Assessing high resolution oxidation-reduction potential and soluble reactive phosphorus variation across vertical sediments and water layers in Xinghu Lake: A novel laboratory approach

Yingzhi Li[1,2], Beicheng Xia[1,*], Jiaying Zhang[1],
Chuanhong Li[2], Wenzhuan Zhu[1]

1. School of Environmental Sciences and Engineering, Sun Yat-sen University, Guangzhou 510275, China. E-mail: zsulyz@126.com
2. Huizhou Institution of Environmental Science, Huizhou 516001, China

Abstract

To understand the transfer process of soluble reactive phosphorus (SRP) on the lake sediment-water interface in a mesotrophic shallow lake in South China, the SRP concentrations and the oxidation-reduction potential (ORP) across the sediment-water interfaces were continually monitored. Sediment samples were collected from Xinghu Lake in Guangdong Province. The ORP dynamics at different layers of overlying water was similar for six experimental systems, whereas those in porewater were significantly different. The ORP in overlying water was 200–300 mV higher than those in sediments. The oxygen penetration depth ranged from 2 to 10 mm in Xiannu Lake sediments. The variation amplitudes of ORP increased with sediment depth, but the mean ORP values were all about 218 mV. The SRP concentrations in porewater maintained at a low level of about 0.049 mg/L because of high atom ratio of total iron and total manganese to total phosphorus. The SRP concentrations and variation amplitudes in porewater increased with sediment depth. The SRP in overlying water mainly originated from SRP transference of the porewater of middle and bottom sediments (3–15 cm). The ORP variation and SRP transfer in porewater played important roles in changing SRP concentrations. A distinct SRP concentration gradient appeared in overlying water when intense exchange occurred at the sediment-water interface; therefore, it was necessary to monitor the SRP concentration profiles to accurately estimate the internal loading.

Key words: sediment-water interface; soluble reactive phosphorus; oxidation-reduction potential

DOI: 10.1016/S1001-0742(09)60208-4

Introduction

The sediment-water interface is where acute biogeochemical processes take place, such as those controlling and regulating the phosphorus transference and phosphorus transformation from one phase to another between water and sediments (Boström et al., 1988; Gächter et al., 1988; Kim et al., 2003; Spears et al., 2007). Such processes are an important part of the biogeochemical cycle of material elements. The biogeochemical cycle of nutritional matter at the sediment-water interface is one of the key research topics in the field of limnology. Most researches focused on phosphate exchange at the interface and the interaction among sediment composition, environmental factors, and the capacities of sediment to adsorb phosphorus (House and Deniso, 2000; Jensen and Andersen, 1992; Lopez et al., 1996). However, there exist few data about the transfer and diffusion processes of phosphorus between different layers of overlying water and porewater or about the influence of environmental conditions, such as oxidation-reduction potential (ORP), on the transference processes of phosphorus.

The ORP is one of the indicators of redox-sensitive chemical processes in sediments and water. However, both spatial (i.e., between sediment-sediment, sediment-water, and water-water vertical layers) and temporal dynamics of ORP variation have not been well documented, because of the limitations *in situ* measurement technology (Song et al., 2000; Teasdale et al., 1998; Viollier et al., 2003). ORP is the most important factor influencing the exchange process of phosphorus (House and Deniso, 2000). However, the ORP, especially those in sediments (because little dissolved oxygen (DO) could penetrate in sediments), is susceptible to environment changes.

In order to understand the rule of soluble reactive phosphorus (SRP) exchange across sediment-water interface in mesotrophic shallow lake in the semi-tropical zone, the influences of environmental conditions especially ORP on SRP dynamic across vertical sediments and water column in Xianhu Lake were investigated with the application of a novel laboratory approach.

1 Materials and methods

1.1 Study site

Xinghu Lake is a national key scenic spot of China and it is an urban and recreational lake located in Zhaoqing City, West of Guangdong Province in the semi-tropical zone. Xinghu Lake consists of five sub-lakes (Bohai Lake, Li Lake, Qinglian Lake, Xiannu Lake, Zhongxin Lake) which covers 6.24 km² and has an mean depth of 2.2 m (Fig. 1). Xiannu Lake has a surface area of 1.42 km² and it has a maximum depth of 25.3 m and a mean depth of 2.2 m. Xinghu Lake is a freshwater lake and the sub-lake of Xiannu Lake has a salinity of 255 μS/cm. Xiannu Lake is a developing eutrophic lake.
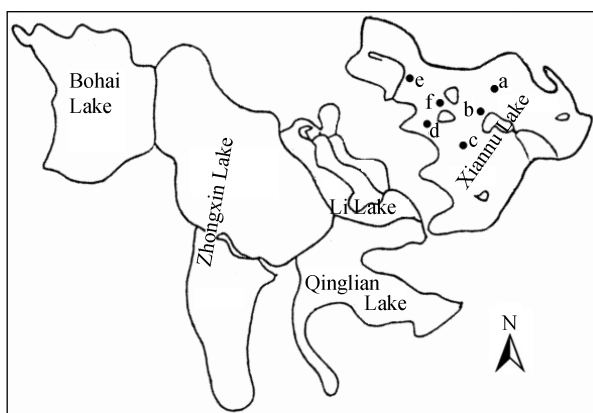

Fig. 1   Schematic diagram of sampling locations in Xinghu Lake.

1.2 Field sampling

On 7 December 2006, six sediment cores were collected from Xiannu Lake, and their codes and sampling sites were as follows: a (23°04′55.5″N, 112°29′05.9″E); b (23°04′53.3″N, 112°28′48.2″E); c (23°04′48.6″N, 112°28′45.6″E); d (23°04′49.6″N, 112°28′35.7″E); e (23°04′59.2″N, 112°28′18.4″E); and f (23°04′53.9″N, 112°28′39.1″E). Transparent polymethyl methacrylate tubes were used to sample sediment cores and act as experimental systems. Six small holes were drilled in line on each tube. These small holes were designed to sample overlying water and sediment porewater (Fig. 2). Before sampling, a tube was set on a stainless steel sampling apparatus (Yuan et al., 1992) and its six small holes were sealed with rubber plugs. At each site, several sediment cores > 17 cm in length were taken and some of them were then subdivided into 0–3 cm, 3–6 cm, and 6–15 cm sections and bagged, and water samples were collected at the depth of 0.5 m below the water interface. The transparence (SD) was measured at each site, and the DO concentrations and ORP were measured at the water depth of 0.5 m below the water interface, the middle of water column and 0.5 m above the lake bottom, respectively. Water samplers were collected at the depth of 0.5 m below the water interface. For retrieval, the bottom of the tube was sealed with a polymethyl methacrylate plug and
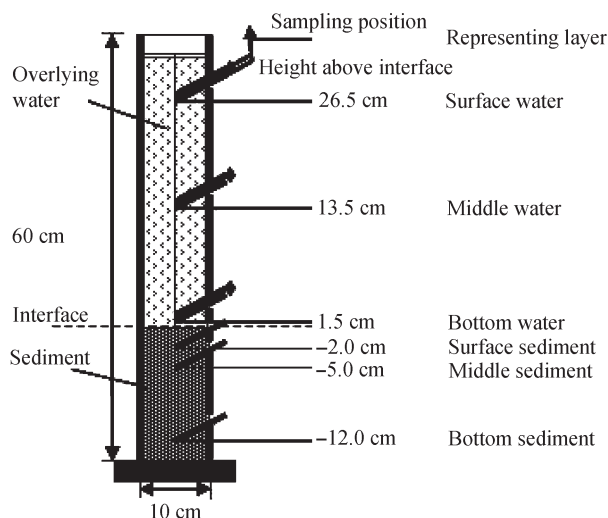

Fig. 2   Experimental apparatus.

the overlying water was carefully removed with minimal disturbance. The tubes were kept upright on return to the laboratory.

1.3 Analysis of basic parameters

For water parameters, total phosphorus (TP) was determined by using PMA-malachite green spectrophotometry after digestion ($K_2S_2O_8$, 0.5 hr, 120°C), while the Chlorophyll-a (Chl-a), chemical oxygen demand (COD_{Mn}) and total nitrogen (TN) were determined using corresponding measurements as described in Standards of National Environmental Protection Department (2002). The mean concentrations of Chl-a, COD_{Mn}, TP, TN and SD were (mean ± SD) (8.82 ± 0.77) mg/m³, (3.2 ± 0.3) mg/L, (0.020 ± 0.004) mg/L and (0.37 ± 0.02) mg/L, respectively. The vertical variations of DO concentrations and ORP in Xiannu Lake determined in the field are showed in Table 1.

For the sediments, the concentrations of TP, total iron (TFe) and total manganese (TMn) were analyzed by previously reported standard methods (Bao, 2000). The organic matter (OM) content was obtained by ashing (Heiri et al., 2001). The mean contents of OM, TP, TFe and TMn in vertical section of sediments are shown in Table 2.

1.4 Experimental system setup

The overlying water in tubes was carefully siphoned off without disturbing the sediments. And then, the plug in the bottom of the tube was removed to allow the sediments to flow out the tube slowly and smoothly; the length of the sediment core inside the tube was carefully regulated

Table 1   Vertical variation of dissolved oxygen (DO) concentration and oxidation-reduction potential (ORP) in Xiannu Lake

Vertical position	DO (mg/L)	ORP (mV)
Surface (0.5 m below water surface)	6.9 ± 0.2	407.2 ± 6.5
Middle	6.2 ± 0.1	372 ± 12.6
Bottom (0.5 m above lake bottom)	5.4 ± 0.4	357 ± 14.8

Data are expressed as mean ± SD.

Table 2 Mean contents of OM, TP, TFe and TMn in vertical section of sediments

Vertical section	OM (g/kg)	TP (mg/kg)	TFe (g/kg)	TMn (g/kg)
0–3 cm	15.9 ± 4.3	459 ± 57	53.1 ± 6.3	4.4 ± 0.6
3–6 cm	14.4 ± 3.1	553 ± 60	40.2 ± 5.5	4.2 ± 0.5
6–15 cm	10.5 ± 2.2	594 ± 50	35.0 ± 4.9	3.2 ± 0.5

OM: organic matter; TP: total phosphorus; TFe: total iron; TMn: total manganese.

to exactly 17.0 cm. Then, the extruded sediment core was carefully cut and the bottom of the tube was quickly sealed and kept upright. The rubber plugs in sediments were substituted by the rhizon soil moisture samplers (Rhizon SMS) (Rhizosphere Research Products, Doderstraat, Doderstraat 62, NL 6706 JG Wageningen, The Netherlands). These Rhinzon SMS were used to sample porewater. The experimental equipment is shown in Fig. 2.

At the beginning of the experiment, 3000 mL of purified water were slowly added to each experimental system against the inner wall of the tubes (the water column was 38.0 cm high) with minimal disturbance.

1.5 Experimental procedures and methods

Six experimental systems were kept in laboratory. Temperature naturally fluctuated at $(22 ± 4)$°C. Water samples were drew from different layers (Fig. 2) at 4, 24, 48, 144, 216, 288, 360, and 432 hr. For the overlying water, the 10-mL or 20-mL syringes were used to draw 7–8 mL (or to draw 13–14 mL for repeated analysis) to analyze SRP concentration. To sample porewater from sediments, we used vacuum tubes and Rhizon SMS to draw 6–6.5 mL for analysis of SRP and ORP; the equivalent volume of purified water was added to experimental system to compensate for their own loss of water and evaporation.

1.6 Detection of ORP, pH, DO and SRP concentration

Before the experiment, the ORION STAR instrument (Thermo Electron Corporation, USA) (which is used to measure ORP and pH) was equipped with an ORP probe that was calibrated using standard redox solutions (with nominal potentials of 420 mV at 25°C) in laboratory temperature. And DO instrument was automatically calibrated with air. Within 15 min of removing porewater samples from the experimental systems, the ORP and pH of porewater were successively measured by inserting the corresponding probes into the sampling tubes. The ORP and pH of different layers of overlying water were successively detected by inserting the corresponding probe directly into the overlying water. The DO concentrations of overlying water were detected by DO instrument (YSI model 55, USA) that was directly inserted into corresponding layers.

SRP concentrations were measured by using PMA-malachite green spectrophotometry (Standards of National Environmental Protection Department, 2002) (UV-spectrophotometer 752, Shanghai High Exactitude Technology Company, Shanghai, China). Its detection limit was 1 μg/L. The standard sample of phosphate (Center for Standard Sample Research of the National Environmental Protection Department, Beijing, China) was used to control the quality in this experiment.

1.7 Data analysis

The SRP flux at the sediment-water interface was calculated using the following Eq. (1).

$$\phi_{i+1} = 240(Mo_{i+1} - (Mo_i - Mo_{ei}))/(\pi R^2)/(T_{i+1} - T_i) \tag{1}$$

where, ϕ_{i+1} (mg/(m^2·day)) is the flux; Mo_i (μg) is the total amount of SRP in the overlying water before the i-time sampling; Mo_{ei} (μg) is the total amount of SRP in all of the overlying water samples from the i-time sampling; and R is the radius of the tube used in the experimental system (R = 5.0 cm).

Mo_i and Mo_{ei} were calculated from the following Eqs. (2) and (3), respectively:

$$Mo_i = \pi R^2(C_{1i}(H_i - h_1) + (h_1 - h_2)(C_{1i} + C_{2i})/2 + (h_2 - h_3)(C_{2i} + C_{3i})/2 + h_3(C_{3i} - h_3(C_{3i} - C_{4i})/(h_3 - h_4)/2)) \tag{2}$$

$$Mo_{ei} = (V_{1i}C_{1i} + V_{2i}C_{2i} + V_{3i}C_{3i}) \tag{3}$$

where, H_i (cm) is the height of the water surface before the i-time sampling; h (cm) is the sampling height above sediment-water interface (h_1 = 26.5, h_2 = 13.5, h_3 = 1.5, h_4 = –2.0); C_{1i}, C_{2i}, C_{3i} and C_{4i} (mg/L) are the SRP concentrations of the water samples collecting the i-time at the height of 26.5, 13.5, 1.5 cm and –2.0 cm from the sediment-water interface, respectively; V_{1i}, V_{2i} and V_{3i} (mL) are the volumes of the water samples collecting the i-time at the height of 26.5, 13.5 and 1.5 cm above the sediment-water interface, respectively.

H_i was calculated from the following Eq. (4):

$$H_i = 55 - hv(T_{i+1} - T_i)/24 \tag{4}$$

where, hv is the average thickness of the water column lost because of evaporation during the experiment (hv = 0.10 cm).

The relationships between different parameters or between different layers were tested statistically using general correlation coefficient (Pearson) procedures in SPSS Version 13.0. The differences in some parameters (such as DO, ORP, pH and SRP) between different layers were analyzed statistically with ANOVA followed by comparison of mean by t-test.

2 Results

2.1 Dynamic characteristics of the ORP

Figure 3 shows the ORP dynamics at different layers in the six experimental systems. The ORP of the overlying water layers were about 200–300 mV higher than those of porewater. The variation coefficients of ORP were less than 5% in the different layers of overlying water, while those
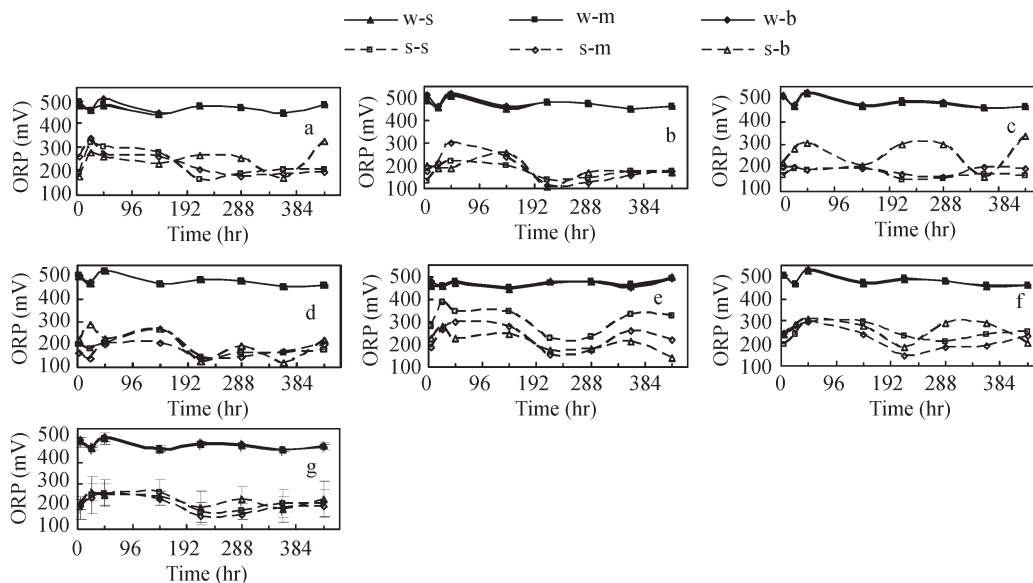
Fig. 3 ORP dynamics at different layers. Figures a–f recorded in the six different simulated systems a–f (the sediments of systems a–f were collected from the six sampling sites a–f, respectively. Each of the six experimental systems was regarded as a replication and the average values taken from all systems at the same sampling depth were plotted in Fig. 3g). w–s: surface layer in water column, sampling at the height of 26.5 cm above the sediment-water interface; w–m: middle layer in water column, sampling at the height of 13.5 cm above the interface; w–b: bottom layer in water column, sampling at the height of 1.5 cm above the interface; s–s: surface layer in sediments, sampling at the depth of 2.0 cm below the interface; s–m: middle layer in sediments, sampling at the depth of 5.0 cm below the interface; s–b: bottom layer in sediments, sampling at the depth of 12.0 cm below the interface.

at the surface (2 cm depth below interface), middle (5 cm depth below interface), and bottom (12 cm depth below interface) layers in sediments was 17.8%, 21.2%, and 22.3%, respectively. Within each system, the correlation coefficients (Pearson) indicated that relationships between different layers' ORP dynamics were significantly positive ($p < 0.001$) in overlying water.

In contrast, the ORP dynamics in the sediment porewater differed both between different experimental systems and between different layers within the same system. The correlative relationships between different layers' ORP dynamics in porewater were positive but not significant. No significant relationship was detected between the bottom layer of water column (1.5 cm height above the interface) and the surface layer of sediments (2.0 cm depth below the interface).

Each of the six experimental systems was regarded as a replication (Fig. 3g). Significant correlations in ORP dynamics between different layers were observed both in overlying water and in sediments. The effects of depth and time on ORP were analyzed statistically using 2-way (or repeated measures) ANOVA in SPSS 13.0. The results indicated that, either in overlying water or in sediments, ORP was significantly influenced by time ($p < 0.001$) but not by depth ($p > 0.05$) and not by the interaction of depth and time ($p > 0.05$). However, the great standard variations at different layer of sediment porewater indicated significant spatial variations in ORP in the six sediment cores (Fig. 3g).

2.2 Dynamics of DO

Each of the six experimental systems was regarded as a replication. The dynamics of DO concentrations are showed in Fig. 4. DO concentrations decreased with water depth and the differences of DO concentration between
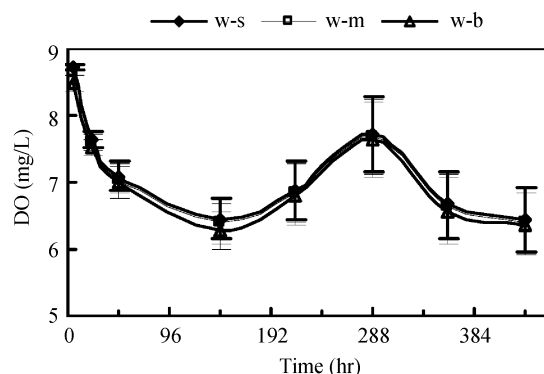

Fig. 4 DO dynamics at different layers in experimental systems.

different layers were significant ($p < 0.05$).

2.3 Dynamics of pH

Each of the six experimental systems was regarded as a replication. The pH dynamics are shown in Fig. 5. Significant correlations between different layers were observed in overlying water but not in porewater. The average variation coefficients of pH in sediment porewater were much lower than that in overlying water.

The effects of depth and time on pH were analyzed statistically using 2-way (or repeated measures) ANOVA. In overlying water, pH values were significantly affected by time ($p < 0.001$) but not by depth ($p > 0.05$). However, in sediment porewater, pH values were significantly affected by depth ($p < 0.001$) but not by time ($p > 0.05$). In addition, the depth-time interaction on pH was not significant ($p > 0.05$) either in overlying water or in porewater.

2.4 Dynamics of SRP concentration

Figure 6 shows that SRP concentrations of overlying water were lower than those of porewater. The linear
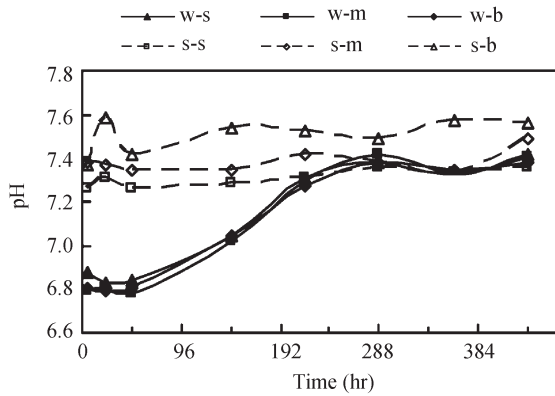
Fig. 5   pH dynamics at different layers in experimental systems.

regression analysis showed that the relationships between average SRP concentrations in porewater and that in overlying water were negative for systems a, c, d, e and f, but for system b.

The SRP concentrations in overlying water tended to rise with water depth increased, and ranged from 0.009 to 0.014 mg/L. The statistical relationships between different layers' SRP dynamics were positive and significant ($p < 0.01$) in each experimental system.

The variation coefficients of SRP concentrations for the surface, middle and bottom layers in sediments were 20.6%, 34.2%, and 45.3%, respectively. SRP concentrations increased with sediment depth. The relationships between SRP dynamics at different layers of porewater were unclear and more complicated than those of overlying water.

The SRP concentrations of the bottom layer of water column and surface layer of sediments in experimental systems a, c, d, e, and f were positively related, whereas they were negative in system b.

2.5 SRP flux

The SRP fluxes (ϕ_{i+1}) across the sediment-water interface are shown in Fig. 6. The SRP fluxes fluctuated strongly in the six experimental systems and varied among

different systems in the first 48 hr; after that the SRP exchange was steady and slow, and fluxes ranged from −1.1 to 1.2 mg/(m²·day). That SRP was diffused from sediment porewater to overlying water, which was the main exchange process of SRP across the sediment-water interface.

2.6 Relationship between SRP dynamics and ORP

The SRP concentrations and ORP in the middle or bottom layers in sediments usually fluctuated strongly comparing with that in the surface layer of sediments (Figs. 3 and 6). In the middle or bottom layers in sediments, the large changes in SRP concentration were usually coupled with opposite changes in ORP (Figs. 3 and 6).

However, both SRP concentrations and ORP values sometimes decreased or increased simultaneously (Figs. 3 and 6). Transference of SRP between different layers in porewater probably was a vital factor, and it influenced the variation of SRP concentration or counteracted the effect of environmental factors on the variation of SRP concentration.

3 Discussion

3.1 ORP and SRP dynamics across

3.1.1 Water-water interface

In overlying water, not only were the ORP dynamics in different layers similar, but also the ORP values also were almost uniform in the vertical direction; this is attributable to steady environmental conditions, especially to DO concentrations which are important to the ORP, those were always > 5.5 mg/L (Fig. 4). In winter, lots of aquatic vegetable in Xiannu Lake decayed and consumed plenty of DO in water column, but part of them could still grow well. Therefore, DO concentrations and ORP significantly decreased with water depth in Xiannu Lake, and the water column maintained the aerobic condition (Table 1).

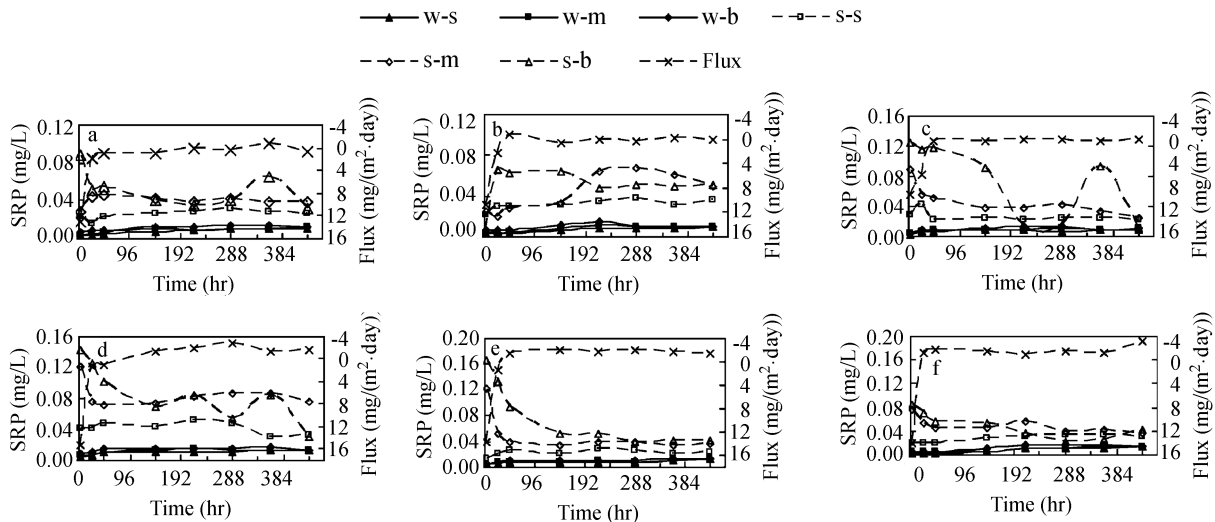Based on the data of water quality, the trophic level

Fig. 6   SRP dynamics at different layers and fluxes across interface in six experimental systems (a–f).

of Xiannu Lake was evaluated using the Score Method (Jin and Tu, 1990). The result indicated Xiannu Lake was under mesotrophic lake conditions. But in simulative experiments, the SRP concentrations in overlying waters were very low, which may be attributed to the facts: the atom ratio between TFe and TP in sediments was much higher than 8 which may effectively restrain the SRP release (Christensen and Jensen, 1997). Significant differences in SRP concentration between different layers in the overlying water were due to the frequent SRP exchange at the sediment-water interface. Significantly positive correlations between the SRP dynamics of different layers indicated that the changes in SRP concentrations in different layers occurred simultaneously in the same direction. This could be explained by the fact that Xiannu Lake was a shallow lake so that SRP could diffuse easily between different layers in overlying water.

3.1.2 Sediment-water interface

The ORP in sediment porewater was 200–300 mV lower than that in overlying water. The DO concentration in lake bottom and reactive OM content in sediments were the most important factors determining the oxygen penetration depth (Aller, 1994; Katsev et al., 2006). The mean content of OM in sediments (0–15 cm) was 1.4% and DO concentration in the bottom of water column was about 5.5 mg/L, therefore, it may be estimated that oxygen penetration depth usually ranged from 2 to 10 mm. And, the oxidized boundary in Xiannu Lake sediments maybe ranged from 2 to 10 mm in winter. The positive but not significant relationship between the SRP dynamics of the bottom layer in water column and the surface layer in sediments indicated that the intense SRP exchange occurred between the overlying water and porewater. Factors that could influence this process included variable environmental factors and surface sediment absorption or release of SRP.

The SRP concentrations in surface sediment porewater maintained a very low level. It may be explained by the following reasons: (1) the surface (1–3 cm) sediments were abundant in iron oxide and manganese oxide, strongly adsorbing phosphate; (2) the ORP of surface sediments maintained a relatively steady state, helping to maintain the balance between adsorption and desorption of SRP under a certain environmental condition.

3.1.3 Sediment-sediment interface

The differences in ORP among different layers and variation of pH with depth in sediments resulted from sediments of uneven media and significant variations in their physicochemical characteristics. Insignificant pH variation with time in sediments indicated that the buffering capacity of sediments was high and also implied that sudden changes in SRP concentration could not be attributed to pH variation with time. With increasing depth of the sediment, it becomes more and more difficult for DO to penetrate and maintain steady environmental conditions. The oxygen penetration depth in different sediments ranging from 2 to 50 mm has been detected previously (Müller et al., 2006; Stief and Beer, 2006; Werner et al., 2006). These studies showed that the active organic matter in sediments and DO concentration in bottom water play important roles in oxygen penetration depth. Based on these finding, oxygen penetration depth in Xiannu Lake sediments was estimated 2–10 mm. Thereby, it can be explained why the ORP in the surface sediment was steadier than that in the substrate.

The transfer of SRP between layers of porewater was complicated and different from which occurred in overlying water. Three factors may responsible for this difference: (1) spatial variation in the physicochemical characteristics resulting from spatial variation in sediment composition, which can lead to different sorption capabilities for phosphorus and different responses to changes in environmental conditions (Jones et al., 1993; Mesnage et al., 2007; Spears et al., 2006); (2) different environmental conditions in different sediment layers (Carignan and Lean, 1991); and (3) SRP transfer in sediment porewater was hampered by sediment particulates (Ullman and Aller, 1982).

In South China, the sediments of semitropical lakes usually are abundant in iron and manganese. This may be an important reason for the SRP concentrations of porewater in Xinanu Lake being obviously lower than that in Taihu Lake, Xianwu Lake (Gong et al., 2006; Zhu et al., 2003). In Xiannu Lake, the atom ration of TFe and TMn to TP in surface (1–3 cm) sediments was much higher than that in the middle (3–6 cm) and bottom (6–15 cm) sediments. These were the most important reasons for that the mean SRP concentration in the surface layers was much lower and much steadier than that in the middle and bottom layers in sediments.

The frequent and great changes in environmental conditions such as the ORP in the middle and bottom layers in sediments resulted in frequent and strong changes in their SRP concentrations. Based on the SRP dynamics of different layers in porewater, it could be concluded that the SRP of overlying water mainly originated from SRP transference of the middle and bottom layers in sediments. Because the regulation effects of sediments on porewater SRP concentration, the changes in SRP concentration of the bottom layer in sediments could not result in/from the corresponding variation in SRP concentration of the middle layer in sediments. In other words, the transference magnitude of SRP between the bottom and middle layers in sediments is not equal to the variation magnitude in SRP of the bottom layer in sediments.

3.2 Spatial and temporal covariation between ORP and SRP

The ORP is one of the most important factors influencing the SRP concentration in porewater. In this experiment, the relationship between the ORP and SRP concentration was not strictly linear. The correlation analysis got a negative relative coefficient but not significant by statistical test. It is well known that a decrease of ORP results in a deoxidization of metal-oxides, which might lead to a release of SRP, whereas a rise of ORP helps to cause more SRP to be absorbed. In fact, the SRP concentration of porewater was usually changed with the environmental

conditions, especially ORP in sediments. Subsequently, the SRP concentrations of overlying water were changed with SRP diffusion across the sediment-water interface. Therefore, the SRP concentration of overlying water is governed not only by environmental conditions in sediments and overlying water but also by the direction and velocity of SRP diffusion (Søndergaard et al., 2003). SRP concentrations of overlying water increased with water depth within 288 hr, while SRP concentrations at different layers in overlying water trended to be identical after 288 hr. The effects of space and time on ORP dynamics in overlying water were insignificant.

DO and pH were regarded as very important environmental factors regulating SRP release and uptake. DO is an important electron acceptor regulating microorganism metabolism and oxidation-reduction reactions in sediments, and then DO indirectly act on SRP uptake and release processes across sediment-water interface (Ishikawa and Nishimura, 1989; Schön et al., 1993). However, the penetration depth of DO was restricted within several millimeters in Xiannu Lake sediments. The pH in sediments not only plays an important role in sorption state of phosphorus and adsorption capacity for phosphorus, but also closely relates to microorganism activity and the alkaline phosphatase activity. However, high buffering capacity of Xiannu Lake sediments made pH of each layers maintain steady with time. Therefore, the significant influences of DO concentration and pH on SRP concentrations of the middle and bottom layers in sediment porewater were not observed in Xiannu Lake sediments. In fact, the content of iron and manganese in sediments was the most important factor influencing the SRP concentration and ORP in Xiannu Lake. In addition, the changes of SRP concentration were also influenced both by the ORP and by SRP diffusion. Therefore, the negative relationship between the ORP and SRP concentration did not exist in each layer of porewater and their relationship was complicated. Although SRP concentration was mainly dominated by ORP, other factors could not be ignored. Benthic algae, bacteria, yeast and fungi can play a direct role in uptake and released of SRP in sediments, and can change environmental conditions such as ORP, pH and DO concentration (Carlton and Wetzel, 1988; Currie and Kalff, 1984; Gächter et al., 1988; Steinman and Mulholland, 2007). In the field, benthic invertebrate can increase the release of SRP and accelerate SRP transfer, furthermore, can indirectly affect SRP transfer by increasing the availability of DO and NO_3^- in sediments (Chen and Liu, 1995; Stief and Beer, 2006).

3.3 Implications for accurate measurement of internal loading: how should this be measured?

Internal loading originating from sediments is one of important sources contributing most to the nutrient status and budgets of lakes (Rossi and Premazzi, 1991; Søndergaard et al., 2003). In order to better assess the influence of SRP release from sediments on water quality, internal loading should be accurately estimated.

Internal loading was usually inferred from diffusion

calculations based on the SRP gradients near sediment-water interface using Fick's first law (Berner, 1980):

$$F = -\phi D_s (\partial C / \partial Z)_{z=0} \tag{5}$$

$$D_s = \phi^n D_o$$

when $\phi \leqslant 0.7$, $n = 1$; when $\phi > 0.7$, $n = 1.5 - 2$ (6)

(Lerman,1979; Ullman and Aller, 1982)

where, ø is porosity; D_s is the diffusion coefficient in porewater and $(\partial C / \partial Z)_{z=0}$ is the porewater concentration gradient. D_o is the diffusion coefficient at infinite dilution. The porosity was assumed to average 0.61 for the entire sediments (0–15 cm).

According to Fick's first law, the estimated fluxes (F) of SRP across sediment-water interface ranged from 0.008 to 0.048 mg/(m²·day), which were much lower than the factual fluxes (ϕ) (Fig. 6), especially within the first 48 hr. Therefore, it was obviously inappropriate to dynamically estimate fluxes with Fick's first law in this study. Slomp et al. (1998) indicated that the SRP flux measured directly far higher than that calculated by Fick's first law resulting from the influence of adsorption at sediment-water interface. Similar observations were reported by Shi et al. (2004). The following factors might be ignored. (1) The SRP release caused by the mineralization of OM. The OM contents of surface sediments was 1.59% dry sediments, and OM content of sediments decreased with sediment depth increasing because of the mineralization (Table 2). The mineralization of OM was one of important SRP-releasing ways in Xiannu Lake. (2) The sediment physicochemical characteristics and environmental factors influence the exchange across sediment-water interface (Holdren and Armstrong, 1980; Kim et al., 2003; Slomp et al., 1998; Wang et al., 2005). (3) The SRP concentrations in the surface layer maintained steady and were lower than those in the middle and bottom layers in sediments (Fig. 6), which resulted in SRP being transported from deeper layers upward to surface layers in sediments and to overlying water. The fluxes varied with SRP concentrations of deeper layers, especially within the first 48 hr (Fig. 6), suggesting that the deeper (3–15 cm) sediments contribute strongly to the SRP concentration of overlying water.

Therefore, internal loading should be calculated according to the variation in SRP concentrations in overlying water. SRP concentrations increased with water depth when SRP in sediments was released to overlying water. In order to accurately estimate the internal loading, it is necessary to measure the SRP concentration profiles in overlying water.

4 Conclusions

(1) The changes in SRP concentrations in different layers occurred simultaneously and in the same direction in Xiannu Lake. The high content of iron oxide and manganese oxide in sediments was an important factor influencing both the SRP contents of overlying water and sediment porewater and ORP in sediments. The SRP concentrations in overlying water and surface sediment

porewater maintained very low state because of the high atom ration of TFe and TMn to TP in sediments.

The SRP of overlying water mainly originated from SRP transference of the middle and bottom layers in sediments. The significant influences of DO concentration and pH on SRP concentrations of the middle and bottom layers in sediment porewater were not observed in sediments.

(2) It was hard to accurately estimate the flux across sediment-water interface using Fick first law when diffusion was not a main approach for exchange. Internal loading could be accurately calculated according to the variations in SRP concentration profiles in overlying water.

Acknowledgments

References

Aller R C, 1994. Bioturbation and remineralization of sedimentary organic matter: Effects of redox oscillation. *Chemical Geology*, 114: 331–345.

Bao, 2000. Soil and Agricultural Chemistry Analysis (3rd ed.). Chinese Agriculture Publishing House, Beijing. 71–76, 217–219, 225–228.

Berner R A, 1980. Early Diagenesis: A Theoretical Approach. Princeton Universitiy Press, Princeton, NJ.

Boström B, Anderson J M, Fleischer S, Jansson M, 1988. Exchange of phosphorus across the sediment-water interface. *Hydrobiologia*, 170: 229–244.

Carignan R, Lean D R S, 1991. Regeneration of dissolved substances in a seasonally anoxic lake: The relative importance of processes occurring in the water column and in the sediments. *Limnology and Oceanography*, 36: 683–707.

Carlton R G, Wetzel R G, 1988. Phosphorus flux from lake sediments: effect of epipelic algal oxygen production. *Limnology and Oceanography*, 33: 562–570.

Chen T Y, Liu Z, 1995. Influence of chironomid larvae on nitrogen and phosphorus release from sediment to overlying water. *Acta Entomologica Sinca*, 38(4): 448–451.

Christensen K F, Jensen H S, 1997. Comparison of iron, manganese, and phosphorus retention in freshwater littoral sediment with growth of *Littorella uiflora* and benthic microalge. *Biogeo-Chemistry*, 38: 149–171.

Currie D J, Kalff J, 1984. The relative importance of bacterioplankton and phytoplankton in phosphorus uptake in freshwater. *Limnology and Oceanography*, 32: 476–482.

Gächter R, Meyer J S, Mares A, 1988. Contribution of bacteria to release and fixation of phosphorus in lake sediments. *Limnology and Oceanography*, 33: 1542–1558.

Gong C S, Yao Q, Fang C X, Dong H P, Zheng C H, Bao X M, 2006. Release fluxes estimate of phosphorus in a urban shallow lake: Lake Xuanwu, Nanjing. *Journal of Lake Science*, 18(2):179–183.

Heiri O, Lotter A F, Lemcke G, 2001. Loss on ignition as a method fro estimating organic and carbonate content in sediments: reproducibility and comparability of results. *Journal of Paleolimnology*, 25: 101–110.

Holdren G C, Armstrong D E, 1980. Factors affecting phosphorus release from intact lake sediment cores. *Water Science and Technology*, 1: 79–89.

House W A, Deniso F H, 2000. Factors influencing the measurement of equilibrium phosphate concentration in river sediments. *Water Research*, 34: 1187–1200.

Ishikawa M, Nishimura H, 1989. Mathematical model of phosphate release rate from sediments considering the effect of dissolved oxygen in overlying water. *Water Research*, 23(3): 351–359.

Jensen H S, Andersen F Ø, 1992. Importance of temperature, nitrate, and pH for phosphate release from aerobic sediments of four shallow, eutrophic lakes. *Limnology and Oceanography*, 37: 577–589.

Jin X C, Tu Q Y, 1990. Investigation Criterion of Lake Eutrophication (2nd ed.). Chinese Environmental Sciences Press. Beijing, China.

Jones R I, Shaw P J, Haan H E, 1993. Effects of dissolved humic substances on the speciation of iron and phosphate at different pH and ionic strength. *Environmental Science & Technology*, 27: 1052–1059.

Katsev S, Sundby B, Mucci A, 2006. Modeling vertical excursions of the redox boundary in sediments: Application to deep basins of the Arctic Ocean. *Limnology and Oceanography*, 51(4): 1581–1593.

Kim L H, Choi E, Stenstrom M K, 2003. Sediment characteristics, phosphorus types and phosphorus release rates between river and lake sediments. *Chemosphere*, 50: 53–61.

Lerman A, 1979. Chemical exchange across sediment-water interface. *Annual Review of Earth and Planetary Sciences*, 6: 281–303.

Lopez P, Lluch X, Vidal M, Morgui J A, 1996. Adsorption of phosphorus on sediments of the Balearic (Span) related to their composition. *Estuarine Coastal and Shelf Science*, 42: 185–195.

Mesnage V, Ogier S, Bally G, Disnar J R, Lottier N, Dedieu K et al., 2007. Nutrient dynamics at the sediment-water interface in a Mediterranean lagoon (Thau, France): Influence of biodeposition by shellfish farming activities. *Marine Environmental Research*, 63(3): 257–277.

Müller B, Wang Y, Wehrli B, 2006. Cycling of calcite in hard water lakes of different trophic states. *Limnology and Oceanography*, 51(4): 1678–1688.

Rossi G, Premazzi G, 1991. Delay in lake recovery caused by internal loading. *Water Research*, 25:567–575.

Schön G, Geywitz S, Mertens F, 1993. Influence of dissolved oxygen and oxidation-reduction potential on phosphate release and uptake by activated sludge from sewage plants with enhanced biological phosphorus removal. *Water Research*, 27(3): 349–354.

Shi F, Wang X L, Shi X Y, Zhang C S, Jiang F H, Zhu C J et al., 2004. Benthic flux of dissolved nutrients at the sediment-water interface in the East China Sea. *Marine Environmental Science*, 23(1): 5–8.

Slomp C P, Malschaert J F P, Raaphorst W V, 1998. The role of adsorption in sediment-water exchange of phosphate in North Sea continental margin sediments. *Limnology and Oceanography*, 43(5): 832–846.

Søndergaard M, Jensen J D, Jeppesen E, 2003. Role of sediment and internal loading of phosphorus in shallow lakes. *Hydro-*

biologia, 506(1): 135–145.

Song J, Luo Y M, Zhao Q G, Zhu Y M, Wu L H, Wu S C, 2000. Nutrient release at sediment-water interface: application of rhizon-SMS in study of nitrogen release from sediments. *Acta Pedologica Sinica*, 37: 515–520.

Spears B M, Carvalho L, Perkins R, Kirika A, Paterson D M, 2006. Spatial and historical variation in sediment phosphorus fractions and mobility in a large shallow lake. *Water Research*, 40: 383–391.

Spears B M, Carvalho L, Perkins R, Kirika A, Paterson D M, 2007. Sediment phosphorus cycling in a large shallow lake: Spatio-temporal variation in phosphorus pools and release. *Hydrobiologia*, 584: 37–48.

Standards of National Environmental Protection Department, 2002. Analysis Methods for the Examination Water and Wasterwater (4th ed.). Chinese Environmental Sciences, Beijing, China.

Steinman A D, Mulholland P J, 2007. Phosphorus limitation, uptake, and turnover in benthic stream algae. In: Methods in Stream Ecology (Hauer F R, Lamberti G A, eds.). Academic Press, San Diego, CA. 187–212.

Stief P, Beer D, 2006. Probing the microenvironment of freshwater sediment macrofauna: Implications of deposit-feeding and bioirrigation for nitrogen cycling. *Limnology and Oceanography*, 51: 2538–2548.

Teasdale P R, Minett A I, Dixon K, Lewis T W, Batley G, 1998. Practical improvements for redox potential (E_H) measurements and the application of a multiple-electrode redox probe (MERP) for chacterising sediment *in situ*. *Analytica Chimica Acta*, 367(1): 201–213.

Ullman W J, Aller R C, 1982. Diffusion coefficients in nearshore marine sediment. *Limnology and Oceanography*, 27: 552–553.

Viollier E, Rabouille C, Apitz S E, Breuer E, Chaillou G, Dedieu K et al., 2003. Benthic biogeochemistry: state of the art technologies and guidelines for the future of *in situ* survey. *Journal of Experimental Marine Biology and Ecology*, 285/286: 5–31.

Wang S R, Jin X C, Pang Y, Zhao H C, Zhou X N, Wu F C, 2005. Phosphorus fractions and phosphate sorption characteristics in relation to the sediment compositions of shallow lakes in the middle and lower reaches of Yangtze River region, China. *Journal of Colloid and Interface Science*, 289: 339–346.

Werner U, Billerbeck M, Polerecky, L, Franke U, Huettel M, 2006. Spatial and temporal patterns of mineralization rates and oxygen distribution in a permeable intertidal sand flat (Sylt, Germany). *Limnology and Oceanography*, 51(6): 2549–2563.

Yuan Z Q, Wu D S, Huang R G, Chen Z L, Wu F C, Wan G J, 1992. Manufacturer of a series of sampling apparatuses applied for lake sediment-water interface. *Environmental Sciences*, 14(1): 70–72.

Zhu G W, Gao G, Qin B Q, Zhang L, Luo L C, 2003. Geochemical characteristics of phosphorus in sediments of a large shallow lake. *Advances in Water Science*, 14(6): 714–719.