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Distribution and Release Fluxes of Phosphorus from Sediments in the Lake Caohai, Guizhou

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Abstract: *A typical grass-type lake, Caohai, Guizhou, was used as the study object. The morphology and release flux of phosphorus in Caohai sediment were analyzed by the chemical continuous extraction method and pore water diffusion model. The results showed that the TP content of Caohai sediment was 559.75 mg/kg, much lower than that of other lakes on the Yunnan-Guizhou Plateau; the release flux was -0.0009-0.0518 mg/(m^2-d); the phosphorus form content was Res-P>NaOH-NRP>NaOH-SRP>BD-P>HCl-P>NH4Cl-P in descending order. However, due to the high proportion of organic phosphorus in the Caohai, the ecological risk of its potential release was high. In this study, the author found that the sediment phosphorus content and release flux of grass-type lakes, represented by Guizhou Caohai, were lower than those of algal-type lakes, which had important implications for the conservation management of grass-type lakes.*

Keywords: *Caohai, Guizhou, Interstitial water, Sediment, Phosphorus morphology, Release flux*

1. Introduction

Phosphorus is a major factor limiting the productivity of lakes, and the input of large amounts of phosphorus can lead to the eutrophication of lakes[1]. Phosphorus in sediments is both a 'sink' and a 'source' of pollution[2]. When the input of exogenous phosphorus is effectively controlled, the phosphorus in the overlying water mainly comes from the release of endogenous phosphorus in the sediment, which affects the lake's water quality and eutrophication process[3-5]. Therefore, it is important to elucidate the transport and transformation characteristics of sediment phosphorus for the management of eutrophic lakes and the restoration of aquatic vegetation.

The phosphorus loading pattern in sediments determines the amount of phosphorus that can participate in interfacial exchange and is bioavailable, and the sorption and release characteristics of phosphorus and its stable mineralization also depend on the loading pattern of phosphorus[6-7]. Much of the phosphorus in sediments is unstable and not completely buried in the sediment[8]. Using chemical sequential extraction, total phosphorus in sediments can be classified into six forms, namely loosely adsorbed phosphorus (NH_4CI-P), calcium-bound phosphorus(HCl-P), aluminum-bound phosphorus (NaOH-SRP), iron-bound phosphorus(BD-P), organic phosphorus (NaOH-NRP),and residual state phosphorus (Res-p)[9].

Caohai in Guizhou is located in Weining County, west of Bijie City, and is a precious plateau karst freshwater lake, which has been known as a "bird's paradise", "underwater forest", "species gene bank" and "open-air museum", The lake is known as an "open-air museum" and has extremely important ecological value. Due to reckless discharge and poor management in the early years, pollutants were discharged into the Caohai, accumulating a large number of nutrients and organic pollutants such as nitrogen and phosphorus in the sediments. In recent years, the government has built a large number of artificial wetlands and sewage treatment plants in the inlet and key discharge areas around the Caohai, and the treatment and control of the Caohai has gradually matured, effectively controlling the input of exogenous pollutants, and the endogenous pollution load has become the key to the management of the Caohai. This study investigates the distribution characteristics of phosphorus in the overlying water of the Caohai and estimates the risk of static release of phosphorus, combined with the factors influencing the temporal and spatial differences in sediment phosphorus patterns, with a view to providing a basis for further research on the characteristics of endogenous phosphorus release from the Caohai and subsequent treatment measures.[10-12]

2. Materials and methods

2.1. Overview of the study area

Caohai (26°47′35″ ~ 26°52′10″N, 104°9′23″ ~ 104°20′10″E) is located in Weining Yi Hui Miao Autonomous County, Guizhou Province, and is the largest grass-type freshwater lake in Guizhou Province. The total area of Caohai is 120.00 km², and the water area reaches 22.39 km². It belongs to the mountainous subtropical plateau monsoon climate, with a rainy season from May to October and an average annual precipitation of about 950.9mm[13-14]. (Figure 1)

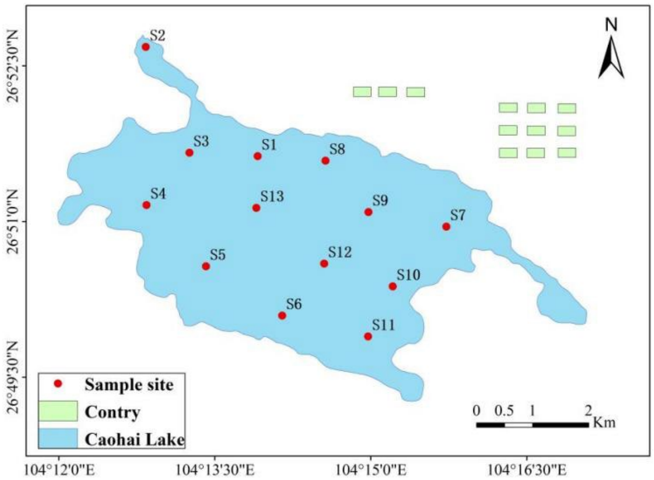

Figure 1: Location of field observation sites in Caohai Lake

2.2. Sample collection

In February 2022, 13 points were selected for sediment column sample collection in the whole lake of Caohai by GPS positioning. The column sediment was collected using a rigid Plexiglas tube gravity sampler with a tube diameter of 90mm, sealed at both ends and brought back to the laboratory. The overlying water was aspirated with a siphon tube and water quality was experimentally determined. Interstitial water was obtained by filtration through a 0.45 μm mixed fibre membrane.

2.3. Analytical methods

The physical and chemical indicators of the water bodies were measured according to the water quality standard method of the Environmental Quality Standard for Surface Water, including total phosphorus (TP)in the interstitial water, total nitrogen (TN) in the overlying water, total phosphorus (TP) in the overlying water, ammonia nitrogen ($NH_4^{+)}$ in the overlying water, permanganate index ($COD_{Mn)}$ in the overlying water and chlorophyll a (Chl.*a*) in the overlying water. Overlying water dissolved oxygen (DO), pH and water temperature (WT) were measured in situ using a portable water quality analyzer.

Sediment pH and Eh were determined in situ using a portable instrument. Sediment indicators were determined according to the Methods of Agricultural Chemical Analysis of Soils. Organic carbon content was determined using the externally heated potassium dichromate oxidation-volume method, total nitrogen content was determined using the Kjeldahl method, and total phosphorus content was determined using the SMT method. The continuous chemical extraction method for sediment phosphorus morphology developed by Hupffer[15] and others determined the phosphorus morphology.

2.4. Data processing

Microsoft Excel was used for basic processing of the data, SPSS 22 software was used for correlation analysis, and the spatial distribution of sediment phosphorus morphology was analysed and processed by Arcgis interpolation method, and the correlation mapping in the text was done by Origin2021 software.

Phosphorus diffusion fluxes at the sediment-water interface are calculated according to first law [16], Eq:

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$$F = \Phi \cdot D \frac{\partial c}{\partial z}\Big|_{z=0} \quad (1)$$

The formula is as follows: represents the porosity of surface sediment, represents the actual diffusion coefficient, and $\frac{\partial c}{\partial z}\Big|_{z=0}$ represents the concentration gradient [mg/(L·cm)] at the sediment-water interface. These can be calculated using an empirical formula [17]:

$$D = \Phi D_0 (\Phi < 0.7)$$
$$D = \Phi^2 D_0 (\Phi > 0.7) \quad (2)$$

Where D_0 is the ideal diffusion coefficient of the infinite dilution solution. The ideal diffusion coefficient of nutrients at different temperatures can be converted from the ideal diffusion coefficient at 25°C. The ideal diffusion coefficient of PO_4^{3-}-P at 25°C is 6.12×10^{-6} cm²/s. F is positive when diffusing from the sediment to the overlying water and negative when diffusing from the overlying water to the sediment. Porosity equation [18]:

$$\Phi = \frac{(W_w - W_d) \times 100\%}{(W_w - W_d) + \frac{W_d}{2.5}} \quad (3)$$

Where is the wet weight of sediment (g), is the dry weight of sediment (g), and 2.5 is the average ratio of wet sediment density to water density.

The comprehensive pollution index of sediment is evaluated by the formula (4) of single pollution index and formula (5) of comprehensive pollution index [19]:

$$S_i = \frac{C_i}{C_S} \quad (4)$$

Where is the single evaluation index or standard index, and C_i is the measured value of the evaluation factor *i*, and C_s is the evaluation standard value of the evaluation factor *i*. C_s of TN in sediment is 0.55 g/kg, and C_s of TP is 0.60 g/kg.

$$FF = \frac{\sqrt{F^2 + F_{MAX}^2}}{2} \quad (5)$$

Where F represents the average value of n pollution indices (S_{TN} and S_{TP}), and F_{MAX} represents the maximum single pollution index (the maximum of S_{TN} and S_{TP}).

The comprehensive nutrient status index of the water body [20] is:

$$TLI(\Sigma) = \sum W_j \times TLI(j) \quad (6)$$

Where *TLI(j)* represents the nutrient status index of the jth parameter, and *Wj* represents the relevant weight of the nutrient status index of the jth parameter.

3. Results and analysis

3.1. Basic information on overlying water

Table 1: Physicochemical properties of water column in Caohai

Parameters	Maximum value	Minimum value	Average value
pH	8.30	8.90	8.30
Transparency SD/(cm)	100.0	15.0	65.6
Total Nitrogen TN/(mg/L)	2.65	2.13	2.34
Total Phosphorus TP/ (mg/L)	0.02	0.04	0.03
Ammonia Nitrogen NH_3-N/ (mg/L)	1.80	2.21	1.98
Chlorophyll a Chl.*a*/(μg/L)	1.40	5.58	2.68
Permanganate index COD_{Mn}/(mg/L)	8.95	7.42	7.95
Integrated Eutrophication Index *TLI*	57.77	46.49	49.72

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As can be seen from Table 1, the pH of the overlying water at the sampling sites ranged from 8.30 to 8.90, which was generally weakly alkaline; the chlorophyll a (Chl.a) content ranged from 1.40 to 5.58 μg/L, with a mean value of 2.68 μg/L, the mean value of TN in the overlying water was 2.34 mg/L, while the mean value of TP in the overlying water was 0.03 mg/L; the mean value of permanganate index (CODMn) was 7.95 mg/L. The water quality of the overlying water was evaluated with reference to the Carlson integrated nutrient index method, and the calculation of the weight size was carried out using five parameters: SD, CODMn, TN, Chla and TP. The results of the calculations showed that the combined eutrophication index (TLI) of Caohai ranged from 46.49 to 57.77, with a mean value of 49.72. The lake was classified as a mesotrophic lake according to the *TLI* classification.

3.2. Characteristics of total phosphorus distribution

The pH of sediment in Caohai Lake ranged from 6.90 to 7.09, with a mean value of 7.01, and was generally weakly alkaline; the maximum value of sediment redox potential was -51, the minimum value was -193, and the mean value was -110, which was reductive; the porosity of surface sediment ranged from 0.56 to 0.77, with a mean value of 0.66. The TP content of sediment was 559.75 mg/kg. A kriging difference analysis of the TP values, as shown in Figure 2, shows a clear spatial distribution of sediment TP, with the eastern part of the lake being the area of high human activity with the highest TP content and the central part of the lake having the lowest.

Using the lowest level of ecological risk sediment TP concentration (600 mg/kg) issued by the Ministry of Environment and Energy of Ontario, Canada (1992) as the reference standard, the single factor index method was applied to evaluate the sediment TP pollution, and the results showed that the phosphorus pollution index in the Caohai Lake area was 0.76-1.34. The results indicated that the total phosphorus pollution in the surface sediment of Caohai was level 2 pollution and there was a certain risk of pollution. The overall pollution index (*FF* value) of sediment is 7.91, which is a level 4 pollution.

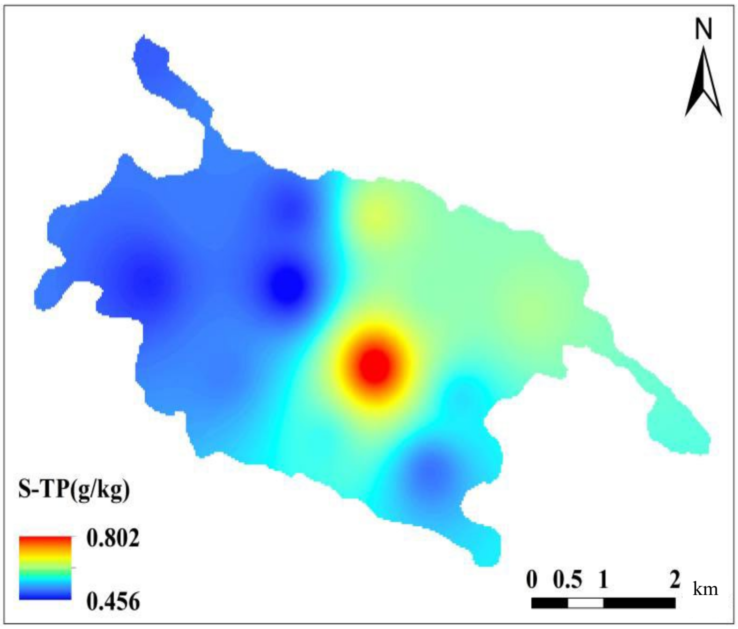

Figure 2: Spatial distribution of TP content in Caohai Lake

3.3. Spatial heterogeneity of phosphorus by form in Caohai sediments

The distribution of different forms of phosphorus in Caohai sediments is shown in Figure 3, with the magnitude of Res-P>NaOH-NRP>NaOH-SRP>BD-P>HCl-P>NH4Cl-P. The phosphorus forms in the surface sediments of the Caohai are mainly organic phosphorus (NaOH-NRP), aluminium-bound phosphorus (NaOH-SRP), iron-bound phosphorus (BD-P) and residual phosphorus (Res-P) are dominant.

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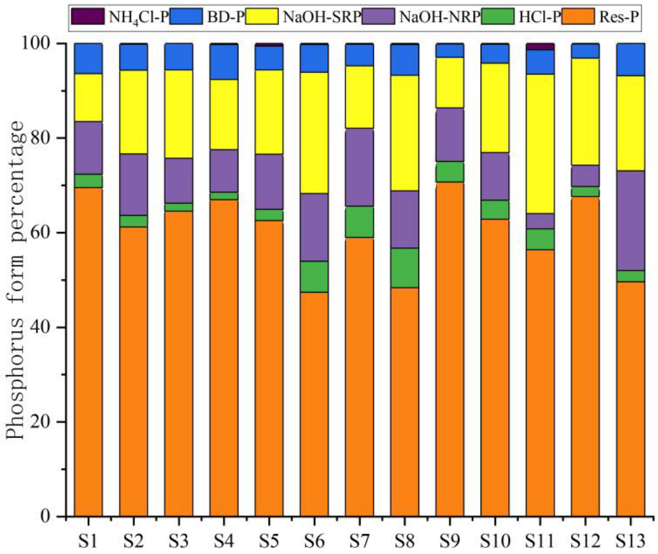

Figure 3: The content and distribution of phosphorus fractions in the sediments

The spatial distribution of surface sediment phosphorus patterns is shown in Figure 4, with the spatial distribution of Res-P similar to that of sediment TP.

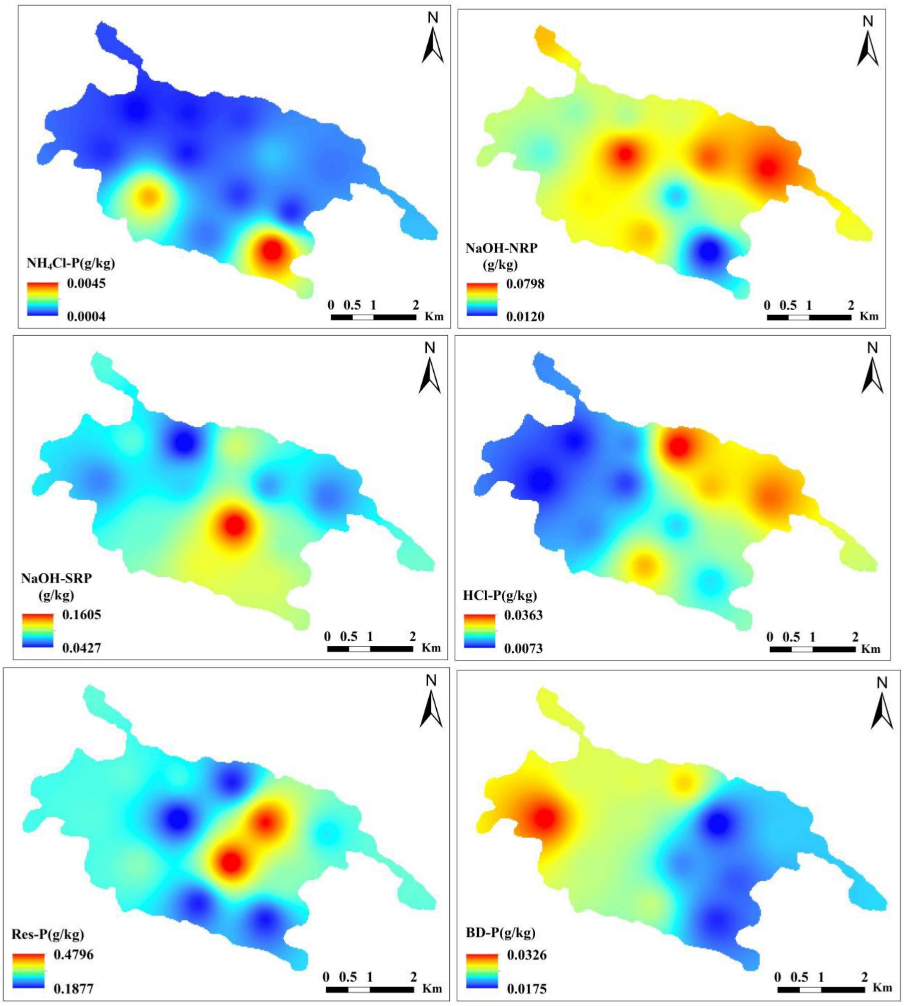

Figure 4: Space distribution of phosphorus speciation content in spring sediments

Under the concentration gradient, phosphorus in the sediment will diffuse from the interstitial water to the overlying water thus affecting the water quality of the lake. The results of phosphorus diffusion fluxes at each sampling site are shown in Table 2. The diffusion fluxes of phosphorus in sediments from

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Caohai [-0.0009-0.0518 mg/(m^2·d)] were found to be much lower than those from Dianchi [0.90-2.06 mg/(m^2·d)] [21] and Taihu [2.06 mg/(m^2 · d)] [22], which are heavily eutrophic lakes, when compared with those from other lakes.

Table 2: Diffusion flux of phosphorus at sediment water interface

Sampling Points	Φ	F/ [mg/(m^2·d)]
S1	0.62	0.0392
S2	0.56	-0.0009
S5	0.65	0.0315
S6	0.63	0.0355
S7	0.77	0.0518
S9	0.62	0.0217
S12	0.62	0.0400
S13	0.66	0.0258

4. Discussion

This study found that the sediment TP content of Caohai was low and it was a low phosphorus lake. The average TP content of Caohai was 559.75 mg/kg, which was lower than other lakes in the Yunnan-Guizhou Plateau, such as Erhai with an average content of 1442.30 mg/kg[23] and Dianchi with an average content of 2171.81 mg/kg, and similar to lakes in the middle and lower reaches of the Yangtze River, such as Taihu Lake. The average content of NH4Cl-P was 1 mg/kg and the average content of HCl-P was 18 mg/kg. The average content of NaOH-NRP was 53 mg/kg, NaOH-SRP was 89 mg/kg, Res-P was 296 mg/kg and BD-P was 24 mg/kg. The high value of HCl-P content was in the northeast part of the lake, and the overall content was lower in the west part of the lake; the high value of NaOH-NRP content was in the northeast and central part of the lake, and the lowest value was in the southeast part of the lake; the high value of NaOH-SRP content was in the deep water area in the central part of the lake, and the overall content was lower in the north than in the south; the highest value of Res-P content was in the The highest value of BD-P content occurs in the southwest part of the lake, while the eastern part of the lake has a lower content, showing an overall trend of gradually decreasing from the western part of the lake to the eastern part of the lake. NH4Cl-P refers to the loosely adsorbed phosphorus extracted from NH4Cl, and although it only accounts for a small proportion, it is seen as a valid indicator of lake pollution. Caohai is a typical grass-type lake with lush aquatic vegetation and high organic matter content, but low HCl-P content, which may be related to the particle size composition of Caohai sediments. Caohai sediments show strong reduction throughout the year, facilitating the dissolution of NaOH-SRP into the overlying water. NaOH-NRP is readily converted to bioavailable phosphorus for release into the pore water by changes in dissolved oxygen and microbial action. Sediments in large shallow lakes in late summer, autumn and winter are often anoxic due to the decomposition of organic matter. Res-P, or residual phosphorus, makes up the highest proportion of S-TP in the Caohai and is also known as inactive organic phosphorus, which has low solubility and is difficult to extract and use by phytoplankton.

The diffusive flux of phosphorus in Caohai sediments [-0.0009-0.0518 mg/(m^2 · d)] was much lower than that in eutrophic lakes such as Dianchi and Taihu Lake [21-22], which may be related to the more luxuriant aquatic plants in Caohai.

5. Conclusion

The mean TP content of Caohai sediment was 559.75 mg/kg, with low phosphorus content, but there was significant spatial variation. The diffusive flux of phosphorus in Caohai sediments ranged from -0.0009 to 0.0518 mg/(m^2·d), and the magnitude of different forms of phosphorus was Res-P>NaOH-NRP>NaOH-SRP>BD-P>HCl-P>NH4Cl-P.

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