ORIGINAL ARTICLE



# Effects of temperature on phosphorus release in sediments of Hongfeng Lake, southwest China: an experimental study using diffusive gradients in thin-films (DGT) technique

Jingfu Wang<sup>1</sup> · Jingan Chen<sup>1</sup> · Shiming Ding<sup>2</sup> · Jing Luo<sup>3</sup> · Yang Xu<sup>3</sup>

Received: 25 November 2014/Accepted: 2 June 2015/Published online: 16 June 2015 © Springer-Verlag Berlin Heidelberg 2015

Abstract The effects of temperature on phosphorus (P) release in sediments of Hongfeng Lake, southwest China, were investigated under simulation condition. The distributions of labile P in sediments were measured in situ using a diffusive gradients in thin-films (DGT) technique (Zr-oxide DGT) at a two-dimensional, sub-millimeter spatial resolution. The changes of P fractions in sediments at different temperatures were also investigated using a chemical fractionation technique which divided sediment P into NH<sub>4</sub>Cl-P, BD-P, NaOH-P, HCl-P, and Residual P. The results showed that the concentrations of labile P in sediments increased rapidly as the simulating temperature increased, reflecting a rapid P release from sediments. The NaOH-P concentrations in sediments showed the greatest decrease (accounting for 79.3 % of total decrease) during the experiment, suggesting that the increase of labile P in sediments was mainly due to the transformation of NaOH-P. The release of HCl-P also occurred in sediments, increasing the labile P concentration in pore waters. The seasonal variation of temperature and its induced biological-chemical changes at the sediment-water interface (such as organic matter degradation, and respiration) might be an important factor affecting the P release in sediments

Jingan Chen chenjingan@vip.skleg.cn of Hongfeng Lake. Our results provide new information for illuminating P biogeochemical cycling processes at the interface in eutrophic lakes.

**Keywords** DGT · Temperature · Phosphorus release · Sediments · Hongfeng Lake

# Introduction

Phosphorus (P) is widely regarded as the primary factor responsible for lake eutrophication (Carpenter 2005), and P release from sediments may be a major source of P to the water column (Conley et al. 2009; Nausch et al. 2009). Intensive internal P loading can prevent improvement of water quality and cause a delay in lake recovery for a long period after the external loading reduction (Jeppesen et al. 2005; Genkai-Kato and Carpenter 2005). Previous studies showed that sediment P release was mainly controlled by the physicochemical and biological conditions at the sediment-water interface (SWI), e.g., temperature, dissolved oxygen (DO), pH, wind disturbance, and bioturbation (Søndergaard et al. 1992; Fan et al. 2004; Jin et al. 2006a, b; Jiang et al. 2008; Tang et al. 2013). Temperature increase and anaerobic conditions were beneficial to the release of P from sediments. Increasing temperature can obviously enhance the biomass and growth of bacteria and autotrophic alga, and the increase was beneficial to the removal of P from the sediments (Jiang et al. 2008). The low DO concentrations at SWI induced the reduction of Fe(III)-host minerals to Fe(II) and finally resulted in Febound P release, which was commonly regarded as a major P-release mechanism (Steinberg 2011). The release of Fe-P ordinarily occurred at alkaline condition, and low pH promoted the release of Ca-P, and little P release occurred

<sup>&</sup>lt;sup>1</sup> State Key Laboratory of Environmental Geochemistry, Institute of Geochemistry, Chinese Academy of Sciences, Guiyang 550002, China

<sup>&</sup>lt;sup>2</sup> State Key Laboratory of Lake Science and Environment, Nanjing Institute of Geography and Limnology, Chinese Academy of Sciences, Nanjing 210008, China

<sup>&</sup>lt;sup>3</sup> College of Resources and Environmental Engineering, Guizhou University, Guiyang 550025, China

under neutral conditions (Jin et al. 2006a, b). In shallow lakes, e.g., Taihu Lake, China, and Arresoe Lake, Denmark, the internal P loading can be primarily attributed to resuspension of sediment caused by wind-waves (Søndergaard et al. 1992; Fan et al. 2004).

Most experimental studies have set the simulating conditions in large ranges, testing the effects of the physicochemical parameters on P release in sediments (Jin et al. 2006a, b; Jiang et al. 2008). In fact, in most natural lake ecosystems, the physicochemical parameters at the SWI, except for temperature, are relatively stable. First, although some studies reported extremely high pH values up to 9.5 in lake waters (Schrenk-Bergt et al. 2004), diurnal pH of 7.0-8.0 appeared to be very common. Second, permanent anaerobic widely existed at the SWI, especially in the deep-water lakes. Additionally, resuspension reduced by wind disturbance can only affect on some shallow lakes located in typical monsoon regions, and rarely occurred in other shallow lakes and deep-waters. Therefore, seasonal variation of temperature and its induced biological-chemical changes (such as organic matter degradation, and sulfate reduction) may be an important force affecting P release at the SWI in lakes.

During the past decades, a number of studies had paid attention to the effects of temperature on P release from the sediments (Jiang et al. 2008; Anthony and Lewis 2012; Li et al. 2013; Wu et al. 2014). These observations suggested that with the temperature increasing, the activity of microorganisms was increased significantly, meanwhile, the mineralization of organic matter can be enhanced, which may favor the release of Fe/Al-P or Ca-P. Although those studies were carried out, the processes and the mechanisms of P release affected by the temperature at SWI were not well illuminated, due to lacking in situ, highresolution monitoring techniques. Recently, the diffusive gradients in thin-films (DGT) technique have been well developed and proved to be an available tool in situ detection of labile solutes in sediments (Davison et al. 1997; Warnken et al. 2004; Jezequel et al. 2007; Stockdale et al. 2008; Robertson et al. 2008). Ding et al. (2010, 2013) developed a powerful Zr-oxide DGT technique for the oneor two-dimensional (2D) measurement of labile P in sediments at a millimeter or submillimeter spatial resolution. This technique has been applied in high-resolution studies on P cycling in lake sediments (Ding et al. 2012; Xu et al. 2012). In this study, the Zr-oxide DGT in combination with other techniques (e.g., microelectrode, chemical sequential extraction) was employed to study the effects of temperature on P release in lake sediments. In situ simulating experiments were conducted using sediment cores collected from Hongfeng Lake, a eutrophic deep-water lake, Southwestern China. The objective of this study was (1) to observe the in situ 2D concentration distributions and changes of labile P in sediments during the temperature increasing processes; and (2) to investigate the synchronous changes of physicochemical parameters and sediment P fractions at the SWI, and discuss the mechanisms controlling the release of P in sediments of Hongfeng lake.

## Materials and methods

## Study site

Hongfeng Lake (N 106.24°, E 26.30°) is one of the largest manmade lakes located on the Yunnan-Guizhou Plateau in southwestern China (Fig. 1). It was constructed in the 1960s. It has a surface area of 57.2 km<sup>2</sup>, a mean water depth of 10.5 m (max. 45 m), and holds  $6.01 \times 10^8$  m<sup>3</sup> of water. Hongfeng Lake supplies drinking water to Guiyang City, is the provincial capital with a population of over 3 million, and also provides services for hydropower, flood control, shipping, recreation, and commercial aquaculture. Hongfeng Lake is currently in the mesotrophic state (Yang et al. 2014). Concentrations of the total P, total N, and Chla in waters of Hongfeng Lake ranged of 0.03-0.10 mg/L, 1.0-2.5 mg/L, and 2-75 mg/L, respectively. It is monomictic and strongly stratified during the summer, with anoxic hypolimnion (below 12 m depth) from June to September. The concentrations of soluble reactive P in the water column after the onset of anoxia can accumulate rapidly in the hypolimnion, reaching high concentrations (i.e., >0.20 mg/L) over the summer.

#### Sampling and experiment

Sediment core was collected from the outlet area (water depth  $\sim 40$  m) of Hongfeng Lake in May, 2014 (Fig. 1). A plastic static gravity corer (6 cm i.d.) was employed to minimize the disturbance of the surface sediment layer. The core was only used if it had a visibly undisturbed sediment surface and clear overlying water. As soon as the core was obtained, the sampling core (polymethyl methacrylate glass tube) was immediately covered with tinfoil to keep in dark and transferred to laboratory.

In order to study the effects of temperature on P release in sediments, simulating experiments were conducted in a transparent rectangular Perspex box  $(20 \times 20 \times 50 \text{ cm},$ width  $\times$  length  $\times$  height) filled with filtered lake water. The sampling core was then put in the water and placed together with the Perspex box into an illumination incubator (SPX-70BIII, Taisite Instrument Co., Ltd., Tianjing, China). Three incubation temperature stages were set at 8, 15, and 22 °C, according to the monitored seasonal temperature of the overlying water in Hongfeng Lake.



Fig. 1 Location of the study area and the sampling site

Experiments for each stage lasted for 7 days. In order to minimize the effect of the varied DO to the P release, the whole processes of the experiment were conducted under the same anoxic condition, which were produced by purging nitrogen (99 %) to the overlying water for 2 h twice every day.

The Zr-oxide gel DGT made by Ding et al. (2012) and the flat-type DGT holder obtained from DGT Research Limited (Lancaster, U.K.) were employed in this study. The DGT probes with exposure window of  $1.8 \times 16.0$  cm (width  $\times$  length) were deployed in the collected sediment core on the 7th, 14th, and 21st day, respectively. The deployment time was 24 h. Two-dimensional distributions of P concentrations on the Zr-oxide gel were analyzed after retrieval. To ensure that the three measured profiles were produced at the same location in the sediment core, a blank DGT device was previously inserted into a fixed position on the sediment surface. During settling and between deployments of the Zr-oxide DGT, the blank probes were deployed to maintain sediment integrity. Probe changeover was performed by rapidly sliding the deployed probe out of the sediments and replacing it with a new probe. This process took for a short time (less than 60 s) to minimize the disturbance and sinking of the sediments near the monitored profile. Considerable care was taken to avoid artificial changes of the SWI during settling and deployments.

## Analysis of labile P in sediments using DGT

After retrieval, the Zr-oxide gel was immersed in the mixed reagent for coloration in an incubator for 45 min with the temperature stabilized at  $35 \pm 1$  degrees according to a previous report (Ding et al. 2013). The surfaces on the Zr-oxide settled sides were then scanned using a flat-bed scanner (Canon 5600F) at a resolution of 300 dpi, corresponding to a pixel size of  $169 \times 169 \mu m$ . The grayscale intensity of the scanned images corresponding to the open window of the solution DGT unit was finally analyzed with ImageJ 1.46.

Calibration of the P measurement was performed by establishing the relationship between the grayscale intensities of the Zr-oxide gel and its accumulated masses of P after the DGT deployments. The relationship between the masses of P accumulated in the gels and their corresponding grayscale intensities was fitted using an exponential equation (Fig. 2; Eq. 1).

Grayscale = 
$$270.26 \times (1 - e^{-1.32M_0}).$$
 (1)

Grayscale is the grayscale intensity of the gel surface,  $M_0$  is the mass of P accumulated in the gel per unit area (µg/cm<sup>2</sup>). In this study, each Zr-oxide gel of  $1.7 \times 1.5$  cm (width × length) was immerged into a series of 25 mL well-stirred solutions containing 0.03 mol/L NaNO<sub>3</sub> and certain concentrations of P (0–1.6 mg/L) for 24 h,



Fig. 2 The calibration curve for P measurement based on the analysis of the relation between the mass of P accumulated in the gel and the grayscale intensity of the gel surface

respectively. *M* (the total mass of P accumulated in each Zr-oxide gel,  $\mu$ g) was calculated by the concentration differences and volume of the well-stirred solutions before and after P uptake of the Zr-oxide gels. Then,  $M_0$  was equal to *M* divided by the gel area (2.55 cm<sup>2</sup>).

The concentrations of labile P in sediments were calculated using the DGT equation (Eq. 2):

$$C_{\rm DGT} = \frac{M\Delta g}{DAt} = \frac{M_0 \Delta g}{Dt}, \qquad (2)$$

where  $\Delta g$  is the thickness of the diffusive layer (cm), *D* is the diffusion coefficient of the phosphate in the diffusive layer (cm<sup>2</sup>/sec), the values of *D* for H<sub>2</sub>PO<sub>4</sub><sup>-</sup>(aq) have been reported elsewhere (Zhang et al. 1998), *A* is the exposure area of a pixel size defined in scanning of the gel (cm<sup>2</sup>), and *t* is the deployment time (s).

The relationship between the masses of P accumulated in the gels and their corresponding grayscale intensities was analyzed by sigmaplot 12.0 software (Systat Software Inc., USA). High-resolution 2D distribution of labile P in sediments was drawn with Origin 8.6 software (OriginLab Corporation, USA).

#### Microsensors and measurement

Microsensors are widely used not only due to its examination of microenvironments and microgradients, but also due to the minimal disturbance to the system (Kühl and Jørgensen 1992; Santegoeds et al. 1998). High-resolution vertical distributions of  $O_2$ ,  $H_2S$ , and pH in the collected sediment core were obtained by a powerful and versatile four-channel Microsensor Multimeter (Unisense, Science Park Aarhus, Denmark) with a spatial resolution of 300 µm.

- 1. The applied  $O_2$  microsensor was of the micro-Clarktype described by Revsbech (1989), with a sensing-tip diameter of <10 µm, a 90 %-response time of 1 s, and a velocity sensitivity of <1-2 %. A two-point linearly calibration of the microsensor was done in air-saturated calibration solution and in the anoxic solution (~2 g sodium ascorbate in 100 mL of 0.1 M NaOH).
- 2. The H<sub>2</sub>S microsensor is a miniaturized amperometric sensor with an internal reference, a sensing, and a guard anode (Jeroschewski et al. 1996). Calibration was done in a dilution series of a sulfide standard solution buffered to the same pH (7.2–7.3) as the synthetic biofilm medium and with the same salinity (flushed with nitrogen to avoid oxidation of the sulfide).
- 3. The pH microelectrode is a miniaturized glass pH electrode with tip diameters down to 10 microns. The electrodes were calibrated at room temperature (20 °C) in three standard pH buffers. It responds linearly between the three points with a slop of 52–60 mV/pH-unit and a 90 % response time of <10–20 s.

## Analysis of P fractions in sediments

To determine how the chemical fractions of P in sediments change in the P-release processes, P fractionation of the surface sediments (0-4 cm, sectioned into 1 cm intervals) was analyzed before and after the cultivation experiment. At the beginning of the experiment, a PVC tube (2.5 cm i.d.) was inserted along an edge area into the core (6 cm i.d.) to avoid the disturbance during sampling. Then, 1-cm interval samples were taken out from the PVC tube by the small Teflon spoon. The PVC tube was left in situ until the end of the experiment. After the experiment, the left core profile was sliced into 1-cm interval. Surface sediment samples (0-4 cm) were collected. All collected samples were immediately freeze-dried. Afterwards, the samples were ground and sieved with a standard 100-mesh sieve for P fraction analysis. Although the pretreatment of drying was widely used in the sediment P-fractionation analysis (Ruban et al. 2001; Jin et al. 2006a, b), recent study suggested that fresh sediment should be used for a accurate P-fractionation (Zhang et al. 2014). In this study, we focused on the variation of sediment P forms at different temperatures other than P-fractionation analysis, so the traditional method (drying) was used for its easy handling of the material for comparison between different temperature treatments.

Sediment P fractionations and total P concentrations were performed using the sequential extraction scheme based on Psenner et al. (1988) and Hupfer et al. (1995). Three parallel samples for each sediment sample were analyzed for data quality control. The determination of different P fractions was as following: (1) NH<sub>4</sub>Cl–P (extracted with 1 M NH<sub>4</sub>Cl solution, 0.5 h); (2) BD–P (extracted with 0.11 M bicarbonate/dithionite solution, 1 h); (3) NaOH–P (total P extracted with 1 M NaOH solution, 16 h); (4) HCl–P (extracted with 0.5 M HCl solution, 16 h); (5) Residual P (digestion with 30 % (v/v) H<sub>2</sub>SO<sub>4</sub> and 8 % K<sub>2</sub>S<sub>2</sub>O<sub>4</sub> at 121 °C for 30 min, extracted with 1 M HCl solution, 16 h). The concentrations of P in the extraction solution were determined using the method of Murphy and Riley (1962).

## Analysis of sediment properties

Total organic carbon (TOC) and total nitrogen (TN) in the sediments were analyzed using an elemental analyzer (Vario MACRO cube, Elementar, Germany). Before TOC and TN analysis, the sediments were pretreated by an excess of 1 mol/L HCl to remove carbonates. Total concentrations of Fe, Mn, and Al were measured by the use of inductively coupled plasma optical-emission spectrometry (ICP-OES) after micro-acid (HNO<sub>3</sub>–HCl–HF) wet digestion of sediments. Properties of sediments from different regions of Lake Tai are shown (Table 1).

### Results

# Chemical characteristics of sediments

TOC content in the sediments ranged from 6.15 to 7.38 % with a mean value of 6.75 %. TN content in the sediments ranged from 0.54 to 0.72 % with a mean value of 0.64 %. The molar ratio of TOC/TN ranged from 11.4 to 13.3, which is in the range of typical mixed sources including both autochthonous sources and allochthonous sources. Moreover, the sediments had a high aluminium content, and relatively low iron and manganese contents (Table 1).

## Changes of O<sub>2</sub>, pH, and H<sub>2</sub>S in sediments

Changes of  $O_2$ , pH, and  $H_2S$  in sediment profiles measured by microsensors are shown in Fig. 3. Compared of these parameters under three temperature conditions, similar ranges for  $O_2$  and pH curves were detected, but not for  $H_2S$ . In general,  $O_2$  were consumed completely on surface layers of the all three profiles, and the penetration depth was all smaller than 7 mm. The pH in the core profiles was near neutral (6.7–7.9) for all depths, and exhibited a decreasing tendency from the surface to the 20 mm depth. As the temperature increased, the pH value slightly changed to be more acidic. H<sub>2</sub>S was detected at a depth of about 8 mm. At 8 °C, the concentrations of H<sub>2</sub>S reached its maximum (6.1  $\mu$ M) by ~28 mm, then decreased gradually to a low value (2.0  $\mu$ M), and remained relatively constant from ~40 mm downwards. While at 15 and 22 °C, the concentrations of H<sub>2</sub>S increased more rapidly upon ~25 mm, and reached a relative higher level (11.3  $\mu$ M for 15 °C, and 15.6  $\mu$ M for 22 °C), revealing the occurrence of more intense sulfate reduction reactions.

## Changes of labile P in sediments

The 1D and 2D distributions of labile P concentrations in sediments at different temperatures are shown in Fig. 4. In the three core profiles, the concentrations of labile P in the 2D scales increased with sediment depth in the surface 0–5 cm layers, and then decreased slightly in the deeper layers (Figs. 4a, 3b, c). Figure 4 also showed that the concentrations of labile P increased markedly both in the 1D and 2D scales as the temperature increased. At 8 °C, the concentrations of labile P in the sediment core varied from 0.153 to 0.601 mg/L with an mean value of ~0.400 mg/L (Fig. 4a). At 15 and 22 °C, the mean values of labile P concentrations raised respectively to ~0.600 and ~0.700 mg/L. At 22 °C, the maximal value of labile P concentrations in the core profile reached to 0.929 mg/L.

In the sub-millimeter scale, large spatial heterogeneity occurred both in the vertical and the horizontal direction (Figs. 4d, e, and 5). In Fig. 4d and e, the hot spots with diameters less than 5 mm have high labile P concentrations, exhibiting a large chemical range (from 0.50 to 0.75 mg/L) with significant differences in the millimeter-scale regions. The variation of the labile P concentrations in the temperature increasing processes exhibited subtle differences in 2-dimensional space of the hot spots, likely revealing the difference of P-release rate in 2-dimensional millimeterscale space. In addition, the horizontal heterogeneity generally occurred in varied depth positions of the collected core profile. Figure 5 shows the horizontal heterogeneity of the labile P concentrations in sediments at 15 °C. The average concentrations of labile P of 30, 60, and 90 mm depth were 0.639, 0.710, and 0.625 mg/L, respectively. However, at the same depth, e.g., 9 mm, the relative standard deviation (RSD) of labile P concentrations reached to

Table 1Chemicalcharacteristics of sedimentscollected from Hongfeng Lake

	TOC (% d.w.)	TN (% d.w.)	TOC/TN	Fe (g/kg d.w.)	Al (g/kg d.w.)	Mn (g/kg d.w.)
Mean	6.75	0.64	12.3	52.8	81.2	1.02
SD	0.56	0.08	-	_	_	_



Fig. 3 Chemical parameters of sediments in the core profile, including oxygen, hydrogen sulfide, and pH value. The depth zero represents the water-sediment interface

6.6 % along the horizontal direction. The absolute value of the concentration difference reached to 0.180 mg/L, showing a large heterogeneity in the centimeter (sub-millimetre)-scale horizontal distance.

## Changes of P fractions in sediments

The change of P fraction concentrations in the surface 0–4 cm sediments before and after the experiment is shown in Fig. 6. NaOH–P was the first major P fraction in all sediment samples, accounting for  $45.5 \pm 4.7$  % (before the experiment) and  $59.6 \pm 6.2$  % (after the experiment) of the total P, respectively. Generally, the total P concentrations had a decreasing trend upward toward the sediment surface in the top 4 cm layers. There was a similar tendency for NaOH–P, HCl–P, and total P. The BD–P and residual-P concentrations changed slightly throughout the sediment profile. Distinguished from the relative P fractions, NH<sub>4</sub>Cl–P concentrations increased from the depth of 4 cm to the sediment surface.

At the beginning, the mean concentration of the sediment P for the four depth layers was 1144.6 mg/kg. After the experiment (21 days), the mean P concentration in sediments decreased down to 907.7 mg/kg. First, NaOH–P and HCl–P concentrations were reduced by an average of 187.9 and 66.2 mg/kg, respectively, which was the main reason that caused the notable reduction of total P. Additionally, the average concentrations of BD–P and residual-P also slightly decreased by 6.5 and 5.4 mg/kg. However, NH<sub>4</sub>Cl–P presented distinct tendency. The mean concentrations of the most active P (NH<sub>4</sub>Cl–P) in sediments increased remarkably from 24.9 to 43.3 mg/kg.

#### Discussion

# Release of NaOH-P in sediments

Previous studies suggested that the P re-cycle in sediments mainly depends on the changes in P chemical fractions in surface sediments, which may result from continuous transport of chemical species across the SWI (Jin et al. 2006a, b; Jorcin and Nogueira 2005; Tang et al. 2013). During the experiment, the total P concentrations in sediments significantly reduced, with a mean value of 236.9 mg/kg ( $\sim$ 15 % of total P) (Fig. 6). In all sediment samples, NaOH-P was the first major P fraction. The decrease of NaOH-P concentrations was the greatest in all P fractions of the sediments (187.9 mg/kg on average, accounting for 79.3 % of total decrease). Meanwhile, the NH<sub>4</sub>Cl-P concentrations obviously increased in the every sediment layer. NH<sub>4</sub>Cl-P represented weakly adsorbed inorganic P that easily converted through the desorption reaction to be dissolved reactive P (DRP) in the pore waters (Pettersson 2001). Therefore, our results suggested that the increasing labile P detected by DGT was mainly due to the transformation of NaOH-P to NH<sub>4</sub>Cl-P or DRP under high-temperature conditions.

According to the sequential extraction method of Hupfer et al. (1995), the NaOH–P is composed of two parts, i.e., NaOH–srP and NaOH–nrP. NaOH–srP represents P bound to metal oxides, primarily of Fe and Al, which is exchangeable again with OH<sup>–</sup> and inorganic P compounds soluble in bases. The NaOH–nrP primarily represents the polyphosphate (poly-P) in NaOH and/or EDTA extracts of the sediments. The NaOH-srP (Fe/Al-P) in sediments was



(d) Hot spot of P at 15 degrees

(e) Hot spot of P at 22 degrees

Fig. 4 The one- and two-dimensional vertical profiles of the P concentrations under the temperatures of  $8^{\circ}$ ,  $15^{\circ}$ , and  $22^{\circ}$ , respectively. The one-dimensional P concentration curve was made up of

usually considered to be an important potential P resource for overlying water, which is sensitive to pH (Jiang et al. 2008; Wilson et al. 2008). Because the OH<sup>-</sup> has stronger coordination competition capacity than phosphate, NaOHsrP will be released massively from Fe/Al metal oxides under alkaline conditions. With the incubation temperature increased from 8 to 22 °C, the coordination competition between OH<sup>-</sup> and phosphate became more intense. Increasing incubation temperature promoted the release of NaOH-srP in this experiment.

The release of NaOH–nrP (poly-P) was primarily controlled by degradation of organic matters in sediments, which was mainly effected by microbial activities. In this experiment, the BD–P (redox sensitive P forms primarily bound to Fe-hydroxides and Mn compounds) did not changed significantly, indicating that the SWI has been in a stable reducing environment. Although ORP did not

579 points of P concentrations in the vertical direction, and *each point* represented the mean value calculated by 104 points of P concentrations in the horizontal direction

change significantly, the concentrations of  $H_2S$  exhibited a tendency of increase with increasing temperature.  $H_2S$  is an important product by the dissimilatory reduction of sulfate by anaerobic respiration of sulfate reducing bacteria (SRB) (Howarth 1984; Hockin and Gadd 2003). The increasing  $H_2S$  concentrations with a peak at ~25 mm depth in sediments indicated an increasing activity and/or growing population density of SRB under high temperature conditions. Accordingly, the activities and population density of other microorganisms may also increase, promoting the degradation of organic matters and the release of NaOHnrP.

Our results indicated that as the temperature increased, although other simulating apparatus was nearly the same, numerous NaOH–P rapidly transformed into  $NH_4Cl$ –P in sediments or DRP in the pore waters. This might be due to the more intense coordination competition between  $OH^-$ 



**Fig. 5** The horizontal heterogeneity of the labile P concentrations in sediments at 15 degrees. The *red line (circle), green line (circle),* and *blue line (triangle)* represented the horizontal variation of labile P concentrations of 30, 60, and 90 mm depth

and phosphate, and the induced microbial activities (e.g., respiration, degradation of organic matters) in sediments by temperature increase. This classical P-release model may explain the phenomenon of seasonal changes of water P in lake ecosystems (Boström et al. 1988; Steinberg 2011).

## Release of HCl-P in sediments

The HCl–P represents P forms that are sensitive to low pH and are assumed to consist mainly of apatite P and P bound to carbonates. The Ca–P fraction was generally considered

to be stable, but sensitive to pH changes (Jin et al. 2006a. b). In the experiment, the release of HCl-P occurred in nearly all sediment layers (Fig. 6), especially in the depths of 3-4 cm. The high-resolution chemical profiles showed that oxygen was depleted within the depth of 7 mm. In the aerobic condition, the deposited organic matter in the reduction state was likely to be oxidized by O<sub>2</sub> to generate organic matter in the oxidation state, meanwhile,  $H^+$  will be released into the pore water (Urban et al. 1994; Risgaard-Petersen et al. 2012). It was probably the main reason of pH in pore water in sediments declining rapidly. In addition, the sufficient supply of H<sub>2</sub>S in deep sediments impelled reactive Fe<sup>2+</sup> to form FeS in sediments, also releasing H<sup>+</sup> (Rickard 1995). All of the acid producing reactions may cause transformation of HCl-P from Ca-P to DRP, then released to the sediment pore waters.

#### Conclusion

Effects of temperature on P release in sediments collected from Hongfeng Lake, southwest China, have been experimentally investigated using Zr-oxide DGT technique. Our results showed that as the incubation temperature increased, the labile P concentrations rapidly increased in the two-dimensional scales, reflecting a rapid release of P from sediments. In all P fractions of the sediments, the decrease of NaOH–P concentrations accounted for 79.3 % of total P decrease in the experiment, suggesting that the increased labile P in sediments should be mainly attributed



Fig. 6 The concentration variation of P forms in sediments before (blue cylinder) and after (red cylinder) the experiment

to the transformation of NaOH–P to  $NH_4Cl-P$  or DRP under high-temperature conditions. The release of HCl–P also occurred in surface sediments, effecting the labile P concentration in pore waters. The variation of temperature and its induced biological–chemical changes at the SWI (such as organic matter degradation, and respiration) might be an important factor affecting the seasonal P release in sediments of Hongfeng Lake.

**Acknowledgments** This research was funded by Natural Science Foundation of China (Nos. 41173125 and 41403113).

## References

- Anthony JL, Lewis WM (2012) Low boundary layer response and temperature dependence of nitrogen and phosphorus releases from oxic sediments of an oligotrophic lake. Aquat Sci 74(3):611–617
- Boström B, Andersen JM, Fleischer S, Jansson M (1988) Exchange of phosphorus across the sediment–water interface. Hydrobiologia 170:229–244
- Carpenter SR (2005) Eutrophication of aquatic ecosystems: bistability and soil P. Proc Natl Acad Sci 102:10002–10005
- Conley DJ, Paerl HW, Howarth RW, Boesch DF, Seitzinger SP, Havens KE, Lancelot C, Likens GE (2009) Controlling eutrophication: nitrogen and phosphorus. Science 323:1014–1015
- Davison W, Fones GR, Grime GW (1997) Dissolved metals in surface sediment and a microbial mat at 100-µm resolution. Nature 387(6636):885–888
- Ding SM, Xu D, Sun Q et al (2010) Measurement of dissolved reactive phosphorus using the diffusive gradients in thin films technique with a high-capacity binding phase. Environ Sci Technol 44(21):8169–8174
- Ding SM, Sun Q, Xu D, Jia F, He X, Zhang CS (2012) Highresolution simultaneous measurements of dissolved reactive phosphorus and dissolved sulfide: the first observation of their simultaneous release in sediments. Environ Sci Technol 46(15):8297–8304
- Ding SM, Wang Y, Xu D et al (2013) Gel-based coloration technique for the submillimeter-scale imaging of labile phosphorus in sediments and soils with diffusive gradients in thin films. Environ Sci Technol 47(14):7821–7829
- Fan CX, Zhang L, Qin BQ, Wang SM, Hu WP, Zhang C (2004) Estimation on dynamic release of phosphorus from windinduced suspended particulate matter in Lake Taihu. Sci China Ser 47(8):710–719
- Genkai-Kato M, Carpenter SR (2005) Eutrophication due to P recycling in relation to lake morphometry, temperature, and macrophytes. Ecology 86:210–219
- Hockin SL, Gadd GM (2003) Linked redox precipitation of sulfur and selenium under anaerobic conditions by sulfate-reducing bacterial biofilms. Appl Environ Microbiol 69:7063–7072
- Howarth RW (1984) The ecological significance of sulfur in the energy dynamics of salt marsh and coastal marine sediments. Biogeochemistry 1:5–27
- Hupfer M, Gächter R, Giovanoli R (1995) Transformation of phosphorus species in settling seston and during early sediment diagenesis. Aquat Sci 57(4):305–324
- Jeppesen E, Søndergaard M, Jensen JP, Havens KE, Anneville O, Carvalho L, Coveney MF, Deneke R, Dokulil MT, Foy B, Gerdeux D, Hampton SE, Hilt S, Kangur KL, Hler JK, Lammens EHHR, Lauridsen TL, Manca M, Miracle MAR, Moss B, Ges

PN, Persson G, Phillips G, Portielje B, Romo S, Schelske CL, Straile D, Tatrai I, Wille E, Winder M (2005) Lake responses to reduced nutrient loading—an analysis of contemporary longterm data from 5 case studies. Freshw Biol 50:1747–1771

- Jeroschewski P, Steuckart C, Kühl M (1996) An amperometric microsensor for the determination of H<sub>2</sub>S in aquatic environments. Anal Chem 68(24):4351–4357
- Jezequel D, Brayner R, Metzger E, Viollier E, Prevot F, Fievet F (2007) Two-dimensional determination of dissolved iron and sulfur species in marine sediment pore-waters by thin-film based imaging. Thau lagoon (France). Estuar Coast Shelf Sci 72(3):420–431
- Jiang X, Jin XC, Yao Y, Li LH, Wu FC (2008) Effects of biological activity, light, temperature and oxygen on phosphorus release processes at the sediment and water interface of Taihu Lake, China. Water Res 42(8–9):2251–2259
- Jin XC, Wang SR, Pang Y, Wu FC (2006a) Phosphorus fractions and the effect of pH on the phosphorus release of the sediments from different trophic areas in Taihu Lake, China. Environ Pollut 139:288–295
- Jin XC, Wang SR, Bu QY, Wu FC (2006b) Laboratory experiments on phosphorous release from the sediments of 9 lakes in the middle and lower reaches of Yangtze River region, China. Water Air Soil Pollut 176(1–4):233–251
- Jorcin A, Nogueira MG (2005) Temporal and spatial patterns based on sediment and sediment–water interface characteristics along a cascade of reservoirs (Parana-panema River, south-east Brazil). Lakes Reserv 10:1–12
- Kühl M, Jørgensen BB (1992) Microsensor measurements of sulfate reduction and sulfide oxidation in compact microbial communities of aerobic biofilms. Appl Environ Microbiol 58:1164–1174
- Li HY, Liu L, Li MY, Zhang XR (2013) Effects of pH, temperature, dissolved oxygen, and flow rate on phosphorus release processes at the sediment and water interface in storm sewer. J Anal Methods Chem. doi:10.1155/2013/104316
- Murphy J, Riley JP (1962) A modified single solution method for the determination of phosphate in natural waters. Anal Chim Acta 27:31–36
- Nausch M, Nausch G, Lass HU, Mohrholz V, Nagel K, Siegel H, Wasmund N (2009) P input by upwelling in the eastern Gotland Basin (Baltic Sea) in summer and its effects on filamentous cyanobacteria. Estuar Coast Shelf Sci 83:434–442
- Pettersson K (2001) P characteristics of settling and suspended particles in Lake Erken. Sci Total Environ 266:79–86
- Psenner R, Boström B, Dinka M, Pettersson K, Puckso R (1988) Fractionation of suspended matter and sediment. Archiv für Hydrobiologie Beiheft. Ergebnisse der Limnologie 30:98–103
- Revsbech NP (1989) An oxygen microelectrode with a guard cathode. Limnol Oceanogr 34:474–478
- Rickard D (1995) Kinetics of FeS precipitation: part 1. Competing reaction mechanisms. Geochim Cosmochim Acta 59:4367–4379
- Risgaard-Petersen N, Revil A, Meister P, Nielsen LP (2012) Sulfur, iron, and calcium cycling associated with natural electric currents running through marine sediment. Geochim Cosmochim Acta 92:1–13
- Robertson D, Teasdale PR, Welsh DT (2008) A novel gel-based technique for the high resolution, two-dimensional determination of iron (II) and sulfide in sediment. Limnol Oceanogr Methods 6:502–512
- Ruban V, Lopez-Sanchez JF, Pardo P, Rauret G, Muntau H, Quevauviller P (2001) Harmonized protocol and certified reference material for the determination of extractable contents of phosphorus in freshwater sediments—a synthesis of recent works. Fresenius J Anal Chem 370(2–3):224–228
- Santegoeds CM, Ferdelman TG, Muyzer G, de Beer D (1998) Structural and functional dynamics of sulfate-reducing

populations in bacterial biofilms. Appl Environ Microbiol 64:3731-3739

- Schrenk-Bergt C, Krause D, Prawitt O, Lewandowski J, Steinberg CE (2004) Eutrophication problems and their potential solutions in the artificial shallow Lake Altmühlsee (Germany). Stud Quat 21:73–86
- Søndergaard M, Kristensen P, Jeppesen E (1992) Phosphorus release from resuspended sediment in the shallow and wind-exposed Lake Arresoe, Denmark. Hydrobiologia 228(1):91–99
- Steinberg CEW (2011) Aerobic phosphorus release from shallow lake sediments. Sci Total Environ 409(21):4640–4641
- Stockdale A, Davison W, Zhang H (2008) High-resolution two dimensional quantitative analysis of phosphorus, vanadium and arsenic, and qualitative analysis of sulfide, in a freshwater sediment. Environ Chem 5(2):143–149
- Tang W, Zhang H, Zhang WQ, Wang C, Shan BQ (2013) Biological invasions induced phosphorus release from sediments in freshwater ecosystems. Colloids Surf, A 436:873–880
- Urban N, Brezonik P, Baker L, Sherman L (1994) Sulfate reduction and diffusion in sediments of Little Rock Lake, Wisconsin. Limnol Oceanogr 39:797–815
- Warnken KW, Zhang H, Davison W (2004) Analysis of polyacrylamide gels for trace metals using diffusive gradients in thin

films and laser ablation inductively coupled plasma mass spectrometry. Anal Chem 76(20):6077-6084

- Wilson TA, Norton SA, Lake BA, Amirbahman A (2008) Sediment geochemistry of Al, Fe, and P for two historically acidic, oligotrophic Maine lakes. Sci Total Environ 404:269–275
- Wu YH, Wen YJ, Zhou JX, Wu YY (2014) Phosphorus release from lake sediments: effects of pH, temperature and dissolved oxygen. KSCE J Civil Eng 18(1):323–329
- Xu D, Ding SM, Sun Q, Zhong JC, Wu W, Jia F (2012) Evaluation of in situ capping with clean soils to control phosphate release from sediments. Sci Total Environ 438:334–341
- Yang TG, Liu HY, Yu YH (2014) Variation trend of water quality and its casing effect to the Hongfeng Lake. Resour Environ Yangtze Basin 23(1):96–102 (in Chinese with English abstract)
- Zhang H, Davison W, Gadi R, Kobayashi T (1998) In situ measurement of dissolved phosphorus in natural waters using DGT. Anal. Chim. Acta 370(1):29–38
- Zhang L, Liao QJH, Zeng C, Mo QL, Fan CX (2014) Effects of pretreatment on the sequential phosphorus fractionation of anaerobic sediment. J Limnol 73(2):274–281