Postprint: Characteristics of Heavy Metal Contamination in Inter-dam Cultivated Soils of the Liao River Mainstream

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Abstract

Through determination of heavy metal copper, cadmium, zinc, and lead contents in the 0–5 cm, 5–15 cm, and 15–30 cm sediment layers of cultivated soil at 10 cross-sections between dams in the Liao River main stream, the degree of soil heavy metal pollution in this area was evaluated, and the geoaccumulation index method was employed to assess the pollution status of individual heavy metals and the potential ecological risk index, providing a comprehensive evaluation of the degree of heavy metal ecological hazard. The results indicate that the mean contents of copper, lead, zinc, and cadmium in the soil of this area are 32.42 mg · kg ^{1}, 38.23 mg · kg ^{1}, 47.35 mg · kg ^{1}, and 1.625 mg · kg ^{1}, respectively. The mean contents of lead and zinc are highest at Danidukou, being 55.54 mg · kg ^{1} and 80.51 mg · kg ^{1}, respectively; the mean contents of copper and cadmium are highest at Tongjiangkou, being 50.24 mg · kg ^{1} and 3.103 mg · kg ^{1}, respectively. Except for cadmium, the concentrations of lead, copper, and zinc at all cross-sections and different depths are below the National Soil Environmental Quality Standard Grade II; the mean cadmium content is 1.70 times the National Soil Environmental Quality Standard Grade II, with a maximum value of 3.402 mg · kg ^{1}. The cadmium content in the upstream main stream of the Liao River Bridge is 6.47 times that in the downstream. The geoaccumulation index values of cadmium indicate pollution between dams, among which all cross-sections above the Liao River Bridge indicate strong pollution. The potential ecological risk index values for heavy metals are highest from Tongjiangkou to Yubaotai Bridge. The contribution of cadmium to the potential ecological risk index values for multiple metals at each cross-section reaches 78.77%~98.23%, and the contribution rate is positively correlated with the potential ecological risk index (RI). The variation trend of the potential ecological risk index values for multiple heavy metals is consistent with the distribution trend of the cadmium

geoaccumulation index, with the maximum value appearing at the Tongjiangkou cross-section.

Full Text

Preamble

Characteristics of Soil Heavy Metal Pollution in Cultivated Land in Zones Between Ipsilateral Dams of the Liaohe River

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Abstract: This study investigated heavy metal (copper, cadmium, zinc, and lead) concentrations in cultivated soils at depths of 0-5 cm, 5-15 cm, and 15-30 cm across ten sections in the zones between ipsilateral dams of the Liaohe River main stream. The degree of soil heavy metal pollution was evaluated using the geoaccumulation index method to assess single-metal contamination status and potential ecological risk index to comprehensively evaluate the ecological hazard level. Results showed that average concentrations of Cu, Pb, Zn, and Cd were 32.42 mg · kg ^{1}, 38.23 mg · kg ^{1}, 47.35 mg · kg ^{1}, and 1.625 mg · kg ^{1}, respectively. The highest mean concentrations of Pb and Zn occurred at Daniu Ferry (55.54 mg · kg ^{1} and 80.51 mg · kg ^{1}), while Cu and Cd peaked at Tongjiangkou (50.24 mg · kg ^{1} and 3.103 mg · kg ^{1}). Except for Cd, mean concentrations of Pb, Cu, and Zn at all sections and depths were below the Grade II National Soil Environmental Quality Standard. The mean Cd concentration was 1.70 times the Grade II standard, with a maximum value of 3.402 mg · kg ^{1}. Cadmium content upstream of the Liaohe Bridge was 6.47 times that downstream. Geoaccumulation index values indicated Cd pollution throughout the dam zones, with strong pollution (exceeding Grade V) occurring primarily upstream of the Liaohe Bridge. The potential ecological risk index was highest between Tongjiangkou and Yubaotai Grand Bridge. Cadmium contributed 78.77%-98.23% to the multi-metal potential ecological risk index, with contribution rates positively correlated with the risk index. The spatial pattern of multi-metal potential ecological risk index mirrored that of the Cd geoaccumulation index, with maximum values observed at Tongjiangkou.

Keywords: Heavy metal pollution; Zone between ipsilateral dams of Liaohe River; Cultivated soil; Geoaccumulation index; Potential ecological risk index

The zone between dams refers to the area between inner and outer embankments in large rivers, constituting part of the riparian zone, typically several hundred meters wide. Its primary function is secondary buffering, directing river flow along established channels while protecting surrounding residents and farmland. During flood seasons, river water entering these zones carries substantial sediment rich in nutrients and pollutants. Heavy metals are major components of watershed contaminants, and their distribution in watershed soils reflects environmental health status. Analysis of soil heavy metal content is essential for evaluating watershed soil environmental quality [1]. As heavy metal loading increases, the proportion of exchangeable metals in soil rises while residual fractions decline, enhancing bioavailability and environmental threat, ultimately entering the human body through the food chain and causing disease [2]. Currently, research on heavy metal pollution in river dam zones and soil safety in the Liaohe main stream remains scarce. However, studies of the Liaohe River system have shown that pollutant deposition exceeds both Liaoning provincial background values and national soil quality standards (Grade II) [3-4]. Investigations of heavy metals in residents' hair also indicate significantly elevated levels near certain river sections compared to rural averages [5].

Field surveys reveal that zones between dams along the Liaohe main stream are commonly cultivated by local residents, who express considerable concern about river contamination and potential health impacts. Historical incidents in Japan (Minamata and Itai-itai diseases) demonstrated diseases caused by heavy metal accumulation through food chains. Therefore, investigation and assessment of soils in these cultivated dam zones are necessary. This study collected soils at 0–5 cm, 5–15 cm, and 15–30 cm depths to measure Pb, Zn, Cu, and Cd concentrations, evaluating pollution levels to reveal agricultural safety in Liaohe main stream dam zones.

1.1 Sampling Time and Locations

The study area encompassed the Liaohe River main stream from the confluence of East and West Liaohe Rivers at Fudedian, Changtu County, Liaoning Province, to the river mouth, spanning approximately 516 km [3]. Sampling sites from upstream to downstream included: upstream—Fudedian (A), Tongjiangkou (B), Zhu' ershan (C), Mahushan Bridge (D), and Yubaotai Grand Bridge (E); midstream—Daniu Ferry (F) and Zhanghuangdi Liaohe Bridge (G); downstream—Panjin Lengdong Bridge (H), Shuguang Bridge (I), and Zhaoquanhe Estuary (J). The landscape from Fudedian (A) to Liaohe Bridge (G) consisted of uncultivated cornfields, while from Lengdong Bridge (H) to the estuary (J) comprised uncultivated rice paddies. All sampling points were georeferenced using GPS. A total of 30 soil sample sets were collected in May 2011, with specific locations shown in [Figure 1: see original paper].

1.2 Sample Collection and Pretreatment

Soil samples were collected using a five-point composite method. Samples were taken at different depths using a shovel, mixing five subsamples from the same depth before quartering to 3–5 kg and placing in sample bags. Samples were air-dried at room temperature, ground, and passed through a 2 mm nylon sieve for analysis. Heavy metal analysis employed HNO -HClO -HF tri-acid digestion [6].

1.3 Sample Measurement and Data Processing

Copper, cadmium, zinc, and lead concentrations were determined using a flame atomic absorption spectrophotometer (Beijing Purkinje General TAS-990). Liaoning provincial soil background values [7] and Liaohe River system sediment averages [8] served as references for interpreting contamination status. The Grade II soil standard from the National Soil Environmental Quality Standard GB 15618-1995 [9] was used to evaluate whether concentrations exceeded limits for normal crop growth and human health protection. Single-sample t-tests and rank correlation analysis among Cu, Cd, Zn, and Pb were performed using SPSS 18.0, with Origin 7.0 software used for graphical presentation.

1.4 Evaluation Methods

This study employed the geoaccumulation index method (Igeo) [10] to assess single heavy metal pollution status and the potential ecological risk index (RI) method [11] to evaluate ecological hazards to cultivated soils in dam zones.

2.1 Heavy Metal Pollution Degree in Liaohe Dam Zones

As shown in , mean concentrations of Cu, Pb, and Zn in Liaohe dam zone cultivated soils were 32.42 mg · kg ^{1}, 38.23 mg · kg ^{1}, and 47.35 mg · kg ^{1}, respectively, all significantly lower than the Grade II soil standard ($P<0.01$). Coefficients of variation across the watershed were 36.15%, 38.79%, and 51.05%, respectively, indicating individual Cu, Pb, and Zn concentrations did not exceed Grade II standards. Mean Cu concentration exceeded background values but was below river sediment values, with non-significant differences ($P>0.05$) and low variation (36.15%), suggesting minor Cu pollution with relatively stable distribution. Mean Pb concentration exceeded background values ($P<0.05$) but was below sediment values ($P>0.05$), likely due to deposition of Pb-bearing pollutants from river water. Mean Zn concentration was below both background ($P>0.05$) and sediment values ($P<0.01$), with 51.05% variation but a maximum of 135.35 mg · kg ^{1}, indicating minor but uneven Zn contamination. Mean Cd concentration was 1.625 mg · kg ^{1}, 13 times the background value, 1.7 times the Grade II standard, and 0.47 times the sediment value, with 65.54% variation and a maximum of 3.402 mg · kg ^{1}, indicating severe Cd contamination.

2.2 Longitudinal Distribution of Heavy Metals in Liaohe Dam Zones

Spearman rank correlation analysis was performed from upstream (Fudedian) to downstream to assess concentration trends. Results showed no significant trend for Pb; Zn and Cu showed increasing trends at 11% of sections and no trend at 89%; Cd showed increasing trends at 33% of sections, decreasing trends at 11%, and no trend at 56% ().

As shown in [Figure 2: see original paper], Pb and Zn concentrations peaked at

Daniu Ferry (F) (55.54 mg · kg^{1} and 80.51 mg · kg^{1}), while Cu and Cd peaked at Tongjiangkou (B) (50.24 mg · kg^{1} and 3.103 mg · kg^{1}). All four elements showed declining trends from Tongjiangkou (B) to Zhu' ershan (C), with highly significant differences ($P<0.01$) for Pb, Cu, and Cd and significant difference ($P<0.05$) for Zn, suggesting reduced contamination impact in this reach. Concentrations of Pb, Cu, and Zn increased from Zhu'ershan (C) to Daniu Ferry (F), peaking at Daniu Ferry, then decreased significantly to Lengdong Bridge (H) ($P<0.01$). From Lengdong Bridge (H) to Shuguang Bridge (I), Pb showed no significant change ($P>0.05$), Cu increased slightly ($P<0.05$), and Zn increased significantly ($P<0.01$). From Shuguang Bridge (I) to the estuary (J), Pb, Cu, and Zn showed no significant changes.

Cadmium increased from Zhu' ershan (C) to Yubaotai Grand Bridge (E) ($P<0.01$), then decreased to the estuary ($P<0.01$), dropping from 2.778 mg · kg^{1} to 0.195 mg · kg^{1}—a 14-fold difference. Lower Cd concentrations downstream may relate to rice cultivation and seawater intrusion.

Mean Pb, Cu, and Zn concentrations at all sections were below Grade II standards ($P<0.01$). Cadmium pollution was more severe upstream, with a mean concentration of 2.177 mg · kg^{1} above Liaohe Bridge (G), 6.47 times the 0.336 mg · kg^{1} mean below Lengdong Bridge (H), indicating regionally constrained contamination. New pollution sources were unlikely between Tongjiangkou (B) and Zhu'ershan (C) and between Daniu Ferry (F) and Lengdong Bridge (H), but potential sources may exist upstream of Fudedian (A), between Zhu' ershan (C) and Daniu Ferry (F), and between Lengdong Bridge (H) and Shuguang Bridge (I).

2.3 Vertical Profile Distribution of Heavy Metals in Liaohe Dam Zones

Heavy metal deposition in soils records historical contamination patterns in space and time [8], enabling reconstruction of pollution history through vertical distribution analysis.

2.3.1 Lead Profile Distribution

Mean Pb concentration at 5-15 cm depth (40.26 mg · kg^{1}) exceeded both 15-30 cm (37.37 mg · kg^{1}) and 0-5 cm (37.05 mg · kg^{1}) depths ($P<0.05$), indicating an overall historical trend of initial increase followed by recent decrease, with current pollution lower than historical levels.

Pb concentrations at all depths and sections remained below Grade II standards. Minimum concentrations at Zhu' ershan (C) reached background values (21.40 mg · kg^{1}). Maximum concentrations occurred at Daniu Ferry (F) (59.91 mg · kg^{1} at 0-5 cm and 70.71 mg · kg^{1} at 15-30 cm) and Mahushan Bridge (D) (54.7 mg · kg^{1} at 5-15 cm), exceeding the sediment value of 51.00 mg · kg^{1} ($P<0.01$). No consistent depth pattern was observed across sections, likely due to large regional variations. No significant depth differences (P>0.05) occurred between Tongjiangkou (B) and the estuary (J), but significant differences (P<0.05) were found between Zhu' ershan (C) and Daniu Ferry (F), suggesting stable downstream impacts but historical changes upstream, possibly due to differences between cornfields (upstream) and rice paddies (downstream) where water movement homogenizes surface soil Pb.

2.3.2 Copper Profile Distribution

Mean Cu concentration at 0-5 cm depth (34.63 mg · kg^{1}) exceeded 5-15 cm (31.38 mg · kg^{1}) and 15-30 cm (31.26 mg · kg^{1}), indicating an overall increasing historical trend.

Cu concentrations at most depths fell between background and sediment values with no consistent depth pattern. Maximum concentrations occurred at Tongjiangkou (B) (79.48 mg · kg^{1} at 0-5 cm), Daniu Ferry (F) (50.20 mg · kg^{1} at 5-15 cm), and Fudedian (A) (40.52 mg · kg^{1} at 15-30 cm). Concentrations at Mahushan Bridge (D) exceeded those at Zhu' ershan (C) and Yubaotai Grand Bridge (E) (highly significant differences, P<0.01, except between C and D at 5-15 cm), and concentrations at Daniu Ferry (F) exceeded those at Yubaotai (E) and Liaohe Bridge (G) (P<0.01), suggesting pollution sources between Zhu' ershan (C)-Mahushan Bridge (D) and Yubaotai (E)-Daniu Ferry (F).

2.3.3 Zinc Profile Distribution

Mean Zn concentration at 0-5 cm depth (49.97 mg · kg^{1}) exceeded 15-30 cm (48.38 mg · kg^{1}) and 5-15 cm (43.70 mg · kg^{1}), indicating a historical trend of initial decrease followed by recent increase.

Zn concentrations were generally below background values, except at Fudedian (A) and Daniu Ferry (F) at 15-30 cm depth (P<0.01), suggesting historical Zn pollution. Overall, Zn contamination in dam zones was minimal.

2.3.4 Cadmium Profile Distribution

Mean Cd concentration at 15-30 cm depth (1.713 mg · kg^{1}) exceeded 0-5 cm (1.596 mg · kg^{1}) and 5-15 cm (1.566 mg · kg^{1}), indicating a historical trend of initial decrease followed by recent increase.

Cadmium showed clear variation across dam zones. Except at Fudedian (A) (0-5 cm) and Daniu Ferry (F) (5-15 cm), all depths above Liaohe Bridge (G) exceeded downstream concentrations (P<0.01), Grade II limits (P<0.01), sediment values (P<0.01), and background values (P<0.01). All depth maxima originated at Tongjiangkou (B): 3.003 mg · kg^{1} (0-5 cm), 3.209 mg · kg^{1} (5-15 cm), and 3.097 mg · kg^{1} (15-30 cm). No significant depth differences (P>0.05) occurred between Tongjiangkou (B) and Yubaotai Grand Bridge (E), except at Mahushan Bridge (D) (P<0.01), indicating severe recent Cd pollution above

Liaohe Bridge far exceeding agricultural and human health safety limits. Concentrations increased from Fudedian (A) to Tongjiangkou (B) (P<0.01), with Fudedian (A) 0-5 cm concentration (0.472 mg·kg ¹) much lower than 5-15 cm (2.193 mg·kg ¹), suggesting a Cd source between these sites and historical contamination at Fudedian. Below Liaohe Bridge (G), all depths were below sediment values (P<0.01) but above background values, indicating reduced but persistent contamination.

2.4.1 Geoaccumulation Index Evaluation of Dam Zone Heavy Metal Pollution

Using Liaoning soil background values () as the Igeo reference, [Figure 4: see original paper] shows Cd Igeo values significantly exceeded those of Pb, Cu, and Zn, peaking at 4.23 (Class 6, strong to extreme pollution) at Tongjiangkou (B). Upstream of Liaohe Bridge (G), pollution levels were primarily Class 5 and above; Shuguang Bridge (I) showed Class 3 (moderate pollution); Lengdong Bridge (H) and Zhaoquanhe Estuary (J) showed Class 2 (unpolluted to moderately polluted). Thus, Cd pollution affected nearly all dam zones, with upstream contamination markedly more severe than downstream. Pb and Cu Igeo values were below 1 (below moderate pollution), while Zn Igeo values were negative, indicating negligible Pb and Cu pollution and no Zn pollution.

2.4.2 Potential Ecological Risk Index Evaluation of Dam Zone Heavy Metal Pollution

Using Liaoning soil background values as the reference, RI evaluation () indicated very strong potential ecological risk from Tongjiangkou (B) to Yubaotai Grand Bridge (E). Fudedian (A) and Daniu Ferry (F) to Liaohe Bridge (G) showed strong ecological risk; Shuguang Bridge (I) showed moderate risk; Lengdong Bridge (H) and Zhaoquanhe Estuary (J) showed slight risk. RI values upstream of Liaohe Bridge (G) exceeded downstream values, particularly at Tongjiangkou (B) (871.59) and Yubaotai (E) (774.56). The RI spatial pattern matched the Cd geoaccumulation index distribution ([Figure 4: see original paper]), confirming Cd as the dominant contributor. Single-metal potential ecological risk coefficients (Er) verified this, with Cd contributing 78.77%-98.23% to RI across sections, and higher RI values corresponding to greater Cd contributions.

2.5 Correlation Analysis of Heavy Metal Sources

Correlation analysis () revealed highly significant positive correlations (P<0.01) among Pb, Cu, and Zn (r = 0.931-0.977), suggesting common pollution sources. Cadmium showed no significant correlation with Pb, Cu, or Zn, indicating independent sources.

3 Discussion and Conclusions

Field surveys revealed that Liaohe dam zones primarily consist of cultivated land, trees, and open grassland. Upstream of Liaohe Bridge, dam zone crops are mainly corn and rice. Due to fertile soils and potential flood impacts during high-water periods, these lands typically receive no fertilizer or pesticide applications, with harvested corn considered "green" products despite unverified safety. This study found minor Zn pollution, light Pb or Cu contamination in some reaches, but ubiquitous Cd pollution, with some sections severely exceeding limits for normal crop growth and human health protection, rendering them unsuitable for cultivation.

Studies by Shan Ting [12] on Liaohe Estuary wetlands, Deng Baole [13] on Liaohe River sediments, and Qi Wei et al. [14] on regional geochemistry all identified Cd as the most prominent contaminant, reaching moderate to severe pollution levels. Recent statistics [15] confirm industrial heavy metal emissions in the Liaohe Basin are dominated by Cd, with basin-wide severe contamination making cultivation inadvisable. The National Soil Pollution Survey Bulletin [16] reported overall soil exceedance rates of 16.1%, with 19.4% for cultivated land and 7.0% specifically for Cd, including 0.5% of sites with severe Cd pollution. Thus, Cd pollution has become a major safety concern, with the Liaohe Basin widely contaminated and requiring urgent remediation.

Mean concentrations of Cu, Pb, and Zn in Liaohe dam zone soils, as well as section-specific means, were below Grade II standards, while nearly all sampling points exceeded Grade II for Cd. This likely reflects extensive industrial Cd use. Cadmium pollution was more severe in the mid-upstream region, with trends similar to those in exposed and submerged sediments at the same sections [3,8]. Upstream of Liaohe Bridge, Igeo values indicated Class 5 (strong pollution) and above, while RI values between Tongjiangkou and Yubaotai Grand Bridge reached "very strong" risk, corresponding to Class 4 (moderate to high pollution) in adjacent zones, indicating higher mid-upstream risk. Heavy metal sources in sediments include mining, industry, wastewater treatment plants, urban areas, erosion, groundwater, atmospheric deposition, irrigation, and runoff. The Liaohe main stream gently slopes north-south through a flat landscape of protective forests and farmland. Based on field investigations, potential dam zone heavy metal sources include: (1) erosion by contaminated river water [4], with floodwaters carrying substantial sediment; estuarine heavy metal distribution is influenced by runoff, tides, and wind disturbance [17]; (2) fertilizer application, with Cd and Zn from phosphate fertilizers and Pb from pesticides [18]; though fertilization is rare due to soil fertility, occasional applications may occur; (3) traffic on dam roads, with vehicle exhaust and tires emitting Pb, Zn, Cu, and Cd [19]; (4) industrial production, with smelting and chemical plants along the river; (5) atmospheric deposition, with wind-blown farmland soil and precipitating airborne metals during windy spring/autumn periods [20]; (6) domestic waste disposal from riverside villages, including heavy metal-containing items like batteries [21]; and (7) wastewater irrigation [22].

This study indicates Pb, Cu, and Zn likely share common sources, while Cd has independent sources.

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Note: Figure translations are in progress. See original paper for figures.