Diffusion flux of phosphorus nutrients at the sediment–water interface of the Ulansuhai Lake in northern China

Shengnan Zhao, Xiaohong Shi, Changyou Li, Sheng Zhang, Biao Sun, Yong Wu and Shuixia Zhao

ABSTRACT

Overlying water and sediment samples were collected from 11 locations in Ulansuhai Lake in June of 2012 to determine the concentration of dissolved inorganic phosphorus (DIP) in the interstitial water, overlying water and sediment and to estimate the diffusion flux of DIP at the sediment–water interface. The DIP levels in overlying water were 0.004–0.185 mg/L (average = 0.062 mg/L), while they were 0.05–0.25 mg/L (average = 0.124 mg/L) in the interstitial water in the 0–2 cm surface sediment. Moreover, the annual mean exchange flux of DIP in the sediment was between -0.092 mg/m^2·d and 0.053 mg/m^2·d, and this occurred via internal source action in most areas. After area weighting, it is estimated that the exchange capacity of DIP at the sediment–water interface of the Ulansuhai Lake is 1.30 t/a. These findings indicate internal loading of phosphorus in sediment of the Ulansuhai Lake; thus, the diffusion of DIP in the interstitial water has effects on the lake, with a degree of influence of 2.7% to 81.5%.

Key words | dissolved inorganic phosphorus, Fick's first law, flux, interstitial water, sediment–water interface, Ulansuhai Lake

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INTRODUCTION

Evaluation of nutrient equilibrium is essential to the investigation of eutrophic lakes. Determining the flux and direction of dissolved inorganic phosphorus (DIP) can help explain the contribution of internal pollution. Phosphorus is an essential factor that influences water function and water ecosystem composition and structure, as well as being one of the key elements leading to eutrophication. Most eutrophic lakes in China, including Ulansuhai Lake, are phosphorus-controlled (Wang 2013). The phosphorus in Ulansuhai Lake is both exogenous and endogenous. Exogenous phosphorus refers to that contained in domestic wastewater, industrial wastewater from chemical fertilizer plants and food processing plants and cropland recession water, while endogenous phosphorus is mainly released from sediment to the lake under the influence of the external environment (Qin & Zhu 2009; Li et al. 2011).

There are two physical methods by which phosphorus is released from sediment, diffusion under the concentration gradient of the overlying water and sediment (Cowan & Boynton 1996) and wind disturbance that leads to sediment resuspension and enhanced phosphorus release. In general,

nutrient salts released from sediment exist in the interstitial water of sediment first, after which they are diffused into the overlying water under the concentration gradient, contributing to eutrophication of lakes. Therefore, the concentration gradient of overlying water and interstitial water of sediment is used to estimate diffusion phosphorus flux from sediments (Urban et al. 1997).

Phosphorus primarily consists of orthophosphate, polyphosphate and organophosphorus, with orthophosphate being the major part taken up by plants. The United States Environmental Protection Agency has set upper limit values for total phosphorus and orthophosphate in lakes of 0.025 mg/L and 0.05 mg/L, respectively. In general, DIP is the major part in the phosphorus cycle in water, which can be taken up by microorganisms easily. It improves the algae primary productivity and enhances the biogeochemical cycling of phosphorus and also contributes to the eutrophication of lakes. The phosphorus in the water, especially orthophosphate, decreases due to the microorganism consumption, which is transformed to organophosphorus. However, some of the phosphorus can be released because

of aerobic decomposition of organic matter, and some of the phosphorus will be taken up to become organophosphorus again. The phosphorus release from sediments is one of the most important sources and has a significant effect on eutrophication levels. The process of phosphorus release from sediment includes four parts: desorption, diffusion, ligand exchange and hydrolysis. As the phosphorus fraction of DIP exists in sediments, it can be released into overlying water by diffusion, resuspension, and destabilization. Therefore, DIP is important for the phosphorus biogeochemistry cycle in lakes. Fan *et al.* (2006) found that static endogenous phosphorus accounted for 46.6% of the total load in Taihu Lake. Li *et al.* (2008a, 2008b) discovered that the release of endogenous nitrogen and phosphorus from the sediment of Fubao Bay in Dian Lake was higher than that of Taihu Lake. However, few studies have investigated these properties in lakes of northern China. In a study of Lake Coeurd Alene in the United States, Kuwabara *et al.* (2003) found that the release of endogenous phosphorus nutrient salts was equivalent to the input of exogenous phosphorus nutrient salts. In China, most studies have focused on southern lakes (Li *et al.* 2008a, 2008b, 2012; Tang *et al.* 2009; Xiang *et al.* 2011; Zhang *et al.* 2012a, 2012b).

Therefore, in this study, on-site sampling and monitoring of Ulansuhai Lake were conducted to determine the physicochemical properties of water and sediments, as well as the contents of different forms of phosphorus in the surface water, bottom water and interstitial water in sediments. Fick's first law was then employed to estimate the diffusion flux of phosphorus at the sediment–water interface and quantify the effects of sediment phosphorus pollution on the overlying water. This information was subsequently utilized to elucidate the migration and transformation mechanism of phosphorus at the sediment–water interface and compare this with those of lakes in southern China. The results presented herein will enable comprehensive assessment of the rate of contribution made by endogenous nutrients to lake pollution.

MATERIALS AND METHODS

Ulansuhai Lake is located in the Urad Front Banner of Bayan Nur in the Inner Mongolia Autonomous Region at $40°36'$–$41°03'$N and $108°43'$–$108°57'$E. The lake covers an area of $293 \, km^2$, including $118.97 \, km^2$ of reed area and $111.13 \, km^2$ of visible water area, while $85.7 \, km^2$ of the visible water area has crowded submerged plants. The lake begins to freeze at the beginning of November every year, and the ice does not melt until late March or early April of the following year. Temperature changes in the area vary, and the perennial mean temperature is $7.3 \, °C$. The annual sunshine duration is $3,185.5 \, h$, the average annual rainfall is $224 \, mm$ and the evaporation capacity is $1,502 \, mm$ (Zhang *et al.* 2012a, 2012b). Ulansuhai Lake is the only discharging channel of cropland recession water and industrial and domestic wastewater in the area. Every year, about $5 \times 10^8 \, m^3$ of cropland recession water and industrial and domestic wastewater are discharged into the lake, including a large volume of pollutants (Ma *et al.* 2012). At present, the lake is severely polluted, which is characterized by eutrophication, high levels of organic contaminants and salinization. As Ulansuhai Lake drains into the Yellow River through its southern outlet, its water quality influences the water security of people living downstream. Based on field data collected in June 2012, the nitrogen level in the water is about 2.24–4.92 mg/L and the phosphorus level is about 0.02–0.26 mg/L. The ratio of nitrogen to phosphorus for all samples was greater than 16, indicating that the lake is eutrophic and phosphorus is the main controlling factor.

Eleven water and sediment sampling and monitoring points were constructed based on the area of the lake and its water flow direction (Figure 1) using GPS, and samples were collected in June 2012. A self-made hydrophore (patent no. ZL201020680966.1) was utilized to collect samples from the surface and bottom water (Figure 2(a)) into polypropylene bottles. A self-made columnar mud sampler was applied to collect two 30–40 cm thick columnar samples (Figure 2(b)), and layers were divided into 2 cm sections in the field, then placed in clean sample bags. Air was squeezed out of the bags, after which the water and sediment samples were sealed and preserved in a dark place at low temperature until being transported to the laboratory, where they were prepared for analysis immediately.

Sampling with the self-made columnar mud sampler was conducted as follows: the piston (7) was pushed to the ground (8), after which the handle (4) was held to place the sampling head into the water through the ice hole. The sampler was then hit with a rubber hammer to force the sediment upwards until it was filled with sediment, at which time the piston push-pull rod (7) was constrained by the guide pad (5). The globe valve (2) was then installed with a fast joint (3) and filled with water through an inlet (1). Air was exhausted out of the tube, after which the valve was closed immediately and the sampler was lifted using the handle (4). The sediment was then picked up and held in the sampling tube due to the pressure difference.
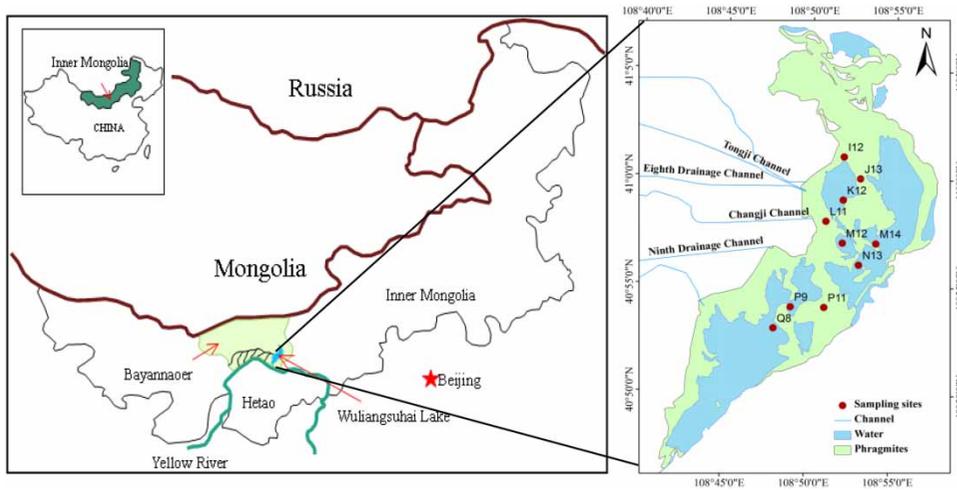
Figure 1 | Location of different sampling sites of Ulansuhai Lake, Inner Mongolia, China.
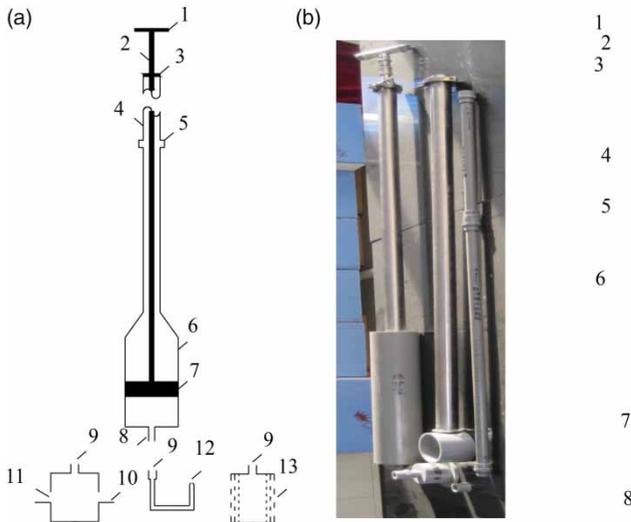

Figure 2 | Water sampler (a) and core sediment sampler (b). See text for explanation of numbered parts.

Once lifted, the columnar sediment was pushed out using the push-pull rod (Figure 2(b)).

Sampling with the self-made hydrophore was as follows: the handle (1) lifted the piston, the shaft (2) connected the piston (7) and the handle, and the fixing (3) prevented the shaft (2) from moving. The lengthening bar (4), assembled with pipe clamps, collected deep-water samples. The water container (6) contained samples, (8) is a water inlet and can be connected to interface (9) with the upper screw to enable sampling as a multifunctional device. The thief rod, with scales on, collected samples from specified spots (Figure 2(a)).

To prepare interstitial water, fresh sediment samples were centrifuged at 4,000 rpm for 30 min, after which the supernatant was passed through a 0.45 μm filter membrane. The dissolved oxygen, DIP, pH and conductivity were measured immediately, as previously described (Jiang *et al.* 2010a, 2010b).

The DIP in overlying and interstitial water was measured according to the specifications for lake eutrophication with the ammonium molybdate spectrophotometric method (Jin & Tu 1990). The moisture content of the sediment was computed based on the mass difference. The sediment pH and conductivity were determined according to the specifications for lake eutrophication (Jiang *et al.* 2010a, 2010b).

Statistical analysis

The diffusion transfer flux of the nutrient salts at the sediment–water interface primarily depends on diffusion caused by the concentration gradient between the overlying and interstitial water. If the concentration of a chemical substance in the aqueous phase near the interface changes almost linearly with variations in sediment concentration, its net flux can be determined based on Fick's first law (Martinova 1993; Jiang *et al.* 2010a, 2010b):

$$F = \varphi \times D_s \times \left(\frac{\delta_c}{\delta_x}\right) \tag{1}$$

where F is the diffusion flux of nutrient salt at the sediment–water interface in mg/m^2·d, φ is the sediment porosity, $\delta c/\delta x$ is the concentration gradient of the interface in mg/L·cm, which is computed with the d-value, i.e. the difference between the interstitial water and overlying water concentration in the surface sediment, and D_s is the diffusion coefficient of sediment mass, indicating the real molecular diffusion coefficient considering the bending effect of sediments.

The empirical correlation between D_s and φ (Borowski *et al.* 1996) was determined according to Ullman & Aller (1982) as follows: if $\varphi < 0.7$, $D_s = \varphi D_0$; if $\varphi \geq 0.7$, $D_s = \varphi D_0$, where D_0 is the diffusion coefficient of a 25 °C ideal solution. Both temperature and ionic form can influence D_0. This experiment was conducted in June, when the average temperature of the lake was 25 °C; thus, the D_0 value at 25 °C was used. For PO_4^{3-}, $D_0 = 6.12 \times 10^{-6}$ cm^2/s (Li 1974).

Release was computed as follows:

$$W = \sum_{j}^{n} \sum_{i}^{n} r_{ij} A_j \Delta T_i \times 10^{-3} \qquad (2)$$

where W is the total diffusing capacity of phosphorus nutrient salt (t/a), r_{ij} is the rate of release of sediment in area j at temperature i (mg/m^2·d), A_j is the area of area j (km^2) and ΔT_i is the time period (a) at temperature i.

The effect of phosphorus diffusion on water without considering temperature layering, and on the premise that the water is intensively mixed and the sediment release to the overlying water through the interstitial water is only influenced by molecular diffusion, is given by:

$$CR = \frac{C_d}{C_w} \quad C_d = \frac{F_V \times T_w}{H} \quad T_w = \frac{V}{Q} \qquad (3)$$

where CR is the contribution rate of the diffusion of total dissolved phosphorus nutrient to the overlying water (%), C_d is the concentration of the total dissolved phosphorus nutrient (mg/L) diffused and migrated from the sediment interstitial water, C_w is the concentration of the total dissolved phosphorus nutrient (mg/L) in the overlying water, F is the diffusion flux (mg/m^2·d), T_w is the retention time of water (a), H is the depth of water (m), V is the storage capacity of the lake (m^3) and Q is the water flow velocity (m^3/s).

RESULTS

DIP content at the sediment–water interface

Figure 3 shows the vertical profile characteristics of DIP at the sediment–water interface of Ulansuhai Lake. The distribution of DIP in the overlying water at the sediment–water interface was 0.004–0.185 mg/L, with an average of 0.062 mg/L. The surface sediment (0–2 cm) interstitial water is an important interchange medium in the

transportation of phosphorus at the sediment–water interface. The DIP in the interstitial water in the 0–2 cm surface sediment from most sampling points was much higher than that in the overlying water, ranging from 0.05 to 0.25 mg/L, with an average of 0.124. The average variation of DIP in the sediment interstitial water (0–30 cm) from different sampling points was 0.031–0.158 mg/L.

At I12, L11, M12 and N13, the maximum DIP concentration in the interstitial water in the columnar sediment was observed in the 0–2 cm surface layer. As the depth increased to 2–6 cm, the DIP concentration declined rapidly, after which it stabilized. The maximum DIP concentration in the interstitial water in the columnar sediment of J13, M14, P9 and Q8 was observed at 4–8 cm, below which it declined rapidly to 14 cm, after which it stabilized. The DIP concentration in interstitial water at K12 varied significantly, with the maximum value appearing at a greater depth of 14–16 cm. The DIP concentration in the interstitial water did not change significantly at P11, where the maximum value appeared at 0–2 cm, then declined gradually with depth until slowly stabilizing. Vertically, there was no obvious fluctuation in concentration observed. In general, the DIP concentration in the interstitial water in the columnar sediment of I12, L11, M12, N13 and P11 declined slowly with increasing depth, while the DIP concentration in the interstitial water in the columnar sediment of J13, K12, M14, P9 and Q8 declined, then increased with depth.

Diffusive fluxes across the sediment–water interface of DIP

The transformation of nutrients at the sediment–water interface primarily includes convective flux and diffusion flux. Normally, when the flow velocity is low, the convective flux is much smaller than the diffusion flux. The migration of nutrients is primarily controlled by the diffusion transfer caused by the concentration gradient between the upper and lower interface, while the contribution of nutrients is mainly controlled by the one-dimensional vertical transmission and reaction. Therefore, nutrient diffusion at the sediment–water interface follows Fick's first law. This process can be described by the content of nutrients in the interstitial water in the surface sediment. Normally, the variation in nutrient content with depth in the interstitial water should follow the exponential distribution law. Therefore, the exponential curve fitting of depth was conducted using the DIP content in the upper layer of the interstitial water (0–8 cm) and in the 3–5 cm layer of the interstitial water above the interface. The derivative of the depth, x, was determined based on the fitting expression,
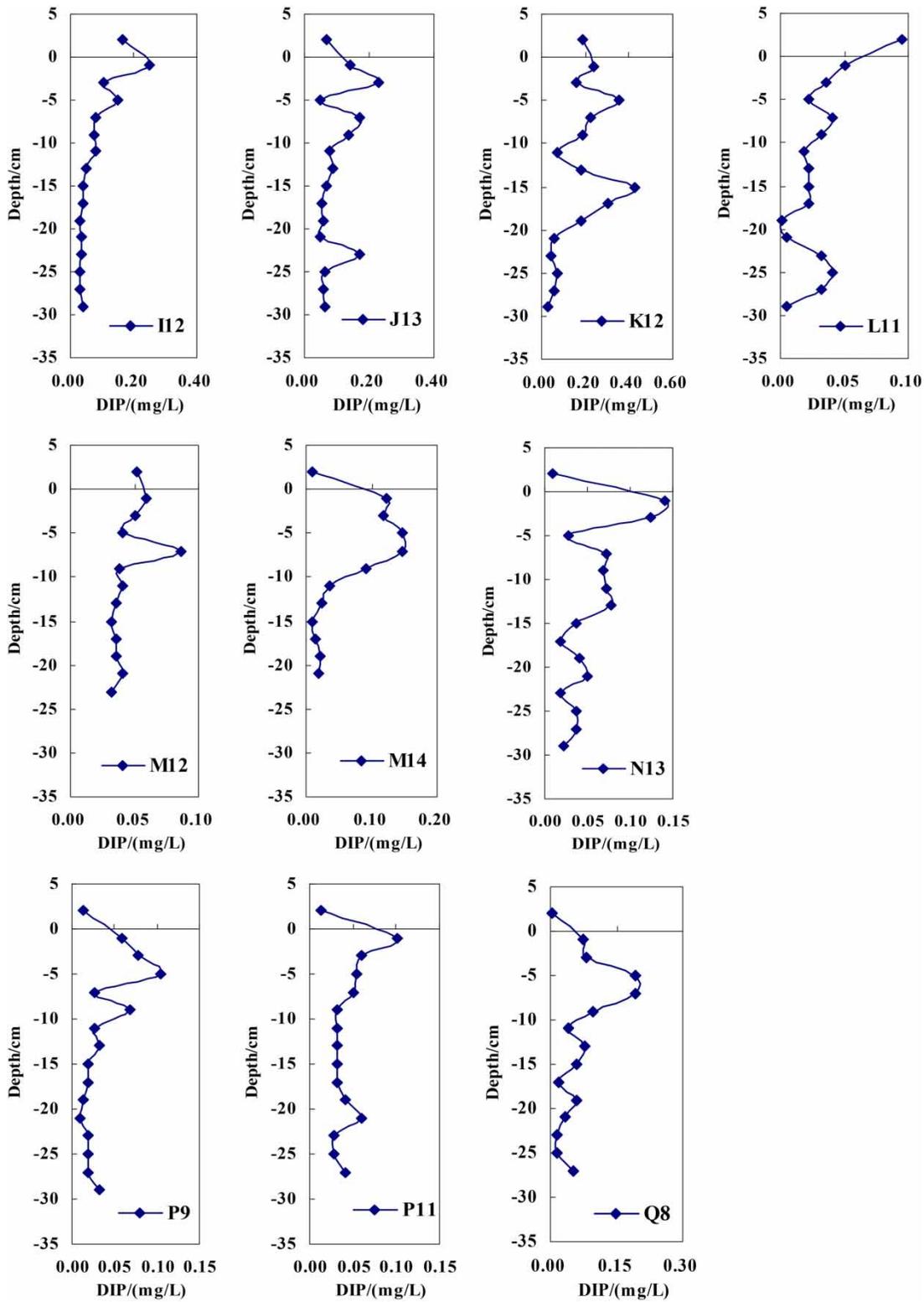
Figure 3 | Vertical variation of DIP content at the sediment–water interface of different sampling spots.

dc/dx at the sediment–water surface was acquired and the diffusion flux of DIP content at the sediment–water surface was computed with Fick's first law.

The results of the exponential curve fitting of depth based on DIP concentration in the interstitial and overlying water show that correlation coefficients of all sampling spots of the Ulansuhai Lake are high, and the value of R^2 is between 0.554 and 0.983, indicating that it is appropriate to describe the diffusion of endogenous nutrients of the Ulansuhai Lake with first-order reaction kinetics.

Table 1 shows the exchange rates of DIP at the interface of Ulansuhai Lake computed based on measured data from different lake spots and Fick's Law. As suggested in Table 1, different areas of Lake Ulansuhai followed different laws with respect to DIP absorption and release. The diffusion flux of I12, L11 and M12 was -0.092 mg/m^2·d, -0.072 mg/m^2·d and -0.014 mg/m^2·d, respectively.

With the exception of the three aforementioned spots, the diffusion flux was positive. These findings indicate that the nutrients in the pores of the sediments diffuse toward the overlying water, after which they are released. K12 had the highest diffusion rate of 0.053 mg/m^2·d, followed by N13, Q8, P9, J13 and M14, which had diffusion rates of 0.036, 0.034, 0.026, 0.020 and 0.006 mg/m^2·d, respectively.

DISCUSSION

Profile characteristics and effect factors for DIP at the sediment–water interface

Surface sediment interstitial water is closely related to the overlying water, and its concentration ratio can reflect the release of endogenous pollutants to a certain extent. Bostrom *et al.* (1982) revealed that, when the concentration of DIP in interstitial water of sediment is 5 to 20 times that of overlying water, the DIP can be released into the overlying water. Generally, the DIP in the interstitial water of Ulansuhai Lake tends to release toward the overlying water, but the diffusion varies. The concentration ratio between DIP in overlying water and interstitial water in the surface sediment (0–2 cm) of Ulansuhai Lake ranged from 0.53 to 16.7. At I12, J13, K12 and L11, where the overlying and interstitial water is more concentrated, the ratio was smaller (0.53–2.0), while in areas with lower concentrations of DIP in the overlying and interstitial water, there were obvious concentration gradients and higher ratios. The concentration ratio was highest at Q8 (16.72), while it was 13.79 and 15.84 at M14 and N13, respectively. These findings indicate that the endogenous phosphorus tends to release from the interstitial water to overlying water.

Based on the spatial distribution of DIP in Ulansuhai Lake, the highest DIP contents in the 0–2 cm surface sediment interstitial water were at J13, K12, M14 and N13. This is mainly because the northwest area of the lake is greatly affected by human activities, containing discharge outlets of exogenous pollutants from different channels. This results in a large amount of phosphorus entering this portion of the lake, increasing the likelihood of its deposition on the bottom. It is also connected to the 'oxbow' appearance of this part of the lake. Vortex flows are caused when water discharged to the lake mixes with water flowing from the northern part of the lake. As a result, the flow velocity decreases and phosphorus nutrients are deposited in the surface sediments. Therefore, this area has the highest content of phosphorus nutrients in the

Table 1 | Diffusive fluxes across the sediment–water interface of DIP

Site	Fitting curve	R^2	dc/dx mg/L·cm	Porosity φ	D_0 10^{-6} cm^2/s	D_s 10^{-6} cm^2/s	F mg/m^2·d
I12	$y = 0.21e^{-0.0966x}$	0.554	-0.0207	0.95	6.12	5.52	-0.092
J13	$y = 0.1023e^{0.1723x}$	0.745	0.0178	0.46	6.12	2.82	0.020
K12	$y = 0.207e^{0.102x}$	0.953	0.0211	0.78	6.12	3.72	0.053
L11	$y = 0.0706e^{-0.231x}$	0.983	-0.0079	0.94	6.12	5.41	-0.072
M12	$y = 0.0554e^{-0.0532x}$	0.779	-0.0029	0.97	6.12	5.72	-0.014
M14	$y = 0.0287e^{0.4173x}$	0.649	0.0120	0.30	6.12	1.84	0.006
N13	$y = 0.0279e^{0.6561x}$	0.711	0.0177	0.72	6.12	3.17	0.036
P9	$y = 0.0266e^{0.321x}$	0.830	0.0085	0.83	6.12	4.22	0.026
P11	$y = 0.0298e^{0.3696x}$	0.505	0.0107	0.43	6.12	2.63	0.010
Q8	$y = 0.0174e^{0.4267x}$	0.751	0.0073	0.95	6.12	5.54	0.034

surface sediment interstitial water. The highest contents of DIP in the overlying water were observed in the lake inlet and the northwestern portion of the lake, at I12, J13, K12 and L11. Overall, DIP was found to decline significantly from the northern to the southern part of the lake.

The minimum DIP content of all sampling spots was observed at the lowest level of the sediment interstitial water. This was mainly because sediment in this lake is lithologically dense and therefore not affected by overlying water and other disturbances. In addition, there is less active organic detritus, fewer organic materials and lower microbial activity at the bottom of the lake; therefore, the DIP content in the sediment interstitial water is lower. Furthermore, sediment pH, moisture content and conductivity can influence the vertical distributional characteristics of dissolved phosphate in interstitial water to a certain degree, and integrated factors are the reason for the declining trend of dissolved phosphate content in interstitial water.

As shown in Figure 4, the sediment pH tended to rise gradually with increasing depth, eventually becoming alkaline. The maximum pH of the underlying sediment was 8.18 and alkalescent characteristics are shown. This could be explained by buffering of pH changes in the sediment by carbonate dissolution, which would lead to an increase

of pH, as previously described (Blackford & Kita 2013). The total phosphorus in the surface sediment of Ulansuhai Lake primarily consists of inorganic phosphorus, which accounted for 56.80%–90.44% of the total phosphorus. Inorganic phosphorus was primarily Ca-bound, which accounted for 23.1%–41.5% of the total phosphorus. Since carbonate salt and calcium carbonate dissolve as pH decreases, low pH facilitates the release of phosphorus from Ca-bound phosphorus, while high pH hinders its release. Diagenesis becomes stronger below a certain depth, while potentially releasable inorganic phosphorus tends to be converted into stable mineral-bound phosphorus under alkaline conditions, which is difficult to release. As a result, the content of dissolved phosphate in interstitial water tends to decline.

As shown from the vertical distribution of sediment conductivity, the conductivity in sediment is higher at 0–15 cm. As depth increased, the conductivity declined slowly. Since there is a 10 cm layer of organic detritus on the upper sediment, the mineralization and decomposition of organic matter is obvious in this layer, where a high level of organic materials is decomposed into inorganic materials; therefore, the ion content is higher in the interstitial water. As depth increases, free organic ions are slowly converted into stable carbonate and silicate, and the ion content is reduced
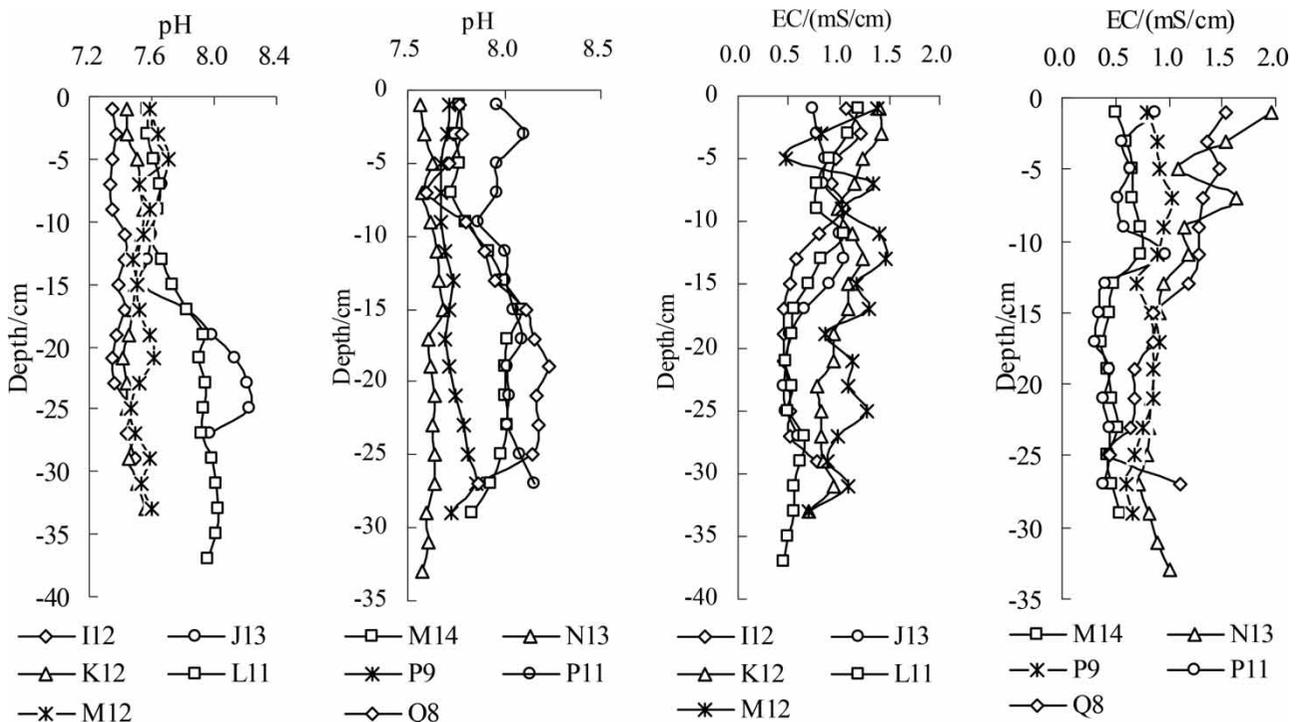

Figure 4 │ Vertical changes of pH and electrical conductivity (EC) at the sediment–water interface of different sampling locations.

in the interstitial water. Moreover, the moisture content of the sediment declines gradually with increasing depth, which lowers microbial and enzymatic activity, reducing the mineralization of organic materials. As a result, the rate of conversion from organic phosphorus to inorganic phosphorus decreases significantly.

Diffusion flux of DIP at the sediment–water interface

Analysis of the location of the lake suggests that areas with negative exchange rates are primarily located near Xidatan County, where the main drain, No. 8 drain, and No. 9 drain are nearby. Evaluation of algal blooms in recent years indicates that Xidatan, where I12 and L11 are located, is at high risk for yellow algae. The mass propagation and growth of algae is likely influenced by the adsorption of phosphorus in the water by sediment. For this study, samples were collected in June, which is a high-yield period of algae. The peak season for the growth of chlorophyta in Ulansuhai Lake is June, and high values are usually observed around I12 and L11, where the density of green algae and cyanobacteria is high. The rapid growth of algae can significantly reduce the bio-available phosphorus content in the water environment. A portion of the phosphorus consumed during primary production is imported exogenously, while the rest is provided by recycling within the system. During the algal growth period, sediments likely provide algae with phosphorus, as does the overlying water. With the rapidly improving demand for phosphorus, the requirement of the overlying water for phosphorus supplementation cannot be satisfied, which results in its having to adsorb phosphorus from sediments instead. As a result, the phosphorus content of the interstitial water in

sediments will slowly decrease, leading to a phosphorus deficiency, which causes phosphorus in the overlying water to migrate to the sediments and form a phosphorus sink. Therefore, the growth of algae leads to an internal sink of phosphorus nutrients at Xidatan, where I12 and L11 are located. Moreover, Fan *et al.* (2006) found that in open lake areas, the content of suspended particles disturbed by water movement is high. These surface particles have large specific surface areas under high reoxygenation and high temperature conditions, which enables them to easily adsorb anionic phosphate radicals in water. M12, located in the visible water area in the middle of the lake, has sediments that can easily adsorb phosphorus from the water.

Although the phosphorus content in the sediment at K12 was not high, the silt in this area has a high median size and release rate, resulting in a smaller total specific surface area, which results in a higher release of phosphorus. The high release rate of N13, Q8, P9 and P11 was mainly because these sites are located in the southern lake near the outlet, which is influenced by waves and varying forms of the lakebed. Moreover, the lake becomes narrower from north to south, and wastewater discharged through the outlet flows to the south, carrying large amounts of phosphorus. The phosphorus is then absorbed by a large number of reeds, waterweeds and other aquatic plants in this region, resulting in lower levels of phosphorus in the water. As a result, the gradient increases and the release of phosphorus in the surface sediments is accelerated. Moreover, the algal density of Q8 is higher than that of other areas. Algae are perennial and produce more death in wracks. Detritus is generally not completely decomposed in the lakebed, and the generated residues are buried. Anaerobic degradation by microorganisms then results in DIP dissolving into the interstitial water.

Comparative analysis of the phosphorus diffusion flux of Ulansuhai Lake and other lakes in southern China (Table 2) revealed that the diffusion flux of DIP in Lake Ulansuhai is smaller than that of other listed water bodies. This is primarily because Ulansuhai Lake is located in a cold region of China characterized by a 4-month period in which the air temperature is approximately $-15\,°C$ and there is an ice depth of 0.3–0.6 m. As a result, less phosphorus is released from sediments than in lakes in warmer regions, resulting in a lower annual release volume relative to southern lakes. Overall, the results of this study indicated that temperature, dissolved oxygen and hydrodynamic conditions are the main factors affecting endogenous phosphorus release in the lake.

Table 2 | Diffusive fluxes across the sediment–water interface of DIP

	Range (mg/m²·d)	Average (mg/m²·d)	Reference
Ulansuhai Lake, China	(−0.092)–0.053	0.026	This study
East Taihu Lake, China	(−0.17)–0.76	0.38	Zhang *et al.* (2006)
Meiliang Bay in Taihu Lake, China	0.02–0.41	0.23	Zhang *et al.* (2006)
Fubao Bay in Dianchi Lake, China	0.118–0.265	0.18	Li *et al.* (2008a, 2008b)
Xuanwu Lake, China	1.296–1.584	1.46	Gong *et al.* (2006)

Contribution of sediment to DIP release to the lake

Analysis of the aforementioned diffusion flux of DIP at the sediment–water interface of Ulansuhai Lake indicated that lake sediment is the primary internal source of phosphorus. Under certain environmental conditions, lake sediments tend to release phosphorus to the overlying water, which causes increased phosphorus concentrations in water and aggravates water pollution.

In a shallow lake with slow metabolism (water depth less than 10 m; detention time about 2 years), the high phosphorus concentration is one of the important factors to support algae growth at high density. Also, organic matter decomposition causes the anaerobic condition at the lake bottom, which promotes the 200 mV potential threshold line shift to the surface sediment (van Kessel 1978). Ulansuhai Lake is a shallow lake with an average depth of 1.4 m, and a dissolved oxygen (DO) range of 0.02–2.04 mg/L (average = 0.31 mg/L). Moreover, 90% of the lake has DO levels below 1.0 mg/L, indicating that the bottom of the lake is anaerobic. Under anaerobic conditions, $Fe(OH)PO_4$ can be dissolved and release DIP and Fe_4^{3-} into the overlying water. To explain the dynamic process of sediment release, the release strength of sediments was measured and the overall amounts of DIP released in different spots and from all lake sediments were calculated. During the computational process, the water quality of Xiaohaizi was not measured because this area is not impacted by ship traffic. Thus, this area was excluded from the computation. The total area of the lake is 293 km^2, while the actual data used for the analysis corresponded to 237.33 km^2. The amounts of DIP released at the sediment–water interface

of Lake Ulansuhai, acquired based on Formula (2), are as shown in Table 3. With the exception of I12, L11 and M12, the amount of DIP released was positive. The exchange capacity of DIP at the sediment–water interface of the entire Ulansuhai Lake was 1.30 t/a. Overall, these findings indicate that the sediment of Lake Ulansuhai is characterized by internal loading of phosphorus.

Table 3 shows the exchange rates of DIP at the interface of Ulansuhai Lake, acquired based on measured data collected from different areas using Fick's law. Different areas of the lake showed different patterns of DIP absorption and release. Specifically, the flux of DIP at I12, L11 and M12 was −0.092, −0.072 and −0.014 mg/m²·d, respectively. The negative diffusion flux indicates that phosphorus nutrients in the overlying water were adsorbed and fixed by sediments. Such release to sediment is referred to as 'internal source', while adsorption of the substance by sediment is known as 'internal sink'.

The sediment–water interface of the lake was acquired based on Formula (3), without considering temperature layering and on the premise that the water is intensively mixed and the sediment release to the overlying water through the interstitial water is only influenced by molecular diffusion. Specifically, for the performance of all tested spots, Q8 is biggest (81.5%), N13 (38.5%) is more than P9 (21.2%), which is greater than P11 (8.59%), and K12 is smallest (2.7%) at positive contribution rate. The deviation from the law of phosphorus diffusion flux is mainly because the influencing factors of W include the retention duration of water, water depth and DIP concentration. Although K12 had the highest DIP diffusion flux, the water depth there was 2.12 m, which reduced the contribution of DIP release

Table 3 | Release amounts of DIP at the sediment–water interface of Lake Ulansuhai and the contribution rate of sediment phosphorus release to the water

Site	Area km²	F mg/m²·d	Released t/a	C_w mg/L	H m	T_w d	C_d mg/L	CR %
I12	7.61	−0.092	−0.26	0.167	2.04	200.00	−0.009	−5.40
J13	29.88	0.020	0.22	0.071	2.00	200.00	0.002	2.79
K12	10.48	0.053	0.20	0.185	2.12	200.00	0.005	2.70
L11	11.58	−0.072	−0.30	0.095	1.52	200.00	−0.009	−9.92
M12	11.1	−0.014	−0.06	0.052	2.30	200.00	−0.001	−2.34
M14	29.44	0.006	0.06	0.009	1.80	200.00	0.001	7.09
N13	12.94	0.036	0.17	0.009	2.10	200.00	0.003	38.51
P9	23.79	0.026	0.22	0.014	1.80	200.00	0.003	21.24
P11	22.83	0.010	0.09	0.014	1.80	200.00	0.001	8.59
Q8	77.68	0.034	0.96	0.004	1.90	200.00	0.004	81.50
Total	237.33		1.30					

to the water. Among all source phases, the degree of DIP release was smallest here. In contrast, the DIP diffusion flux of spot Q8 was 0.034 mg/m^2·d. Although this was not the maximum level observed, it had the highest effect on water, up to 81.5%. This is mainly because the concentration of DIP is low in the overlying water, there is a large diffusion gradient and the depth is shallow. Thus, the interstitial water diffusion at Q8 has a greater effect on the overlying water. Spots M14 and N13 have smaller diffusion flux, but the concentration of the overlying water is lower. Once the exogenous pollutants of Ulansuhai Lake are under control, sediment interstitial water and differences in the nutrient concentration of the overlying water will determine the release of endogenous nutrient loading from the sediment. Therefore, even for spots with small diffusion flux, the degree of the overlying water concentration and water depth should be considered.

In real sediment–interstitial water–overlying water lake systems, diffusion flux is also influenced by ion exchange, absorption, storm and waves. Diffusion flux acquired based on the interstitial water formula will only reflect the trends in DIP exchange between the sediment and water. In addition, only the effects of diffusion flux, water depth, phosphorus concentration and seasonal water retention duration have been focused on with respect to the contribution made by interstitial water diffusion to water, while factors such as temperature layering and water retention duration have not been considered.

CONCLUSION

There is an obvious gradient between the concentration of DIP in the surface interstitial water and overlying water of Ulansuhai Lake. The ratio is small at the lake entrance and large in the central and southern portions of the lake, indicating that the internal phosphorus of Ulansuhai Lake tends to release from the interstitial water to the overlying water. The release rate of DIP from different areas of Ulansuhai Lake was calculated using an interstitial water concentration diffusion model, and these values were then used to determine the overall release from the lake. The results showed that DIP release occurred via internal action in most lake areas, and the exchange capacity of DIP at the sediment–water interface was 1.30 t/a. The lakebed of the central and southern part of the lake and water in areas with perennial plants affected by the anaerobic conditions caused by waves and decaying plant matter often have internal sinks in the sediment. Comparative

analysis of the amount released and the concentration in the overlying water and interstitial water showed that the effects of endogenous pollutants on the aquatic environment are influenced by the concentration of the overlying water, the rate of its release, and water depth.

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