High-resolution characterization of labile phosphorus, iron, and manganese in sediments of different trophic waters in Lake Taihu, China

Liqing Zeng, Fan Yang, Changzhou Yan and Xinhong Wang

ABSTRACT

High-resolution combined ZrO-Chelex diffusive gradients in thin film (DGT) probes were arranged to synchronously monitor the characteristics of labile phosphorus (P), iron (Fe), and manganese (Mn) in sediments from regions of varying trophic levels in Lake Taihu, China. Results showed that P release was closely related to the lake region’s trophic level. Labile P in sediments and the apparent diffusion flux ($F_d$) of P were higher in hyper-eutrophic algae-dominated regions than those in macrophyte-algae-dominated and macrophyte-dominated regions, indicating that P released from sediments may be facilitated in eutrophic environments. A positive correlation observed between DGT-labile P and Fe or Mn, which had similar regional spatial distributions to P, showed that reductive dissolution of Fe-Mn (oxyhydr)oxides (FeOOH-MnOOH) in sediments was responsible for internal P release, which was strengthened in eutrophic environments. Ratios of labile Fe or Mn/labile P ($L_{Fe}/L_{P}$ and $L_{Mn}/L_{P}$) in sediments in algae-dominated regions showed lower values than those in macrophyte-algae-dominated and macrophyte-dominated regions, further confirming that FeOOH-MnOOH in algae-dominated regions were less able to fix P, which brought higher pollution risks for the overlying water. $L_{Fe}/L_{P}$ or $L_{Mn}/L_{P}$ also had a significantly positive correlation with $F_d$, further testament that labile Fe or Mn was much more relevant to the sediment P cycle.

Key words | DGT, eutrophication, iron and manganese, labile phosphorus, Lake Taihu, sediment

INTRODUCTION

Phosphorus (P) accumulation and release in fresh water have been studied extensively in recent decades. Excessive P release caused by human activities leads to widespread eutrophication and algal blooms (Schindler 2006). Once P enters the freshwater system, it is likely to accumulate in sediments through deposition and adsorption, resulting in high sediment P loading (Hupfer et al. 2007). In terms of lake management, even if external P sources are effectively controlled, the internal release of P accumulated in the sediment also contributes to continuous eutrophication (Sondergaard et al. 2005). At present, it is widely believed that the oxidation-reduction of iron and manganese (oxyhydr)oxides (FeOOH-MnOOH) plays an important role in sediment P cycling (Lovley 1991; Smith et al. 2011). Under reductive conditions, FeOOH-MnOOH is reduced to Fe$^{2+}$ and Mn$^{2+}$, which results in P release (coprecipitated with or adsorbed on to FeOOH-MnOOH) to pore waters and even to overlying waters. Under oxidative conditions, Fe$^{2+}$ and Mn$^{2+}$ are reoxidized to FeOOH-MnOOH, which can adsorb labile P and form a precipitate. Therefore, sediment P participates in early diagenetic processes in sediments through oxidation-reduction of FeOOH-MnOOH. As lake sediments have high spatial heterogeneity, composition is liable to vary, and thus, acquiring spatial distribution information of Fe, Mn, and P in high resolution was very important for detailed studies of P release in sediment.

Diffusive gradients in thin films (DGT) is a passive sampling technique capable of tracking bioavailable fractions of elements in sediment, water, and soil (Zhang et al. 2014). DGT technology not only reflects labile elements in dynamic equilibrium between the solid and liquid phases, but also helps to simplify complicated operations and to minimize analytical errors that occur in traditional chemical extraction methods (Zhang et al. 2014). Furthermore, DGT technology has higher resolution, shorter balance time, and better selectivity than the techniques of dialysis.

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and membrane diffusion equilibrium (Stockdale et al. 2008). At present, DGT technology has been successfully used to analyze labile P in sediment profiles (Zhang et al. 2014) and the spatial distribution of labile Fe and Mn (Gao et al. 2017). The latest ZrO-Chelex binding DGT technique (ZrO-Chelex DGT) can synchronously obtain information about labile P, Fe, and Mn in sediments at the millimeter scale (Wang et al. 2016) and, thus, has advantages in monitoring the mobility of these ions at high resolution as well as the ions’ coupling relationships.

Sediments from varying trophic regions in Lake Taihu (Wuxi, China) have different P adsorption capacities (Xiao et al. 2015). When the nutrient adsorption quantity exceeds the sediments’ load, sediment P can be released into the water column under certain conditions, enhancing the internal pollution risk. In this study, sediments from four regions in Lake Taihu with varying trophic levels, namely Zhushan Bay (ZB), Meiliang Bay (MB), Gonghu Bay (GB), and Southern Taihu (ST), were chosen to study the distribution characteristics of labile P, Fe and Mn, and their relationships, through synchronously monitoring the high-resolution information of labile P, Fe, and Mn in sediment profiles. Meanwhile, the apparent diffusion flux ($F_{ad}$) of P in the sediment-water interface (SWI) was also calculated to quantitatively assess P mobility in sediments from these regions. This study provides a multiple-perspective approach to systematically investigating labile P cycling coupled with labile Fe and Mn cycling at the SWI of Lake Taihu. It will also contribute to a better understanding of internal reductive release of labile P in eutrophic environments.

MATERIALS AND METHODS

Study site

Two sampling sites were selected in each region of the lake, including ZB, MB, GB and ST (Figure 1). ZB and MB belong to hyper-eutrophic algae-dominated regions, GB is regarded as a middle eutrophic macrophyte-algae-dominated region, while ST is classified as a mesotrophic macrophyte-dominated region.

Preparation of DGT experiment

DGT probes equipped with ZrO-Chelex gel as a binding layer were used for simultaneous measurements of labile P, Mn, and Fe in sediments (Xu et al. 2013; Wang et al. 2016). Flat probes with $18 \times 160$ mm (width $\times$ length) exposure area were used for measurements. During the
assembly of DGT, the ZrO-Chelex binding gel was laid sequentially as a 0.4-mm-thick diffusive gel and a 0.13-mm-thick cellulose nitrate filter membrane (0.45-mm pore size, Whatman, UK), covered with a plastic plate and tied with fishing line (justron, 0.33 mm in diameter). The ZrO-Chelex DGT probes were deoxygenated with nitrogen overnight and stored in a container of deoxygenated sodium chloride solution (0.1 M) before use.

**Sampling and processing**

In May 2015, water samples were obtained in triplicate at each sampling site. 50 mL of the samples was filtered through a 0.45 μm cellulose acetate membrane and acidified to a pH level of 3 or 4 with HNO₃ for Fe and Mn analyses. All samples were stored at 4 °C and measured within one week of collection. For analysis of total nitrogen (TN), total phosphorus (TP), total dissolved phosphorus (TDP), 500 mL of total phosphorus (TP), total dissolved phosphorus (TDP) was collected, stored at 4 °C, and measured within a 24 h our period. Water parameters in situ, including pH and dissolved oxygen (DO), were measured using a multiple water quality analyzer (YSI 6600v2).

Sediment cores of 80 cm in diameter were collected from each site at 15 cm of overlying water and 25 cm sediment depth. All samples were sealed, stored under darkened conditions, and immediately transported to the laboratory for DGT measurements.

**Experiment and sample analysis**

All cores were kept in an incubator under darkened conditions at a temperature equivalent to the sampling temperature (~20 °C). Each DGT probe was plotted to display the SWI position, then was gently inserted in the sediment core and left for 24 hours. After retrieval, probes were rinsed with lake water and then deionized water to remove visible sediment particles.

The ZrO-Chelex gels were disassembled from the DGT probes and vertically cut into two slices to minimize the possible heterogeneity of the sediment cores, from 0 to 9 mm and from 9 to 18 mm. A 5 mm slice of each vertical binding gel was cut and put into a 1.5 ml centrifuge tube. Each slice was then eluted using 1.00 mL of 1.0 M HNO₃ for 16 hours for Fe and Mn extraction, washed using deoxygenated water, and then eluted using 1.00 mL of 1.0 M NaOH for 16 hours for P extraction.

TP, DTP, and DRP of in-situ water samples as well as eluted P were measured using the molybdenum blue method (Murphy & Riley 1962). TN of water samples was determined after digestion in alkaline potassium persulfate, which was followed by UV spectrophotometric analysis (Thermo Evolution 300). The Mn of in-situ water samples as well as the Mn in DGT elutes were determined by inductively coupled plasma mass spectrometry (ICP-MS, Agilent 7500cx). Fe concentration of in-situ water samples and DGT elutes were measured by the phenanthroline colorimetric method (Tamura et al. 1974). All water samples were analyzed in triplicate.

The surface sediment was used for chemical analysis. Sediments were freeze-dried at ~80 °C and passed through a 0.2-mm sieve for further characterization and analysis. Sediment pH was measured in a 1:2.5 solid (the liquid ratio suspension was determined using a pH electrode). Total organic carbon (TOC) content in sediment samples was analyzed using a TOC analyzer (TOC-VcpH, Elementar, Germany). Total amounts of P, Fe and Mn were determined by X-ray fluorescence (XRF) spectroscopy (AxiosmAX, PANalytical). All analyses were conducted in triplicate. Weakly absorbed and strongly absorbed Fe or Mn were extracted, respectively (Keon et al. 2007; Seddique et al. 2008), and the sum of weakly absorbed and strongly absorbed Fe or Mn was defined as FeOOH or MnOOH. For each step of the extraction procedure, calibration solutions were prepared in the same matrix.

**Data analysis and statistics**

The concentrations of labile P, Fe, and Mn obtained by DGT were calculated using the following equation:

\[
C_{DGT} = \frac{M \Delta g}{DAf}
\]  

where \( \Delta g \) is the thickness of the diffusive layer (cm), \( D \) is the diffusion coefficient of the target elements in the diffusive layer (cm²), \( A \) is the exposure window area (cm²), and \( f \) is the deployment time (s). \( M \) is the accumulated mass of fractions over the deployment time (μg) and varies with the fixed phases and elution agents, so the elution rate needs to be considered as:

\[
M = \frac{C_e (V_e + V_d)}{f_e}
\]

where \( C_e \) is the elution reagent concentration, \( V_e \) is the elution reagent volume, \( V_d \) is the combination phase volume, usually negligible, and \( f_e \) is the elution factor.
The F2 of P across the SWI was quantified from labile P profiles using Equation (3) (Xu et al. 2013). Given the different resupply mechanisms of DGT measurements from the overlying water and sediments, the apparent flux was the sum of the sediment and overlying water flux.

\[
J = J_w + J_s = -D_w \left( \frac{\delta C_{\text{DGT}}}{\delta X_w} \right) (X = 0) - \varphi D_s \left( \frac{\delta C_{\text{DGT}}}{\delta X_s} \right) (X = 0)
\]

where \(J_w\) and \(J_s\) represent the labile P flux from sediments to the SWI and from water to the SWI, respectively. It is important to note that the focus of this study was the area in the vicinity of the SWI. For Equation (3), \(\varphi\) is the sediment porosity, for which a value of 0.9 was selected, based on the results of a study by Gao et al. (Gao et al. 2009); \(D_w\) and \(D_s\) are the P diffusion coefficients in water and sediment, respectively (Xu et al. 2013); and \(\left( \frac{\delta C_{\text{DGT}}}{\delta X_w} \right)_{(X=0)}\) and \(\left( \frac{\delta C_{\text{DGT}}}{\delta X_s} \right)_{(X=0)}\) represent labile concentration gradients in the overlying water and sediment, respectively. A distance of approximately 2 cm from the SWI within the experimental area was selected and gradients were determined within this area.

The spatial differences of each parameter in water and sediment were analyzed by variance analysis (ANOVA) using post-hoc single comparisons (Duncan’s new multiple range test (MRT)). The correlation coefficients between P indicators in sediment and the main geochemical parameters were calculated to assess the influence of the main geochemical parameters on P release. Both statistical analyses were computed using SPSS 19.0 software.

RESULTS AND DISCUSSION

Basic properties of overlying water and sediments

TN, TP, TDP, and DRP content of the overlying water showed spatial differences (\(p < 0.05\), Table 1). The highest concentrations of TN, TP, TDP, and DRP occurred in ZB with corresponding values of 3.91, 0.16, 0.14, and 0.12 mg L\(^{-1}\), respectively. The pH of overlying water was generally weakly alkaline (7.37–8.37). The DO mean values ranged from 6.80 to 9.53 mg L\(^{-1}\), showing that the overlying water of each lake region was aerobic in nature. DO content of ZB was the lowest, which possibly resulted from the intense oxygen decomposition by a large number of phytoplankton.
in this lake region (Yan et al. 2016). At the same time, concentrations of dissolved Fe and Mn in overlying water yielded higher values in this lake region (113.05 and 38.02 mg L$^{-1}$), indicating that the region was in a stronger reductive environment.

The pH values of the sediments were similar to that of the overlying water, i.e. also weakly alkaline (7.36–8.22) (Table 1). The average TOC content was in the range of 0.75–1.46%, and the highest TOC content was observed in algae-dominated lake regions (ZB and MB, 1.46% and 1.09%, respectively), indicating that long-term accumulation of organic matter in eutrophic sediments was extremely significant in such regions. The mean contents of FeOOH and MnOOH were in the range of 16.97–22.11 mg kg$^{-1}$ and 0.29–1.22 mg kg$^{-1}$, respectively. The highest FeOOH and MnOOH were also found in sediments from algae-dominated lake regions (ZB and MB). The order of decreasing average TP in investigated sediments ranked as follows: ZB (1.14 g kg$^{-1}$) > MB (0.68 g kg$^{-1}$) > ST (0.55 g kg$^{-1}$) > GB (0.39 g kg$^{-1}$) (Table 1). The sediment TP distribution was in line with that of the overlying water. Moreover, TP in sediments was also correlated with FeOOH ($r = 0.776$; $p < 0.05$) and MnOOH ($r = 0.981$; $p < 0.01$), demonstrating that the cycling of Fe and Mn may play an important role in P sedimentary partitioning.

**Distribution characteristics of DGT-labile P, Fe, and Mn**

The vertical and transversal distributions of DGT-labile P, Fe, and Mn in the sediments showed that labile P exhibited varying profile trends in different lake regions (Figure 2).

The vertical distribution of labile P in sediments from these regions can generally be classified into three patterns. In algae-dominated lake regions (ZB and MB), the labile P in sediments increased with depth. Although the labile P in site MB-1 increased slowly in the deep zone, it was still different from the labile P profiles obtained in GB and ST regions. Labile P in macrophyte-algae-dominated lake regions (GB) increased with depth and had a peak in the middle zone (~40–80 mm), and then decreased to the bottom. Labile P in sediments from ST were low and increased slightly with depth. These three profile distributions of labile P were basically consistent with the reported literature (Ding et al. 2015).

Labile Fe and Mn in ZB sediments showed similar trends to the labile P in the whole profile (Figure 2(b)). For the other sites, the labile P, Fe, and Mn showed similar trends within the depth of 0–70 mm; however, dissimilar trends occurred below this depth range. Inconsistent trends of labile Fe, Mn, and P in the deep zone might be caused by different diagenesis processes. In GB and ST, the nonsynchronous trends of labile Fe, Mn, and P in the deep zone may be for two reasons: the first reason being that sedimentary diagenesis intensity increased with depth, P adsorbed on mineral particles can be converted into more stable phosphate minerals, leading to the decrease of labile P (Eckert & Nishri 2014). Another possible explanation for decreasing labile P in the deep zone was that, in the macrophyte-algae-dominated and macrophyte-dominated regions, the growth of aquatic plants created a great demand for P from both water and sediment. In MB, Fe-bound P was more abundant in the deep zone and was easier to dissolve in the strongly reductive environment (Yuan et al. 2010), which induced the almost consistent trends of labile Fe and P. Unlike labile Fe, labile Mn in the deep zone was not in step with labile P. Such inconsistent trends likely resulted from the lower MnOOH content in this region (Table 1), which released low labile Mn to react easily with Ca to form Ca-Mn carbonate precipitates (Haese et al. 2000). Therefore, when the reductive dissolution of FeOOH and MnOOH in deep sediments was the dominant factor, the tendencies of labile Fe, Mn, and P in the deep zone moved towards synchronization. When the precipitation or adsorption process played a dominant role, the three trends tended towards non-synchronization.

The average labile Fe, Mn, and P in sediments were calculated to study their spatial differences (Table 2). The mean values of labile P, Fe, and Mn in ZB were 23, 2, and 2 times that of ST, indicating that the algae-dominated region was in a strongly reductive environment which brought about a significant reduction of FeOOH and MnOOH to release P. The significant positive correlation between the labile P content and labile Fe or Mn further indicated that P release was subject to the cycles of Fe and Mn (Smith et al. 2011) (Table 3). At the same time, the correlation analysis between P indicators in sediments and those in the overlying water showed that labile P had a more significant correlation with DRP and DTP than TP in sediments. In particular, at the depth of 0–20 mm, labile P had the most significant correlation with various P species in the overlying water (Table 2). Thus, the labile P can better reflect the activity of sediment P. The significant correlation between P flux and DRP or DTP further supported the above conclusion. Furthermore, both labile P and TP$_{sediment}$ were correlated with TOC (Table 2), indicating that organic matter played an important role in P mobility. TOC promoted the reduction and decomposition of iron oxide, thereby promoting P mobility (Stockdale et al. 2004).
At the same time, the oxidation of organic matter and the accompanying reduction of associated oxidation products could further enhance sediment P release (Withers & Jarvie 2008). Horizontal results indicated that labile P showed significant differences but similar variation tendencies between the two slice samples. This result is evidence that high-resolution measurements greatly facilitate the discovery of small variations caused by sediment
heterogeneity. Meanwhile, such vertical analyses could also minimize geological diversity between parallel sites.

Estimation of apparent diffusion flux of P across the SWI

The apparent diffusion flux of P was calculated from the high-resolution P distribution across the SWI. As shown in Figure 3, the average $F_d$ of P was in the range of $–6.17$ to $17.80$ ng cm$^{-2}$ d$^{-1}$, and $F_d$ in algae-dominated regions (ZB-1, ZB-2, MB-1, and MB-2: $17.80$, $13.40$, $10.83$, and $8.31$ ng cm$^{-2}$ d$^{-1}$, respectively) were far above those measured in macrophyte-algae-dominated and macrophyte-dominated regions (GB-1, GB-2, ST-1, and ST-2: $6.33$, $3.69$, $0.78$, and $–6.17$ ng cm$^{-2}$ d$^{-1}$, respectively). These results showed that labile P in sediments from algae-dominated regions had the stronger release potential to the overlying water, which made the sediments the internal pollution source in Lake Taihu, thus having an important impact on the lake's eutrophication. In contrast, the sediments in macrophyte-algae-dominated and macrophyte-dominated regions displayed low P release potential or existed as a P repository, buffering regional P pollution. This result was in accordance with previous reports that internal P loading in the polluted or algae-dominated lake region was stronger than that in macrophyte-algae-dominated or macrophyte-dominated lake regions (Kisand & Nõges 2003; Zhu et al. 2013).

Comparison of the ability of FeOOH-MnOOH fixing labile P in sediments

The ability of FeOOH-MnOOH to fix P was assessed by calculation of the ratio between labile Fe or Mn and labile P (defined as $LFe/LP$ and $LMn/LP$, respectively), and profiles of the average ratios of $LFe/LP$ and $LMn/LP$ are shown in Figure 4. For sites in macrophyte-algae-dominated or macrophyte-dominated lake regions (GB-1, GB-2, ST-1 and ST-2), both $LFe/LP$ and $LMn/LP$ increased gently or sharply from SWI to the middle zone, then decreased with depth. The distribution features indicated that FeOOH and MnOOH of these surface sediments possessed strong P-fixation ability. For sites in algae-dominated region (MB-1, MB-2, ZB-1, and ZB-2), $LFe/LP$ or $LMn/LP$ increased only slightly with depth, suggesting in these sites both FeOOH and MnOOH showed a relatively weak binding capacity to P, facilitating P release to overlying water. Small peaks of $LFe/LP$ or $LMn/LP$ in MB-1 and MB-2 were likely caused by

| Table 2 | Correlation between DGT-labile P and the each indicator of sediments |
|---|---|---|---|---|
| Sediment | TP, overlying water | TDP | DRP | DGT-labile Mn, sediment (0–120 mm) | DGT-labile Fe, sediment (0–120 mm) | TOC |
| TP | 0.916** | 0.878** | 0.876** | 0.839** | 0.646 | 0.900** |
| DGT-labile P, sediment (0–20 mm) | 0.923** | 0.909** | 0.895** | 0.868** | 0.869** | 0.807* |
| DGT-labile P, sediment (0–120 mm) | 0.920** | 0.898** | 0.883** | 0.860** | 0.850** | 0.845** |
| $F_d$ | 0.713* | 0.759* | 0.727* | 0.602 | 0.721* | 0.820* |

*p < 0.05; **p < 0.01 (n = 8).

| Table 3 | The average values of DGT-labile Fe, Mn and P and the ratios in each sediment |
|---|---|---|---|---|---|---|
| Site | DGT-labile Fe | DGT-labile Mn | DGT-labile P | $LFe/LP$ | $LMn/LP$ |
| ZB-1 | 245.67 | 253.52 | 247.55 | 0.75 | 1.25 |
| ZB-2 | 177.36 | 202.51 | 102.37 | 1.43 | 1.77 |
| MB-1 | 196.19 | 106.91 | 74.91 | 3.34 | 1.26 |
| MB-2 | 149.22 | 110.05 | 69.36 | 2.62 | 4.26 |
| GB-1 | 121.76 | 104.74 | 14.06 | 16.05 | 9.49 |
| GB-2 | 143.42 | 84.59 | 16.95 | 10.32 | 7.79 |
| ST-1 | 64.17 | 72.33 | 6.83 | 8.54 | 12.87 |
| ST-2 | 144.51 | 146.81 | 8.28 | 19.70 | 27.55 |

Each value represents the mean value of the two transverse profiles in each site (0–9 mm, 9–18 mm).

Figure 3 | The apparent diffusion flux of P across the SWI of each sampling site.
by geological heterogeneity. For sites in macrophyte-algae-dominated or macrophyte-dominated lake regions, the values of $L_\text{Fe}/L_\text{P}$ and $L_\text{Mn}/L_\text{P}$ were in the range of 8.54–19.70 and 7.79–27.55, respectively. The corresponding values in sites in algae-dominated lake regions were in the range of 0.75–3.34 and 1.25–4.26, respectively (Table 3). The lower $L_\text{Fe}/L_\text{P}$ and $L_\text{Mn}/L_\text{P}$ suggested that P in sediments from algae-dominated lake regions had stronger potential to release from FeOOH-MnOOH, which brought higher pollution risk to the overlying water.

The linear correlation slope between the labile Fe or Mn and the labile P was calculated to further examine the ability of FeOOH-MnOOH to control the internal P release (Table 4). The slopes of $L_\text{Fe}/L_\text{P}$ and $L_\text{Mn}/L_\text{P}$ in sites in the algae-dominated lake regions (1.21–2.24 and 0.35–2.28) were smaller than those in macrophyte-algae-dominated or macrophyte-dominated lake regions (3.75–15.60 and 1.82–7.59). The results further indicated that FeOOH or MnOOH in sediments from macrophyte-algae-dominated or macrophyte-dominated lake regions were more capable

Table 4 | Correlation between the DGT-labile Fe or Mn and DGT-labile P in profiles of sediments (n = 50)

<table>
<thead>
<tr>
<th>Site</th>
<th>Linear equation between DGT-labile Fe and P</th>
<th>Linear equation between DGT-labile Mn and P</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZB-1</td>
<td>$L_\text{Fe} = 1.29 \cdot L_\text{P} - 72.69$ ($r = 0.960, p &lt; 0.01$)</td>
<td>$L_\text{Mn} = 0.90 \cdot L_\text{P} + 30.06$ ($r = 0.806, p &lt; 0.01$)</td>
</tr>
<tr>
<td>ZB-2</td>
<td>$L_\text{Fe} = 2.25 \cdot L_\text{P} - 52.62$ ($r = 0.868, p &lt; 0.01$)</td>
<td>$L_\text{Mn} = 2.28 \cdot L_\text{P} - 30.87$ ($r = 0.899, p &lt; 0.01$)</td>
</tr>
<tr>
<td>MB-1</td>
<td>$L_\text{Fe} = 1.22 \cdot L_\text{P} + 104.99$ ($r = 0.560, p &lt; 0.01$)</td>
<td>$L_\text{Mn} = 1.64 \cdot L_\text{P} - 15.56$ ($r = 0.844, p &lt; 0.01$)</td>
</tr>
<tr>
<td>MB-2</td>
<td>$L_\text{Fe} = 1.85 \cdot L_\text{P} + 20.66$ ($r = 0.929, p &lt; 0.01$)</td>
<td>$L_\text{Mn} = 0.35 \cdot L_\text{P} + 85.70$ ($r = 0.330, p &lt; 0.05$)</td>
</tr>
<tr>
<td>GB-1</td>
<td>$L_\text{Fe} = 3.76 \cdot L_\text{P} + 101.53$ ($r = 0.377, p &lt; 0.01$)</td>
<td>$L_\text{Mn} = 2.95 \cdot L_\text{P} + 50.03$ ($r = 0.479, p &lt; 0.01$)</td>
</tr>
<tr>
<td>GB-2</td>
<td>$L_\text{Fe} = 4.61 \cdot L_\text{P} + 60.48$ ($r = 0.685, p &lt; 0.01$)</td>
<td>$L_\text{Mn} = 1.82 \cdot L_\text{P} + 51.95$ ($r = 0.372, p &lt; 0.01$)</td>
</tr>
<tr>
<td>ST-1</td>
<td>$L_\text{Fe} = 15.60 \cdot L_\text{P} - 42.35$ ($r = 0.724, p &lt; 0.01$)</td>
<td>$L_\text{Mn} = 7.01 \cdot L_\text{P} + 36.28$ ($r = 0.763, p &lt; 0.01$)</td>
</tr>
<tr>
<td>ST-2</td>
<td>$L_\text{Fe} = 14.70 \cdot L_\text{P} + 19.72$ ($r = 0.795, p &lt; 0.01$)</td>
<td>$L_\text{Mn} = 7.60 \cdot L_\text{P} + 64.77$ ($r = 0.887, p &lt; 0.01$)</td>
</tr>
</tbody>
</table>

Figure 4 | The average distributions of $L_\text{Fe}/L_\text{P}$ and $L_\text{Mn}/L_\text{P}$ in sediment profiles.
of adsorbing P, which was consistent with the ratio of $LFe/LP$ or $LMn/LP$, $F_d$ of P and the labile P concentration. Jensen et al. have proposed a total amount ratio ($TFe/TP$) to assess whether the surface of the oxygenated sediment had sufficient adsorption capacity for P (critical value is 15) (Jensen et al. 1992). Based on this, the ratio of $TFe/TP$ in each site was calculated from Table 1, and the values in ZB, MB, GB and ST were found to be 39.08, 55.97, 84.74 and 69.53, respectively. All these ratios were higher than the critical value, suggesting that FeOOH in all lake sediments had strong P-fixation ability. However, the results were not consistent with the results of $F_d$, which showed that in algae-dominated regions the sediments’ adsorption capacity of fixing P was weak. The $TFe/TP$ ratio which was used to assess the binding capacity of FeOOH to P therefore has its limitations. In addition, the labile ratio slope had a significant negative correlation with $F_d$, while the total amount ratio of $TFe/TP$ and $TMn/TP$ showed no correlation with $F_d$ (Table 5), which further illustrated that labile Fe and Mn were more closely correlated to the cycle of P in sediments than the total Fe and Mn. In summary, compared with the total amount, the labile content can provide a more accurate assessment in determining Fe-coupled and Mn-coupled P release in sediments. Besides, as deep sediments may also be affected by other processes, a more comprehensive study is required to reveal micro-change processes associated with P in these regions.

**CONCLUSION**

In this study, the distribution characteristics of labile P, Fe, and Mn in lake sediments were successfully monitored and assessed using a high-resolution ZrO-Chelex DGT technique. The labile P content and the apparent diffusion flux of P in sediments in algae-dominated lake regions were higher than those in the macrophyte-algae-dominated or macrophyte-dominated lake regions. DGT-labile P in each site was positively correlated with the DGT-labile Fe and Mn, indicating that the oxidation-reduction of FeOOH-MnOOH was important to the sediment P cycle. The values of $LFe/LP$ and $LMn/LP$ in sediments in algae-dominated lake regions were lower than those in macrophyte-algae-dominated or macrophyte-dominated lake regions, indicating that P in sediments in algae-dominated lake regions had stronger potential to release from FeOOH-MnOOH, which brought out a higher pollution risk to the overlying water. The slopes of $LFe/LP$ and $LMn/LP$ in algae-dominated lake regions were smaller than those in macrophyte-algae-dominated or macrophyte-dominated lake regions, indicating that FeOOH-MnOOH in algae-macrophyte-dominated or macrophyte-dominated lake regions were more capable of fixing P. The slopes of $LFe/LP$ and $LMn/LP$ had significant negative correlations with $F_d$, while $TFe/TP$ and $TMn/TP$ had no correlation with $F_d$, suggesting $LFe/LP$ and $LMn/LP$ provided a more accurate assessment in determining Fe-coupled and Mn-coupled P release in sediments.

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