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Research Article

Variations of sediment organic phosphorus and organic carbon during the outbreak and decline of algal blooms in Lake Taihu, China

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ABSTRACT

In this study, sediment organic phosphorus (OP) and organic carbon (OC) in Lake Taihu, China, as well as their relationships, were analyzed during the outbreak and decline of algal blooms (ABs) over a five-month field study. The results showed synchronous temporal changes in the sediment OP and OC contents with the development of ABs. In addition, there was a significant positive correlation between the sediment OP and OC ($p < 0.01$), suggesting simultaneous deposition and consumption during the ABs outbreak. The sediment OP and OC contents decreased significantly at the early and last stages of the ABs outbreak and increased at the peak of the ABs outbreak and during the ABs decline. These temporal variation patterns suggest that the sediment OC and OP contents did not consistently increase during the ABs outbreak, even though algae are an important source of organic matter in sediments. The depletion or enrichment of OC and OP in sediments may also depend on the scale of the ABs outbreak. The obtained results revealed significant differences in the sediment OC and OP contents between the months ($p < 0.05$). In addition, OP in the sediments was dominated by orthophosphate diester (phospholipids and DNA-P) and orthophosphate monoester during the ABs outbreak and decline, respectively. The active OC contents and proportions in the sediments in the ABs outbreak were significantly lower than those observed in the ABs decline period, demonstrating the significant impacts of the ABs outbreak and decline on the sediment OC and OP in Lake Taihu.

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Introduction

Phosphorus (P) is a key nutrient for lake eutrophication and plays a dominant role in the promotion of algal blooms (ABs) (Daniel et al., 2009; Xie et al., 2003; Xu et al., 2015). Lake sediments are important storage pools for P and continuously exchange P with the overlying water (Søndergaard et al., 2001). The release of P from shallow lake sediments can substantially accelerate the eutrophication process even with low external P inputs (Hupfer and Lewandowski, 2008; Søndergaard et al., 2003; Zhang et al., 2021). Organic P (OP) is one of the major sediment P forms in lakes (Bai et al., 2009; Shinohara et al., 2017). The decomposition of OP is an important component of the P cycle in sediments, providing a source of P for algal growth in lakes (Ni et al., 2016; Shinohara et al., 2017; Yu et al., 2022a; Zhang et al., 2015). Spears et al. (2007) indicated that the decomposition of OP potentially maintains a low magnitude and long-term release of bioavailable P. High pH values and low dissolved oxygen (DO) levels associated with ABs outbreak can promote the release of OP from sediments, persistently maintaining ABs in lakes even under externally controlled P loading or low soluble reactive P (SRP) levels in water (Ni et al., 2019a). In addition, algal debris deposits can enhance the accumulation of bioavailable OP in sediments (Zhou et al., 2022). Similar to inorganic P (IP), Ni et al. (2022) pointed out a very close relationship between the biogeochemical cycle of sediment OP and ABs development in eutrophic lakes. The contents and compositions of sediment OP may be strongly altered as a result of changes in the lake environment induced by ABs outbreak and decline. However, previous studies on sediment P during ABs have mainly focused on IP fractions and rarely assessed the effects of ABs on sediment OP (Han et al., 2015; Yuan et al., 2017). Therefore, it is necessary to investigate the variations in the sediment OP content and composition during the ABs outbreak and decline to better understand the biogeochemistry cycle of internal OP in lakes.

The role of lakes in carbon (C) sequestration may become increasingly important as terrestrial C sequestration continues to decrease along with increasing atmospheric carbon dioxide (CO_2) concentrations (Tranvik et al., 2009). Algae, as an important component of the primary production of water bodies, play a vital role in the biogeochemical cycle of C in aquatic ecosystems (Yu et al., 2022b). Inorganic C can be transformed into organic C (OC) through algal photosynthesis (Wyatt et al., 2014). Algal-derived OC can be released into water and sediments following algal cell death (Wang et al., 2021; Zhou et al., 2022). The deposited OC in lake surface sediments can subsequently be buried over time and/or mineralized to methane (CH_4) and CO_2 (Diesing et al., 2021). The contribution of algal-derived OC to sediment OC contents may be substantial due to the high algal productivity during the ABs process (Fujibayashi et al., 2019). Whereas the increase in pH values induced by ABs can enhance the OC mineralization, affecting the occurrence of OC in lake sediments (Anderson et al., 2014; Wang et al., 2021). Thus, it is presumed that sediment OC contents may not increase consistently during ABs because OC accumulation in sediments depends on the balance between C sequestration and mineralization.

In addition, OC is one of the main factors affecting the transformation of OP in aquatic environments (Filippelli, 2001; Zhao et al., 2020). Microbial degradation of dissolved organic carbon (DOC) in aquatic environments can lead to oxygen depletion and water acidification, which may potentially promote the release of OP from sediments (Li et al., 2016). In addition, DOC can promote the production of alkaline phosphatase, which may contribute to the mineralization of OP in lake sediments (Anderson, 2018; Dong et al., 2022). Yu et al. (2022b) highlighted that the biogeochemical cycles of C and P are closely related to lake primary production and organic matter (OM) degradation. Indeed, large proportions of C and P are deposited at the sediment-water interface as OC and OP of OM, suggesting possible direct interactions between sediment OC and OP.

Lake Taihu is a large shallow lake with an average water depth of about 2.0 m, covering a surface area of 2340 km^2 (Qin, 2020). In fact, this lake has been affected by severe eutrophication and ABs since the 1960s (Ding et al., 2015). As a typical shallow lake, Lake Taihu sediments play a prominent role in the C and P cycles of the lake ecosystem. Most previous studies have mainly focused on either the sediment OP or OC in Lake Taihu. For example, Yu et al. (2022b) revealed a range of the OC deposition rate in Lake Taihu sediments of 31.91-114.47 g C/m^2/year. On the other hand, Zhang et al. (2008) and Bai et al. (2009) showed high OP accumulations in the heavily polluted sediments of Lake Taihu. However, there is little information regarding the relationship between sediment OC and OP in Lake Taihu, especially during the ABs process. Therefore, the present study aims to: (1) investigate the variation in the OC and OP contents and fractions in the surface sediments of Lake Taihu during the outbreak and decline of ABs; (2) assess the effects of ABs on the sediment OP and OC; and (3) elucidate the OC-OP relationships during the ABs outbreak in Lake Taihu.

1. Materials and methods

1.1. *Study area and sample collection*

Lake Taihu is the third largest freshwater lake in China, located in the highly developed and most densely populated Yangtze Delta (Ding et al., 2015). The regional climate in the study area is subtropical monsoon, with a long-term annual average temperature range of 16-18°C and annual precipitation of 1100-1150 mm. A large volume of domestic and industrial wastewater from surrounding cities has been discharged into the lake since the 1960s, resulting in serious eutrophication issues (Qin et al., 2016). Zhushan Bay is located in the downwind direction of the prevailing southeastern wind in the northeastern area of Lake Taihu (Fig. 1), thereby resulting in the accumulation of algae in this area from the wider lake area (Zhou et al., 2016). Qin (2020) highlighted the occurrence of ABs in Zhushan Bay mainly in summer.

In this study, sediment samples were collected from Zhushan Bay (31°27′24"N; 120°2′37"E) over the June-October 2016 period on June 5th, July 21st, August 24th, September

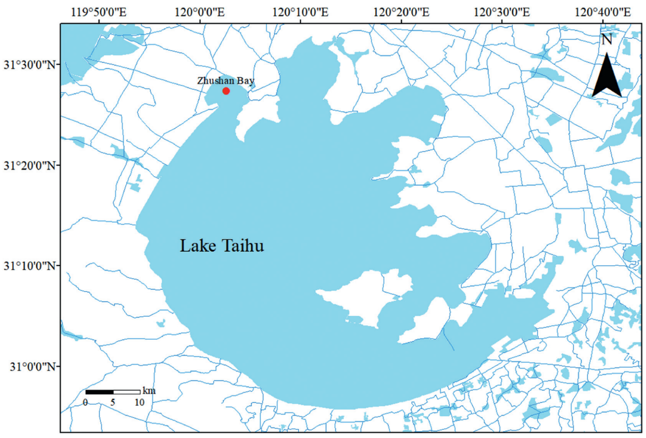

Fig. 1 – Sampling site in Lake Taihu.

23rd, and October 29th, covering the outbreak and decline periods of ABs (Bai et al., 2017). In order to ensure the reliability of monitoring data, the geographic coordinate (longitude and latitude) of the sampling site was recorded on the first sampling date (June 5th) to collect sediment samples from the same sampling site on the subsequent dates. In total, six parallel surface sediment cores (0-2 cm depth) and overlying water were collected each month. The collected samples were first evenly mixed, then stored in refrigerators at 4°C for further analysis.

1.2. *Determination of water quality and sediment properties*

In this study, chlorophyll-a (Chl-a) contents in lake water were determined by spectrophotometry at 665 and 750 nm wavelengths following extraction with a 90% ethanol solution (Chen et al., 2006). Water DO concentrations and water temperatures were measured synchronously using a fiberoptic oxygen meter (FirestingO_2, Pyro Science, Germany). In addition, the wet sediment samples were centrifuged to obtain pore water. The pore water was then filtered through a 0.45 µm membrane before analyzing the filtrates for DOC contents using a total organic carbon (TOC) analyzer (Vario TOC select, Elementor, Germany). The sediment moisture contents were determined using the gravimetric method, while the sediment pH values were determined using a pH meter (PHS-3C, Rex Electric Chemical, China). The collected sediment samples were first calcinated for 3 hr at 450°C, then total P (TP) was extracted using 3.5 mol/L HCl solutions. Sediment IP was extracted from sediments with 1 mol/L HCl, while OP was extracted using a 1 mol/L HCl solution following the calcination of the solid residue from IP extraction at 450°C for 1 hr (Ruban et al., 2001). The P contents in the extracts were analyzed using the molybdenum blue method (Murphy and Riley, 1962).

The TOC and active organic carbon (AOC) contents in the collected sediment samples were determined using the K_2CrO_4-external heating and permanganate oxidation methods, respectively (Institute of Soil Science, Chinese Academy of Sciences, 1978). Sediment DOC was first extracted from the sediment samples using ultrapure water, then the extracted DOC solution was filtered through a 0.45 µm membrane filter and analyzed using a TOC analyzer (Vario TOC select, Elementor, Germany). Furthermore, the filtered DOC solution was analyzed in a 1 cm quartz cuvette using a UV-VIS spectrophotometer (UV3600, Shimadzu, Japan) at a wavelength range of 200-700 nm to determine the UV-visible spectral parameters of dissolved organic matter (DOM) (Ni et al., 2019a). The 253:203 nm UV absorbance ratio of the extracted solution (E253/E203) was used to reflect the concentrations of DOM substitution groups. The E253/E203 ratio values can increase with increasing the concentrations of the aromatic substitution groups in DOM (Korshin et al., 1997; Wang et al., 2009). SUVA254 is an effective index for estimating the proportion of aromatic compounds in DOM (Pang et al., 2020). This index was calculated in this study as 100 times the ratio of UV absorbance at 254 nm to the corresponding DOC concentration. The SUVA254 values increase with increasing the humification and aromaticity degrees (Weishaar et al., 2003). Furthermore, the Abs285 value can also reflect the DOM aromatization degree. A high Abs285 value also indicates a high DOM aromaticity degree (Kalbitz et al., 2000).

1.3. *P extraction and ^{31}P NMR analysis*

Phosphorus-31 nuclear magnetic resonance spectroscopy (^{31}P NMR) is a non-destructive and non-invasive technique used to identify P forms, allowing simultaneous characterization of multiple P compounds with distinct binding properties (Bai et al., 2017; Spears et al., 2007; Zhang et al., 2013). Moreover, this technique can overcome the complexity of OP composition and structure (Kwak et al., 2018; Wen et al., 2020). Several sediment P compound classes can be detected using ^{31}P NMR, including phosphonate, orthophosphate (Ortho-P), orthophosphate monoesters (Mono-P), orthophosphate diesters (Diester-P), pyrophosphate (Pyro-P), and polyphosphate (Poly-P), thus providing insight into the composition of OP in lake sediments (Ahlgren et al., 2006; Shinohara et al., 2012).

In this study, sediment P was pre-extracted by adding 1 g of sediment to an 8 mL solution of 0.5 mol/L NaOH and 0.1 mol/L ethylenediaminetetraacetic acid disodium salt (Na_2-EDTA), followed by orbital stirring at 20°C for 16 hr and centrifugation at 4000 r/min for 10 min (Bai et al., 2017). The IP contents in the NaOH-EDTA extracts were analyzed using the molybdenum blue method (Murphy and Riley, 1962). Whereas the TP contents in the NaOH-EDTA extracts were analyzed using the molybdenum blue method after digestion with $K_2S_2O_8$ (Murphy and Riley, 1962). The OP contents in the NaOH-EDTA extracts were determined by calculating the difference between the TP and IP contents. The remaining NaOH-EDTA extracts were concentrated to approximately 1 mL at 28°C using a rotary vacuum evaporator, then stored at -18°C until ^{31}P NMR spectroscopy analysis.

The extracts were placed into 5-mm NMR tubes with deuterium oxide (D_2O) (10%) prior to ^{31}P NMR spectroscopy analysis to capture the signals. The solution ^{31}P NMR spectra were obtained at 161.84 MHz using an Agilent AV 400 spectrometer, with a pulse angle, relaxation delay, and acquisition time of 45°, 1 sec, and 0.4 sec, respectively (50 ppm window centered at 0 ppm). The analysis of each sample lasted over 15 hr.

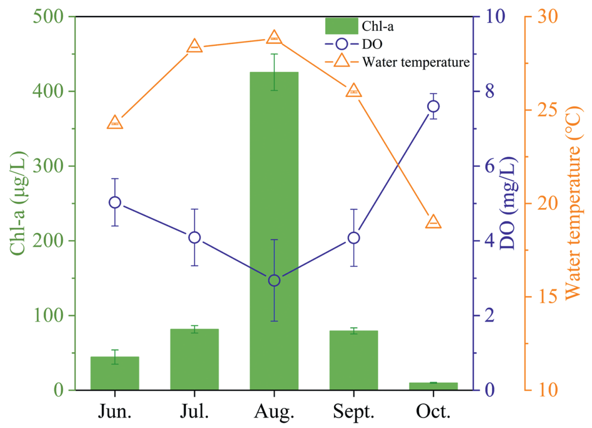

Fig. 2 – Variations of chlorophyll-a (Chl-a), dissolved oxygen (DO), and temperature in the water of Zhushan Bay from June to October.

Spectra were obtained based on approximately 20,000 scans. Chemical shifts were recorded with respect to 85% H_3PO_4 via the signal lock. Peaks were assigned using a ^{31}P NMR chemical shift of phosphonate (18-20 ppm), Ortho-P (6-7 ppm), Mono-P (4-6 ppm), phospholipids (1-3 ppm), deoxyribonucleic acid (DNA-P) (0 ppm), Pyro-P (-3.5 to -4.5 ppm), and Poly-P (-17 to -19 ppm) (Turner et al., 2003). While peak areas were calculated by integration.

1.4. *Data analysis*

In this study, ^{31}P NMR spectral data were analyzed using MestReNova14.0. In addition, the Pearson correlation analysis was performed in this study to assess the correlations between different sediment parameters. While the one-way analysis of variance (ANOVA) was performed to determine whether the temporal variations in the sediment parameters are significant at the $p < 0.05$ level. All statistical tests were performed using IBM SPSS25.0 statistics software.

2. Results

2.1. *Water and sediment properties*

As shown in Fig. 2, the DO concentrations in the overlying water decreased from June (5.03 mg/L) to August (2.94 mg/L) and increased to 7.60 mg/L in October. The higher water temperatures were observed in July (28.4°C) and August (28.8°C), while the lowest water temperature was observed in October (18.9°C). Chl-a concentrations showed increasing and decreasing trends from June (44.50 μg/L) to August (425.53 μg/L) and from September (79.49 μg/L) to October (9.90 μg/L), respectively.

The physicochemical properties of pore water and sediment from June to October are reported in Table 1. The mean DOC concentrations in pore water were 16.25 and 11.74 mg/L in July and October, respectively, showing significantly higher concentrations than those observed in June (7.61 mg/L), August (6.67 mg/L), and September (7.37 mg/L). The average sediment moisture contents in the sampling period ranged from 57.49% to 73.42%, showing a slight monthly variation. The lowest sediment pH value was 7.23 in June, while the pH values in other months were similar, oscillating around 7.54.

Table 1 – Properties of pore water and sediments in Zhushan Bay.

Month	Pore water DOC (mg/L)	Sediment Moisture content (%)	pH
June	7.61	69.73	7.23
July	16.25	57.49	7.59
August	6.67	73.42	7.49
September	7.37	60.42	7.52
October	11.74	67.48	7.55

2.2. *Variations in OC and OP contents in the surface sediments*

The TOC, AOC, and DOC contents in the surface sediments from June to October are shown in Fig. 3a-c. The mean TOC contents were 24.42 mg/g and 23.46 mg/g in June and August, respectively (Fig. 3a), which were significantly higher than those observed in July (17.88 mg/g), September (15.01 mg/g), and October (18.63 mg/g). The mean sediment AOC contents were 6.56 and 6.41 mg/g in June and August, then decreased considerably to 3.31 and 4.46 mg/g in July and September, respectively (Fig. 3b). The highest mean sediment AOC content was 8.16 mg/g in October. The AOC proportion in sediments ranged from 18.27% to 44.60% of TOC, showing the lowest and highest levels in July and October, respectively (Fig. 4a), while the values in other months were similar, oscillating around 28%. The average sediment DOC content in the collected surface sediments ranged from 0.07 mg/g in July to 0.27 mg/g in September (Fig. 3c). Whereas the average sediment DOC contents in June, August, and October were 0.18, 0.15, and 0.20 mg/g, respectively. The DOC proportion in sediments ranged from 0.45% to 1.49% of TOC, showing the lowest and highest levels in September and July October, respectively (Fig. 4b).

The TP, IP, and OP contents in the surface sediments from June to October are shown in Fig. 3d-f. The average TP content in the surface sediments ranged from 1181.93 mg/kg in September to 2340.40 mg/kg in June (Fig. 3d). The highest TP content was slightly higher than that observed in August (2045.93 mg/kg) and significantly higher than those revealed in July (1890.60 mg/kg) and October (1760.73 mg/kg). The average IP and OP contents in the surface sediments ranged from 1164.73 to 1884.87 mg/kg and 169.63 to 252.73 mg/kg, respectively (Fig. 3e and Fig.3f). The sediment IP and OP content trends were similar to that of the sediment TP contents. The proportions of the OP in TP contents ranged from 9.64% to 14.6%, showing relatively high values in September and October (Fig. 4c).

The correlation analysis results showed a significant positive correlation between the TP and OP contents in the surface sediments ($p < 0.01$), while the sediment pH values showed significant negative correlations with the sediment TP and OP contents ($p < 0.05$) (Table 2). In addition, the sediment TP con-

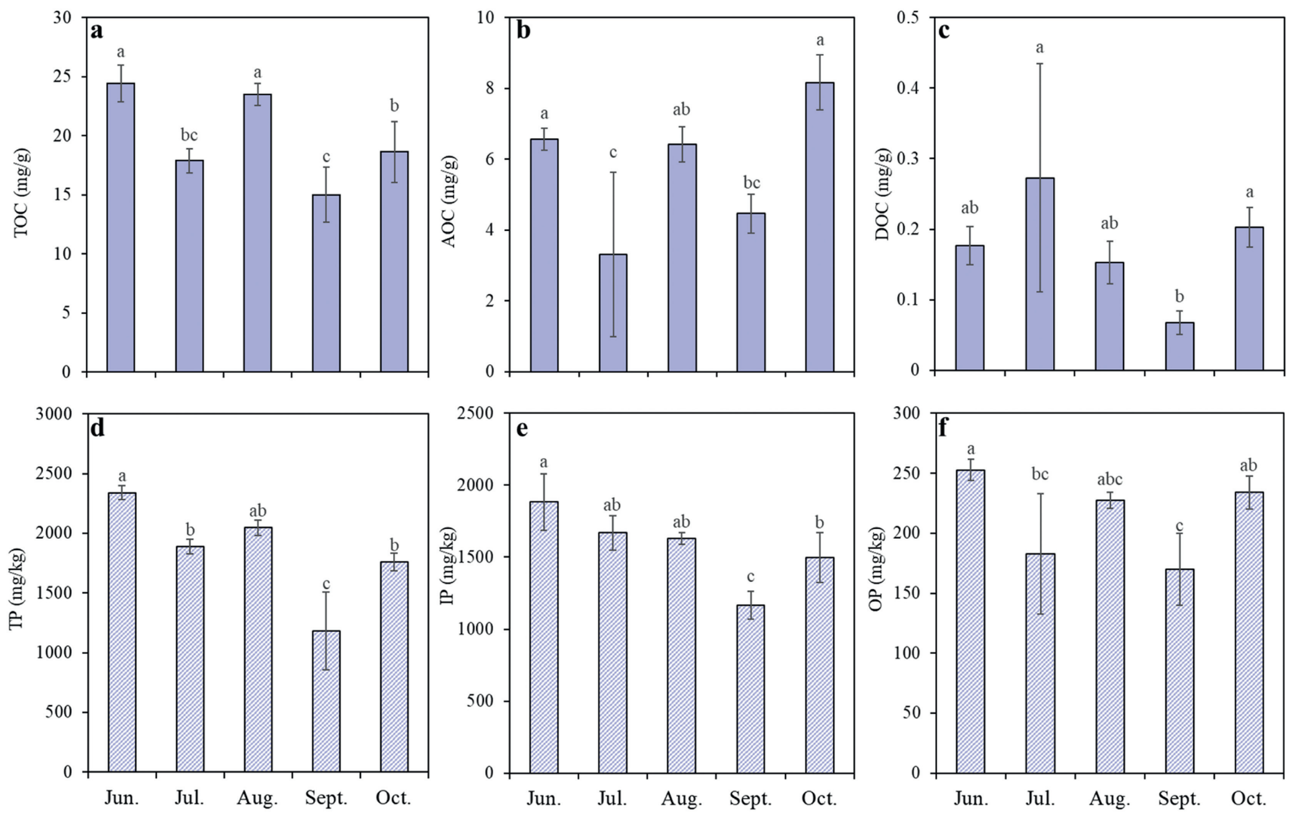

Fig. 3 – Variations of different C and P forms in the surface sediment of Zhushan Bay from June to October. (a) variation of TOC; (b) variation of AOC; (c) variation of DOC; (d) variation of TP; (e) variation of IP; and (f) variation of OP. Different lowercase letters above the error bars indicate that the contents are significantly different among months ($p < 0.05$).

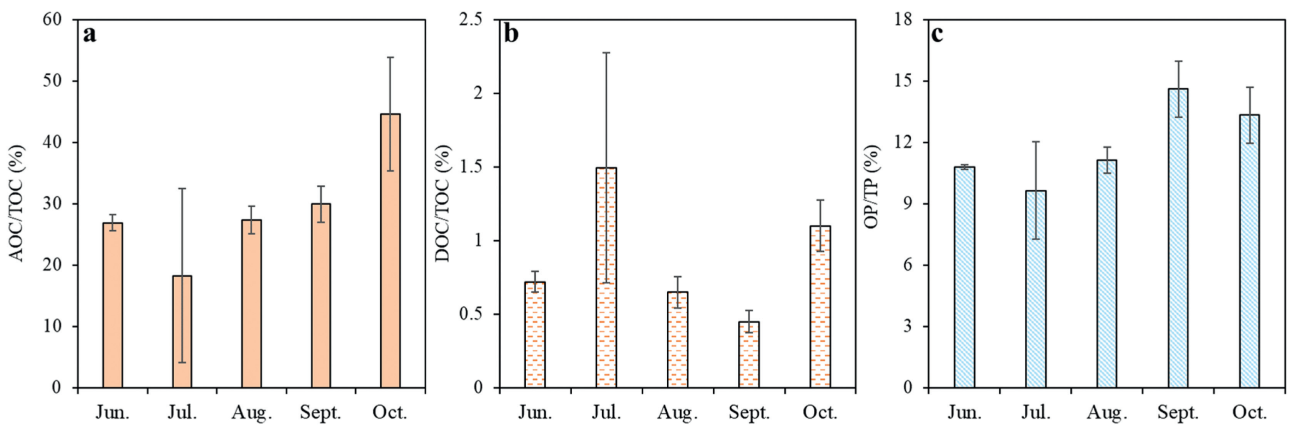

Fig. 4 – The percentage changes of (a) AOC in TOC, (b) DOC in TOC, and (c) OP in TP in the surface sediments of Zhushan Bay from June to October.

tents were significantly and positively correlated with the sediment TOC contents ($p < 0.01$). Whereas the sediment OP contents were significantly and positively correlated with the sediment TOC and AOC contents ($p < 0.01$).

2.3. *UV spectral characteristics of sediment DOM*

The UV-visible spectral parameters of DOM in the collected surface sediments are shown in Fig. 5. The E253/E203 ratio ranged from 0.22 in June to 0.29 in October. The maximum Abs285 value was 0.37 in June, then decreased significantly in July, August, and September to 0.17, 0.20, and 0.12, respectively, before increasing to 0.29 in October. The SUVA254 value was 2.84 in June, then decreased to 1.25 in July before showing an increasing trend from August (1.79) to October (3.31).

On the other hand, the Abs285 values showed a significant negative correlation with the sediment pH values ($p < 0.01$) (Table 2). In addition, the Abs285 values were significantly and

Table 2 – Correlation coefficients between OP fractions and other parameters in surface sediments.

	TOC	AOC	DOC	TP	OP	Moisture content	pH	E253/E203	Abs285	SUVA254	Mono-P	Phospho -lipids	DNA-P	Pyro-P
TOC	1													
AOC	0.348	1												
DOC	0.304	-0.118	1											
TP	0.859**	0.349	0.474	1										
OP	0.712**	0.743**	0.038	0.677**	1									
Moisture content	0.791**	0.528	0.108	0.580*	0.703**	1								
pH	-0.588*	-0.192	0.049	-0.592*	-0.562*	-0.414	1							
E253/E203	-0.064	0.384	0.013	0.083	0.102	0.134	0.161	1						
Abs285	0.629*	0.560*	0.286	0.712**	0.720**	0.521*	-0.679**	0.345	1					
SUVA254	-0.115	0.530	-0.453	-0.147	0.396	0.141	-0.319	0.415	0.512	1				
Mono-P	-0.621*	0.246	0.081	-0.422	-0.120	-0.305	0.504	0.455	-0.035	0.397	1			
Phospholipids	0.895**	0.353	0.073	0.748**	0.649**	0.684**	-0.695**	0.001	0.575*	0.009	-0.704**	1		
DNA-P	0.817**	0.260	-0.015	0.628*	0.481	0.606*	-0.680**	-0.123	0.509	-0.001	-0.757**	0.904**	1	
Pyro-P	-0.104	0.553*	0.268	-0.047	0.224	0.150	0.118	0.350	0.401	0.503	0.745**	-0.250	-0.238	1

*: p <0.05, **: p < 0.01.

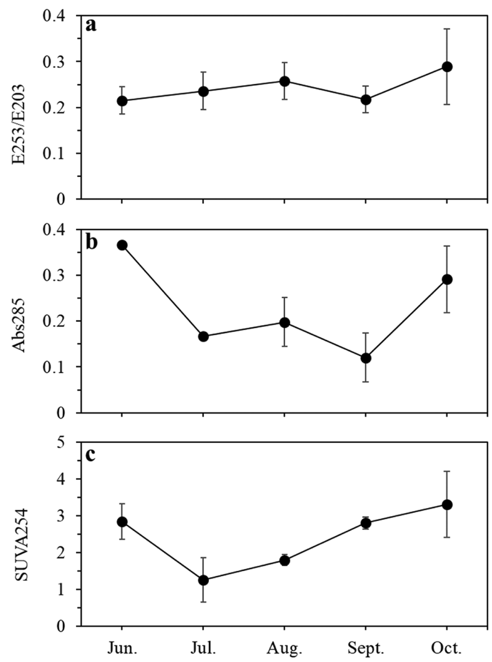

Fig. 5 – UV-visible spectral parameters of DOM in the surface sediments in Zhushan Bay. (a) E253/E203; (b) Abs285; and (c) SUVA254.

positively correlated with the sediment TOC and OP contents at the $p < 0.05$ and $p < 0.01$ levels, respectively.

2.4. *P fractions detected by ^{31}P NMR spectroscopy analysis*

In this study, five P compound classes were detected in the surface sediments using ^{31}P NMR spectroscopy, namely Ortho-P, Mono-P, phospholipid, DNA-P, and Pyro-P (Fig. 6). The results showed that Ortho-P was the main P component in the sediments, accounting for more than 90% (Table 3). In addition, Mono-P was observed only in July in the early sampling period (June to August), with an average sediment Mono-P content of 19.57 mg/kg, accounting for about 3.23% of the TP contents in the NaOH-EDTA extracts. In the later sampling period from September to October, the proportion of Mono-P in TP increased. The average sediment Mono-P contents in September and October were 17.37 and 38.76 mg/kg, accounting for 4.66% and 6.20% of the sediment TP content, respectively.

The proportions of phospholipids in TP ranged from 0.30% to 1.32%. The highest and lowest proportions were observed in August and September, respectively. In addition, the average phospholipid contents in June and August were 9.24 and 9.11 mg/kg, respectively, significantly higher than those observed in the remaining months. The lowest phospholipid content was 1.13 mg/kg in September. The average DNA-P contents were 17.15 and 14.08 mg/kg in June and August, accounting for 1.81% and 2.04% of the TP content in the NaOH-EDTA extracts, respectively. In contrast, significantly lower average DNA-P contents were observed in July, September, and October of 1.12, 2.06, and 1.76 mg/kg, accounting for 0.19%, 0.55%, and 0.28% of the TP contents in the NaOH-EDTA ex-

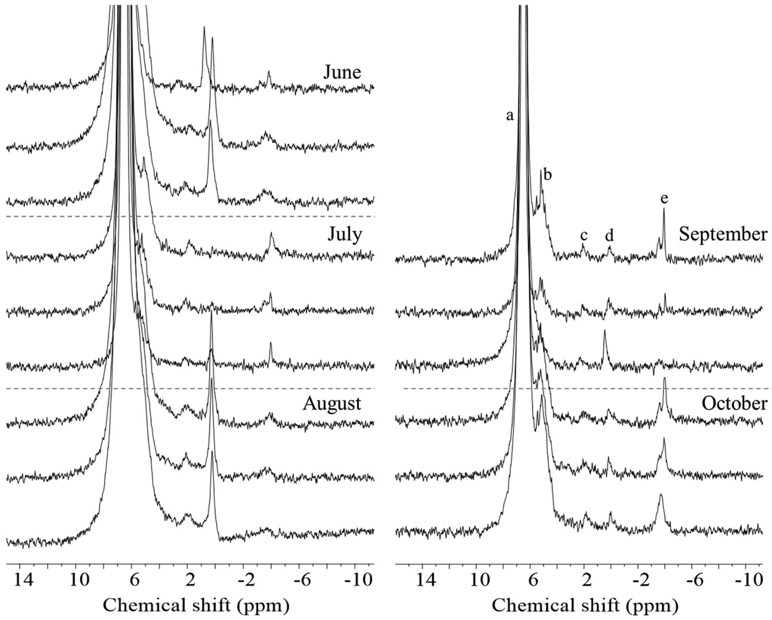

Fig. 6 – ^{31}P NMR spectra of dissolved P compound classes in NaOH-EDTA extracts of the surface sediments in Zhushan Bay (a: orthophosphate; b: orthophosphate monoesters; c: phospholipids; d: DNA-P; e: pyrophosphate).

Table 3 – TP and OP contents in surface sediments detected using ^{31}P NMR spectroscopy.

Month	TP in NaOH-EDTA extracts (mg/kg)	OP in NaOH-EDTA extracts	Ortho-P	Mono-P	Phospholipids	DNA	Pyro-P
June	942.57±331.65a	294.34±39.81a	919.72±325.37a (96.91)	n.d	9.24±0.94a (0.97)	17.15±6.93a (1.81)	2.91±1.8b (0.31)
July	606.78±13.21b	44.48±6.58c	581.77±15.2b (95.88)	19.57±5.36b (3.23)	1.84±0.45b (0.30)	1.12±1.27b (0.19)	2.47±0.47b (0.41)
August	689.61±7.12ab	85.96±6.36b	665.36±7.89ab (96.42)	n.d	9.11±1.56a (1.32)	14.08±3.82a (2.04)	1.53±0.18b (0.22)
September	363.69±151.3b	66.75±5.04bc	349.67±139.43b (93.81)	17.37±4.13b (4.66)	1.13±0.54b (0.30)	2.06±1.55b (0.55)	2.5±1.08b (0.67)
October	625.65±7.77ab	85.59±5.24b	575.41±7.02b (91.97)	38.76±6.86a (6.20)	2.95±1.41b (0.47)	1.76±0.23b (0.28)	6.77±0.2a (1.08)

n.d means that the P fraction was not detected.
*Numbers in parentheses are the percentages (mean) of P components.
Different letters within the same column indicate that contents are significantly different ($p < 0.05$) among different months. Values are means ± sd ($n = 3$).

tracts, respectively. The sediment Pyro-P gradually decreased from June (2.91 mg/kg) to August (1.53 mg/kg) and increased from September (2.50 mg/kg) to October (6.77 mg/kg).

On the other hand, phospholipids and DNA-P contents in the sediments were negatively correlated with the sediment pH values ($p < 0.01$) (Table 2). In addition, phospholipids contents showed significant correlations with the sediment TOC and OP contents ($p < 0.01$).

3. Discussion

3.1. *Effects of ABs on sediment OC*

The concentration of Chl-a is recognized as a marker of phytoplankton biomass in the water environment (Chen et al., 2018). Xu et al. (2015) highlighted the occurrence of ABs in Lake Taihu at a Chl-a concentration above 20 µg/L. The results of the present study showed a substantial increase in the Chl-a concentrations from June to August, reaching a very high concentration range of 44.50-425.53 µg/L, suggesting the occurrence of the ABs outbreak phase, with a peak outbreak of ABs in August. Chl-a concentrations drastically decreased from 79.49 µg/L in September to 9.9 µg/L in October, suggesting the senescence and decline phases of the ABs.

The variation in the sediment TOC contents is affected by the accumulation and decomposition of the sediment OC. During the early ABs outbreak period, a decrease in the sediment TOC content was observed in July (Fig. 3a), suggesting lower accumulation rates than the mineralization rates of the sediment OC from June to July. On the other hand, no significant decreases in the water DO concentrations were observed in the early ABs outbreak period ($p > 0.05$), showing DO concentrations of 5.03 and 4.09 mg/L in June and July, respectively (Fig. 2). In contrast, the water temperature values showed a significant increase from 24.3°C in June to 28.4°C in July ($p < 0.05$). Long exposure to oxygen and high water temperatures can promote the mineralization of OC in lake sediments (Sobek et al., 2009). In addition, sediment pH can affect the OC-related microbial activity and cation exchange (Yu et al., 2022b), decreasing the OC content with increasing the pH values (Yang et al., 2021). In this study, the sediment TOC contents were significantly and negatively correlated with the sediment pH values (Table 2), indicating that increased pH values due to the rapid algal growth might further promote the sediment OC mineralization. In addition, the observed sediment AOC contents and AOC/TOC values in June were higher than those observed in July (Fig. 3b and Fig. 4a). AOC refers to the part of OC with poor stability, rapid turnover rates, and rapid mineralization. Therefore, the high observed AOC/TOC values suggest a rapid OC cycle and a high bioavailability of the sediment OC from June to July. The rapid expansion of ABs might further accelerate the OC mineralization process, explaining the significant decreases in the sediment TOC and AOC contents in July. Li et al. (2004) showed a significant positive correlation between the average daily mineralization rates of soil OC and DOC contents. The high DOC concentrations and DOC/TOC values in July further demonstrated the high mineralization degree of the sediment OC (Fig. 3c and Fig. 4b).

In this study, the peak of ABs outbreak in the study area was observed in August, which might greatly contribute to the accumulation of algal-derived OC contents in the surface sediments (Zhang et al., 2014; Zhou et al., 2022). Algal organic matter (AOM) refers to the released metabolite into the water bodies during algal growth and cell death (Zhou et al., 2018). Pang et al. (2020) indicated that AOM is mainly composed of hydrophilic polysaccharides and protein organics, with low aromatic compound contents and SUVA254 values. The results of the present study revealed a significant decrease in the SUVA254 values during the ABs outbreak period from June to August (Fig. 5c), suggesting that AOM supplemented OM in the sediments. In addition, the DO concentrations in the overlying water showed a significant decrease from 5.03 mg/L in June to 2.94 mg/L in August (Fig. 2), which might be beneficial for the stability of OC in the surface sediments (Sobek et al., 2009; Zhu et al., 2020a). Furthermore, the strong association between reactive iron (Fe) phases and OC may inhibit the microbial degradation of OC in sediments (Ma et al., 2020). Indeed, Lalonde et al. (2012) indicated that 21.5% ± 8.6% of the sediment OC was directly bonded to reactive Fe phases by examining sediments from a wide range of environments, including fresh waters, estuaries, river deltas, continental margins, and the deep sea. According to Wang et al. (2022), the ABs-induced anaerobic environment led to the decomposition and release of a large amount of Fe-P in the sediments in Zhushan Bay of Lake Taihu, resulting in a significant increase in the concentration of labile Fe in the sediments in August 2016, thereby potentially promoting the preservation of OC in the sediments. These findings may explain the increase in the sediment TOC content in August 2016 in this study.

Wang et al. (2021) showed a positive priming effect of algal debris on sediment organic matter (SOM) mineralization. In addition, algal debris can increase the total carbon oxidation rate, resulting in denitrification and methanogenesis-dominated SOM mineralization (Zhou et al., 2022). Pang et al. (2020) showed a continuous degradation of SOM, even though the contribution of AOM to SOM decreased sharply at the end of the ABs outbreak, explaining the decrease in the sediment TOC content in this study in September. The results of the present study revealed a substantial decrease in the water temperature values in the decline period of ABs (October) (Fig. 2), weakening relatively the mineralization ability in sediments and, consequently, increasing the sediment TOC contents (Fig. 3a).

3.2. *Effects of ABs on sediment OP*

The sediment OP contents showed decreasing-increasing-decreasing-increasing trends over the ABs outbreak and decline period from June to October (Fig. 3f). In contrast, the OP components detected by ^{31}P NMR showed different trends due to their different properties. The DNA-P contents and proportions were higher and lower than those of other sediment OP components in June and July, respectively (Table 3). Phospholipids and DNA-P are Diester-P compounds easily utilized by microorganisms and characterized by lower stability than that of Mono-P (Yuan et al., 2017). In addition, the simulation results of Bai et al. (2021) showed a significantly higher transformation rate of dissolved OP under anoxic conditions than that under oxic conditions. However, no significant decreases in the water DO concentrations were observed from June to July in this study ($p > 0.05$). Therefore, redox conditions were not the main reason for the decrease in the sediment DNA-P content in July. On the other hand, the increase in the water temperature in July might increase the sediment phosphatase activity, thereby promoting the decomposition of DNA-P (Bai et al., 2017). Furthermore, the results of the present study showed an increase in the sediment pH value in July (Table 1). Yu et al. (2022b) showed an increase in the OP mineralization degree with increasing sediment pH values, which is consistent with the significant negative correlation between the sediment OP contents and pH values ($p < 0.05$) observed in this study (Table 2).

Although Mono-P was the main component of sediment OP in July, it may be influenced by external inputs. Mono-P consists of labile monoester and phytate-like P (Ni et al., 2022). The latter is primarily derived from indigestible P-bearing materials, including legumes, triticeae, and cereals, as well as from indigestible excrement of humans and non-ruminant animals (Ni et al., 2019a). The water level of Lake Taihu showed a significant increase from 3.9 m in June 2016 to 4.87 m in July 2016 due to the occurrence of Typhoon Nepartak (Zhu et al., 2020b), resulting in high amounts of external P inputs in the surface sediments, particularly the particulate P form, and, consequently increasing the Mono-P contents.

The decomposition of algae can also occur during the outbreak of ABs, thereby releasing P from the degraded algal cells (Han et al., 2015). The result of the present study revealed a significant increase in the sediment OP contents in August (Fig. 3f). Moreover, the proportion of Diester-P (phos-

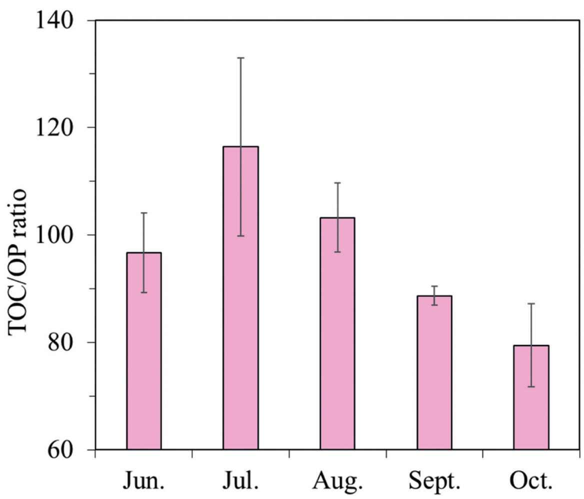

Fig. 7 – Variation of TOC/OP ratios in surface sediments of Zhushan Bay from June to October.

pholipids and DNA-P) in the sediment OP increased significantly in August (Table 3). Indeed, Diester-P is mainly derived from the DNA and RNA of microorganisms, as well as the degradation products of phytoplankton (Yuan et al., 2017), demonstrating that algal deposition is an important source of OP in sediments. Ahlgren et al. (2006) showed that Mono-P is easily decomposed under anaerobic conditions, while Bai et al. (2021) revealed increases in Mono-P transformation rates with phytoplankton growth. The Mono-P contents might be below the detection limit due to the presence of high algal biomass and anaerobic conditions associated with the ABs outbreak in August (Fig. 2 and Table 3). The DO concentrations in the overlying water increased during the decline period of ABs, while Mono-P was the main component of OP in the sediment TP in September and October.

3.3. *Relationship between sediment OC and OP during the ABs outbreak period*

The TOC/OP ratio of phytoplankton is usually close to the Redfield ratio (106) (Filippelli, 2001; Yu et al., 2022a), which is consistent with the results of the present study from June to August (Fig. 7), suggesting that algae were the main source of the sediment OC and OP during the ABs period. The sediment OP contents were significantly and positively correlated with the sediment TOC contents ($p < 0.01$) (Table 2), demonstrating simultaneous deposition of OC and OP in the surface sediments during the outbreak period of ABs. The results of this study showed a significant decrease in the sediment AOC content in July due to the high mineralization rate of sediment OC. On the other hand, DNA-P and phospholipids are the most active OP components (Yuan et al., 2017). The DNA-P and phospholipid contents in the surface sediments also showed significant decreases in July, suggesting simultaneous mineralization of the sediment OC and OP in this month.

Depolymerization and dissolution are the first phases of OC mineralization into CO_2 and CH_4 (Li et al., 2004). In this study, the highest DOC contents in the sediments and pore water were observed in July (Fig. 3c and Table 1), suggesting a high mineralization rate of the sediment OC over the June-July period. Previous studies have reported that bacteria utilize DOC to produce alkaline phosphatase, which may contribute to the mineralization of OP (Anderson, 2018; Dong et al., 2022). Indeed, algae are an important source of DOC (Wyatt et al., 2014), explaining the significant increase in DOC concentrations in sediments and pore water in July, thereby contributing to the decomposition of the sediment OP.

The TOC/OP ratio in sediments can also reflect the degree of OC and OP regeneration from the decomposed SOM (Yu et al., 2022a). Slomp et al. (2002) revealed an enhancement in the OP regeneration compared to OC during SOM decomposition under anoxic conditions, resulting in higher TOC/OP ratio values. The results of the current study showed significant decreases in the DO concentrations during the ABs outbreak period, which may promote the mineralization process of the sediment OP to a certain extent (Wang et al., 2021). Furthermore, the relatively stable DOM structure in sediments (i.e., abundant aromatic substances, functional groups, and high humification) can enhance the stability of the sediment OP (Ni et al., 2019b). However, the SUVA254 value showed a significant decrease during the ABs outbreak period in this study, suggesting significant decreases in the humification and aromaticity of DOM, thereby resulting in a high release potential of OP from the surface sediments. On the other hand, the TOC/OP ratio values in July and August were higher than that observed in June (Fig. 7), suggesting a higher regeneration degree of the sediment OP during the ABs outbreak period.

4. Conclusions

The objective of this study was to investigate the variation characteristics of the sediment OP and OC and their relationships during the ABs outbreak and decline in Lake Taihu. The main conclusions drawn from this study are as follows:

1) The concentrations and proportions of the different OP components in the collected sediments exhibited great differences between the ABs stages. The observed sediment OP was dominated by Diester-P (phospholipids and DNA-P) and Mono-P during the ABs outbreak and decline, respectively.
2) The ABs decline increased significantly the sediment AOC content and proportion.
3) Even though algae are an important source of OM in sediments, the rapid proliferation of algae also hastened the mineralization of sediment OC and OP. The outbreak of ABs may exhibit a dual effect on sediment OC and OP contents, explaining the lack of a consistent increase in the sediment OC and OP contents during the ABs outbreak.
4) The sediment OP and TOC contents showed synchronous temporal variations during the outbreak and decline of ABs from June to October. In addition, the observed significant positive relationship between the sediment OP and TOC demonstrated the simultaneous deposition and consumption of these compounds during the ABs outbreak and decline.

Although the effects of ABs on the sediment OP and OC contents were revealed in this study through field research and analysis, it was difficult to quantify their magnitudes. Therefore, further simulation experiments are required to quantify the effects of ABs at different stages on the sediment OP and OC contents. In addition, the present study was conducted during the outbreak and decline of ABs. It is, therefore, necessary to monitor the changes in sediment OP and OC before the ABs outbreak in future studies to comprehensively evaluate the impacts of the ABs process on sediment OC and OP in Lake Taihu.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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