Buffering effect of suspended particulate matter on Phosphorus cycling during transport from rivers to lakes

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Abstract

How to maintain harmful algal blooms under phosphate-limitation is still an open question in mesotrophic/eutrophic lakes. Little evidence for the importance of suspended particulate matter (SPM) in mediating phosphorus cycling and contributing to eutrophication has been generated for aquatic ecosystems, especially in coupled river-lake systems. In this study, we examined phosphorus transport and redistribution in a river-lake system in the Lake Erhai basin by establishing the relations between phosphorus distribution and phosphorus sorption behavior on SPM, and predicted how quality and quantity changes in SPM might influence phosphorus cycling by laboratory experiments and modeling. During the wet seasons, TP pool shifted from being dominated by total dissolved phosphorus (TDP) in the Miju River and estuary regions (73±5%) to being dominated by total particulate phosphorus (TPP) (74±11%) in Lake Erhai. The detritus-SPM in the Miju River as a P-sink and phytoplankton-SPM in Lake Erhai as a P-source buffered TDP levels during the wet seasons, which attributed to P activity and phytoplankton-POC of SPM. Increasing SPM concentrations could enhance the P-buffering. When $C_0 \leq 5$ μmol/L and phytoplankton-SPM ≥ 16 mg/L, P release increased by 50%-300%; when $C_0 \geq 5$ μmol/L and detritus-SPM ≥ 16 mg/L, P removal could exceed 30%. This study highlights two distinctive roles of SPM in regulating P cycling during transport from rivers to lakes. Especially the phytoplankton-SPM to buffer phosphate-limitation during algal blooms should not be ignored, which could provide theoretical references for the mechanism of continued algal blooms in mesotrophic lakes.

Keywords: Particulate phosphorus; Eutrophication; Suspended particulate matter; Phosphorus partition; Buffering

1. Introduction

Phosphorus (P) is an essential element for organisms and limits primary productivity in most freshwater systems, and understanding P cycling in aquatic systems is important to prevent eutrophication (Conley et al., 2009). In many eutrophic lakes, dissolved inorganic P (DIP), the almost 100% bioavailability, gradually declines during the peak algal bloom period (Reinhard et al., 2017), even below the limit of detection (Björkman and Karl, 2003; Ji et al., 2017), and total particulate phosphorus (TPP) dominates TP pool, such as more than 60% in Lakes Erie, Huron, Taihu and Dianchi (Lin and Guo, 2016; Xu et al., 2010; Wang et al., 2015). Studies have also shown that more than 80% of the fluvial flux of P to lakes may be associated with suspended particulate matter (SPM) (Baker et al., 2014; Pan et al., 2013). SPM can act as a source or sink of P by adsorption/desorption or uptake/release to regulate the abundance, bioavailability, and biogeochemical cycling of P in freshwater environments (Cyr et al., 2009). However, due to the complicated component of SPM and the difficulty of obtaining in water environment, previous studies mainly focused on simulating adsorption/desorption process of P by sediments (Pan et al., 2013; Yi et al., 2017; Deborde et al., 2007). Little has been done to address a quantitative analysis about changes in quality and quantity of P-associated SPM during transport from rivers to lakes, which severely restricts our understanding of how SPM affects the cycling and partition of P (Lin and Guo, 2016).

Adsorption processes and adsorption reversibility of SPM are important for regulating P levels especially when water conditions change. The adsorption capacity, which can be quantified by equilibrium adsorption constants, is determined by the chemical composition and concentration of SPM and adsorbate concentration (Pan et al., 2002). Equilibrium phosphorus concentration at zero sorption (EPC_0), a parameter obtained from phosphate-particles adsorption experiments, has been used to provide quantitative information on whether particles remove or release P to calculate the P flux in the particle-water interface (Pan et al., 2013). P particle-reactivity in the particle-water interface can be defined as the partition coefficient (K_d) with the ratio between the particulate and dissolved phases in aquatic ecosystems (Huang et al., 2017; Lin and Guo, 2016). K_d has been observed to decline with increasing SPM in both marine and freshwater environments, showing the “particle concentration effect” (O’Connor and Connolly, 1980). However, no studies to date have systematically integrated all these adsorption properties to determine the potential effect of SPM on P cycling at an entire river-lake system (Pan et al., 2013, Yi et al., 2017; Lin and Guo, 2016). Studies combining field investigations, laboratory experiments and modeling are still few and would lead to a better understanding of the cycling pathways of P species and SPM.

Lake Erhai, the second largest plateau freshwater lake in southwestern China, is one of the three most concerned lakes with better-quality in China and an important source of domestic and irrigation water in Dali, Yunnan Province (Tong et al., 2017). Because of the increases in anthropogenic discharges and agriculture non-point pollution in recent years on the lake fringes, cyanobacterial blooms frequently occur from July to October of every year in the lake (Zhang et al., 2015). Especially, two massive cyanobacteria blooms occurred in September and October in 2013. It is in a critical period of transformation from mesotrophic status to eutrophication. Lake Erhai is potentially P-limited (Yu et al., 2014). Steep gradients in P species exist from inflowing rivers to the lake. As shown in the figure 1 in this study, average concentrations of DIP (phosphate) dramatically decreased from 8.2 μmol/L in the upstream river to 0.2 μmol/L in open Lake Erhai across the estuary. Especially during algal blooms, DIP concentration in Lake Erhai is often less than 0.1 μmol/L. However, algal blooms often last until November (Chl*a* >20 μg/L). TPP pool can be almost 4 times larger than TDP pool, and over 10 times larger than DIP pool (Ji et al., 2017). The algal blooms are attributed in part to an increase in the concentration of DIP from TPP transformation (Baker et al., 2014). Consequently, we hypothesise that SPM may help P cycling to maintain high algal biomass under DIP-limitation. The interesting problem is further intensified whether SPM is changing and would help or hinder the P cycling or have no effect from river to lake, which is essential for guiding water management and for coupled river–lake modeling in global P cycling (Pan et al., 2002; Yi et al., 2017).

Thus, we carried out a systematic investigation of the spatiotemporal variations of P species and SPM across the boundary from the Miju River to Lake Erhai (Fig.S1). The aims were to (1) determine the potential of SPM as a source or sink of P throughout the entire river-lake; (2) identify the factors that influence P-buffering ability of SPM;

(3) predict how changes in SPM concentration affect P level and K_d by laboratory experiments and modeling; and (4) propose implications of SPM for P cycling during transport from river to lake. A summary of these experiments, as well as their respective objectives, is presented in Fig.S2. These results are important for understanding the nature and controls on P cycling in particle rich rivers-lakes system.

2. Materials and methods

2.1. Study area

Lake Erhai, Yunnan Province, China, is at an altitude of about 1970 m and is between 25.6° and 25.9° N and 100.1° and 100.3° E. The lake covers approximately 250 km^2 and is fed by a watershed that extends across 2565 km^2 (Fig.S1). It is, on average, 10.6 m deep. The area has a subtropical monsoon climate, with annual average, average maximum, and average minimum temperatures of 15.1, 20, and 8.9 °C, respectively. The mean annual rainfall is 1100 mm, of which 90% falls during wet seasons from May to October, and the remaining months are dry seasons. Cyanobacterial blooms usually appear during the wet seasons, and even can persist until November. The relatively long residence time of water (average 2.75 years) could promote accumulation of phytoplankton biomass, nutrients and SPM in the lake, and allow time for particle-water interaction to occur (Zhang et al., 2015). There are 22 main rivers inflowing into the lake as main pollutant sources. The water quality of the rivers is mostly ranked as class V ($9.6 < TP \leq 12.9$ μmol/L), the worst category of Chinese Surface Water Quality Standards (GB3838-2002) (Ji et al., 2017). Of these rivers, Miju, which flows into the northern part of the lake and is the greatest pollutant discharge (accounting for 57%) into the lake, is classified as worse than class V (Lu et al., 2015).

2.2. Sampling and Analysis

The 11 sampling sites were selected with GPS from the Miju River, through the river-lake mixing zone, into Lake Erhai over 4 occasions, in April, July, October of 2013, and January 2014 (Fig. S1, Table S1). Water samples for the lake and the river were collected using a 5 L Plexiglas water sampler at depth of 0.5-1.0 m and 0.2-0.5 m below surface, respectively. Water temperature (WT), pH, and dissolved oxygen (DO) were measured *in situ* using portable YSI electrodes (Xylem Co. New York, USA). The flow was measured *in situ* with a flowmeter (Qliner2, HACH, USA). In the laboratory, SPM was obtained by filtering water samples using precombusted (550°C for 4 h) and preweighed glass-fiber filters (Whatman GF/F; nominal pore size 0.7 μm). The filters were then washed with deionized water and freeze-dried until a constant weight (Yang et al., 2021). Thus, dissolved P species here are operationally defined as those in the < 0.7 μm filtrate, which may contain living biomass and thus overestimate dissolved organic P (DOP) compared to those in the < 0.45 μm filtrates. Water parameters, including TP, TDP, DIP and DOP, were analyzed according to Standard Methods (APHA 2012), details of which are given in Text S1.

2.3. P speciation and organic matter in SPM

SPM concentrations were calculated from the difference between the weights of the precombusted (550°C for 4 h) and weighed GF/F filters and the freeze-dried filter samples per unit volume of water. TPP, particulate inorganic phosphorus (PIP), and particulate organic phosphorus (POP) were determined using the modified method of Solórzano and Sharp (1980), and particulate P fractions were analyzed using a sequential chemical extraction procedure (Psenner and Pucsko,1988), details of which are given in Text S2, Fig. S6. The five-step extraction sequence provides information about a range of fractions, namely (1) NH_4Cl-P (2) BD-P (3) $NaOH_{25}$-rP, $NaOH_{25}$-nrP (4) HCl-P (5) $NaOH_{85}$-P.

Particulate organic carbon (POC) and particulate organic nitrogen (PON) were measured with an element analyzer (Perkin-Elmer 2400 Series II) after vapor acidification to remove carbonates. Particulate organic matter (POM) was colorimetrically determined after treatment of the sample with potassium dichromate/H_2SO_4 according to the Walkey−Black method (Tan, 1995). Particulate inorganic material (PIM) was then defined as the difference between SPM and POM. Chlorophyll-α (Chl*a*) was determined spectrophotometrically after extraction with 90% acetone. The ratio between phytoplankton biomass (mg C /L) and POM (mg/L) was determined to quantify the phytoplankton carbon percentage of the POM (phytoplankton-POC) (Sobczak et al., 2002). Detrital origin POC (detritus-POC) was estimated as the difference between total POC and phytoplankton-POC. Gross primary productivity (GPP) was determined using the light and dark bottle oxygen technique (Vollenweider, 1974). Alkaline phosphatase activity (APA) was estimated using the model substrate p-nitrophenyl phosphate (pNPP, Sigma) (Dore and Priscu, 2001). Samples were analyzed in triplicate, and the standard deviations were always < 5%.

2.4. Partition coefficient of P

The partition of P between the dissolved and particulate phases and its particle reactivity can be quantified by the partition coefficient (K_d) (Lin and Guo, 2016), which is calculated with the following equation:

$$K_d = \frac{C_p}{C_d * [SPM]} \qquad (1)$$

where C_p and C_d are the concentrations of particulate and dissolved P, respectively, in the inorganic, organic, or total P pools (μmol/L). [*SPM*] is the concentration of SPM (mg/L). Values of K_d are expressed in L/mg.

2.5. Degree of P saturation

The degree of P saturation (DPS), which relates a measure of P already adsorbed by SPM to its P adsorption capacity, could be a good indicator of P release potential from SPM to waters (Ohno et al., 2007). Acid ammonium oxalate extraction was used to determine DPS (McKeague and Day, 1966), details of which are given in Text S3. We calculated the DPS with the following equation:

$$DPS = \frac{P_{ox}}{0.5 * (Fe_{ox} + Al_{ox})} \qquad (2)$$

Where P_{ox}, Al_{ox}, and Fe_{ox} are expressed in mg/g.

2.6. Adsorption Isotherms Experiments and Sorption Kinetics of P

I: Experiments details of the adsorption isotherms and sorption kinetics of P are provided in the Text S4. Mathematical descriptions of the adsorption isotherms were described by a modified Freundlich equation as follows: $Q_e = \mathrm{K_f}\,(C_{eq}{}^{n} - \mathrm{EPC_0}{}^{n})$ (3) where Q_e is the amount of net sorption or release of P at equilibrium (mg P /kg), $\mathrm{K_f}$ is the affinity constant (L/μmol), n is the exponential factor, and C_{eq} is the equilibrium P (μmol/L). EPC_0 is a measure of the P concentration at which SPM is neither adsorbing nor releasing P in the equilibrium state (μmol/L). Greater values of K_f and smaller values of EPC_0 indicate stronger P sorption ability of SPM (Jarvie et al., 2005). Model parameters were estimated by a Marquardt nonlinear least-squares fitting routine.

In order to judge whether the SPM acts as a source or sink of P for the water body, a criterion of $\delta = C_{eq}^{n} - EPC_0^{n}$ (4) was defined (Pan et al., 2013)

When $\delta < 0$, $Q_e < 0$ (release), SPM is a source of P.

When $\delta > 0$, $Q_e > 0$ (adsorption), SPM is a sink for P.

The slope of the isotherm curve at Q_e=0 is the distribution coefficient $K_{d\text{-}eq}$, which is calculated by taking the derivative of the modified Freundlich equation with respect to C_{eq} at the EPC_0.

$$K_{d\text{-}eq} = d[K_f\,(C_{eq})^{n}]/d(C_{eq})_{EPC0} = nK_f\,(C_{eq})^{n-1} \qquad (5)$$

The removal rate of DIP can be described by the following equation:

$$DIP\ removal\ (\%) = (C_0 - C_{eq})/C_0 \qquad (6)$$

Mathematical descriptions of the sorption kinetics were established by fitting the data sets with first order sorption functions: $Q_t = Q_{max}\,(1-e^{-kt})$ (7), Q_t (mg P /kg) is the amount of sorbed P at time t (h), Q_{max} (mg P /kg) is the amount of sorbed P in the equilibrium. k is the first-order constant of sorption kinetics (h^{-1}).

II: We conducted the adsorption experiment by changing the mixture mass ratio of detritus-SPM and phytoplankton-SPM from 1:1 to 1:20 to simulate P adsorption behavior of the increasing phytoplankton-SPM when algal blooms. The detritus-SPM came from the station MR-1 in the Miju River in October, while phytoplankton-SPM was obtained by adding fresh algae. After mixture, the remaining details of the experiment are the same as described in Sorption Experiments I.

III: A series of SPM concentrations (2, 6, 10, 16, 25, 35 mg/L) were used to determine the threshold of SPM to reduce or increase the DIP level by adsorption experiments. These SPM concentrations were chosen to bracket the known changes of SPM during different seasons over the past decades in the Miju River and Lake Erhai. The phytoplankton-SPM and the detritus-SPM respectively came from the station LE-2 in Lake Erhai due to its maximum phytoplankton-POC content and the station MR-1 in the Miju River due to its maximum PIM and detritus-POC content. Tubes were spiked with KH_2PO_4 to provide a range of initial P concentrations (C_0, 0.05−12 μmol/L) designed to simulate the typical condition of P input to the river and lake. The remaining details of the experiment are the same as described in Sorption Experiments I.

2.7. Modified K_d model

We modified the K_d model based on the equilibrium between the initial and final TP concentrations used by Prastka (1998) and Turner and Tyler (1997) [eqn (8), (9)]. The modified K_d model can rationalize the apparent contradiction between the source and sink of TDP on SPM under different conditions ([eqn (10)-(12)]). Refer to Text S5 for more details.

$$\overline{A}_{\mathrm{gpp}} = 19.8\,\overline{TP} - 77 \qquad (8)$$

$$C_R+P_R+\frac{\overline{A}_1+77}{19.8}=C_{es}+P_{es}+\frac{\overline{A}_2+77}{19.8} \qquad (9)$$

$$K_d=\frac{P_{es}}{C_{es}*S_{es}} \qquad (10)$$

$$\Delta TDP = C_R\text{-}C_{es}=\frac{C_R K_d S_{es}\text{-}P_R+\frac{\overline{A}_2\text{-}\overline{A}_1}{19.8}}{1+K_d S_{es}} \qquad (11)$$

$$TDP\ removal\ (\%) = \frac{\Delta TDP}{C_R} \times 100 = \frac{K_d S_{es}}{1+K_d S_{es}} - \frac{P_R}{C_R(1+K_d S_{es})} + \frac{\bar{A}_2 - \bar{A}_1}{19.8\ C_R(1+K_d S_{es})} \quad (12)$$

where C_R, P_R are the dissolved and particulate P concentrations in the initial simulation, respectively, in mg/L; C_{es}, P_{es}, S_{es} are the final dissolved and particulate P concentrations and SPM concentration, respectively, measured in mg/L; $\bar{A}_{gpp}$ is the average GPP, measured in g/m^3/d; $\bar{A}_1$, $\bar{A}_2$ are the GPP in the initial and final concentrations, respectively, in g/m^3/d; K_d is the final partition of P species between the dissolved and particulate phase for the steady state, in L/mg.

2.8 Generalized additive model

In this study, GAM was used to identify the relative influence of various factors on P adsorption of SPM. Refer to Text S6 for more details. The GAM model can be described as below (Zou et al., 2020):

$$g(y) = s_0 + s_1(x_1) + \cdots + s_m(x_m) + \varphi \quad (13)$$

where, $s(x)$ represent smooth functions of linking explanatory variables; φ is the random residual term; $g(y)$ represent response variables.

2.9. Statistical analysis

Differences between treatments were determined using one-way analysis of variance (ANOVA, SPSS, version 16.0). Tukey's multiple comparison test (honest significant difference, HSD) was used to identify variances among groups ($P \leq 0.05$).

3. Results and Discussion

3.1. Variations in the species and partition of P during transport from rivers to lakes

Concentrations of different P species and SPM in the Miju river and Lake Erhai significantly varied between the dry and wet seasons (Fig. 1a). In the Miju River, concentrations of DIP, PIP and POP increased from 2.7±0.9, 0.3±0.23, 0.5±0.3 μmol/L during the dry season to 7.7±2.8, 1.8±0.3, 1.2±0.6 μmol/L during the wet season, respectively, a 3-6 times increase, which were significantly correlated with the flow ($P < 0.05$) (Table. S2), indicating an increase in non-point loading during rainfall events (Lu et al., 2015). In Lake Erhai, concentrations of DOP, PIP and POP increased from 0.3±0.2, 0.3±0.07 and 0.5±0.2 μmol/L during the dry season to 0.7±0.2, 2.1±0.4 and 2.0±0.5 μmol/L during the wet season, respectively, a 3-7 times increase. But a triple decrease in the DIP concentration from 0.45±0.05 μmol/L during the dry season to 0.11 ±0.02 μmol/L during the wet season was observed, which may be attributed to algal uptake due to a double increase in Chl*a*. Furthermore, APA during the wet season was almost double that of the dry season (Fig. S3). SPM was positively correlated with Chla and GPP in Lake Erhai and flow in the Miju River ($P < 0.05$) (Table.S2), indicating increases in SPM during the wet season might be related to plankton biomass in Lake Erhai and terrigenous input in the Miju River, respectively. Higher WT (average 21.7± 1.7 °C) and lower DO (4.0±1.4 mg/L) happened during the wet season than that in the dry season (14.4±3.3°C for WT; 7.5±1.1 mg/L for DO), while pH changed little (Fig. S4).

The nutrient regimes were very different in the Miju River and Lake Erhai and gradually changed across the estuary. During the wet season, TP pool shifted from being dominated by TDP in the Miju River and estuary regions (73±5%) to being dominated by TPP (74±11%) in Lake Erhai. Especially DIP concentrations decreased dramatically from the Miju River (8.0±0.9 μmol/L) across the estuary (4.1±0.2 μmol/L), to Lake Erhai (0.14±0.02 μmol/L), a 60-fold decrease, and TPP pool increased by 1.5-fold from the Miju River (3.0±0.2 μmol/L) across the estuary (2.1±0.4 μmol/L), to Lake Erhai (4.3±1.6 μmol/L). Comparison with some other rivers and lakes (Table S3) shows that the dominant contribution of TPP to TP also occurs in Lakes Huron, Erie, Taihu and Dianchi (accounting for 54-88%) and in rivers (accounting for 56-91%), such as Mississippi River, Maumee River, Jourdon River, Chena River, Yellow River and inflowing rivers of Lake Taihu, etc. Higher TPP abundance indicates a stronger water-particulate exchange activity (Zhang and Huang, 2011). K_d values of DIP (1.6±0.6 vs. 0.03 ± 0.01 L/mg) and TDP (0.33 ± 0.15 vs. 0.05 ± 0.03 L/mg) in Lake Erhai are apparently higher than that in the Miju River ($P < 0.05$) (Fig.1b), indicating the higher particle-reactivity of SPM in the lake in regulating the abundance, distribution and cycling of P in lakes, which also happens in other rivers and lakes (Table S3).

3.2. P-buffering potential of SPM as a source or sink

The K_f, EPC_0, the criterion δ values and $K_{d\text{-}eq}$ calculated of the isotherms using eq (3)−(5) for all 11 stations are presented in Fig. 2 and Fig. S5. Results demonstrated that there were different sorption behaviors of SPM between the Miju River and Lake Erhai during different sampling months. During the wet seasons, P sorption ability of SPM in the Miju River was higher with larger K_f values (1.1±0.03 L/mg) compared to the dry seasons (0.88±0.07 L/mg), but the SPM in Lake Erhai showed lower P sorption ability compared to the dry seasons, with smaller K_f values (0.47±0.08 vs. 0.76±0.02 L/mg) and larger EPC_0 values (5.03±2.69 vs. 0.61±0.65 μmol/L). Meanwhile, the SPM in Lake Erhai showed lower P sorption ability than that in the Miju River, with smaller K_f values (0.47±0.08 vs. 1.1±0.03 L/mg) and larger EPC_0 values (5.03±2.69 vs. 2.52±0.69 μmol/L).

By comparison between DIP and EPC_0, $K_{d\text{-TDP}}$ and $K_{d\text{-}eq}$ (TDP) (Zhang and Chi, 2002), respectively, we can predict whether SPM was a source or sink of P in the Miju River and Lake Erhai (Fig. 2). During the dry season, with relatively low SPM and P input, $K_{d\text{-TDP}}$ was equal to the $K_{d\text{-}eq}$, and δ values in the river (average 0.03±0.02 μmol/L) and the lake (0.06±0.03 μmol/L) were very low and close to zero, i.e. DIP was roughly in equilibrium with the SPM. During the wet season, in the Miju river, the $K_{d\text{-}eq}$ (TDP) was about 40 times higher $K_{d\text{-TDP}}$ (the slope close to zero), and δ was positive, and on average, adsorbed 2.17±1.12 μmol/L, and potentially removed 45.1±0.5% of DIP concentrations, i.e. the SPM played a strong P-sink to buffer additional P loading into the lake after rainfall. However, for Lake Erhai, $K_{d\text{-TDP}}$ was about triple $K_{d\text{-}eq}$ (TDP), and δ was negative, and on average, released P up to 2.52±1.14 μmol/L, accounting for 52.5% of TPP, causing a 25-fold increase in DIP concentration. This could explain why "secondary" algal blooms occur under the DIP-limitation in mesotrophic lakes. Particulates can also contribute to soluble P when the DPS exceeds 25% or 30% (Ohno et al., 2007). During the wet season, the DPS (60.1±12.1%) was higher in Lake Erhai as compared to 16.7±4.7% in the Miju River, indicating the stronger driving force for P-release of the SPM in Lake Erhai (Fig. 3). Therefore, the SPM could serve as a strong P-sink in the river and a P-source in the lake to buffer dissolved P level. Especially, the risk of SPM as a P-source to lake eutrophication should not be ignored.

3.3. Factors influencing P-buffering of SPM

3.3.1 Effect of particulate organic matter

The P sorption ability of SPM is governed by its chemical composition and biological activity. Pearson correlation (Table S4) showed P sorption ability of SPM, characterized by δ, K_f and $K_{d\text{-}eq}$, was significantly negatively correlated to POM, phytoplankton-POC and APA ($P < 0.01$), and positively correlated to C:N and C:P ($P < 0.01$), respectively. GAM model further identified (Table 1) that the phytoplankton-POC, APA and C:N were significant explanatory variables ($P < 0.001$), which could explain more than 60% variability of δ and EPC_0 and more than 30% variability of K_f and $K_{d\text{-}eq}$. The mean contributions of phytoplankton-POC, APA and C:N were 79%, 64% and 49%, respectively. Consequently, the phytoplankton-POC and its biodegradability (APA, C:N and C:P) were important factors inducing P release from SPM. Previous studies have confirmed that phytoplankton-POC is strongly related to the number of carboxylic (-COOH) groups, so P release may be enhanced if monocarboxylic acid increases (Staunton and Leprince, 1996).

This was consistent with the spatiotemporal patterns of POC fractions of SPM in Lake Erhai and the Miju River (Fig.3, Fig.S3). In Lake Erhai from the dry seasons to wet seasons, the significantly increased ratio of phytoplankton-POC (30±3% vs.

68±11%), the consistently lower organic C:N (23.5±5.5 vs. 8.0±1.6) and C:P (223.4±56.6 vs. 92.5±20.5) ratios, and the higher APA (0.018±0.006 vs.0.038±0.006 mmol/L/h) of the SPM can all prove its autochthonous origin from algae and organic debris of planktonic microorganisms with biolabile compounds for SPM in Lake Erhai during the wet seasons (called phytoplankton-SPM), indicating greater metabolic availability and higher turnover of POP by mineralization of microbial activity (Feng et al., 2018). Therefore, the SPM in the wet season enriched in phytoplankton-POC helps P release due to the high reactivity in aquatic environments.

But for the Miju River, PIM dominated SPM, accounting for 65±14%. The more abundant detritus-POC (0.55±0.21 mg/L) than phytoplankton-POC (0.24±0.1 mg/L) all year round and the higher organic C:N (22.6±9.9) and C:P (229±121) ratios of the SPM indicate its terrestrial plant or soil derived sources (called detritus-SPM) including clay minerals, silt, insoluble salts and colloidal aggregates (Turner and Millward, 2002), which may be refractory, inhibiting P release.

3.3.2 Effect of P activity of SPM

The P activity of SPM is governed by P species, which reflects P potential bioavailability transported in particle-water interface (Tang et al., 2018). The P (NH_4Cl+BD) fraction is fully mobile under natural conditions (Yi et al., 2017), and the POP pool, such as $NaOH_{25}$-nrP, also release P from polyphosphate-incorporating bacteria mineralization or bacterial respiration (Hupfer et al., 2004; Zhang et al., 2020). Consequently, the fractions of NH_4Cl-P, BD-P, and $NaOH_{25}$-nrP were all considered as the labile or bioavailable fractions (BAP) in this study.

Significant correlation occurred between P fractions and adsorption parameters across the sampling sites (Table S4). BAP fractions were significantly negatively correlated with P sorption ability of SPM, characterized by δ, K_f and $K_{d\text{-}eq}$, and positively correlated with EPC_0; while inert fractions (HCl-P and $NaOH_{25}$-rP) of SPM were positively correlated with δ, K_f and $K_{d\text{-}eq}$, and negatively correlated with EPC_0, respectively. GAM model (Table 1) further confirmed that $NaOH_{25}$-nrP, NH_4Cl-P, $NaOH_{25}$-rP and HCl-P were identified as significant explanatory variables ($P < 0.001$), which could explain 46.8%~90.6%, 50.1%~83.7%, 33.1%~82.8% and 31.8%~79.2% of variations in the P sorption ability of SPM, and explain 84.5%, 90.2%, 73.6% and 55.3% variations of EPC_0, respectively. Therefore, the P release capacity of SPM could be attributed to the proportions of BAP; while for P adsorption capacity of SPM, the aluminum and calcium oxides might be a key driver rather than iron compounds (Kerr et al., 2011). As shown in Fig.2 and Fig.3, in Lake Erhai, the BAP concentrations increased from 479 ± 105 mg/kg to 1260 ± 210 mg/kg leading to higher P-release potential from 0.17±0.07 μmol/L to 5.72±1.84 μmol/L; while in the Miju River, P-adsorption potential increased from 0.07±0.06 μmol/L to 5.97±1.12 μmol/L as the inert fractions increased from 205±30 mg/kg to 539±112 mg/kg. Consistently, in other well-known rivers (Rydin, 2000), the higher proportion of inert fractions in SPM, such as Nile and Mississippi Rivers (54%~57%), the Amazon River (67%~72%), and the Yellow River (82%), could reflect its higher P adsorption potential (Pan et al., 2013; Sutula et al., 2004).

P adsorption experiment (Fig.4) also confirmed that P adsorption amount (Q_e) of the phytoplankton-SPM in Lake Erhai (-11.5~13.3 mg/kg) was much lower than that of the detritus-SPM in the Miju River (-1.8~70.9 mg/kg). In Lake Erhai, this quasi-positive correlation among BAP fractions, phytoplankton-POC and Q_e revealed that the low Q_e might be attributed to BAP fractions and phytoplankton-POC, as described by Zhu et al. 2015 that phytoplankton-POC complexes with surface-bound Fe to form soluble organic-metal compounds can replace and release previously-sorbed P by competitive adsorption or ligand exchange. Furthermore, this quasi-negative correlation between APA and Q_e suggests the higher APA could stimulate visible P-release of phytoplankton-SPM. However, in the Miju River, the inert fractions significantly increased from 27% to 54% with increasing Q_e of detritus-SPM, indicating P could be resorbed and immobilized to enriched Al/Ca metal oxides. Similarly, for the Yellow River, the elevated concentrations of $Al(OH)_3$ and Ca metal oxides in particles can prevent P release by adsorbing P due to their stability under both oxic and anoxic conditions (Huser et al., 2016).

In addition, the DO and WT were identified as significant explanatory variables ($P < 0.001$), explaining 40~67.8% of the variations in the $K_{d(DIP)}$, $K_{d(DOP)}$ and $K_{d(TDP)}$ (Table. 1). $K_{d(DIP)}$ and $K_{d(DOP)}$ of SPM were significantly positively correlated with DO, and negatively correlated with WT (Table. S4), indicating that higher WT (21.7±1.7 °C) and anoxia (DO<5 mg/L) during the wet season can stimulate P release of SPM. Consequently, P exchange in the particle-water interface is largely controlled by POC and P species of SPM and water environment. Nevertheless, under which conditions the coupling of POC and metal oxyhydoxides or metal ions affects the P release and how fast the release happens needs to be further studied.

3.4. Effect of increasing SPM on P-buffering

Results from the adsorption isotherm experiment by changing mixing ratio of phytoplankton-SPM and detritus-SPM showed that P sorption capacity dropped down as the phytoplankton-SPM proportion increased, with smaller Q_e and K_f and higher EPC_0 (Fig.5a). The phytoplankton-SPM showed the minimum Q_e (-11.5~13.2 mg/kg) and K_f (0.35 L/mg) and maximum EPC_0 (5.11 mg/L); while the detritus-SPM showed the maximum Q_e (20.1~70.9 mg/k) and K_f (0.95 L/mg) and the minimum EPC_0 (0.15 mg/L). These results confirmed significant differences in P sorption capacity between the phytoplankton-SPM and detritus-SPM ($P < 0.05$).

Moreover, when detritus-SPM concentrations increased from 2 to 35 mg/L, DIP removal proportion increased up to more than 50% in the Miju River, but decreased to below -50% (indicating P-release) when phytoplankton-SPM concentrations increased from 2 to 35 mg/L in Lake Erhai (Fig. 5 b, c). Especially when $C_0 \leq 5$ μmol/L and phytoplankton-SPM ≥ 16 mg/L, the release amount of P could lead to 0.5- and 3-fold increase in the DIP flux; While when detritus-SPM ≥ 16 mg/L, P removal exceeds 30% at $C_0 \geq 5$ μmol/L and 50% at $C_0 \geq 7$ μmol/L. Consequently, the higher phytoplankton-SPM concentration could release more DIP, especially at lower DIP concentration, while the higher detritus-SPM concentration could remove more DIP, especially at higher DIP concentration. The conclusion again reflected P-buffering of phytoplankton-SPM as a P-source and detritus-SPM as a P-sink, which may also apply to other rivers and lakes rich in SPM (Table S3), such as Lake Dianchi with the 29.6±8 mg/L SPM concentration, and the Yellow River, the inflowing rivers to Lakes Taihu and Dianchi with a range of SPM concentration from 27 to 656.3 mg/L.

The relationships between $K_{d\text{-}eq}$ (DIP) and SPM concentration were fitted at different initial DIP levels in Lake Erhai and the Miju River (Fig.5 d, e). In Lake Erhai, the significantly inverse correlation between $K_{d\text{-eq}}$ (DIP) and phytoplankton-SPM ($P < 0.01$) demonstrated a strong “particle concentration effect” (Lin and Guo, 2016), indicating higher phytoplankton-SPM concentration enhances P-buffering. However, in the Miju River, the inverse correlation between $K_{d\text{-eq}}$ (DIP) and detritus-SPM is not significant, demonstrating the P adsorption capacity of detritus-SPM was relatively stable (Lin et al., 2012).

We used the modified K_d model with realistic estimates of the input parameters, and biological uptake of P from the relationship between TP and GPP reported by Smith (1979) to determine the relationship of SPM and TDP (Text S4, Fig.6). We hypothesise that the removal of dissolved P from aquatic ecosystems mainly reflects the combination of biological uptake and particle adsorption (Huang and Zhang, 2010).

For similar initial and final values of GPP (based on simulations over the range A_2-A_1=0–0.9 g/m^3/d) i.e., moderate or negligible biological uptake of P in the Miju River, the model predicted that TDP removal would increase significantly as SPM concentration increased, mainly because of adsorption by physicochemical control (Fig.6a). The SPM could therefore shift from a source to sink of P, depending on its concentrations and K_d. In the Miju River, during the wet season, the detritus-SPM concentration averaged 10.3 mg/L and was above the critical thresholds of 7.2 mg/L at average K_d values of 0.07, suggesting the detritus-SPM was a P-sink, which was consistent with the adsorption isotherms. If TDP inputs continued to increase (i.e., the K_d decline), more SPM would be needed to buffer the additional TDP loading.

However, if GPP is much higher at the end than at the beginning ($A_2 - A_1 > 0.9$ g/m^3/d) i.e., biological uptake of P dominates, as algae biomass sharply increase in Lake Erhai during the wet season. Interestingly, the TDP removal decreased sharply as the SPM concentration increased (Fig.6b). i.e., autotrophs can facilitate the accumulation of P on phytoplankton-SPM and enhance P lability, which in turn increases the bioavailable P for reuse, thereby promoting outbreak of algal blooms (Xie et al., 2003).

Both experiments and modeling confirmed that increasing SPM concentrations could enhance P-buffering. Especially the phytoplankton-SPM to buffer DIP-limitation during algae blooms should not be ignored, not just focused on eliminating sediments loading through sediment capping, sediment dredging (Liu et al., 2016; Wen et al., 2020).

3.5. Implications of SPM for P cycling during transport from river to lake

We drew a mechanism diagram of P-buffering of SPM during transport in the river-lake system (Fig.7). From the dry season to wet season, the increased SPM along with more P nutrient from terrestrial sources flows to the rivers and lakes due to the rainfall and runoff increase (Zhang et al., 2014). For rivers, the detritus-SPM enriched with PIM adsorbs P to form inert P fractions (K_d increase), which tend to sedimentation rather than re-release into water, thus could reduce 45% of P input to lakes. Global warming will increase the chemical and physical weathering rates, and the rainfall will increase weathered particles content and agricultural nonpoint sources into rivers (Pan et al., 2013). However, the detritus-SPM content was not enough to fully buffer the increased loading. Therefore, plenty of P loading into lakes at the proper temperature (>20°C) can trigger phytoplankton growth, leading to the increase of phytoplankton-SPM from algae metabolism. When the DIP is insufficient to satisfy the algae growth, the increasing phytoplankton-SPM enriched with BAP fractions could release more DIP (K_d decrease), causing a 25-fold increase for algae reuse, which creates a vicious cycling among algae-SPM-P to worsen water quality. Furthermore, anoxic, higher WT and enhanced APA in the wet season had positive effects on P liberation from the phytoplankton-SPM. This could explain why algal blooms in Lake Erhai can persist until November under DIP-limitation. The SPM shifted from a P-sink to a P-source to buffer P levels and promote P cycling during transport from rivers to lakes.

4. Conclusions

Our study offers a rare insight into two distinctive P cycling regimes between rivers and lakes, and provides new evidences of SPM as a P-sink in rivers and a P-source in lakes to buffer the level and partition of P, which was closely linked to the quality and quantity of SPM. The seasonal differences in POM components and P activity of SPM can influence P balance in the SPM-water interface, i.e., from the dry seasons to wet seasons, the significantly increased phytoplankton-POC and BAP fractions of SPM induced more P-release from SPM. Moreover, increasing SPM concentrations could enhance the P-buffering effect. When phytoplankton-SPM $\geq$ 16 mg/L at $C_0 \leq 5$ μmol/L, P release increased by 50%-300%; when detritus-SPM ≥ 16 mg/L at $C_0 \geq 5$ μmol/L, P removal could exceed 30%. This study highlights the importance of SPM as a sink or source of P in regulating P cycling cannot be ignored, and helps water managers to rethink the inner loop among algae-SPM-P under DIP-limitation.

Supplementary information

Supplementary information contains Figures S1–S7, Tables S1–S4, and six parts: Text S1–Text S6.

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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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Table 1. The GAM fitting results between major factors and parameters (δ, EPC_0, K_f and $K_{d\text{-}eq}$) of Freundlich crossover-type equations calculated by a nonlinear fit for the P adsorption isotherms of SPM; and between major factors and K_d ($K_{d(DOP)}$, $K_{d(TDP)}$ and $K_{d(DIP)}$) in field investigation in the Miju River and Lake Erhai.

Response variables		Explanatory variable	Edf	*F*	*p*	Dev.expl (%)	R^2
Simulation Experiment	δ	$NaOH_{25}$-nrP	3.59	85.98	$<2\times10^{-16}$ ***	90.6%	0.898
		NH_4Cl-P	4.14	39.04	$<2\times10^{-16}$ ***	83.7%	0.824
		$NaOH_{25}$-rP	4.07	37.14	$<2\times10^{-16}$ ***	82.8%	0.813
		APA	6.77	20.84	$<2\times10^{-16}$ ***	82.3%	0.795
		Phyto-POC	5.68	22.39	$<2\times10^{-16}$ ***	80.9%	0.779
		C:N	3.52	18.41	4.17×10^{-10} ***	67.2%	0.643
		HCl-P	3.01	8.45	5.57×10^{-5} ***	46.2%	0.422
		$NaOH_{85}$-P	5.84	3.07	0.0115 *	40.4%	0.306
		POM	2.01	9.25	0.000262 ***	36.8%	0.337
		C:P	2.05	8.48	0.000459 ***	35.4%	0.321
	EPC_0	NH_4Cl-P	8.45	35.19	$<2\times10^{-16}$ ***	90.2%	0.879
		$NaOH_{25}$-nrP	7.39	22.84	$<2\times10^{-16}$ ***	84.5%	0.813
		APA	5.59	24.46	$<2\times10^{-16}$ ***	82.8%	0.793
		Phyto-POC	4.29	23.94	7.8×10^{-15} ***	77.1%	0.746
		$NaOH_{25}$-rP	4.47	19.09	3.72×10^{-12} ***	73.6%	0.705
		C:N	3.61	16.41	2.9×10^{-9} ***	65.4%	0.622
		HCl-P	3.08	12.18	1.03×10^{-6} ***	55.3%	0.519
		C:P	5.46	5.07	0.00039***	49.4%	0.42
		POM	2.15	9.44	0.000149***	39.5%	0.364
	K_f	HCl-P	0.22	17.34	5.66×10^{-14} ***	79.2%	0.752
		Phyto-POC	6.39	3.27	0.00911 **	62.6%	0.325
		$NaOH_{25}$-rP	3.61	4.02	0.00778 **	53.1%	0.274
		NH_4Cl-P	1.35	9.53	0.000651 ***	50.1%	0.278
		APA	3.21	3.64	0.0139 *	49.4%	0.237
		$NaOH_{25}$-nrP	2.79	3.67	0.0145 *	46.8%	0.218
		C:N	6.63	1.16	0.324	36.5%	0.131
		C:P	3.34	2.07	0.102	21.3%	0.144
	$K_{d\text{-}eq}$	Phyto-POC	6.11	379.70	$<2\times10^{-16}$ ***	97.0%	0.951
		NH_4Cl-P	3.21	31.93	$<2\times10^{-16}$ ***	64.9%	0.604
		BD-P	6.36	4.98	2.98×10^{-6} ***	56.0%	0.564
		$NaOH_{25}$-nrP	5.97	12.25	1.47×10^{-11} ***	54.8%	0.515
		APA	7.51	3.79	0.000658 ***	41.1%	0.373
		$NaOH_{25}$-rP	7.50	3.89	0.000658 ***	33.1%	0.283
		HCl-P	5.59	5.48	6.61×10^{-5} ***	31.8%	0.263
		C:N	4.58	5.14	7.44×10^{-5} ***	30.1%	0.233
		PIM	3.79	5.08	6.61×10^{-5} ***	28.4%	0.219

Field Investigation	$K_{d(TDP)}$	DIP	4.851	22.03	1.25e-14 ***	77.40%	0.746
		DO	6.629	8.571	4.76e-07 ***	66.50%	0.604
		Chla	6.299	7.909	2.2e-06 ***	62.70%	0.563
		SPM	6.17	7.298	6.83e-06 ***	60.70%	0.541
		NH_4Cl-P	2.138	20.41	3.05e-08 ***	58%	0.558
		HCl-P	6.09	6.024	6.06e-05 ***	56.40%	0.492
		$NaOH_{25}$-rP	4.425	8.08	1.05e-05 ***	55.30%	0.501
		POM	3.61	9.779	4.4e-06 ***	53.80%	0.496
		Phyto-POC	3.762	8.851	1.2e-05 ***	52.20%	0.477
		$NaOH_{25}$-nrP	2.681	10.1	2e-05 ***	46.60%	0.431
		WT	3.693	6.126	0.000401 ***	43.80%	0.385
		TPP	4.469	4.685	0.00132 **	42.50%	0.359
		APA	3.658	6.078	0.000445 ***	42.50%	0.372
	$K_{d(DIP)}$	$NaOH_{25}$-nrP	6.652	26.26	<2e-16 ***	85%	0.823
		C:N	5.552	30.98	<2e-16 ***	84.70%	0.824
		NH_4Cl-P	4.92	32.87	<2e-16 ***	83.90%	0.819
		DIP	8.224	17.68	1e-15 ***	82.30%	0.781
		Chl a	7.475	19.2	<2e-16 ***	82.20%	0.784
		Phyto-POC	6.656	19.09	1.38e-15 ***	80.70%	0.772
		APA	3.971	29.78	<2e-16 ***	79.20%	0.771
		SPM	7.049	12.46	1.79e-10 ***	74.30%	0.693
		DO	6.872	9.006	1.68e-07 ***	67.80%	0.616
		$NaOH_{25}$-rP	6.236	4.338	0.00113 **	49%	0.403
		TPP	2.675	10.87	9.21e-06 ***	48.80%	0.455
		WT	6.326	3.764	0.00339 **	45.20%	0.358
		PIP	1.798	12.1	4.21e-05 ***	40.50%	0.379
	$K_{d(DOP)}$	DOP	5.526	25.35	<2e-16 ***	81.8%	0.791
		WT	6.797	7.29	4.14e-06 ***	62.60%	0.556
		PIP	6.945	5.132	0.000186 ***	55.40%	0.469
		TPP	6.266	4.687	0.00054 ***	51.50%	0.433
		DO	2.023	10.18	9.44e-05 ***	40%	0.37
		BD-P	2.779	4.451	0.0066 **	30.10%	0.252

$*p \leqslant 0.05, **p \leqslant 0.01, ***p \leqslant 0.001$

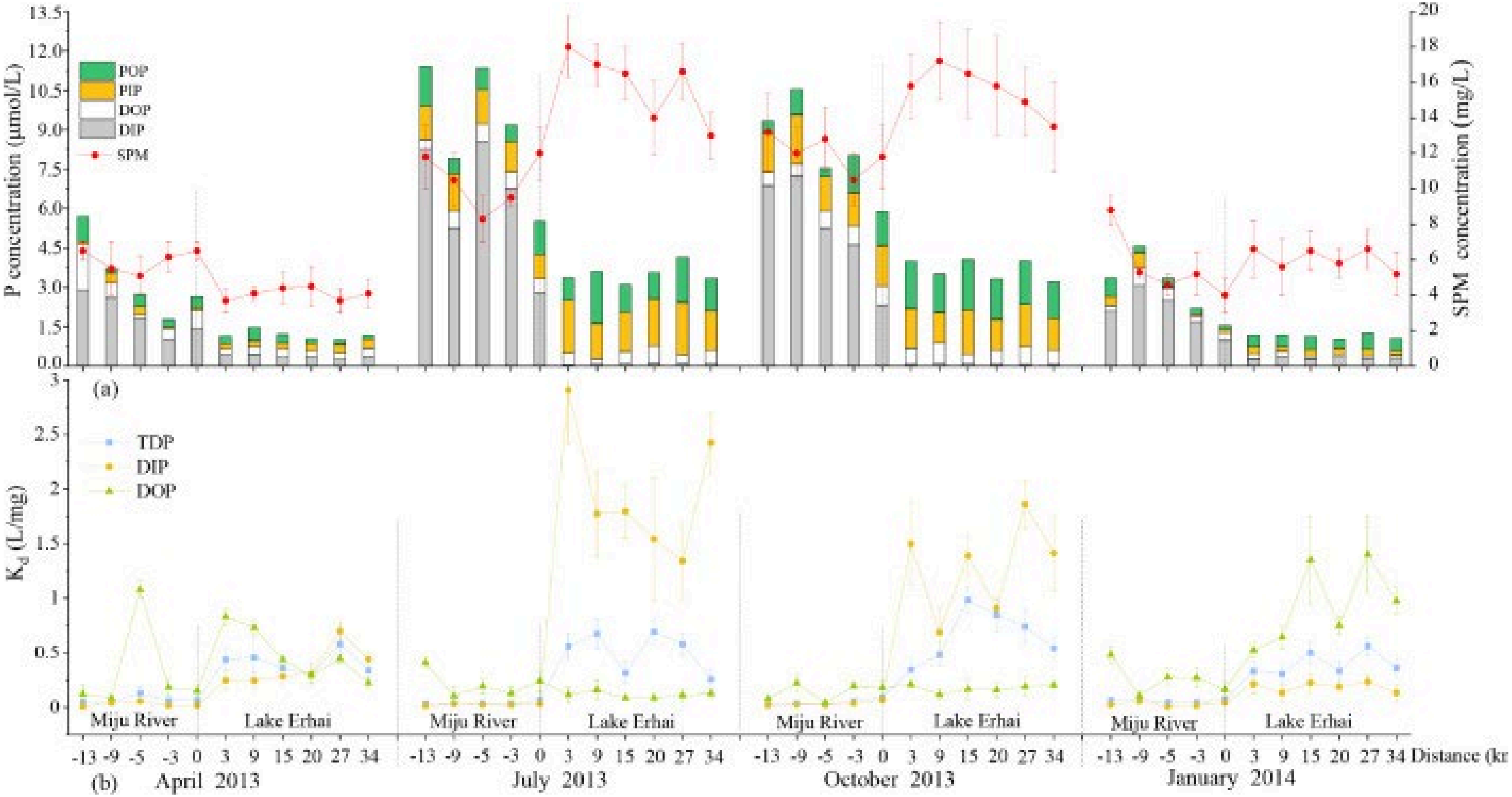

Fig. 1. (a) Spatial-temporal distribution of P species and suspended particulate matter (SPM) and (b) average partition of different P forms across the transition from the Miju River to Lake Erhai during different sampling months. The dashed line represents the estuary at the river-lake interface.

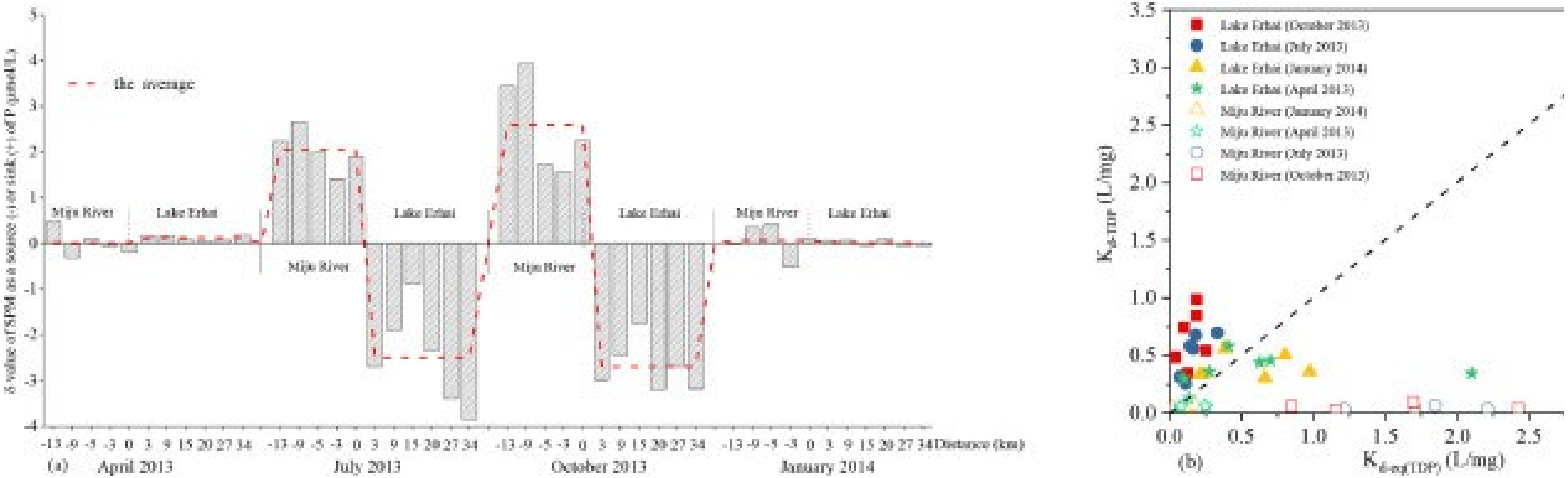

Fig.2. (a) The calculated potential of each SPM as a sink or source of P calculated by δ in the Miju River and Lake Erhai during different sampling months. (b) Correlations between $K_{d\text{-}eq}$ (TDP) and $K_{d\text{-}TDP}$ in the Miju River and Lake Erhai during different sampling months.

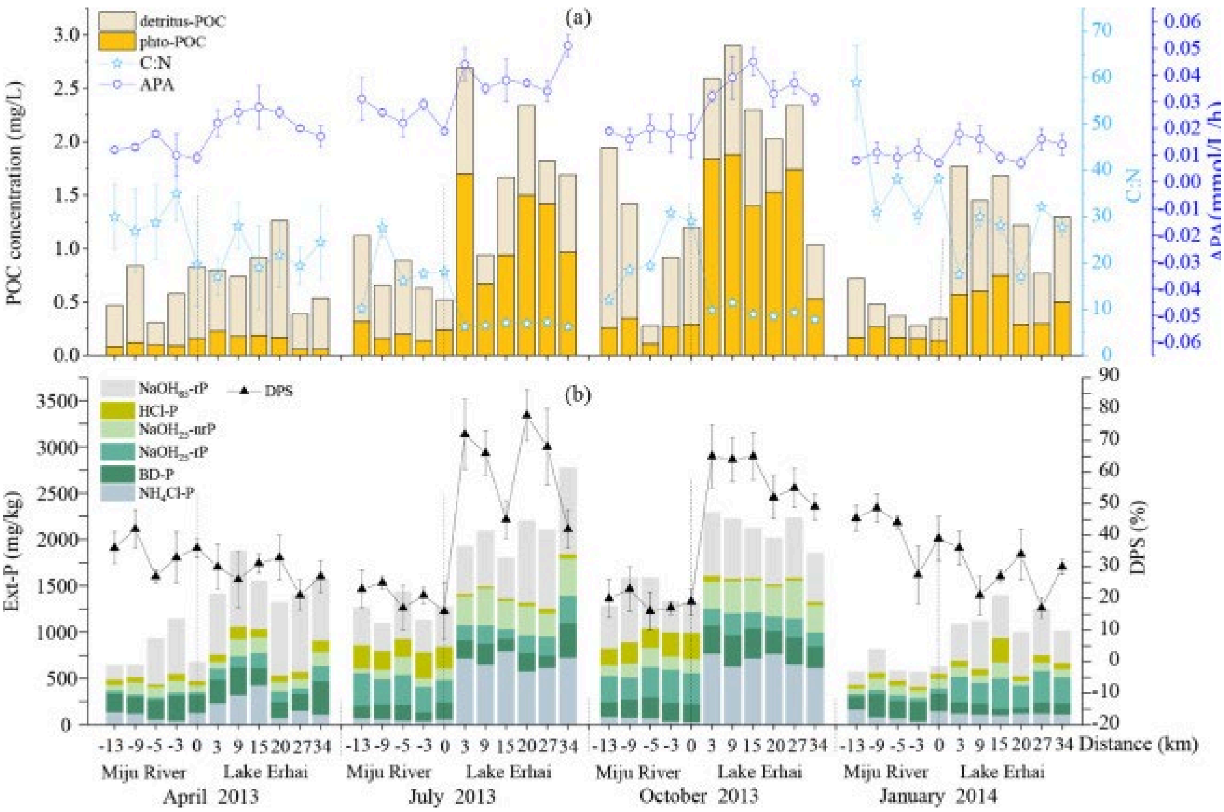

Fig.3. (a) Spatial-temporal variations in the POC from phytoplankton (phyto-POC) and detritus (detritus-POC), the organic C:N ratio in SPM and alkaline phosphatase activity (APA); (b) Different P species in SPM and the degree of phosphorus saturation (DPS) from the Miju River to Lake Erhai during different sampling months.

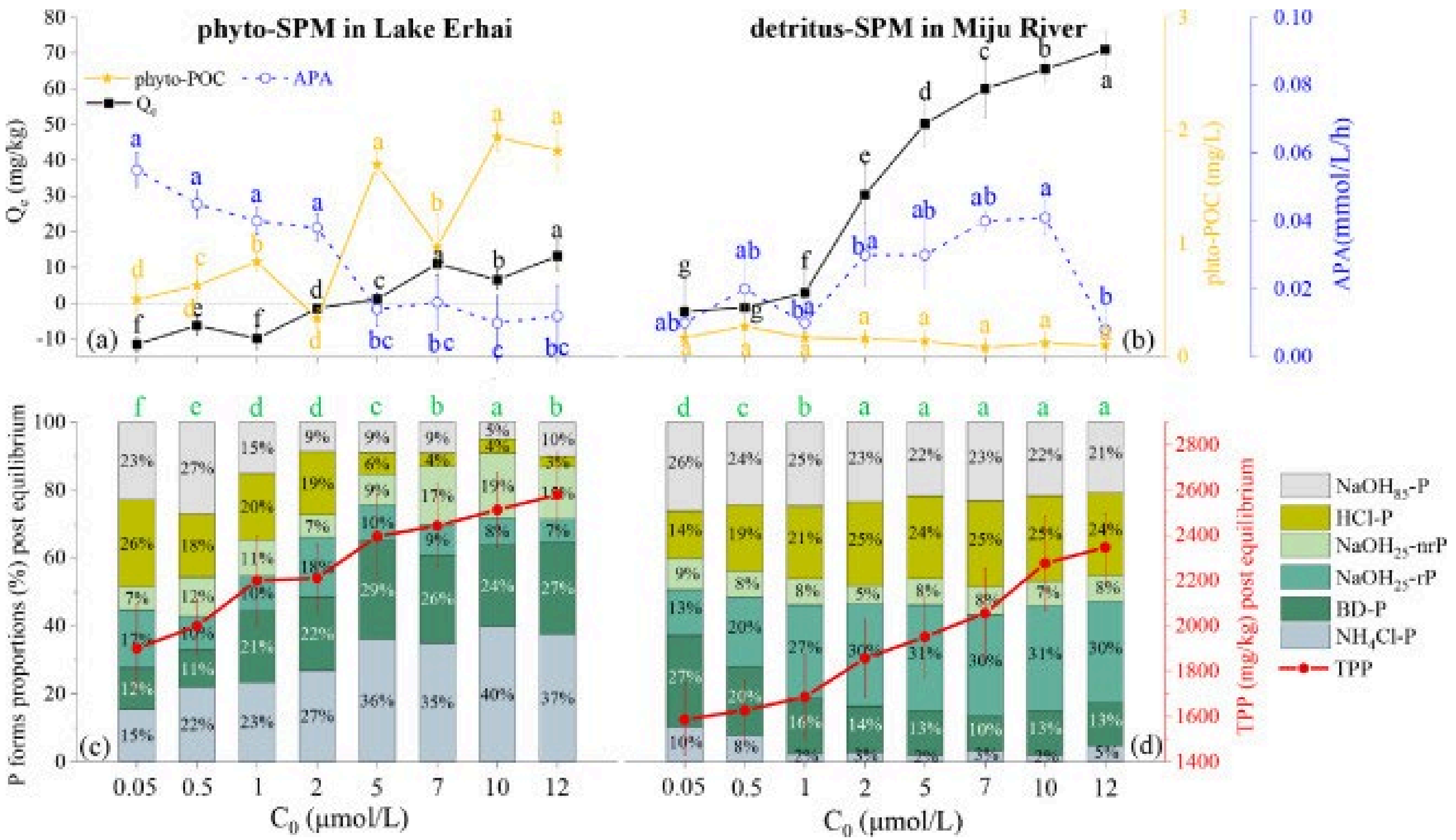

Fig.4. Variations of the P sorption capacity (Q_e), phyto-POC, APA and proportions of particulate P species with at equilibrium at different initial DIP concentrations (C_0) in Lake Erhai (a, c) and the Miju River (b, d) by adsorption isotherms of SPM. The phyto-SPM came from the station LE-2 in Lake Erhai, and the detritus-SPM came from the station MR-1 in the Miju River in October. The different letters (i.e., a–c) indicate significant differences among C_0 (one-way ANOVA, $p \leqslant 0.05$). Different letters in green represent significant differences of BAP fractions (NH_4Cl-P+BD-P+$NaOH_{25}$-nrP) (c) and inert fractions of HCl-P+$NaOH_{25}$-rP (d) among C_0.

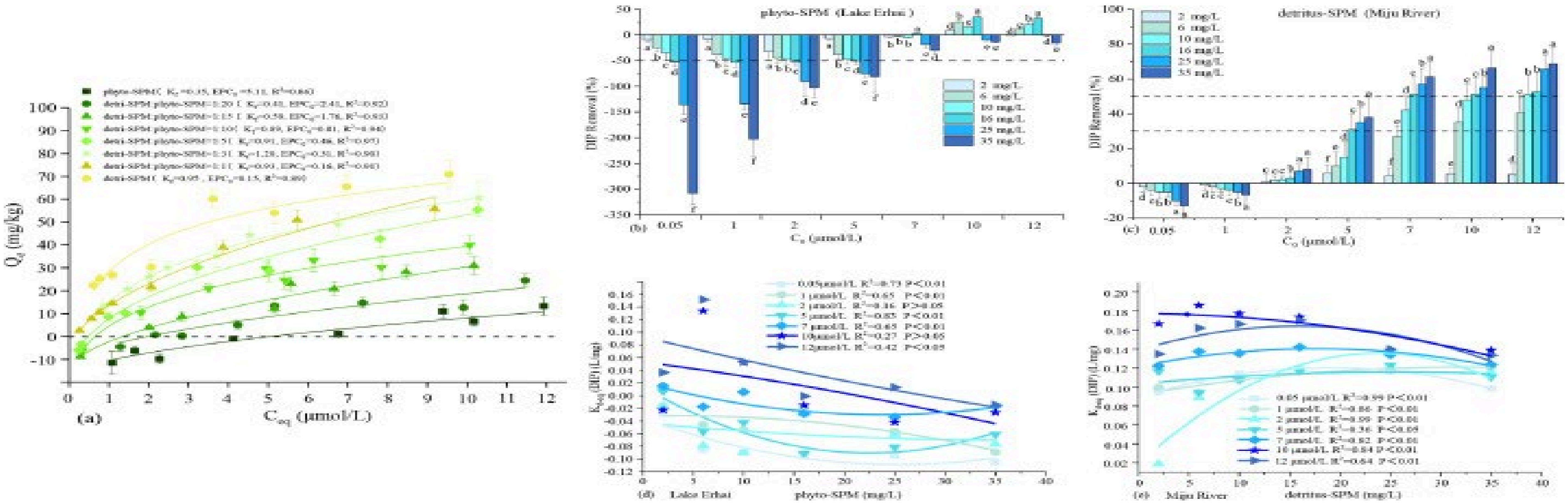

Fig.5. (a) P adsorption isotherms by the mixture of detritus-SPM and phyto-SPM, and changed the mixture mass ratio from 1:1 to 1:20; The detritus-SPM came from the station MR-1 in the Miju River in October, while phyto-SPM was obtained by adding fresh algae. The influence of different SPM concentrations (2, 6, 10, 16, 25 and 35 mg/L) on DIP removal (%) and $K_{d\text{-}eq}$ (DIP) at different initial DIP concentration in Lake Erhai (b, d) and the Miju River (c, e). The different letters (i.e., a–c) above the bars indicate significant differences among SPM concentrations (one-way ANOVA, $p \leq 0.05$).

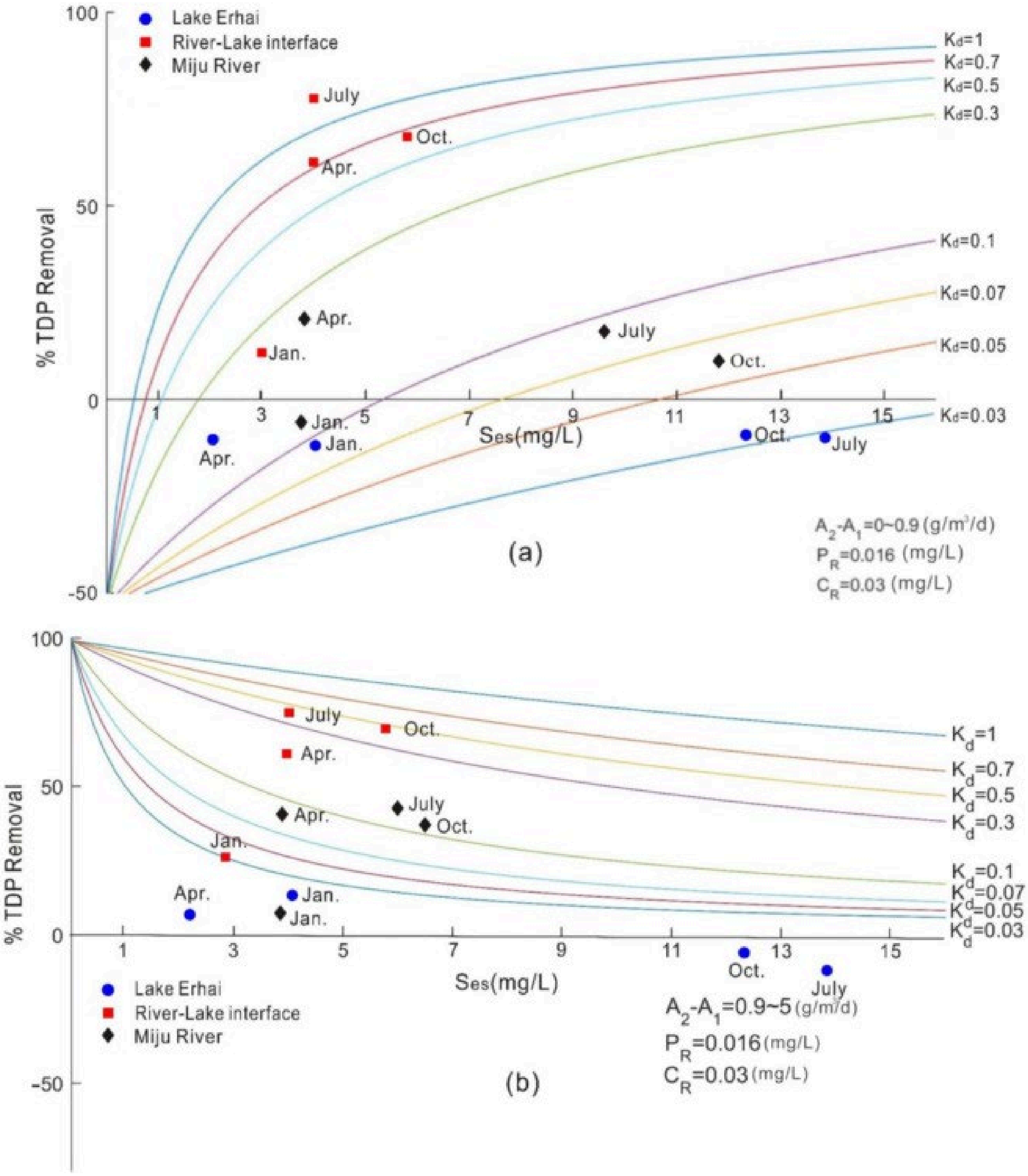

Fig.6. Model predicted % removal (+) or release (-) of TDP as a function of the SPM concentrations (S_{es}) at various values of K_d at low algal biomass (a) and high algal biomass (b). K_d and S_{es} values in the simulations are consistent with realistic changes in the Miju River and Lake Erhai. The values of the other parameters were the mean of realistic estimates.

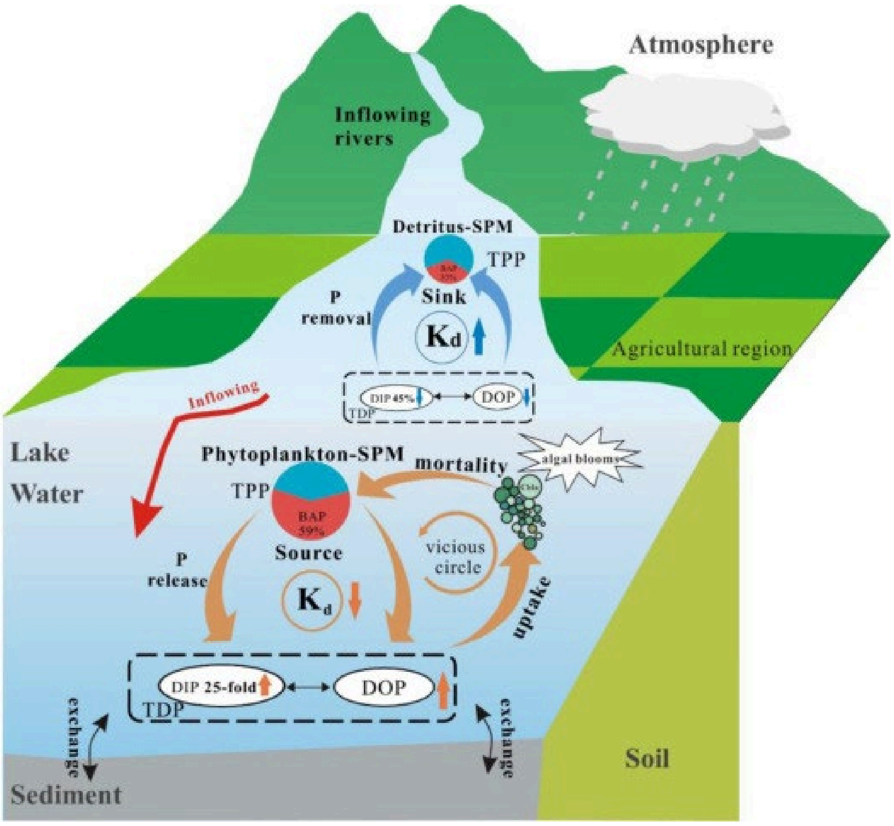

Fig.7. Mechanism diagram of P buffering effect of SPM as a P-sink in rivers and P-source in lakes on P cycling and K_d during transport in the river-lake system.