Distribution Characteristics and Pollution Assessment of Heavy Metals in Sediments of Zhushan Bay

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Abstract: The distribution characteristics of heavy metals in the columnar sediments of Zhushan Bay, Taihu Lake are studied. The Pearson correlation analysis and principal component analysis are carried out, and the pollution of heavy metals is evaluated. The highest mean concentration is found for zinc (Zn), followed by chromium (Cr), copper (Cu), nickel (Ni), lead (Pb), arsenic (As), cadmium (Cd). The content of heavy metals in estuaries and open water is significantly higher than those in aquatic-terrestrial ecotone, and pollution accumulation occurs in the deep sediments. There is a significant positive correlation between Cr, Cu, Ni and Zn, which indicates their similar sources. The geoaccumulation index (Igeo) shows that Cr has the highest value, with moderately to heavily polluted. The pollution situation of the study area is improved after the desilting project of Taihu Lake, but the potential ecological risk index (RI) is still moderate to severe, among which Cd is the single factor that contributes the most to RI.

1. Introduction
Taihu Lake Basin is the third largest freshwater lake in China with a surface area of 36900 km² at the southern edge of the Yangtze River Delta Plain[1]. In 2007, the "cyanobacteria crisis" broke out in a large area, which caused people to pay close attention to the water pollution of Taihu Lake. In order to improve the water environment quality of Taihu Lake and restore the ecological function of water, the management department of Taihu Lake Basin has started the a “Desilting Plan” since 2008 and completed on the 30th of September 2014. Zhushan Bay is located in the northwest of Taihu Lake and is one of the most polluted areas. A large number of industrial wastewater and domestic sewage are discharged into the area through lakes and rivers, and most of the heavy metals are rapidly transferred to sediments through various physical and chemical processes, showing a strong cumulative effect[2]. Although researchers have carried out some researches on heavy metal pollution in the sediments of the Zhushan Bay basin in the past, it is limited to the physical and chemical properties and pollution evaluation of the heavy metals in the surface sediments[3-4]. In this paper, the sampling sites are selected in agricultural areas, industrial zones, estuarine and aquatic-terrestrial ecotone, where the surface and deep water sediments are collected after the ecological restoration projects. The spatial distribution of heavy metal elements in the horizontal direction and vertical depth direction from the shore to the center of the lake is studied, and the source of pollutants in sediments is found by correlation analysis in order to find out the migration law of heavy metal elements. Finally, the pollution after treatment is evaluated by means of the geoaccumulation index (Igeo) and the potential ecological risk index (RI).
2. Methods and Materials
Zhushan Bay is a semi-closed eutrophic lake in northwestern Taihu, which is surrounded by township factories. The water quality is inferior to classⅤall year round[5-6]. The location of the sampling points is near the estuary and perpendicular to the lakeshore line extending from the ecotone to the open water body. Sampling of aquatic-terrestrial ecotone are set 60 meters apart. Setting sampling point S1 (120°1′6″E, 31°26′59″N), point S2 (120°1′6″E, 31°27′1″N) and point M (120°1′8″E, 31°27′2″N), the distribution of sampling points is shown in fig.1.

Figure 1. Plot of sampling points in Zhushan Bay

Using piston cylindrical samplers to collect deep layer (about 100cm) columnar sediment samples at point S1, point S2 and point M. When the sample is taken out, the visible plant remains, shells, and rubble will be removed. Soil sample length will be measured quickly and cut with 10cm segments, which are sealed with a clean polyethylene bag, labeled inside and outside the bag and shipped back to the laboratory as soon as possible. The soil sample should be kept away from light and the temperature should be controlled at 0~4 ℃ before the test. Soil samples will be dried naturally at room temperature, ground evenly and then sealed and stored after 100 mesh nylon sieve.

The content of Cd, Pb, Cu, Zn, Cr, Ni is determined by TAS-990AFG atomic absorption spectrophotometer and the content of As is determined by AFS8220 atomic fluorescence photometer after the soil samples are digested by HCI-HNO 3-HF-HCIO 4. In the process of determination, two parallel samples are set up, the relative standard deviations are kept within 20% and the recovery rate is 100%.

3. Results and Discussion
3.1 Distribution characteristics of heavy metals in sediments of Zhushan Bay
From the comparative analysis of the distribution of heavy metals in different sampling sites in fig. 2, it can be found that the order of average contents of heavy metals is as follows: Zn > Cr > Cu > Ni > Pb > As > Cd. The average content of Zn, Cr, Cu, Ni and Pb from the interlaced water to the open water is S2 > M > S1, that is, the content of heavy metals in estuaries and open water is obviously higher than those in aquatic-terrestrial ecotone. It is consistent with the study of Chen X et al.[7] that the content of heavy metals in the sediments decreases with the distance from the distance to the discharge outlet from the coast to the lake and reaches a high value of the lake heart. However, in the three sampling sites, the point S2 is located in the estuarine flow scouring area, and the velocity of sediment brought in by the current slows down, and the particles adsorbing heavy metals are first deposited in the estuary area[8]. The point M in the center of the lake is far away from the estuary and is less affected by the river, so the heavy metal content in the sediment is lower than that in the estuary area. The contents of As and Cd at point S2, i.e. estuarine area, are obviously smaller than those in other two sampling points, which may be due to the fact that the contents of these two heavy metals are relatively small and disturbed by the water flow in the estuary, so the contents of these two heavy metals decrease.
Figure 2. Distribution of average heavy metal contents in sediments of the Zhushan Bay

Fig. 3 shows the distribution of heavy metals in sediments with depth. The vertical distribution of heavy metals in sediments can directly reflect the accumulation of pollution\[9\]. By comparing the vertical distribution of seven heavy metals in Zhushan Wan and the background value of heavy metal environment in Jiangsu Province, it can be found that the content of Cd and Cr in the sediments is much higher than the background value, while most of Cu, Ni and Zn in the three sampling points exceed the background value. The vertical distribution of Pb and As is only partially exceeds the background value, and the pollution degree is relatively light. The content of Cd is the minimum, which increases with the increase of depth in three sampling sites, reaches the maximum at the depth of 70cm, and then decreases gradually under the depth of 70cm. The same patterns of heavy metals are also found in Cr, Cu, Ni and Zn. The contents of these heavy metals fluctuates with the increase of depth, and then begin to decrease at a certain depth (50-70cm). This is related to the accumulation of heavy metals in the corresponding years of sediment\[10\], and the sediment at 50-70cm corresponds to the accumulation of the rising period of modern industry and agriculture in Taihu Basin.
3.2 Correlation and principal component analysis of heavy metals
The correlation between heavy metals in sediments from all sampling sites is shown in Table 1. There is a significant positive correlation between Cr, Cu, Ni and Zn at 0.01 level, and the correlation coefficient is 0.854 to 0.963, indicating that the four heavy metals may have the same source and similar migration path. There is a significant negative correlation between Cd and Cr, Cu, Ni, Zn at 0.01 level or 0.05 level, which indicates that Cd has its own source of pollution. There is no significant correlation between Pb and As and other elements. The total amount of these two heavy metals is relatively small and close to the soil background value of Jiangsu Province, the pollution degree is relatively light, and there might be no obvious exogenous pollution.

As shown in Fig.4, we extract two principal components of 7 heavy metal elements from three sampling sites in Zhushan Bay, contributing 59.50% and 20.39% of the total variance, respectively. Principal component 1 contributes most to the total variance and is the main factor controlling the distribution and source of heavy metals in sediments. Its characteristic is that the factor variables have higher loads on the heavy metal elements Cr, Cu, Ni and Zn, which are 0.953, 0.978, 0.931 and 0.963, respectively. The results are consistent with the correlation analysis of heavy metals, indicating that the sources of heavy metals in the sediments of Zhushan Bay can be divided into two categories. The first major source is industrial pollution. Due to the three industrial zones in Yixing at the upper reaches of the estuary of Zhushan Bay, the metal processing industry, leather and chemical industry in the zone are well developed. Among them, the contribution rate and the higher Cu, Zn element come from the waste water from the metal plating process, while a large amount of Cr containing waste water will be produced in the leather production process[11]. The second type of pollution is mainly agricultural pollution. Cd, the main element of principal component 2, is one of the iconic elements in the process of pesticide and the use of chemical fertilizer [12].
### Table 1. Relativity analysis of heavy metals

| Heavy metal | Cd  | Pb   | Cr   | Cu   | Ni   | Zn   | As  |
|-------------|-----|------|------|------|------|------|-----|
| Cd          | 1   | -0.306 | -0.481** | -0.466** | -0.507** | -0.399* | 0.158 |
| Pb          | 1   | -0.306 | 0.238 | 0.922** | 0.013 | 0.301 | -0.232 |
| Cr          | -0.481** | 0.238 | 1     | 0.854** | 0.963** | 0.905** | 0.327 |
| Cu          | -0.466** | 0.207 | 0.922** | 1     | 0.934** | 0.865** | 0.296 |
| Ni          | -0.507** | 0.013 | 0.854** | 0.934** | 1     |         | 0.274 |
| Zn          | -0.399*  | 0.301 | 0.905** | 0.963** | 0.865** | 1     | 0.395 |
| As          | 0.158  | -0.232 | 0.327 | 0.296 | 0.274 | 0.395 | 1   |

Note: ** Indicates significant correlation at 0.01 level, * Indicates significant correlation at 0.05 level.

![Figure 4. Principal component analysis of heavy metal sediments in Zhushan Bay](image)

### 3.3 Methods for assessment of heavy metal pollution

The geoaccumulation index (Table 2) proposed by German scholar Müller[13] and the potential ecological index of heavy metals (Table 3) proposed by Swedish scholar Hakanson[14] are used to evaluate the pollution of heavy metals in sediments. Among them, the influence of environmental geochemical background value on the evaluation result is fully considered by the geoaccumulation index, and the environmental background value of heavy metals in the soil of Jiangsu Province[15] is adopted in this paper. Differently, the potential ecological index takes into account the general migration and transformation of heavy metal toxicity in sediments and the sensitivity of the assessment area to heavy metal pollution[16].

The Igeo range of heavy metals in the sediments of Zhushan Bay is shown in Fig.5, based on the environmental content of heavy metals in soils of Jiangsu Province. The overall pollution degree is Cr > Cd > Zn > Cu > Ni > As > Pb. The pollution of Cr is the most serious, the pollution index is 1.97-3.57, which is moderately contaminated to heavily contaminated. The pollution class of Cd is 1 to 3. For Cu and Zn, their pollution class are both 0 to 2. The contamination level of Ni and As is absent to moderately contaminated, and Pb is absence of contamination. Although the content of Cd in soil is the least among the seven kinds of heavy metals, the accumulation of Cd in soil is more obvious because of the small background value of environment. Compared with the box chart of three sampling points, it is not difficult to find that the dispersion of the Igeo values of various heavy metals at point S2 is much smaller than that of the other two points, and especially for Cr, Cu, Ni, Zn. These four heavy metals mainly come from the estuary discharge, and the upstream of the river pass through many industrial parks.
Table 2. Classification of cumulative index and degree of contamination

| $I_{geo}$ | Class | Contamination level                        |
|-----------|-------|-------------------------------------------|
| $\leq0$   | 0     | Absence of contamination                  |
| 0–1       | 1     | From absent to moderately contaminated    |
| 1–2       | 2     | Moderately contaminated                   |
| 2–3       | 3     | From moderate to heavily contaminated     |
| 3–4       | 4     | Heavily contaminated                      |
| 4–5       | 5     | From heavily to extremely contaminated    |
| $>5$      | 6     | Extremely contaminated                    |

Table 3. The relationship between potential ecological risk index and pollution level

| Item | $E_r/10$ | $E_{r,10}$ | RI/10 | Risk | Class |
|------|----------|------------|-------|------|-------|
|      | 4–8      | 8–16       | ≥32   | <15  | 0     |
|      | 4–8      | 8–16       | ≥32   | 15–30| 1     |
|      | 16–32    | ≥32        | ≥60   | 30–60| 2     |
|      | ≥32      | ≥60        |       | ≥60  | 3     |
|      | Low      | Moderate   | Considerable | High | Serious | Low | Moderate | Considerable | Serious | 0 | 1 | 2 | 3 |
| Note: $RI$ is the potential ecological risk index, $E_r$ is the potential ecological risk parameters for single metal. The ecological risk parameter $E_r$ of single heavy metal factor is Cd > Cr > Cu > As > Ni > Pb > Zn. Cd contributes the most to $RI$, accounting for 59.22% to 74.62%. The range of the sediment ecological risk parameter $E_r$ is 71.25 ~ 356.25, and the pollution degree of the section is moderate to serious. In the three sampling sites, the single factor ecological risk parameter $E_r$ of these six heavy metal factors is less than 40, and the pollution grade is lower. It can be seen that Cd is the largest pollutant in the assessment of the potential ecological hazard index of heavy metals in the sediments of Zhushan Bay. From the vertical direction (fig. 6), the ecological risk parameter $E_r$ of single heavy metal factor of Cd increase from the surface layer down, and then decrease to a certain depth. This result is consistent with the vertical distribution of heavy metals in sediments, indicating that agricultural activities, especially the use of chemical fertilizers, are frequently used in the corresponding years of the sediment depth. The range of potential ecological risk index (RI) of seven heavy metals in sediments is 186.51 ~ 242.59, and the pollution grade is moderate to severe. The results showed that the whole water quality of Zhushan Bay is improved after desilting, but there is still a risk of pollution.

4. Conclusion
(1) The average content of 7 heavy metal elements in the three sampling point sediments of the Yeshan Bay in the Taihu Lake is as follows: Zn> Cr> Cu> Ni> Pb> As> Cd. The contents of heavy metals in estuary and open water are obviously higher than those in land-water interlaced zone, and the
difference of heavy metal content in estuarine area is smaller. The vertical distribution of heavy metals in sediments indicates that heavy metals are accumulated in sediments.

(2) Through the Pearson correlation analysis and principal component analysis of seven heavy metal elements, Cr, Cu, Ni, Zn and As are significantly positively correlated, which are the first principal component elements. The main source of pollution lies in the long-term discharge of wastewater from non-ferrous smelting, electroplating, chemical, printing and dyeing industries into the river. The second principal component, Cd, is a large amount of substance contained in pesticides. There is no significant correlation between heavy metal element Pb and other elements.

(3) The method of land accumulation index show that Cr pollution is the most serious, which is moderate to moderate serious pollution. Although the content of heavy metals in Cd is the lowest, it is far higher than the background value of soil in Jiangsu Province, showing mild to moderate 2 pollution. The pollution degree of Pb is the least, which is in clean state.

(4) The results of potential ecological risk index show that the contribution of Cd to RI is the largest, accounting for 59.22% to 74.62%, and the pollution grade of the profile is from heavy to serious. The RI value of the whole area is 186.51 ~ 242.59, the pollution grade is moderate to severe, which indicates that the dredging project in Zhushan Bay area has some effect, but the pollution still needs to be further controlled.

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