Distribution Characteristics of Some Heavy Metal Elements in the Polluted Soil in Baiyin Dongdagou

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Abstract. 11 soil samples with different depths were collected in Dongdagou, Baiyin city, and the contents and correlations of Ni, Cu, Zn, Cr, Cd, Pb and Hg in the soil were investigated and analyzed. The results showed that the distribution content of heavy metal in the soil was according the order of Zn > Cu > Pb > Cd > Cr > Ni > Hg. There are significant correlation between Zn and Cd, Zn and Cu in the soil, and the compound pollution characteristics of heavy metal on the soil are revealed. These results would provide theoretical direction and scientific basis for the risk assessment and prevention of soil heavy metal pollution in Dongdagou area of Baiyin city.

1. Introduction
The rapid development of electroplating, chemical industry, mineral industry and other industries discharged a large number of pollutants to environments, which resulted in the increasing of heavy metal pollution in the environment [1,2]. As a result, the heavy metal pollution become a global problem for environmental pollution [3]. Heavy metal pollution for soil, which is the basis for the survival of earth organisms [4,5], is particularly serious [6-9], which has attracted the intensive attention of China’s environmental governance [10,11]. Heavy metals enter plants through contaminated soil, and ultimately endanger human health through the biological chain [12]. Baiyin city is China’s non-ferrous metal industrial base [13]. With extensive mining, smelting and processing of non-ferrous metal in the Dongdagou Watershed of Baiyin city in past decades, this resulted in serious heavy metal pollution on farmland and surrounding ecological environment [14], seriously threatening to the healthy of the local people and hindering the sustainable development of local economy. Some scholars recently investigated the heavy metal pollution of soil in dongdagou area of Baiyin [15,16], but spatial distribution and pollution evaluation of heavy metal pollution in soil are hardly cared. In this paper, soil samples with different depths in 11 different areas of Dongdagou are selected, and the contents of Ni, Cu, Zn, Cr, Cd, Pb and Hg in the soil are investigated. Our result hope to provide the theoretical basis of risk assessment and a direction for ecological improvement. It also help to protect the life health of local residents, as well as rationally utilizing and protecting land resources in the future.

2. Samples and methods
The sampling sites were located in 11 areas, including Lead and zinc Industry Zone, No.3 Smelter and Dongdagou near the Yellow River port. 9 m × 9 m sample method was adopted. The soil samples were collected in three sections of 0-20 cm, 20-40 cm and 40-60 cm in depth. A total of 32 samples were collected, and the sampling points were accurately positioned by GPS. The data of sampling points were shown in Table 1.

The soil samples were dried on the flat plastic film until they were semi-dry. The plant roots, debris and small rocks were removed. The soil was air-dried in the shade and then passed through 80 mesh nylon sieve. 100 g soil samples were taken out by quartering and ground. The samples were put into a self-sealing bag for use after passing through 100 mesh sieve. 20-30 g soil sample was taken out of the bag and put into an aluminum box. It was dried for 4-5 h at 105 ℃ and its constant weight was said. The contents of Ni, Cu, Zn, Cr, Cd and Pb in the samples were determined by atomic absorption spectrophotometry and Hg by ICP-OES. The water used in the experiment was ultrapure water and the reagents were all of superior purity. The sample was measured in parallel for 4 times, Origin 8.0 was used for drawing, and SPSS 21.0 software was used for correlation and factor analysis.

### Table 1. Distribution of soil sample collection sites.

| Collected site | Northern latitude | East longitude | Comment |
|----------------|-------------------|----------------|---------|
| S₁             | 36°36'44.31"      | 104°13'32.66" | (East bank of drainage ditch) the soil was restored, grass plants such as willow, elm, pagoda tree and pigweed were planted |
| S₂             | 36°35'48.92"      | 104°13'14.73" | (the Third Smelter Inspection Station) the riverbed under the small bridge located at the upper reaches of the river |
| S₃(1)          | 36°35'34.65"      | 104°13'02.24" | (6 km away from the Third Smelter) half slope of the river bank, the soil was restored and slope protection soil was taken |
| S₃(2)          | 36°35'34.31"      | 104°13'03.31" | (6 km away from the Third Smelter) Alfalfa land, the soil was restored, rhizosphere soil of Alfalfa land was taken |
| S₃(3)          | 36°35'32.21"      | 104°13'07.64" | (6 km away from the Third Smelter) Natural slopes, the soil was restored, non-rhizosphere soil was taken |
| S₄             | 36°33'25.17"      | 104°12'45.64" | (70-80 m to the east of the sewage outlet of the lead-zinc waste treatment plant) The east side of the river is a natural landscape, and the west side is an artificial slope protection |
| S₅             | 36°32'20.23"      | 104°12'53.45" | (Next to National Highway 109 in Dongdagou Sewage Discharge Section) By the side of the river under Dongdap Dong Bridge, natural landscape, a large amount of industrial and domestic wastewater discharge |
| S₆             | 36°30'34.90"      | 104°15'14.20" | (3 km south of National Highway 109 in Dongdagou Sewage Outlet) |
| S₇             | 36°29'27.10"      | 104°17'01.52" | (Malapai Bridge channel) |
| S₉(1)          | 36°25'32.43"      | 104°18'32.79" | (Minqin Village river beach) |
| S₉(2)          | 36°28'05.35"      | 104°20'39.19" | (Downstream of Yangwan Bridge) An artificial lake is formed by sand dug upstream of the bridge. The surrounding area is covered with plants such as cypress, Kochia sibiricum, Suaeda sibiricus, and the downstream water is clear |
| S₁₀            | 36°26'27.78"      | 104°22'10.81" | (The river channel 1km south of Yongfeng Village in Dongdagou) The full width of the river is 60 m |
| S₁₁(1)         | 36°25'34.32"      | 104°23'31.98" | (50 m away from the riverside, the beach is in the Yellow River Estuary of dongdagou) |
| S₁₁(2)         |                    |                | (100 m away from the riverside, the beach is in the Yellow River Estuary of dongdagou) |

3. Results and discussion
3.1. Distribution of heavy metal content in soil

The content of 7 heavy metal elements in each soil sampling was investigated. The concentration of heavy metal and statistical analysis results of each samples were shown in Figure 1. (The dotted lines represented the national soil environmental quality level-III standards) and Table 3. The corresponding table of sample land and serial number was shown in Table 2.

![Figure 1.](image)
Soil metal concentrations of Zn, Cr, Cu, Pb, Ni, Cd and Hg in different sampling areas.

**Table 2.** Correspondence table between collected site and serial number.

| Collected site | S₁ | S₂ | S₃(1) | S₃(2) | S₄ | S₅ | S₆ | S₇ | S₈(1) | S₈(2) | S₉ | S₁₀ | S₁₁(1) | S₁₁(2) |
|----------------|----|----|-------|-------|----|----|----|----|-------|-------|----|----|--------|--------|
| Serial number  | 1  | 2-4| 5-10  | 11    | 12-20| 21 | 22-23| 24 | 25    | 26    | 27 | 28    | 29     | 30     | 31     | 32     |

The content of Cr and Ni are relatively low in Dongdagou area, while the contents of Zn, Cu, Pb, Hg and Cd are higher, especially near the Third Smelter, which basically exceed the national soil environmental quality level-III standards. The Cd content about 70-80 m from the east of the sewage outlet of the lead-zinc waste treatment plant seriously exceeds the national standard of soil quality (III).
The Cu content near sewage discharge section in the 109 National Highway of Dongdagou seriously exceeds the standard. With a distance of 6 km from the Third Smelter, the contents of all the metals except Pb are significantly reduced, implying the soil has been repaired. The same sampling site with different depths, the deeper of the sampling depth, the higher of the content of Zn and Cd. The Cu content reached a highest value at the depth of 20-40 m while the content of Pb decreases with the deepening of the depth.

The order of the average content value of heavy metal in different sampling area is Zn > Cu > Pb > Cd > Cr > Ni > Hg. The highest content of Zn, Cu and Cd were found near the Third Smelter. The highest levels of Ni and Hg were found in Dongdagou sewage discharge section of National Highway 109. The highest content of Cr was found at the river in Minqin Village. The highest content of Pb was found 6 km away from the Third Smelter. It can be seen from Table 3, the variation coefficients of the five heavy metal contents from the sampling sites in Dongdagou area of Baiyin City are quite different, and the order of the variation coefficients is Zn > Cd > Cu > Hg > Pb > Ni > Cr. The coefficients of variation of Pb, Ni and Cr are relatively low, which are 70.13%, 33.77% and 33.24% respectively. The other four elements, Zn, Cd, Cu and Hg, the coefficients of variation are above 90%. It was shown that these four elements are obviously abundant in some parts of the study area. The coefficient of variation of heavy metals is generally at a relatively low value under natural conditions, and the interference of human activities will cause a larger coefficient of variation[17]. Therefore, the large variability of the four elements Zn, Cd, Cu, and Hg also reflects the large volatility of the distribution of these elements in the soil, which is largely caused by human activities. The unmined areas are the least polluted, and the waste slag produced by the smelter is the direct cause of the serious pollution. It can be seen that the pollution from the mining and smelting of mineral resources is the main source of pollution in this area rather than natural factors.

Table 3. Soil potentially heavy metals content in Baiyin city (mg/kg) (n=32).

| Element | Mix (mg/kg) | Max (mg/kg) | Average (mg/kg) | Median (mg/kg) | SD (mg/kg) | CV (%) | BV (mg/kg) | NSS |
|---------|-------------|-------------|-----------------|----------------|------------|--------|------------|-----|
| Zn      | 53.43       | 18634.58    | 2597.31         | 1042.74        | 4170.28    | 160.56 | 69.3       | 250 |
| Cr      | 34.84       | 155.39      | 93.50           | 98.04          | 31.08      | 33.24  | 70         | 200 |
| Cu      | 11.33       | 3180.84     | 749.67          | 368.23         | 854.00     | 113.92 | 35         | 100 |
| Pb      | 147.71      | 1753.23     | 711.95          | 542.26         | 499.31     | 70.13  | 35         | 300 |
| Cd      | 29.29       | 609.11      | 95.66           | 55.49          | 122.49     | 128.05 | 0.116      | 0.60 |
| Ni      | 11.67       | 61.89       | 33.26           | 32.18          | 11.23      | 33.77  | 38.5       | 50  |
| Hg      | 2.50        | 43.75       | 13.31           | 7.50           | 12.04      | 90.51  | 0.02       | 0.50 |

SD is the standard deviation.
CV is the variable coefficient.
BV is the back ground values of the potentially heavy metals.
NSS is the National soil environmental quality standard values from Chinese Environmental Quality Standard for Soils, (SEPAC,1995).
Standard for soil in China Level II (GB 15618-1995) are soil limited values to ensure the agricultural production and maintain the health of human.

3.2. Correlation analysis of heavy metal elements in soil

SPSS 21.0 software was used for correlation analysis of 7 heavy metal elements, and the results are shown in Table 4. It can be seen from Table 4 that there is a significant correlation between Zn and Cd, and the correlation coefficient is 0.964. There is also a high correlation between Zn and Cu, and the three elements Zn, Cd and Cu have good homology. It can be concluded that heavy metal pollution in the soil shows the characteristics of compound pollution in Dongdagou area of Baiyin city.
Table 4. Correlation analysis of soil heavy metal elements.

| Element | Zn     | Cr   | Cu    | Pb   | Cd   | Ni   | Hg   |
|---------|--------|------|-------|------|------|------|------|
| Zn      | 1      |      |       |      |      |      |      |
| Cr      | -0.440*| 1    |       |      |      |      |      |
| Cu      | 0.804**| -0.426*| 1    |      |      |      |      |
| Pb      | -0.438 | 0.440*| 0.440*| 1    |      |      |      |
| Cd      | 0.964**| -0.439*| 0.710**| 0.319 | 1    |      |      |
| Ni      | 0.069  | -0.054| 0.126 | 0.297| 0.107| 1    |      |
| Hg      | 0.651**| -0.284| 0.713**| 0.365| 0.673**| 0.036| 1    |

*Correlation is significant at the 0.05 level (two-tailed).
**Correlation is significant at the 0.01 level (two-tailed).

4. Conclusions

The high content of Zn, Cu, Pb, Cd, Cr, Ni, and Hg in the sampling soil of the Baiyin Dongdagou is due to human activities, and the waste residue from the smelter is the direct cause of serious pollution in the area. Heavy metal pollution in the soil is showing the characteristics of compound pollution. The high-intensity ecological hazard risk is manifested in the soil in the Baiyindongdagou area, and it is imperative to strengthen the prevention and control of soil heavy metal pollution.

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