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ABSTRACT

Columnar sediment samples were collected from five representative river inflow areas of Dianchi Lake, China. The vertical distribution of each form of P were tested. Results showed that the concentration of TP in the sediments from areas A, B, C, D and E in the order of D > B > A > C > E, and the average concentration of D, B, A, C and E were 2991, 2064, 1308, 879, and 759 mg•kg^{-1}, respectively. The concentration of Ex-P, Fe/Al-P, Ca-P and Org-P all decreased with increasing depth. The release of Ex-P was significantly related to TP whereas the Fe/Al-P was not significantly related to TP in the samples from areas polluted by domestic sewage. However, the release of Ex-P and Fe/Al-P were both significantly related to TP in the samples from areas polluted by phosphate mining and phosphate fertilizer application. The results of equilibrium P concentration (EPC0) analysis showed that P in the sediments of areas A, D and E were the source of P in Dianchi Lake, and the P in the sediments of areas B and C were in relative equilibrium with the overlying water.

1. Introduction

It is well known that Phosphorus (P) is one of the most important limiting factors for lake eutrophication, and sediments play an important role in the metabolism of lake nutrients, representing an important nutrient sink or source [1,2]. The main sources of P in lakes include external loading and internal release [3]. The release of endogenous P often determines the eutrophic state and time of restoration of the lake. In other words, even though the external loading of P can be effectively controlled, the release of a large amount of P that has accumulated in the sediments will represent an important P source for the water body, and the eutrophic state in the lake will continue [1].

In recent years, sequential extraction procedures have been widely used in studies on the morphology of sediment P because it allows the rapid and effective extraction of the various forms of sediment P. Sediment P is usually divided into different forms, including exchangeable P (Ex-P), P bounded to Al and Fe oxides (Fe/Al-P), P bounded to calcium (Ca-P), inorganic P (Inorg-P) and organic P (Org-P) [4–7]. Although the total P (TP) content in the sediments reflects the eutrophic state of the lake to some extent, it is unable to predict the potential release

risk and ecological hazard of P. The speciation distribution of P in the sediments can provide more information and help to understand the P cycles and P release tendency in the lake, and is one of the important parameters to predict the endogenous P release [8–10]. Therefore, the assessment of the risk of lake eutrophication requires not only determine the TP concentration in sediments, but also determine the concentration of P forms, the distribution ratio and release characteristics of each form.

Dianchi Lake, as the sixth largest freshwater lake in China, is located in the central part of the Yunnan-Guizhou Plateau (24°40′–25°02′N, 102°37′–102°48′E), downstream of Kunming City and is one of the lakes that suffered relatively severe eutrophication in China [11]. Dianchi Lake has many inflowing rivers, but it has only one water outlet and the water replacement cycle is 3–8 years. As a result, abundant nutrients accumulate in the sediments of the lake and the water quality deteriorates year by year [2,12]. Water pollution prevention and control measures in Dianchi Lake were initiated in 1990. During a governance process that has lasted nearly 30 years, a series of measures have been taken including wastewater interception, governance of rivers flowing into the lake, governance of agricultural and rural non-point source pollution, ecological restoration and

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construction, and desilting. By August 2013, although exogenous pollutants in Dianchi Lake had been essentially controlled, water quality deterioration has not been improved and blue-green algae and algal blooms continued to occur once per year [13].

In September 2013, the 'Niulanjiang River–Dianchi Lake Water Diversion Project' was officially launched. Two million m³ of clean water are supplied into Dianchi Lake every day to remarkably shortening the replacement cycle of water. At present, the water quality deterioration in Dianchi Lake has been halted, but the water quality itself has yet not been substantially improved. In the 'Niulanjiang River–Dianchi Lake Water Diversion Project', the clean water from Niulanjiang River was pumped to a drainage channel before entering Dianchi Lake at extremely high cost, which was neither economic nor practical for a long-term replacement of Dianchi Lake water. Therefore, a complete solution to the problem of eutrophication in Dianchi Lake needs to focus on gradual restoring the self-purification function of its water body. In addition, in the river inflow area of Dianchi Lake, the transfer and exchange of sediment particles in the vertical and horizontal direction are strong and complex, and the strong hydrodynamic conditions cause considerable sediment resuspension and material exchange, resulting in a stronger diagenetic decomposition of organic matter than that in the central lake area. Study of the forms of occurrence and release characteristics of P in the sediments of these areas will help to understand the role of the sediments in the eutrophication of Dianchi Lake, and to provide a theoretical basis for the development of the measures to restore the self-purification function of Dianchi Lake. The purpose of this study was therefore as follows: (1) to study the vertical distribution characteristics of P form in the sediments of the river inflow area of Dianchi Lake; (2) to study the correlation between the distribution of various forms of P in the sediments from the river inflow area of Dianchi Lake and the physicochemical properties of sediments; (3) to study the release characteristics of P and the release efficiency of various P forms in the sediments from the river inflow area of Dianchi Lake.

2. Materials and methods

2.1. Study area, sediment sampling and overlying water characteristics

Dianchi Lake once had 35 in-flowing rivers. At present, rivers that constantly supply water to Dianchi Lake throughout the year include Panlongjiang River, Baoxianghe River, Luolonghe River, Laoyuhe River, Yunihe River, Guchenghe River and the Xishan brooks near Guanyinshan Mountain and the Baiyukou Scenic Spot. Among these, Panlongjiang River is the largest river flowing into Dianchi Lake (water transferred from the Niulanjiang River flows into Dianchi Lake via Panlongjiang River). The sedimentation and accumulation of silts in the estuaries of Dianchi Lake lead to a comparatively high content of N and P in sediments at these locations, thus the release risk is relatively high. As a result, five representative river inflow areas (A, B, C, D and E) were selected in this study for investigation as follows: A, Panlongjiang River inflow area (P mainly from domestic sewage); B, Laoyuhe River inflow area (P mainly from wastewater from phosphate fertilizer application); C, Yunihe River inflow area (P mainly from domestic sewage); D, Guchenghe River inflow area (P mainly from the phosphate mining wastewater and domestic sewage); E, the Xishan Stream in Guanyinshan and Baiyukou area and rural sewage inflow area (Figure 1).

In March 2016, columnar samples were collected from Areas A, B, C, D, and E with sampling depth of 40 cm by using a self-made columnar sampler. The samples were packaged onsite and stored at the temperature of 4 °C. After transported to the laboratory, the samples were cut into 5 cm subsamples and numbered using the sample cutter (for example, samples collected in Area A were numbered A1, A2, …, A8, representing 0–5 cm, 5–10 cm, …, 35–40 cm, respectively). After freeze-drying, some of the samples were used to analyze the contents of clay (0.02–4 μm), silt (4–63 μm) and sand (>63 μm). The remaining samples were ground through a 100-mesh nylon sieve and stored for later use. The total organic
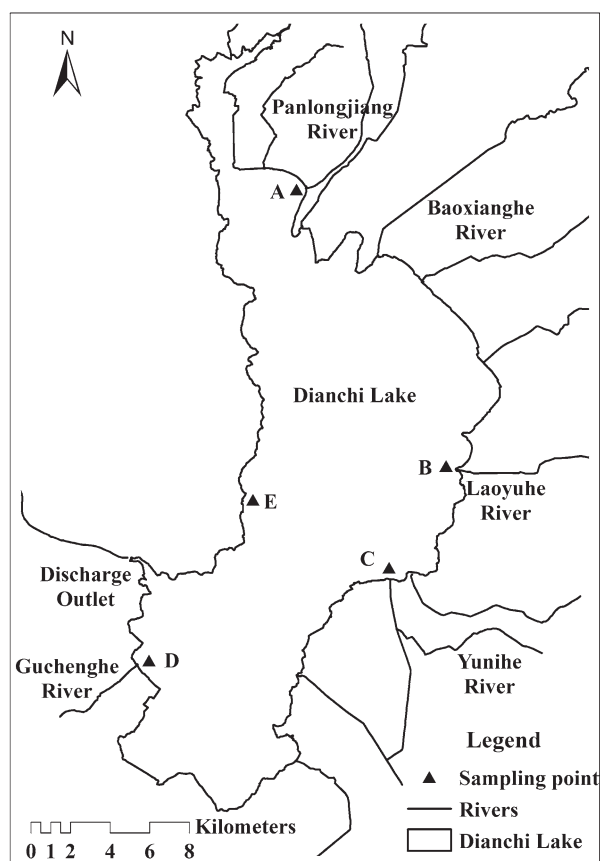

Figure 1. The geographic location of the sampling sites. Source: The Authors.

carbon (TOC), TN, TP and inorganic element components (Si, Fe, Al, Ca, Mg) of ground samples were measured using the standard methods (TOC was determined by hydrated heat potassium dichromate oxidation-colorimetry method; TN was determined by the Kjeldahl method; TP was determined by SMT method; inorganic elements were determined by using IPC-OES (Thermo iCAP 6300) after mixture acid ($HF + HCl + HNO_3 + HClO_4$) digestion) [14]. In addition, the corresponding overlying water was also collected and the parameters including temperature, pH value, oxidation–reduction potential (E_h), dissolved oxygen (DO) were measured in the field. The properties of those studied sediments and overlying water were also reported in our previous studies [15]. The TN, TP, and soluble reactive P (SRP) within the overlying water were measured in the laboratory [16]. The sampling location and the overlying water parameters were listed in Table 1.

2.2. P forms and analysis

The Standard Measurements and Testing (SMT) extraction method was applied to determine the content of each P form (TP, Inorg-P, Org-P, Ex-P, Fe/Al-P and Ca-P) in the core sediments of Dianchi Lake. In the sequential P form, Ex-P was extracted by $MgCl_2$ (1 mol·L^{-1}), Fe/Al-P was extracted by NaOH (1 mol·L^{-1}), and Ca-P was extracted by HCl (1 mol·L^{-1}) [17]. In a separate extraction, Inorg-P was extracted by HCl and TP was determined by treating the samples at 550 °C, followed by HCl extraction [18]. After the extractions, Org-P was determined by the difference between TP and Inorg-P [19,20].

2.3. P release experiments

P release experiments were performed as follow: 3 grams of dried sediment sample was added into 250 mL Pyrex centrifuge tubes, 200 mL 2 mmol·L^{-1} $CaCl_2$ solution was then added. The centrifuge tubes were capped and incubated in dark at 20 °C in an orbital shaker at 150 rpm for 24 h, the sampled solution was then immediately centrifuged for 10 min (at 4000 rpm), and was then filtered through a 0.45-µm GF/C filter membrane. The P concentration in extractions was determined by the molybdenum blue method [21]. The residual sediment was washed with distilled water (3 times) after the residual liquid was removed and then dried at 60 °C (12 h) for the next form extraction analysis [4].

2.4. The equilibrium P concentration determination

The equilibrium P concentration (EPC_0) result can indicate whether the sediments are the source or sink of the aquatic P [22,23]. The EPC_0 of surface sediments (0–5 cm) in each study area was determined with the method mentioned by Tye et al. [24]. The specific measurement steps are as follows: A measured mass of sediment (equivalent to 0.5 g dry weight) was added into six Pyrex screw cap centrifuge tubes (250 mL) with 200 mL 2 mmol·L^{-1} $CaCl_2$ solutions. The tubes were spiked with different concentrations of KH_2PO_4 (the amount of P was equivalent to 0.0, 0.1, 0.2, 0.3, 0.4 and 0.5 mg·L^{-1}; i.e. 0.00, 3.23, 6.45, 9.68, 12.90 and 16.13µmol-P·L^{-1}). The tubes were capped and shaken in the dark at 20 °C in an orbital shaker at 150 rpm for 24 h. Samples were then centrifuged and their SRP concentration determined by the molybdenum blue method.

Data quality was controlled using standard reference materials and method blanks. The analysis procedure was controlled under the same conditions. SMT method is of good accuracy, determination of each P forms is relatively independent, and the measured values can be crosschecked. The procedure was triplicates and the results were reported as their average.

3. Results and discussions

3.1. P forms distributions in core sediments

The vertical distribution characteristics of the concentration of P in various forms (Ex-P, Fe/Al-P, Ca-P, Org-P, and TP) and N/P values in the sediments are shown in Figure 2. The results indicate that the TP sequence in sediments decreased in the order D > B > A > C > E, with means of 2991, 2064, 1308, 879, and 759 mg·kg^{-1}, respectively. TP concentration in sediments of all study areas exhibited a similar trend in the vertical direction, and gradually decreased from top to bottom. It is worth noting that in the five study areas, the TP concentration in the surface layer sediments of Areas A and B were much higher than that of the bottom layer, indicating that the two study areas were significantly affected by human activities. The Panlong River, passing through Kunming City, accumulated a large amount of domestic sewage before the implementation of the water transfer project, resulting the TP concentration of the sediments in Area A is relatively high. The farmland around Area B was mainly used for flower planting, and the use of a large number

Table 1. Sampling location and the N, P concentrations in overlying water of Dianchi Lake.

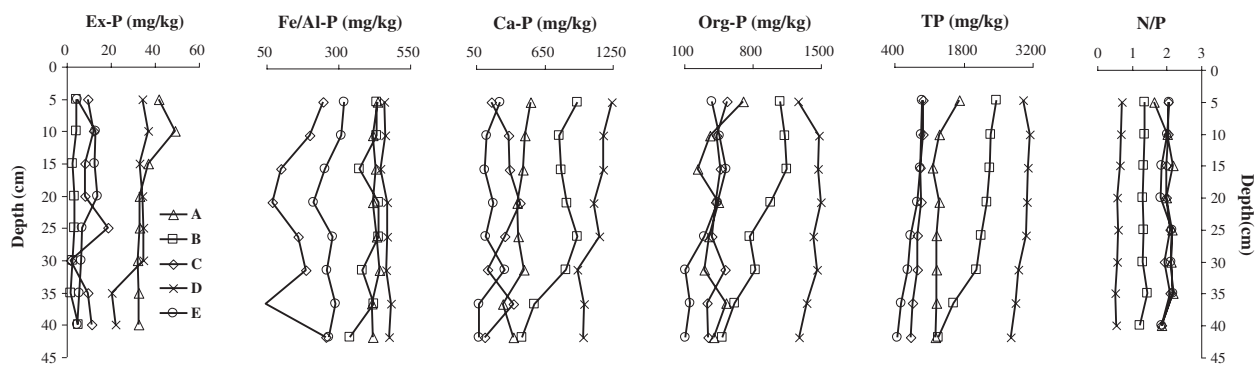| Sample site	Position	Water depth (m)	pH	TN (mg-N·L^{-1})	TP (mg-P·L^{-1})	SRP (mg-P·L^{-1})
A	24°57'10.99"N 102°40'53.76"E	3.0	7.54	1.811	0.180	0.102
B	24°49'40.72"N 102°45'31.68"E	2.5	7.99	1.776	0.116	0.053
C	24°46'51.97"N 102°43'51.96"E	3.0	8.10	1.705	0.146	0.082
D	24°44'13.07"N 102°36'43.56"E	3.0	7.52	1.491	0.209	0.097
E	24°48'40.22"N 102°39'45.00"E	3.0	7.88	1.705	0.257	0.073

Figure 2. Vertical variations of Ex-P, Fe/Al-P, Ca-P, Org-P, TP and N/P in core sediments (different x-axis scales).

of P fertilizers led to a relatively high TP concentration in the sediment of this region. Area D was the inflow area of phosphate mining wastewater, and the inflow area sediment contained numerous phosphate rock particles, resulting in the highest TP concentration. The lowest TP concentration in area E owe to less sewage supplying and some undestroyed natural wetlands surrounding.

The structure of the aquatic biological community of lakes was strongly affected by the amounts of N and P, as well as the interaction between N and P [25]. The values of N/P in overlying water from different area (A, B, C, D, and E) for this study were 10.06, 15.31, 11.68, 7.13, and 6.63, respectively (TN/TP, by mass, calculated by the data listed in Tab.1), which indicated that P was the dominant limiting factor for algal growth in Dianchi Lake according to the nutrient limitation characteristic of the eutrophication assessment standard [26]. However, in this study, the N/P values in the sediments of the study areas showed no obvious change in the vertical direction, and the average values of N/P in the sediments of Areas A, B, C, D and E were 2.02, 1.34, 2.01, 0.61 and 2.01, respectively, which were significantly lower than those in the corresponding overlying waters. This could be associated with the difference of release mechanism between N and P in sediment. In sediments, the release of N depends on the extent of the decomposition of N-containing compounds. The intensity of microbial activity, DO value, E_h value and other factors all affect the release mode and efficiency of sediment N. However, the release of P is mainly related to the forms of its occurrence in sediments. The P in the sediments of Dianchi Lake mainly exists as inorganic P [1]. Once a condition favorable for the dissolution of calcium, aluminum, iron and other insoluble phosphates occurs, P will be released [27].

The changes in the concentration of Ex-P, Fe/Al-P, Ca-P and Org-P in the sediments of the study areas were generally consistent with the changes of TP in the vertical direction, and gradually decreased with the increase of the depth. It is worth noting that the TP concentration of sediments in Area B was higher than those of Areas A, C and E, and the content of Ex-P in Area B was the lowest and was almost constant through the sampled sediment profile. This was primarily due to the wind direction at

Dianchi Lake, where there is a southwest wind throughout most of the year. In Area B, the waves at the river inflow area were relatively large, and thus the material exchange between the sediment and overlying water was high, and the diagenetic decomposition of organic matter was strong, therefore reducing the concentration of Ex-P in the sediments. In addition, the vertical variation of sediment Org-P concentration in Area B was large (the concentration of Org-P decreased sharply below 15 cm), which indicates that the pollution from the exogenous input in Area B has not been effectively controlled in recent years.

The ratios of various forms of sediment P to TP are shown in Figure 3. Studies have shown that Ex-P accounted for the TP concentration of 1–25% in lake sediments, and also was found to contribute more in the sediments of calcareous lakes than that in other lakes because of the high degree of $CaCO_3$ over saturation [3]. In this investigation, the Ex-P concentration in sediments were the lowest among the four P forms (0.11–3.75%) (Figure 3). This suggests that Dianchi Lake was in low degree of $CaCO_3$ saturation.

The Fe/Al-P levels could be used as a pollutant indicator for lake environments [28]. In this investigation, the Fe/Al-P concentration in sediments of A (33.01%) and E (38.66%) areas were the highest among the five study areas (Figure 3). However, in Area D with the highest TP concentration in the sediment, the ratio of Fe/Al-P was reasonably low (only 15.57%), indicating that there were different sources of sediment P in the river inflow area of Dianchi Lake. That is, the sediment P in Areas A and E mainly originated from domestic sewage, whereas the contribution of domestic sewage to the sediment P in Area D was small. The Ca-P, had a detrital origin and was not available to algae, is largely dependent on lake position and naturally occurring background calcium levels in soils within the watershed [28]. It is noteworthy that, although the concentration of Ca-P in the sediments of areas B and D were much higher than those of other areas (Figure 2), the TP concentration in the sediments were high, so the ratios of Ca-P to TP were essentially the same as those in other study areas (Figure 3).
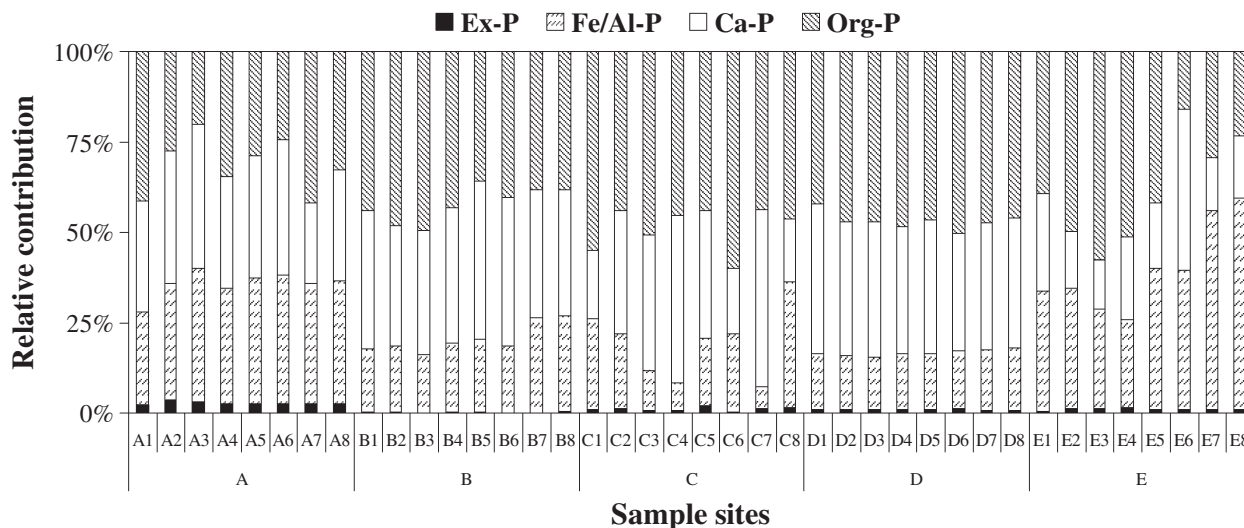
Figure 3. The relative contribution of different P forms to TP in the studied core sediments.

Org-P can be partly utilized by microorganisms and directly affects the P concentration in overlying water for primary production. The ratios of Org-P to TP in the study areas were between 15.98 and 60.01%, showing a relatively wide range, a large fluctuation, and an irregular variation in the vertical direction (Figure 3). Gao et al. showed that the vertical distribution of sediment Org-P in the center of Dianchi Lake exhibited an 'S' shape, and the Org-P concentration in surface sediments was higher than that at the bottom [1]. However, in the current study, there was no clear vertical 'S'-shaped distribution of Org-P, which was mainly because the deposition rate of the sediments in the river inflow area was much higher than that of the center of the lake, and the material exchange effect was large.

3.2. The relationship between different P forms and sediment properties

The distribution of P forms in the sediments depends on the source of the sediments, their mineral composition (i.e. Fe and Al oxides), organic matter content, environmental conditions (i.e. DO, E_h, pH), and bioactivity. Conversely, in different areas of the same lake, the source and composition of the sediments have a relatively strong influence on the distribution of P forms [1]. Therefore, the correlations between the various P forms in the sediments and their physicochemical properties were analyzed to investigate the influence

of sedimentary sources and composition on the distribution of P forms in the sediments (Table 2).

The correlation analysis showed that among various forms of P in the sediment; Ex-P had a significant positive correlation with Fe/Al-P, Ca-P and TP, and was not correlated with Org-P; Fe/Al-P showed a significant positive correlation with Ca-P, Org-P and TP; and Ca-P exhibited a significant positive correlation with Org-P and TP. In terms of the relationship between the various forms of P in the sediment and the physicochemical properties of the sediments, except for Ex-P, the concentration of various forms of P showed a significant positive correlation with the concentration of TOC, clay, silt, TFe_2O_3 and Al_2O_3, and a significant negative correlation with the sand concentration and N/P value ($p < 0.01$). The concentration of various forms of P were significantly correlated with the CaO and MgO concentration ($p < 0.01$), and were not significantly correlated with the SiO_2 concentration (Table 2).

The Ex-P is a type of weakly adsorbed P, and its concentration is related to many factors affecting the P adsorption process on sediment. A higher TOC in the sediment and a smaller particle size leads to a stronger capacity of P adsorption [7]. However, the Ex-P concentration showed no significant positive correlation with the concentration of TOC, clay, and silt in this study, which is consistent with the results of Tye et al. [24]. Although the presence of organic matter may increase sorption of dissolved organic phosphorus, P does not or rarely binds

Table 2. Pearson inter-correlation coefficients between the P forms and the Pearson correlation coefficients between the P forms and sediment properties in the core sediments ($n = 40$).

	Ex-P	Fe/Al-P	Ca-P	Org-P	TOC%	Clay%	Silt%	Sand%	SiO_2	TFe_2O_3	Al_2O_3	CaO+MgO
Ex-P	1.000				0.245	0.297	0.356*	−0.335*	−0.102	0.063	0.331*	0.436**
Fe/Al-P	0.509**	1.000			0.564**	0.652**	0.384*	−0.617**	−0.209	0.643**	0.488**	0.553**
Ca-P	0.326*	0.667**	1.000		0.532**	0.639**	0.494**	−0.640**	−0.233	0.910**	0.635**	0.548**
Org-P	0.267	0.596**	0.908**	1.000	0.430**	0.513**	0.398*	−0.514**	−0.101	0.901**	0.549**	0.594**
TP	0.358*	0.727**	0.972**	0.969**	0.521**	0.620**	0.465**	−0.617**	−0.179	0.923**	0.614**	0.468**

$^*p < 0.05$; $^{**}p < 0.01$.

with organic matter as sorption site where it is blocked by organic acids as well as complexation of exchangeable Al and Fe [29]. Moreover, Ex-P is also a seasonally variable pool of P compounds, and environmental factors, such as temperature, pH, Eh and N concentration in sediments, can also affect the concentration of Ex-P, the final distribution of P forms in sediments is the result of a combined effect of many factors [30].

The Fe/Al-P represents phosphorus bound to Fe and Al oxides, the higher the content of Fe/Al oxide in the sediments is, the higher the Fe/Al-P concentration will be. In the sediments, the release of Fe/Al-P is greatly affected by changes in the environmental E_h value. When the DO is depleted, Fe/Al-P can be released from sediments to overlying water, and becomes the endogenous source of P in water bodies [31]. However, in the present study, Fe/Al-P content exhibited a significant positive correlation with TOC, clay and silt concentration and a negative correlation with the sand concentration, which might be because the blocking effect of clay and silt weakened the release of Fe/Al-P in the sediments [32].

The Ca-P, which represents P bound to calcium/magnesium, is a relatively stable phosphorus fraction and can only be released under acidic conditions. The higher the CaO and MgO concentration in the sediments is, the higher the Ca-P concentration becomes [8]. This was a good explanation for the significant positive correlation between Ca-P concentration and the CaO and MgO concentration in this study.

In the sediments of Dianchi Lake, Org-P primarily originated from autochthonous sources [2]. Thus, although most Org-P was relative stable, the lake sediments would accumulate some bioavailable Org-P in the process of eutrophication. Furthermore, with greater phytoplankton biomass (or organic substances) accumulated in eutrophic lake sediments, activities of phosphatase (e.g. alkaline phosphatase) are usually greater in sediments [33,34]. Therefore, in Dianchi Lake sediments, the higher

the TOC, the higher the Org-P, exhibiting a significant positive correlation between Org-P and TOC.

3.3. P release and EPC_0 determination

When the external loading of P is controlled, the release of P in the sediments becomes one of the main factors affecting the P concentration of overlying water in the lake. The release of various forms of P can be estimated by comparing the changes in the distribution ratios of various P forms in the sediments before and after the release experiment. The release experiment results indicated that the release rate of Org-P was negative, which was not consistent with the actual situation. This could be due to the relative enrichment of Org-P caused by dissolution of soluble materials in the sediment during the release experiment. Therefore, the release rate of Org-P is not shown in Figure 4.

The results of the release experiment showed that in the sediments of the study areas, Ex-P and Fe/Al-P were the dominant forms of released P (accounting for over 90% of total release), and there was no clear trend in the release rate of various forms of P in the vertical direction (Figure 4). However, in different study areas, the release rate was significantly different between P forms. In Areas A and C, the release of Ex-P was dominant, and their release rates were 2.26–3.45% and 0.03–1.25%, respectively. In Areas B and E, the release of Fe/Al-P was dominant, and the release rates were 0.27–0.50% and 1.22–3.17%, respectively. In Area D, the release of Ex-P was dominant in the sediment at 0–30 cm, and the release of Fe/Al-P was dominant in the sediment at 30–40 cm (Figure 4). The difference in the release rate of different P forms in different study areas was mainly affected by the source of P, the hydrodynamic conditions, and the deposition rate of sediments. The Fe/Al-P concentration in the sediments may indicate the source of the pollution, and a high Fe/Al-P ratio indicates a high
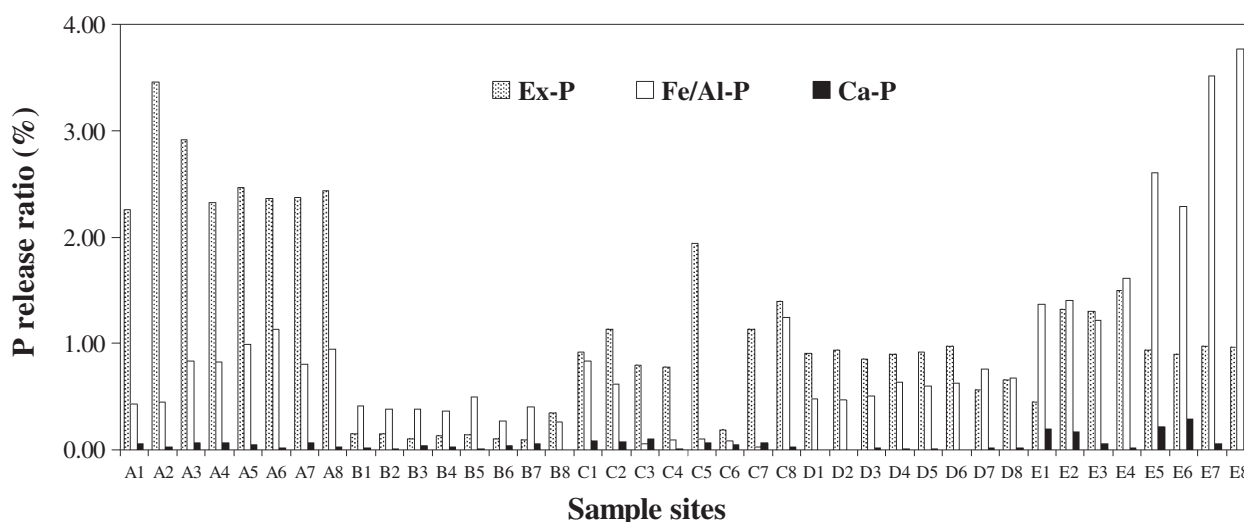

Figure 4. The release ratio of the different P forms to TP in core sediments.
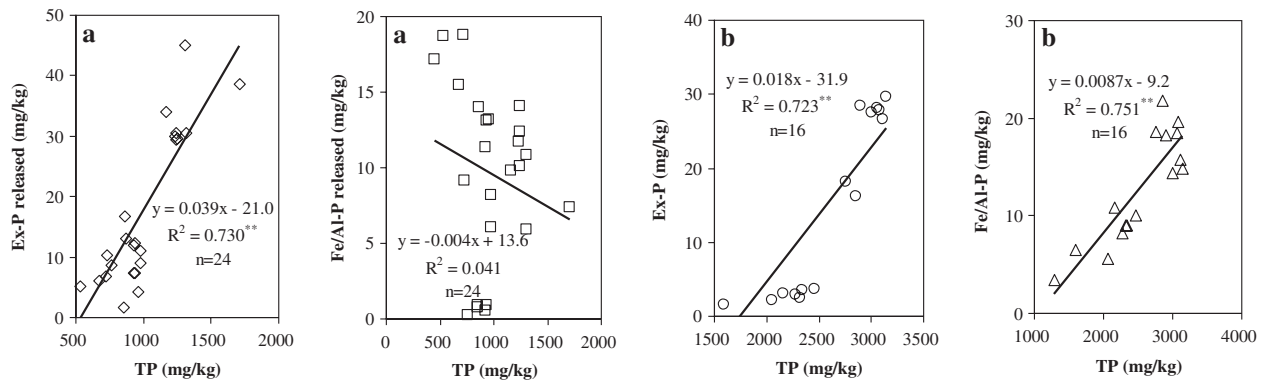
Figure 5. The relationship between the P released of different P forms and TP contents in the sediments (a: domestic sewage polluted area, b: phosphate rock mining and phosphate fertilizer application area).

Table 3. Parameters obtained from Henry isotherm fitting analysis to calculate EPC_0 in sediments.

Sample	Regression equation	EPC_0 (μmol-P·L^{-1})	SRP (μmol-P·L^{-1})	Uptake/release
A	$\Delta N_a = 0.2764C_e - 2.3088$ ($R^2 = 0.9721$)	8.35	3.29	Release
B	$\Delta N_a = 0.3374C_e - 0.5484$ ($R^2 = 0.9691$)	1.62	1.71	Equilibrium
C	$\Delta N_a = 0.2917C_e - 0.8276$ ($R^2 = 0.9468$)	2.84	2.64	Equilibrium
D	$\Delta N_a = 0.2846C_e - 2.1884$ ($R^2 = 0.9512$)	7.69	3.13	Release
E	$\Delta N_a = 0.2421C_e - 0.8410$ ($R^2 = 0.9679$)	3.47	2.35	Release

influence of human activities however, the Ca-P concentration is related to P-containing minerals [28]. In the current study, the Fe/Al-P concentration in the sediments of Areas A and E were relatively high (Figure 3), indicating that the sediment P in Areas A and E had the same source (i.e. all from domestic sewage). On the other hand, the Ca-P concentration in the sediments of Areas B and D were relatively high (Figure 3), indicating that the sediment P in Areas B and D had the same source (i.e. all from P-containing minerals).

In this study, five study areas were divided into two pollution types according to the use of riverside land and the ratios of Fe/Al-P and Ca-P in the sediments. One type, including Areas A, C and E, was domestic sewage pollution with a high Fe/Al-P ratio. Another type was phosphate mining (Area D) and phosphate fertilizer application (Area B) contamination, and showed a high Ca-P ratio. The correlation between the amounts of various forms of P released and TP in the sediments were then assessed (Figure 5).

The correlation analysis showed a significant positive correlation between the ratio of Ex-P released and the concentration of TP in the sediments in both areas with different polluting sources. The ratio of released Fe/Al-P from the sediments of the area polluted by domestic sewage was not significantly correlated with the TP in the sediments. In contrast, the ratio of released Fe/Al-P from the sediments of the area polluted by phosphate mining and wastewater from phosphate fertilizer application was significantly positively correlated with the TP in the sediments ($y = 0.0087x - 9.2$, $p < 0.01$, $n = 16$).

The EPC_0 (measured in μmol·L^{-1}) is calculated by plotting the change in the amount of SRP sorbed after a 24 h incubation, relative to the initial amount (ΔN_a, in

μmol·g^{-1}), against the concentration of SRP in solution after 24 h (C_e, in μmol·L^{-1}), and fitting an isotherm to the data using a least squares method [23]. The Henry linear model was used in this study for this purpose. The Henry model is derived from: $\Delta N_a = K \cdot C_e - N_i$, where K (L·g^{-1}) is the sorption constant, and N_i (μmol·g^{-1}) is the initial sorption amount [22]. The parameters were calculated and summarized in Table 3.

The EPC_0 values of the sediments in Areas A, D and E were much higher than that of the SRP concentrations in the overlying water. Therefore, the sediments of Areas A, D and E were the source of P in Dianchi Lake. In contrast, the EPC_0 values of the sediments in Areas B and C were close to the SRP concentrations in the overlying water. Therefore, the sediment P in Areas B and C was in relative equilibrium with the overlying water.

4. Conclusions

The sediment concentration of TP in area D (polluted by phosphate mining) and area B (polluted by phosphate fertilizer application) were higher than the area A, C, and E (polluted by domestic sewage) indicating the phosphate mining and the application of a large amount of phosphate fertilizer had a major influence on the sediment concentration of TP in Dianchi Lake. Although the sedimentation rate in the river inflow area was not stable and it was difficult to obtain the corresponding relationship between the depth of sediments and the depositional ages, the concentration of Ex-P, Fe/Al-P, Ca-P and TP in the sediments of all study areas gradually decreased with depth. This indicates that with increasing influence of human activities, a large amount of exogenous P accumulated in sediments.

There was no clear trend release rate of each form of P was observed in the vertical direction in the sediments of each study area. In the environment, the probabilities of the exchange between surface sediments and overlying water was stronger than that between deep sediments and overlying water. However, in the laboratory experiment, there was a similar probability of exchange between the sediment sample and the extracts, which may lead to overestimated release rates of various forms of P in deep sediments. Therefore, it is more appropriate to use EPC_0 to determine whether the sediments are sources or sinks of P in the overlying water. The results of EPC_0 in this study indicated that the sediments of areas A, D and E were the 'source' of P in Dianchi Lake, and the sediment P in Areas B and C was in relative equilibrium with the overlying water. However, it is likely that with increased P control measures, the SRP concentration in the overlying water will gradually decrease, resulting in increased risk of release of P in sediment of the river inflow areas of Dianchi Lake will develop a release risk.

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