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RESEARCH ARTICLE

Ecological assessment and source identification based on chemical forms and content of heavy metals in the sediment of Baiyangdian Lake

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Abstract This study reveals the superimposing ecological risk of chemical form and total amount of heavy metals (HMs) and their source in the sediments of Baiyangdian Lake, also provides important scientific basis for environmental protection and sustainable development of the Xiong'an New Area. The total amount and distribution of typical HMs (As, Cd, Cr, Cu, Pb, and Zn) in the sediments of Baiyangdian Lake and its peripheral rivers were analyzed. Moreover, five chemical forms (F1−F5) of HMs in the sediments of Baiyangdian Lake were identified by an improved Tessier five-step method. Risk Assessment Coding Method (RAC) and mean sediment quality guideline quotient (SQG-Q) were used to assess ecological risk. In addition, the improved enrichment coefficient and statistical methods were used to identify the sources of HMs. The contents of HMs in the lake sediment is about 1 to 3 times the background values, with higher concentration in the central area and lower concentration in the northern and southern areas. The pH and organic matter concentrations were 6.99 to 7.28 and 3.98% to 5.69%, respectively. The chemical form of HM in the lake sediments is mainly in residue form. Ion-exchangeable form and carbonate bound form of Cd account for the highest proportion (19% to 42% and 17% to 25%, respectively); Pb and As have a higher proportion of iron and manganese oxidation form (21% to 51% and 15% to 31%, respectively); Cu and Zn have a higher proportion of organic bound form (11% to 39% and 8% to 25%, respectively). RAC indicates a high potential risk for Cd, Pb, and As, and the SQG-Q indicated a high ecological risk for As, Cr and Pb. The form and behavior of HMs, such as bioavailability and toxicity, are largely influenced by the physicochemical properties of the sediments. Organic matter and pH mainly affect the ion exchange form of HMs, while the total amount of HMs mainly affects the binding form and residual form of HMs with organic matter. Changes in the content and morphology of Cu, Zn, and Cd in Baiyangdian sediments are mainly influenced by inflow river, which are mainly from human industrial activities, such as wastewater discharge. There are various sources of HMs, such as Pb, which mainly comes from human life activities such as domestic waste, leaching, aquaculture, and tourism in Baiyangdian village, influenced by lead and natural environment and related to the spatial location of the lake; while the source of chromium is more complex.

Keywords risk assessment, heavy metal, source identification, sediment, Xiong'an New Area

1 Introduction

Pollutants are mainly deposited in the sediments at the bottom of the lake. When the physicochemical environment of the water changes, the pollutants in the sediments will migrate into the water, directly or indirectly causing toxic effects on aquatic organisms, and serious environmental problems may erupt at any time (Goretti et al., 2016). However, some pollutants, such as HMs, can be deposited in lake sediments for long periods of time and are difficult to detect. HMs accumulate in sediments, thus causing toxic effects on water bodies and organisms, and even affecting human health through the food chain. Therefore, the pollution and source of HMs in lake sediment have attracted widespread attention of scholars around the world, and become a research hotspot in environmental area.

Baiyangdian Lake is the most representative lake in

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northern China, playing an irreplaceable role in maintaining the aquatic environment and is known as the “pearl of north China”. The Chinese government attaches great importance to the ecological environment of Baiyangdian Lake, especially after the establishment of Xiong’an New Area around Baiyangdian Lake, the ecological status has become increasingly high and its environmental change has become the focus of widespread attention. At present, the research on the aquatic environment in Baiyangdian Lake mainly focuses on the assessment of HMs pollution (Yang et al., 2005; Dai et al., 2011; Hu et al., 2011; Su et al., 2011; Gao et al., 2018; Gao et al., 2019), benthic community (Zhang et al., 2018a), eutrophication (Zhao et al., 2011; Gao et al., 2013), wetland landscape pattern evolution (Bai et al., 2013), and water quality change and its causes (Wang et al., 2010; Zhuang et al., 2011; Gao et al., 2017; Yuan et al., 2017).

However, previous studies on the assessment and sources of HMs in the Baiyangdian Lake sediment are mostly based on the total amount of HMs, such as geo-accumulation index, enrichment coefficient, and potential ecological risk coefficient, while there are few relevant reports concerning chemical forms. The mobility, bioavailability, ecological effects, and toxicity of HMs are mainly determined by their chemical forms (Gao et al., 2012; Wang et al., 2013). HMs in the form of certain ions or molecules in the soil can change its chemical forms via dissolution, precipitation, coagulation, and complexing adsorption, thus exhibiting different activities and causing different degrees of damage to soil (Cai et al., 2019). Many studies have reported that the chemical forms and bioavailability of HMs in the soil are an important method for assessing the risk of HMs in soil (Liu et al., 2017; Dai et al., 2018). Therefore, the analysis of the chemical form of HMs in lake sediment is beneficial to comprehensively assess their ecological risk. Moreover, HMs from human sources mainly occur in secondary phase, especially extractable chemical forms (Chen et al., 2011). Therefore, chemical form analysis is more critical in determining the sources of HMs. In conclusion, the superimposed influence of chemical forms and total amount of HM was not reflected in the previous analysis of the risk and sources of HM in Baiyangdian Lake.

In addition, studies have shown that the content of HMs in the sediments of Baiyangdian Lake generally shows a decreasing trend (Table 1), but the content of some HMs, such as Cd, fluctuate greatly from year to year. These studies have improved understanding of the sediment and aquatic environment of Baiyangdian Lake, but there are many rivers flowing into the periphery that could potentially affect the content of HMs in the Lake. Therefore, it is necessary to expand the research area to the peripheral rivers. In view of the above issues, this study identified the content and distribution characteristics of typical HMs in the sediments of Baiyangdian Lake and its peripheral rivers. In addition, five chemical forms of HMs in lake sediments were identified, and the relationship between the total amount and their physicochemical properties was discussed based on the chemical forms. Risk Assessment Coding Method (RAC) and mean sediment quality guideline quotient (SQG-Q) were used to comprehensively assess the potential ecological risk of HMs. And the sources of HMs pollution were traced by statistical methods in terms of both total and chemical forms. Thus, the superimposed ecological risk of chemical forms and total amount of HMs in Baiyangdian sediments and their sources were revealed, and the influence of physicochemical properties on HM forms was identified, which also provides an important scientific basis for the environmental protection and sustainable development of Xiong’an New Area.

2 Study area

Baiyangdian Lake, located in Anxin County, Baoding City, is the largest freshwater lake in north China, with a total area of about 366 km^2 and the geographical coordinates of 115°45′E–116°07′E, 38°44′N–38°59′N (Fig. 1).

The villages and water in Baiyangdian Lake area cross each other, and the landforms are connected by trenches. The area is affected by the East Asian monsoon, belonging to the warm temperate semi-arid continental climate, with multi-year average temperature of 7.3℃ to 12.7℃ and an average annual precipitation of 563.9 mm.

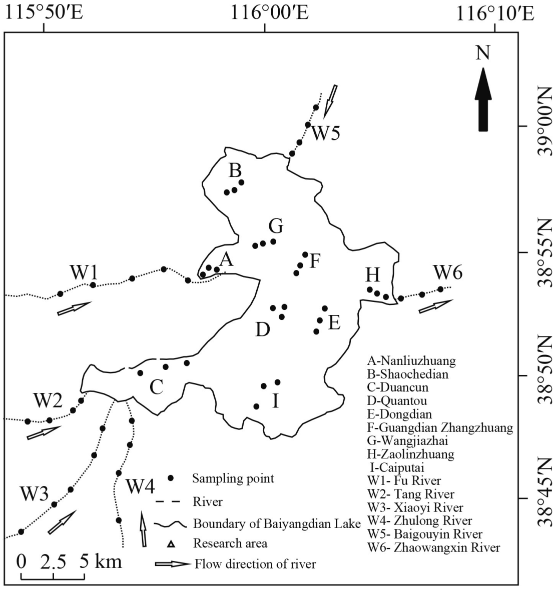


Fig. 1 Location of sampling points in Baiyangdian Lake and peripheral rivers.

Table 1 Average contents of HMs in Baiyangdian sediments obtained by predecessors (mg·kg^{-1})

Cu	Zn	Pb	Cd	Data sources
30.66	112.33	54.61	7.03	Yang et al. (2005)
31.67	118.64	55.43	6.92	Li et al. (2007)
35.00	112.00	30.00	0.90	Su et al. (2011)
28.73	73.25	32.60	1.79	Lu (2016)

In recent years, the economy has developed rapidly year by year in the upstream and surrounding areas of Baiyangdian Lake. By 2013, the resident population of Baoding has exceeded 10 million. At the same time, the population within Baiyangdian aera has also increased rapidly, with about 100000 people living here, posing an increasingly serious threat to the ecological environment of the lake (Zhang et al., 2016). The inflow rivers around Baiyangdian Lake mainly include Fu River, Tang River, Xiaoyi River, Zhulong River, and Baigou River, and the outflow rivers are Zhaowangxin River (Fig. 1). These rivers are the most important source of water, but the development of surrounding industries is also a serious threat to the environment of the watershed (Zhuang et al., 2011; Zhang et al., 2018b).

3 Materials and methods

3.1 Sample collection and preparation

Based on the distribution of rivers and waters around Baiyangdian and the extent of human activities, a total of 52 surface sediment samples ranging from 0 to 10 cm in size were taken using a Peterson Mud Harvester (TC-600 type) in October, 2020 (Fig. 1). Among them, 27 samples were collected in 9 representative regions of Baiyangdian (including Nanliuzhuang (A), Shaochedian (B), Duancun (C), Quantou (D), Dongdian (E), Guangdianzhangzhuang (F), Wangjiazhai (G), Zaolinzhuang (H) and Caiputai (I)), and 25 samples were collected in peripheral rivers (including Fu River, Tang River, Xiaoyi River, Zhulong River, Baigou River and Zhaowangxin River). The collected sediment samples were sealed in clean PTFE bags, numbered, and shipped to the laboratory.

Sediment samples were frozen, dried in a vacuum freeze dryer, and cleared of sand, animal, and plant debris. The samples were ground with an agate bowl and passed through a 100-mesh nylon sieve. Then they were packed in polyethylene plastic self-sealing bags and stored in a refrigerator at −4°C.

3.2 Test methods

3.2.1 Physicochemical properties

The pH value was determined by glass electrode method with a water-soil ratio of 1:5 and the organic matter content (OM) was determined by the potassium dichromate method (Wu, 2017).

3.2.2 Method for determination of total amount of HMs

The content of HMs in sediments were determined by aqua regia extraction-inductively coupled plasma mass spectrometry according to the national environmental protection standards of China (Ministry of Environmental Protection, 2016): this method specifies to drop 15 mL aqua regia into a 100 mL conical flask and add 3 or 4 small glass beads, place the conical flask on the glass funnel, and heat to boiling on the electric heating plate, make aqua regia vapor soak into the inner wall of the conical flask about 30 min, cool and discard, wash the inner wall of the conical flask with deionized water and dry. A sample of 0.1 g (accurate to 0.0001 g) was weighed in a 100 mL conical flask, and then 6 mL of aqua regia was dropped into the conical flask. Again, the conical flask was heated on an electric heating plate to keep the aqua regia slightly boiling for 2 h. After sufficient dissolution, the extracted solution was cooled to room temperature and filtered slowly and quantitatively through filter paper into a 50 mL volumetric flask. The glass funnel, conical flask and filtered residue were washed three times with a quantitative standard solution of nitric acid. The cleaning solution was also filtered into a volumetric flask and deionized water was added to a standard volume. The contents of Cu, Zn, Pb, Cr, As, and Cd in sediment were detected by inductively coupled plasma mass spectrometer (ICP-MS, iCAP Qc, Thermo Fisher, USA). To ensure the accuracy of the results, the content of HMs in the standard reference sample of stream sediment (GSD-9) was tested during the analysis, and the analysis error of each element was within 5%.

3.2.3 Determination method of chemical form of HMs

The chemical forms of HMs were determined by the improved Tessier five-step method as the following simplified steps (Tessier et al., 1979).

Step 1 (ion exchange form, F1). 1.0 g sediment sample was extracted with 10 mL of $MgCl_2$ (1M, pH 8.2) solution at room temperature for 1 h and stirred continuously. The mass of the dried residue was weighed and calculated using a precision balance.

Step 2 (carbonate bound form, F2). The residue of step 1 was washed with 10 mL 1.0 M NaAC (1M, adjusted pH to 5.0 by HOAC) at room temperature with continuous stirring for 5 h.

Step 3 (iron manganese oxidation form, F3). The residue of step 2 was extracted for 5 h at (96±3)°C using a mixed solution of 20 mL NH_4Cl (0.04 M) and 25% (v/v) HOAC with regular stirring.

Step 4 (organic bound form, F4). The residue of step 3 was extracted with a mixed solution of 3 mL HNO_3 (0.02M) and 5 mL H_2O_2 (30%, v/v) (adjusted pH to 2.0 by HNO_3) at (85±2)°C for 3 h, stirring several times. After the solution was cooled, added another mixed solution of 5 mL NH_4OAC (3.2M) and HNO_3 (20%, v/v), and the mixed solution was kept at a constant volume of 20 mL, continuous stirring for 30 min.

Step 5 (residue form, F5). To balance the detected HMs, aqua regia was used to replace $HF\text{-}HClO_4$ used in the Tessier method, and the residue of step 4 was digested with aqua regia in PTFE cup for 2 h.

Continuous extraction of HMs were carried out in a 50 mL centrifuge tube. After each extraction, the sample needed to be centrifuged for 30 min, and the upper solution was transferred to a 25 mL calibration flask with a liquid transfer tube. The precipitate was centrifuged again and washed thoroughly with deionized water. The supernatant was also moved into the calibration flask and deionized water was added to the standard volume. The extraction substances in each step were detected by ICP-MS using the above extracted aqua regia.

To determine the accuracy of this method, three replicates were performed for each sample. To check the accuracy and reproducibility of the successive extraction values of sediment samples, the coverage rate of successive extraction of HMs was calculated as Eq. (1):

$$R = \frac{C_{\mathrm{F1}} + C_{\mathrm{F2}} + C_{\mathrm{F3}} + C_{\mathrm{F4}} + C_{\mathrm{F5}}}{C_{\mathrm{t}}} \times 100, \tag{1}$$

where C_{F1}, C_{F2}, C_{F3}, C_{F4} and C_{F5} are the contents of five forms of HMs; C_{t} is the actual measured total amount of HMs.

3.3 Methods of risk assessment

3.3.1 Risk Assessment Coding Method (RAC)

HM in the form of ionic compounds and carbonates has rapid bioavailability due to its weak chemical bonding and easy exchange with the upper water layer (Ghrefat et al., 2006; Huang et al., 2011). Generally, the higher the bioavailability of HMs, the greater the risk they pose to the environment, and vice versa. Risk Assessment Coding Method (RAC) is a significant risk quantification method for HMs in sediments in recent years (Liu et al., 2008; Liu et al., 2011; Sundaray et al., 2011; Yu et al., 2011). This method assesses the effectiveness (availability) of HMs and their risks to the environment based on the mass fraction of ion-exchange form (F1) and carbonate-bound form (F2). To facilitate the quantitative assessment of environmental risks, RAC classifies the mass fractions of ion exchange form (F1) and carbonate bound form (F2) into 5 levels, as shown in Table 2.

Table 2 Judgment criteria of Risk Assessment Coding Method

Risk level	None	Low	Medium	High	Extremely high
Mass fraction of F1 and F2 in all forms	<1	1–10	11–30	31–50	>50

3.3.2 SQG-Q

The recently revised guidelines were applied in the ecological risk assessment index obtained by using the SQG-Q method and the guidelines had a high degree of confidence and acceptable uncertainty due to the integrated consideration of various contamination factors (Caeiro et al., 2005). This method was based on the probable effect level (PEL), which was used to calculate the SQG-Q, as follows in Eqs. (2) and (3):

$$\text{SQG-Q} = \frac{\sum_{i=1}^{n} (\text{PEL} - \text{Q})_i}{n}, \tag{2}$$

$$(\text{PEL-Q})_i = \frac{C_i}{\text{PEL}_i}, \tag{3}$$

where PEL-Q: the probable effect level quotient; C_i: the actually tested content of HM i; PEL_i: the probable effect level of HM i.

According to the Eq. (2), the SQG-Q can be calculated to assess the ecological risk of HMs in the sediments of the study area. In addition, the threshold of PEL is named TEL.

Generally, SQG-Q⩽0.1 indicates that the region is not affected by HMs, with the lowest potential adverse biological toxicity. If 0.1<SQG-Q<1.0, it indicates that there is a moderate potential adverse biological toxicity effect. If SQG-Q⩾1.0, there is a very high potential adverse biological toxicity effect in this region. Here, PEL or TEL is derived from the Biological Effects Database of North American Sediment (BEDS). In fact, PEL and TEL can also be used to distinguish the biological toxicity of all HMs (MacDonald et al., 2000; Ma et al., 2018). In other words, when the content of HM is lower than TEL, adverse biological toxicity effects rarely occur. When the content of HM is higher than PEL, the adverse biological toxicity effect might occur frequently.

3.3.3 Source identification method based on chemical form of HMs

According to the geochemical theory, many scholars define the residual form (F5) as primary phase, and other forms (F1 + F2 + F3 + F4) as secondary phase (Wang et al., 2010).

Enrichment factor (*EF*) can be used not only to assess the level of HMs pollution, but also identify the sources of HMs in sediments. When *EF* < 1.5, it indicates that HMs mainly come from the natural weathering process of the crust and lithosphere. When *EF* > 1.5, it is believed that HMs mainly come from human activities (Su et al., 2015). However, it is difficult to determine the source of HMs by *EF* value because of its large *EF* value span. Therefore, this study improves the source identification method of *EF*, and makes correlation analysis between *EF* value and content of primary and secondary phase of HMs to determine their sources.

The calculation formula of enrichment coefficient is as Eq. (4):

$$EF = (C_i / C_r) / (B_i / B_r), \tag{4}$$

where C_i: measured contents of studied HM, mg·kg^{-1}; C_r: measured contents of reference HM, mg·kg^{-1}; B_i: environmental background contents of studied HM, mg·kg^{-1}; B_r: environmental background contents of reference HM, mg·kg^{-1}.

Generally, Fe, Al, Ti, and Mn can be selected as reference HMs (Bourliva et al., 2017), especially Mn is used as the reference HM in many studies (Han et al., 2006; Hu et al., 2013; Bourliva et al., 2017), so, Mn was also selected as the reference HM in this study.

3.4 Data processing

Coreldraw was used to draw some figures; EXCEL was used for chart processing of relevant data; SPSS 19.0 for Windows was used for correlation analysis and cluster analysis of relevant data.

4 Results

4.1 The content and distribution of HMs in the sediments

The variation characteristics of HMs in sediments of Baiyangdian and peripheral rivers are shown in Fig. 2. For each peripheral river, except Zn, the average content of other HMs in sediment is higher than that in Hebei soil background. Among them, Pb is significantly enriched in sediments of the Xiaoyi River, and the highest content is 390.12 mg·kg^{-1}, which is about 18.15 times the background value, while the average contents of Cu, Zn, Cd, and Cr in the sediments of the Fu River are the largest, which are 2.67, 4.08, 11.81, and 1.43 times the background value, respectively. Arsenic has the largest average content in sediments of the Xiaoyi River, which is 2.82 times the background value. Overall, the HMs content of inflow rivers (including Fu River, Tang River, Xiaoyi River, Zhalong River, Baigou River) is significantly higher than that of outflow rivers (Zhaowangxin River). Among them, the Xiaoyi River has the highest content of HMs, followed by the Fu and Tang Rivers.

For the sediments of Baiyangdian Lake, the average contents of Pb, Cu, Zn, Cd, Cr, and As are all higher than the soil background value of Hebei Province, which are about 1.85, 1.42, 1.19, 3.4, 1.21, and 1.39 times, respectively (Table 3). Figure 2 shows that Pb has the highest content in Quantou (D), with an average value of 71.24 mg·kg^{-1}; the average contents of Cu, Zn, Cd, and As in Dongdian (E) and Guangdian Zhangzhuang (F) are generally higher than those in other regions; the average contents of Cu, Zn, Cd, and As in the two regions are respectively 41.36, 110.37, 0.45, 32.76 mg·kg^{-1} and 32.36, 120.68, 0.46, 29.12 mg·kg^{-1}, which are 1.90, 1.40, 4.88, 2.4 and 1.48, 1.53, 4.89, 2.14 times the background value, respectively; Cr has the highest content in Zaolinzhuang (H), with an average value of 140.32 mg·kg^{-1}, which is about 2.05 times the background value.

It can be seen from Table 3 that for the variation coefficient of HMs in sediments, As > Pb > Cr > Cd > Zn > Cu. The variation coefficient of all HMs is between 0.1 and 1, indicating that the HMs in Baiyangdian Lake have a medium degree of change. Table 4 shows that the pH of the sediments is 6.99 to 7.28, which is generally near neutral; the organic matter content ranges from 4.06% to 5.65%.

In general, the content of HMs in the sediments of Baiyangdian Lake presents a different spatial distribution pattern (Fig. 2), which is characterized by “higher content in the central regions and lower content in the north and south”. Among them, the HMs content of sediments in Guangdian Zhangzhuang (F), Wangjiazhai (G), and Dongdian (E) is relatively high; while Caiputai is a static water area, and the impact of human activities is relatively small, so the content of HMs is low.

4.2 Chemical forms

The content of HMs in various chemical forms is shown in Table 5. According to Eq. (1), the total coverage (R) of HMs is calculated to be 84% to 113%, indicating that the total amount of various chemical forms of HMs is approximately equal to the measured total amount of HMs, which further reflects the feasibility of the improved Tessier five-step method (Burt et al., 2003).

Figure 3 shows that different HMs in the sediments of different regions presented different chemical form characteristics. In general, the proportion of F5 to all the HMs was relatively large, mostly in the range of 50 to 80%. Except for the F5, F1 and F2 of Cd accounted for the highest proportions, in the range of 19 % to 42% and 17% to 25 %, respectively; F3 of Pb and As accounted for a relatively high proportion, in the range of 21% to 51% and 15% to 31% respectively; Cu and Zn had relatively high F4, in the range of 11% to 39% and 8% to 25% respectively. From the regional perspective, the F1 accounted for a relatively large proportion in Nanliuzhuang (A) and Shaochedian (B) in the northwest of Baiyangdian Lake; while, the F2 accounted for a relatively large proportion in Dongdian (E) and Guangdian Zhangzhuang (F) in the middle and east of Baiyangdian Lake.

4.3 Ecological risk assessment

4.3.1 Ecological risk assessment of sediments based on chemical forms of HMs

The uptake of HMs in lake sediments by organisms depends mainly on their effective forms, the contents of F1 and F2. Under the same conditions, the higher the effective form content of HMs, the higher the ecological and environmental risk. According to the method of RAC, F1 and F2 are the effective forms of HMs. It can be seen from Fig. 4 and Table 5 that the mass fraction of

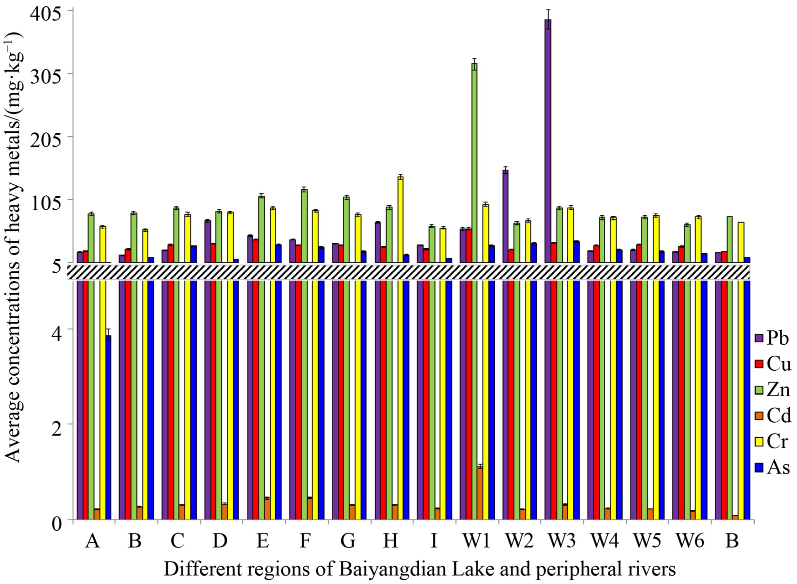


Fig. 2 Average contents of HMs in Baiyangdian Lake and rivers (error bars represent the average error of the HMs content of all samples in each region). A: Nanliuzhuang; B: Shaochedian; C: Duancun; D: Quantou; E: Dongdian; F: Guangdian Zhangzhuang; G: Wangjiazhai; H: Zaolinzhuang; I: Caiputai; W1: Fu River; W2: Tang River; W3: Xiaoyi River; W4: Zhulong River; W5: Baigouyin River; W6: Zhaowangxin River; O: The soil background value of Hebei Province.

Table 3 The contents of HMs in the sediments of Baiyangdian Lake

Item	Pb	Cu	Zn	Cd	Cr	As
Average content1)/(mg·kg^{-1})	39.8	31.02	93.06	0.32	82.56	18.96
Standard deviation2)	18.53	5.08	16.66	0.08	23.75	9.71
Variation coefficient3)	0.47	0.16	0.18	0.24	0.29	0.51
Background value in Hebei Province/(mg·kg^{-1}) (China National Environmental Monitoring Centre, 1990)	21.5	21.8	78.4	0.09	68.3	13.6
Ratio4)	1.85	1.42	1.19	3.42	1.21	1.39

Notes： 1) The average content of each HM of all regions in Baiyangdian Lake. 2) Standard deviation is for average content of each HM of all regions in Baiyangdian Lake. 3) Variation Coefficient = Standard deviation divide average concentration; 4) The ratio of average content to background value in Hebei Province.

Table 4 Average physicochemical properties in sediments of each region in Baiyangdian Lake

District and code	pH	Organic matter/(OM%)
Nanliuzhuang (A)	7.1	4.06
Shaochedian (B)	7.05	3.98
Duancun (C)	7.28	4.08
Quantou (D)	7.13	5.65
Dongdian (E)	6.99	5.21
Guangdian Zhangzhuang (F)	7.16	5.24
Wangjiazhai (G)	7.24	5.14
Zaolinzhuang(H)	7.28	5.54
Caiputai(I)	7.26	5.12

Note: The pH and organic matter content are the average values of each region.

F1+F2 of Cd in all regions of Baiyangdian Lake is greater than 30%. Among them, effective form of Cd accounts for more than 50% in Nanliuzhuang (A), Duancun (C), Dongdian (E), and Guangdian Zhangzhuang (F), suggesting a very high risk of Cd; for the remaining regions, the effective form of Cd accounted for is 31% to 50%, indicating a high risk of Cd. The proportion of effective form of Pb in Shaochedian (B) ranged from 31% to 50%, indicating a high risk of Pb, while that in Nanliuzhuang (A), Dongdian (E), Guangdian Zhangzhuang (F), and Zaolinzhuang (H) ranged from 11% to 30%, there is a medium risk of Pb in these regions; the effective proportion of Pb in the remaining regions ranged from 1% to 10% with a low risk of Pb. The effective form of As ranged from 11% to 30% in Nanliuzhuang (A), Shaochedian (B), and Caiputai (I), indicating a moderate risk of As; for the remaining regions, As ranged from 1% to 10% with a low risk of As. The effective form of the other HMs account for 1% to 10% in all regions, indicating low risk of these HMs in Baiyangdian Lake.

In general, the total effective forms fraction of all HMs in Baiyangdian Lake is about 1%<5.5%<10%. Regardless of the total amount of HMs, the potential ecological environmental risk of the lake is low according to RAC. The potential ecological risk of HMs in the lake is ranked as Cd > Pb > As > Cr > Cu > Zn. However, special attention needs to be paid to the fact that Cd may pose a high risk to the environment. In terms of lake area, the potential risk in Nanliuzhuang (A), Duancun (C), Dongdian (E), and Guangdian Zhangzhuang (F) are the most serious the protential risk in, and the central area of Baiyangdian is a high risk area of HMs. In addition to F1 and F2, the F3 and F4 of HMs also have some potential

Table 5 The average contents of various forms of HMs in the sediments of Baiyangdian Lake

HM	Region	F1/(mg·kg^{-1})	F2/(mg·kg^{-1})	F3/(mg·kg^{-1})	F4/(mg·kg^{-1})	F5/(mg·kg^{-1})	*R*1)/%	Secondary phase content (F1+F2+F3+F4)	Variation coefficient of primary phase	Variation coefficient of secondary phase
Pb	A	2.36	2.12	12.32	1.36	5.66	112.09	18.16	0.62	0.29
	B	2.14	2.53	4.69	0.95	3.99	87.43	10.31		
	C	1.23	1.36	10.24	0.93	13.93	113.76	13.76		
	D	2.16	2.04	14.26	1.04	47.30	93.77	19.5		
	E	4.15	1.99	18.16	1.06	20.40	96.62	25.36		
	F	4.21	2.05	16.24	1.24	22.44	111.64	23.74		
	G	1.56	0.98	15.09	0.89	20.67	110.96	18.52		
	H	1.24	6.27	19.65	1.95	36.68	95.80	29.11		
	I	1.95	1.24	12.16	0.94	18.58	107.77	16.29		
Cu	A	1.29	0.34	1.25	3.45	19.35	110.50	6.33	0.10	0.32
	B	1.36	0.29	1.65	2.94	19.57	97.95	6.24		
	C	0.22	0.31	1.54	14.40	20.24	110.44	16.47		
	D	0.21	0.65	1.95	10.03	18.35	91.01	12.84		
	E	1.42	0.23	1.31	14.02	21.58	93.22	16.975		
	F	1.21	0.61	2.69	11.04	20.68	111.94	15.545		
	G	1.05	0.19	1.27	9.60	18.24	93.77	12.105		
	H	0.69	0.58	0.99	8.81	16.47	92.76	11.07		
	I	0.16	0.21	1.68	7.11	15.27	92.75	9.16		
Zn	A	2.01	3.55	2.45	12.30	68.56	107.90	20.305	0.14	0.37
	B	1.99	2.68	1.36	16.41	64.36	104.27	22.435		
	C	1.23	2.34	3.25	8.52	80.69	105.25	15.34		
	D	0.65	2.14	1.24	13.15	76.57	108.16	17.175		
	E	1.98	1.95	2.38	24.22	86.25	105.81	30.53		
	F	1.68	2.99	3.24	33.68	90.68	109.60	41.585		
	G	1.24	1.06	2.14	26.84	85.49	107.76	31.275		
	H	0.98	2.68	2.33	13.91	69.41	96.69	19.895		
	I	0.25	0.65	1.86	10.51	56.65	112.22	13.265		
Cd	A	0.10	0.04	0.01	0.01	0.08	106.82	0.16	0.21	0.26
	B	0.10	0.05	0.02	0.02	0.12	112.96	0.19		
	C	0.07	0.07	0.01	0.03	0.10	88.71	0.18		
	D	0.04	0.06	0.05	0.03	0.11	90.63	0.18		
	E	0.13	0.11	0.01	0.03	0.14	92.22	0.28		
	F	0.13	0.09	0.02	0.04	0.14	91.58	0.28		
	G	0.06	0.06	0.01	0.02	0.12	87.10	0.15		
	H	0.06	0.05	0.04	0.03	0.09	85.21	0.17		
	I	0.04	0.04	0.01	0.04	0.08	89.58	0.14		
Cr	A	3.83	1.10	4.25	5.65	52.57	109.39	14.83	0.30	0.27
	B	3.28	1.03	3.25	3.47	47.65	103.87	11.03		
	C	1.35	2.14	7.24	8.65	60.36	97.94	19.38		
	D	3.55	1.52	11.65	6.98	62.98	102.82	23.70		
	E	3.87	2.34	11.14	7.69	64.27	97.62	25.05		
	F	1.19	1.49	9.65	8.14	64.82	98.13	20.47		

(*continued*)

HM	Region	F1/(mg·kg^{-1})	F2/(mg·kg^{-1})	F3/(mg·kg^{-1})	F4/(mg·kg^{-1})	F5/(mg·kg^{-1})	$R^{1)}$/%	Secondary phase content (F1+F2+F3+F4)	Variation coefficient of primary phase	Variation coefficient of secondary phase
	G	3.76	1.39	11.13	8.54	60.77	106.11	24.82		
	H	0.22	2.52	14.69	13.24	113.24	102.56	30.67		
	I	0.73	1.18	9.04	5.99	45.79	104.86	16.94		
As	A	0.30	0.03	0.58	0.07	2.28	84.46	0.98	0.52	0.53
	B	0.98	0.24	1.83	0.36	8.74	93.82	3.41		
	C	0.95	0.31	7.58	0.31	21.20	97.75	9.16		
	D	0.72	0.20	1.92	0.49	6.32	96.98	3.33		
	E	2.02	0.91	5.74	0.91	20.66	100.78	9.59		
	F	2.01	0.90	7.27	1.20	18.86	103.85	11.38		
	G	1.05	0.92	5.58	1.15	14.51	105.45	8.70		
	H	0.66	0.36	5.88	0.36	11.09	106.99	7.27		
	I	0.87	0.34	2.31	0.33	7.18	93.31	3.84		

Notes: *R*: coverage rate, Calculated by Eq. (1). A: Nanliuzhuang; B: Shaochedian; C: Duancun; D: Quantou; E: Dongdian; F: Guangdian Zhangzhuang; G: Wangjiazhai; H: Zaolinzhuang; I: Caiputai.

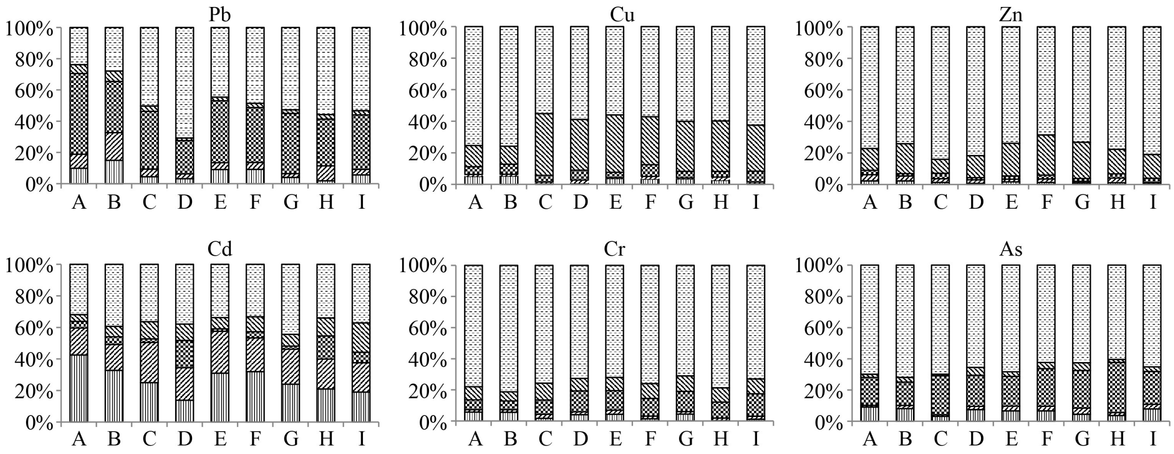


Fig. 3 The proportions of various forms of HMs in each region of Baiyangdian Lake. *Y*-axis: The average mass fraction of different forms; *X*-axis: Different regions of Baiyangdian Lake. ░: residue form(F5); ▧: organic bound form(F4); ▦: iron manganese oxidation form (F3); ▨: carbonate bound form (F2); ▥: ion exchange form (F1); A: Nanliuzhuang; B: Shaochedian; C: Duancun; D: Quantou; E: Dongdian; F: Guangdian Zhangzhuang; G: Wangjiazhai; H: Zaolinzhuang; I: Caiputai.

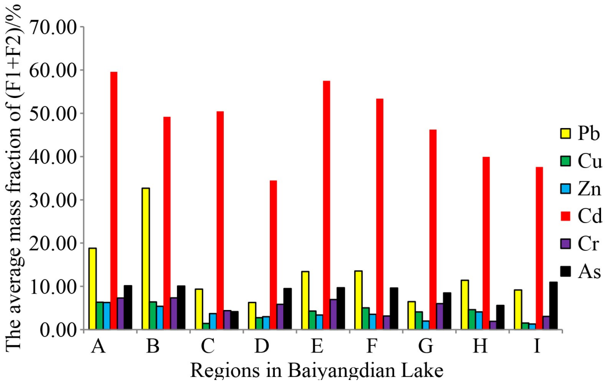


Fig. 4 The average mass fraction of effective form (F1 + F2) of HMs in Baiyangdian Lake. A: Nanliuzhuang; B: Shaochedian; C: Duancun; D: Quantou; E: Dongdian; F: Guangdian Zhangzhuang; G: Wangjiazhai; H: Zaolinzhuang; I: Caiputai.

bioavailability, and can be released in relatively strong acidic media and becomes bioabsorbable. Therefore, F3 and F4 are also direct provider of bioabsorbable HMs. Pb, As, Cr, Zn, and Cu have considerable contents of F3 and F4 in most regions, thereby increasing the potential ecological risk of these HMs in Baiyangdian Lake.

4.3.2 Ecological risk assessment of sediments based on total amount of HMs

According to the SQG-Q method, this paper adopts the Canadian Freshwater Sediment Quality Standard established by the biological effects database (Li et al., 2013), and uses the data of the HMs content in the sediments to further assess the risk of HMs in the sediments of Baiyangdian Lake. Table 6 lists the baseline values of PEL and threshold effect level (TEL) of several HMs.

Table 6 Baseline values of PEL and TEL ($mg \cdot kg^{-1}$) (Li et al., 2013)

Item	Pb	Cu	Zn	Cd	Cr	As
PEL	91.00	197.00	315.00	3.50	90.00	17.00
TEL	35.00	36.00	123.00	0.60	37.00	5.90

The PEL baseline value is selected to calculate the SQG-Q coefficient, and the average PEL-Q values of Pb, Cu, Zn, Cd, Cr, and As in different regions can be calculated from Eq. (3), as shown in Table 7. According to Eq. (2), the average SQG-Q coefficient of each region is further calculated (Table 7). Obviously, the highest value of SQG-Q appears in Dongdian (E), followed by Guangdian Zhangzhuang (F) and Zaolinzhuang (H). The SQG-Q values of all sampling points range from 0.1 to 1.0, indicating that the sediments of Baiyangdian Lake had been moderately polluted by HMs and exhibits moderate potential biological toxicity, especially in the middle and east regions of Baiyangdian Lake.

Table 7 PEL-Q and SQG-Q values of different regions

Region	PEL-Q/($mg \cdot kg^{-1}$)						SQG-Q
	Pb	Cu	Zn	Cd	Cr	As	
Nanliuzhuang (A)	0.23	0.12	0.26	0.06	0.68	0.23	0.26
Shaochedian (B)	0.18	0.13	0.26	0.08	0.63	0.76	0.34
Duancun (C)	0.27	0.17	0.29	0.09	0.90	1.83	0.59
Quantou (D)	0.78	0.17	0.28	0.09	0.94	0.59	0.47
Dongdian (E)	0.52	0.21	0.35	0.13	1.02	1.93	0.69
Guangdian Zhangzhuang (F)	0.45	0.16	0.38	0.13	0.97	1.71	0.64
Wangjiazhai (G)	0.39	0.16	0.34	0.09	0.90	1.29	0.53
Zaolinzhuang (H)	0.75	0.15	0.29	0.09	1.56	1.01	0.64
Caiputai (I)	0.36	0.13	0.20	0.07	0.66	0.69	0.35

Compared the average content of each HMs in each region (Fig. 2) with the HMs quality standard of the sediment (Table 6), the average content of As in Dongdian (D), Guangdian Zhangzhuang (F), Wangjiazhai (G), and Zaolinzhuang (H) and the average content of Cr in Zaolinzhuang (H) exceeds PEL, which are 1.93, 1.71, 1.29, 1.01, and 1.56 times of the PEL value, respectively. The average contents of other HMs in each region do not exceed the PEL value, but the average contents of As, Cr, and Pb in most regions are much higher than the TEL value, and those of other HMs are close to the TEL value. Accordingly, the potential biological toxicity of As, Cr, and Pb in Baiyangdian Lake may be very high, and adverse biological effects may occur frequently; however, the potential biological toxicity of other HMs cannot be ignored. Therefore, it is necessary and urgent to strengthen the preventive and control measures for HMs pollution in Baiyangdian Lake.

5 Discussion

5.1 Analysis of potential risks

According to the above assessment results of HMs pollution in Baiyangdian Lake, there is little regional difference in the risk assessment of HMs between the two methods. The risk of HMs is generally higher in the central region and the lowest in the south. However, in terms of the potential risk assessment of each HM, the two methods gave different results. RAC identified that Cd, Pb, and As had great potential risks, especially Cd had high potential risks, while SQG-Q identified that As, Cr, and Pb had high ecological risks. Here the biggest difference in HM is Cd.

It can be seen that the assessment results of Cd based on the chemical form of HMs are different from those based on the total amount of HMs. This may be related to the more active chemical form of Cd, such as strong affinity between Cd and carbonates, and co-precipitation with carbonates in water at higher pH. Tessier et al. (1979) found that Cd mainly existed in ion exchangeable form and carbonate binding form in sediments of Yamaska and St. Francois Rivers in Canada. With regard to the chemical form of Cd, Fytianos and Lourantou (2004) believed that Cd occurred mainly as exchangeable, carbonate-bound and residual forms. The ion exchange forms (F1) are relatively active and readily absorbed by organisms (Maryam and Afshin, 2017). The human body can assimilate HMs indirectly through the food chain, resulting in serious health issues (Men et al., 2018). Therefore, if Cd has a high content of F2, when the pH decreases, the content of exchangeable Cd will increase rapidly; then, the biological toxicity of Cd may increase sharply, directly or indirectly causing toxic effects on aquatic organisms, and ecosystem and human health will be greatly threatened.

It can be seen from Table 8 that the previous assessment methods are mainly the geoaccumulation index and the potential ecological risk index. These two methods and the SQG-Q method are both based on the total amount of HMs. During 2005–2020, the risk brought by the total amount of HMs in the Baiyangdian area shows a decreasing trend (Table 8). The risk of Cd was high in past years, and gradually decreased in recent years, but the RAC method in this study shows that Cd is still at high and very high risk, which reflects the ecological risk posed by the active chemical form of Cd. So when assessing the risk of Cd, the results should be superimposed on the total amount and chemical form. For other HMs, the proportion of their chemical forms may also change as the environmental conditions change. Even if the total amount of HMs does not change, their risk to the environment will increase. Therefore, the total

Table 8 Comparison with previous assessments

Method	Risk level of single HM						Overall risk level	Data sources
	Cd	As	Pb	Cu	Zn	Cr		
RAC	high– extremely high	low − medium	low-high	low	low	low	low	This paper
SQG-Q	low	high	high	low	low	high	medium	This paper
GA	——	——	low	low	low	low		Hu et al. (2011)
PA	low	low	low	low	low	low	low	Hu et al. (2011)
GA	extremely high		medium	low−medium	low−medium	low−medium		Li et al. (2007)
GA	extremely high	——	medium	non-risk	non-risk	——		Yang et al. (2005)
PA	extremely high	——	non-risk	non-risk	non-risk	——	medium	Yang et al. (2005)

Notes: GA: geo-accumulation index assessment; PA: potential ecological risk assessment.

amount of HM and chemical forms should be taken into account in the risk assessment of HMs pollution in sediments, and their superposition effect should be considered from these two aspects.

5.2 The influence of physicochemical properties on the forms of HMs

Studies have shown that the form and behavior of HMs in river sediments or soils, such as bioavailability, toxicity, etc., are largely affected by the physicochemical properties (Sahuquillo et al., 1999). To discuss the influence of physicochemical properties on the forms of HMs, this paper has analyzed their correlation as shown in Table 9. Except for As, the F1 forms of HMs are significantly negatively correlated with pH at the level of 0.05. The F2 forms of Cd, Cr, As are positively correlated with the total amount of HMs. The F3 forms of Cr and Pb are positively correlated with total amount and organic matter. The F4 and F5 forms of most HMs have a significant positive correlation with total amount at 0.01 level.

The pH is an important physical and chemical index of the water-sediment system, which will directly affect the structure, fertility, and organisms of the sediments, and also has an important impact on the forms of HMs in the sediments. The F1 forms of almost all HMs in the sediments of Baiyangdian Lake are significantly negatively correlated with pH. According to geochemical theory, as the pH value of the sediments increases, the number of negative charges on the surface of oxides, minerals, and other substances in the sediments will increase. Exchangeable HMs are mostly positively charged, which may increase the adsorption probability of exchangeable HMs in the sediments, thereby reducing the content of exchangeable HMs. The increase of pH will gradually stabilize the organic matter HMs complexes in the sediments. Therefore, the content of organic bound HMs

Table 9 Correlation coefficients between forms and physicochemical properties of HMs in the sediments

Form	Influencing factor	Pb	Cu	Zn	Cd	Cr	As
	pH	−0.680*	−0.681*	−0.692*	−0.667*	−0.711*	−0.362
F1	OM	0.196	−0.252	−0.526	−0.273	−0.209	0.280
	Total	0.04	0.062	0.489	0.605	−0.435	0.780*
	pH	0.148	0.085	−0.338	−0.419	0.177	−0.083
F2	OM	0.278	0.467	−0.382	0.265	0.366	0.437
	Total	0.525	0.062	0.219	0.943*	0.834**	0.742*
	pH	0.146	−0.103	0.292	0.150	0.357	0.361
F3	OM	0.787*	0.146	−0.163	0.654	0.914**	0.234
	Total	0.740*	0.090	0.510	0.099	0.814**	0.931**
	pH	0.194	0.173	−0.283	0.316	0.564	−0.106
F4	OM	0.286	0.393	0.342	0.563*	0.547*	0.482
	Total	0.490	0.868**	0.857**	0.497	0.940**	0.637
	pH	0.245	−0.632	−0.145	−0.515	0.347	0.058
F5	OM	0.873**	−0.335	0.256	0.217	0.510	0.093
	Total	0.964**	0.506	0.937**	0.855*	0.980**	0.998**

Notes: **, Significantly correlated at 0.01 level, *, Significantly correlated at 0.05 level.

will increase. At the same time, the increase of the pH value will cause the formation of iron and manganese and other cations and OH^- in the sediments, which can increase the F3 in the sediments. Therefore, the correlation coefficients between F3 and pH and F4 and pH are mostly positive in the sediments of Baiyangdian Lake. The chemical properties of the HM residues in the sediment are relatively stable and are not easily affected by the pH value. Therefore, the F5 forms of the HMs in Baiyangdian Lake has no obvious correlation with the pH value. Many scholars have found through experiments that the ion exchangeable form of most HMs in the soil is significantly negatively correlated with pH. The contents of F2, F3, F4, and F5 are significantly positive in relation with soil pH (Cai et al., 2019), which is more consistent with Baiyangdian Lake sediment. Therefore, it can be concluded that the F1 is less in alkaline lakes, and the biological toxicity of HMs is also relatively weak.

Except for Pb and As in the sediments of Baiyangdian Lake, the F1 forms of other HMs are negatively correlated with organic matter. The reason may be that the organic matter in the sediment contains a large number of active functional groups, such as hydroxyl and carboxyl groups. After releasing H^+, it has a negative charge and has a good adsorption and ion exchange effect on positively charged metal ions, the F1 forms of HMs will decrease accordingly. In addition, organic matter can indirectly increase the pH value of sediments and increase the adsorption of HMs ions in sediments, which will also reduce the F1 forms in the sediments (Guan et al., 2011). The F3 forms of Pb and Cr and the F4 forms of Cr and Cd of sediments in the Baiyangdian Lake are significantly positively correlated with organic matter. This is roughly in line with the results of previous experiments on soil organic matter (Hua et al., 2002). The carbonate bound form (F2) of most HMs has no obvious correlation with organic matter. This may be affected comprehensively by the types of HMs, type and content of organic matter, CEC, pH value, micro-organisms, and other aspects.

5.3 Source identification of HMs

5.3.1 Source identification based on total amount

After standardizing the total amount of HMs in the sediments of Baiyangdian Lake and peripheral rivers, they were analyzed for correlation with SPSS software (Table 10 and Table 11). Zn, Cu, Cd, and As in the sediments of Baiyangdian Lake were significantly correlated, and Pb and Cr were significantly correlated. While, there is a significant correlation between Zn, Cu, Cd, and Cr in the peripheral rivers, and a significant correlation between Pb and As. Obviously, Zn, Cu, Cd in Baiyangdian Lake and peripheral rivers have similar correlation characteristics, indicating that these HMs in the lake and rivers may be inherited or have the same source. However, the correlation of Pb, Cr, and As in Baiyangdian Lake and rivers is quite different, which may be due to the stronger spatial variability and multiple sources of Pb, Cr, and As.

To further discuss the source of HMs, cluster analysis is conducted on the total amount of HMs in sediments of Baiyangdian Lake and peripheral rivers. The analysis results show good approximation between Baiyangdian Lake and rivers (Figs. 5(a) and 5(b)). Especially when all HMs are divided into two categories, for Baiyangdian Lake, Zn, Cu, Cd, and As are clustered into one category and Pb and Cr are clustered into one category; for peripheral rivers, Zn, Cu, Cd, Cr are clustered into one category and Pb, As are clustered into one category. This is consistent with the above correlation analysis, indicating that the geochemical effects of Zn, Cu, and Cd in rivers and Baiyangdian Lake are related or have common sources. Since Fuhe River, Tanghe River, Xiaoyi River and Zhulong River are the main water supply of Baiyangdian Lake, these rivers are the main factors affecting the spatial changes of Zn, Cu, and Cd in the sediments of Baiyangdian Lake. The above different analysis result of HMs between peripheral rivers and Baiyangdian Lake lies in the assemblages of Pb, As, and Pb, Cr assemblages, which may also be related to human activities and sedimentary environments.

Table 10 Correlation coefficients of HMs in sediment of Baiyangdian Lake

	Pb	Cu	Zn	Cd	Cr	As
Pb	1	0.232	0.206	0.173	0.764*	0.088
Cu	0.232	1	0.755*	0.786*	0.164	0.869**
Zn	0.206	0.755*	1	0.811**	0.176	0.691*
Cd	0.173	0.786*	0.811**	1	0.076	0.675*
Cr	0.764*	0.164	0.176	0.076	1	0.227
As	0.088	0.869**	0.691*	0.675*	0.227	1

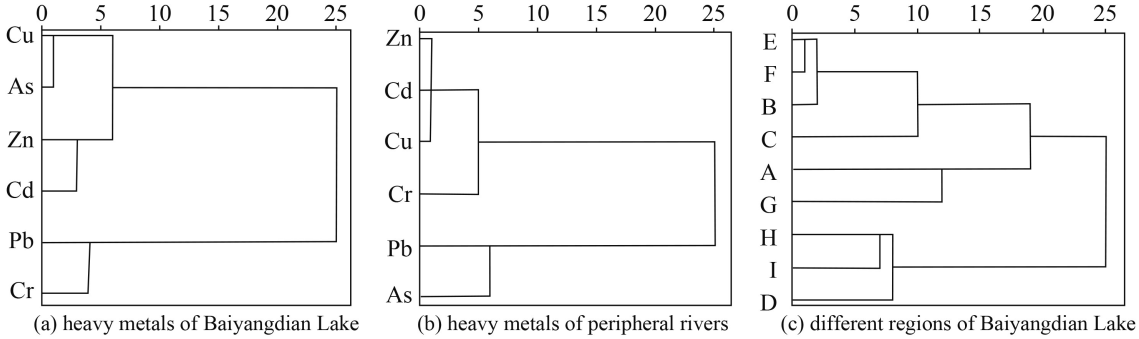
Notes: *, Significantly correlated at the 0.05 level; **, Significantly correlated at the 0.01 level.

Table 11 Correlation coefficients of HMs in sediments of peripheral rivers

	Pb	Cu	Zn	Cd	Cr	As
Pb	1	−0.044	−0.110	−0.073	0.337	0.817*
Cu	−0.044	1	0.969**	0.971**	0.900*	0.185
Zn	−0.110	0.969**	1	0.999**	0.803	0.229
Cd	−0.073	0.971**	0.999**	1	0.819*	0.260
Cr	0.337	0.900*	0.803	0.819*	1	0.361
As	0.817*	0.185	0.229	0.260	0.361	1

Note: *, Significantly correlated at the 0.05 level; **, Significantly correlated at the 0.01 level.

Figure 5(c) is the cluster analysis results of HMs in different areas of Baiyangdian. When the Baiyangdian area is divided into two categories, Nanliuzhuang (A), Shaochedian (B), Duancun (C), Dongdian (E), Guangdian Zhangzhuang (F), and Wangjiazhai (G) are classified into



(a) heavy metals of Baiyangdian Lake (b) heavy metals of peripheral rivers (c) different regions of Baiyangdian Lake

Fig. 5 Tree diagram of cluster analysis of HMs in Baiyangdian Lake and peripheral rivers.

one category, which are close to the inflow river, indicating that these areas are mainly affected by inflow rivers. Quantou (D), Zaolinzhuang (H), and Caiputai (I) are classified into one category, which are far away from the inflow river. Quantou (D) is located in the southcentral Baiyangdian. Caiputai (I), located in the south of Baiyangdian Lake, is characterized by quiet water. Zaolinzhuang (H) is close to the outflow river. It is difficult for the three regions to maintain the characteristics of HMs of inflow river for a long time, while some HMs levels are susceptible to change due to spatial location and human activities. For example, the proportion of Cr in Zaolinzhuang (H) is significantly higher than that in the inflow river and other regions, the proportion of As in Caiputai (I) and Quantou (D) is significantly lower than that in the inflow river and other regions, and the proportion of Pb in Quantou (D) is significantly higher than that in other regions. The variation of Pb, Cr, and As is consistent with the above correlation analysis, which shows that the point source pollution in the village is also an important factor for the spatial variation of Pb, Cr, and As.

In summary, the sources of Zn, Cu, and Cd in the sediments of Baiyangdian Lake are mainly affected by the inflow rivers, and the sources of Pb, As, and Cr may be more related to the human activities of villages or spatial location of Baiyangdian Lake.

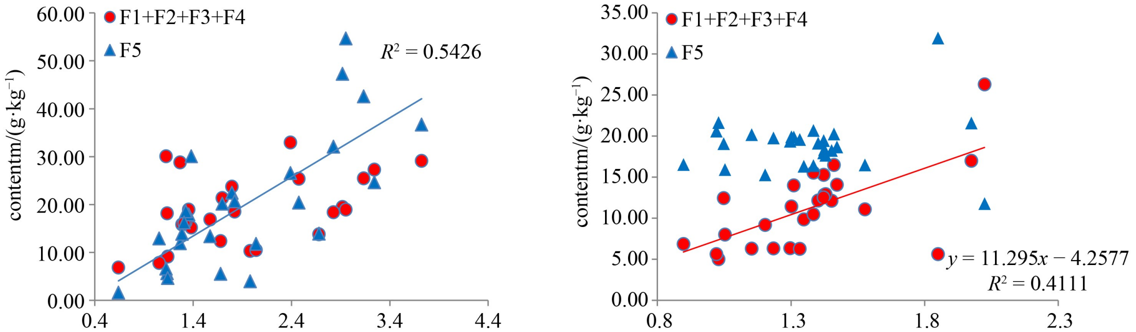
5.3.2 Source identification based on chemical forms

Previous studies have shown that the chemical form (F5) of the primary phase of HMs in sediments has high stability, and generally does not participate in the rebalancing distribution of the water-sediment system (He et al., 2003). The chemical forms of secondary phase (F1+ F2+F3+F4) have great bioavailability and toxicity (Zhang et al., 2018b) and strong migration, which are mainly produced by human activities. Therefore, the primary chemical forms of HMs are related to natural deposition and diagenesis, which are natural sources, while the secondary chemical forms are mainly related to human activities, which are human sources (Li et al., 2019).

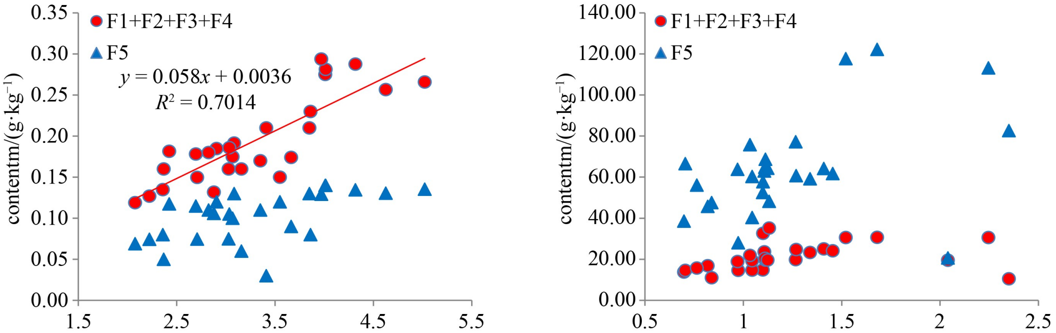
As shown in Table 5 and Fig. 3, the average contents of secondary phases (F1+F2+F3+F4) of Pb, Cu, Zn, Cd, Cr, and As in sediments of Baiyangdian Lake are 10.31 to 29.11, 6.24 to 16.98, 13.27 to 41.59, 0.14 to 0.28,11.03 to 30.67 and 0.98 to 11.38 mg·kg^{-1}, respectively. The average contents of primary phase (F5) are 3.99 to 47.30, 15.27 to 20.68, 56.65 to 90.68, 0.08 to 0.12, 45.79 to 113.24, and 2.28 to 21.20 mg·kg^{-1}, respectively. The variation coefficients of secondary phase content are 0.46, 3.2, 2.58, 1.23, 0.92, and 1.01 times higher than that of primary phase, respectively, indicating that the variation of Cu, Zn, Cd, and As in Baiyangdian Lake are mainly caused by the secondary phase, which is more related to human activities, while Pb is mainly caused by the primary phase. The change of Cr may be related to secondary phase and primary phase.

The correlation analysis between the enrichment coefficient (*EF*) of HMs and the contents of their primary and secondary phases at all sampling sites in Baiyangdian Lake is shown in Fig. 6. It shows that there is a significant correlation between the secondary phases and *EF* for Cu, Zn, Cd, and As, and the R^2 values are 0.4111, 0.5735, 0.7014, and 0.4171, respectively, indicating that these HMs are mainly derived from human activities (secondary activities). There is a significant correlation between the primary phase of Pb and its *EF*, and the R^2 value is 0.5426, indicating that Pb is more closely related to natural factors, mainly natural sources. Yet there is no obvious correlation between the secondary and primary phases and EF for Cr, which further indicates that Cr may be a natural and human mixed source.

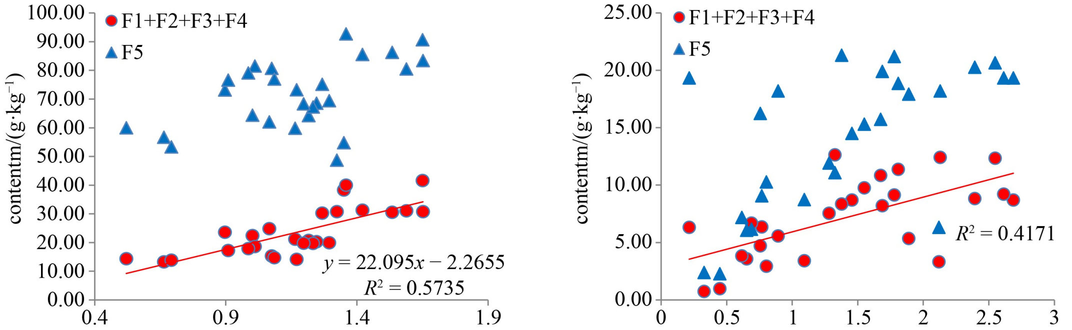
Based on the aforementioned analysis of the total amount of HMs, it is pointed out that Cu, Zn, and Cd in the sediments of Baiyangdian Lake are strongly correlated with the inflow rivers, so it is inferred that Cu, Zn, and Cd in the inflow rivers are mainly derived from human activities too. According to the survey, for a long time wastewater from Baoding sewage treatment plant, battery production plant, and printing industry plant often enter Baiyangdian Lake through the Fuhe River, Tanghe River, and Xiaoyihe River, respectively. According to these discharge phenomena, combined with the analysis of the total amount and chemical form of HMs in sediments, it is shown that the variations of Cu, Zn, and Cd in sediments of Baiyangdian Lake are mainly affected by inflow rivers, and Cu, Zn, and Cd in inflow rivers mainly derive from various human industrial activities such as wastewater discharge. Although As is related to human activities, it is not affected by the inflow river



(a) *EF*-Pb (b) *EF*-Cu



(c) *EF*-Cd (d) *EF*-Cr



(e) *EF*-Zn (f) *EF*-As

Fig. 6 Enrichment coefficient of HMs in surface sediments of Baiyangdian Lake and their correlation with chemical form (the fitting line of the secondary phase is red, and the fitting line of the primary phase is blue).

according to total amount analysis, so it is judged to be related to human life activities such as domestic garbage, leaching, aquaculture and tourism in Baiyangdian village. Pb is related to the natural effects and the spatial location of lake, and Cr has a mixed source of human activities of villages and natural effects.

6 Conclusions

1) The proportion of residue forms of all HMs in the sediments of Baiyangdian Lake is relatively large. Except for the F5, F1 and F2 of Cd account for the highest proportion; Pb and As have a higher proportion of F3; Cu and Zn have a higher proportion of F4. Regionally, the ion-exchange HMs are mainly in the northwest of Baiyangdian Lake; the carbonate bound HMs are mainly in the middle and east of Baiyangdian Lake.

2) The RAC obtains the ranking of potential ecological risks of HMs in Baiyangdian Lake: Cd > Pb > As > Cr > Cu > Zn. Cd has the possibility of posing a high risk to the environment; the F3 and F4 forms of other elements increase the potential ecological risk of HMs in the lake. The SQG-Q shows that the sediments of Baiyangdian Lake has been polluted by HMs at a moderate level and exhibits a moderate potential biological toxicity effect. The total amount of HMs and chemical forms should be taken into account in the risk assessment of HMs pollution in sediments, and their superposition effect should be considered from these two aspects.

3) The analysis of the correlation between the form and physicochemical properties of HMs in the sediments of Baiyangdian Lake shows that the form and behavior of HMs, such as bioavailability and toxicity, are largely affected by the physicochemical properties of the

sediments. Organic matter and pH mainly affect the F1 of HMs, and the total amount of HMs mainly affects the F4 and F5 of HMs.

4) The variations of Cu, Zn, and Cd in sediments of Baiyangdian Lake are mainly affected by inflow rivers, and Cu, Zn, and Cd in inflow rivers mainly derive from various human industrial activities such as wastewater discharge. As is mainly related to human life activities such asdomestic garbage, leaching, aquaculture, and tourism in Baiyangdian village, Pb is related to the natural effects and the spatial location of lake, and Cr has a mixed source of human activities of villages and natural effects.

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