZSIA are often fed rice chaff, which in the SZIA may well contain high Cd concentrations. Cadmium concentrations in pig meat and liver of one-year old (100-125 kg) pigs in the ZSIA are in the range 0.08 - 0.09, and 0.40 - 4.20 mg/kg, respectively (Wu et al 1986). These levels are statistically significantly higher than those found in pigs in the control area (meat, 0.01 - 0.10; liver, 0.06 - 0.39 mg/kg, respectively).

From an historical perspective, the SZIA may have been an agricultural success in terms of increased product and farmer incomes, but not an ecological or social one. All soils have their own metal assimilative capacity below which the soil retains its normal ecological function (Xiong 1997). Therefore, an essential prerequisite for the application of contaminated wastewater onto land, either for irrigation or to use the soils for purification itself (land treatment), is to follow an assimilative capacity model. Unfortunately, when wastewater irrigation in the SZIA commenced, proponents of the scheme were not aware of the importance of assimilative capacity of heavy metals in soil, and did not follow such a model. Thus, Cd was transported via the irrigation channel, accumulated in paddy soil and rice grain, and migrated through the food chain to humans. Once the soils are polluted with metals, severe environmental and social problems can arise from the survival and intractability of metals in soils. If soils are contaminated, the simplest solution may be to choose a land use that fits the site's condition, rather than adjust the site's conditions to suit a particularly sensitive re-use. In the SZIA, retirement of the most severely affected agricultural land has been the main method used to keep heavy metals out of the food chain. Much of the land has been re-zoned for industrial use. This has allowed investment by foreign countries, especially Japan, Korea, United States and European countries, in industries near a labour force that has been swelled by retired farmers. Re-zoning has a secondary impact, in that the local food chain is less contaminated and the scope for a public health problem greatly reduced.

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