



## Enhanced release of sedimentary phosphorous following nitrate decline in a nitrate-rich reservoir and its management implications

Zengwen Gao<sup>a,\*</sup>, Hong Li<sup>a</sup>, Xilai Zheng<sup>b</sup>

<sup>a</sup>School of Environmental Science and Engineering, Qingdao University, Shandong 266071, China, Tel. +86 13864220611; email: gaozengwen@163.com (Z. Gao), Tel. +86 18354263319; email: lihongqdu@163.com (H. Li)

<sup>b</sup>College of Environmental Science & Engineering, Ocean University of China, Shandong 266100, China, Tel. +86 532 66781759; email: zhxilai@ouc.edu.cn

Received 7 August 2017; Accepted 15 August 2018

### ABSTRACT

Nitrate in aquatic systems is controlled to protect human health, whereas it is also used as an inhibitor of sedimentary phosphorus (P) release to prevent freshwater eutrophication. This study was conducted to investigate the effects of nitrate decline on P release from sediments in Tianzhuang Reservoir (Yiyuan County, Shandong, China), which has a high nitrate concentration in the water column and high ferric-bound P to total P (Fe-P/TP) and total iron to total P (T-Fe/TP) ratios in the surficial sediments. We investigated the nitrate and soluble reactive phosphorus (SRP) profiles in sediment porewaters, estimated their fluxes on the sediment side of the sediment–water interface, and calculated the net production ratio of nitrogen (N) to phosphorus in the surface sediments. We also conducted P release experiments in the laboratory. SRP was significantly negatively correlated with nitrate in porewaters of the surficial 7.5-cm sediments. The diffusional SRP flux in Tianzhuang Reservoir was only 0.191 mg/(m<sup>2</sup>·d). The net production ratio of N:P was 2,372:1 in the surface sediments. Laboratory experiments showed that the concentration of SRP in nitrate-free water was clearly higher than that in nitrate-rich water under the effects of the sedimentary P release. These findings indicated that nitrate was the key factor controlling the sedimentary P release in the reservoir, and that nitrate decline would enhance the release of P from redox-sensitive sediments. Therefore, we recommend that measures for controlling P should be implemented simultaneously when treatments for nitrate pollution are employed in aquatic systems with redox-sensitive, iron-rich sediments.

*Keywords:* Nitrate; Phosphate; Sediment–water interface; Release enhancement

### 1. Introduction

The natural cycle of nitrogen has been heavily disturbed by the tremendous consumption of nitrogen fertilizer and fossil fuel for industrial processes [1,2], which has led to increased nitrate and ammonium in water bodies. Excessive nitrogen in water is an important factor for eutrophication of surface waters [3]. Furthermore, nitrate at levels exceeding the threshold concentration for drinking water is usually thought to be harmful to the public, especially to young

children [4]. Therefore, nitrogen pollution is being treated mainly by implementing external measures (e.g., land management practices [5,6], nitrate removal by adsorption [7,8]) in many countries.

Substantial human and financial resources have been invested to control water nitrogen pollution; however, some researchers and technicians tend to add nitrate to the hypolimnion water or surficial sediments to control the eutrophication of surface water by reducing P release from polluted sediments [9–13]. It is done because oxygen is a key factor in the sedimentary phosphorus cycle related to the coupling

\* Corresponding author.

between Fe and P. Under aerobic conditions, phosphorus release from Fe-rich sediments can be suppressed, whereas under anoxic conditions, the previously ferric-bound P (Fe–P) is released to the water as the ferric iron is reduced to ferrous iron [14–17]. Nitrate is an oxidizing agent that maintains the relatively oxidized state of surficial sediments in aquatic systems; therefore, it is used as a suppressant of Fe–P release from sediments [9,10]. When oxygen and nitrate are consumed by biochemical processes (the oxidation of organic matter) near the sediment–water interface, a high sulfate reduction rate can inhibit the Fe mobilization via the formation of solid  $\text{FeS}_x$  [18]. Therefore, the reduction of sulfate can enhance the release of P from sediments. This coupling cycle between Fe and P is commonly termed as the classical model of internal P loading [19]. However, this classical model is only valid in special cases because of the complexity of actual systems [20,21]. In addition, Schauser et al. [22] reported that nitrate cannot suppress the release of P from sediments with low P sorption capacity under intensive mineralization conditions. Therefore, not all aquatic systems agree with this classical model.

Tianzhuang Reservoir is a mesotrophic reservoir located in southwest Shandong Province, China. The total nitrogen (TN) (average concentration of 11.0 mg/L monitored in 2005 and 2006) in the water column of the reservoir has exceeded the Chinese environmental quality standard for surface water (1 mg/L) (GB 3838-2002) because of discharges from a local nitrogenous fertilizer plant and runoff from agricultural watersheds. TN in the reservoir usually exceeds 10 mg/L, and the nitrate level is about 5–12 mg N/L [23]. Tianzhuang Reservoir is a potential source of drinking water for Yiyuan County. To improve the quality of drinking water, the local government plans to divert the discharge from the nitrogenous fertilizer plant and decrease nitrogen loading from the associated watersheds. It should be noted that the sulfate in the water was about 100 mg/L and that Fe–P ranged from 500 to 600 mg/kg dry sediments, which constitutes up to 60% of the total phosphorus (TP) in the sediments [24].

Most studies of the relationship between nitrate and phosphorus in aquatic systems conducted to date have focused on the resistant effects of increased nitrate on phosphate release from sediments (e.g., the addition of 24 g N/m<sup>2</sup> of nitrate to the sediment of White Lough [11]), while few have investigated the effects of nitrate concentration decline due to its control. Through field monitoring, Andersen [10] and Beutel et al. [13] identified the increase of phosphate concentration with the nitrate concentration decreasing in anoxic hypolimnions, and verified the resistant effects of increased nitrate on phosphate release from sediments. Kleeberg et al. [25] calculated the enhanced release amount of P from sediments of Lake Jabel with the decrease of nitrate input, and suggested that the diversion of its main tributary, which would reduce the nitrate loading of waters, should be rejected. Therefore, this study was to explore the potential effects of controlling nitrate pollution on the sedimentary release of P from Tianzhuang Reservoir and implications for reservoir management. We hypothesize that the decline of nitrate concentration would increase the phosphorus release from the sediments of Tianzhuang Reservoir based on the preliminary survey results. In this study, we investigated the relationship between nitrate and SRP in porewaters and calculated the

net production ratio of N:P in surficial sediments using the PROFILE program to elucidate the role of nitrate in phosphorus release. We then conducted sediment–water exchange experiments to explore the effects of the nitrate decline in water on phosphorus release from the sediments.

## 2. Material and methods

### 2.1. Study area

Tianzhuang Reservoir (36°10'N and 118°06'E) is located in the upstream portion of Yiyuan County, Shandong Province (Fig. 1). The reservoir has a surface area of about 3.43 km<sup>2</sup> and a watershed area of about 424 km<sup>2</sup>. The watershed is mainly covered by forest and farmland, with many iron and gypsum mines underground. The average depth of the reservoir is about 12 m and the maximum depth is 17 m. And it experiences a slight stratification during summer [23]. The reservoir bed is almost completely covered by muddy sediments with thicknesses ranging from 2.5 to 5.5 m. About 1,000 m<sup>3</sup>/d wastewater that contains high-concentration ammonium (50 mg N/L) and low-concentration nitrate (7.5 mg N/L) is discharged from a nitrogenous fertilizer plant situated on the north bank into the reservoir. Four inflows are included (Fig. 1), and the nitrate concentration in these rivers ranges from 5.5 to 9.6 mg N/L. The hydraulic residence time of the reservoir is about 195 d calculated over a time scale of 1 year. The chemical characteristics of the reservoir water (monitored in April 2006) are shown in Table 1.

### 2.2. Sampling and analysis

Sediments were collected in April 2006 from C1 (close to the outflow) and C2 (central reservoir) (Fig. 1). The water depths at the two sites were 17 and 12 m, respectively. Sediments cores (10 cm in diameter and about 20 cm long) were collected with minor disturbance using a gravity sampler. Four cores were collected from site C1 and one from site C2. All sediment cores were kept vertical and chilled in dark boxes when transported to the laboratory. Two sediment cores from C1 and one from C2 were used to analyze the constituents of the porewaters and sediments, while the

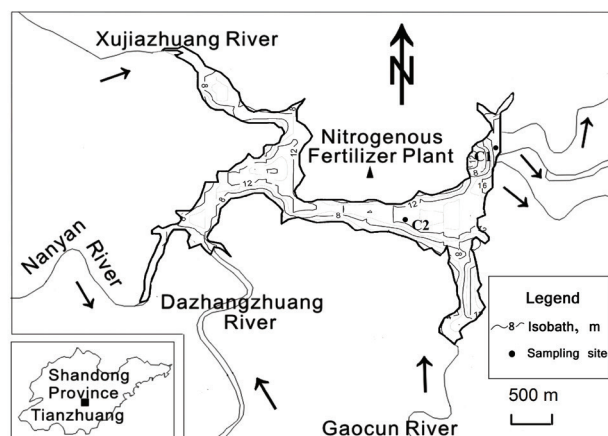


Fig. 1. Map of Tianzhuang Reservoir and sampling sites.

Table 1  
Chemical characteristics of the reservoir water

Major ions	Concentration
NO <sub>3</sub> <sup>-</sup> -N, mg/L	6.74 (4.4%)
SO <sub>4</sub> <sup>2-</sup> , mg/L	97.8 (8.1%)
Cl <sup>-</sup> , mg/L	39.3 (5.2%)
Na <sup>+</sup> , mg/L	24.2 (3.4%)
K <sup>+</sup> , mg/L	1.7 (5.4%)
Mg <sup>2+</sup> , mg/L	14.0 (4.9%)
Ca <sup>2+</sup> , mg/L	33.8 (3.3%)
PO <sub>4</sub> <sup>3-</sup> -P, mg/L	0.01 (16.8%)
pH	8.16
NH <sub>4</sub> <sup>+</sup> -N, mg/L	2.50 (4.4%)

Note: Value in parentheses is the relative standard deviation of the monitoring method.

remaining cores were used for the incubation experiments. Water at about 0.5 m above the sediments at different sites was sampled using a HL-CS poly (methyl methacrylate) sampler. The temperature of the water just above the sediment–water interface was measured using a multiparameter water quality monitor (YSI Inc., USA).

Sediment cores were sectioned into 2–4 cm slices in a glove bag under N<sub>2</sub>-filled conditions. The sectioned sediments were then placed in 50 mL centrifuge tubes and centrifuged for 30 min at 4,000 rpm. Next, the supernatants were filtered through cellulose acetate filters (0.45 μm), while the sediments were dried at room temperature and then stored for later analysis. TP in the sediments was analyzed according to Aspila et al.'s [26] method. The total iron (T-Fe) was measured in HCl extracts of the remaining ash after ignition [27]. Additionally, Fe–P in the sediments was extracted from sediment samples by Rutterberg's method [28] and measured by a modified method for the determination of P in citrate-dithionite-bicarbonate extraction solutions [29].

The nitrate and SRP in the porewaters and waters above sediments were determined by ion chromatography (DX 80 Ion Analyzer, Dionex Corporation, USA) (the relative standard deviation (RSD), 4.6% for nitrate and 16.8% for SRP) [30]. The ammonia nitrogen (NH<sub>4</sub><sup>+</sup>-N) was determined by UV spectrophotometry (the RSD, 4.4%) [30].

### 2.3. Flux calculation

The diffusional fluxes of SRP and nitrate on the sediment side of the sediment–water interface (flux) were calculated by Fick's First Law of Diffusion [31]:

$$\text{Flux} = -\phi D_s \left. \frac{\partial C}{\partial x} \right|_{x=0} \quad (1)$$

where  $\phi$ ,  $D_s$  and  $\partial C/\partial x$  are the porosity of surficial sediments, the molecular diffusion coefficient in the sediments, and the concentration gradient of the solute just below the sediment–water interface, respectively. Porosity, measured as weight loss upon drying of sediments at 60°C, was 0.904 ± 0.006 for the investigated sediments. The diffusion coefficient

( $D_s$ ) was estimated from the empirical relationship  $D_s = \phi^2 D_0$  [32], where  $D_0$  is the diffusion coefficient at infinite dilution corrected by the Stokes–Einstein relationship [33,34] at the in-situ temperature of 12°C measured near the sediment–water interface. And the solute flux errors introduced from the estimation of the diffusion coefficients in sediment porewaters would be less than 20% [31,35]. The concentration gradient was estimated from the difference in concentration between the bottom water and the porewater in the surficial sediments. The presence of a diffusive boundary layer (DBL) on the water side of the sediment–water interface would provide a supplementary resistance to solutes release from sediments [36]. This resistance effect of a DBL was not taken into account in the flux calculation. The solute fluxes calculated are simply a maximum estimation, and the diffusive fluxes would likely be slower in the presence of a DBL, as it is the case at in-situ conditions.

### 2.4. Net production of nitrogen and phosphorus

Assuming a steady-state solutes distribution in the sediment porewaters, the net productions of nitrogen and phosphorus per unit volume of sediment, calculated by the difference of the generation rate from organic matter decomposition and the rate of adsorption onto the sediments [37,38] were calculated according to the concentration profiles of NH<sub>4</sub><sup>+</sup>-N and SRP. The approach was implemented by the PROFILE program [37]. In our simulation, bioturbation and irrigation were neglected as no animals were found when the sediments were sieved.

### 2.5. Sediment–water interaction experiments

Experiments were conducted to investigate the sediment–water interaction and to evaluate the effects of declining water nitrate on sedimentary P release. The experiments were conducted using distilled water (pH, 8.16; nitrate, 0 mg N/L) or reservoir water (pH, 8.16; nitrate, 6.7 mg N/L) as the overlying water of the sediments. The apparatus used consisted of two plexiglass columns, 50 cm high with a 10 cm internal diameter. The bottom of each column was closed and the top was sealed with a stopper that had two holes, one for sampling and one for venting. The sediment cores sampled from C1 were about 20 cm high and the overlying water was 25 cm deep in the column. The overlying water was gently bubbled with nitrogen gas for 2 h every day, and the water was assumed to be in anoxic status during the experiments. Overlying water was sampled after ventilation every 2 d and the nitrate and phosphate levels were measured. Following sampling, the water was replaced with an equal amount of distilled or reservoir water. The pH of the overlying water was measured at the end of the incubation period. Experiments were performed in the dark at 13°C ± 2°C for 16 d.

Although the two kinds of waters for the incubation experiments are different from chemistry, impurities and ionic strength, the main factors affecting the sedimentary phosphorus release are likely to be calcium ion and nitrate ion. Therefore, another experiment was conducted to examine the potential effects of calcium ion on the phosphate concentration in the reservoir water. The same amount of phosphate (KH<sub>2</sub>PO<sub>4</sub>) was added to two volumetric flasks,

one containing distilled water and the other reservoir water. The pH of the distilled water was then adjusted to 8.16 with 1 mol/L NaOH solution before the  $\text{KH}_2\text{PO}_4$  added. The flasks were shaken immediately by hand, after which they were incubated in darkness for 24 h. Following incubation, the SRP of each sample was measured. The SRP was measured by the molybdenum-antimony anti-spectrophotometric method (the RSD, 13.2%) [30] and the nitrate was measured by the ultraviolet spectrophotometric method (the RSD, 5.1%) [30]. SAS (Statistical Analysis System) was used for the statistical analyses.

### 3. Results and discussion

#### 3.1. Role of nitrate on phosphorus release

The chemical characteristics of the surficial sediments (0–2 cm) are presented in Table 2. The Fe–P accounted for about 60% of the TP in the surface sediments, indicating that the sediments were sensitive to redox potential with respect to P.

The nitrate and SRP in the sediment porewaters had a negative correlation (Fig. 2). Specifically, the concentrations of SRP increased from the sediment–water interface down to about 7.5 cm (Column C1) or 10 cm (Column C2), below which they decreased (Fig. 2(a)). Conversely, the concentrations of nitrate decreased from the interface to about 7.5 cm, below which they were lower than the detection limit (Fig. 2(b)). Comparison of Fig. 2(a) with Fig. 2(b) revealed that the increase of SRP concentration corresponded to the decrease of nitrate concentration in the porewaters of the upper sediments. There was also a significantly negative correlation between nitrate and SRP in the porewaters of the upper 7.5 cm sediments ( $r = -0.821$ ,  $p = 0.0124$ ,  $n = 8$ ), suggesting that nitrate may inhibit the liberation of Fe–P from the sediments.

The SRP flux on the sediment side of the sediment–water interface was  $0.191 \text{ mg}/(\text{m}^2\cdot\text{d})$  (Table 3), which was significantly lower than Nürnberg's statistical value for mesotrophic lakes ( $2\text{--}10 \text{ mg}/(\text{m}^2\cdot\text{d})$ ) [39]. The SRP flux of Tianzhuang Reservoir was also significantly lower than the value of Lake Hongfeng (Table 4), although the Fe–P in the surface sediments of the former system was only slightly less than that of the latter, which had a depth similar to Tianzhuang Reservoir. The main difference in water characteristics between the two aquatic environments lay in the nitrate concentration. Specifically, the nitrate concentration in Tianzhuang Reservoir was markedly higher than that in Lake Hongfeng. The high nitrate concentration in the reservoir

Table 2  
Chemical characteristics of surficial sediments

	C1	C2
TP, mg/kg dw	870.6	856.4
Fe–P, mg/kg dw	566.0	531.5
Fe–P/TP, %	65.0	62.1
T-Fe, mg/kg dw	25,280	23,164
T-Fe/TP	29	27

C1, close to the outflow; C2, central of the reservoir; dw, dry weight.

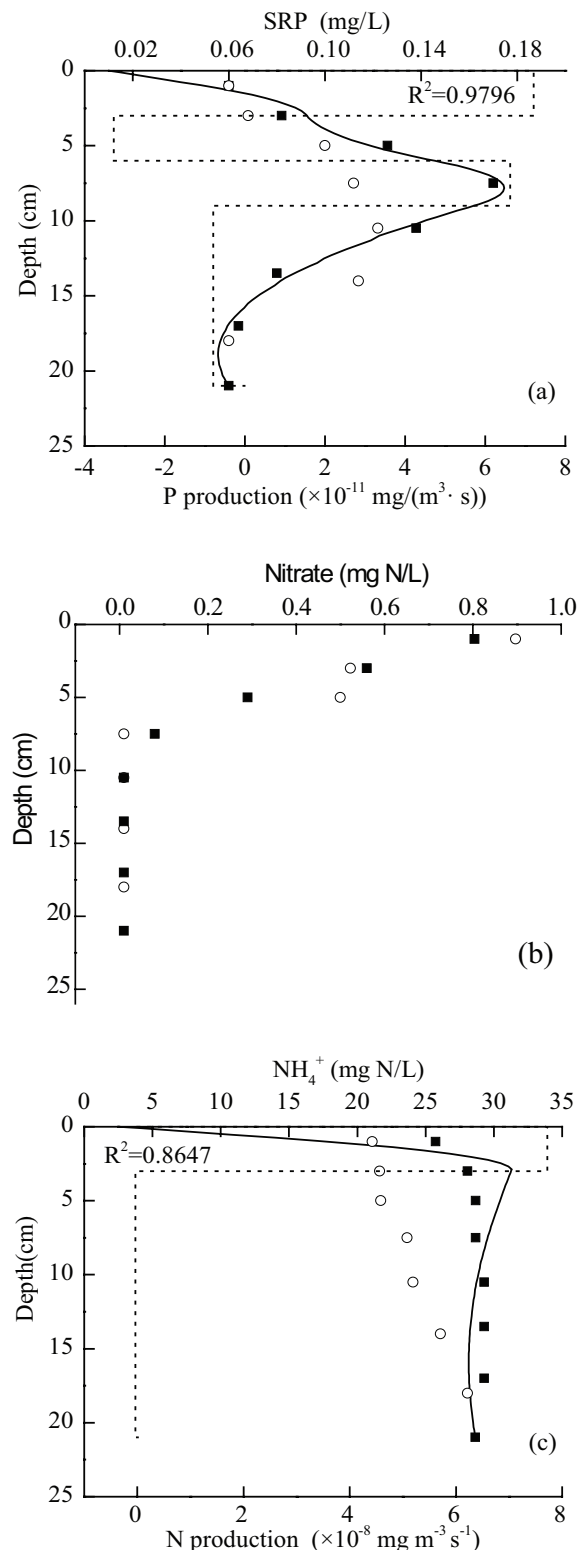


Fig. 2. Nutrient profiles (soluble reactive phosphorus (SRP) (a), nitrate (b), and  $\text{NH}_4^+$  (c) in porewaters of sediments). Data points (square of site C1 and circle of C2) were the measured concentration profiles. The best fitting concentration profile (solid line) and the net production profile (dotted line) were calculated by the PROFILE program according to the measured concentration profile of site C1.



Table 3  
Nutrient fluxes on the sediment side of the sediment–water interface

	$D_s \times 10^{-5} \text{ m}^2/\text{d}$	$\delta C/\delta x \times 10^5 \text{ mg}/\text{m}^4$		Flux <sup>a</sup> $\text{mg}/(\text{m}^2 \cdot \text{d})$	
		C1	C2	C1	C2
$\text{NO}_3^- \text{-N}$	9.741	5.94	5.78	$-52.307 \pm 10.822$	$-50.898 \pm 10.546$
SRP	4.229	-0.05	-0.05	$0.191 \pm 0.054$	$0.191 \pm 0.054$

<sup>a</sup>Positive flux denotes that the nutrient moves from sediments to overlying water; C1, close to the outflow; C2, central of the reservoir.

Table 4  
Comparison of surface water nitrate, porewater phosphate, and interfacial phosphate flux between Tianzhuang Reservoir and Lake Hongfeng

	Tianzhuang Reservoir	Lake Hongfeng <sup>a</sup>
Nitrate in surface water, $\text{mg}/\text{L}$	5–12	1.5
Fe–P in sediments, $\text{mg}/\text{kg}$	500–600	700–900
Fe–P/TP of sediments, %	60	30–40
SRP in porewater, $\text{mg}/\text{L}$	0.06	0.1–0.2
SRP release flux, $\text{mg}/(\text{m}^2 \cdot \text{d})$	0.191	1.46–2.88

<sup>a</sup>Data were from Wang [41].

water resulted in high nitrate flux into sediments (about  $50 \text{ mg N}/(\text{m}^2 \cdot \text{d})$ , Table 3). In addition, the penetration depth of nitrate was about 7.5 cm (Fig. 2(b)). Knowles [40] reported that only upper 1 to 5 cm sediment layer was the denitrification zone, and that the penetration depth depends on the rate of nitrate diffusion into the sediments. The deeper penetration of nitrate in our investigation was believed to result from the high rate of nitrate flux into the sediments, which indicated that the activity of denitrification in the surface sediments of Tianzhuang Reservoir was stronger. The active denitrification then suppressed the release of Fe–P, resulting in lower SRP in the porewaters of sediments in Tianzhuang Reservoir than in Lake Hongfeng. Accordingly, the P flux on the sediment side of the sediment–water interface was only about  $0.191 \text{ mg}/(\text{m}^2 \cdot \text{d})$ .

The net production ratio of N:P was 2,372:1 in the surface sediment in Tianzhuang Reservoir (reference data 16:1 according to the Redfield ratio). The net production ratio is affected by differential adsorption. The dimensionless adsorption constant for SRP (5) is usually larger than that for  $\text{NH}_4^+ \text{-N}$  (1.6) in anoxic sediments [42]. The high value of the ratio indicates that the SRP liberated from the decomposition of organic materials was strongly adsorbed by the surficial sediments in the denitrification zone.

Overall, the high ratio of Fe–P/TP, negative correlation of SRP and nitrate concentration profiles, low SRP flux and high net production ratio of N:P indicated that the high nitrate concentration is an important factor for controlling P release from redox-sensitive sediments in Tianzhuang Reservoir.

### 3.2. Effects of nitrate decline on phosphorus release

The column experiments were not designed to determine exact rates of sedimentary P release under different nitrate-bearing water conditions, but to test whether the

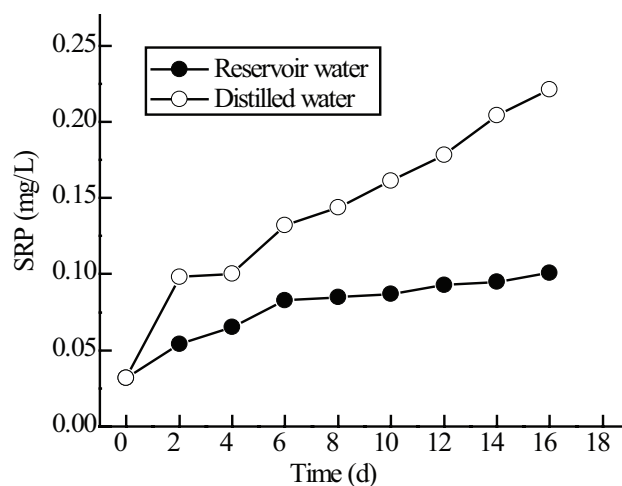


Fig. 3. Variation in soluble reactive phosphorus (SRP) concentrations in the overlying water.

nitrate decline (from 6.7 to 0  $\text{mg N}/\text{L}$ ) in reservoir water would lead to enhanced P release from the redox-sensitive sediments.

The SRP concentrations in the two kinds of overlying waters (distilled water and reservoir water) tended to increase with time. However, the increasing rate of SRP in the distilled water was significantly larger than that in the reservoir water. At the end of the incubation, the SRP concentrations in the distilled water and the reservoir water were 0.22 and 0.10  $\text{mg}/\text{L}$ , respectively (Fig. 3). The main difference influencing the SRP concentration lay in the high levels of calcium and nitrate in the reservoir water. The calcium and phosphate may generate precipitation, which is beneficial to P removal from reservoir water. In our experiment, the effects of  $\text{Ca}^{2+}$  were not significant (Fig. 4). Therefore, the difference in SRP concentration in the contrast experiments was mainly a result of nitrate effects. During incubation, the nitrate concentration in the overlying water (reservoir water) decreased with time, and the value was 2.9  $\text{mg N}/\text{L}$  at the endpoint of the experiment (Fig. 5), whereas the nitrate was always below the detection limit in the distilled water overlying the sediment.

Comparison of the two column experiments showed that a decrease in nitrate concentration from 6.7 to 0  $\text{mg N}/\text{L}$  would significantly enhance the release of P from sediments of Tianzhuang Reservoir. Andersen [10] and Beutel et al. [13] found an increase of phosphate concentration with decreasing nitrate concentration seasonally in anoxic hypolimnions. Jensen et al. [43] reported that, if the ratio of T-Fe:TP in surficial sediments was above 15 (by weight), it may be

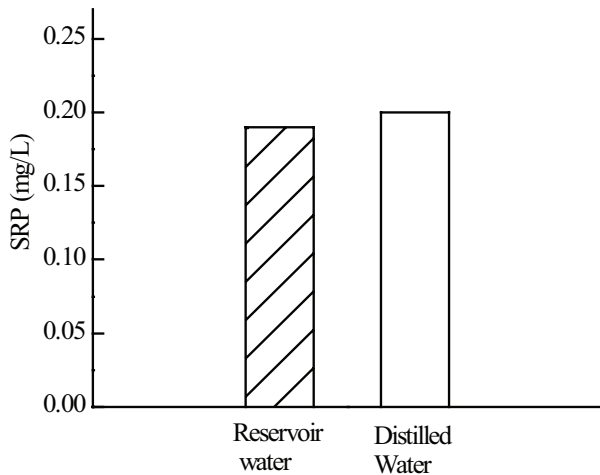


Fig. 4. Comparison of soluble reactive phosphorus (SRP) concentrations between distilled and reservoir water after addition of the same amount of  $\text{KH}_2\text{PO}_4$ .

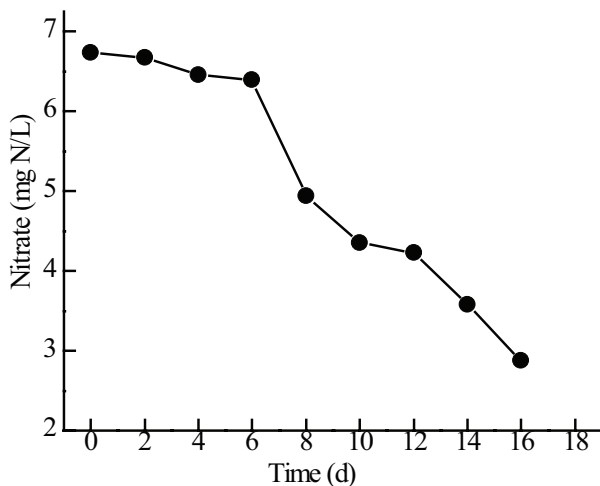


Fig. 5. Variation in nitrate concentrations in the overlying water (reservoir water) with time.

possible to control sediment P release via maintenance of an oxidized surface sediment layer. The T-Fe:TP ratio of the sediments investigated in the present study exceeded 27 (Table 2), indicating that the surface sediments had a high potential sorption capacity for P [44]. Therefore, the release of P from the sediments was retarded under high nitrate levels, and the release rate was lower than that under nitrate-free conditions.

Andersen [10] pointed that no P was released from sediments if the nitrate concentration exceeded 0.5 mg N/L. Moreover, complete resistance of P in response to lower levels of nitrate (0.23 mg N/L) has been reported in laboratory experiments [13]. In contrast, even under the high nitrate concentration (5 mg N/L) conditions in our experiment, an obvious release of P occurred. P can also be released from oxic surface sediments to the overlying water through diffusion [45]. The diffusion flux of SRP in Tianzhuang Reservoir was about 0.191  $\text{mg}/(\text{m}^2\text{-d})$  (calculated from P profiles), but it was only about one-fifth of the incubation flux

( $1.078 \pm 0.212 \text{ mg}/(\text{m}^2\text{-d})$ ) roughly determined from the mass balance in our experiment. Clearly, some factors other than the redox condition have a major effect on P release under a high T-Fe:TP ratio and a high nitrate concentration. Curtis [46] and Jin et al. [47] reported that high pH benefits the release of P attached to iron compounds at the sediment surface. The release of P from sediments containing high Fe-P is enhanced when the pH is about 7.7 [47]. Active denitrification near the sediments leads to increased pH in the overlying water [48,49]. The pH of the water (reservoir water) at the end of our experiment was 8.56, whereas the value was 7.85 in the other column. Therefore, the elevated pH (from 8.16 to 8.56) might be the main reason for the release of P under high nitrate conditions in our experiment, although the T-Fe/TP ratio in the surface sediments was high. In natural waters, the enhanced release effect of elevated pH is expected to be negligible because of the buffering capacity of water.

### 3.3. Implications for reservoir management

The sediments in Tianzhuang Reservoir were redox-sensitive and P release would be enhanced if the nitrate concentration declined. Moreover, this decline might decouple the Fe-P cycle because of the high sulfate concentration in the reservoir water, resulting in a further release of P from the sediments. The sulfate concentration was about 1,000  $\mu\text{m}/\text{L}$  in Tianzhuang Reservoir, which is more than the average value of 10–500  $\mu\text{m}/\text{L}$  for freshwater [50]. The existence of nitrate near the sediment–water interface resisted the reduction of sulfate in the surface sediments. In addition, the TN:TP ratio in the water column of Tianzhuang Reservoir exceeded 200, indicating that P was the key factor limiting eutrophication. Moreover, the TP concentration in the reservoir ranged from 0.010 to 0.028 mg/L in 2006, approaching the eutrophic TP standard of the OECD (0.035 mg/L). The depth of nitrate penetration into sediments reached up to 7.5 cm; therefore, more P would be released to the water column under low nitrate concentrations or the nitrate-free condition. Accordingly, the additional P released from nitrate concentration decline may trigger seasonal algal blooms in this reservoir.

To ensure the safety of drinking water, the local government plans to control the nitrate pollution of Tianzhuang Reservoir by diverting discharges from the nitrogenous fertilizer plant and diminishing nitrate loading from the catchments. Wastewater from the nitrogenous fertilizer plant should be diverted because it is a major source of ammonium to the reservoir, and it also contains other toxic compounds. The main nitrate loading of the reservoir originated from the associated agricultural areas. Controlling nitrogen from diffuse sources is a considerably expensive and usually ineffective measure [51]. Control of nitrate pollution in Tianzhuang Reservoir would alleviate the adverse effects of nitrate on human health; however, the enhanced release of P from sediments might trigger eutrophication, resulting in even worse water quality problems. The plan to divert the polluted inflows of Lake Jabel was rejected because the decline of the nitrate loading of the lake would result in a large amount of P being released [25]. Additionally, the nitrate concentration in Tianzhuang Reservoir water after June 2005 did not exceed the guideline value for drinking water (11 mg N/L) set by the World Health Organization. For the T-Fe:TP ratio

in the surface sediments was above 15 markedly, the sediments under the high nitrate concentration condition would be beneficial to more P retention. Accordingly, the effects of nitrate on P release from redox-sensitive sediments should be addressed while diminishing the diffuse source loads to control nitrate pollution. If the nitrate concentration declines gradually in Tianzhuang Reservoir, measures should be implemented to avoid or alleviate the release of P in the surface sediments.

It is important to note that this study was based on only a few sediment investigations and laboratory experiments. Tianzhuang Reservoir appears to be an ideal site for exploring the interaction among P–Fe–N–S cycles. Therefore, more sediment investigations and precise experiments should be conducted to further elucidate the mechanism of sedimentary P release and the effects of chemical characteristics of the drainage basin on reservoir water quality. Because of the high ratios of Fe–P:TP and T–Fe:TP in surficial sediments of Tianzhuang Reservoir, the P exchange between the sediments and overlying water agrees with the classical Fe–P coupling model. Therefore, measures controlling P release from sediments within Tianzhuang Reservoir should be practiced synchronously with nitrate concentration decrease. The results may help to optimize the management strategies for Tianzhuang Reservoir. Moreover, the findings indicate that interactions among biogeochemical cycles should be understood from a holistic perspective before making management decisions for other lakes, especially under the tendency of elevated nitrate concentration or expanding eutrophication [52]. In addition, it is important to understand the potential water quality improvement of discharging nitrified wastewater effluent to surface waters [53,54]. It may be helpful in deciding whether there is a need for nitrate elimination by denitrifying nitrified wastewater effluent in all sewage treatment plants [51].

#### 4. Conclusions

Exchange of P between sediments and water is a complex result of physical, chemical and biological processes. Here, we discussed the effects of chemical processes on sedimentary P release from redox-sensitive sediments. The sedimentary P release in Tianzhuang Reservoir agreed with the classical Fe–P coupling model between iron and phosphorus. The high level of nitrate in the water column improved the P retention capacity of sediments with a high T–Fe:TP ratio. The decline of nitrate concentration in surface waters would enhance the release of phosphorus from redox-sensitive sediments seasonally, especially in waters with high sulfate concentrations; therefore, it is expected to increase the risk of eutrophication of Tianzhuang Reservoir. Accordingly, the interaction between nitrate and phosphorus and the reservoir-specific characteristics should be emphasized when decisions are made to control nitrate pollution of surface waters.

#### Acknowledgements

This research was financed by the National Natural Science Foundation of China (No. 51279075). The authors are very grateful to Lu Xuewei, Li Wei and Song Shuai for their assistance with the samples.

#### References

- [1] J.N. Galloway, F.J. Dentener, D.G. Capone, E.W. Boyer, R.W. Howarth, S.P. Seitzinger, G.P. Asner, C.C. Cleveland, P.A. Green, E.A. Holland, D.M. Karl, A.F. Michaels, J.H. Porter, A.R. Townsend, C.J. Vörösmarty, Nitrogen cycles: past, present, and future, *Biogeochemistry*, 70 (2004) 153–226.
- [2] P.M. Vitousek, J.D. Aber, R.W. Howarth, G.E. Likens, P.A. Matson, D.W. Schindler, W.H. Schlesinger, D.G. Tilman, Human alteration of the global nitrogen cycle: sources and consequences, *Ecol. Appl.*, 7 (1997) 737–750.
- [3] A.S. Moffat, Global nitrogen overload problem grows critical, *Science*, 279 (1998) 988–989.
- [4] P.N. Magee, Nitrogen as a potential health hazard, *Philos. Trans. R. Soc. Lond. B. Biol. Sci.*, 296 (1982) 543–550.
- [5] S. Krause, J. Jacobs, A. Voss, A. Bronstert, E. Zehe, Assessing the impact of changes in land use and management practices on the diffuse pollution and retention of nitrate in a riparian floodplain, *Sci. Total. Environ.*, 389 (2008) 149–164.
- [6] F. Laurent, D. Ruelland, Assessing impacts of alternative land use and agricultural practices on nitrate pollution at the catchment scale, *J. Hydrol.*, 409 (2011) 440–450.
- [7] Y.H. Zhan, J.W. Lin, Z.L. Zhu, Removal of nitrate from aqueous solution using cetylpyridinium bromide (CPB) modified zeolite as adsorbent, *J. Hazard. Mater.*, 186 (2011) 1972–1978.
- [8] M. Islam, R. Patel, Synthesis and physicochemical characterization of Zn/Al chloride layered double hydroxide and evaluation of its nitrate removal efficiency, *Desalination*, 256 (2010) 120–128.
- [9] W. Ripl, Biochemical oxidation of polluted lake sediment with nitrate—a new lake restoration method, *Ambio*, 5 (1976) 132–135.
- [10] J.M. Andersen, Effect of nitrate concentration in lake water on phosphate release from the sediment, *Water Res.*, 16 (1982) 1119–1126.
- [11] R.H. Foy, Suppression of phosphorus release from lake sediments by the addition of nitrate, *Water Res.*, 20 (1986) 1345–1351.
- [12] M. Søndergaard, E. Jeppesen, J.P. Jensen, Hypolimnetic nitrate treatment to reduce internal phosphorus loading in a stratified lake, *Lake Reserv. Manage.*, 16 (2000) 195–204.
- [13] M.W. Beutel, A.J. Horne, W.D. Taylor, R.F. Losee, R.D. Whitney, Effects of oxygen and nitrate on nutrient release from profundal sediments of a large, oligo-mesotrophic reservoir, Lake Mathews, California, *Lake Reserv. Manage.*, 24 (2008) 18–29.
- [14] C.H. Mortimer, The exchange of dissolved substances between mud and water in lakes. I & II, *J. Ecology*, 30 (1941) 147–201.
- [15] W.F. James, P.W. Sorge, P.J. Garrison, Managing internal phosphorus loading and vertical entrainment in a weekly stratified eutrophic lake, *Lake Reserv. Manage.*, 31 (2015) 292–305.
- [16] S.M. Ding, Y. Wang, D. Wang, Y.Y. Li, M.D. Gong, C.S. Zhang, In situ, high-resolution evidence for iron-coupled mobilization of phosphorus in sediments, *Sci. Rep.*, 6 (2016) 24341.
- [17] C.D. Giles, P.D.F. Isles, T. Manley, Y.Y. Xu, G.K. Druschel, A.W. Schroth, The mobility of phosphorus, iron, and manganese through the sediment-water continuum of a shallow eutrophic freshwater lake under stratified and mixed water-column conditions, *Biogeochemistry*, 127 (2016) 15–34.
- [18] N.F. Caraco, J.J. Cole, G.E. Likens, Evidence for sulphate-controlled phosphorus release from sediments of aquatic systems, *Nature*, 341 (1989) 316–318.
- [19] D.M. Orihel, H.M. Baulch, N.J. Casson, R.L. North, C.T. Parsons, D.C.M. Seckar, J.J. Venkiteswaran, Internal phosphorus loading in Canadian fresh water: a critical review and data analysis, *Can. J. Fish. Aquat. Sci.*, 74 (2017) 2005–2029.
- [20] M. Hupfer, J. Lewandowski, Oxygen controls the phosphorus release from lake sediments—a long-lasting paradigm in limnology, *Int. Rev. Hydrobiol.*, 93 (2008) 415–432.
- [21] K. Song, A.J. Burgin, Perpetual phosphorus cycling: eutrophication amplifies biological control on internal phosphorus loading in agricultural reservoirs, *Ecosystems*, 20 (2017) 1483–1493.

- [22] L. Schauser, L. Chorus, J. Lewandowski, Effects of nitrate on phosphorus release: comparison of two Berlin lakes, *Acta Hydrochim. Hydrobiol.*, 34 (2006) 325–332.
- [23] Z.W. Gao, J. Wang, X.L. Zheng, Water Quality Assessment and Spatial-Temporal Distribution of Nitrogen in the Tianzhuang Reservoir, *Proc. iCBBE: Environmental Pollution and Public Health Track*, 2010, pp. 6898–6902.
- [24] Z.W. Gao, X.L. Zheng, W. Li, Determination of Nutrient Fluxes across the Sediment-Water Interface in a Nitrate-Rich Reservoir, *Proc. iCBBE: Environmental Pollution and Public Health Track*, 2008, pp. 3319–3322.
- [25] A. Kleeberg, B. Nixdorf, J. Mathes, Lake Jabel restoration project: phosphorus status and possibilities and limitations of diversion of its nutrient-rich main inflow, *Lakes Reserv. Res. Manage.*, 5 (2000) 23–33.
- [26] K.I. Aspila, H. Agemina, A.S. Chau, A semi-automated method for the determination of inorganic, organic and total phosphate in sediments, *Analyst*, 101 (1976) 187–197.
- [27] J.M. Andersen, An ignition method for determination of total phosphorus in lake sediments, *Water Res.*, 10 (1976) 329–331.
- [28] K.C. Rutterberg, Development of a sequential extraction method for different forms of phosphorus in marine sediments, *Limnol. Oceanogr.*, 37 (1992) 1460–1482.
- [29] M.A. Huerta-Diaz, A. Tovar-Sánchez, G. Filippelli, J. Latimer, S.A. Sañudo-wilhelmy, A combined CDB-MAGIC method for the determination of phosphorus associated with sedimentary iron oxyhydroxides, *Appl. Geochem.*, 20 (2005) 2108–2115.
- [30] Editorial board of Environment Protection Bureau of China, *Monitoring and Determination Methods for Water and Wastewater*, 4th ed., China Environmental Science Press, Beijing, 2002.
- [31] R.A. Berner, *Early Diagenesis: A Theoretical Approach*, Princeton University Press, New Jersey, 1980, pp. 26–41.
- [32] W.J. Ullman, R.C. Aller, Diffusion coefficients in nearshore marine-sediment, *Limnol. Oceanogr.*, 27 (1982) 552–556.
- [33] Y.H. Li, S. Gregory, Diffusion of ions in seawater and in deep-sea sediment, *Geochim. Cosmochim. Acta*, 38 (1974) 703–714.
- [34] A. Lerman, *Geochemical Processes: Water and Sediment Environments*, A Wiley-Interscience Publication, New York, 1979, pp. 79–94.
- [35] M.D. Krom, R.A. Berner, The diffusion coefficients of sulfate, ammonium, and phosphate ions in anoxic marine sediments, *Limnol. Oceanogr.*, 25 (1980) 327–337.
- [36] B.P. Boudreau, N.L.J. Guinasso, The Influence of a Diffusive Sublayer on Accretion, Dissolution, and Diagenesis at the Sea Floor, in *The Dynamic Environment at the Ocean Floor*, K.A. Fanning, F.T. Manheim, Eds., Lexington, Lexington, Mass, 1982, pp. 115–145.
- [37] P. Berg, N. Risgaard-Petersen, S. Rysgaard, Interpretation of measured concentration profiles in sediment pore water, *Limnol. Oceanogr.*, 43 (1998) 1500–1510.
- [38] B.P. Boudreau, *Diagenetic Models and Their Implementation: Modelling Transport and Reactions in Aquatic Sediments*, Springer-Verlag Berlin Heidelberg, 1997, pp. 165–190.
- [39] G.K. Nürnberg, Prediction of phosphorus release rates from total and reductant-soluble phosphorus in anoxic lake sediments, *Can. J. Fish. Aquat. Sci.*, 45 (1988) 453–462.
- [40] R. Knowles, Denitrification, *Microbiol. Rev.*, 46 (1982) 43–70.
- [41] Y.C. Wang, Biogeochemical Processes of Nutrients (P, N and C) at the Sediment-Water Interface in Two Reservoirs: Lake HongFeng and Baihua, Guizhou, China, Institute of Geochemistry, Academia Sinica, 2001.
- [42] R.A. Berner, Stoichiometric models for nutrient regeneration in anoxic sediments, *Limnol. Oceanogr.*, 22 (1977) 781–786.
- [43] H.S. Jensen, P. Kristensen, E. Jeppesen, A. Skytthe, Iron:phosphorus ratio in surface sediment as an indicator of phosphate release from aerobic sediments in shallow lakes, *Hydrobiologia*, 235/236 (1992) 731–743.
- [44] R.Y. Zhang, L.Y. Wang, F.C. Wu, B.A. Song, Phosphorus speciation in the sediment profile of Lake Erhai, southwestern China: Fractionation and  $^{31}\text{P}$  NMR, *J. Environ. Sci.*, 25 (2013) 1124–1130.
- [45] H. Cyr, S.K. McCabe, G.K. Nürnberg, Phosphorus sorption experiments and the potential for internal phosphorus loading in littoral areas of a stratified lake, *Water Res.*, 43 (2009) 1654–1666.
- [46] P.J. Curtis, Effects of hydrogen ion and sulphate on the phosphorus cycle of a Precambrian Shield lake, *Nature*, 337 (1989) 156–158.
- [47] X.C. Jin, S.R. Wang, Y. Pang, F.C. Wu, Phosphorus fractions and the effect of pH on the phosphorus release of the sediments from different trophic areas in Taihu Lake, China, *Environ. Pollut.*, 139 (2006) 288–295.
- [48] T. Tirén, K. Pettersson, The influence of nitrate on the phosphorus flux to and from oxygen depleted lake sediment, *Hydrobiologia*, 120 (1985) 207–223.
- [49] J.A. Tomaszek, Relationship between denitrification and redox potential in two sediment-water systems, *Mar. Freshwater Res.*, 46 (1995) 27–32.
- [50] M. Holmer, P. Storkholm, Sulphate reduction and sulphur cycling in lake sediments: a review, *Freshwater Biol.*, 46 (2001) 431–451.
- [51] T. Petzoldt, D. Uhlmann, Nitrogen emissions into freshwater ecosystems: is there a need for nitrate elimination in all wastewater treatment plants, *Acta Hydrochim. Hydrobiol.*, 34 (2006) 305–324.
- [52] S.R. Carpenter, Phosphorus control is critical to mitigating eutrophication, *PNAS*, 105 (2008) 11039–11040.
- [53] F.J. Cubas, J.T. Novak, A.N. Godrej, T.J. Grizzard, Effects of nitrate input from a water reclamation facility on the Occoquan Reservoir water quality, *Water Environ. Res.*, 86 (2014) 123–133.
- [54] M.W. Beutel, R. Duvil, F.J. Cubas, D.A. Matthews, F.M. Wilhelm, T.J. Grizzard, D. Austin, A.J. Horne, S. Gebremariam, A review of managed nitrate addition to enhance surface water quality, *Crit. Rev. Environ. Sci. Technol.*, 46 (2016) 673–700.