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To cite this article: Zhiping Yang, Tao Liang, Kexin Li, Qian Zhang & Lingqing Wang (2016): The diffusion fluxes and sediment activity of phosphorus in the sediment–water interface of Poyang Lake, Journal of Freshwater Ecology, DOI: 10.1080/02705060.2016.1181113

To link to this article: http://dx.doi.org/10.1080/02705060.2016.1181113
The diffusion fluxes and sediment activity of phosphorus in the sediment–water interface of Poyang Lake

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ABSTRACT
The dissolved reactive phosphorous (DRP) in pore water releases into the water body through the sediment–water interface. The DRP concentrations in the water and sediment of Poyang Lake were determined by high-resolution pore diffusion balance (HR-Peeper) and Zr-oxide diffusive gradients in thin films (Zr-oxide DGT) techniques. The range of the DRP concentrations in the pore water samples of different sampling sites was 30–360 ng/cm³. The diffusion fluxes of DRP in the sediment–water interface were calculated based on the DRP concentration gradients. The range of DRP flux in Poyang Lake was 4.78–40.5 ng m⁻² d⁻¹ with an average value of 14.7 ng m⁻² d⁻¹. The results showed that the P diffusion flux was higher in the middle of the Poyang Lake than both upstream and downstream of the lake.

KEYWORDS
Phosphorous; high-resolution pore water diffusion balance technology (HR-Peeper); Zr-oxide diffusive gradients in thin films (Zr-oxide DGT); pore water; sediment; lake

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JOURNAL OF FRESHWATER ECOLOGY, 2016
http://dx.doi.org/10.1080/02705060.2016.1181113

Introduction

Phosphorus (P) is a major nutrient for aquatic biota and plays a critical role in limiting primary productivity in aquatic ecosystems (Hong 2011; Martínez-Soto & Martínez 2012). Increased P input can cause eutrophication, which causes floating algae overgrowth and can even lead to algae blooms (Berelson et al. 1998; Jiang et al. 2010). Phosphorous in sediments releases into the water body by two ways: sediment disturbance and interstitial water diffusion (Mitchell and Baldwin 1998; Spears et al. 2013; Wang and Liang 2015). The dissolved reactive phosphorous (DRP) in the pore water releases into the water body through the sediment–water interface which is an important avenue for P release and a sensitive indicator of the geochemical characteristics of sediment P (Pitkanen et al. 2001; Kuwabara et al. 2003). The sediment–water interface is the boundary environment that varies widely in physical, chemical, and biological characteristics (Ullman & Sandstron 1987; Perkins and Underwood 2001; Jiang et al. 2008). The migration and transformation of P at the sediment–water interface is quite complicated, so high-resolution technologies are needed to characterize these complex mechanisms (Ding et al. 2012; Zhang et al. 2014).

Interface processes, especially the migration and transformation of nutrients, and the corresponding ecological effects are not only significant to lake biogeochemistry but also constitute the scientific basis for evaluation, prediction, and control of lake eutrophication (Chen et al. 2003; Tian and Zhou 2007; Hickey & Gibbs 2009; Testa et al. 2013). The evaluation of the reactivation process and calculation of the flux of sediment P rely on a high spatial resolution of the concentration
gradient of pore water P (Rozan et al. 2002; Kopacek et al. 2007). The traditional method to isolate pore water is centrifugation (Xu et al. 2012; Zhang et al. 2014). Although the method is simple, the vertical stratification is ruined and the overlying water is difficult to collect (Zhang & Davison 1995; Ding et al. 2012).

In recent years, many new methods have been developed and have facilitated research of the environmental micro-interface. The diffusive gradients in thin films (DGT) and the high-resolution dialysis technique (HR-Peeper) can provide high vertical spatial resolution for DRP as low as millimeters (Monbet et al. 2007; Ding et al. 2012; Xu et al. 2012). The Zr-oxide DGT is an in situ, dynamic, and high-resolution technique for sampling DRP in sediments and it is based on the DGT theory developed by Davison and Zhang (1994). These techniques have been used successfully for imaging the heterogeneous distribution of labile P, especially its concentration gradient in the vicinity of the sediment–water interface (Chen et al. 2016).

In this research, HR-Peeper and Zr-oxide DGT techniques were used to obtain the vertical distribution of DRP in sediments from Poyang Lake. In order to analyze the DRP buffering characteristics of solid reactive P in pore water, the diffusion fluxes of P at the sediment–water interface were calculated. The P reaction processes in shallow lakes are discussed based on the analysis of the environmental micro-interface. The micro-interface behavior and mechanism of internal P cycling will provide the scientific basis for studying internal pollution in shallow lakes.

Methods

Site description

Poyang Lake is the largest freshwater lake in China and an important freshwater resource. The lake is a seasonally shallow lake in the middle and lower reaches of the Yangtze River (28° 24’ N—29° 46’ N, 115° 49’ E—116° 46’ E; Figure 1). The flow of Poyang Lake into the Yangtze River accounts for one-fifth of the mainstream flow of the river. The basin area is 1.622 × 10^5 km^2, accounting for 9% of the Yangtze River Basin. The average annual run-off is 145 billion m^3, accounting for 15% of water in the Yangtze River Basin.

Poyang Lake has a humid subtropical monsoon climate with an annual average temperature of 16.5—17.8 °C and an average annual precipitation of 1570 mm. The flood season of the lake is from April to September and the dry season is from October to March. The area and volume of Poyang Lake differ greatly between the two seasons. The length of the lake is 173 km, the maximum width is 70 km, and the average width is 16.9 km. Poyang Lake basin is surrounded by Shi Zhong, Lu, San Qing, and Long Hu Mountains, the Yangtze River is to the north, and the Ganjian and Fuhe Rivers are to the south. Water drains into the Yangtze River in Hukou County. With the rapid economic development of the Poyang Lake River Basin in recent years, environmental problems have become increasingly prominent, especially the decline in water quality and increasing eutrophication.

Sampling devices

The Peeper device is made of organic glass and comprises a series of chambers (Figure 2). Each chamber side is covered with a layer of a dialysis membrane that is biologically inert and has a pore size of 0.45 μm. Ultra-pure water is placed into these chambers prior to analysis. Equilibrium of soluble ions and molecules on either side of the dialysis membrane is reached after diffusion through the membrane. The volume of each chamber and the space between chambers can be changed according to the experimental need. Peepers can acquire the complete profile of the interface between the overlying water and pore water. However, peepers have the disadvantage that the sampler needs to be in the sediments for a certain period of time to reach equilibrium before the pore water is sampled. In this study, the equilibrium time was two days (Yang et al. 2011).
The Zr-oxide DGT device (2.5 × 18 cm) comprises layers of filtration, diffusion, and fixed films (Figure 3). The filtration film, generally made of cellulose nitrate, is located on the external side of the DGT device. It has a uniform surface pore diameter, stable structure, and 0.13 mm thickness. The diffusion film is generally made of polyacrylamide gel (Zhang & Davison 1995) and the diffusion coefficients at different temperatures can be found at http://dgtresearch.com. The fixed film is
made by adding fixing agent to a gel solution and its ability to fix is dependent on the type of fixing agent and its performance.

Ions diffuse through the diffusion film and then are quickly captured by the fixed film. The active ion concentration near the fixed film is kept at zero, keeping the diffusion gradient constant. A linear concentration gradient is formed within the diffusion film. During the enrichment time, the concentration of target ions outside the external medium ($C_{DGT}$) can be calculated after determining the quantity of ions in the fixed film:

$$C_{DGT} = \frac{M\Delta g}{DAt}$$  \hspace{1cm} (1)

where $M$ equals the amount of accumulated ions in the fixed film ($\mu$g); $\Delta g$ equals the thickness of the diffusion film (cm, can be chosen according to the actual need; Heinen and McManus 2004); $D$ equals the diffusion rate of ions in the diffusion film ($7.34 \text{ cm}^2/\text{s}$ at $25^\circ \text{C}$), which is related to temperature, the composition of the diffusion film, and the characteristics of the ion itself; $A$ equals the contact area of the DGT device to outside ($\text{cm}^2$); $t$ equals the diffusion time (s); and $C_{DGT}$ equals the average concentration of ions in the external solution during the sampling period ($\text{mg/cm}^3$).

**Sampling and analysis**

Six sediment cores were taken from Poyang Lake with a gravity sampler with an organic glass tube ($\Phi 110 \times 500 \text{ mm}$). The location of samples, which was determined by GPS, is shown in Figure 1. In order to avoid disturbance to the sediment interface, both ends of the tube were sealed with a rubber stopper. All samples were stored vertically within 6 h.
A Zr-oxide DGT device was used in combination with an HR-Peeper device. Deionized water was added to the devices and left for 24 h. After incubation with deionized water, the sampling devices were vertically placed into the cores. After 48 h, the devices were removed, and the location of the sediment–water interface was determined. The surface of the DGT was then flushed with ultra-pure water and it was placed in a plastic bag. HR-Peeper samples were frozen with dry ice and stored at $-17 \, ^\circ\text{C}$. The film was cut into approximately 3 mm fragments and sequentially transferred to 1.5 mL centrifuge tubes. Sodium hydroxide (0.2 M) was added to the films according to the quantity volume ratio of the film (1:10) and incubated for 16 h. The concentration of DRP was determined using ammonium molybdate colorimetry.

**Flux calculation**

The diffusive flux of DRP, $F$ (mol cm$^{-2}$ s$^{-1}$) at the sediment–water interface can be estimated from the pore water profile of DRP using Fick’s first law:

$$ F = \phi_0 D \frac{\partial C}{\partial x} \bigg|_{x = 0} $$

(2)
where $\Phi_0$ is the porosity of the surface sediments, $D_s$ (cm$^2$/s) is the diffusion coefficient for the DRP in the diffusion layer, and $(\delta C/\delta x)$ at $x = 0$ is the pore-water concentration gradient.

The sediment curvature is difficult to directly measure. Ullman gave the empirical relationship between the true diffusion coefficient $D_s$ and porosity $\varphi$:

$$D_s = \varphi D_0 \quad \varphi < 0.7 \quad (3)$$

$$D_s = \varphi^2 D_0 \quad \varphi > 0.7 \quad (4)$$

In these formulas, $D_0$ is the diffusion coefficient of an infinitely diluted solution.

Temperature and ionic form have an impact on $D_0$. The diffusion coefficient used in this study was corrected for the in-situ temperature (28 °C) at Poyang Lake. This study was performed at 25 °C, so for $\text{PO}_4^{3-}$, $D_0 = 7.34$ cm$^2$/s. The amount of DRP diffusive release from the sediment-water interface obeyed Fick’s first law. Pore water and overlying water P concentrations were exponentially fitted with depth. The first derivative ratio spectra of depth x can then be calculated.

**Results and discussion**

**Distribution of DRP in pore water**

Measured with the HR-Peeper, the DRP concentrations in the pore water of different sampling points, P1 through P6 were 30, 360, 52, 30, 244, and 55 ng/cm$^3$, respectively. The active DRP concentrations in the pore water and sediments were measured by HR-Peeper and DGT techniques, respectively (Figure 4).

The DRP concentration in P1 increased sharply from a depth of −4 to −50 mm, and then slightly decreased until a depth of −80 mm, followed by a slight increase until the final depth of −100 mm. The DRP concentration in P2 (Xingzi County) was relatively stable and increased sharply from a depth of −10 mm to −24 mm, then sharply decreased from −24 to −45 mm, followed by a slight increase until the lowest depth. The DRP concentration in P3 (Laoye Temple) increased with depth. The DRP concentration in P4 (Mid-lake) increased from a depth of −20 to −50 mm, sharply decreased until −60 mm, then slightly increased until −80 mm, and then slightly decreased until the largest depth of −106 mm. In P5 (Army Hill Lake north), the DRP concentration increased with depth while in P6 (Army Hill Lake West), the DRP concentration increased intermittently with depth. The increasing reduction potential with depth is conducive to the release of mineral P and, therefore, the DRP concentration increased with the sediment depth. However, with increasing sediment depths, sediment porosity and water flow gradually declined and the pH gradually returned to be weakly alkaline (Jin et al. 2006; Xu et al. 2012). Weakly alkaline pH resulted in a gradually strengthened diagenesis and transformation of inorganic P with release potential to stable phosphorus minerals. As well, the decrease of water flow in the sediments resulted in a decrease in microbial activity and gradual decrease of organic compound mineralization (Spohn & Kuzyakov 2013; Zhu et al. 2013). The conversion rate of organic phosphorus to inorganic P also decreased. The DRP concentration first increased with the depth but then decreased with increasing depth. The maximum value of the DRP concentration at a certain depth can be considered an indicator of the dissolved P generated from P minerals plus the degradation of organic P in the sediments.

Overall, the DRP concentration in Poyang Lake sediments increased with depth. The distributions of DRP in sediments and the corresponding pore waters were similar, as measured with DGT ($C_{\text{DGT}}$) and HR-Peeper, respectively. The $C_{\text{DGT}}$ in sediments was much lower than that in the corresponding pore waters. This difference was due to the fact that Peeper analysis is based on a dynamic equilibrium, while DGT is based on the kinetic theory.
**Sediment reactivity and resupply kinetics**

The ratio, $R$, of the DRP concentration measured by HR-Peeper and the DRP concentration measured by Zr-oxide DGT (DRP$_{DGT}$/DRP$_{PEEPER}$) can reflect the buffering ability of sediment solids in the pore water (Ding et al. 2015). A value close to 1 indicates very rapid resupplying, while a value...
close to 0.05 indicates very slow resupplying. The \( R \) values for the six sampling sites P1 through P6 were 0.269, 0.290, 1.177, 1.422, 0.392, and 1.562, respectively.

The \( R \) values for the native sediments remained steady in the overlying water, with an average value of 0.029 ± 0.006 (Figure 5). The highest \( R \) values were observed between the surface water interface and −12 mm depth, with a maximum of 0.46. Below −12 mm and −36 mm depth, the \( R \) values were constant, followed by a linear increase until the greatest depth. The average value of \( R \) in pore waters was 0.30, indicating a partial resupply of DRP from the solid phase of sediments. The \( R \) values from the overlying water to a depth of −74 mm for the capped sediments had a similar distribution, with average values of 0.026 and 0.13 in the overlying water and pore waters of this region, respectively. The latter was only 43% of the native sediments, implying a much lower

Figure 5. The \( R \) (DRP\(_{DGT}\)/DRP\(_{PEEPER}\)) distribution of Poyang Lake sediments.
resupply of DRP from the solid phase for the capping treatment. Below the depth of −84 mm, the values increased sharply and exceeded those in the native sediments. The spatial heterogeneity of DRP was very high, which was more likely to reflect that the bottom sediments had a higher DRP releasing ability to pore water than upper sediments.

**DRP fluxes at the sediment–water interface**

Because the porosity of P1 sediment was more than 0.7, the equation \( D_s = \phi^2 D_0 \) was used to calculate the real flux coefficients. The porosity values of the other five sample sites were all less than 0.7, and therefore, \( D_s = \phi^2 D_0 \) was used to calculate the real flux coefficients. Calculated according to Fick’s law, the DRP fluxes, \( F \), at the sediment–water interface are shown in **Table 1** for all samples. The diffusive DRP fluxes were 40.5, 5.24, 4.78, 7.60, 11.1, and 19.1 ng P m\(^{-2}\) d\(^{-1}\) in P1–P6, respectively. The P fluxes across the sediment–water interface in a large eutrophic lake reported by Ding et al. (2015) ranged from −21 to 65 ng P m\(^{-2}\) d\(^{-1}\). The range of DRP flux in this study was 4.78–40.5 ng P m\(^{-2}\) d\(^{-1}\) with an average value of 14.7 ng P m\(^{-2}\) d\(^{-1}\). It was demonstrated that sediment acted as a sink or a source of P to the overlying water in Poyang Lake. The P concentration gradient between sediment and overlying water, porosity, particle size, as well as some other factors were considered to have influenced the DRP fluxes (Torres et al. 2014). Since this model did not consider the influence of bio-perturbation, the horizontal migration of phosphorous in the water body, and the wave disturbance of sediments, the results of Fick’s Law were, in general, slightly lower than the real diffusion flux.

**Conclusions**

The DRP vertical distribution in the sediment of Poyang Lake was obtained using HR-Peeper and Zr-oxide DGT devices and the DRP interface diffusion fluxes were calculated. The results showed that the sediments of Poyang Lake had the ability to release P and with increasing depth, this ability was strengthened. In addition, the diffusion flux was higher in the middle of Poyang Lake than in both upstream and downstream areas. The trophic status and trophic development of the lake were influenced by the P concentration in lake sediments. It is, therefore, important to characterize the P dynamics at the sediment–water interface, which will be useful in predicting and understanding the eutrophication status and the potential risks.

**Acknowledgments**

This study was sponsored by the National Key Project for Basic Research (No. 2012CB417004). The authors wish to express thanks to Yifan Liu for the help in the experiment.

**Table 1. Fluxes of dissolved reactive P (DRP) at the sediment–water interface in Poyang Lake, China, at five sampling sites (P1–P5, see Figure 1 for locations). The curves represent best fit exponential equation for DRP concentration as a function of depth x. The \( r \) value is the correlation coefficient for the curve. \( D_s \) is the diffusion coefficient, porosity is the porosity of the sediment and \( F \) is the calculated DRP flux.**

<table>
<thead>
<tr>
<th>Sample sites</th>
<th>Curves</th>
<th>( r )</th>
<th>( dC/dx )</th>
<th>( D_s ) ( (10^6 \text{ cm}^2 \text{ s}^{-1}) )</th>
<th>Porosity</th>
<th>( F ) ( (\text{ng m}^{-2} \text{ d}^{-1}) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>P1</td>
<td>( y = 0.2538e^{0.0034x} )</td>
<td>0.871</td>
<td>0.0110</td>
<td>4.627</td>
<td>0.794</td>
<td>40.5</td>
</tr>
<tr>
<td>P2</td>
<td>( y = 0.5163e^{0.0046x} )</td>
<td>0.217</td>
<td>0.00227</td>
<td>3.930</td>
<td>0.535</td>
<td>4.78</td>
</tr>
<tr>
<td>P3</td>
<td>( y = 0.3206e^{0.0075x} )</td>
<td>0.584</td>
<td>0.00401</td>
<td>4.518</td>
<td>0.616</td>
<td>4.78</td>
</tr>
<tr>
<td>P4</td>
<td>( y = 0.3230e^{0.0073x} )</td>
<td>0.801</td>
<td>0.00817</td>
<td>4.139</td>
<td>0.564</td>
<td>19.1</td>
</tr>
<tr>
<td>P5</td>
<td>( y = 0.3261e^{0.0085x} )</td>
<td>0.737</td>
<td>0.00238</td>
<td>4.840</td>
<td>0.659</td>
<td>7.60</td>
</tr>
<tr>
<td>P6</td>
<td>( y = 0.1764e^{0.0085x} )</td>
<td>0.275</td>
<td>0.0015</td>
<td>5.062</td>
<td>0.690</td>
<td>5.235</td>
</tr>
</tbody>
</table>
Disclosure statement

The authors declare that they have no conflict of interest.

Notes on contributors

Zhiping Yang gained his PhD in environmental science at the Chinese Academy of Sciences in 2015. His research interests are nutrients dynamics in lakes. He is currently working on a research project about nitrogen and phosphorus release characteristics of Poyang Lake.

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