Research Paper

Release of reactive phosphorus from sediments in Dongting Lake linked with the Yangtze River

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Environmental context. Eutrophication caused by excessive inputs of phosphorus is a prevalent global environmental problem. Reactive phosphorus released from sediments was measured by two new in situ passive sampling techniques capable of high-resolution measurements of phosphorus concentration. The methods provide the scientific evidence for solving the problems associated with deteriorating surface water quality.

Abstract. Internal phosphorus (P) loading is regarded as a major eutrophication factor and may prevent improvements in lake water quality. Two new in situ passive sampling techniques, high-resolution pore-water equilibrators (HR-Peeper) and zirconium oxide-based diffusive gradients in thin films (Zr-oxide DGT), were combined to measure dissolved reactive phosphorus (DRP) (C_{Peeper}) and labile phosphorus (C_{DGT}) at five sites in South Dongting and West Dongting Lakes. The vertical distribution of C_{Peeper} and C_{DGT} displayed similarity, which demonstrated that the buffering capacity of the labile P in sediments was similar at different depths. The diffusion flux of P from the sediments at the sediment–water interface ranged from 1.9 to 88 ng m^{-2} day^{-1}, with an average value of 38 ng m^{-2} day^{-1}. The P flux at the entrances to the Yuan, Li and Zi Rivers was fairly large at all five sites. The sediments at the five sites released P into overlying water, indicating that the sediments are an important source of P for Dongting Lake.

Introduction

Eutrophication of closed water bodies, such as lakes and reservoirs, has become a global issue in recent years due to rapid economic growth and population increase. Approximately 75 % of closed water bodies are affected by eutrophication.[1] Out of the 131 main lakes in China, an estimated 67 are in a eutrophic state.[2] Although Dongting Lake is currently stable at a meso-trophic level, the lake contains high levels of phosphorus and nitrogen and is in the transition stage to eutrophication. The highest degree of eutrophication is found in West Dongting Lake, followed by South Dongting Lake, with East Dongting Lake displaying the lowest degree of eutrophication.[3]

Phosphorous (P) is a key nutrient required for primary production in aquatic ecosystems; however, excess P can result in extreme propagation of planktonic algae and lead to water eutrophication.[2] The sources of P in lakes can be divided into external and internal sources.[4,5] Internal P refers to the P in sediment that is released into overlying water as dissolved inorganic P through adsorption and desorption, decomposition, ligand exchange and enzymatic hydrolysis, as well as by sediment resuspension induced by wind, biological disturbance, advection and other processes.[6–8] The release of P from sediment is controlled by P concentration and morphology,

sediment composition, pH, Fe redox cycling and dissolved oxygen.[9–11] In lake ecosystems, sediment contains a stock pool of nutrients and other contaminants. The sediment–water interface is a key site of material exchange and is involved in internal load formation, which is closely related to complex physical, chemical and biological processes.[2] Dissolved reactive phosphorous (DRP) is the most biologically active form of P in pore water.[6,12] There are two basic processes involved in the release of P from the sediment to the overlying water: P diffusion from pore water and P resupply from the solid P fraction. The mobile P fraction is referred to as labile P.[13]

Traditional methods for measuring sediment activity generally require collection and transportation of samples to the laboratory, which can lead to changes in the sample environment.[13] In addition, the low resolution (centimetres) of conventional active sampling techniques can cause difficulties in achieving rapid and accurate results.[14] In situ passive sampling is a non-destructive method based on the principle of material free diffusion that can be used to study the characteristics of pore water.[15,16] High-resolution measurement of P is of particular importance owing to the large spatial heterogeneity of natural sediments.[13] Representative passive sampling techniques include pore water equilibrators (Peeper), a suction technique

based on the principle of negative pressure, the Rhizon technique, diffusive equilibration in thin films (DET),[17] and diffusive gradients in thin films (DGT).[13,15–21]

In the present research, high-resolution pore water equilibrators (HR-Peeper) and zirconium oxide-based DGT were used to measure P distribution (C_{Peeper}, C_{DGT}) at five sites in South Dongting Lake and West Dongting Lake. DGT-labile P was used to estimate the diffusion flux of P from the sediment layer at the sediment–water interface. Zr-oxide DGT provided information about the distribution of highly labile P, including P dissolved in pore water and P desorbed from sediments.

Experimental

Study area

Dongting Lake is a shallow lake in China with location coordinates of latitude 28°30′–30°20′N and longitude 110°40′–113°10′E (Fig. 1). The lake is located on the southern bank of the Jingjiang River and serves as an important storage lake for the Yangtze River. Based on geographical location and topography, Dongting Lake can be divided into three regions: East Dongting Lake, South Dongting Lake and West Dongting Lake, with areas of 1217, 897 and 284 km^2 respectively.[3]

In order to investigate the characteristics of internal P in Dongting Lake, three sites in West Dongting Lake and two sites in South Dongting Lake were selected for sampling. South Dongting Lake is a semi-enclosed lake with fairly slow wind, wave and water velocities. South Dongting Lake receives fresh water, municipal wastewater and industrial wastewater from West Dongting Lake, the Zi River, and Yiyang City, and is categorised as mesotrophic.[3] West Dongting Lake is a fluid lake, and there are many emergent plants and a growing fish culture. The emergent plants can dissipate the effects of waves. West Dongting Lake is also mesotrophic.[22]

Operating principles of HR-Peeper and ZR-oxide DGT techniques

HR-Peeper technique

HR-Peeper is a recently developed high-resolution in situ sampling technique based on inner and outer membrane permeation equilibrium theory.[23] In this technique, a membrane is used to separate a chamber from the sediment and water sample. The chamber contains a sampling medium, such as deionised water or an electrolyte solution. Soluble ions and molecules in the pore water can be exchanged into the sampling medium in the chamber through the membrane.[15] The vertical spatial resolution of the pore water can reach 2 mm, which fulfils the requirements for high spatial and temporal resolution. This technique allows the measurement of a sample after an equilibrium time of ∼1–2 days using a volume of only 15 μL, which is well below the volume required by conventional colorimetric analysis (∼1 mL).[13,22] Peeper equipment for the current study was purchased from DGT Research Ltd (Lancaster, UK).

The HR-Peeper comprises a handle, a main body and a frame. The main body houses the chambers, and the frame is used to fix permeable membranes on the chamber surface. The chamber is composed of concave holes, and the size of each chamber is
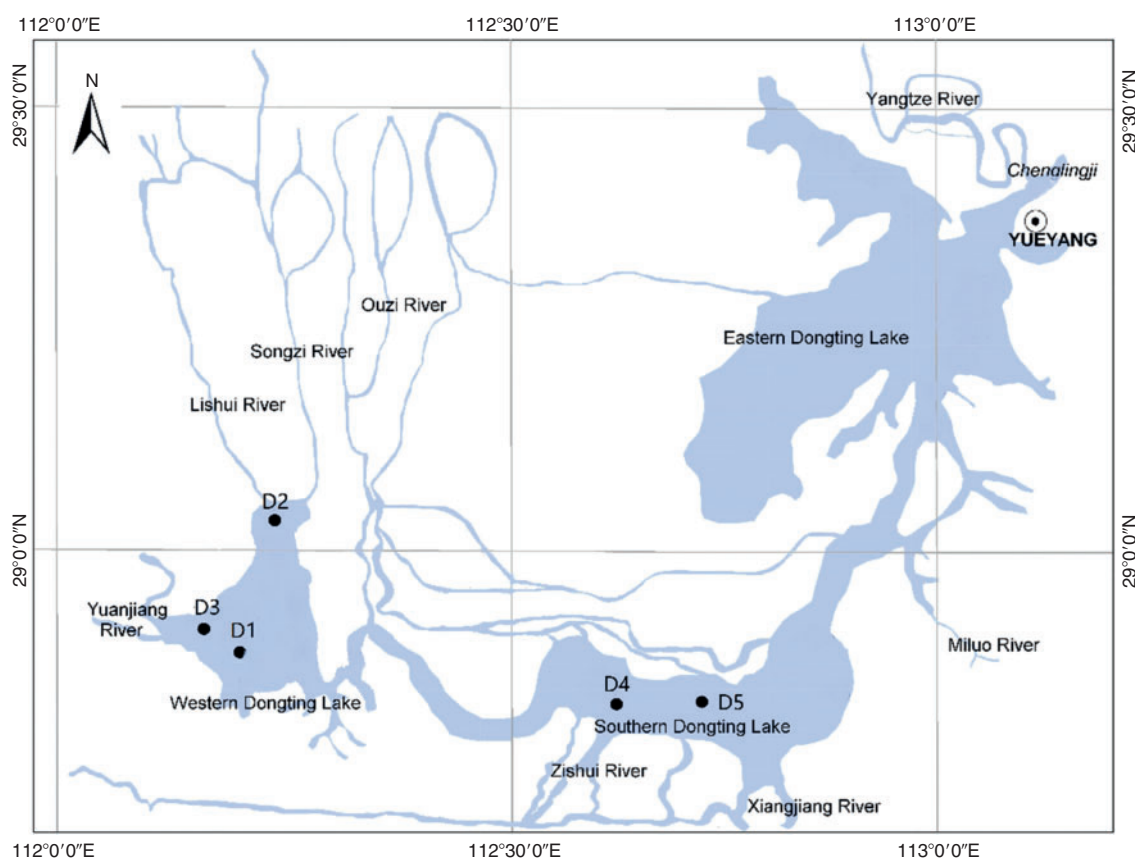

Fig. 1. The location of Dongting Lake and the sampling sites. The labelled black dots indicate the sampling sites. Yuanjiang channel (D1), the Li River entrance (D2) and the Yuan River entrance (D3) are located in West Dongting Lake; and the Zi River entrance (D4) and Fanggangzi (D5) are located in South Dongting Lake.

20 mm (length) $\times$ 1 mm (width) $\times$ 1 mm (height). The distance between two adjacent chambers is 1.0 mm, so the resolution can reach 2.0 mm.

Zr-oxide DGT technique

The Zr-oxide DGT is a novel in situ passive sampling technique that can be used to obtain high-resolution measurements of DRP distribution in sediments.[24] The DGT technique is based on Fick's first law. In order to form a stable concentration gradient between the hydrogel and the external water body, the binding phase can be quickly combined with the hydrogel and monitored substances at the binding phase interface. Assuming that the gradient remains constant during the setting time, the specific ion concentration in solution can be calculated using the transformation Eqn 1.[12] Zr-oxide DGT can only measure soluble forms that accumulate in the binding phase after passing through the diffusion layer.[13]

The DGT instrument comprises four elements: a permeable membrane, a diffusion membrane, a fixed film and a plastic jacket that fixes these three layers in place. In the present study, the fixed film consisted of Zr oxide, which has a high capacity for DRP and allows passage of DRP for a long time. Further details regarding the materials and equipment settings for the DGT technique can be found in previous reports.[25]

Equipment installation

The HR-Peeper equipment and DGT equipment were tied together and placed in water that was sparged with nitrogen for 16 h to remove oxygen. The combined device was then sealed in oxygen-free water and transferred to the sampling sites. After 4 h in the sampling sites, the device was removed, and sediments from the two sides of the device were placed on wet filter paper. An in-house built columnar sampler (internal diameter = 6.2 cm) was used to collect columnar sediments at each sample site. Columnar samples were cut into 1-cm segments and sealed in plastic bags. The 1-cm segments were tested for water content and porosity.[15,26]

Sampling analysis

The HR-Peeper samples were analysed according to the methods of Ding et al.[25] The DGT samples were analysed according to the methods of Ding et al.[26] The fixed film was removed and cut into slices with a length of 1 mm. Each slice was extracted by incubation in 0.4 mL of 1.0 M NaOH for 24 h, and the extraction solution was measured by a 96-microwell colorimetric method to obtain C_{DGT}.

Data processing

DGT-labile P calculation

The concentration of labile P measured by DGT was calculated from the following formula:[13]

$$C_{DGT} = \frac{M\Delta g}{D_g A t} \tag{1}$$

where Δg is the thickness of the diffusive layer, D_g is the diffusion coefficient of P in the diffusive layer, t is the deployment time, A is the exposed area of the gel, and M is the accumulated mass of P calibrated from the greyscale intensity on the Zr oxide gel surface. M can also be calculated according to Eqn 2 when it is eluted using a known volume of 1 M NaOH (V_e).

$$M = \frac{C_e(V_e + V_g)}{f_e} \tag{2}$$

where C_e is the DRP concentration in the alkaline eluate, V_g is the volume of the gel, and f_e is the elution efficiency (0.95).[26]

P diffusion flux at sediment–water interface

If the diffusion of P is considered to occur only in one direction, from the sediment to the water, then Fick's first law can be used to calculate the diffusion flux of P:

$$F = -\varphi D_s \left(\frac{\delta c}{\delta x}\right)_{(x-0)} \tag{3}$$

where F is the diffusion flux from the sediment (ng (cm day)$^{-2}$); δC is the DGT labile P concentration in the sediment; $\left(\frac{\delta c}{\delta x}\right)_{(x-0)}$ is the DGT labile P concentration gradient (i.e. the slope) in the sediment; φ is the porosity (estimated as 0.9 in the top 5-mm layer);[27] D_s is the diffusion coefficient (m^2 s^{-1}) and was calculated from the diffusion coefficient of H_2PO_4 in water using φ^3 for $\varphi \geq 0.7$.[26] If $F > 0$, P is released from the sediment to the overlying water; if $F < 0$, P is adsorbed by the sediment.[14,26]

Buffering capacity of the labile P in sediment

The ratio of C_{DGT}/C_{Peeper} (R) was calculated to analyse the buffering capacity of the labile P in sediment. R reflects the buffering capacity under three conditions. First, in the 'total buffer' condition, the labile P that diffuses into the DGT can be replenished by the P originating from the sediment. Thus, the sediment provides sufficient buffering capacity for the DRP in the pore water, so $C_{DGT} = C_{Peeper}$ and R = 1. Second, in the 'no buffer' condition, the sediment has no buffering capacity for the DRP in the pore water. Thus, the labile P that diffuses into the DGT comes only from the pore water, so $C_{DGT} \leq C_{Peeper}$ and R < 0.1. Third, in the 'partial buffer' condition, there is a partial DRP in the sediment that cannot replenish the pore water. Thus the buffering capacity is not sufficient to maintain the amount of P in the pore water that diffuses into DGT; thus, 0.1 < R < 1 (Table 1).[14,25] Excel 2013 (Microsoft Corporation, Redmond, Washington DC) was used to perform these calculations and to plot the results.

Results and discussion

The physical and chemical characteristics of sediments

Trends in porosity and water content of sediments suggest both compaction and partial resuspension of sediments.[28,29] Biological disturbance of benthic organisms is known to increase the water content and porosity of upper sediments.[15] Water

Table 1. Classification of sediment buffer capacity for dissolved reactive phosphorous (DRP)
DRP$_{DGT}$, DRP concentration that diffuses into diffusive gradients in thin films; DRP$_{Peeper}$, DRP concentration obtained by high-resolution Peeper

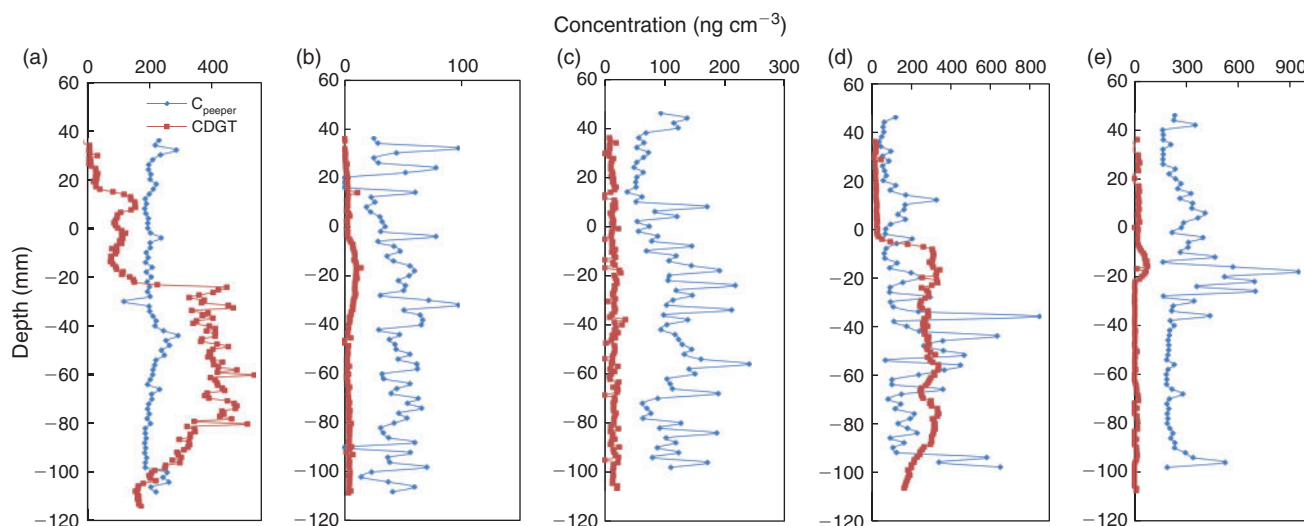| Classification	Relationship between DRP$_{DGT}$ and DRP$_{Peeper}$	R
Total buffer	DRP$_{DGT}$ = DRP$_{Peeper}$	1
No buffer	DRP$_{DGT}$ $\leq$ DRP$_{Peeper}$	R < 0.1
Partial buffer	DRP$_{DGT}$ = DRP$_{Peeper}$ or	0.1 < R < 1
	DRP$_{DGT}$ $\leq$ DRP$_{Peeper}$	

Fig. 2. The distribution profile of DRP$_{Peeper}$ (dissolved reactive phosphorous concentration obtained by high-resolution Peeper) and DRP$_{DGT}$ (DRP concentration that diffuses into diffusive gradients in thin films) in sediments: (a) Yuanjiang channel (D1); (b) Li River entrance (D2); (c) Yuan River entrance (D3); (d) Zi River (D4); and (e) Fanggangzi (D5).

content can also influence the microbial community in upper sediments and can alter the biogeochemical cycling of nutrients in sediments.[30,31]

The measured porosity and water content at five sites in Donting Lake indicated that the sediment resuspension capacity of West Dongting Lake is much greater than that of South Dongting Lake. The sediment porosity in Dongting Lake ranged from 50 to 83 % and was found to decrease gradually with sediment depth. The water content of the upper sediments at the Li River entrance was determined to be ~65 % and was considerably larger than that of the other four sites (25–47 %). The water content of the deep sediments at the five sites was similar. The water content of West Dongting Lake and South Dongting Lake sediments decreased as the sediment depth increased, also suggesting a compaction effect. The pore space of the upper sediment was greater than that of the deep sediment, as more pore water was able to fill the upper sediment space.

The distribution of C$_{Peeper}$ and C$_{DGT}$

The P distributions in the sediments at five sites were shown in Fig. 2. The average values (and ranges) of C$_{Peeper}$ and C$_{DGT}$ in the Yuanjiang channel (site D1) were 207.4 (117.2–290.1) and 241.3 (0–533.4) ng cm^{-3} respectively. C$_{Peeper}$ and C$_{DGT}$ tended to first increase and then decrease with increasing sediment depth. C$_{Peeper}$ and C$_{DGT}$ at the Yuan River entrance (D3) exhibited similar distributions, with average values (and ranges) of 106.9 (37.9–240.2) and 14.7 (0–35.1) ng cm^{-3} respectively. At these two sites, the DRP concentration in the pore water was fairly high.

The average values (and ranges) of C$_{Peeper}$ at the Zi River entrance (D4), Fanggangzi (D5) and the Li River entrance (D2) were 184.3 (37.9–845.6), 275.6 (163.5–945.4) and 43.2 (0–95.8) ng cm^{-3} respectively. C$_{DGT}$ values at Fanggangzi (D5) and the Li River entrance (D2) were much lower, with average values (and ranges) of 13.25 (0–72.1) and 4.2 (0–11.0) ng cm^{-3} respectively. The average value (and range) of C$_{DGT}$ measured at the Zi River entrance (D4) was 204.9 (9.1–344.1) ng cm^{-3}. The C$_{DGT}$ values measured between depths of −10 and −20 cm were similar to those measured between depths of −80 and

−120 cm. This similarity was attributed to several possibilities. First, sediments at different depths possessed different DRP buffering capacities. Second, spatial dislocation of the device occurred when the combined device was inserted into the sediments. Third, there were gaps between the surface of the DGT equipment and the measured sediment, which caused the overlying water to penetrate deeper into the sediment and resulted in an abnormal local reading for C$_{Peeper}$.

C$_{Peeper}$ and C$_{DGT}$ were found to increase quickly at a certain sediment depth, which indicated that the sediment was spatially heterogeneous. The C$_{DGT}$ reading at the Yuanjiang channel (D1) increased quickly at −22 cm. At the Yuan River entrance (D3), C$_{Peeper}$ fluctuated significantly. At the Zi River entrance (D4), C$_{DGT}$ increased quickly at −13 cm, and C$_{Peeper}$ increased quickly at −50 cm. At Fanggangzi (D5), C$_{Peeper}$ increased at −50 cm. At the Li River entrance (D2), C$_{Peeper}$ increased quickly at −2, −32 and −78 cm. The points at which DRP quickly increased may indicate locations of microniches. These may arise from environmental changes in the sediment induced by the rapid degradation of local organic matter or the reduction of sulfur or iron content, which could affect the DRP distribution.[7,32] At the same time, these disturbances may also redistribute the sediment particles, thereby increasing spatial heterogeneity of the sediment.[33] Upper sediments are easily disturbed by winds, waves, aquatic organisms and human activities, whereas deep sediments are primarily disturbed by microorganisms.[32,34–36] The Yuanjiang channel, the Yuan River entrance and the Li River are located in West Dongting Lake in regions covered by reeds. The roots of large aquatic plants, such as reeds, can change the redox conditions of the sediment–water interface through the release of oxygen or through respiration.[37] These processes can, in turn, alter the concentration gradient of nutrients in the pore water.[38–40]

The sediment activity of Dongting Lake

The distribution of R as a function of sediment depth is shown in Fig. 3. The average R values at Yuanjiang channel, the Li River entrance, the Yuan River entrance, the Zi River entrance and Fanggangzi were 1.49, 0.14, 0.14, 1.77 and 0.09 respectively.
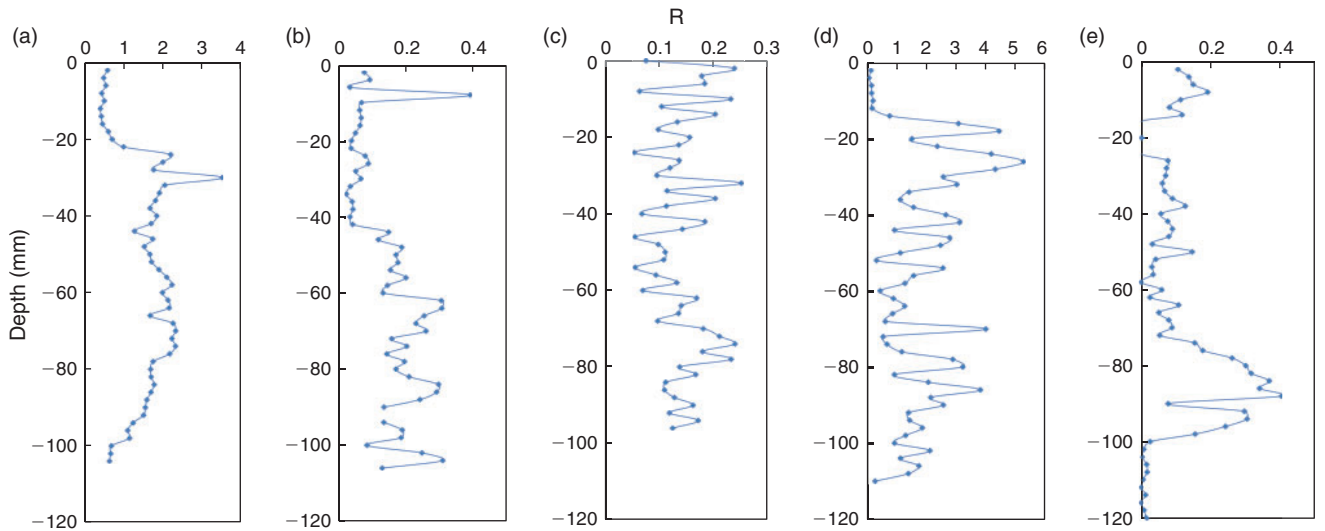
Fig. 3. The distribution profile of R in sediments: (a) Yuanjiang channel (D1); (b) Li River entrance (D2); (c) Yuan River entrance (D3); (d) Zi River (D4); and (e) Fanggangzi (D5).

These results suggest that the buffering capacity of Dongting Lake sediments varied spatially. The maximum R values for Yuanjiang channel, the Yuan River entrance and the Zi River entrance were calculated for a depth range of 20–40 mm below the sediment–water interface and were found to be similar to that found in studies of Chaohu Lake and Taihu Lake.[13]

The measured R values in sediments from the Li River entrance ranged from 0.02 to 0.40, indicating that a segment of the sediments provided buffering capacity and that the sediments at the Li River entrance were fairly inert. In addition, R tended to increase with increasing sediment depth, suggesting that the deeper sediments tended to release P into the pore water, thus causing the P in the sediments to release into the overlying water. R varied from 0.39 to 3.47 in the Yuanjiang channel and from 0.08 to 5.26 at the Zi River entrance; thus, the sediments at these two sites exhibited high spatial heterogeneity. At these sites, R was relatively high at depths of 20–100 mm below the sediment–water interface, indicating that sediments at these depths possessed high buffering capacity. However, as the depth increased, R exhibited a larger variation at the Zi River entrance compared with the Yuanjiang channel, and the spatial heterogeneity of the sediment was greater at the Zi River entrance than at Yuanjiang channel. At the Yuan River entrance, R values were in the range of 0.05–0.25, suggesting that the sediments had fairly low buffering capacity, and R did not vary significantly with depth, indicating that the sediments were inert. At Fanggangzi, R < 0.4, and the sediments were also inert. R increased significantly at depth of 70–100 mm below the sediment–water interface, which indicated that the sediments had fairly high buffering capacity at these depths. Overall, the R values for the sediments at Yuanjiang channel, the Li River, the Zi River entrance and Fanggangzi at depths of 20–100 mm below the sediment–water interface were 1- to 5-fold higher than the R values at depths of 0–20 mm below the sediment–water interface. The R values also tended to decrease when the sediment depth was greater than −100 mm.

The Zi River entrance and the Yuanjiang channel, which displayed high R values, are both located in an estuarine area with high sediment activity and a stable supply of P for pore water. The sediments in the Li River and Fanggangzi exhibited fairly high buffering capacity at depths of 60–100 mm below the sediment–water interface, which can be attributed to their proximity to reeds in West Dongting Lake. Emergent plant roots are beneficial to the migration of labile P from the sediments to the pore water. The buffering capacity near the sediment–water interface was found to be similar at the five sites owing to similarities in the basic physical and chemical properties of the sediment–water interface among the sites. Sediments in West Dongting Lake were relatively more active compared with those in South Dongting Lake.

P diffusion flux at the sediment–water interface

Assuming that the diffusion in pore water follows first-order reaction kinetics, the variation of P concentration with sediment depth should display an exponential distribution.[39] Therefore, the C_{DGT} (C) at 3–4 cm of the upper disturbed layer of the pore water and 3 cm above the sediment–water interface were fitted with sediment depth using an exponential relationship. According to the fitting equation (Table 2), the derivation of depth (x) was used to calculate dC/dx at the sediment–water interface. The correlation coefficients of the estuary regions (Yuan River entrance: 0.67, Li River entrance: 0.53, Zi River entrance: 0.58) were greater than those of the sites in the middle of the lake (Yuanjiang channel: 0.066, Fanggangzi: 0.073). These results suggest that the dynamic conditions of the estuary region are more suitable for the application of first-order reaction kinetics to describe the internal nutrient diffusion process.

The P diffusion flux (F) from sediments at the sediment–water interface was calculated with Fick's law (Table 3).

Table 2. Dissolved reactive phosphorous (DRP) concentration gradients at the sediment–water interface

Sites	Fitting curves	R^2	dC/dx
Yuanjiang channel	$y = 0.19828e^{-0.0003x}$	0.07	0.000059
Yuan River entrance	$y = 0.08287e^{-0.0246x}$	0.67	0.002
Li River entrance	$y = 0.0331e^{-0.0207x}$	0.53	0.00069
Zi River entrance	$y = 0.0969e^{-0.0261x}$	0.58	0.0025
Fanggangzi	$y = 0.2033e^{-0.0017x}$	0.07	0.00035

Table 3. P diffusion flux (F) at the sediment–water interface

Sites	Ds (10^6 cm^{-2} s^{-1})	Porosity	F (ng m^{-2} day^{-1})
Yuanjiang channel	4.35	0.59	1.9
Yuan River entrance	4.46	0.61	67
Li River entrance	4.78	0.65	24
Zi River entrance	4.74	0.80	88
Fanggangzi	4.14	0.56	10

F values were positive for all five sites, and the diffusion flux ranged from 1.9 to 88 ng m^{-2} day^{-1}, with an average value of 38 ng m^{-2} day^{-1}. The maximum values for F were located at the Zi River entrance and the Yuanjiang channel, which demonstrated that the internal source of P is of primary importance for South and West Dongting Lakes. The Yuan River entrance, Li River entrance and Zi River entrance are located in the estuary region and possess relatively high F values. In the current study, the calculation for F only considered the P gradient between the sediment and the overlying water, but the influence of porosity and the particle-blocking factor on the dissolved state were ignored. The effects of emergent plants, horizontal diffusion and overlying water turbulence were not considered; thus, the F values calculated using Fick's Law are considerably lower than the actual diffusion flux. The P flux measured by DGT is an apparent flux, which can be regarded as an indicator of the actual flux induced by the gradient of dissolved P.

Conclusion

HR-Peeper and Zr-oxide DGT instrumentation were combined to collect in situ measurements of C_{Peeper} and C_{DGT} at five sites in South Dongting and West Dongting Lakes. The combination of the HR-Peeper and Zr-oxide DGT techniques provides information related to sediment activity. The distribution of C_{Peeper} at each site was similar to that of C_{DGT}, which indicated that the buffering capacity of the sediments for pore water at different depths was similar. There was no obvious difference in buffering capacity near the sediment–water interface among the five sites because there were minimal differences in the physical and chemical properties of the sediments near the sediment–water interface. Sediments at the Zi River entrance (0.33–5.26) and the Yuanjiang channel (0.67–3.47) displayed fairly high R values at depths of 20–100 mm below the sediment–water interface, which demonstrated that the sediments could provide sufficient buffering capacity for DRP in the pore water. The P diffusion flux values at the Zi River entrance and the Yuanjiang channel were 88 and 67 ng m^{-2} day^{-1} respectively. Internal P is therefore an important source of P for Dongting Lake.

Acknowledgement

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