

Original Research

Source Apportionment and Risk Assessment of Heavy Metals (Cd, Cu, Ni, Pb, Zn, and Mn) in Surface Sediments from the Dragon Lake, Bengbu, China

Li Ma*, Lanbao Zhu, Jing Wang

School of Civil Engineering, Bengbu University, Bengbu 233030, China

Received: 5 August 2020

Accepted: 25 September 2020

Abstract

Heavy metal concentrations in surface sediments of the Dragon Lake were studied based on the field investigation, sampling, indoor test and statistical analysis. Pollution risk was assessed using geoaccumulation index (I_{geo}), potential ecological risk index (PERI) and sediment quality guidelines (SQGs). The enrichment level of heavy metals in surface sediments decreased in the order of $Cd > Zn > Cu > Ni > Pb > Mn$. I_{geo} and PERI indicated Cd had the highest biological risk among the six heavy metals. The concentrations of Cd, Ni and Zn were between threshold effect level (TEL) and probable effect level (PEL), suggesting adverse biological effect occasionally occurred. Comparing the north and south of Dragon lake, the north part should be given more attention due to the higher heavy metal concentrations. The metals (Cd, Zn, Cu, Ni, and Pb) were attributed to anthropogenic sources, including agriculture, industrial emissions and traffic pollution, whereas Mn was mainly from natural sources. The results can provide reference for water quality management of Dragon Lake.

Keywords: heavy metals, sediments, assessment, source, Dragon Lake

Introduction

Heavy metals have become a worldwide concern due to their characteristics of toxicity, persistence, and non-degradability, they are easily accumulated in environmental medium, and pose a threat to human health through the food chain [1-3]. In aqueous ecosystem, heavy metals derived from both natural (e.g.

rock weathering and soil erosion) and anthropogenic sources (such as agriculture, industrial and coal mining activities, transportation). After entering into the aquatic ecosystem, only a small portion of free metal ions remain dissolved, the rest get deposited in surface sediments [4]. In certain conditions, they can be released back into the water again posing ecological risk to aquatic organisms. Thus, sediments not only act as a carrier of pollutants, but also the potential sources of contamination in the water itself [5-6]. In the water, trace amounts of heavy metals such as Zn, Cu, Ni, and Mn are indispensable for the function of biological systems, but their over-accumulation can be harmful

*e-mail: marivy_2006@163.com

for living creatures. However, other metals such as Pb and Cd are unnecessary and thus are toxic to the water ecosystem [7-9]. Therefore, understanding the risk assessment and their sources in aqueous ecosystem has become a meaningful research field and lake sediments are always chosen as an indicator to monitor the contamination, which could reflect the overall pollution of heavy metals in aquatic ecosystem.

Bengbu is an important comprehensive industrial base in northern Anhui province, China. (116°45'-118°04'E and 32°43'-33°30'N), which covers a total area of 5952 km² and has a population of 3.863 million inhabitants. The area belongs to the transitional zone of subtropics and south temperate zone, with an average annual temperature 15.1°C. The average annual rainfall and sunlight amount to about 905.4 mm and 4429.2 h, respectively. Plains account for most of the area. Dragon Lake is located in the east of Bengbu main urban area, which is national 4A tourist spot and national ecological demonstration zone integrated with leisure, tourism, outdoor sports, popular science, eco-adventure and other themes. As the largest urban inner lake in Eastern China, this lake covers 8.4 km² and has the total storage volume of 1.25×10⁷m³, originating from the confluence of the channels among the mountains around Dragon Lake, and flowing northward into Huai River. The functions of Dragon lake include sightseeing, aquaculture, flood control and regulating climate. However, with the development of the urbanization and dramatic growth of population in this area, Dragon Lake has been polluted at a certain degree, especially in the lakeshore area, which caused negative environmental effects. In recent year, a few of studies processed on the level of water eutrophication, monitoring and evaluation of water quality in Dragon Lake [10-11]. Nevertheless, similar work related to the pollution of heavy metals in surface sediments has not been processed. Therefore, in this paper, a total of 22 representative sampling sites have been chosen along the lakeshore and the content, ecological risks level and source identification of heavy metals have been conducted. The main goal of this study are to: (1) investigate the concentrations of cadmium (Cd), copper (Cu), lead (Pb), zinc (Zn), nickel (Ni), and manganese (Mn) in surface sediments of Dragon Lake; (2) assess the ecological risk of heavy metals; (3) identify the natural and anthropogenic sources of the heavy metals using multivariate statistical analyses.

Material and Methods

Study Area

The study was carried out in Dragon Lake. As can be seen in Fig. 1, a high bridge on Donghai avenue crosses this lake, and the part in the north of the bridge is usually called north lake, and the other part is south lake. South lake is relatively in the undeveloped

condition, marsh and fishing villages as the main land around the lakeshore. Compared to the south lake, north lake has been completely developed, many communities and restaurants are located along the lake, anthropogenic activities in this region increases the potential pollution risk. Additionally, it is worth mentioning that the well-known traditional industry zone in Bengbu lies in the east of the north lake, and therefore, discharge of industrial wastes cannot be ruled out in this area.

Sediment Sampling and Chemical Analysis

Surface sediments samples were collected from 22 sites along the Dragon Lake (Fig. 1). Each sample was acquired using peterson grab, then were placed in the acid-rinsed polyethylene bags and sealed. Global Position System (GPS) was taken to locate the exact longitudes and latitudes of each site. All samples were sent to the laboratory and stored in the freezer for further analysis.

Before laboratory processing, samples were air-dried, homogenized, passed through a 100-mesh sieve and stored in pre-washed glass containers at room temperature. Afterward, about 0.10 g of milled surface sediments from each site was put in 100 ml conical flask containing 6ml aqua regia solution (HNO₃:HCl = 1:3, v/v). The solution kept faint boiling for 2 h on an electric heating thermostat. The above step of acid digestion was repeated until the mixture was evaporated to semi-dryness. All extracts were transferred to 50 mL volumetric flasks with slow filter paper. After filtration, a small amount of nitric acid solution was used to clean glass funnel, conical flask and filter residue at least three times to ensure that the residues were into the volumetric flasks. In the process,

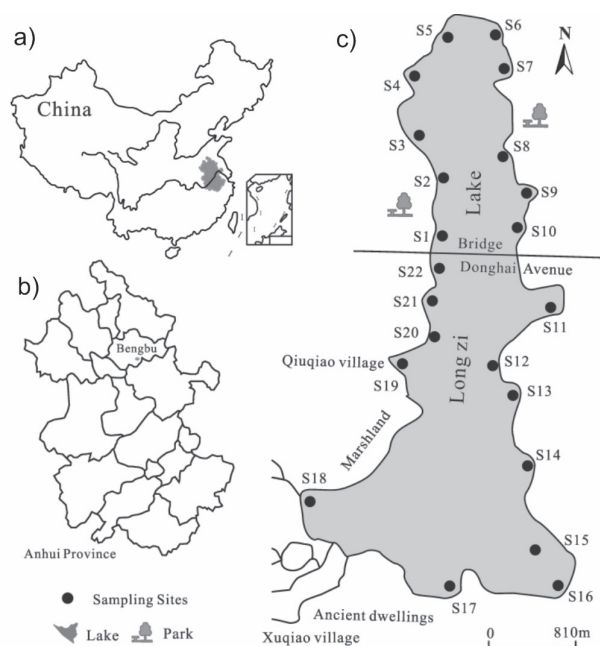


Fig. 1. Location of the study area and sampling sites.

high purity acids were used in the analysis, glassware was cleaned and decontaminated in a 5% nitric acid solution for 24 h and then rinsed with distilled water.

Analytical processes were conducted in experimental center of environmental science, and heavy metal concentrations were determined by Flame atomic absorption spectrometry (TAS, Beijing Purkinje General Instrument Co., China, TAS-990AFG). Quality control was evaluated using duplicates, blanks, and sediment reference materials. All samples were analyzed in triplicate to guarantee the accuracy, and the relative standard deviations (RSD) were less than 10%. Recoveries for six heavy metals were between 98.5% and 103.6%.

Geoaccumulation Index (I_{geo})

This method was proposed by Muller and had widely used in the study of sediment contamination [12-15]. This method clearly presented the levels of heavy metal contamination, with the consideration of anthropogenic pollution factors and geochemistry background value, especially the change of background value caused by diagenesis. This indicator was defined as follows:

$$I_{geo} = \log_2 \left(\frac{C_n}{1.5B_n} \right) \quad (1)$$

...where C_n is the concentration of heavy metal (n) in surface sediments; B_n is geochemistry background value of heavy metal (n); 1.5 is the background value correction factor due to lithological variations. The pollution condition in sediments based on I_{geo} was classified into seven levels [16]: Level 0 ($I_{geo} < 0$, practically unpolluted); Level 1 ($0 \leq I_{geo} < 1$, unpolluted to moderately polluted); Level 2 ($1 \leq I_{geo} < 2$, moderately polluted); Level 3 ($2 \leq I_{geo} < 3$, moderately to heavily polluted); Level 4 ($3 \leq I_{geo} < 4$, heavily polluted); Level 5 ($4 \leq I_{geo} < 5$, heavily to extremely polluted); Level 6 ($I_{geo} \geq 5$, extremely polluted).

Potential Ecological Risk Index (PERI)

The PERI was introduced by Hakanson to comprehensively assess the ecological risk of heavy

metals in sediments [17]. This method not only considered the variations of background value, but also contained environmental sensitivity and heavy metal toxicity. PERI was calculated by the following equations:

$$E_r^i = T_r^i \times \frac{C_i}{C_n} \quad RI = \sum_{i=1}^n E_r^i \quad (2)$$

...where C_i is the concentration of heavy metal i, C_n is the background value of heavy metal i, T_r^i is the toxicity coefficient of a certain heavy metal. Based on previously research, the toxicity coefficients of Cd, Cu, Mn, Ni, Pb and Zn used in analysis were 30, 5, 1, 5, 5, and 1, respectively. E_r^i is the potential ecological assessment coefficient for a certain metal, RI is the comprehensive potential ecological risk index. The criteria for ecological potential risk of heavy metals were presented in Table 1 [18].

Sediment Quality Guidelines (SQGs)

To clearly interpret the relationship between environmental pollution and adverse biological effect, SQGs were introduced. The guidelines consist of two types of limit values, TEL (threshold effect level) and PEL (probable effect level) [19]. The concentrations below the TEL represent a better benthic environment, where adverse biological effects are not expected to occur. Concentrations higher than PEL indicate serious pollution, where adverse biological effects occur frequently. While concentrations between TEL and PEL stand for adverse biological effect occasionally occur [20-21].

Statistical Analysis

Independent sample *t*-test ($p < 0.05$) was conducted to identify the significant differences of heavy metal concentrations in surface sediments. Pearson correlation matrix (PCM), hierarchical cluster analysis (HCA) and principal component analysis (PCA) were used to distinguish the sources of heavy metals. All statistical analyses were performed by SPSS 19.0. Coreldraw 12 was applied for graphic processing.

Table 1. Criteria for ecological potential risk of heavy metals.

| Ranges of E_r^i | Risk grades | Ranges of RI | Risk grades |
|------------------------|--------------|---------------------|-------------|
| <40 | Low | <110 | Low |
| $40 \leq E_r^i < 80$ | Moderate | $110 \leq RI < 220$ | Moderate |
| $80 \leq E_r^i < 160$ | Considerable | $220 \leq RI < 440$ | High |
| $160 \leq E_r^i < 320$ | High | ≥ 440 | Very high |
| ≥ 320 | Very high | | |

Table 2. Summary statistics of heavy metal concentrations in surface sediments (mg/kg).

| Parameters | Cd | Cu | Ni | Pb | Zn | Mn |
|-------------------------|-------|-------|-------|-------|--------|--------|
| Minimum | 0.01 | 14.25 | 15.05 | 9.47 | 25.99 | 215.01 |
| Maximum | 5.57 | 50.92 | 49.35 | 74.05 | 376.02 | 888.73 |
| Mean | 1.27 | 28.74 | 30.54 | 26.95 | 146.45 | 428.63 |
| CV ^a | 1.07 | 0.40 | 0.30 | 0.56 | 0.85 | 0.36 |
| TEL | 0.596 | 35.7 | 18 | 35 | 123 | - |
| PEL | 3.53 | 197 | 36 | 91.3 | 315 | - |
| Background ^b | 0.097 | 20.4 | 29.8 | 26.6 | 62 | 530 |

^a CV: variation coefficient; ^b Background: the background values of heavy metals in surface sediments from Anhui province.

Results and Discussion

Concentrations and Spatial Distribution Patterns of Heavy Metals

The basic statistics related to the heavy metal concentrations as well as the background value and

SQGs were summarized in Table 2. According to the background values of heavy metals in Anhui province [22], the mean concentrations of the heavy metals (Cd, Cu, Ni, Pb, Zn, and Mn) in surface sediments were 1.27, 28.74, 30.54, 26.95, 146.45, and 428.63 mg/kg, respectively; by comparing these values to background concentrations (0.097, 20.4, 29.8, 26.6, 62, and

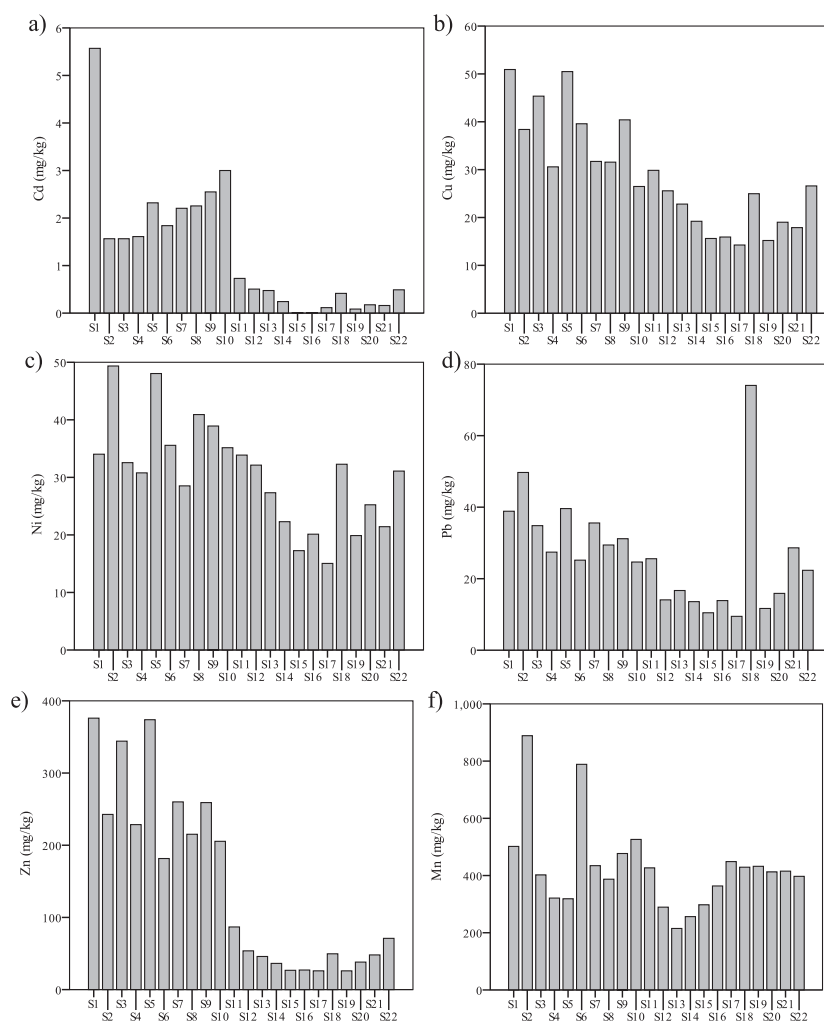


Fig. 2. Spatial distribution of the concentrations of heavy metals in surface sediments.

530 mg/kg, respectively), it can be seen that Cd content greatly exceeded the environmental background values. This finding was consistent with our previous reports in other regions of Bengbu city [23-24]. The CV reflected the average variability level of each site, the greater the CV value was, the more stronger human activities disturbed. As can be seen from Table 2, the CV of five heavy metals (Cu, Ni, Pb, Zn, and Mn) ranged from 30% to 85%, which showed moderate variability. However, the CV of Cd exceeded 100%, implying the possible effect of human activities on this metal. Compared with TEL and PEL, the mean concentrations of Cu and Pb were lower than TEL value, but the mean concentrations of Cd, Ni and Zn were between TEL and PEL, thus the adverse biological effect may occasionally occur for the latter three metals.

The heavy metal concentrations in surface sediments showed different spatial distribution patterns (Fig. 2). The Cd concentrations in sediments were highest at S1 and lowest at S15-S16. Otherwise, it can be obviously seen that the contents in the north lake (S1-S10) were

greater than that in the south lake (S11-S22). The Cu concentrations in sediments were also highest at S1 and lowest at S17, the higher concentrations occurred at S2-S3, S5-S6, and S9. The Ni concentrations were highest at S2 and lowest at S17, being higher at S1, S3-S6, S8-12, S18, and S22 than at S7, S13-S16, and S19-S21. The Pb concentrations were highest at S18 and lowest at S17, they were higher at S1-S5, S7-S9, and S21 than at S6, S10-S16, S19-S20, and S22. The abnormal concentration occurred in S18 may be due to the construction of the ancient dwellings. The Zn concentrations were highest at S1 and lowest at S19, just like the metal Cd, the contents in the north lake (S1-S10) were obviously greater than that in the south lake (S11-S22). The Mn concentrations were highest at S2 and lowest at S13, and it was another content peak occurred at S6 except for S2. In order to understand the difference between the north lake and the south lake, independent sample *t*-test was conducted for the comparison of heavy metal contamination. The result indicated that Cd (Fig. 2a), Cu (Fig. 2b), Ni

Table 3. I_{geo} assessment data of heavy metals in surface sediments and their levels.

| | I_{geo} values | | | | | | I_{geo} level | | | | | |
|------|------------------|-------|-------|-------|-------|-------|-----------------|----|----|----|----|----|
| | Cd | Cu | Ni | Pb | Zn | Mn | Cd | Cu | Ni | Pb | Zn | Mn |
| S1 | 5.26 | 0.73 | -0.39 | -0.04 | 2.02 | -0.66 | 6 | 1 | 0 | 0 | 3 | 0 |
| S2 | 3.43 | 0.33 | 0.14 | 0.32 | 1.38 | 0.16 | 4 | 1 | 1 | 1 | 2 | 1 |
| S3 | 3.43 | 0.57 | -0.46 | -0.20 | 1.89 | -0.98 | 4 | 1 | 0 | 0 | 2 | 0 |
| S4 | 3.47 | 0.00 | -0.54 | -0.54 | 1.30 | -1.31 | 4 | 1 | 0 | 0 | 2 | 0 |
| S5 | 4.00 | 0.72 | 0.10 | -0.01 | 2.01 | -1.32 | 4 | 1 | 1 | 0 | 3 | 0 |
| S6 | 3.66 | 0.37 | -0.33 | -0.66 | 0.97 | -0.01 | 4 | 1 | 0 | 0 | 1 | 0 |
| S7 | 3.92 | 0.05 | -0.65 | -0.17 | 1.48 | -0.87 | 4 | 1 | 0 | 0 | 2 | 0 |
| S8 | 3.95 | 0.04 | -0.13 | -0.44 | 1.21 | -1.04 | 4 | 1 | 0 | 0 | 2 | 0 |
| S9 | 4.13 | 0.40 | -0.20 | -0.36 | 1.48 | -0.74 | 5 | 1 | 0 | 0 | 2 | 0 |
| S10 | 4.37 | -0.21 | -0.35 | -0.69 | 1.14 | -0.60 | 5 | 0 | 0 | 0 | 2 | 0 |
| S11 | 2.33 | -0.04 | -0.40 | -0.64 | -0.10 | -0.90 | 3 | 0 | 0 | 0 | 0 | 0 |
| S12 | 1.80 | -0.26 | -0.48 | -1.50 | -0.79 | -1.46 | 2 | 0 | 0 | 0 | 0 | 0 |
| S13 | 1.71 | -0.42 | -0.71 | -1.26 | -1.02 | -1.89 | 2 | 0 | 0 | 0 | 0 | 0 |
| S14 | 0.74 | -0.67 | -1.00 | -1.55 | -1.36 | -1.63 | 1 | 0 | 0 | 0 | 0 | 0 |
| S15 | -3.86 | -0.97 | -1.37 | -1.93 | -1.80 | -1.42 | 0 | 0 | 0 | 0 | 0 | 0 |
| S16 | -3.86 | -0.94 | -1.15 | -1.52 | -1.78 | -1.13 | 0 | 0 | 0 | 0 | 0 | 0 |
| S17 | -0.34 | -1.10 | -1.57 | -2.07 | -1.84 | -0.83 | 0 | 0 | 0 | 0 | 0 | 0 |
| S18 | 1.51 | -0.29 | -0.47 | 0.89 | -0.91 | -0.89 | 2 | 0 | 0 | 1 | 0 | 0 |
| S19 | -0.78 | -1.01 | -1.17 | -1.77 | -1.84 | -0.88 | 0 | 0 | 0 | 0 | 0 | 0 |
| S20 | 0.27 | -0.69 | -0.82 | -1.33 | -1.29 | -0.95 | 1 | 0 | 0 | 0 | 0 | 0 |
| S21 | 0.14 | -0.77 | -1.06 | -0.48 | -0.95 | -0.94 | 1 | 0 | 0 | 0 | 0 | 0 |
| S22 | 1.75 | -0.20 | -0.52 | -0.84 | -0.39 | -1.00 | 2 | 0 | 0 | 0 | 0 | 0 |
| Mean | 1.86 | -0.20 | -0.61 | -0.76 | 0.04 | -0.97 | 2 | 0 | 0 | 0 | 1 | 0 |

(Fig. 2c), Zn (Fig. 2e), and Mn (Fig. 2f) concentration in surface sediments had significant variation ($p < 0.05$) from the two districts. However, it is no significant variation ($p > 0.05$) for Pb (Fig. 2d) in surface sediments.

I_{geo} Assessment

The I_{geo} values of the sampling sites are presented in Table 3. Among the metals, Cd showed the highest accumulation in the north lake, and the values ranged from 3.43 (S2, S3) to 5.26 (S1) which belonged to level 4 of heavily polluted sediment samples and level 6 of an extremely polluted sediment sample. While, in the south lake, the greatest value occurred in site 11, which is near Donghai Avenue, human activities take a direct role to the enrichment. Cd is not an essential element for life, but a highly toxic environmental pollutant that has an adverse impact on plants, animals, and human beings. Application of phosphate fertilization and waste

discharge may be the major anthropogenic sources of Cd in our study area. Except for S2, S18 (Pb), S5 (Ni), the I_{geo} value of Ni, Pb, and Mn indicated no pollution in sediments. Zn (mean: $I_{geo} = 0.04$) showed no pollution to moderate pollution due to the contribution of the higher I_{geo} value in the north lake, and the I_{geo} level of which belonged to level 1 (no pollution to moderate pollution) to level 3 (moderately to heavily polluted). All the sites except S10 indicated level 1 of Cu geo-accumulation in the north lake. Meanwhile, there was no Cu pollution in the south Lake. In general, Cd pollution along the Dragon Lake deserves attention, and the geoaccumulation of Zn and Cu in the north lake also need concern.

PERI Assessment

PERI assessment results of heavy metals in sediments are listed in Table 4. E_r^i and RI were obtained,

Table 4. PEPI assessment data of heavy metals in surface sediments.

| | E_r^i | | | | | | RI |
|-------|-----------|-------|------|-------|------|------|---------|
| | Cd | Cu | Ni | Pb | Zn | Mn | |
| S1 | 1722.68 | 12.48 | 5.71 | 7.31 | 6.06 | 0.95 | 1755.19 |
| S2 | 484.02 | 9.41 | 8.28 | 9.34 | 3.91 | 1.68 | 516.65 |
| S3 | 484.02 | 11.12 | 5.46 | 6.55 | 5.55 | 0.76 | 513.46 |
| S4 | 497.94 | 7.50 | 5.16 | 5.16 | 3.69 | 0.61 | 520.05 |
| S5 | 717.53 | 12.37 | 8.06 | 7.45 | 6.03 | 0.60 | 752.04 |
| S6 | 569.07 | 9.70 | 5.97 | 4.73 | 2.93 | 1.49 | 593.89 |
| S7 | 681.96 | 7.77 | 4.79 | 6.69 | 4.19 | 0.82 | 706.22 |
| S8 | 697.42 | 7.73 | 6.86 | 5.53 | 3.47 | 0.73 | 721.76 |
| S9 | 788.66 | 9.90 | 6.53 | 5.86 | 4.18 | 0.90 | 816.03 |
| S10 | 927.84 | 6.49 | 5.90 | 4.64 | 3.31 | 0.99 | 949.17 |
| S11 | 225.77 | 7.32 | 5.68 | 4.81 | 1.40 | 0.80 | 245.79 |
| S12 | 156.19 | 6.27 | 5.39 | 2.65 | 0.87 | 0.55 | 171.90 |
| S13 | 146.91 | 5.59 | 4.59 | 3.14 | 0.74 | 0.41 | 161.37 |
| S14 | 75.00 | 4.71 | 3.74 | 2.55 | 0.59 | 0.48 | 87.07 |
| S15 | 3.09 | 3.83 | 2.90 | 1.97 | 0.43 | 0.56 | 12.78 |
| S16 | 3.09 | 3.90 | 3.38 | 2.61 | 0.44 | 0.69 | 14.10 |
| S17 | 35.57 | 3.49 | 2.52 | 1.78 | 0.42 | 0.85 | 44.63 |
| S18 | 128.35 | 6.12 | 5.42 | 13.92 | 0.80 | 0.81 | 155.42 |
| S19 | 26.29 | 3.72 | 3.34 | 2.19 | 0.42 | 0.82 | 36.78 |
| S20 | 54.12 | 4.66 | 4.23 | 2.99 | 0.61 | 0.79 | 67.40 |
| S21 | 49.48 | 4.38 | 3.60 | 5.38 | 0.78 | 0.78 | 64.40 |
| S22 | 151.55 | 6.52 | 5.22 | 4.20 | 1.15 | 0.75 | 169.38 |
| Mean | 392.12 | 7.05 | 5.12 | 5.07 | 2.36 | 0.81 | 412.52 |
| Grade | Very high | Low | Low | Low | Low | Low | High |

Table 5. Result of correlation analysis.

| | Cd | Cu | Ni | Pb | Zn | Mn |
|----|---------|---------|---------|---------|-------|-------|
| Cd | 1.000 | | | | | |
| Cu | 0.824** | 1.000 | | | | |
| Ni | 0.749** | 0.805** | 1.000 | | | |
| Pb | 0.613** | 0.717** | 0.760** | 1.000 | | |
| Zn | 0.872** | 0.931** | 0.768** | 0.775** | 1.000 | |
| Mn | 0.379 | 0.324 | 0.323 | 0.345 | 0.271 | 1.000 |

** Coefficient is significant at P<0.01 (two-tailed).

and the pollution degree of the six heavy metals decreased in the order of Cd>Cu>Ni>Pb>Zn>Mn. Cd exhibited serious ecological risk, whereas the others had a low ecological risk. Specifically, all of the sampling points (S1-S10) for Cd showed very high ecological risk in the north lake, and the highest E_r^i appeared in S1 ($E_r^i = 1722.68$). While, in the south lake, one site (S11) presented high ecological risk, four sites (S12, S13, S18, and S22) posed considerable ecological risk, three sites (S14, S20, and S21) exhibited moderate ecological risk, and the rest sites (S15, S16, S17, and S19) were identified as the low ecological risk.

The *RI* values showed the overall pollution level of the study area. As can be seen from Table 4, *RI* ranged from 12.78~1755.19, with a mean value of 412.52 (high risk). All the sample points presented low to very high potential ecological risk, with the proportion of 31.82%, 18.18%, 4.55%, and 45.45%, respectively. These results

were dominated by Cd ecological risk. Therefore, Cd must be put in high attention and be of the prior contaminants considered to control.

Pollution Source Identification Based on PCM, HCA, and PCA

The correlation can provide useful information to understand the relationship among the heavy metals. PCM requires data that is correspondent to normal distribution [25]. In our study, Shapiro-Wilk test were performed to analyse data distribution. The results showed that Cu and Ni concentrations coincided with normal distributions ($p>0.05$), but the concentrations of Cd, Mn, Pb, and Zn could not pass the normality test ($p<0.05$) and needed data processing. In this study, rank cases were used for the data transformation and the relevant coefficients of heavy metal concentrations were presented in Table 5.

As can be seen from Table 5, there is a significantly positive correlation at $P<0.01$ level among the five heavy metals (Cd, Cu, Ni, Pb, and Zn), Mn had no significant relation with the other five heavy metals, indicating its different behaviors, sources or migration in surface sediments of the Dragon Lake.

Based on the data of heavy metal concentrations in different sites, HCA was performed using between-groups linkage method and squared Euclidean distance to analyze the similarity for the cases and the variables, then tested the differences between the groups. HCA classified the cases (sampling sites) and variables (heavy metals) into two clusters, and there were significant differences between them. As can be observed in Fig. 3, the first cluster includes all the sampling sites of north lake (S1-S10) linked with three sites of south lake (S11, S18, and S22), which have high enrichment of heavy metals. Cluster 2 comprises of the remaining sites of south lake (S12-S17, S19-S21), representing relatively low contamination area. The dendrogram (Fig. 4) showed two main clusters, metals (Cu, Zn, Cd, Ni, and Pb) in one cluster, and Mn in another group, indicating similar sources for metals (Cu, Zn, Cd, Ni, and Pb) and independent sources for Mn. This finding showed good agreement with PCM.

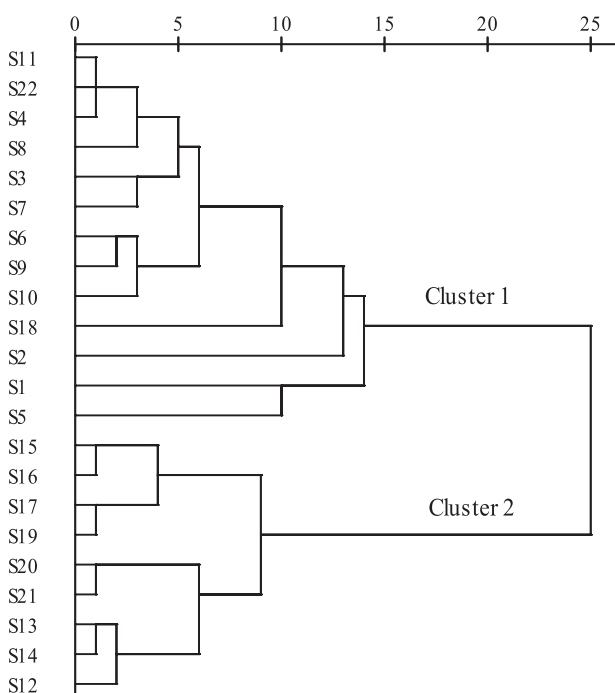


Fig. 3. Dendrogram of the sampling sites.

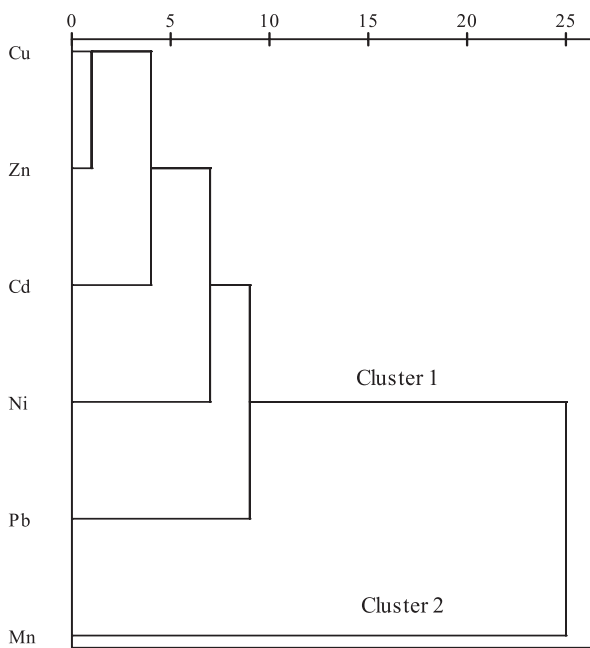


Fig. 4. Dendrogram of heavy metals.

To further discriminate the possible source of heavy metals, PCA was conducted on the normalized data of heavy metal concentrations in surface sediments of the Dragon Lake. The Kaiser-Meyer-Olkin value was 0.864 and Bartlett's test was 0 ($p < 0.05$) showed that PCA was effective to identify the sources of heavy metals in sediments [26]. As presented in Table 6, a total of two principal components were extracted with eigenvalues higher than 1.0. The first principal component (PC1) explained 65.97% of the total variance loaded heavily on Cd, Cu, Ni, Pb, and Zn, with the coefficients rotated 0.908, 0.926, 0.871, 0.772, and

0.938, respectively. The second principal component (PC2) dominated by Mn only, accounted for 19.95% of the total variance. The component plot in rotated space was shown in Fig. 5, the heavy metals (Cd, Cu, Ni, Pb and Zn) associated with PC1 were very close to each other, suggesting that these heavy metals may share the same source. However, Mn was far away from the other five metals, implying the different origin in surface sediments of the Dragon Lake. The results of PCA were well consistent with the results of PCM and HCA.

Two main sources of the heavy metals in sediments of the Dragon Lake could be identified by PCM, HCA, and PCA. Generally, the enrichment of Cd, Cu, Ni, Pb, and Zn are the superposition of anthropogenic source upon the natural background. As can be seen from Fig. 2, the concentrations of Cd, Cu, Ni, Pb, and Zn exceeded their background values, with the proportion 100%, 68.2%, 59.1%, 45.5%, and 59.1%, respectively, and the heavily polluted sites mainly located at the north lake and part of the south lake near Donghai Avenue. According to the investigation, the surrounding area used to be some villages in Bengbu city, agriculture land use was dominant in the past. Therefore, the long history of farming along with the use of fertilizers may result in extensive Cd accumulation in sediments [27-28]. Further, there used to be eastern traditional industrial zone near the north lake, so atmospheric deposition of pollutant and sewage sludge also have contributions to the increases of Cd contents. Pb was mainly contributed by fuel combustion and automobile exhaust, Zn originated from automobile tire wear whereas Cu and Ni may also derive from exhaust fumes to a lesser extent [29-34]. Usually, Cu, Zn, and Pb are indicative elements related to human activities in local scale [35-36]. In the study area, these four metals were primarily distributed in sediments located in close vicinity to the main city roads (such as Donghai avenue) and construction land. Therefore, PC1 can be explained to be the sources related to anthropogenic sources, including the use of fertilizers in agriculture,

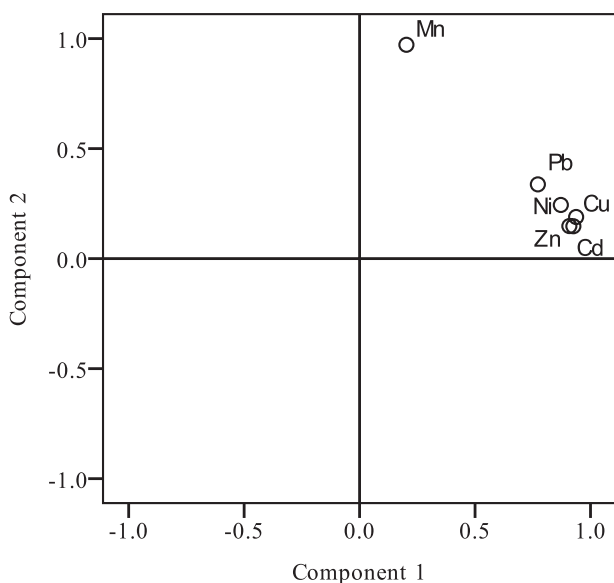


Fig. 5. Component plot in rotated space.

Table 6. Rotation component matrix.

| Elements | Component | |
|-----------------------|-----------|-------|
| | PC1 | PC2 |
| Cd | 0.908 | 0.148 |
| Cu | 0.926 | 0.147 |
| Mn | 0.203 | 0.972 |
| Ni | 0.871 | 0.244 |
| Pb | 0.772 | 0.337 |
| Zn | 0.938 | 0.189 |
| Eigenvalue | 3.958 | 1.197 |
| % of variance explain | 65.97 | 19.95 |
| % of cumulative | 65.97 | 85.92 |

industrial emissions and traffic pollution. For the PC2, Mn was shown to have higher loads and can be explained to be the source related to geological weathering or dissolution. That is because the concentration of Mn was lower than the background value, and the I_{geo} and PERI assessment of Mn content also present zero or a low potential ecological risk. Moreover, previous studies revealed that the metal is always released by silicate weathering processes and adsorbed by clays [37-40].

Conclusions

Six heavy metals of 22 sites were studied in the nearshore surface sediments of Dragon Lake, Bengbu, China. Results showed that the mean contents of the heavy metals (Cd, Cu, Ni, Pb, and Zn) exceeded their background values in local natural soils by 13.1, 1.41, 1.02, 1.01, and 2.36 times, respectively, and the concentration of Mn was within the background value. Compared with some Lakes in China and abroad, Cd concentration in Dragon Lake were at the moderate level, and the others metals were at a low level in general. I_{geo} and PERI assessment indicated that Cd showed the highest accumulation and ecological risk among the six heavy metals, due to the contribution of Cd, the pollution level of the study area was high overall. Spatial pattern implied that high Cd values were mainly located in north lake with frequent human activities. These findings indicated that the heavy metals in sediments were influenced by anthropogenic factors. The combined analyses of multivariate techniques (PCM, HCA, and PCA) showed that the metals (Cd, Cu, Ni, Pb, and Zn) were mainly from anthropogenic sources, including agriculture, industrial emissions and traffic pollution. Mn was dominantly related to natural source. Based on our study, it is proposed to move the heavy polluted industries to the other places, reduce vehicle exhaust, and control phosphate fertilizer input in the study area, and the north part of Dragon Lake should be given priority for water management.

Acknowledgements

This work was supported by National Natural Science Foundation of China (41773100), the Plan for Excellent Young Talents of Anhui Higher Education Institutions of China (gxyqZD2019082, gxyq2018106), Natural Science Foundation of Bengbu University (2018ZR04zd) and College-enterprise Cooperative Project (BBXYHX2017017).

Conflict of Interest

The authors declare no conflict of interest.

References

1. JI Z.H., ZHANG H., ZHANG Y., CHEN T., LONG Z.W., LI M., PEI Y.S. Distribution, ecological risk and source identification of heavy metals in sediments from the Baiyangdian Lake, Northern China. *Chemosphere*, **237**, 124425, **2019**.
2. KE X., GUI S.F., HUANG H., ZHANG H.J., WANG C.Y., GUO W. Ecological risk assessment and source identification for heavy metals in surface sediment from the Liaohe River protected area, China. *Chemosphere*, **175**, 473, **2017**.
3. DUODU G.O., GOONETILLEKE A., AYOKO G.A. Comparison of pollution indices for the assessment of heavy metal in Brisbane River sediment. *Environmental Pollution*, **219**, 1077, **2016**.
4. MALVANDI H. Preliminary evaluation of heavy metal contamination in the Zarrin-Gol River sediments, Iran. *Marine Pollution Bulletin*, **117** (1-2), 547, **2017**.
5. WANG R., ZHANG C., HUANG X.T., ZHAO L., YANG S.Y., STRUCK U., YIN D.Q. Distribution and source of heavy metals in the sediments of the coastal East China sea: Geochemical controls and typhoon impact. *Environmental Pollution*, **260**, 11936, **2020**.
6. DING X.G., YE S.Y., LAWS E.A., MOZDZER T.J., YUAN H.M., ZHAO G.M., YANG S.X., HE L., WANG J. The concentration distribution and pollution assessment of heavy metals in surface sediments of the Bohai Bay, China. *Marine Pollution Bulletin*, **149**, 110497, **2019**.
7. ZHONG W.J., ZHANG Y.F., WU Z.H., YANG R.Y., CHEN X.Y., YANG J., ZHU L.Y. Health risk assessment of heavy metals in freshwater fish in the central and eastern North China. *Ecotoxicology and Environmental Safety*, **157**, 343, **2018**.
8. ARFAEINIA H., DOBARADARAN S., MORADI M., PASALARI H., MEHRIZI E.A., TAGHIZADEH F., ESMAILI A., ANSARIZADEH M. The effect of land use configurations on concentration, spatial distribution, and ecological risk of heavy metals in coastal sediments of northern part along the Persian Gulf. *Science of the Total Environment*, **653**, 78, **2019**.
9. BOSCH A.C., O'NEILL B., SIGGE G.O., KERWATH S.E., HOFFMAN L.C. Heavy metals in marine fish meat and consumer health: a review. *Journal of the Science of Food and Agriculture*, **96** (1), 32, **2016**.
10. SHENG D., ZHU L.B., SHAO F.W. Water quality monitoring and evaluation of Longzi Lake in Bengbu City. *Journal of Changchun Normal University*, **4** (3), 35, **2015** [In Chinese].
11. SHENG D., ZHU L.B. Species and bioavailability of phosphorus in surface sediments of Longzihu Lake. *Journal of Bengbu University*, **34** (2), 90, **2015** [In Chinese].
12. MULLER G. Index of geoaccumulation in sediments of the Rhine River. *Geojournal*, **2** (3), 108, **1969**.
13. ALVES C.M., FERREIRA C.M.H., SOARES H.M.V.M. Relation between different metal pollution criteria in sediments and its contribution on assessing toxicity. *Chemosphere*, **208**, 390, **2018**.
14. DUNG T.T.T., CAPPUYNS V., SWENNEN R., PHUNG N.K. From geochemical background determination to pollution assessment of heavy metals in sediments and soils. *Reviews in Environmental Science and Bio-Technology*, **12** (4), 335, **2013**.

15. JONATHAN M.P., SHUMILIN E., RODRIGUEZ-FIGUEROA G.M., RODRIGUEZ-ESPINOSA P.F., SUJITHA S.B. Potential toxicity of chemical elements in beach sediments near Santa Rosalia copper mine, Baja California Peninsula, Mexico. *Estuarine Coastal and Shelf Science*, **180**, 91, **2016**.
16. CHOWDHURY R., FAVAS P.J.C., PRATAS J., JONATHAN M.P., GANESH P.S., SARKAR S.K. Accumulation of Trace Metals by Mangrove Plants in Indian Sundarban Wetland: Prospects for Phytoremediation. *International Journal of Phytoremediation*, **17** (9), 885, **2015**.
17. HAKANSON L. An Ecological Risk Index for Aquatic Pollution-Control-a Sedimentological Approach. *Water Research*, **14** (8), 975, **1980**.
18. CAO Q.Q., SONG Y., ZHANG Y.R., WANG R.Q., LIU J. Risk analysis on heavy metal contamination in sediments of rivers flowing into Nansi Lake. *Environmental Science and Pollution Research*, **24** (35), 26910, **2017**.
19. MACDONALD D.D., CARR R.S., CALDER F.D., LONG E.R., INGERSOLL C.G. Development and evaluation of sediment quality guidelines for Florida coastal waters. *Ecotoxicology*, **5** (4), 253, **1996**.
20. BRAMHA S.N., MOHANTY A.K., SATPATHY K.K., KANAGASABAPATHY K.V., PANIGRAHI S., SAMANTARA M.K., PRASAD M.V.R. Heavy metal content in the beach sediment with respect to contamination levels and sediment quality guidelines: a study at Kalpakkam coast, southeast coast of India. *Environmental Earth Sciences*, **72** (11), 4463, **2014**.
21. ZHANG Y.F., HAN Y.W., YANG J.X., ZHU L.Y., ZHONG W.J. Toxicities and risk assessment of heavy metals in sediments of Taihu Lake, China, based on sediment quality guidelines. *Journal of Environmental Sciences*, **62**, 31, **2017**.
22. LI J., ZHENG C., GUO X. Manual data of environmental background value. China Environment Science Press, Beijing, China, **1989**.
23. MA L., GUI H.R. Anthropogenic impacts on heavy metal concentrations in surface soils from the typical polluted area of Bengbu, Anhui province, Eastern China. *Human and Ecological Risk Assessment*, **23** (7), 1763, **2017**.
24. MA L., GUI H.R. Accumulation of Heavy Metals in Surface Soils of Bengbu Higher Education Mega Center, China. *Fresenius Environmental Bulletin*, **26** (7), 4697, **2017**.
25. LI F., HUANG J.H., ZENG G.M., YUAN X.Z., LI X.D., LIANG J., WANG X.Y., TANG X.J., BAI B. Spatial risk assessment and sources identification of heavy metals in surface sediments from the Dongting Lake, Middle China. *Journal of Geochemical Exploration*, **132**, 75, **2013**.
26. MA L., YANG Z.G., LI L., WANG L. Source identification and risk assessment of heavy metal contaminations in urban soils of Changsha, a mine-impacted city in Southern China. *Environmental Science and Pollution Research*, **23** (17), 17058, **2016**.
27. NIU Y., JIANG X., WANG K., XIA J.D., JIAO W., NIU Y., YU H. Meta analysis of heavy metal pollution and sources in surface sediments of Lake Taihu, China. *Science of the Total Environment*, **700**, 134509, **2020**.
28. LI B., WANG H., YU Q.G., WEI F., ZHANG Q. Ecological assessment of heavy metals in sediments from Jianhu Lake in Yunnan Province, China. *Polish Journal of Environmental studies*, **29** (6), 1, **2020**.
29. XIA P., MENG X.W., YIN P., CAO Z.M., WANG X.Q. Eighty-year sedimentary record of heavy metal inputs in the intertidal sediments from the Nanliu River estuary, Beibu Gulf of South China Sea. *Environmental Pollution*, **159** (1), 92, **2011**.
30. BOURLIVA A., CHRISTOPHORIDIS C., PAPADOPOULOU L., GIOURI K., PAPADOPOULOS A., MITSIKA E., FYTIANOS K. Characterization, heavy metal content and health risk assessment of urban road dusts from the historic center of the city of Thessaloniki, Greece. *Environmental Geochemistry and Health*, **39** (3), 611, **2017**.
31. KESHAVARZI B., TAZARVI Z., RAJABZADEH M.A., NAJMEDDIN A. Chemical speciation, human health risk assessment and pollution level of selected heavy metals in urban street dust of Shiraz, Iran. *Atmospheric Environment*, **119**, 1, **2015**.
32. LIN M.L., GUI H.R., WANG Y., PENG W.H. Pollution characteristics, source apportionment, and health risk of heavy metals in street dust of Suzhou, China. *Environmental Science and Pollution Research*, **24** (2), 1987, **2017**.
33. LI F., ZHANG J.D., HUANG J.H., HUANG D.W., YANG J., SONG Y.W., ZENG G.M. Heavy metals in road dust from Xiandao District, Changsha City, China: characteristics, health risk assessment, and integrated source identification. *Environmental Science and Pollution Research*, **23** (13), 13100, **2016**.
34. PATHAK A.K., YADAV S., KUMAR P., KUMAR R. Source apportionment and spatial-temporal variations in the metal content of surface dust collected from an industrial area adjoining Delhi, India. *Science of the Total Environment*, **443**, 662, **2013**.
35. SUN L.H., FENG S.B. Heavy Metals in the Surface Soil around a Coalmine: Pollution Assessment and Source Identification. *Polish Journal of Environmental Studies*, **28** (4), 2717, **2019**.
36. LIANG X.M., SONG J.M., DUAN L.Q., YUAN H.M., LI X.G., LI N., QU B.X., WANG Q.D., XING J.W. Source identification and risk assessment based on fractionation of heavy metals in surface sediments of Jiaozhou Bay, China. *Marine Pollution Bulletin*, **128**, 548, **2018**.
37. ZAHRA A., HASHMI M.Z., MALIK R.N., AHMED Z. Enrichment and geo-accumulation of heavy metals and risk assessment of sediments of the Kurang Nallah-Feeding tributary of the Rawal Lake Reservoir, Pakistan. *Science of the Total Environment*, **470**, 925, **2014**.
38. CHEN X.D., LU X.W., YANG G. Sources identification of heavy metals in urban topsoil from inside the Xi'an Second Ringroad, NW China using multivariate statistical methods. *Catena*, **98**, 73, **2012**.
39. DRAGOVIC S., MIHAILOVIC N., GAJIC B. Heavy metals in soils: Distribution, relationship with soil characteristics and radionuclides and multivariate assessment of contamination sources. *Chemosphere*, **72** (3), 491, **2008**.
40. SUN L.H. Pollution Assessment and Source Approximation of Trace Elements in the Farmland Soil near the Trafficway. *Journal of Environmental Engineering and Landscape Management*, **28** (1), 20, **2020**.