

Total phosphorus-precipitation and Chlorophyll *a*-phosphorus relationships of lakes and reservoirs mediated by soil iron at regional scale

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ABSTRACT

Phosphorus is a critical element determining trophic status and Chlorophyll *a* (Chl *a*) level in natural lakes and reservoirs, and total phosphorus (TP) concentrations can be predicted from data on phosphorus loading, hydraulic flushing rate and sedimentation. Due to their interactions with phosphorus, iron (hydr) oxides in suspended particles, originally derived from watershed soil, can strongly influence the phosphorus sedimentation and phosphorus bioavailability in water columns. Thus, the TP-precipitation relationship and the response of Chl *a* to TP are likely associated with watersheds soil iron. To test this assumption, we built hierarchical linear models for summer observation of natural lakes and reservoirs across a large geographic gradient. The intercepts and slopes of TP-precipitation relationships are higher in natural lakes than those in reservoirs, and these model coefficients exhibit latitudinal variations that are explained by the natural soil iron gradient. Soil iron, operating at a regional level, significantly mediates the effect of precipitation on TP concentration in both natural lakes and reservoirs, and drives the latitudinal variation in the Chl *a*-TP relationships for reservoirs. Our results imply that the increase in extreme precipitation events anticipated under future climate conditions may substantially mitigate eutrophication in tropical and subtropical reservoirs, but may worsen conditions in temperate lakes.

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1. Introduction

Phosphorus is the common limiting nutrient for aquatic primary production, and its concentration is usually used as an indicator for evaluating the trophic status and water quality of natural lakes and artificial lakes (reservoirs) (Edmondson, 1970; Schindler, 1974). Identifying the cause of phosphorus concentration variations in lakes can improve our ability to anticipate the effectiveness of management practices (Schindler, 2006). TP concentrations in lakes are closely associated with precipitation (Dillon, 1975; Jones and Bachmann, 1976; Chapra and Tarapchak, 1976; Mosley, 2015). An intensive precipitation can induce a strong runoff and subsequently increase the input of soil particles and external phosphorus to lakes (Carpenter et al., 1998; Ekholm and Lehtoranta, 2012). However, intensive precipitation could reduce hydraulic retention time and

facilitate water exchange, and may dilute the phosphorus in water columns. In addition, the sedimentation of particulate phosphorus also brings about a decrease in TP concentration in water columns. Thus, the effect of precipitation on TP concentration in water columns not only depends on phosphorus loading but also on flushing out and sedimentation. Due to the difference in nutrient input and limnological factors between natural lakes and reservoirs (Straškraba, 1996; Doubek and Carey, 2017), these two lake types might have distinct TP-precipitation relationships.

Simple empirical models have been developed to predict TP concentrations in both natural lakes and reservoirs from data on phosphorus loading, hydraulic flushing rates and sedimentation (Vollenweider, 1975; Jones and Bachmann, 1976). Although such models often have favorable goodness-of-fit statistics, there is still a high unexplained variance (Kalf, 2002), which greatly depends on how well the phosphorus sedimentation is estimated. By examining the phosphorus input-output relationships of a large number of natural and artificial lakes, Canfield and Bachmann (1981) gave a statistical estimate for the sedimentation coefficient. Because of the input dependence of phosphorus loading, their estimate implicitly

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shows that phosphorus sedimentation is critical for TP-precipitation relationships of lakes and reservoirs.

Iron (hydr) oxides are involved in phosphorus sedimentation in lakes, in which phosphorus sorption/desorption and co-precipitation/dissolution react on the interface between iron (hydr) oxides and water phase (Boström et al., 1988; Holtan et al., 1988; Slomp et al., 1996; Hongve, 1997; Ruttenberg, 2003). Suspended particle and surface sediment can be both a sink and a source of phosphorus in water columns depending on the sedimentation/resuspension equilibrium (Jensen et al., 1992; Forsgren et al., 1996; Koski-Vähälä and Hartikainen, 2000; Søndergaard et al., 2003; Hoffman et al., 2013). Iron (hydr) oxides in water columns and in sediments are ultimately derived from catchment soil (Dillon and Molot, 2005). Soil iron content, which has a regional pattern connected to climate conditions and geology (Buol et al., 2011), therefore determines the iron content in suspended particles and sediments which can influence TP concentration in water columns. Hence, precipitation has a potential to mediate TP concentration by soil iron.

Phosphorus concentration determines Chl *a* level to a great extent in aquatic ecosystems (Schindler, 1974; Schindler, 2006). The Chl *a*-TP relationships have been extensively examined and the regression models reflect the response of phytoplankton to phosphorus and the phosphorus utilization efficiency in lakes and reservoirs (Dillon and Rigler, 1974; Vollenweider and Kerekes, 1980; Prairie et al., 1989; Filstrup et al., 2014). Because iron (hydro) oxides may strongly influence TP concentrations and modify the bioavailable proportion of TP in water columns (Hoyer and Jones, 1983; Caraco et al., 1990; Håkanson et al., 2005), the intercepts and slopes of Chl *a*-TP regression models for natural lakes and reservoirs may be affected indirectly by soil iron at regional level. Compared to reservoirs, natural lakes typically have higher P loadings but smaller watershed. Consequently, the effect of soil iron on the Chl *a*-TP relationship is expected to be lesser for lakes than that for reservoirs. Thus, we predict that soil iron is able to explain the regional variation in Chl *a*-TP relationships, but depending on lake type.

To test whether TP-precipitation and Chl *a*-TP relationships in lakes and reservoirs are mediated by soil iron at the regional scale, we investigated 38 reservoirs in southern China and collected data from published works on 77 lakes and 74 reservoirs throughout China. The data set was divided into 12 groups based on region (large river basins, topography or soil iron) and lake type (natural lake or reservoir). We used a multilevel/hierarchical modeling approach to analyze such structural data with soil iron as a regional variable.

2. Materials and methods

2.1. Data

We compiled a data set that encompassed TP and Chl *a* concentration data of 77 lakes (196 observations) and 112 reservoirs (268 observations) in China. The data were obtained from our field investigation in southern China (36 reservoirs) and the published literature in CNKI (<http://www.cnki.net>) and ISI Web of Science. The basic information for each lake/reservoir and the reference of our data were shown in supplementary material (CSV file). These lakes and reservoirs cover a broad latitudinal range from tropical to temperate regions (Fig. 1). Brackish lakes and coastal lakes potentially affected by salt tide were excluded. Artificial scenic lakes were classified as natural lakes because of their similarities to natural lakes. Only summer (June, July and August) observations were included in our dataset. There were repeated observations for 35 lakes and 53 reservoirs. Here, each 'observation' corresponds to a single sampling occasion and reflects the monthly average value.

All samples were taken from the epilimnion in the pelagic zone of water bodies during 2000–2014. TP concentration in our dataset was determined according to standard methods for water quality (APHA, 1989). Chl *a* concentration was determined by spectrophotometric method after acetone or hot ethanol extraction (Jin and Tu, 1990; Lin et al., 2005).

Lakes were divided into 12 groups based on region and lake type (Table 1). Seven regions were classified on the basis of large river basins, topography or soil iron (from north to south): (1) Songhuajiang River and Liao River Basin; (2) Hai River, Yellow River Basin and Huai River Basin; (3) Middle and Lower Yangtze River Basin; (4) Sichuan Basin; (5) Guizhou Plateau; (6) Yunnan Plateau; and (7) Pearl River Basin. According to the similarity of soil characteristic, lakes in Zhejiang Province were included in the Yangzi River Basin, and lakes in east and west of Guangdong Province were included in the Pearl River Basin. Data on TP and Chl *a* concentration from natural lakes in Sichuan Basin and Guizhou Plateau were not available. Consequently, there are only 5 groups of natural lakes, compared to 7 groups of reservoirs. Table 1 shows the morphological parameters (lake depth, surface area, and volume), number of sampling sites (one 'site' refers to a single lake or reservoir), and number of observations for each group of lakes. The regional average iron content in soil was calculated based on provincial average values reported by Wei et al. (1990). Soil samples were digested by nitric acid and perchloric acid, and iron was measured by ICP-AES (inductively coupled plasma atomic emission spectrometry). The background value of soil iron content is primarily determined by geology and climate condition. It is relatively stable and is less affected by human activity. The reported data of soil iron, dated back to 1990, is similar to the contemporary soil iron content during 2000 and 2014 in our study. The monthly air temperature and precipitation were obtained from government statistical yearbooks (<http://nianjian.cnki.net>). Data on Chl *a*, TP, soil iron, air temperature and precipitation for each group of lakes are summarized in Table 2.

2.2. Multilevel/hierarchical modeling

Exploratory analysis of the data (Fig. S1 and Table S1; Fig. S2 and

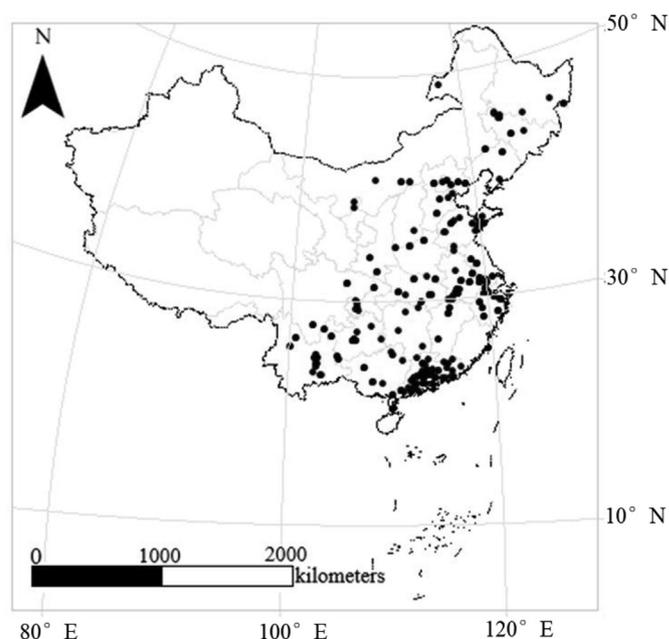


Fig. 1. Map of study area showing locations of 77 natural lakes and 112 reservoirs.

Table 1
Sample size and morphological parameters (mean \pm standard deviation) of lakes and reservoirs in the present study.

Groups	Description	Sites	Observations	Depth (m)	Surface Area (m ²)	Volume (10 ⁸ m ³)
R ₁	Reservoirs in Pearl River Basin	42	86	18.1 \pm 9.80	55.1 \pm 96.20	11.6 \pm 27.20
R ₂	Reservoirs in Yunnan Plateau	2	7	47.4 \pm 3.20	5.7 \pm 2.14	2.7 \pm 0.82
R ₃	Reservoirs in Guizhou Plateau	8	21	14.7 \pm 11.87	108.2 \pm 236.64	15.1 \pm 30.33
R ₄	Reservoirs in Sichuan Basin	8	20	16.6 \pm 7.50	23.2 \pm 25.25	4.8 \pm 6.18
R ₅	Reservoirs in Middle and Lower Yangtze River Basin	18	62	18.2 \pm 11.94	156.6 \pm 327.54	52.3 \pm 119.08
R ₆	Reservoirs in Hai River, Yellow River and Huai River Basin	24	50	14.0 \pm 8.54	91.9 \pm 107.26	11.3 \pm 16.46
R ₇	Reservoirs in Songhuajiang River and Liao River Basin	10	22	17.4 \pm 5.86	51.0 \pm 118.74	8.3 \pm 22.37
L ₁	Natural lakes in Pearl River Basin	13	34	1.8 \pm 0.38	1.4 \pm 1.63	0.03 \pm 0.038
L ₂	Natural lakes in Yunnan Plateau	12	30	14.4 \pm 16.49	81.9 \pm 92.72	14.3 \pm 34.05
L ₅	Natural lakes in Middle and Lower Yangtze River Basin	31	93	2.3 \pm 1.11	547.4 \pm 970.78	17.3 \pm 45.12
L ₆	Natural lakes in Hai River, Yellow River and Huai River Basin	16	31	2.6 \pm 1.49	101.2 \pm 236.40	3.5 \pm 9.94
L ₇	Natural lakes in Songhuajiang River and Liao River Basin	5	8	3.5 \pm 1.87	2425.5 \pm 2024.90	111.3 \pm 93.74
All		189	464	11.8 \pm 11.96	220.2 \pm 640.91	18.9 \pm 56.42

Table S2) shows the difference in TP-precipitation and Chl *a*-TP relationships among 12 groups. By grouping lakes/reservoirs, we introduce a hierarchical structure into the data: observations nested with each lake, lakes nested in individual groups, and so on. Because of the imbalance in sample sizes (number of observations in each lake and number of lakes in each group), multilevel/hierarchical modeling approach is the most appropriate method for analyzing such data. This approach is able to link individual observations with group-level variables and make the statistical inference based on two pieces of information: group means and overall mean (Malve and Qian, 2006; Qian, 2017). A log-log linear model is used as the basic model form for both TP-precipitation and Chl *a*-TP relationships. The log-log linear regression represents a proportional change relationship between the response and the predictor (Qian, 2017; pages 186–187). That is, the model assumes an increase of 1% in the predictor variable will lead to a fixed percentage increase in the response variable. This is a reasonable assumption. When using the natural logarithm, the fitted slope (β or δ) is the fixed percentage ($\beta\%$ or $\delta\%$).

At the observational level, we assume that the natural log-transformed TP concentration can be modeled by a normal distribution with the mean as a linear function of the log precipitation:

$$\text{Level 1: } \ln(TP)_{ijk} \sim N(\alpha_{jk} + \beta_{jk} \ln(Prec)_{ijk}, \sigma_{\ln(TP)}^2) \quad (1)$$

Where the subscript *i*, *j*, *k* represent the *i* th observation from the *j* th group in lake type *k* (natural lake or reservoir). α_{jk} and β_{jk} are the group-type-specific intercept and slope of the TP-precipitation regression model. $\ln(Prec)_{ijk}$ is the natural log-transformed and grand-centered precipitation (individual data value minus overall mean). The intercept α_{jk} is the log-mean TP concentration when the precipitation is equal to the grand mean precipitation. The slope

(β_{jk}) indicates the extent to which precipitation increase or decrease the TP concentration in lakes. $\sigma_{\ln(TP)}^2$ is the residual variance after accounting for precipitation.

The group-type-specific model coefficients are further modeled using a multivariate normal distribution (MVN) with the mean as linear functions of average soil iron. As air temperature determines the thermal regime of water columns and thereby influences the phosphorus transport processes in water columns, air temperature was used as a regional variable in the alternative model (Table 3). Deviance information criterion (DIC), a measure of model complexity and fit in Bayesian framework (Spiegelhalter et al., 2002), and between-group standard deviance in group-specific model coefficients was used for model comparison and selection.

$$\text{Level 2: } \begin{pmatrix} \alpha_{jk} \\ \beta_{jk} \end{pmatrix} = \begin{pmatrix} a_0^\alpha + a_1^\alpha \text{iron}_j \\ b_0^\beta + b_1^\beta \text{iron}_j \end{pmatrix} + \begin{pmatrix} \delta_{\alpha}^{\text{type}_k} \\ \delta_{\beta}^{\text{type}_k} \end{pmatrix} + \begin{pmatrix} \delta_{\alpha}^{\text{group}_j} \\ \delta_{\beta}^{\text{group}_j} \end{pmatrix},$$

$$\begin{pmatrix} \delta_{\alpha}^{\text{type}_k} \\ \delta_{\beta}^{\text{type}_k} \end{pmatrix} \sim \text{MVN} \left(\begin{pmatrix} 0 \\ 0 \end{pmatrix}, \Sigma_k \right),$$

$$\begin{pmatrix} \delta_{\alpha}^{\text{group}_j} \\ \delta_{\beta}^{\text{group}_j} \end{pmatrix} \sim \text{MVN} \left(\begin{pmatrix} 0 \\ 0 \end{pmatrix}, \begin{pmatrix} \sigma_{\alpha}^2 & \rho\sigma_{\alpha}\sigma_{\beta} \\ \rho\sigma_{\alpha}\sigma_{\beta} & \sigma_{\beta}^2 \end{pmatrix} \right). \quad (2)$$

In level 2, soil iron (iron_j) is incorporated into the model as a regional covariate to account for the between-group variation in the intercepts and slopes of TP-precipitation relationships. a_0^α and b_0^β are the intercept and slope of TP-precipitation relationships,

Table 2
Summary statistics of Chl *a*, TP, precipitation, soil iron and air temperature (T) for each group of lakes and reservoirs in the present study.

Groups	Chl <i>a</i> ($\mu\text{g/L}$, mean \pm SD)	TP ($\mu\text{g/L}$, mean \pm SD)	Precipitation (mm, mean \pm SD)	Soil iron (%)	T ($^{\circ}\text{C}$, mean \pm SD)
R ₁	14.4 \pm 25.17	26.4 \pm 32.71	168.5 \pm 109.63	4.40 \pm 0.951	26.1 \pm 3.81
R ₂	66.7 \pm 68.76	43.8 \pm 27.83	167.9 \pm 35.99	5.22 \pm 1.702	19.8 \pm 0.86
R ₃	15.2 \pm 12.00	33 \pm 25.54	147.6 \pm 47.65	4.17 \pm 1.492	22.1 \pm 2.85
R ₄	18.3 \pm 14.10	60 \pm 25.94	128.2 \pm 73.77	3.30 \pm 0.753	25.1 \pm 3.24
R ₅	16.1 \pm 23.38	41.9 \pm 28.10	159.1 \pm 100.13	3.21 \pm 0.571	25.3 \pm 3.33
R ₆	17.3 \pm 29.24	65.6 \pm 84.21	106.9 \pm 63.86	2.89 \pm 0.267	23.5 \pm 2.58
R ₇	13.8 \pm 16.11	88.7 \pm 64.03	91.1 \pm 49.87	2.83 \pm 0.090	22.0 \pm 2.15
L ₁	45.2 \pm 57.12	89.8 \pm 59.49	155.4 \pm 107.60	4.40 \pm 0.951	25.8 \pm 3.62
L ₂	21.1 \pm 27.74	65 \pm 60.78	144.5 \pm 60.81	5.22 \pm 1.702	20.9 \pm 1.77
L ₅	34.6 \pm 35.37	128.5 \pm 104.84	134.1 \pm 95.57	3.21 \pm 0.571	24.6 \pm 3.51
L ₆	83.5 \pm 102.26	323.9 \pm 480.2	109.7 \pm 81.95	2.89 \pm 0.267	24.4 \pm 2.47
L ₇	19.2 \pm 18.72	225 \pm 238.22	91.7 \pm 52.51	2.83 \pm 0.090	21.9 \pm 1.59
All	27.8 \pm 44.43	91.1 \pm 162.14	136.5 \pm 89.82	3.71 \pm 0.750	24.2 \pm 3.51

Table 3The estimated between-group standard deviance in group-specific intercepts (σ_α) and slopes (σ_β), and the DIC value for TP-precipitation regression models.

Basic model form	Group level variable	σ_α	σ_β	DIC
$\ln(TP)_{ijk} \sim N(\alpha_{jk} + \beta_{jk} \ln(Prec)_{ijk}, \sigma_{\ln(TP)}^2)$	None	0.41	0.09	1058
$\ln(TP)_{ijk} \sim N(\alpha_{jk} + \beta_{jk} \ln(Prec)_{ijk}, \sigma_{\ln(TP)}^2)$	Soil iron	0.19	0.04	1039
$\ln(TP)_{ijk} \sim N(\alpha_{jk} + \beta_{jk} \ln(Prec)_{ijk}, \sigma_{\ln(TP)}^2)$	Temperature	0.44	0.10	1049

respectively. a_1^α and b_1^β are the effect of iron on the intercept and slope of TP-precipitation relationships, respectively. Σ_k is the variance-covariance matrix for the lake-type specific model coefficients δ_α^{typek} and δ_β^{typek} . σ_α and σ_β are the between-group standard deviance of group-specific model coefficients δ_α^{groupj} and δ_β^{groupj} , respectively. ρ is the correlation coefficients between δ_α^{groupj} and δ_β^{groupj} .

Similar models are used to address the regional variation in the Chl *a*-TP relationships in lakes and reservoirs. As air temperature has an effect on Chl *a* level in water columns, air temperature was used as a regional variable in the alternative model (Table 4). Total phosphorus was also centered on the overall mean, and the intercept (γ_{jk}) is interpreted as the predicted log Chl *a* concentration in an observation when the TP concentration is equal to the overall mean. The slope (δ_{jk}) indicates the response of Chl *a* to TP concentration change in lakes (for every 1% increase in TP, we expect to see a δ_{jk} % change in Chl *a*).

$$\text{Level 1: } \ln(Chla)_{ijk} \sim N(\gamma_{jk} + \delta_{jk} \ln(TP)_{ijk}, \sigma_{\ln(TP)}^2) \quad (3)$$

$$\text{Level 2: } \begin{pmatrix} \gamma_{jk} \\ \delta_{jk} \end{pmatrix} = \begin{pmatrix} a_0^\gamma + a_1^\gamma \text{iron}_j \\ b_0^\delta + b_1^\delta \text{iron}_j \end{pmatrix} + \begin{pmatrix} \eta_\gamma^{typek} \\ \eta_\delta^{typek} \end{pmatrix} + \begin{pmatrix} \eta_\gamma^{groupj} \\ \eta_\delta^{groupj} \end{pmatrix},$$

$$\begin{pmatrix} \eta_\gamma^{typek} \\ \eta_\delta^{typek} \end{pmatrix} \sim MVN \left(\begin{pmatrix} \eta_0^\gamma + \eta_1^\gamma \text{iron}_j \\ \eta_0^\delta + \eta_1^\delta \text{iron}_j \end{pmatrix}, \Sigma_k' \right),$$

$$\begin{pmatrix} \eta_\gamma^{groupj} \\ \eta_\delta^{groupj} \end{pmatrix} \sim MVN \left(\begin{pmatrix} 0 \\ 0 \end{pmatrix}, \begin{pmatrix} \sigma_\gamma^2 & \rho \sigma_\gamma \sigma_\delta \\ \rho \sigma_\gamma \sigma_\delta & \sigma_\delta^2 \end{pmatrix} \right). \quad (4)$$

All analyses were performed in R (<https://www.r-project.org>) using function lmer in package lme4 (Bates, 2010). The computation of model parameters follows restricted maximum likelihood (REML) estimation and the R codes were modified from Qian (2017).

3. Results

The mean depths of reservoirs were higher than that of lakes (Table 1), indicating that thermal stratification in summer was likely to be more stable in reservoirs than that in lakes. Lakes and

reservoirs in Yunnan Plateau were deeper than the ones in other regions, which shows low regional variation in mean depths (Table 1).

Average monthly precipitation showed a low regional variation (Table 2). TP and Chl *a* concentrations among groups were highly variable with an overall average of $27.8 \pm 44.4 \mu\text{g/L}$ and $91.1 \pm 162.1 \mu\text{g/L}$, respectively (Table 2). The regional average soil iron content ranged from 2.83% to 5.22%. The overall average summer air temperature was $24.2 \pm 3.5^\circ\text{C}$, and there existed no latitudinal variation (Table 2).

3.1. TP-precipitation relationships

Reservoirs have significantly lower intercepts (α_{jk}) of TP-precipitation model than lakes (Fig. 2), indicating that regional average TP concentration in reservoirs is lower than that in lakes when precipitation is similar for these two lake types. The slopes (β_{jk}) of TP-precipitation model are negative for reservoirs (below the red line in Fig. 2B), but positive for lakes except in Yunnan Plateau (L_2 in Fig. 2). There was substantial regional variation in the parameters of TP-precipitation regression models. The intercepts and slopes shown a latitudinal pattern with relatively high values in temperate regions ($L_5, L_6, L_7, R_4, R_5, R_6$ and R_7 in Fig. 2), but low values in tropical and subtropical regions (L_1, L_2, R_1, R_2 and R_3 in Fig. 2). Precipitation has a more negative effect on TP concentration of reservoirs in tropical and subtropical regions than that in temperate regions (Fig. 2B).

As suggested by the DIC value and the between-group standard deviance in group-specific model coefficients (Table 3), soil iron is the variable that best explains the latitudinal pattern in the coefficients of TP-precipitation regression model. The estimated intercepts and slopes of TP-precipitation regression models were negatively correlated with soil iron for both natural lakes and reservoirs (Fig. 2).

3.2. Chl *a*-TP relationships

Intercepts (γ_{jk}) and slopes (δ_{jk}) of Chl *a*-TP regression models were highly variable among regions with relatively high values in tropical and subtropical reservoirs (L_1, L_2, R_1, R_2 and R_3 in Fig. 3). The indication is that Chl *a* concentration at a given TP concentration tends to be higher, and its response to TP variation is more sensitive, in tropical and subtropical reservoirs than those in the temperate reservoirs. The coefficients of Chl *a*-TP regression models for natural lakes were less variable among regions.

Both soil iron and mean temperature can partially explain the

Table 4The estimated between-group standard deviance in group-specific intercepts (σ_γ) and slopes (σ_δ), and the DIC value for Chl *a*-TP regression models.

Basic model form	Group level variable	σ_γ	σ_δ	DIC
$\ln(Chla)_{ijk} \sim N(\gamma_{jk} + \delta_{jk} \ln(TP)_{ijk}, \sigma_{\ln(TP)}^2)$	None	0.44	0.32	1486
$\ln(Chla)_{ijk} \sim N(\gamma_{jk} + \delta_{jk} \ln(TP)_{ijk}, \sigma_{\ln(TP)}^2)$	Soil iron	0.28	0.25	1473
$\ln(Chla)_{ijk} \sim N(\gamma_{jk} + \delta_{jk} \ln(TP)_{ijk}, \sigma_{\ln(TP)}^2)$	Temperature	0.39	0.18	1473

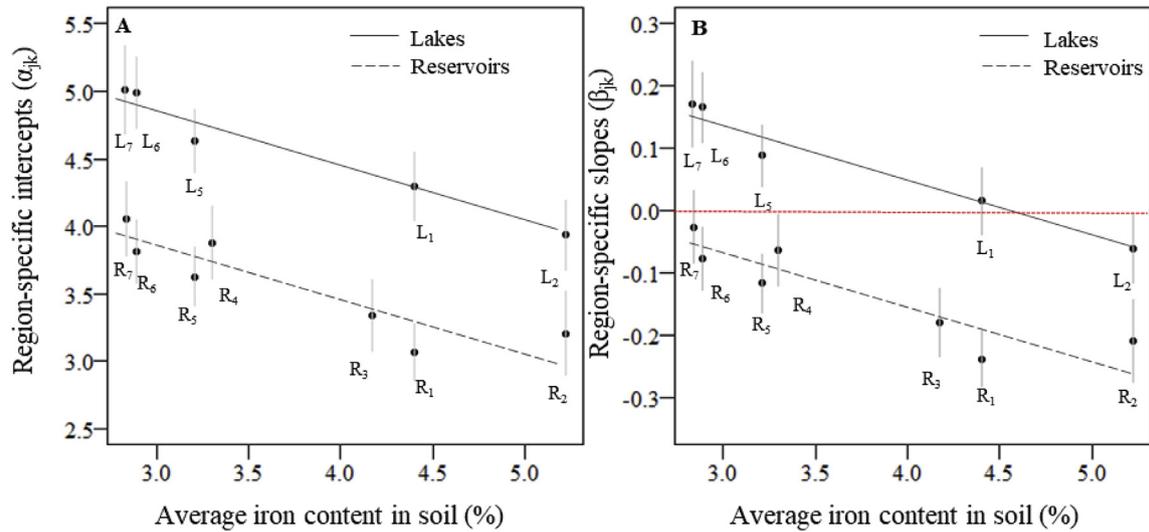


Fig. 2. TP-precipitation regression models showing (A) region-specific intercepts (α_{jk}) versus soil iron, and (B) region-specific slopes (β_{jk}) versus soil iron. The dots are the estimated posterior means, the vertical line segments are the posterior 95% credible intervals, group code R represents reservoirs, L represents natural lakes, and the numerical subscripts of group code represent regions. The red line in Fig. 2B represents a boundary for the positive/negative slopes of the models. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

regional variation in the coefficients of Chl *a*-TP regression models (Table 4), but only soil iron has a latitudinal pattern in our dataset (soil iron ~ latitude: $F_{10, 1} = 18.4$, adjusted $R^2 = 0.61$, $P < 0.01$; temperature ~ latitude: $F_{10, 1} = 0.4$, adjusted $R^2 = -0.05$, $P = 0.52$). Regional difference in soil iron can alone explain the latitudinal pattern in Chl *a*-TP relationships.

The regional level soil iron content is positively correlated with the intercepts and slopes of Chl *a*-TP relationships in reservoirs (Fig. 3).

4. Discussion

Precipitation promotes diffused phosphorus loss from watershed, and has a profound influence on phosphorus dynamics in lakes (Carpenter et al., 1998). Our hierarchical TP-precipitation

model showed that natural lakes have higher intercepts and slopes of TP-precipitation relationships than reservoirs. This is likely because these natural lakes had higher phosphorus loadings. Reservoirs are usually more isolated and receive less nutrient input than natural lakes (Straškraba, 1996; Doubek and Carey, 2017). In addition, this might be explained by the difference in depths between the two lake types. Lakes included in this study are shallow (mean depth < 6 m) except for lakes in Yunnan Plateau (Table 1). These shallow lakes are at best weakly stratified in summer (Qin, 2001; Le et al., 2010), and the mixing may increase the particulate phosphorus release from sediment (James and Barko, 1993; Kristensen et al., 1992). Reservoirs are generally deeper than natural lakes and usually exhibit strong stratification in wet seasons (Brooks and Edgington, 1994; Wang et al., 2012; Doubek and Carey, 2017), which block the diffusion of phosphorus from hypolimnion

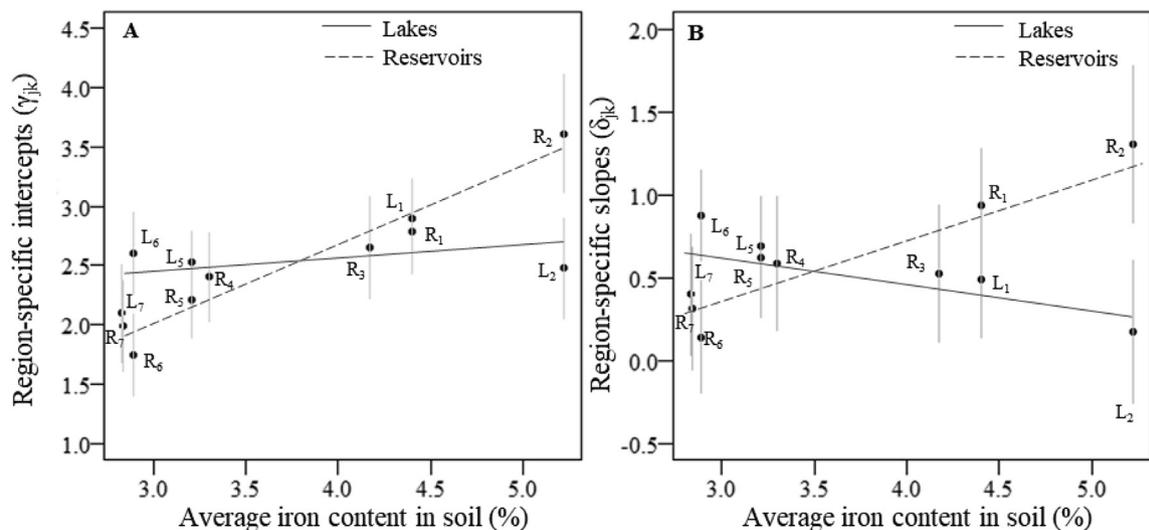


Fig. 3. Chl *a*-TP regression models showing (A) region-specific intercepts (γ_{jk}) versus soil iron, and (B) region-specific slopes (δ_{jk}) versus soil iron. The dots are the estimated posterior means, the vertical line segments are the posterior 95% credible intervals, group code R represents reservoirs, L represents natural lakes, and the numerical subscripts of group code represent regions.

to epilimnion in water columns. Furthermore, deep-water withdrawal in reservoirs lead to deeper thermoclines (Han et al., 2000). Unlike natural lakes, reservoirs can discharge water through outlets at depths reaching phosphorus-enriched hypolimnion (Wang et al., 2011, 2012), and may increase the flushing out of phosphorus (Barbiero et al., 1997). Overall, sedimentation flux minus release flux from surface sediment is equal to the net sedimentation flux. Net sedimentation plus flushing out reflects the ‘dilution effect’ of precipitation on TP concentration. The negative slopes of TP-precipitation models for reservoirs suggest that the ‘dilution effect’ of precipitation to some extent surpasses the ‘enrichment effect’ of TP loading on TP concentration in reservoirs (Fig. 4). The positive slopes of TP-precipitation models indicate that the ‘enrichment effect’ of TP loading is greater than ‘dilution effect’ of precipitation for natural lakes (Fig. 4).

The intercepts and slopes of our TP-precipitation regression models are lower in (sub) tropical region than that in temperate region. As there is no latitudinal gradient in the external loading of phosphorus for natural lakes and reservoirs in China (Zhang et al., 2004), it suggests that TP loading is independent of climate zone in our study. That is, TP loading in south China is not significant different from that in northeast China, and it is reasonable to assume that average TP loading is roughly the same for our lakes and reservoirs at the regional scale. Based upon this assumption, it might be expected that the TP concentration pattern is attributed to the alteration of phosphorus sedimentation process occurring in the water columns, not the variation in external phosphorus input. TP loading probably play a minor role in determining the TP pattern.

TP concentrations in natural lakes and reservoirs with similar precipitation (intercepts) change as a function of soil iron content. The effect of precipitation on TP concentrations (slopes) in both natural lakes and reservoirs are associated with iron content in catchment soil. Although phosphorus also interacts with other metal elements (e.g., calcium, manganese and aluminum), dissolved organic carbon and carbonates, iron acts as a carrier in natural waters (Van der Grift et al., 2018). Compared with other elements in soil, iron is more likely to strongly influence

phosphorus sedimentation in lakes and reservoirs. Phosphorus sedimentation is usually coupled with iron in water columns (Hongve, 1997). With an increasing gradient of soil iron from north to south, we expect to see a more intensive net sedimentation (sedimentation minus internal release) of phosphorus in the water column (Fig. 4), because of the strong phosphorus sorption and coprecipitation with iron (hydr) oxides and the subsequent sedimentation of iron-phosphorus complexes (Stauffer, 1987; Gunnars et al., 2002; Hoffman et al., 2013). Iron hydroxyphosphate is the main chemical form of such iron-phosphorus complexes (Baken et al., 2016; Van der Grift et al., 2016). The TP pattern we observed suggests that there would be a decreasing proportion of phosphorus in the water column and an increasing proportion of phosphorus in the sediment, as we move from high to low latitudes. In other words, high soil iron may considerably counteract the effect of TP loading, and thereby result in the relatively low TP concentration in subtropical lakes and reservoirs. Other factor, such as temperature, largely determines the formation of thermocline and influences the phosphorus flux in water columns (Kalf, 2002). Lakes and reservoirs in tropical and subtropical regions have no ice-on season and have longer stratification period, which might decrease to a larger degree the phosphorus diffusion from hypolimnion. However, the regional average temperature in our dataset do not substantially differ among climate zones. This is probably because altitude also has an influence on temperature in summer and offsets the dependence of temperature on latitude. Therefore, temperature may contribute less to the TP pattern. In addition, low pH increases the phosphorus binding capacity of iron in lakes (Boström et al., 1988), and might change the phosphorus flux in water columns. Nevertheless, no remarkable difference in average pH between tropical and temperate waters was reported so far. The TP pattern could be less related to water pH.

Our TP-precipitation model has implications for the effect of climate change on lake TP concentration. Global climate change is expected to bring not only an increase in temperatures but also an increase in the frequency of flooding events (Khan et al., 2015; Mo et al., 2016). The slopes of our TP-precipitation model suggests that extreme precipitation can lead to an increase in TP concentration in temperate lakes, but a decrease in TP concentration in reservoirs. An intensive might decrease to a greater extent the TP concentration of reservoirs in tropical and subtropical regions than that in temperate regions. Contrary to the conventional wisdom, soil erosion after intensive precipitation is likely to reduce the phosphorus concentration of reservoirs, particularly in tropical and subtropical regions.

Soil iron influences TP concentrations in water columns and alters the fraction of bioavailable phosphorus through chemical immobilization (Caraco et al., 1990; Håkanson et al., 2005). Both TP concentration and the bioavailable proportion of TP are related to the coefficients of Chl *a*-TP regression models (Hoyer and Jones, 1983). In the present study, regional variation in the Chl *a*-TP relationships in reservoirs can be explained by the iron content in watershed soil. Because the intercept is the expected log Chl *a* concentration when TP concentration is at the same level (grand mean of the data), a higher intercept suggests a higher phosphorus utilization efficiency (i.e., the same level of TP leads to a higher Chl *a*; Fig. 3A). A higher slope indicates that a lake is more sensitive to TP. In other words, high soil iron may enhance phosphorus limitation and drive the parameters of Chl *a*-TP regression model in reservoirs to increase from temperate to tropical and subtropical regions. As natural lakes have higher TP concentrations than reservoirs, the phosphorus limitation in lakes could be weaker. This may explain why soil iron content has a lesser effect on the coefficients of regression model for natural lakes.

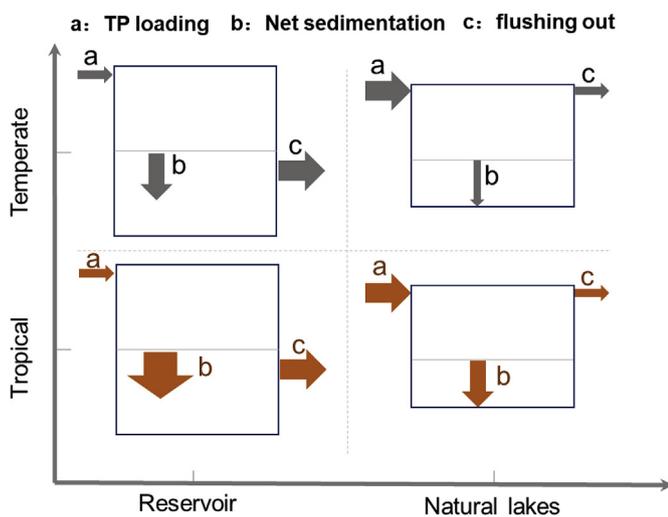


Fig. 4. A conceptual diagram presenting the mechanism explaining the pattern suggested by our TP-regression regression model. Net sedimentation means sedimentation minus the release from lake surface sediment. Each box represents a water column, and the height of box represents water depth. The horizontal line in each box represents thermocline, above which it is epilimnion. Arrows represent the phosphorus flux in water columns and a thicker arrow indicates a more intensive flux.

5. Conclusions

Soil iron can act as a critical variable at the regional scale for mediating the impact of precipitation on TP concentration in lakes and reservoirs. This in turn drives the latitudinal variation in Chl *a*-TP relationship in reservoirs. Our study implies that the increase in extreme precipitation events anticipated under future climate conditions may substantially mitigate eutrophication in tropical and subtropical reservoirs, but worsening the conditions in temperate lakes.

Declarations of interest

None.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.watres.2019.01.038>.

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