Analysis and evaluation of heavy metal pollution characteristics contaminated soil in land-lake ecotone

Xing Weishuai, Chen Xinmin, Chen Fangyuan, Liu Zhaoxin
College of Transportation Science & Engineering, Nanjing Tech University, Nanjing, Jiangsu 210009, China
xingbaobao@njtech.edu.cn, xmchen@njtech.edu.cn, 1024721959qq.com, 1059243431@qq.com

Abstract. In this paper, systematic sampling with elf-made piston sampler and experiment were applied to research on the distribution characteristics of heavy metals (Cd, Pb, Cu, Zn, Cr, Ni, As) pollution in the surface and 1m depth sediments in Zhushan Bay in Zhoutie Town, Yixing City, Jiangsu Province. Spatial distribution characteristics of heavy metal elements and the relationships between heavy metals and the pH were analysed. Results show that surface and deep sediments are weakly alkaline. At the same time, the distribution of seven heavy metal elements in surface sediments in the land-water interlaced zone, estuarine and open water bodies are different. Among them, the contents of Zn and Cr are the highest, the content of Cd is the lowest, and only the content of Pb does not exceed the natural background value. The contents of heavy metals in sediments at different depths all show the distribution characteristics of Zn> Cr> Cu> Ni> Pb> As> Cd. Zn and Cr have the highest concentrations and are most likely to be pollution factors. Only Pb has no obvious accumulation and pollution is lighter. The sediments are shallow and deep, and the contents of heavy metal elements fluctuate locally. The concentration increases recently and the content in the estuary area is significantly higher. The contents of Zn, Cr, Cu and Ni are high and have a significant correlation. The correlation coefficient is between 0.680 and 0.920, showing the homogeneity of the pollutants.

1. Introduction
The land-lake ecotone, which has the ecological characteristics of fragile, heterogeneous, dynamic and complex biological diversity, is an important transitional zone between the lake aquatic ecosystem and the terrestrial ecosystem. The waterway ecotone is a zone of low resistance, weak buffer capacity and high sensitive. And its stability and balance depend on two aspects of nature and human beings[1]. The heavy metal pollution of land-lake ecotone has a long-lasting, cyclical, and accumulative hazard to the ecological environment. The pollution is not limited to the water and soil directly contacted with it, but also can poison the aquatic animals and plants through the release of the overlying water body, which in turn directly or indirectly affect terrestrial humans and other living things.

Taihu Lake is the third largest freshwater lake in China, located in the economically developed and densely populated areas[4]. Zhushan Bay is located in the northwest of Taihu Lake, close to Yixing City, which has a large industrial development, and has a huge consumption of coal, oil and other fossil fuels. With the development of economy and population growth, the pollution status of Zhu Shan Bay is even more obvious due to the failure to get rid of the old path of "development first and
post-management". Lake water pollution, algae outbreak and serious heavy metal pollution have even threatened the water supply sources of the surrounding cities.

This paper takes Zhoutie town basin in Taihu Lake as the research target. Put heart on heavy metal pollution characteristics of land-lake ecotone in Zhushan Bay, Taihu Lake through Site sampling and indoor test. The sampling line is selected in the agricultural area, industrial areas, wetlands phase, and land-lake ecotone no obvious enrichment of algae. According to Soil Environmental Quality Standard (GB15618-1995), the concentrations of seven heavy metals (Cd, Pb, Cu, Zn, Cr, Ni, As) in the sediment sampled were determined by the relevant instruments. In order to find out the spatial distribution of heavy metal elements and pH in the surface and deep sediments of industrial areas where industrial agriculture is relatively concentrated, heavily polluted and sensitive, determine pollution history and environmental risks, evaluate the effectiveness of existing environmental management project. In addition, it has provided a basis for the comprehensive management of Zhushan Bay by analyzing the rules of heavy metal elements migration, finding out the identification sources of pollutants in sediments and predicting the future trend of environmental evolution.

2. Materials and methods

2.1. Set the sampling point
Zhoutie Town is located west of Zhuhan Bay, industrial development earlier. In the 1980s, the rapid development of industry and agriculture in the Taihu Lake basin led to the gradual formation of an industrial structure based on chemical and Mechanical[8]. With the development of economic, Zhoutie Town have developed more than 100 chemical enterprises in a single town since started the construction of industrial parks in 2003. However, the lack of pre-planning led to the concentration of agricultural land and industrial land and serious environmental pollution. In 2009, about 150 gathered chemical companies began to be rehabilitated. Zhuxi Industrial Park and Jinao Industrial Park, located in the northeast of Zhou Iron Town, about 3 km long and 1 km wide, had gathered about 50 factories, and some factories in the residential area and the township upwind.

According to research[11], in terms of the degree of heavy metal pollution, the water of Zhushan Bay is higher than that of Lake District and Lake District is higher than that of the East Taihu. In terms of ecological environment, a large area of cyanobacteria and Algal blooms frequently occur in the area of Zhushan Bay. In terms of long-term results, dredging engineering in Zhushan Bay and Meiliang Bay, the construction of lakeside buffer zone in Zhushan Bay has a uncertain effect on the improvement of water quality and the heavy metal content of sediment, so , long-term observation is needed. At last, Zhoutie Town, as the target area, setted sampling points. There is a high degree of pollution, prone to the accumulation of algal blooms, building an important ecological restoration project of the lake estuarine area.

The sample location is close to the estuary of wetlands and industrial and agricultural land in Zhushan Bay. And it is obviously affected by Industrial and agricultural, ecological restoration projects, into-lake rivers. The length of the sampling route is about 60m. The sampling points are arranged near the estuary and perpendicular to the shoreline. Each interval of sampling point is about 30 meters from the land-lake ecotone extends to the open water. The sampling points Y1, Y2, Y3 are set in the land-lake ecotone, point D is set in the open water. Water depth changes more obviously with the seasons, in the land-lake ecotone. And this sampling time is August, when Zhushan Bay is in the wet season. There it is affected by the rainy season and typhoon, with deep water, storms, water quality yellow, muddy, and significant sediment.

Sampling point layout and cross-sectional plan are shown respectively in Figure 1 and Figure 2.

2.2. Soil sample collection and treatment
In order to study the pollution characteristics of heavy metal elements in a three-dimensionally manner, the mud samples were taken from the surface layer and the column-like samples, respectively.
Surface sediments (0-10 cm) were collected at points Y1, Y2, Y3 and D using a grab Peterson sampler. This paper selects independently designed piston columnar sampler, and this device has the advantages of controlled depth, simple operation, small disturbance, easy to carry and lower sampling costs. Design drawing of piston sampler is shown in Figure 3.

Depth (about 100 cm) columnar sediment samples were taken at Y1, Y3 and D points using a piston columnar sampler. When sampling, the sampler is kept in vertical angle and tapped into deep deposits using a rubber mallet. When the samples were taken out, it would be placed flat on the deck and in order to kept the shape of the sample, the piston rod was slowly pushed in. Measuring of its length rapidly, scraping the ends of the soil, cutting by 10cm in the site. Columnar soil samples in site are shown in Figure 4.

In order to ensure the accuracy of soil samples, the samples were sealed with a clean polyethylene bag, labeled inside and outside the bag, and shipped back to the laboratory as soon as possible. The samples were kept dark and saved closely in a foam incubator with a temperature be controlled at 0 ~ 4 ℃ by placing the ice bag before analysis. The specific location of the sampling point and water depth as shown in Table 1.
Surface sediments are floating mud, the color is brown, its traits is paste-like, with a strong flow. The top of columnar sample is a thin paste-like soil, with brown color and no obvious odor, and also is obvious to the lower part; The center of the columnar sample is a flow-like shape, the bottom of which is soft and soft, with no obvious delamination, all of which are black. The sample is performed with elastic and fine feels when touched by hand, and also with worse decayed plants smell. The columnar samples are stratified according to "dredging geotechnical classification standards", the research of Jiang Xia et al, and the color, odor, state and humidity of the sediment[14]. The upper part of the columnar sample is an oxide layer. The middle and lower part are contaminated layers to contaminated transition layers. There is no obvious delamination between the contaminated transition layers and the upper layer, but more dense existing.

| Position | Region     | Longitude | Latitude | Depth of water |
|----------|------------|-----------|----------|----------------|
| Y1       | Ecotone    | 120°1′6″E | 31°26′59″N | 1.0            |
| Y2       | Ecotone    | 120°1′6″E | 31°27′0″N  | 1.2            |
| Y3       | Ecotone    | 120°1′6″E | 31°27′1″N  | 1.5            |
| D        | Open water zone | 120°1′8″E | 31°27′2″N  | 1.7            |

2.3. Processing and analysis of soil sample

In order to study the heavy metal pollution in the area of water-land ecotone in Zhoutie town, in the cases of area affected by human activities, modern industrial and agricultural activities pollution, in accordance with the requirements of Soil Environmental Quality Standard (GB15618-1995) to control of pollutants, According to the situation of environmental pollution in Zhoutie town, pollution severity in the pollution history of Taihu Lake, the size of heavy metals toxicity and other factors, selected monitoring the content of seven heavy metals.

Dried samples after blending with the method of fourfold division shrink to about 110 g, and then natural air drying, remove the stones and animal residues in the soil sample, milled, through 2 mm nylon mesh, blending. with agate mortar grinding soil samples which though the 2mm nylon sieve to pass 100 mesh, mixed standby.

3. Results and analysis

3.1. Pollution characteristics of heavy metal elements

3.1.1. Content and distribution characteristics of heavy metal elements in surface sediments. The surface soil samples were analysed in the points of Y2, Y2, Y3 and D in the west side of the Zhushan Bay, the maximum, minimum, and average values of its Cd, Pb, Cu, Zn, Cr, Ni, As content are shown in Table 2.

Numerically, the content of Zn is the highest in the sediments, Cr is the second, and the content of Cd is the lowest, but only the content of Pb does not exceed the natural background value. The heavy metal content of surface sediments is shown in Figure 5. The dotted line in the figure shows the natural background value of national level 1 standard.

The content of Zn at points Y1, Y2, Y3 and D is far beyond the natural background value,It has little difference in the water-land ecotone and the estuarine zone, on the contrary, the content in the open water is more significant. The content of Cr in the water-land ecotone and the open water zone is far over average value and remains stable. The content of Cd at points Y1 and Y2 was significantly higher than that at Y3 and D, and the water-land ecotone and estuarine zones were the highest and decreased with the increase of offshore distance. The content of Cu has little difference at points Y1, Y2 and Y3 and it is far from the natural background value, but in the open water, the concentration is significantly higher than that of the water-land ecotone. The content of Ni has little difference at four sampling points and far beyond the natural background value. The content of As is lower than the
natural background value at points Y1 and Y3, and far beyond the natural background value at points Y2 and D. The content of Pb is lower than the natural background value in the water-land ecotone and open water zone. Therefore, Zn, Cr, Cu and Ni have obvious enrichment in the open water zone, while Cd has a significant concentration in the water-land ecotone, and the content of As has great fluctuations.

Table 2 Level of heavy metal pollution in surface sediments

| Element | Max values (mg/kg) | Min values (mg/kg) | Average values (mg/kg) | Standard values (mg/kg) |
|---------|-------------------|-------------------|------------------------|------------------------|
| Cd      | 0.39              | 0.24              | 0.27                   | 0.20                   |
| Pb      | 32.4              | 11.4              | 22.0                   | 35                     |
| Cu      | 127.0             | 93.5              | 103.4                  | 35                     |
| Zn      | 295.0             | 245.0             | 257.0                  | 100                    |
| Cr      | 194.0             | 183.0             | 199.0                  | 90                     |
| Ni      | 89.0              | 69.6              | 75.2                   | 40                     |
| As      | 25.4              | 10.5              | 15.3                   | 15                     |

The content of heavy metal elements in the surface sediments is unevenly distributed in the water-land ecotone, estuaries and open water zone, and the content of estuary area is not significantly higher than that of other points, which is not consistent with previous studies. Studies from Wang Peifang\(^5\) has shown that after the sediment entered the lake from the river channel, the particles that
absorb the heavy metals are first settled in the estuary area due to the slow speed, and with the increasing distance from the estuary, the small influence of channel input and the low content of heavy metals in sediments, which result in the content of heavy metal in sediments in the middle of the lake lower than the estuary. This may be due to the disturbance of the wind and waves, causing the resuspension and migration of the sediments, and the heavy metal elements in the sediments will also be released into the water when the water environment condition changes.

3.1.2. Contents and distribution characteristics of heavy metals in sediments at different depths. The contaminants such as heavy metals, which are produced by human activities, are discharged into the lake and will settle with the suspended matter. As time goes on, the sedimentary layers with chronological characteristics will be formed. These heavy metals accumulated in the sediment layer will be released into the water again under the external disturbance, and become the potential pollution source of the lake. Therefore, the study of the distribution of heavy metals in different depth sediments can reflect the change of heavy metals in the study area with time. According to the analysis of heavy metals in different depth soil samples, the content of each metal element varies with depth at different sampling locations, as shown in Figures 6, Figure 7, Figure 8.

From the contrast analysis of Figure 6, we can see the accumulation characteristics of heavy metal elements with depth at different sampling points, compared with the natural background value, Pb has no obvious accumulation, and lighter pollution, which is different from the results of sampling and analysis by Jiang Xia et al. in 2010 of Zhushan Bay[15].

At point Y1, the content of Cd and Cr elements is always greater than that of the natural background value, and the other four elements are zigzagged from bottom to top. The content of As elements in the upper layer is far below the natural background value, and the bottom-up concentration increases rapidly and decreases rapidly. The contents of Ni, Cu and Zn increased from the bottom up to the zigzag waves smaller than the natural background values. The surface concentration reached the maximum and the overall trend increased rapidly. At point Y3, the content of Pb and As elements is always less than the natural background value, and there is a zigzag fluctuation from the bottom to the top, without obvious change in the content. The contents of Cr, Ni, Cu and Zn are always larger than the natural background values. The magnitude varies from bottom to top, and the content reaches the maximum at depth 5cm, and decreases rapidly on surface. The content of Cd elements is only a little lower than the natural background value, and the bottom-up content gradually decreases[6]. At point D, the content of each element is the same as that at the point Y1, and the content of Cd and Cr elements is always greater than that of the natural background value. The content of Ni, Cu, Cr and Zn increases rapidly from bottom to top and exceeds the natural background value. It reaches the most value at 55cm, and the content of the middle to the surface decreases rapidly.

The contents of Y1 and D showed a similar upward trend from bottom to top, which may be related to the nearest distance from Y1 point and the open water at D point. The weaker hydrodynamic environment and lower deposition rate lead to no accumulation of heavy metals in the bottom sediments. The trend of elemental concentration at Y3 points is obviously different from the other two points, and the pollution is more serious. It may be due to the flow of rivers into lakes at the point of Y3, and the reduction of water flow rate. The river passes through towns and industrial areas, and receives more terrestrial pollutants, and rapidly subsidence in a short time, resulting in accumulation of heavy metals in the bottom sediments.

At depths ranging from 60cm to 55cm, there is an obvious upward trend at three points. The concentration of elements in the lower sediments is obviously lower. Therefore, it is concluded that there may be new sources of pollution entering the river compared with the past time. After that, the concentrations of heavy metals were always kept at a high level. The contents of Ni, Cu, Cr and Zn changed drastically in the depth of 15cm to the surface layer, which may be related to human activities.

On the whole, the heavy metal content in the study area is high, especially Zn and Cr. The main pollution source is the long-term discharge of wastewater from non-ferrous metal smelting, electroplating, chemical industry, printing and dyeing and other industries into the river. Zhu Xi
industrial park, South Jinwo Industrial Park are in this area. Forging factories, printing and dyeing factories, steel factories, leather factories, rubber factories gathered, including Zn, Cr and Wuxi discharge sewage into the lake, the waste gas and fly ash by atmospheric transfer eventually reached the bottom sediments. Adjacent to the sampling point is farmland, long term use of heavy metal element water to irrigate farmland, and also lead to the transfer of heavy metal elements to the land and water ecotone. Especially in this area, the population is large, the farmland is in bulk, and a lot of small and medium-sized chemical plants are gathered. At the same time, dense water networks, developed fisheries, and human activities such as gasoline burning and mechanical wear make the heavy metal content of the bottom sediment accumulate.

3.1.3. Analysis of deposition rate and change of heavy metal elements. According to the research of Liu et al [18], the average sedimentation rate of the upper core of the West Taihu coast is 1.7mm/a. Considering that the particle size and lithology of the upper sediment in the test area changed little, the extrapolation method was used to calculate the sedimentary age and depth at 15cm below the water and soil interface, corresponding to the mid 20s of last century. The following 5cm is the mid 80s of last century. In the middle of the 20s to the middle of 80s, the metal elements were rising rapidly. After the middle of the 80s, the results showed some metal elements reached the peak at a lower state, but the peak is not the history of the highest concentration because the selection of soil sample is longer and the interval of deposition time is larger. At the end of the 80s, a period of rapid development has caused serious heavy metal pollution accident. However, since 90s, the treatment of industrial waste gas and waste water has been started. The heavy metal content in Taihu has been reduced relatively, and the trend of heavy metal pollution in sediments has been slow relatively. This is consistent with the economic development of the river basin and the research of Zhu Guangwei, Liu Enfeng, etc [11].
3.1.4. Analysis of the correlation between heavy metals in sediments. The Pearson analysis method in spss19.0 was used to analyze the correlation of heavy metal content and pH in each layer. The correlation coefficients between heavy metals and their pH in each point are shown in tables 3, 4 and 5. In the table, there is a significant negative correlation between Cr, Cu, Ni, Zn. There is no significant correlation between Cd, Pb and As in Y1 point sediments. At point D, there is a significant negative correlation between Cu and Ni. There is a significant negative correlation in Zn. There is no significant correlation between Cd, Pb, Cr and As.

Table 3 Y1 Relativity analysis of heavy metals at point Y1

| Project | Cd  | Pb | Cr  | Cu  | Ni  | Zn  | As  |
|---------|-----|----|-----|-----|-----|-----|-----|
| Cd      | 1   |    |     |     |     |     |     |
| Pb      | 0.004 |    |     |     |     |     |     |
| Cr      | -0.699* | 0.317 |     |     |     |     |     |
| Cu      | -0.608 | 0.314 | 0.970** | 1 | | |
| Ni      | -0.642* | 0.032 | 0.926** | 0.944** | 1 | | |
| Zn      | -0.449 | 0.585 | 0.902** | 0.927** | 0.797** | 1 | | |
| As      | 0.032 | 0.824** | 0.033 | 0.009 | -0.211 | 0.343 | 1 |

Table 4 Relativity analysis of heavy metals at point Y3

| Project | Cd  | Pb | Cr  | Cu  | Ni  | Zn  | As  |
|---------|-----|----|-----|-----|-----|-----|-----|
| Cd      | 1   |    |     |     |     |     |     |
| Pb      | 0.009 |    |     |     |     |     |     |
| Cr      | 0.127 | -0.231 |     |     |     |     |     |
| Cu      | 0.032 | -0.403 | 0.871** | 1 | | |
| Ni      | -0.419 | -0.055 | 0.680* | 0.57 | 1 | | |
| Zn      | 0.352 | -0.353 | 0.750** | 0.792** | 0.205 | 1 | | |
| As      | -0.032 | -0.221 | 0.655* | 0.728* | 0.409 | 0.707* | 1 | | |

Table 5 Relativity analysis of heavy metals at point D

| Project | Cd  | Pb | Cr  | Cu  | Ni  | Zn  | As  |
|---------|-----|----|-----|-----|-----|-----|-----|
| Cd      | 1   |    |     |     |     |     |     |
| Pb      | -0.435 |    |     |     |     |     |     |
| Cr      | -0.466 | 0.356 |     |     |     |     |     |
| Cu      | -0.453 | 0.26 | 0.886** | 1 | | |
| Ni      | -0.477 | 0.088 | 0.807** | 0.972** | 1 | | |
| Zn      | -0.391 | 0.34 | 0.887** | 0.981** | 0.916** | 1 | | |
| As      | -0.054 | 0.12 | 0.756** | 0.766** | 0.671* | 0.834** | 1 | | |

Note: ** indicates significant correlation at the 0.01 level; * indicates significant correlation at the 0.05 level.

4. Conclusion

According to the analysis of seven kinds of heavy metal elements (Cd, Pb, Cu, Zn, Cr, Ni, As) changes, sedimentation rate and other indicators and their correlation which are related to the sediments in the surface water and land transition zone and 1m depth range of the watershed, which is located in Zhoutie Town, Zhushan Bay, Taihu Lake, the following conclusions can be got:

(1) The contents of heavy metal elements in the four samples were the highest in Zn, the second in Cr, the lowest in Cd, and only Pb content did not exceed the natural background value. The heavy metal elements in the surface sediments are unevenly distributed in the water-land crisscross zone, estuarine and open water, with great uncertainty.

(2) The contents of heavy metal elements in sediments of three deep sampling sites were both Zn> Cr> Cu> Ni> Pb> As> Cd. Zn and Cr are most likely to become a pollution factor, Pb has no
significant accumulation and has light pollution. From the bottom up, the content of heavy metal elements fluctuates locally and rises overall.

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