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Characterization and pollution evaluation of TOC, TN and TP in sediments of Caohai Lake, Guizhou Province, China

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Abstract
Little is known about the distribution and risk levels of biological elements and nutrients in surface sediment of a closed, shallow, and eutrophication lake in a karst plateau wetland. Sediment/soil samples in Caohai lake, Guizhou Province, China and adjacent upland lakeshore were collected. The abundances of total organic carbon (TOC), total nitrogen (TN), TOC:TN, TOC: total phosphorus (TP), and TN:TP in the lake sediments were significantly higher than those in the surrounding lakeshore soils. 42.86% of the surface sediments exhibited TOC and TN concentrations above the severe effect level, whereas all selected TP concentrations fell between the lowest effect and severe effect levels. Sediment-bound TOC and TN were mainly derived from the endogenous residues, while TP was primary deposited in the form of inorganic phosphorus. Targeted measures should be implemented to reduce the levels of sediment-bound TOC and TN in Caohai Lake.

Keywords: *Total nitrogen; Total phosphorus; Surface sediment; Caohai Lake*

Introduction

Closed shallow lakes are an important ecological resource and habitat for various organisms and play a crucial role in regulating nutrient cycling (Zhuo et al.., 2022). The amounts of total nitrogen (TN) and total phosphorus (TP) in sediments can reportedly reflect the degree of lake eutrophication, frequency of algal blooms, climate variations, human activities, and the long-term evolution of lake environments (Anderson et al., 2014; Deng et al., 2022; Zhuo et al., 2022). Compared to open lakes, close inland lakes with higher primary productivity tend to exhibit greater enrichment of total organic carbon (TOC), TN and TP in the sediment (Zhuo et al., 2022). With changes in human activities over the past century, the excessive loading of TN and TP has prolonged eutrophication, contributed to surface water deterioration, and raised human health concerns in lakes such as Caohai Lake (Yu et al., 2021) and Taihu Lake (Deng et al, 2022; Yin et al., 2023).

Thus, elucidating the distribution of nutrient concentrations and their ecological stoichiometry in lake sediments is critically important for ensuring water security (Yin *et al.* 2023). The levels of TN and TP in lake sediments is influenced by the external and internal sources (Pearce *et al.* 2017; Wang *et al.* 2017; Deng *et al.* 2022). Exogenous loads of nitrogen and phosphorus generally enter the lake through atmospheric deposition, riverine inflows, and municipal wastewater discharges (Wang *et al.* 2017; Deng *et al.* 2022), whereas endogenous nutriment loads are mainly derived from the release of lake sediments (Pearce *et al.* 2017; Wang *et al.* 2017; Yin *et al.* 2023). Even when external specific elements are effectively controlled, the release of endogenous nutrients from the contaminated sediments can partially sustain the risk of lake eutrophication for decades (Wang *et al.* 2017; Yu *et al.* 2021; Yin *et al.* 2023). Thus, understanding the distribution characteristics of nutrients in

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lake sediments provides essential scientific data for informing lake health management (Li *et al.* 2024a). Caohai Lake, the closed shallow eutrophication lake in the karst plateau wetland (Dong *et al.* 2023; Zhang *et al.* 2023), is mainly polluted by agricultural nonpoint sources (Hu *et al.* 2025). The water quality of Caohai Lake is grade IV or worse than grade V (Yang *et al.* 2024). Thus far, the attention on Caohai Lake has primarily concentrated on nutrient levels and heavy metal contamination in both sediments and the water columns (Dong *et al.* 2023; Chao *et al.* 2024; Li *et al.* 2024a). Several studies on sediment nutrient pollution in this lake have been mainly limited to preliminary analysis of the
source and fate of specific elements (Yu *et al.* 2021; Dong *et al.* 2023). The aim of this study was (1) to determine the overall pattern of TOC, TN, and TP in lake sediments and surrounding lakeshore soils (LSs), (2) identify the interrelationship among TOC, TN, and TP in the sediments of Caohai Lake, and (3) evaluate the pollution status of sediment-bound TOC, TN, and TP.

Materials and methods

Study area

Caohai Lake (104°10'–104°20'E, 26°47'–26°52'N) is the largest overwintering habitat of migratory birds in Guizhou Province, China (Yin *et al.* 2020; Zhang *et al.* 2023). It experiences a distinct wet and dry season, with a mean annual precipitation of 950 mm and an annual temperature of 10.6℃ (Yin *et al.* 2020; Zhang *et al.* 2023). Caohai Lake is an inland closed lake with an average annual inflow of 0.48 × 10^8 m^3 and an outflow of 0.45 × 10^8 m^3 (Yin *et al.* 2020). The freshwater shallow lake has a total water storage area of 25 km^2 at an average water depth of 1.5 m (Zhang *et al.* 2023). The concentrations of TN, TP, and chlorophyll α in lake wake were 0.59–1.21 mg L^{-1}, 0.08–0.11 mg L^{-1}, and 7.54–20.46 μg L^{-1} (Dong *et al.* 2023), respectively.
All sampling points of the surface sediment (SSs) in the Caohai Lake and surrounding LSs are shown in Fig. 1. The sediment samples (0–10 cm) were collected using a stainless steel grab sampler within 2-m square collection locations at each sampling station. The soil samples (0–10 cm) were collected using a stainless spade. Each soil sample consisted of three subsamples. All samples were air-dried in the shade at 25±3 ℃, ground, and sieved using a 100-mesh sieve.

Laboratory analysis

TOC and TN were determined using a TOC analyzer (Vario TOC Select, Germany) after removing the carbonates using a 6% sulfurous acid (Kang *et al.* 2022). TP was quantified using inductively coupled plasma-atomic emission spectroscopy (Horiba Jobin Yvon, France) following digestion with $HClO_4$-HF (Shen *et al.* 2020). Available phosphorus (AP) was quantified the molybdenum–antimony colorimetric method (Shen

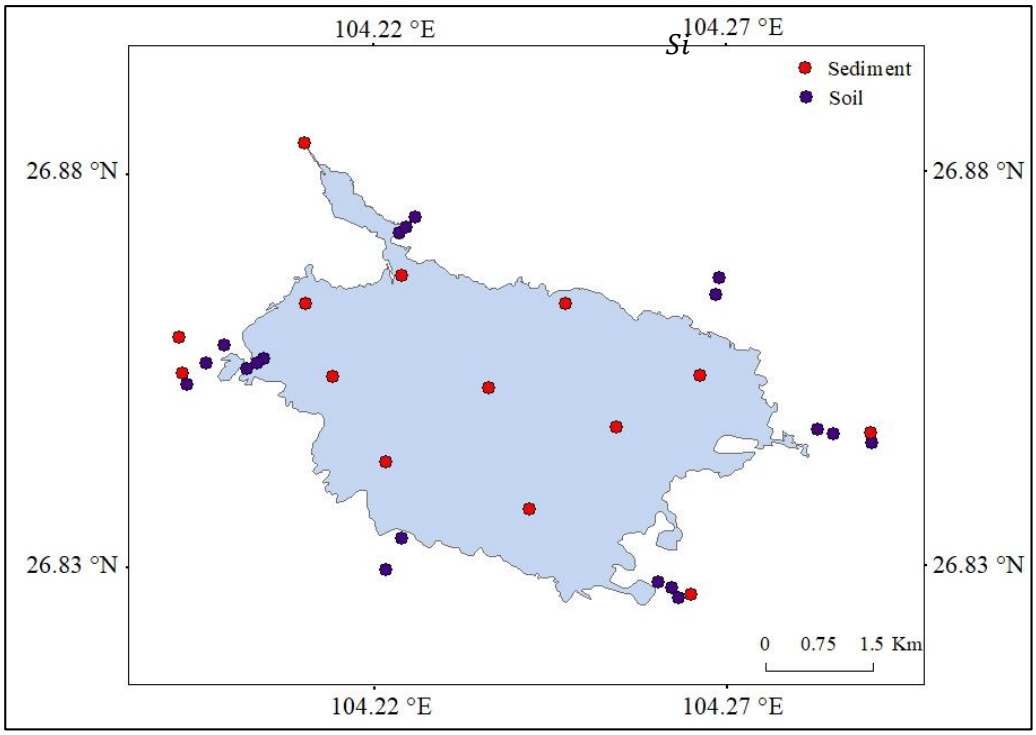

Figure 1
Location of the sampling sites in Caohai Lake

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et al. 2020), while nitrite was determined by the AA3 continuous flowanalyzer (Seal Co, Germany).

Sediment contamination evaluation

The nutrient status of SSs was assessed using the organic carbon index (OI) (equation [1]) and organic nitrogen index (ON) (equation [2]), and subsequently categorized as previously reported by (Zhang *et al.* 2015; Zhu *et al.* 2023; Li *et al.* 2024b).

$$OI = TOC \times ON \quad [1]$$

$$ON = TN \times 0.95 \quad [2]$$

The nutrient pollution index (Si) was calculated using equation [3] and categorized based on previous studies (Zhang *et al.* 2015; Qiu *et al.* 2023; Zhu *et al.* 2023).

$$Si = Ci / Cs \quad [3]$$

where Ci is the measured concentration of nutrient i, Cs denotes the screening value for the sediment environment (0.055 %, and 0.06 % for TN and TP respectively).

Results and discussion

Variation in the biological elements and nutrients

TOC and TN in SSs were higher than those in LSs (Fig. 2a-b). Compared with the non flooding upland soils, the permanent flooding water sediments are inconducive to the mineralization and decomposition of organic nitrogen (Shen *et al.* 2022). As shown in Figure 2c, a small positive TN intercept at zero TOC reflected the contribution of nitrate, nitrite and ammonium to TN were not ignored (Yang *et al.* 2019). The high ratio of TOC:TN favored the accumulation of TOC, whereas the low ratio of TOC:TN was conducive to the increasing available nitrogen (Zhang *et al.* 2017; Lu *et al.* 2024). Similar to the results of (Shen *et al.* 2022) in Poyang Lake, the TOC/TN ratio observed in LSs was lower than that in SSs (Fig. 2d). These results partially revealed that the rate of TOC accumulation was greater than the rate of TOC decomposition in SSs (Lu *et al.* 2024). The relatively large coefficient of variation in the sediment-bound TOC (Fig. 2a) was attributed to aquatic residues (Yuan *et al.* 2012; Deng *et al.* 2022; Lu *et al.* 2024). The relatively lower nitrite in SSs than in LSs (Fig. 3a) also implied the relatively weak denitrification rate in SSs. The mean TOC:TN in SSs (Fig. 2d) was lower than that in peatland wetlands in China (26.72) (Zhang *et al.* 2017) but higher than that in Chinese soils (11.9) (Tian *et al.* 2010) and global soils (14.3) (Xue *et al.* 2019). TOC and TN were mainly derived from the endogenous residues. The mean concentrations of sedi-

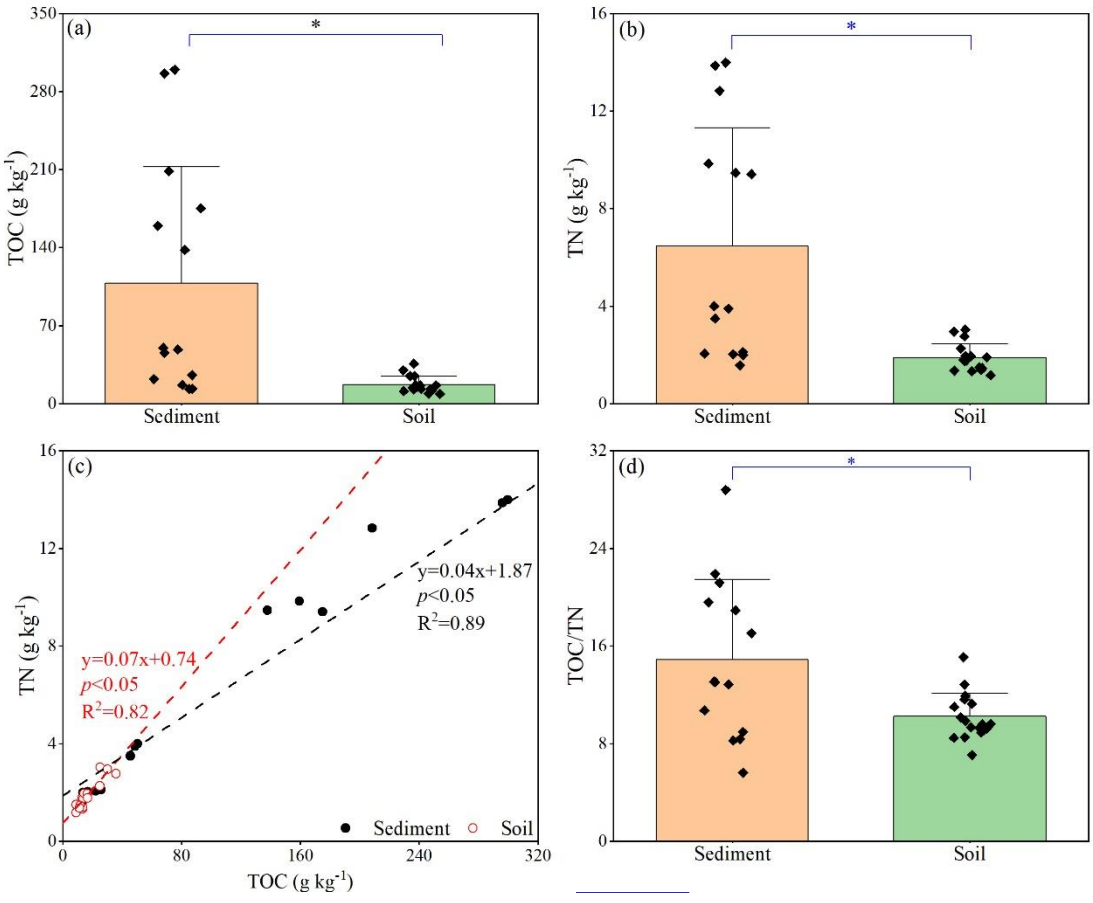

Figure 2
Variation in total organic carbon and total nitrogen

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ment-bound TOC and TN in Caohai Lake were higher than those in Dongting Lake (Lu *et al.* 2024), Daye lake (Qiu *et al.* 2023), and Jangseong Lake (Kang *et al.* 2022). This highlighted that the anaerobic environment in Caohai Lake is more conductive to the TOC accumulation with a limited rate of TN mineralization. The abundance of TP was more sensitive to the parent material but less affected by TOC and exogenous pollution (Kamiya *et al.* 2017; Lu *et al.* 2024). The long-term anaerobic treatment increased the dissolution and dif-fusion of the soil phosphorus (Tammeorg *et al.* 2018), thereby leading to a high TOC:TP. The higher the soil TOC:TP, the lower the bioavailability of soil phosphorus (Zhang *et al.* 2017; Wu *et al.* 2023; Lu *et al.* 2024). A TOC/TP ratio smaller than 200 can result in the net mineralization of organic phosphorus (Zhang *et al.* 2017; Wu *et al.* 2023). In this study, all TP concentrations in Caohai Lake (Fig. 3b) were lower than those in shallow eutrophic lakes, e.g., Finnish (Tammeorg *et al.* 2018) and Kasumigaura (Kamiya *et al.,* 2017). The mean value of the TOC/TP ratios in the SSs (Fig. 3c) fell above the Chinese soils (62.0) (Tian *et al.* 2010), global soils 186.0 (Xue *et al.* 2019) and the threshold corresponding to the net fixation of organophosphates (300) (Wu *et al.* 2023) but lower than those recorded in the peatland soils of China (1186.00) (Zhang *et al.* 2017). AP were significantly lower in SSs than in LSs (Fig. 3d), indicating higher availability and net mineralization of organophosphates in LSs (Lu *et al.* 2024). A significant positive relationship between TOC

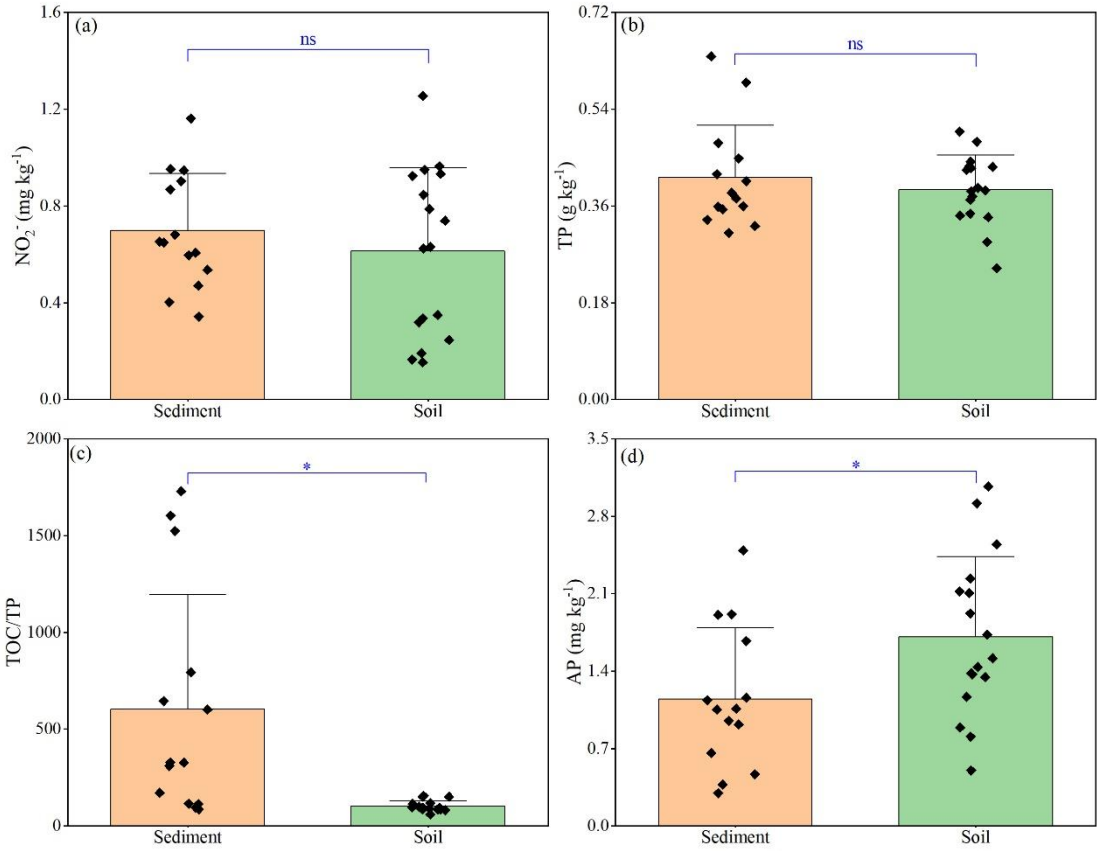

Figure 3
Variation in NO_2^- (a), total phosphorus (b), TOC:TP (c) and available phosphorus (d)

and the ratio of TOC:TP (Fig. 4a) confirmed the internal relationship between the decomposition of TOC and phosphorus bioavailability. The soil TN:TP ratio is related to growth rates (Lu *et al.* 2024) and a low soil TN:TP ratio implies greater soil nitrogen limitation (Zhang *et al.* 2017). Increasing TN:TP ratios have also been observed in large rivers and lakes (Pandey and Pandey 2015; Tong *et al.* 2020). The sediment mean TN/TP ratio (Fig. 4b) was almost above the estimate of 13.1 for global soils (Xue *et al.* 2019), 5.2 for China soils (Tian *et al.* 2010), and 3.26 for herbaceous lake wetlands (Chang *et al.* 2023) but notably lower than those recorded in the peatland soils of China (46.58) (Zhang *et al.* 2017), indicating a P-limited environment. The levels of the sediment TN:TP ratio and TOC concentration were closely correlated (Fig. 4c), highlighting the internal relationship between the sediment TN:TP ratio and TOC (Liu *et al.* 2010).

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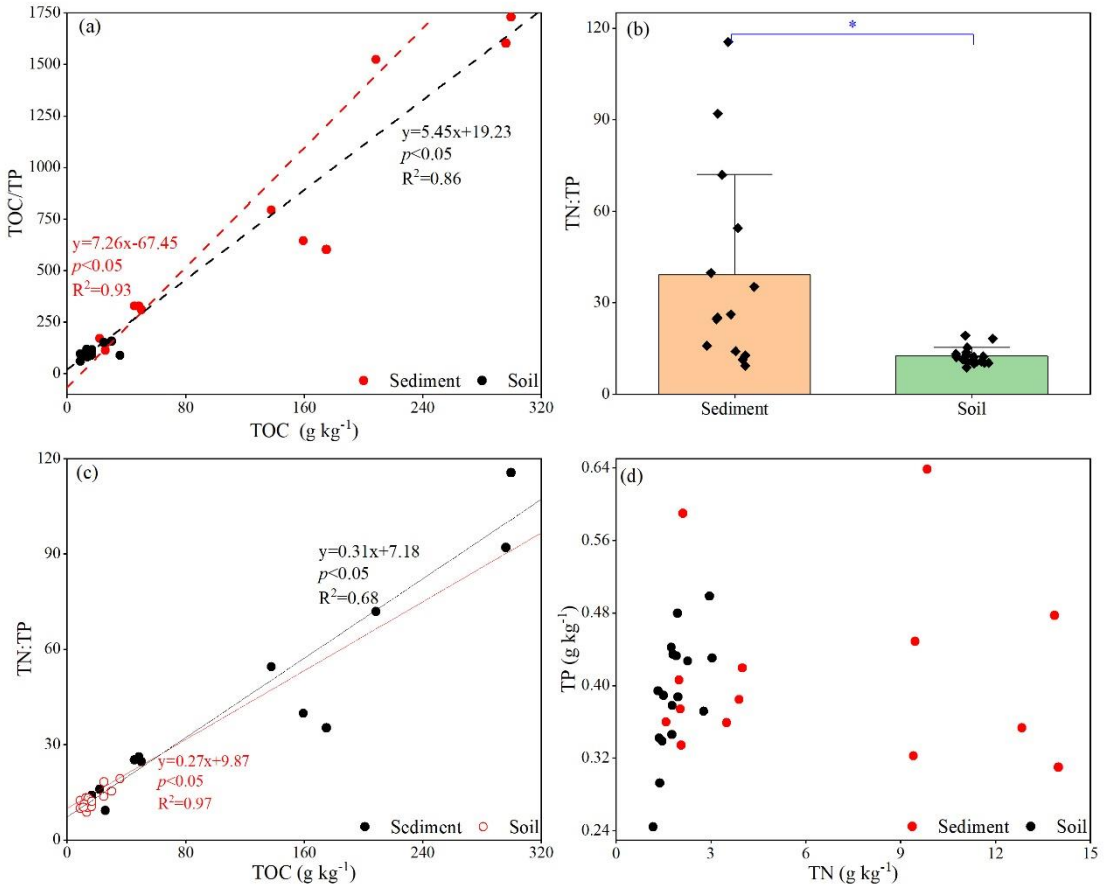

Figure 4
TOC vs TOC:TP (a), distribution of TN:TP (b), TOC vs TN:TP (c) and TN vs TP (d)

Toxicity evaluation

The higher the concentration of specific nutrients in the lake sediments, the greater the potential for biological toxicity to benthic organisms (Persaud *et al.* 1993; Kang *et al.* 2022; Qiu *et al.* 2023). In Caohai Lake, 42.86% of the sediment samples had TN and TOC concentrations exceeding the severe effect levels (TOC = 10%, TN = 4.8 g kg^{-1}), indicating a high likelihood of toxicity to benthic organisms (Persaud *et al.* 1993; Kang *et al.* 2022; Qiu *et al.* 2023). Under such conditions, the sediment becomes inhabitable for dwelling organisms. All TP concentrations fell within the range between the lowest effect and severe effect levels (0.06%–0.2 %) (Kang *et al.* 2022; Qiu *et al.* 2023), and TP was expected to cause occasional adverse consequences on the benthic community. The sediment OI in Caohai Lake ranged from 0.2–52.66, with over 71% of the selected sediment classified as heavily polluted with an OI greater than 0.50% (Fig. 5a). ON exceeded 0.133% across all data points, indicating that the severe

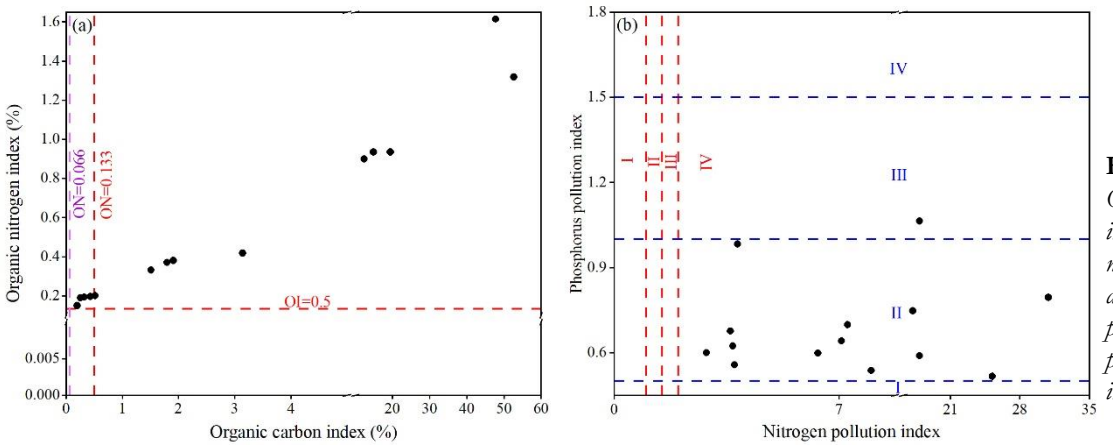

Figure 5
Organic carbon index vs organic nitrogen index (a) and nitrogen pollution index vs phosphorus pollution index (b)

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ON pollution in these lakes was rather severe (Zhang *et al.* 2015; Li *et al.* 2021; Zhu *et al.* 2023). The pollution index of TN and TP were 2.87–30.89 and 0.52–1.06, respectively (Fig. 5b). A relatively high pollution index of TN and TP in Caohai Lake was also recorded in 2012 (Yuan *et al.* 2012) and 2022 (Dong *et al.* 2023). TOC and TN depleted oxygen in the sediment and overlying water than TP in Caohai Lake (Yuan *et al.*,2012). Further research on the TOC release from the Caohai Lake sediment should be undertaken to determine the adverse effects of TOC release on the overlying water quality.

Conclusions

The levels of TOC, TN, TOC:TN, TOC:TP, and TN:TP in the SSs were significantly higher than those in the LSs. A total of 42.86% of the SSs had a TN concentration over 4.8 g kg^{-1}. The mean ratios of TOC:TN, TOC:TP, and TN:TP in SSs fluctuated 14.87 ±6.12, 603.00 ±552.76, and 39.16 ±30.62, respectively. The data showed an insignificant positive corre-lation between TP and both TOC and TN, whereas the levels of TOC and TN were closely correlated. Sediment-bound TOC and TN were mainly derived from the endogenous source, whereas TP was primarily derived from the pa-rent mineral weathering. The sediments in the Caohai Lake were severely enriched in TOC, TN, and organic nitrogen and showed moderate to severe enrichment of TP. These findings suggested that some measures should be implemented to reduce the potential enrichment of sediment-bound TN and TOC in Caohai Lake.

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Ethics declarations CRediT authorship contribution statement

Xu Zhang and Shinong Liu: Writing, Investigation, Software, Methodology, Formal analysis. Xiaolong Huang: Methodology, Investigation, Data curation. Jingcheng Ran and Dan Yang: Supervision, Funding acquisition, Conceptualization.

Competing Interest

The authors declare no competing interests.

Data availability

Data will be made available on request.

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