

Heavy Metal Contamination in a Soil-Rice Ecosystem in the Vicinity of Abandoned Rural Unsanitary Landfill

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The ecosystem adjacent to the abandoned rural unsanitary landfill has been contaminated. The soil cadmium was higher than the maximum allowable content of agricultural soil. There was a remarkable bioaccumulation trend of heavy metals in the rice organs. Chromium and lead contents in rice grain were much higher than the threshold levels, 2.9-6.7 folds and 1.0-1.5 folds of the legislation limits, respectively. Linear correlation analysis showed that the slightly alkaline leachate from the unsanitary landfill was one of the main factors causing the higher soil pH and then affecting the absorption of rice on the cadmium.

Key Words: Rural unsanitary landfill, Heavy metals, Soil, Rice, Leachate.

INTRODUCTION

Rural waste is combined solid waste in rural residents' daily life. After 1990, the components of rural waste changed remarkably as well, parts of hazardous and industrial wastes were commingled into these sites due to the rapid development of township enterprises and the lack of effective administration. Rural waste is no longer to be one favorable agricultural fertilizer. Because of the giant imbalance between the shrinking resource utilization approach and the increasing production of the rural waste, large amounts of rural waste accumulated in the countryside. It is estimated that there were over one hundred million tons of rural waste which were abandoned in rural areas of China each year (http://www.china.com.cn/zhibo/2008-02/18/content_10048366.htm). In such conditions, almost each village constructed one or two unsanitary landfills to dispose these rural wastes. After 2000s, those sites were replaced with the standardized municipal landfills, and were gradually closed and abandoned. However, our field investigation proved that the unsanitary landfills still discharged the contaminants, especially leachate to the environment continuously.

Usually, the heavy metal contamination seems not to be one important issue owing to the low metal contents in leachates for most of the sanitary landfills¹. The other reason was that the trace metals in leachates were strongly reduced through adsorption and precipitation process under the anaerobic

condition of the sanitary landfills². However, because there were lack of the necessary decontamination facilities for the unsanitary landfills, especially the bottom and lateral linear³ and the unsanitary landfills were widely spread in rural areas of China⁴. Moreover, it was found that some of the landfills were surrounded by farmland, especially the paddy field. Since Zn and Cd in the solid waste mostly was found in reducible form and was more susceptible to be leached⁵. When the surface water was used as the irrigation water of the farmland, it was possible that the metals may be accumulated in the human body through the food chain after part of the metals was adsorbed by the soil⁶, then the agricultural ecosystem was under the threatening of metal contamination.

Rice is one of the dominant agricultural crops in China and in the world and the elevated rice metals may cause many debilitating diseases through the bioaccumulation effect of rice⁷. Whereas, to our best of knowledge, there were little data available and few research reports about the contamination report of abandoned rural waste unsanitary landfills in China so far. The main aim of this work is (1) to understand the potential metal contamination in a soil-rice ecosystem in the vicinity of abandoned rural unsanitary landfill; (2) to determine the soil factors influencing the metal bioavailability in a soil-rice system. This research would be helpful to provide useful information to agricultural management and environmental management for the abandoned rural unsanitary landfill.

EXPERIMENTAL

Description of study area: Gaoqiao unsanitary landfill was one abandoned rural waste located in Qishan village, Ningbo city. The site was constructed in 1990s and closed in 2005 and mainly assumed the responsibility of disposing the farmers' daily waste. Its daily waste input, service population, land area and accumulated waste volume of the unsanitary landfill were 50 ton/day, 135000 people, 7500 m² and 52500 m³, respectively.

Ningbo is located in the middle part of the coastline in southeast China (latitude of 28°51' E~30°33' N) and is a classical subtropical monsoon climate region with an average annual precipitation of 1500 mm⁸. The city has a population of 6.9 million in 2007 and the rural land accounts for 74.9 % of the total area in the region.

Sampling: During the period of maturity for rice (at the end of September, 2008), four pairs of rice (*Oryza sativa* L.) and soil samples with same location were collected in a distance of 0-120 m to the unsanitary landfill (Fig. 1). The reference (CK) of soil and rice were sampled in the paddy field far from the unsanitary landfill. Each sample was the composite of 3 sub-samples within a distance of 0.5 m surrounding a specific sampling location. The rice samples included root, stem and leaf and rice grain. Soil samples, from 0-20 cm in depth, were collected at each sampling point and mixed thoroughly to get a representative sample of 1.5-2.0 kg.

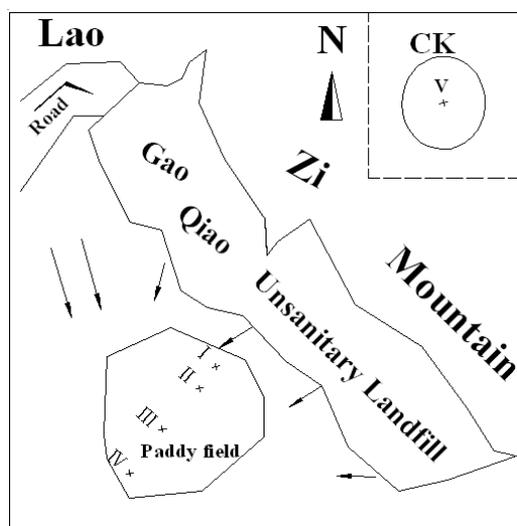


Fig. 1. Rural uncontrolled landfill in Gaoqiao. Note: X, sampling point of rice and soil. Arrow indicates the flow direction of the leachate

Sampling preparation and analysis: The soil samples were air dried in shady and cool conditions until a constant weight was reached. Then the soil samples were passed a 1 mm mesh sieve and the ≤ 1 mm fraction was collected. By quartering each soil sample, ca. 50-100 g samples were ground with a wood bar and sieved with 0.15 mm mesh to collect fine particles (< 0.15 mm). The prepared soil and rice samples were sealed in polyethylene bags and stored at 4 °C for further analyses. The total nitrogen, NH₄-N, total phosphorus and organic matter (OM) of the soil and solid waste were measured using standard procedures⁹. For heavy metal analysis of soil, 0.25 g soil was digested with 4 mL HNO₃, 1 mL HF and 1 mL

HClO₄ under sealed Teflon tank for 10 h. The metal analysis of rice was conducted as following: the fresh rice was washed in tap water and rinsed with deionized water, then dried at 80 °C for 24 h, grounded with agate mortar, digested with HNO₃:H₂SO₄:HClO₄ (8 mL:1 mL:1 mL) under sealed Teflon tank. The Heavy metals of soil and rice were measured using ICP-MS (Agilent 7500a). All the analyzed results were expressed on a dry weight basis.

Assessment method of soil contamination: Geoaccumulation index (I_{geo}) was calculated to assess the degree of heavy metal pollution in soil surrounding the unsanitary landfills. I_{geo} was calculated by the following equation: $I_{geo} = \log_2 [C_n/1.5B_n]$, where C_n represents the measured concentration of the metal n and B_n is the background values of the soils^{10,11}. The background soil was collected from the paddy field far away (over 500 m) from the Gaoqiao landfill and its background values were used as the reference values.

Data analysis: Student's *t*-test (comparison analysis of paired values) was used to compare the soil pH in the vicinity of landfill with that of CK. Pearson correlation was used to measure the correlation between the observations. Data analysis and figure plot were carried out by using SPSS 14 and Origin 8, respectively.

RESULTS AND DISCUSSION

Metal contents in soils and rice: Fig. 2A illustrates the contamination of soils surrounding the unsanitary landfill. The results show the metal contents of soil were in the order of Zn > Pb > Cr > Cu > Cd and their average values were 118.92 ± 33.62 , 45.64 ± 11.85 , 33.28 ± 4.90 , 24.14 ± 2.69 , 1.45 ± 0.59 mg/kg, respectively and they were 1.6, 1.9, 4.8, 1.5 and 1.6-folds of CK. The average metal contents of soils were much higher than that of CK, implying the obvious anthropogenic effect. The coefficient variation (CV) of the five metals were 14.7, 11.1, 41.0, 28.3 and 26.0 %, respectively and the metal CVs did not show a great variability, indicating that the distribution of the trace metal in the sampling region were evenly. Compared with maximum allowable concentrations (MAC) (GB 15618-1995) of metals in agricultural soils in China, soil Cd contents were 2.29 ± 0.37 , 0.72 ± 0.15 , 1.55 ± 0.12 and 1.08 ± 0.37 mg/kg at sampling points I, II, III and IV, respectively and were higher than maximum allowable concentration value. Soil Zn, Pb, Cu and Cr contents were all below the maximum allowable concentration levels.

The metal contents in rice root, rice stem-leaf and rice grain were given in Fig. 2B-2D. The metal contents of rice were ranked in the order of root > stem-leaf > grain. Chromium contents in rice root, rice stem-leaf and rice grain were 26.6, 8.7 and 4.0 mg/kg, respectively and the CVs of corresponding rice organs were 68.6, 34.9 and 47.3 %; Cu contents in root, stem-leaf and grain were 40.1, 7.4 and 5.5 mg/kg and the CVs of corresponding rice organs were 38.8, 17.8 and 8.7 %; Zn contents in root, stem-leaf and grain were 84.5, 34.5 and 25.9 mg/kg and the corresponding CVs were 27.4, 28.4 and 3.3 %; Cd contents in root, stem-leaf and grain were 1.33, 0.12 and 0.03 mg/kg and the corresponding CVs were 25.3, 30.0 and 53.6 %; Pb contents in root, stem-leaf and grain were 14.1, 1.2 and 0.2 mg/kg, with the corresponding CVs, 31.6, 45.3 and 17.3 %, respectively.

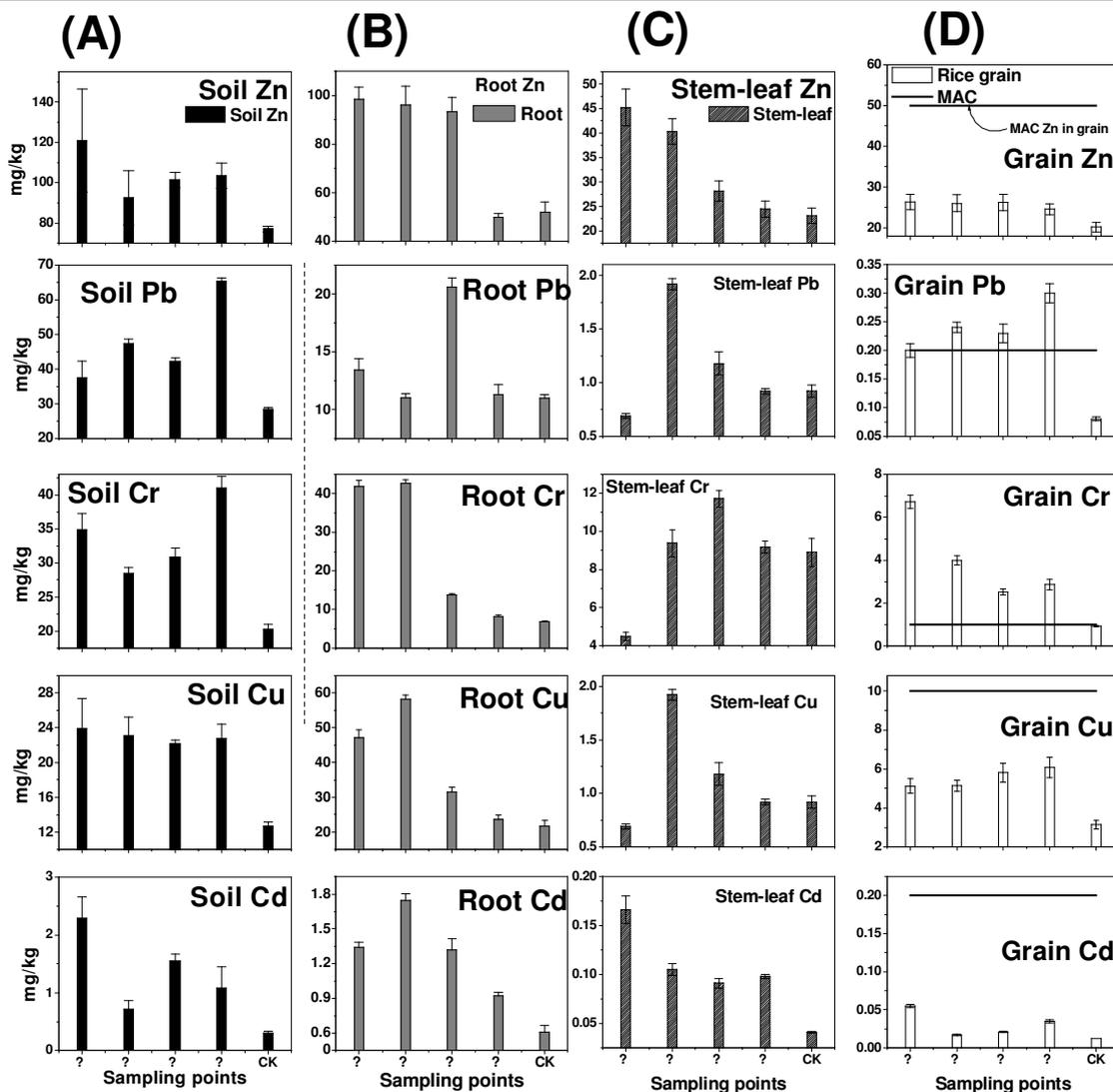


Fig. 2. Heavy metal contents in soil and rice surrounding the abandoned rural unsanitary landfill in Gaoqiao (A: soil; B: rice root; C: rice stem-leaf; D: rice grain). Note: maximum allowable concentration of soil Zn, Pb, Cr, Cu and Cd were 200, 250, 250, 50 and 0.3 mg/kg, respectively (GB 15618-1995) and the corresponding threshold values in rice grain were 50, 0.2, 1, 10 and 0.2 mg/kg, respectively (GB 2762-2005)

Contamination assessment of soil and rice: To describe the overall metal contents of soil and rice (including root, stem-leaf and grain) surrounding the unsanitary landfill, the arithmetic metal contents in different sampling points from the unsanitary landfill (Table-1) were used as the mean values. As shown in Table-1, the higher Igeo of Cd indicates that the soil was moderately polluted with Cd and were unpolluted-moderately with Pb, Cr and Cu and the soil was not contaminated with Zn overall.

Fig. 2 shows that the average contents of rice root, stem-leaf and grain were evidently higher than that of CK, implying

that there was clear metal accumulation trend in rice organs. The result means that the rice was very possibly contaminated with metals within the sampling region. To quantify the contamination degree, the grain metal contents were compared with the food thresholds (maximum allowable concentration) of rice. Here, the Cr and Pb contents in rice grain were much higher than the thresholds (especially Cr) and their mean values were 2.9-6.7 folds and 1.0-1.5 folds of the thresholds, respectively (1.0 mg/kg for Cr and 0.2 mg/kg for Pb, GB 2762-2005), while the Cr and Pb content of rice CK was 0.92 and 0.08 mg/kg, respectively, below the maximum allowable concentration

TABLE-1
HEAVY METALS IN SOIL IN THE VICINITY OF GAOQIAO UNSANITARY LANDFILL

	Zn (mg/kg)	Pb (mg/kg)	Cr (mg/kg)	Cu (mg/kg)	Cd (mg/kg)
Average ± SD	104.6 ± 11.8	48.1 ± 12.1	33.8 ± 5.5	23.0 ± 0.7	1.4 ± 0.7
Range	92.6-120.9	37.5-65.3	28.4-41.0	22.1-23.9	0.7-2.3
Reference	77.1	28.4	20.23	12.69	0.3
Igeo*	-0.15	0.14	0.14	0.27	1.52
Soil MAC (GB 15618-1995)	200	250	250	50	0.3

*Igeo has no unit.

level. The rice was the main staple in the southeast China (including Ningbo). Therefore, the long-term consumption of the rice with metal contamination could bear risk of heavy metal exposure to the consumers.

Factors affecting the metal accumulation in soil-rice ecosystem near the unsanitary landfill: Cadmium migration was active in soil-rice ecosystem and it was assumed that Cd was more susceptible to be released into the food chain and poses a potential threat to the human body¹². The soil was moderately polluted with Cd. However, there was one noteworthy phenomenon, *i.e.*, in rice grain Cd was much lower than the thresholds.

In the normal Cd addition experiment, the bioavailability of soil Cd was relatively high, since the Cd chemicals added were in the form of Cd(NO₃)₂ or CdCl₂, *etc.* However, in our research, the leachate should be one of the main processes to transport Cd into soil. The soil pH and soil Cd were affected by the landfill condition and then affected the rice Cd content. The linear correlation analysis could be help to explain the question, which was listed on Table-2. Table-2 shows that the stem-leaf Cd was correlated with grain Cd and soil pH and grain Cd content was significantly ($p < 0.05$) correlated with soil Cd. Soil pH generally was consider to have the significant effect on the rice grain^{6,13} and it was consistent with the result of Table-2.

TABLE-2
PEARSON CORRELATION COEFFICIENTS BETWEEN
Cd CONTENTS IN DIFFERENT RICE ORGANS WITH
SOIL pH AND SOIL Cd CONTENTS (n = 5)

	Soil pH	Soil Cd
Root Cd	0.244	0.614
Stem-leaf Cd	0.776	0.895*
Grain Cd	0.953**	0.857*
Soil Cd	0.711	–

*,**Denote significant level at $p < 0.05$ and 0.01 , respectively.

The soil pH in the vicinity of Gaoqiao landfill increased to 5.5-6.6, while the average pH of soil CK was 5.0. The result of a one-sample *t*-test shows that they had significant difference ($t = 3.119$, $p = 0.026$) and suggests that the unsanitary landfill contributed noticeable effect on the soil pH. The leachate entered the surface soil continuously under the precipitation and raised the soil pH due to the slightly alkaline characteristic of leachate (pH between 7.3 and 8.3). On the other side, the soil organic mater, total nitrogen, total phosphorus and metal contents in the vicinity of Gaoqiao landfill increased gradually and were evidently higher than that of soil CK (Fig. 2), because the leachate contained a certain amount of organic matter, nutrients and trace elements and a part of these materials were adsorbed by the soil in the process of leachate flowing. Therefore, this resulted in the two interrelated factors affecting the

metal uptake of rice: the higher soil pH would be helpful to increase the Cd absorption of rice, but the Cd uptake of rice would be hampered for the Cd bioavailability of rice would be lowered under higher soil pH¹⁴. In addition, the higher soil Zn and P would be reduce the uptake of rice Cd¹³.

Conclusion

The soil-rice ecosystem adjacent to the abandoned rural unsanitary landfill had been contaminated. The soil Cd was higher than the maximum allowable content of agricultural soil. Geoaccumulation index values of soil Cd suggests that the soil was moderately polluted with Cd, while the soils were unpolluted-moderately overall by Cr, Cu as well as Pb. There was a remarkable bioaccumulation trend of heavy metals in the rice organs (rice root, stem-leaf and grain). The Cr and Pb contents in rice grain were, 2.9-6.7 folds and 1.0-1.5 folds of the threshold levels, , respectively and much higher than the legislation limits. The slightly alkaline leachate from the unsanitary landfill was one of the main factors causing the higher soil pH and then affecting the absorption of rice on the Cd.

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