



Effects of seasonal hypoxia on the release of phosphorus from sediments in deep-water ecosystem: A case study in Hongfeng Reservoir, Southwest China[☆]



Jingfu Wang^a, Jingan Chen^{a,*}, Shiming Ding^b, Jianyang Guo^a, Dallimore Christopher^c, Zihui Dai^a, Haiquan Yang^a

^a State Key Laboratory of Environmental Geochemistry, Institute of Geochemistry, Chinese Academy of Sciences, Guiyang 550002, PR China

^b State Key Laboratory of Lake Science and Environment, Nanjing Institute of Geography and Limnology, Chinese Academy of Sciences, Nanjing 210008, PR China

^c Hydronumerics, Level 1 272 Lygon St, Carlton, Vic 3053, Australia

ARTICLE INFO

Article history:

Received 29 February 2016

Received in revised form

20 July 2016

Accepted 3 August 2016

Available online 20 August 2016

Keywords:

Hypoxia

Phosphorus

Diffusive gradients in thin films technique

Microelectrode

ABSTRACT

Using the diffusive gradients in thin films (DGT) technique and microelectrode technique, hypoxia and its effects on the release of phosphorus (P) from sediments were carefully investigated in Hongfeng Reservoir, a typical deep-water ecosystem where eutrophication and hypoxia is still an environmental challenge in Southwest China. The results suggested that hypoxia significantly promotes the release of P from sediments and the release of P under hypoxic condition mostly comes from the release of BD–P. Together with the *in-situ* and high resolution evidences from DGT and microelectrode, the release of P from sediments under hypoxic condition was assumed to be coupled processes which are associated with the combined cycles of “P–Fe–S”. Evidences from the present work implied that the internal P-loadings induced by hypoxia, especially after a reduction of external P-loading, should be paid more attention in eutrophic deep-water reservoirs, Southwest China.

© 2016 Elsevier Ltd. All rights reserved.

1. Introduction

Hypoxia, defined as dissolved oxygen (DO) levels less than 2 mg/L, has becoming a global environmental challenge (Diaz, 2001; Rabalais et al., 2007; Alvisi and Cozzi, 2016). The expansion of hypoxic areas is largely associated with eutrophication (Conley et al., 2009a), because excess nutrient input results in the rapid consumption of DO (Bianchi, 2007; Djakovac et al., 2014). Hypoxia not only destroys the benthic communities, but also promotes the release of phosphorus (P) from sediments (Conley et al., 2009b; Bianchi et al., 2010). Such sedimentary P loadings (internal P-loadings) may create positive feedback loop, further enhancing prolonged hypoxia (Reddy et al., 2011; Roy et al., 2012; Adhikari et al., 2015). Previous researches on hypoxia were mainly conducted in the estuarine and coastal ecosystem. However, little is known in the freshwater ecosystems (Breitburg, 2002; Howarth

et al., 2011; Lin et al., 2016), especially in deep-water ecosystems, where hypoxia is an environmental challenge (Wang et al., 2015a, b). Southwest China is home to many deep-water (>10 m) reservoirs (Yang and Lu, 2014), where hypoxia often occurs during the summer (Zhang et al., 2015; Bunch et al., 2015).

Many works have proven that, at low level of DO, Fe(III)-host minerals are easily reduced to Fe(II), resulting in the release of Fe-bound P. This process was regarded as the major mechanism of the release of P from sediments (Steinberg, 2011). Meanwhile, under the hypoxic condition, elevated temperature and the mineralization of organic matter can also accelerate the release of P from the sediments (Pizarro et al., 1995; Wang et al., 2007, 2008; Jiang et al., 2008). Understanding on the release of P from sediments under hypoxic condition has been significantly improved in recent decade (Fan et al., 2004; Qin et al., 2006; Kuster-Heins et al., 2010; Lin et al., 2016). However, the release of P from sediments is a complicated process, which involves a number of micro-scale physical, chemical and biological processes at the sediment–water interface (SWI) (Søndergaard et al., 2003). Available knowledge is largely obtained by the traditional methods and there remains a

[☆] This paper has been recommended for acceptance by Eddy Y. Zeng.

* Corresponding author.

E-mail address: chenjingan@vip.skleg.cn (J. Chen).

great gap to fully understanding the mechanisms of P release from sediments, due to lacking of *in-situ* and high resolution evidences. Fortunately, the diffusive gradients in thin films (DGT) technique has been developed and proved to be an effective tool for *in-situ* detecting the labile solutes in sediments (Davison et al., 1997; Warnken et al., 2004; Stockdale et al., 2008; Robertson et al., 2008). Using Zr-oxide DGT, this technique was further improved to have the capacity of one or two dimensional measurement of labile P in sediment at millimeter or submillimeter level (Ding et al., 2010, 2013). On the other hand, more and more investigations showed that high resolution microelectrode with small needle-shaped probe (a tip diameter of 1–20 μm) had great advantage in microscale studies, especially for obtaining distributions of oxygen, pH, and hydrogen sulfide at the SWI (Revsbech, 1989; Pedersen et al., 2011).

Hongfeng Reservoir (HF) is a typical deep-water ecosystem in Southwest China (Wang et al., 2015b). Though biogeochemical forms of P and their distribution in sediments from HF have been carefully investigated, detailed information were extremely scanty associated to the biogeochemical cycles of P under seasonal hypoxia and the release of P from sediments at sub-millimeter resolution. In this study, Zr-oxide DGT, together with microelectrode, were employed to determine the physical and chemical characteristics at the SWI. The objectives of this study are: 1) to explore the effects of hypoxia on the release of P in deep-water ecosystem; and 2) to get a deep insight in the release of P from sediments.

2. Materials and methods

2.1. Study site

Hongfeng Reservoir (N 106.24°, E 26.30°), a seasonal hypoxic water body heavily polluted by P, is an ideal field for investigating the release of P under hypoxic condition (Wang et al., 2015b). It has a surface area of 57.2 km², a mean water depth of 10.5 m (max. 45 m), and holds 6.01×10^8 m³ of water (Fig. 1). The average annual

inflow and outflow of HF were 7.06×10^8 m³ and 6.20×10^8 m³ during 1961–2010 (Data source: the Administration Bureau of Hongfeng, Baihua, and Aha Reservoirs). HF provides drinking water for over 3 million people, and any slight deterioration in water quality may cause serious problems. HF is a P-limited eutrophic reservoir with total P (TP) concentration of 0.03–0.10 mg/L and TN/TP ratio of ~30 (Zhu et al., 2013). The concentrations of TP in surface sediments (0–5 cm) ranged from 766 to 4306 mg/kg, with a mean value of 1815 mg/kg (Wang et al., 2015b).

2.2. Sample collection

Sediment cores were collected from the North Central (NC), South Central (SC), and Houwu (HW) on July 27 and December 10, 2014 (Fig. 1). Selecting of these sites was due to the relatively higher concentrations and the release potential of nutrients in sediments (Wang et al., 2015b). The water depth at NC, SC, and HW was 23 m, 16 m, and 9 m, respectively. Sediment cores were taken each time from each site using a gravity corer. Upon collecting, sediment cores were transported to the laboratory immediately, where DGT device was inserted into the cores as soon as possible and cultured for 24 h. The cultivation temperature was set close to the temperature of benthic region. All the cores were sealed by rubber plug and warped with aluminum foil.

2.3. Laboratory experiment of P release from sediments

Surface sediments were collected at NC in April 2016. Upon collecting, all samples were put in sealed bags and carried to the laboratory immediately. After mixed together, these samples were divided into three parts and put into three organic glass cores as quickly as possible. Each core was then filled with filtered benthic water via a siphon and sealed with an organic glass cover. Experiment was conducted in a Perspex box (20 × 20 × 50 cm, width × length × height). The incubation temperature was set at 20 ± 1 °C, close to the temperature of bottom water during summer.

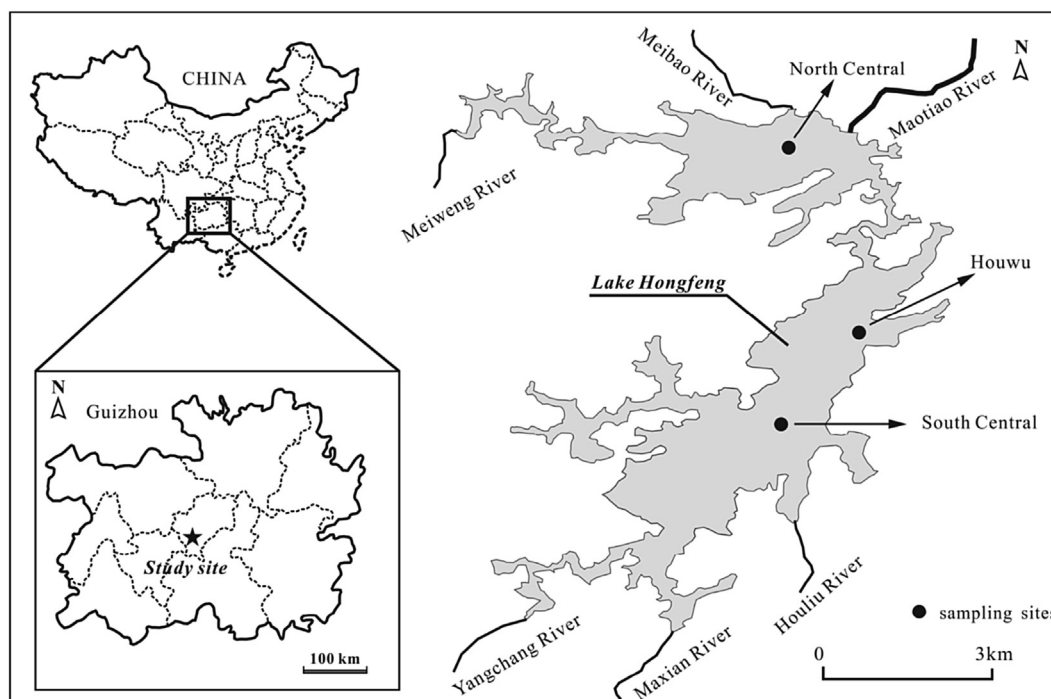


Fig. 1. Study area and the sampling sites.

The experiment was conducted under three DO conditions (i.e., DO < 1.0 mg/L, DO > 9.0 mg/L, and DO ≈ 4–6 mg/L). The hypoxic condition was maintained by purging nitrogen (99%) and air to the overlying water for 2 h twice per day. The incubation lasted for 14 days to ensure a chemical kinetic equilibrium. After that, Zr-oxide gel DGT probes were deployed for 24 h. The 2D distribution of P concentrations on the Zr-oxide gel was analyzed after retrieval. The dissolved active P in the overlying water was analyzed during the incubation experiment.

2.4. Analysis of labile P in sediments

Zr-oxide gel DGT was employed for the analysis of labile P in sediments (Ding et al., 2012). After retrieval, images of labile P in sediments at submillimeter-level were obtained via Gel-based Coloration Technique (Ding et al., 2013). The grayscale intensities of gel surface were obtained using a flat-bed scanner (Canon 5600F) at a resolution of 300 dpi, and then analyzed with Image J (Version 1.46). Concentrations of DGT-labile P in sediments were calculated using the DGT equations (1) and (2) (Zhang et al., 1998; Wang et al., 2015a):

$$C_{DGT} = \frac{M\Delta g}{DA t} = \frac{M_0 \Delta g}{Dt} \quad (1)$$

$$\text{Grayscale} = 270.26 \times \left(1 - e^{-1.32M_0}\right) \quad (2)$$

Where Δg is the diffusive layer thickness (cm), D is the diffusion coefficient of the phosphate in the diffusive layer (cm^2/sec), A is the exposure area of a pixel size (cm^2), t is the deployment time (sec), M_0 is the mass of P accumulated in the gel per unit area ($\mu\text{g}/\text{cm}^2$), and *Grayscale* is the grayscale intensity of the gel surface.

High resolution distributions of labile P in sediments were finally drawn with SigmaPlot (V. 12.0, Systat Software, Inc., USA).

2.5. Microsensors and measurement

A four-channel Microsensor Multimeter (Unisense, Denmark) was employed to determine the vertical profiles of O_2 , H_2S , and pH in sediment core. The spatial resolution of these data was 300 μm . Microsensor (micro-Clark-type) used for O_2 measurement has a sensing-tip diameter of <10 μm , a 90%-response time of 1 s, and a velocity sensitivity of <1–2% (Revsbech, 1989). Before measurement, microsensor was calibrated using an air-saturated calibration solution and a hypoxic solution (~2 g sodium ascorbate in 100 ml of 0.1 M NaOH). H_2S microsensor is a miniaturized amperometric sensor with an internal reference (Jeroschewski et al., 1996). A sulfide standard solution was used for calibration. During the calibration, the sulfide solutions were flushed with nitrogen to avoid oxidation. pH was determined using a miniaturized glass pH electrode with tip diameter down to 10 μm . The pH electrode was calibrated with buffer solution at pH 7 and pH 10 at room temperature and the slope was normally of 52–60 mV/pH-unit.

2.6. Analysis of P fractions in sediments

After the DGT and Microsensor analysis, surface sediments (0–5 cm) in the cores were sectioned at 1-cm interval, and then freeze-dried, ground and sieved (100-mesh) for analysis. TP was determined by the $\text{HClO}_4\text{-H}_2\text{SO}_4$ digestion method (Frankowski et al., 2002). The different forms of P were obtained by a sequential extraction method (Hupfer et al., 1995): 1) $\text{NH}_4\text{Cl-P}$, extracted with 1 M NH_4Cl for 0.5 h; 2) BD-P , extracted with 0.11 M bicarbonate/dithionite for 1 h; 3) NaOH-P , composed of NaOH-srP and

NaOH-nrP (Hupfer et al., 1995), extracted with 1 M NaOH for 16 h; (4) HCl-P , extracted with 0.5 M HCl for 16 h; (5) Residual P, digestion with 30% (v/v) H_2SO_4 and 8% $\text{K}_2\text{S}_2\text{O}_8$ at 121 °C for 30 min, extracted with 1 M HCl for 16 h. Concentrations of P in the extractions were determined using the method developed by Murphy and Riley (1962).

2.7. Analysis of sediment properties

Total organic carbon (TOC) and total nitrogen (TN) were measured by an elemental analyzer (Vario MACRO cube, Elementar, Germany). Before TOC and TN analysis, all samples were pretreated with 1 M HCl overnight to remove carbonates (Horwath and Kessel, 2001). After digested by micro-acid ($\text{HNO}_3\text{-HCl-HF}$), Fe, Mn, and Al in sediments were analyzed by the Inductively Coupled Plasma/Optical Emission Spectrometry. All these data were presented as dry wet basis.

3. Results

3.1. Sediment properties

General characteristics of sediments from different sites were displayed in Table 1. TOC content in sediments ranged from 4.92% to 10.6%, with the highest value at HW, where extensive culture activities occurred in this region during the period of 1987–1999. TN content in sediments was in the range of 0.41%–0.54%, with the highest value at NC. The ratio of TOC/TN ranged from 11.4 to 22.3, indicating a typical mixed origin of organic matter (Meyers, 1997). Relatively high levels of Fe and Al were found both in sediments from NC and HW. However, Mn content in sediments from HW was much less than that in sediments from NC.

3.2. Temporal variation of water chemistry

The vertical profiles of water temperature showed that the water body had a significant thermal stratification at SC and NC from August to September (Fig. 2a). The difference in temperature reached 12 °C between surface water and bottom water. The thermocline was at the depth of 8–14 m. Fig. 2b showed that DO concentration at SC and NC was at least 8.0 mg/L in surface water, but declined sharply below the depth of 4 m and was generally lower than 0.5 mg/L in bottom waters (<12 m).

Monthly profiles of water temperature and DO in water column of HF during 2014 were shown in Fig. 3. Strong temperature and oxygen gradients presented in the warm season (April–September). The depth of the thermocline was at the depth of ~8 m. During June to September, DO concentrations in the bottom water were close to zero near the SWI. The water column was generally well mixed in the cold season (October to December) (Fig. 3).

The vertical variation of TP in the water column of HF was shown in Fig. 4. Although stratification occurred during the period of July to September, variation of TP concentration was small above the thermocline, with a mean value of 0.05 mg/L. Below the thermocline (>12 m), concentration of TP increased sharply at all sites as the depth increased, especially at SC. The maximum

Table 1
Chemical characteristics of sediments from NC, SC, and HW.

Location	TOC(%)	TN(%)	TOC/TN	Fe (g/kg)	Al (g/kg)	Mn (g/kg)
NC	6.15	0.54	11.4	53.7	78.6	0.99
SC	4.92	0.41	11.9	50.5	64.3	0.64
HW	10.6	0.48	22.3	56.3	76.3	0.47

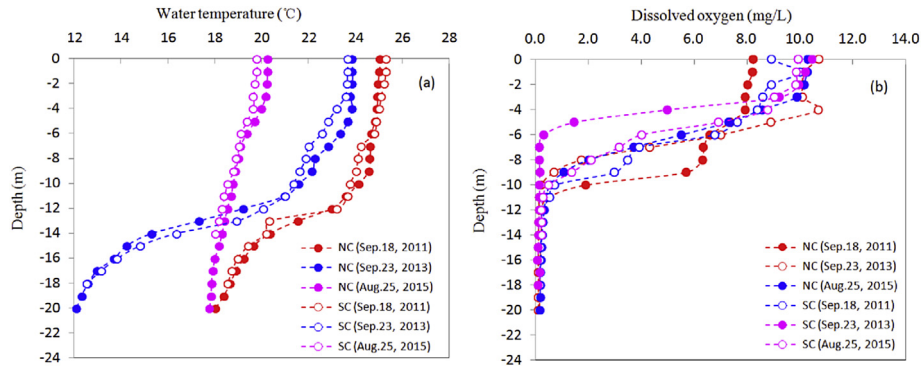


Fig. 2. Profiles of water temperature and dissolved oxygen at SC and NC.

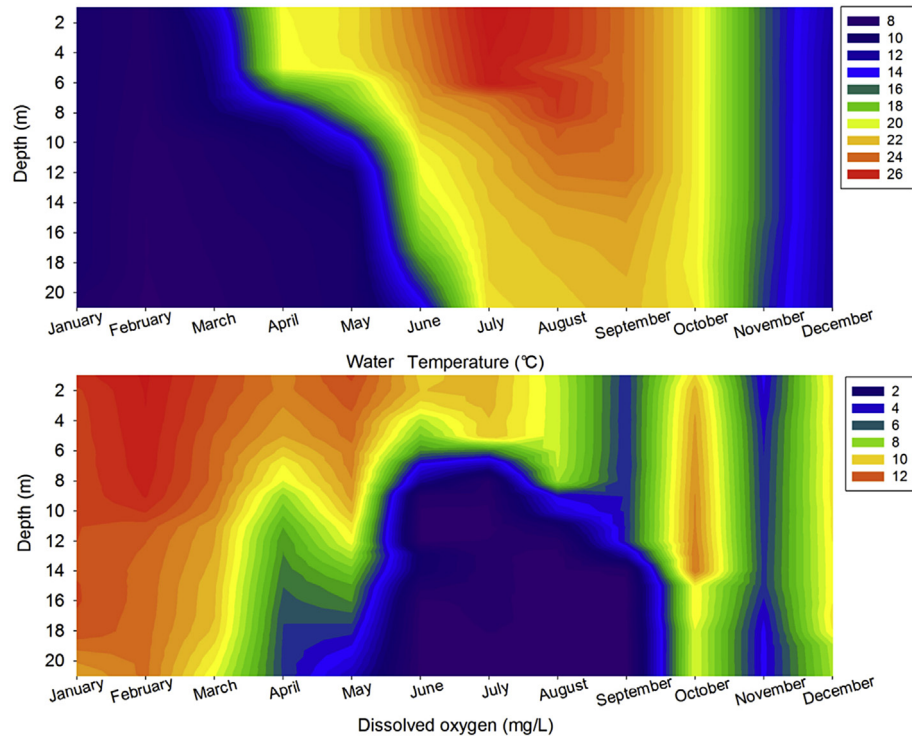


Fig. 3. Variation of water temperature and dissolved oxygen concentrations in water column during 2014.

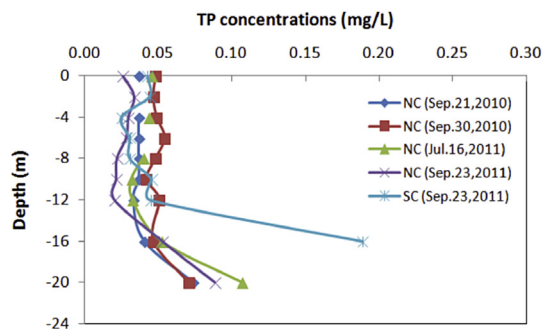


Fig. 4. Vertical profiles of total P in the water column at different sites.

concentration of TP occurred near the SWI. This indicated that the high concentration of TP in bottom waters came from sediments.

3.3. Seasonal variation of labile P in sediments

Seasonal variations of labile P at NC, SC, and HW were shown in Fig. 5. Within the surface layer (0–5 cm), concentrations of labile P were generally increased with depth, although heterogeneity of labile P might occur both in vertical and horizontal direction. At all sites, the mean concentrations of labile P in surface sediments were much higher in summer compared to that in winter. The mean values of the labile P (0–5 cm) at NC, SC, and HW were 0.46, 0.57, and 0.60 mg/L in summer and 0.37, 0.43 and 0.36 mg/L in winter, respectively. As for the labile P at the SWI, the average concentrations at NC, SC, and HW were 0.31, 0.44 and 0.43 mg/L in summer and 0.17, 0.23 and 0.19 mg/L in winter, respectively. The results suggested that large spatial heterogeneity of labile P occurred in the sub-millimeter scale, especially at the horizontal dimension. The relative standard deviation of labile P concentrations within a depth of 35 mm reached 13.8% in the horizontal dimension in summer. Similar phenomena also occurred in the other sediment profiles.

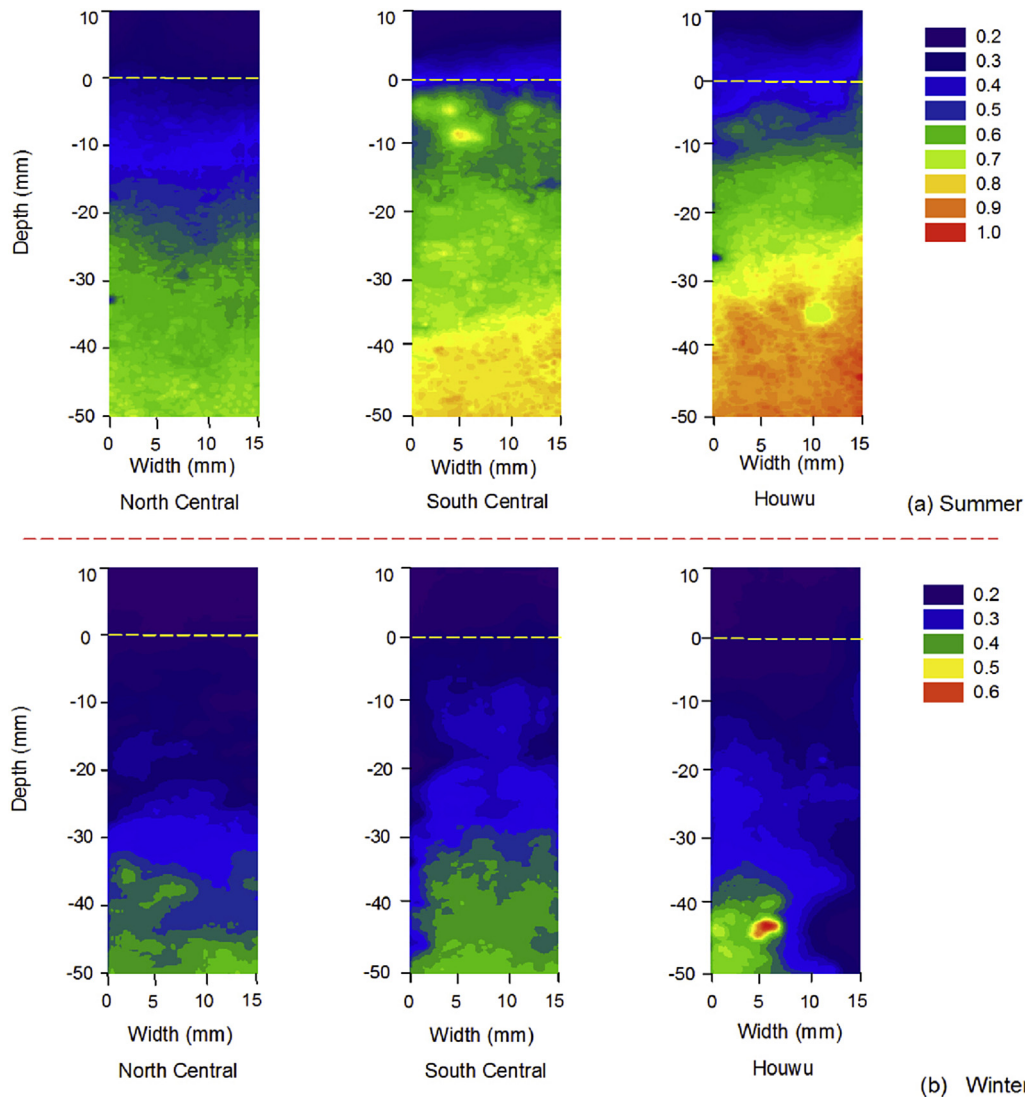


Fig. 5. High-resolution of DGT-labile P at the sediment-water interface at NC, SC, and HW (sediment-water interface is corresponding to the depth of zero).

3.4. Seasonal variation of P fractions in sediments

Seasonal variation of different P fractions in surface sediments was shown in Table 2. In summer, TP concentrations were in the range of 1859–1974 mg/kg (mean of 1941 mg/kg) and the corresponding values were 1917–2151 mg/kg (2070 mg/kg) in winter. NaOH-P was the major fraction of P in sediments, accounting for $43.7 \pm 5.3\%$ of TP in summer and $43.6 \pm 2.0\%$ of TP in winter, followed by Residual-P content, accounting for $22.9 \pm 3.3\%$ of TP in summer and $22.1 \pm 1.6\%$ in winter. Concentrations of BD-P were

slightly higher than that of HCl-P (with mean values of 254 ± 127 mg/kg in summer and 225 ± 70.9 mg/kg in winter), and were much less than that of NaOH-P and Residual-P, with mean values of 342 ± 66.3 mg/kg in summer and 426 ± 31.0 mg/kg in winter. As for concentrations of $\text{NH}_4\text{Cl-P}$, they were very limited in all sediments, accounting for only $\sim 3\%$ of TP in an average. Statistical analysis (*t*-test) showed that significant difference ($P \leq 0.001$, $n = 15$) in content was found only for BD-P between summer and winter. TP concentrations in sediments were lower in summer compared to those in winter, with the difference in values of 177,

Table 2
Seasonal variation of P fractions in sediments from NC, SC, and HW.

Site	Season	P fractions (mg/kg)					
		$\text{NH}_4\text{Cl-P}$	BD-P	NaOH-P	HCl-P	Residual-P	Total-P
NC	Summer	94.0 ± 65.8	273 ± 97.4	932 ± 108.4	232 ± 49.1	444 ± 47.2	1970 ± 215
	Winter	89.5 ± 60.6	393 ± 26.1	963 ± 66.6	262 ± 20.6	444 ± 33.2	2150 ± 145
SC	Summer	21.9 ± 4.7	347 ± 6.0	859 ± 106	140 ± 21.8	490 ± 31.9	1860 ± 106
	Winter	25.4 ± 15.6	433 ± 24.4	860 ± 87.3	143 ± 32.3	456 ± 31.8	1920 ± 88.7
HW	Summer	52.7 ± 3.1	405 ± 35.8	749 ± 69.4	391 ± 31.0	393 ± 21.8	1990 ± 22.9
	Winter	63.4 ± 22.0	454 ± 25.5	886 ± 118	270 ± 53.8	470 ± 14.1	2140 ± 177

58.1, and 151 mg/kg at NC, SC, and HW, respectively. Clearly, this difference was mostly originated from BD–P, accounting for 65.8% of the total variation.

3.5. Seasonal variation of O₂, H₂S and pH in sediments

Seasonal variations of O₂, H₂S and pH in sediments were shown in Fig. 6. In general, O₂ was consumed completely at the surface layers. The penetration depths of O₂ were all less than 4 mm, with the mean value of 1.3 mm in summer and 3.2 mm in winter. H₂S was detectable at the depth of approximate 4 mm in summer and 10 mm in winter. In summer, concentrations of H₂S were rapidly increased with depth and peaked at the depth of ~20 mm, with the maximum values of 4.62 mg/L, 0.22 mg/L, and 0.20 mg/L at NC, SC, and HW, respectively. This indicated that intense reduction of sulfate must have occurred at the surface layer. While in winter, H₂S concentrations increased slowly downward and peaked at the depth of ~30 mm, with the maximum values of 1.26 mg/L, 0.21 mg/L, and 0.09 mg/L at NC, SC, and HW, respectively. The values of pH were in the range of 6.2–7.8, exhibiting a decreasing tendency from the surface to the depth of 20 mm. The pH level was slightly lower in winter than in summer.

3.6. Dissolved active P in overlying water under experimental condition

Under low oxygen (DO < 1.0 mg/L) condition, concentrations of dissolved active P in overlying water evidently increased during the early stage of incubation (0–4 days) and maintained a relatively

high level of 0.15 ± 0.02 mg/L (Fig. 7). This was approximately two or three folds higher than concentrations of dissolved active P in overlying water under DO of 4–6 mg/L or higher than 9 mg/L (Table 3). This implied that hypoxia really facilitates the release of P from sediments.

4. Discussion

4.1. Release of P from sediments

Many mechanisms of the release of P from sediments have been proposed (Fan et al., 2004; Jorcin and Nogueira, 2005; Tang et al., 2013). Potential candidates include the release of BD–P under hypoxic condition (Gomez et al., 1999; Steinberg, 2011), the release of NaOH–srP under alkaline condition (Wilson et al., 2008; Jiang et al., 2008), and the release of NaOH–nrP along with the degradation of organic matter (Wang et al., 2008), etc. Primarily bound to Fe-hydroxides, BD–P is sensitive to oxidation–reduction potential (ORP) (Wilson et al., 2008). It has been widely accepted that anoxia induces the reduction of Fe(III) to Fe(II), resulting in the release of BD–P from sediments (Gomez et al., 1999). NaOH–srP, representing the form of P bound to metal oxides (primarily Fe and Al), is sensitive to pH and is prone to release under alkaline condition (Jiang et al., 2008). NaOH–nrP represents the polyphosphate (poly-P) in sediments. The release of NaOH–nrP from sediments was basically controlled by the degradation of organic matter (OM), associated with the content of TOC, DO and temperature in sediments (Wang et al., 2008). In a word, many factors may influence the release of P from sediments, including the geochemical forms of P and their relative abundance in sediments, the nature of sediment itself and the environmental conditions, such as pH, temperature, and ORP (Nürnberg, 1988; Jorcin and Nogueira, 2005; Rydin et al., 2011; Tang et al., 2013).

In the present work, TP concentrations in sediments in summer were less than that in winter. If the geochemical forms of P are taken into account, this difference was mainly originated from BD–P in sediments (Table 2), because other forms of P in sediments were little varied between summer and winter. Meanwhile, concentrations of labile P both at the SWI and in the surface sediments were markedly higher in summer than in winter. These suggested that the P release from sediments happened in summer and was

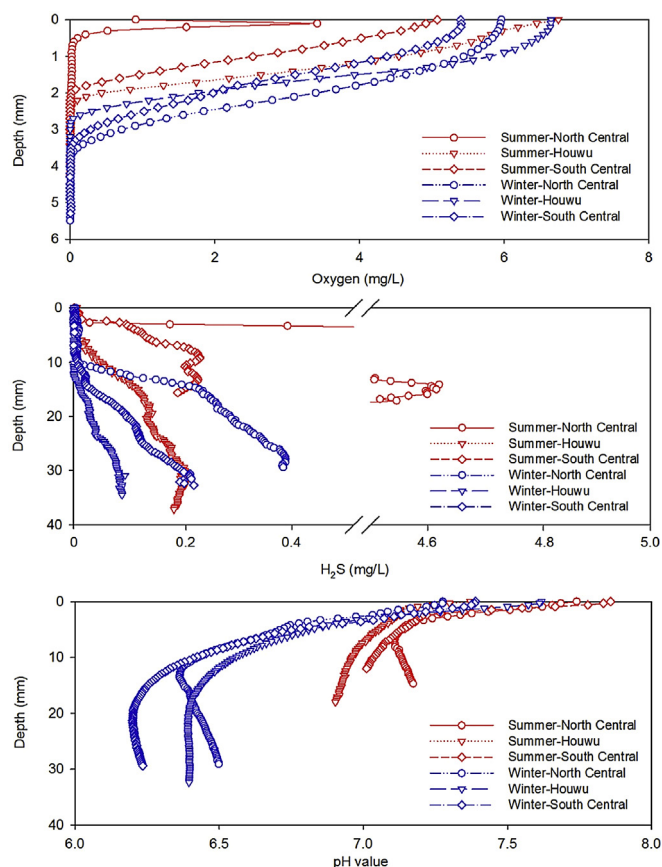


Fig. 6. Seasonal profiles of the chemical parameters (oxygen, hydrogen sulfide, and pH) at the sediment-water interface of NC, SC, and HW.

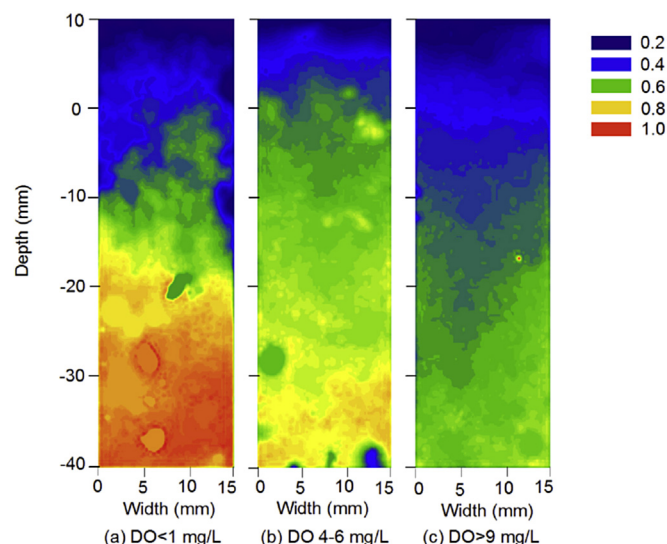


Fig. 7. Two-dimension distributions of DGT-labile P at the sediment-water interface of sediments under different conditions (incubation temperature: 20 ± 1 °C).

Table 3
Dissolved active P in overlying water during incubation.

Incubation time (day)	Dissolved active P (mg/L)		
	DO < 1 mg/L	DO ≈ 4–6 mg/L	DO > 9 mg/L
0	0.03	0.02	0.02
2	0.11	0.04	0.04
4	0.15	0.05	0.06
6	0.16	0.04	0.06
8	0.17	0.05	0.04
10	0.14	0.06	0.03
14	0.12	0.03	0.04

mainly due to the release of BD–P from sediments. If other environmental factors are taken into account, the values of pH in sediments from HF (pH = 6.2–7.8) varied insignificantly both in summer and in winter. pH variation is impossible to cause the significant release of NaOH–srP from sediments (Jin et al., 2006). As for the release of NaOH–nrP from sediments, it was basically controlled by the degradation of organic matter (OM). High DO and temperature in sediments are helpful for the degradation of OM. However, sediments are clearly in hypoxic condition in summer (Figs. 2 and 3). This implied that the possibility of the release of NaOH–nrP from sediments was also quite low. In addition, no significant difference was found for the content of NaOH–P between summer and winter. Results from the incubation experiments positively supported that hypoxia promotes the release of P from sediments.

All in all, all evidences point to these facts that: 1) hypoxia promotes the release of P from sediments, 2) the release of P from sediments under hypoxic condition mostly comes from the release of BD–P, and 3) the huge burden of P and BD–P in sediments (Wang et al., 2015b), increase the possibility of eutrophication in HF, especially in summer.

4.2. Deep insight in the release of P from sediments

The P release across the SWI has been demonstrated to occur at micro-scale level (Ding et al., 2012). In fact, the release of P is a collective result of several geochemical processes, which is often coupled with the geochemical cycle of iron and sulfur in sediments (Caraco et al., 1989; Jensen et al., 1992; Motelica-Heino et al., 2003; Kuster-Heins et al., 2010; Martynova, 2011). The simultaneous release of Fe and S(-II) strongly suggests the coexistence of iron and sulfide in the same sediment layer where Fe(III) and sulfate might act as electron acceptors for oxidations of reactive organic matter (Lehtoranta and Heiskanen, 2003; Naylor et al., 2004). In addition, the process of sulfate reduction was also proved to affect the P release from sediments (Roden and Edmonds, 1997; Sinkko et al., 2013). On the one hand, the product of sulfate reduction (H_2S) promoted the formation of iron sulfides, inducing the activation of Fe–P. Besides, sulfate reduction resulted in acidification of the SWI, causing desorption of PO_4^{3-} from iron compounds. In short, not only a reduction of ferric iron, but also a conversion of Fe(II) to iron sulfide resulted in PO_4^{3-} release. Thus, the cycle of iron and sulfide can influence P availability in sediments.

In the present study, the simultaneous release of P and S(-II) was also observed (Figs. 5 and 6). Concentrations of labile P in sediments were much higher in summer than that in winter (Fig. 5), and the concentrations of hydrogen sulfide in all sediment profiles had similar characteristics (Fig. 6), indicating simultaneous release of P and S(-II). In HF, a large BD–P (Fe-bound P) pool was detectable in the surficial sediment layer (Table 2) with legible seasonal variation. This is consistent with the records of redox condition at the SWI (Fig. 6). Concentrations of BD–P were relatively low when

sediment was sulfidic and reduced in summer, and reached its maximal level when the sediment was well oxidized in winter. The synchronization between BD–P and sulfide implied that the coupled cycle of Fe–P–S in sediments under seasonal hypoxic condition. In summer (hypoxic condition), phosphate will be released as the oxyhydroxides reacts with sulfide to form iron sulfide. The release of P from iron-bound pool would significantly alter the P status in sediments and the diffusive fluxes into the water column, because iron-bound P represents one of the major fractions of TP in sediments from HF. These findings suggested that the release of P from sediments under hypoxia condition is associated with coupled cycles of “P–Fe–S”. This is also supported by the fact that Fe plays a central role in the remobilization of P in sediments (Amirbahman et al., 2003).

Evidences from the present work confirmed that hypoxia strongly promotes the release of P from sediments. The release of P from sediments was assumed to be jointly controlled by DO and temperature based on the field investigation. However, results from the incubation experiment implied that DO is the all-important factor controlling the release of P from sediments, because significant difference in sediment P release existed even if temperature was set to be the same. Interestingly, micro-scale profiles of oxygen detected by microelectrodes showed that oxygen was present at the SWI both in summer and in winter (Fig. 6). Although exact reasons remain unclear how this can happen at the SWI, this phenomenon deserves more efforts.

5. Conclusion

Seasonal hypoxia stimulated the release of P from sediments and resulted in the seasonal variation of labile P in sediments in Hongfeng Reservoir. The concentrations of the labile P in the surface 5-cm sediments were markedly higher in summer than in winter. The concentrations of TP in sediments were reduced by ~6% within ~150 days (from April to September), among which 65.8% was BD–P. High concentrations of H_2S in sediments promoted the formation of iron sulfides and the release BD–P in summer. The internal P-loadings induced by hypoxia, especially after a reduction of external P-loading, should be paid more attention in eutrophic deep-water reservoirs, Southwest China.

Acknowledgements

This work was financially supported by the National Key Research and Development Project by MOST of China (No. 2016YFA0601003), the Chinese NSF projects (No. 41403113 and No. 41303097), and the Environmental Science and Technology Project and the Major Application of Basic Research Project of Guizhou province ([2015]2001).

Appendix A. Supplementary data

Supplementary data related to this article can be found at <http://dx.doi.org/10.1016/j.envpol.2016.08.013>.

References

- Adhikari, P.L., White, J.R., Maiti, K., Nguyen, N., 2015. Phosphorus speciation and sedimentary phosphorus release from the Gulf of Mexico sediments: implication for hypoxia. *Estuar. Coast. Shelf S.* 164, 77–85.
- Alvisi, F., Cozzi, S., 2016. Seasonal dynamics and long-term trend of hypoxia in the coastal zone of Emilia Romagna (NW Adriatic Sea, Italy). *Sci. Total Environ.* 541, 1448–1462.
- Amirbahman, A., Pearce, A.R., Bouchard, R.J., Norton, S.A., Kahl, J.S., 2003. Relationship between hypolimnetic phosphorus and iron release from eleven lakes in Maine, USA. *Biogeochemistry* 65 (3), 369–385.
- Bianchi, T.S., 2007. *Biogeochemistry of Estuaries*. Oxford University Press pp706.

- Bianchi, T.S., DiMarco, S.F., Cowan, J.H., Hetland, R.D., Chapman, P., Day, J.W., Allison, M.A., 2010. The science of hypoxia in the Northern Gulf of Mexico: a review. *Sci. Total Environ.* 408 (7), 1471–1484.
- Breitburg, D., 2002. Effects of hypoxia, and the balance between hypoxia and enrichment, on coastal fishes and fisheries. *Estuar. Coast.* 25 (4B), 767–781.
- Bunch, A.J., Allen, M.S., Gwinn, D.C., 2015. Influence of macrophyte-induced hypoxia on fish communities in lakes with altered hydrology. *Lake Reserv. Manag.* 31 (1), 11–19.
- Caraco, N.F., Cole, J.J., Likens, G.E., 1989. Evidence for sulfate-controlled phosphorus release from sediments of aquatic systems. *Nature* 341 (6240), 316–318.
- Conley, D.J., Björck, S., Bonsdorff, E., Carstensen, J., Destouni, G., Gustafsson, B.G., Hietanen, S., Kortekaas, M., Kuosa, H., Markus Meier, H.E., Müller-Karulis, B., Nordberg, K., Norkko, A., Nürnberg, G., Pitkänen, H., Rabalais, N.N., Rosenberg, R., Savchuk, O.P., Slomp, C.P., Voss, M., Wulff, F., Zillén, L., 2009a. Hypoxia-related processes in the Baltic sea. *Environ. Sci. Technol.* 43 (10), 3412–3420.
- Conley, D.J., Paerl, H.W., Howarth, R.W., Boesch, D.F., Seitzinger, S.P., Havens, K.E., Lancelot, C., Likens, G.E., 2009b. Controlling eutrophication: nitrogen and phosphorus. *Science* 323, 1014–1015.
- Davison, W., Fones, G.R., Grime, G.W., 1997. Dissolved metals in surface sediment and a microbial mat at 100- μm resolution. *Nature* 387 (6636), 885–888.
- Diaz, R.J., 2001. Overview of hypoxia around the world. *J. Environ. Qual.* 30 (2), 275–281.
- Ding, S.M., Sun, Q., Xu, D., Jia, F., He, X., Zhang, C.S., 2012. High-resolution 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, S.M., Wang, Y., Xu, D., Zhu, C.G., Zhang, C.S., 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.
- Ding, S.M., Xu, D., Sun, Q., Yin, H.B., Zhang, C.S., 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.
- Djakovic, T., Supic, N., Aubry, F.B., Degobbis, D., Giani, M., 2014. Mechanisms of hypoxia frequency changes in the northern Adriatic Sea during the period 1972–2012. *J. Mar. Syst.* 141, 179–189.
- Fan, C.X., Zhang, L., Qin, B.Q., Wang, S.M., Hu, W.P., Zhang, C., 2004. Estimation on dynamic release of phosphorus from wind-induced suspended particulate matter in Lake Taihu. *Sci. China Ser. D* 47 (8), 710–719.
- Frankowski, L., Bolaiek, J., Szostek, A., 2002. Phosphorus in bottom sediments of Pomeranian Bay (Southern Baltic-Poland). *Estuar. Coast. Shelf S.* 54, 1027–1038.
- Gomez, E., Durillon, C., Rofes, G., Picot, B., 1999. Phosphate adsorption and release from sediments of brackish lagoons: pH, O₂ and loading influence. *Water Res.* 33, 2437–2447.
- Horwath, W.R., Kessel, C.V., 2001. Acid fumigation of soils to remove carbonates prior to total carbon or carbon-13 isotopic analysis. *Soil Sci. Soc. Am. J.* 65 (6), 1853–1856.
- Howarth, R., Chan, F., Conley, D.J., Garnier, J., Doney, S.C., Marino, R., Billen, G., 2011. Coupled biogeochemical cycles: eutrophication and hypoxia in temperate estuaries and coastal marine ecosystems. *Front. Ecol. Environ.* 9 (1), 18–26.
- 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.
- Jensen, H.S., Kristensen, P., Jeppesen, E., Skytthe, A., 1992. Iron:phosphorus ratio in surface sediment as an indicator of phosphate release from aerobic sediments in shallow lakes. *Hydrobiologia* 235/236, 731–743.
- Jeroschewski, P., Steuckart, C., Kühl, M., 1996. An amperometric microsensor for the determination of H₂S in aquatic environments. *Anal. Chem.* 68 (24), 4351–4357.
- Jiang, X., Jin, X.C., Yao, Y., Li, L.H., Wu, F.C., 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, X.C., Wang, S.R., Pang, Y., Wu, F.C., 2006. 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 (2), 288–295.
- Jorcin, A., Nogueira, M.G., 2005. Temporal and spatial patterns based on sediment and sediment–water interface characteristics along a cascade of reservoirs (Parana-panama River, south-east Brazil). *Lakes Reserv. Manag.* 10, 1–12.
- Kuster-Heins, K., de Lange, G.J., Zabel, M., 2010. Benthic phosphorus and iron budgets for three NW African slope sediments: a balance approach. *Biogeochemistry* 7 (2), 469–480.
- Lehtoranta, J., Heiskanen, A.S., 2003. Dissolved iron:phosphate ratio as an indicator of phosphate release to oxic water of the inner and outer coastal Baltic Sea. *Hydrobiologia* 492 (1), 69–84.
- Lin, P., Klump, J.V., Guo, L.D., 2016. Dynamics of dissolved and particulate phosphorus influenced by seasonal hypoxia in Green Bay, Lake Mich. *Sci. Total Environ.* 541, 1070–1082.
- Martynova, M.V., 2011. Fe/P concentration ratio in Mozhaisk reservoir deposits as an indicator of phosphate sorption. *Water Res.* 38 (2), 211–219.
- Meyers, P.A., 1997. Organic geochemical proxies of paleoceanographic and paleolimnologic, and paleoclimatic processes. *Org. Geochem.* 27 (5–6), 213–250.
- Motelica-Heino, M., Naylor, C., Zhang, H., Davison, W., 2003. Simultaneous release of metals and sulfide in lacustrine sediment. *Environ. Sci. Technol.* 37 (19), 4374–4381.
- Murphy, J., Riley, J.P., 1962. A modified single solution method for the determination of phosphate in natural waters. *Anal. Chim. Acta* 27, 31–36.
- Naylor, C., Davison, W., Motelica-Heino, M., Van Den Berg, G.A., Van Der Heijden, L.M., 2004. Simultaneous release of sulfide with Fe, Mn, Ni and Zn in marine harbour sediment measured using a combined metal/sulfide DGT probe. *Sci. Total Environ.* 328 (1–3), 275–286.
- Nürnberg, G.K., 1988. Prediction of phosphorus release rates from total and reductant-soluble phosphorus in hypoxic lake sediments. *Can. J. Fish. Aquat. Sci.* 45 (3), 453–462.
- Pedersen, O., Pulido, C., Rich, S.M., Colmer, T.D., 2011. *In situ* O₂ dynamics in submerged isoetes Australis: varied leaf gas permeability influences underwater photosynthesis and internal O₂. *J. Exp. Bot.* 62 (13), 4691–4700.
- Pizarro, J., Belzile, N., Filella, M., Leppard, G.G., Negre, J.C., Perret, D., Buffle, J., 1995. Coagulation/sedimentation of submicron iron particles in a eutrophic lake. *Water Res.* 29 (2), 617–632.
- Qin, B.Q., Zhu, G.W., Luo, L.C., Gao, G., Gu, B.H., 2006. Estimation of internal nutrient release in large shallow Lake Taihu, China. *Sci. China Ser. D* 49, 38–50.
- Rabalais, N.N., Turner, R.E., Sen Gupta, B.K., Boesch, D.F., Chapman, P., Murrell, M.C., 2007. Hypoxia in the northern Gulf of Mexico: does the science support the plan to reduce, mitigate, and control hypoxia? *Estuar. Coast.* 30 (5), 753–772.
- Reddy, K.R., Newman, S., Osborne, T.Z., White, J.R., Fitz, H.C., 2011. Phosphorus cycling in the greater Everglades Ecosystem: legacy phosphorus implications for management and restoration. *Crit. Rev. Environ. Sci. Technol.* 41 (S1), 149–186.
- Revsbech, N.P., 1989. An oxygen microelectrode with a guard cathode. *Limnol. Oceanogr.* 34, 474–478.
- Robertson, D., Teasdale, P.R., Welsh, D.T., 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.
- Roden, E.E., Edmonds, J.W., 1997. Phosphate mobilization in iron-rich anaerobic sediments microbial Fe(III) oxides reduction versus iron-sulfide formation. *Arch. Hydrobiol.* 139, 347–378.
- Roy, E.D., Nguyen, N.T., Bargu, S., White, J.R., 2012. Internal loading of phosphorus from sediments of Lake Pontchartrain (Louisiana, USA) with implications for eutrophication. *Hydrobiologia* 684 (1), 69–82.
- Rydin, E., Karlsson, M.J.M., Jonsson, P., 2011. P release from coastal Baltic Sea sediments as estimated from sediment profiles. *Estuar. Coast. Shelf S.* 92, 111–117.
- Sinkko, H., Lukkari, K., Sihvonen, L.M., Sivonen, K., Leivuori, M., Rantanen, M., Paulin, L., Lyra, C., 2013. Bacteria contribute to sediment nutrient release and reflect progressed Eutrophication-driven hypoxia in an organic-rich continental sea. *Plos One* 8 (6), 61–67.
- Søndergaard, M., Jensen, J.P., Jeppesen, E., 2003. Role of sediment and internal loading of P in shallow lakes. *Hydrobiologia* 506, 135–145.
- Steinberg, C.E.W., 2011. Aerobic phosphorus release from shallow lake sediments. *Sci. Total Environ.* 409 (21), 4640–4641.
- Stockdale, A., Davison, W., Zhang, H., 2008. High-resolution twodimensional 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, W.Q., Wang, C., Shan, B.Q., 2013. Biological invasions induced phosphorus release from sediments in freshwater ecosystems. *Colloid Surf. A* 436 (35), 873–880.
- Wang, J.F., Chen, J.A., Ding, S.M., Luo, J., Xu, Y., 2015a. Effects of temperature on phosphorus release in sediments of Hongfeng Reservoir, southwest China: an experimental study using diffusive gradients in thin-films (DGT) technique. *Environ. Earth Sci.* 74, 5885–5894.
- Wang, J.F., Chen, J.A., Christopher, D., Yang, H.Q., Dai, Z.H., 2015b. Spatial distribution, fractions, and potential release of sediment phosphorus in the Hongfeng Reservoir, southwest China. *Lake Reserv. Manag.* 31, 214–224.
- Wang, S.R., Jin, X.C., Zhao, H.C., Zhou, X.N., Wu, F.C., 2007. Effect of organic matter on the sorption of dissolved organic and inorganic phosphorus in lake sediments. *Colloid Surf. A* 297 (1–3), 154–162.
- Wang, S.R., Jin, X.C., Zhao, H.C., Zhou, X.N., Wu, F.C., 2008. Effects of organic matter on phosphorus release kinetics in different trophic lake sediments and application of transition state theory. *J. Environ. Manag.* 88 (4), 845–852.
- Warnken, K.W., 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, T.A., Norton, S.A., Lake, B.A., Amirbahman, A., 2008. Sediment geochemistry of Al, Fe, and P for two historically acidic, oligotrophic Maine lakes. *Sci. Total Environ.* 404, 269–275.
- Yang, X.K., Lu, X.X., 2014. Drastic change in China's lakes and reservoirs over the past decades. *Sci. Rep.* 4, 6041. <http://dx.doi.org/10.1038/srep06041>.
- 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, Y.L., Wu, Z.X., Liu, M.L., He, J.B., Shi, K., Zhou, Y.Q., Wang, M.Z., Liu, X.H., 2015. Dissolved oxygen stratification and response to thermal structure and long-term climate change in a large and deep subtropical reservoir (Lake Qian-daohu, China). *Water Res.* 75, 249–258.
- Zhu, Y.R., Zhang, R.Y., Wu, F.C., Qu, X.X., Xie, F.Z., Fu, Z.Y., 2013. Phosphorus fractions and bioavailability in relation to particle size characteristics in sediments from Lake Hongfeng, Southwest China. *Environ. Earth Sci.* 69 (1), 305–305.