Effects of pH on phosphorus form transformation in lake sediments

Zhao, Shengnan

2022-02-01

Zhao , S , Shi , X , Sun , B , Liu , Y , Tian , Z & Huotari , J 2022 , ' Effects of pH on phosphorus form transformation in lake sediments ' , Water Science and Technology: Water Supply , vol. 22 , no. 2 , pp. 1231-1243 . https://doi.org/10.2166/ws.2021.356

http://hdl.handle.net/10138/342747
https://doi.org/10.2166/ws.2021.356

Water Supply

Water Supply Vol 22 No 2, 1231 doi: 10.2166/ws.2021.356

Effects of pH on phosphorus form transformation in lake sediments

Shengnan Zhao[a], Xiaohong Shi[a,*], Biao Sun[a], Yu Liu[a], Zhiqiang Tian[a,b] and Jussi Huotari[c]

[a] College of Water Conservancy and Civil Engineering, Inner Mongolia Agricultural University, Huhhot 010018, China
[b] Civil Engineering Department, Hetao College, Bayenaoer 015000, China
[c] Lammi Biological Station, Ecosystems and Environment Research Programme, Faculty of Biological and Environmental Sciences, Helsinki University, Lammi FI-16900, Finland
*Corresponding author. E-mail: imaushixiaohong@163.com

SZ, 0000-0002-9684-9361

ABSTRACT

The pH value of lake water varies with the lake environment, which has an effect on the form of phosphorus in sediment, and then the release of sediment phosphorus. The form of phosphorus in sediments was analyzed using field sampling. The environmental conditions with pH values of 4.0, 7.0 and 10.0 were simulated indoors to estimate the effects of pH on phosphorus release from sediments and the content change of various forms of phosphorus was studied. The results showed that in Wuliangsuhai Lake, Ca-P accounted for 54.3%, which was the largest portion of the TP. Phosphorus release was favored under acidic and alkaline conditions, and the alkaline condition was more favorable. The proportion of Fe/Mn-P and Fe/Al-P in the TP decreased with an increase in the pH, while the proportion of Ca-P in the TP increased with an increase in the pH. Under the alkaline condition ($pH = 10$), Ca-P in the sediment increased significantly, with an increase of 22.5%. However, Fe/Mn-P and Fe/Al-P decreased significantly, with drops of 37.3% and 44.9%, respectively. Under the acidic condition ($pH = 4$), Fe/Mn-P and Fe/Al-P in the sediment increased significantly, and the increases were 63.1% and 37.1%, respectively. However, Ca-P decreased significantly, with a drop of 39.2%. In general, low pH promoted the release of Ca-P, and a high pH promoted the release of Fe/Mn-P and Fe/Al-P. Wuliangsuhai Lake water is characterized by weak alkaline characteristics throughout the year, and biological available phosphorus accounts for 13.3%–20.9% of the TP, with Fe/Mn-P being the dominant form. This study revealed that the risk of phosphorus release from sediments to the overlying water was greater under alkaline conditions.

Key words: pH, phosphorus forms, sediment

HIGHLIGHTS

- Evaluate the effect of pH change on different phosphorus forms content in sediments of lake.
- Determine phosphorus forms and the effects of pH on their fraction transformation based on indoor simulation experiments.
- To explore which part of phosphorus form was affected by pH change, and which resulted in the change of phosphorus content in sediments, which is the focus of this study.

1. INTRODUCTION

Phosphorus is an important factor that affects lake water function, as well as water ecosystem composition and structure, and it is one of the key nutrient elements in the eutrophication of lake water (Bao *et al.* 2017; Daneshgar *et al.* 2018; Yang *et al.* 2018; Ja *et al.* 2020). Internal P loading is the important factor in eutrophication, and the eutrophication state can be maintained for a long time (Yang *et al.* 2020). Phosphorus release from sediments is a key process that affects the effectiveness of eutrophication mitigation (Ma *et al.* 2021). The primary reason for the change in phosphorus content in sediments is the adsorption and release of phosphorus in sediments. In essence, a change in the external environmental conditions causes a change in the phosphorus form in sediments. It is speculated that a change in the phosphorus form is the primary reason for a change in the phosphorus content in water and sediments. In addition, a change in the phosphorus form can affect the migration and transformation of phosphorus through the sediment–water interface. Different forms of phosphorus have different activities and cause different effects in water (Ja *et al.* 2020). One form of phosphorus in sediments can be

---

converted into another, affecting the bioavailability of phosphorus, as well as phosphorus release to the overlying water, which further influences the eutrophication degree of lake water.

Influences of the phosphorus exchange between sediments and the water column can be physical, chemical, and biological (Wu *et al.* 2014). pH is one of these factors, and it has been the subject of several studies (Bostrom 1988; Wu *et al.* 2014; He *et al.* 2017; Temporetti *et al.* 2019). Jin and colleagues found that, in alkaline conditions, P release increased with rising pH (Jin *et al.* 2006). Variations in water column pH had a significant impact on sediment mobile P, including OP (Kong *et al.* 2021). These studies were performed in laboratories, where a pH gradient was simulated, and the release amount was determined. However, the change of each form of phosphorus was not determined. The question of how a change in pH changes the form of phosphorus in sediments remains undetermined. Therefore, it is necessary to study the forms of phosphorus in sediments under different pH gradients. Wuliangsuhai Lake is located in a cold and arid region with obvious seasonal characteristics, resulting in significant changes in its external environmental conditions. These changes would inevitably change the forms of phosphorus, affect the transfer and conversion of phosphorus at the sediment–water interface, and thereby affect the phosphorus content in the lake.

The aim of this study is to evaluate the effect of pH change on the different phosphorus form contents in the sediments of the lake. Therefore, in this study, the phosphorus forms and the effects of pH on their fraction transformation are determined based on laboratory simulation experiments. The focus of this study is to explore the part of the phosphorus form that is affected by pH change, which results in a change in the phosphorus content in the sediments.

2. MATERIALS AND METHODS

2.1. Study site

Wuliangsuhai Lake (40°36′ to 41°03′N, 108°43′ to 108°57′E) is located in Urad Qianqi, Bayandao City, in Inner Mongolia. The water area is 293 km^2, with an average lake elevation of 1,018.5 m, and the water depth is 1.1–2.8 m, with an average depth of 1.8 m. The annual average precipitation in Wuliangsuhai Lake is 224 mm, and the annual evaporation is 2,456 mm. The annual sunshine duration is 3,185.5 h, and the daily illumination rate can reach 72%. The annual average temperature is 5.8 °C, the extreme maximum temperature is 37.7 °C, and the extreme minimum temperature is −30.8 °C. The average frost-free period over the years is approximately 152 days. The lake freezes in early November and melts in early April of the following year. The frozen period typically lasts 5–6 months, and the thickness of the ice is approximately 0.3–0.6 m (Liu *et al.* 2017; Tian *et al.* 2020).

2.2. Sampling sites and dates

In this study, in total 10 sampling sites were established in Wuliangsuhai Lake (Figure 1). The site locations were determined using a geographic positioning system (GPS). Surface sediment samples were collected on June 27, 2016 using a column sampler.

2.3. Field methods

Water samples were collected from each site with a plastic bottle (10 L). The pH, dissolved oxygen, total dissolved solids (TDS), water temperature, and conductivity were measured using a YSI Professional Plus instrument *in situ*.

All of the surface sediment samples were placed into clean sealed bags, and the air in the bags was drained. The samples were stored in the dark at low temperature and then brought back to the laboratory for analysis.

2.4. Laboratory methods

2.4.1. Processing of the sediments samples

The sediment samples from each same sampling point were divided into fresh and air-dried soil samples and then treated separately. The air-dried soil samples were naturally dried in a cool and ventilated place at room temperature. They were then crushed with wooden sticks to remove impurities such as large and small stones, animal residues, and plant roots. After grinding, the substances were put through 100 mesh sieves, mixed well, and bagged for the index determination.

2.4.2. Analysis of samples

2.4.2.1. Physical and chemical characterization. For the determination of pH of the sediments, 10 g of sediment samples that were air-dried and ground through a 100-mesh sieve (accurate to 0.0001 g) were placed in a 50-ml beaker, and 25 ml deionized water was added (ratio of soil to water was 1:2.5). This was mixed and stirred for 1 min using a glass

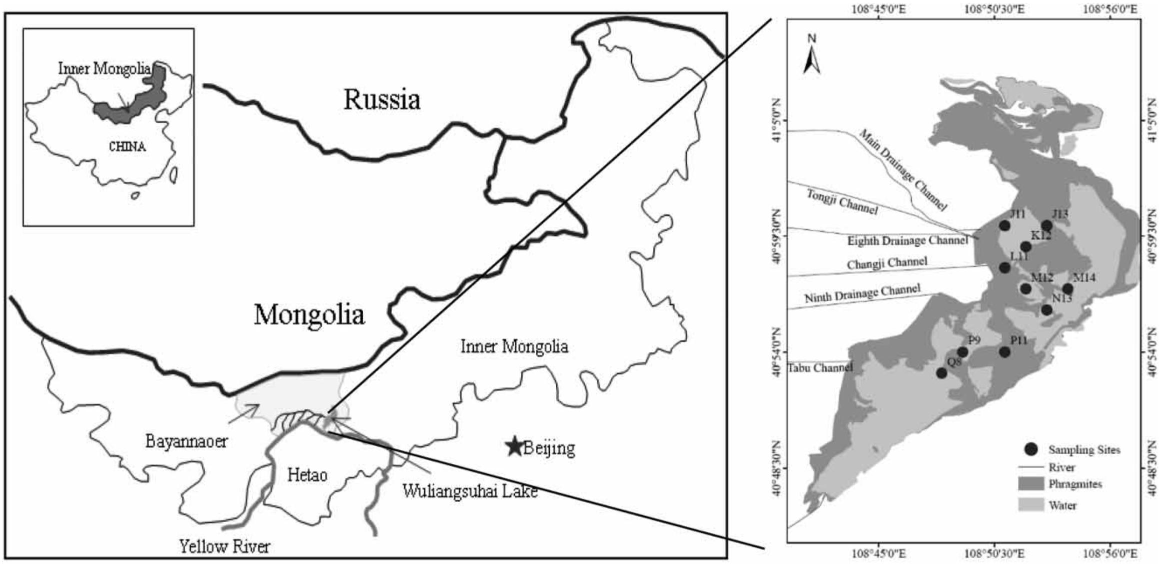

Figure 1 | Sampling sites.

rod until the soil particles were well dispersed, and left to sit for 30 min. An electrode with a pH meter was then inserted into the sample suspension (at the mud–water interface) to measure the pH value. The method was carried out according to the China national standard NY-T 1377–2007.

Several fresh sediment samples were collected and dried at 108 °C, and the moisture content was calculated using the mass difference method.

2.4.2.2. The total phosphorus. A total of 0.3 g of the air-dried soil sample was run through a 100-mesh sieve, and 5 ml nitric acid, 2 ml sulfuric acid, and 1 ml hydrogen peroxide were added for digestion. The supernatant was absorbed and placed in a volumetric flask into which one drop of dinitrophenol indicator was added, a 4 mol/L NaOH solution, as drops until the solution turned yellow. Then, one drop of a 2 mol/L sulfuric acid solution was added to make the yellow color of the solution disappear. Then, a molybdenum antimony sulfate reagent was added, and ultra-pure water was used to obtain a constant volume of 50 ml. After 30 min, a wavelength of 660 nm was used for colorimetry on a UV-Vis light spectrophotometer, and the absorbance value of the measured solution was recorded. According to the standard curve, the phosphorus content of the solution tested was obtained, and then the total phosphorus content of the sediment was calculated.

2.4.2.3. Phosphorus fractionation. The different phosphorus form contents were determined using the sequential extraction scheme according to Psenner (1988). The extraction process separated the forms of phosphorus in the sediment into weakly adsorbed phosphorus (NH_4Cl-P), iron-manganese-bound phosphorus (Fe/Mn-P), iron-aluminum-bound phosphorus (Fe/Al-P), calcium-bound phosphorus (Ca-P), and residual phosphorus (Res-P). The continuous extraction steps were as follows:

Step 1. NH_4Cl-P was extracted. A dried and ground soil sample weighing 0.25 g was placed into a 50-ml centrifuge tube, and 25 ml of NH_4Cl (l-mol/L) was added. This was oscillated for 1 h (220 rpm, 25 °C) at a constant temperature and then centrifuged for 10 min (10,000 rpm). The supernatant was removed and extracted again using the same procedure, and this was combined with the supernatant. The content of the dissolved total phosphorus in the extract was determined after being filtered using a 0.45-μm filter membrane.
Step 2. The residue was cleaned, and 25 ml of deionized water was added. This was oscillated for 10 min (220 rpm, 25 °C), centrifuged for 5 min (10,000 rpm), and the liquid was removed.
Step 3. Fe/Mn-P was extracted. A 25 ml solution of 0.11 mol/L $NAHCO_3$ and 0.11 mol/L safety powder–sodium disulfite was added. This was oscillated for 0.5 h (220 rpm, 40 °C), centrifuged for 10 min (10,000 rpm), and then the supernatant was filtered using a 0.45-μm filtration membrane to obtain the extract. Step 2 was repeated to clean the residue. In

order to eliminate the interference of the insurance powder, 5–10 ml of the extract at a constant volume was collected, and 1.6 ml of 5% potassium persulfate was added. The test liquid was then cooled to room temperature. The content of the dissolved total phosphorus in the extract was determined after being filtered using a 0.45-μm filter membrane.

Step 4. Cleaning of the residue was performed by adding 25 ml deionized water, oscillating for 10 min (220 rpm, 25 °C), and centrifuging for 5 min (10,000 rpm); the liquid was then removed.

Step 5. Fe/Al-P was extracted. First, 25 mL of NaOH (1 mol/L) was added, and this was oscillated for 16 h (220 rpm, 25 °C), centrifuged for 10 min (10,000 rpm), and the supernatant was collected. The content of the dissolved total phosphorus in the extract was determined after being filtered using a 0.45-μm filter membrane.

Step 6. Cleaning of the residue was performed by adding 25 ml of deionized water, oscillating for 10 min (220 rpm, 25 °C), and centrifuging for 5 min (10,000 rpm); the liquid was then removed.

Step 7. Ca-P was extracted by adding 25 ml of HCl (0.5 mol/L), oscillating for 16 h (220 rpm, 25 °C), and centrifuging for 10 min (10,000 rpm); then, the supernatant was collected. The content of the dissolved total phosphorus in the extract was determined after being filtered using a 0.45-μm filter membrane.

Step 8. Cleaning of the residue was performed by adding 25 ml of deionized water, oscillating for 10 min (220 rpm, 25 °C), and centrifuging for 5 min (10,000 rpm); then, the liquid was removed.

Step 9. Res-P was extracted by adding 25 mL of NaOH (1 mol/L), oscillating for 24 h (220 rpm, 85 °C), and centrifuging for 10 min (10,000 rpm); then, the supernatant was collected. The content of the dissolved total phosphorus in the extract was determined after being filtered using a 0.45-μm filter membrane.

2.4.3. Laboratory simulation experiment

Point J11, located in the lake center area, was found to accumulate a high phosphorus content in the sediments after long-term monitoring and was chosen as the research object (TP: 1,790.07 mg/kg). The effects of different pH conditions on the phosphorus release in the surface sediments of Wuliangsuhai Lake were studied. The water utilized for the experiment was the overlying water at the origin point after filtering through a 0.45-μm filter (TP: 0.0466 mg/L; pH: 7.65). The specific experiment was as follows.

In total, 20 g of dried surface sediment samples were weighed and placed at the bottom of three 500-ml beakers. The beakers were then slowly injected with 400 ml of experimental water with a modulated pH. The pH value of the beakers was regulated using l mol/L HCl and 1 mol/L NaOH (Wang *et al.* 2009).

According to the pH monitoring data of Wuliangsuhai Lake water from 2002 to 2016, the water pH was between 4.0 and 10.8, and the mean values of pH during winter, spring, summer, and autumn were 8.7, 9.0, 8.2, and 8.4, respectively (Figure 2). The pH value indicated that the water environment of Wuliangsuhai Lake was neutral–alkaline. Hence, the static simulation experiments of phosphorus release in sediments were determined under the pH conditions of pH = 4.0, pH = 7.0, and pH = 10.0.

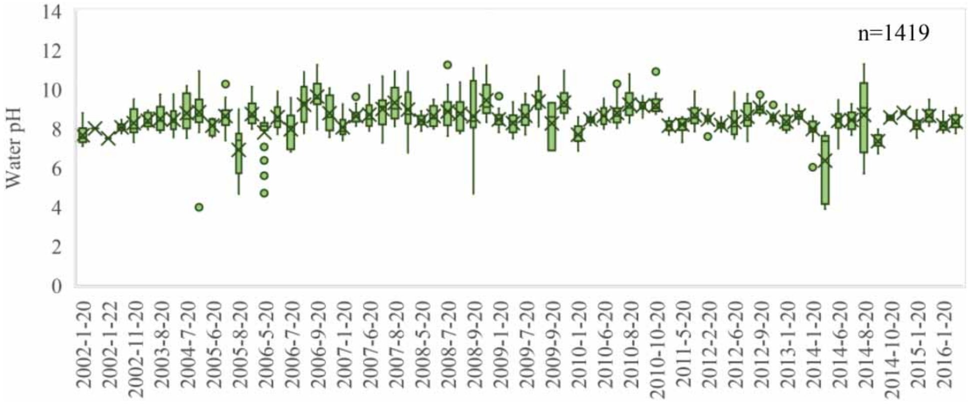

Figure 2 | 2002–2016 pH of Wuliangsuhai lake water. *Note*: The data from Observation and Research Station of Wuliangsuhai Wetland in Inner Mongolia, National Forestry and Grassland Administration, the abscissa represents sampling time. From January 2002 to January 2016, in total 66 samples were taken, with about 20 or 21 water samples taken each time, and 1,419 samples were taken for 66 times. The box diagram in the figure represents the upper Edge, Upper Quartile, Median, Lower Quartile, and Lower Edge of the 21 sampling points sampled at each time.

pH reconditioning was conducted daily. The liquid level scale was recorded, and 50 mL of each water sample were collected with a syringe at intervals of 6, 12, 24, 48, 72, 96, 120, 168, 216, 264, 312, and 360 h. The experiment lasted for 15 days, and in total 12 samples were collected. Three parallel experiments were performed under each pH condition for a total of 108 samples. In addition, a filtered sample water from the original sampling point was added to the original scale and cultured in a 20 °C incubator. The water samples were then collected, centrifuged, and passed through a 0.45-μm filter to determine the TP (Jin *et al.* 2004). After the experiment, the phosphorus forms in the sediments were determined following the same procedures described above. The control is the original sample without pH adjustment.

2.5. Data analysis

The biological available phosphorus (BAP) is the amount of phosphorus that can be released as dissolved phosphate and used by aquatic organisms (Norgbey *et al.* 2020). In the current study, the equation proposed was the following (Ja *et al.* 2020):

$$\mathrm{BAP} = \mathrm{NH_4Cl\text{-}P} + \mathrm{Fe/Mn\text{-}P} + \mathrm{Fe/Al\text{-}P} \quad (1)$$

The potential bioavailable phosphorus can contribute significantly to local primary production when this fraction enters the water column. As such, an assessment of a water ecological ecosystem should recognize not only the phosphorus content but also the phosphorus forms.

3. RESULTS AND DISCUSSION

3.1. Analysis on ecological risk and transfer ability of phosphorus pollution in surface sediments

The TP content in the surface sediments of Wuliangsuhai Lake ranged from 840.1 to 2,709.0 mg/kg, with an average of 1,656.7 mg/kg and a coefficient of variation of 0.2 as shown in Figure 3. Phosphorus in sediments is most closely related to benthic organisms and has an important impact on their habitats. If the content exceeds a certain level, it will exert toxic effects on benthic organisms. At present, experts and scholars refer to ‘the Ministry of Environment and Energy of Ontario, Canada’ for their research. The Canadian baseline values focus on the safety of sediments that have no toxic effects on benthic organisms. In China, there is one standard, which is ‘the thresholds of TN and TP reference values in sediments of typical lakes in eastern China’, the standard is mainly aimed at typical lakes in eastern China. So, according to the guidelines for a sediment quality assessment based on the ecotoxicity effect issued by the Ministry of Environment and Energy of Ontario, Canada, the TP content that generates the lowest ecotoxicity in sediments is 600 mg/kg, and the content that generates severe ecotoxicity is 2,000 mg/kg (Mudroch & Azcue 1995). According to this standard, the TP content of all the sampling points in the surface sediments of Wuliangsuhai Lake was higher than 600 mg/kg, and the TP content value of 20% of the sampling points was higher than 2,000 mg/kg. This indicated that the TP in most of the surface sediments of Wuliangsuhai Lake might have exerted certain ecotoxicity effects on benthic organisms, and some areas might had caused serious ecotoxicity effects. This poses a great threat to the benthic communities and the ecological environment of the Wuliangsuhai Lake area.

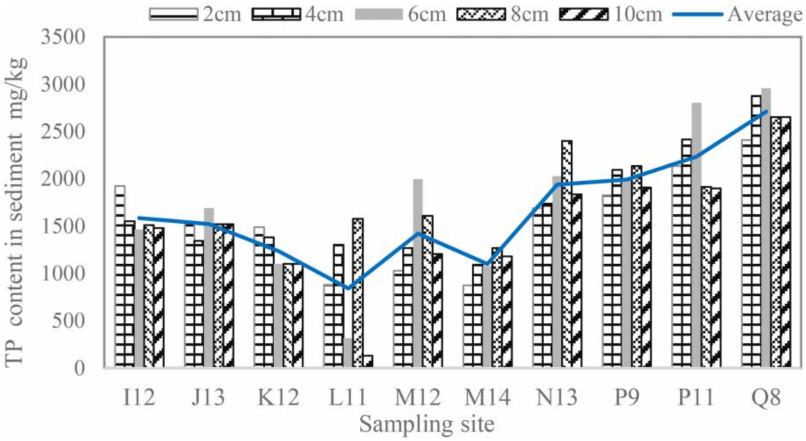

Figure 3 | The spatial distribution of total phosphorus in surface sediments of Wuliangsuhai Lake.

The content of NH_4Cl-P in the surface sediments of Wuliangsuhai Lake was very low, and it ranged from 15.7 to 31.1 mg/kg (Table 1 and Figure 4), with an average of 23.9 mg/kg and a coefficient of variation of 0.4 (Table 1). This accounted for 0.7%–3.6% of the TP and 1.7% of the average percentage of TP. The content of Fe/Mn-P in the surface sediments of Wuliangsuhai Lake ranged from 125.3 to 193.9 mg/kg, with an average of 161.2 mg/kg and a coefficient of variation of 0.1 (Table 1 and Figure 4). Reduction–oxidation reaction (redox)-sensitive phosphorus is very sensitive to the redox potential (Ruban *et al.* 2001). The content of Fe/Al-P in the surface sediments of Wuliangsuhai Lake ranged from 30.1 to 88.1 mg/kg, with an average of 64.0 mg/kg and a coefficient of variation of 0.2 (Table 1 and Figure 4). When the sediment–water interface is anaerobic, Fe/Al-P dissolves and is released into the overlying water. It is then absorbed and utilized by algae and other aquatic plants (Hao *et al.* 2019). The content of Ca-P in the surface sediments of Wuliangsuhai Lake ranged from 249.1 to 1,498.3 mg/kg, with an average of 944.8 mg/kg and a coefficient of variation of 0.2 (Table 1 and Figure 4). The content of Res-P in the surface sediments of Wuliangsuhai Lake ranged from 283.1 to 940.0 mg/kg, with an average of 462.7 mg/kg and a coefficient of variation of 0.2 (Table 1 and Figure 4). Res-P was the most stable among all the forms of phosphorus in the sediments (Kaiserli *et al.* 2002; Lane & Autrey 2016; Parsons *et al.* 2017).

There were large differences in the contents of inorganic phosphorus components in the surface sediments of Wuliangsuhai Lake. The component distribution order was: Ca-P (54.2%) > Res-P (28.7%) > Fe/Mn-P (11.0%) > Fe/Al-P (4.2%) > NH_4Cl-P (1.6%) (Figure 4). Therefore, the primary form of phosphorus in the sediments of Wuliangsuhai Lake was Ca-P.

It was more appropriate to estimate the phosphorus contents derived from the loading of the sediments by the contents of the BAP rather than the TP in the sediments. The single sample non-parametric K-S test showed that the data listed in Table 2 were normal. The BAP content in the sediments of Wuliangsuhai Lake ranged from 179.1 to 307.8 mg/kg, with an average of 247.9 mg/kg, accounting for 9.9%–36.6% of the TP (Figure 5). It can be seen that the phosphorus in the surface sediments of Wuliangsuhai Lake had a certain transfer ability. This was primarily composed of Fe/Mn-P, accounting for 60.2%–70.9% of the BAP (Table 2). Fe/Mn-P is most closely related to the process of phosphorus transfer and conversion in lake water environments. This potentially active phosphorus has an important relationship with loading in lakes.

3.2. Effects of different pH conditions on phosphorus release in sediments

Under the neutral condition of $pH = 7$, the concentration of TP in the overlying water was the lowest. After 24 h of the release experiment, the TP concentration in the overlying water reached a maximum, with a value of 0.17 mg/L (Figure 6(a)). Under the acidic condition of $pH = 4$, the TP concentration in the overlying water was slightly higher than in the neutral condition. After 72 h of the release experiment, the TP concentration in the overlying water reached a maximum of 0.45 mg/L (Figure 6(a)). Under the alkaline condition of $pH = 10$, the TP concentration in the overlying water was the highest. After 48 h of the release experiment, the TP concentration in the overlying water reached a maximum of 0.78 mg/L, and the maximum value appeared one day earlier than that under acidic conditions (Figure 6(a)). The values in Figure 6 are the average of the three samples.

An increase in the pH of the overlying water is beneficial for the release of phosphorus in sediments, and this is primarily because the pH of the overlying water directly affects the existence modes of phosphate. When the overlying water is weakly acidic, the form of phosphorus is primarily HPO_4^{2-}, and when the former is weakly alkaline, the latter is primarily $H_2PO_4^{-}$. The adsorption was the largest in the second condition, and the magnesium salt, silicate, alum inosilicate, ferric hydroxide colloids, and other molecules in the sediments were all involved in the adsorption process. An increase in pH could promote the desorption of phosphate radical ions from the ferric hydroxide colloid and release more phosphate into water, which will enhance the release of phosphorus from sediments. This would result in an increase in the phosphorus content in the overlying water. Therefore, a pH increase favors the release of phosphorus in sediments.

The release content is equal to the total phosphorus content at each sampling time point minus the total phosphorus content in the initial water sample. These observations suggest that phosphorus release from the sediments occurred in both acidic and alkaline conditions, and the alkaline condition was more favorable. However, the least amount of phosphorus was released under the neutral condition (Figure 6(b)).

3.3. Content changes of different forms of phosphorus in sediments before and after phosphorus release experiment

The proportion of NH_4Cl-P in the TP increased with an increase in the pH. NH_4Cl-P accounted for 0.4%, 0.6% and 0.5% of the TP when the pH value was 4.0, 7.0 and 10.0 respectively. (Figure 7). The content of NH_4Cl-P in the original sediment sample was 21.6 mg/kg. After the release experiment, its content in the sediment sample was 3.2, 6.7, and 5.3 mg/kg

Table 1 | Average contents (M ± SE) of P forms in surface sediments of Wuliangsuhai Lake (mg/kg)

	I12	**J13**	**K12**	**L11**	**M12**	**M14**	**N13**	**P9**	**P11**	**Q8**	**Mean**
NH_4Cl-P	24.1 ± 0.01	23.7 ± 1.1	25.4 ± 0.28	30.1 ± 0.12	25.7 ± 0.71	25.6 ± 0.55	31.1 ± 1.46	15.7 ± 0.19	18.7 ± 1.02	19.36 ± 0.68	23.94 ± 0.62
Fe/Mn-P	150.9 ± 0.3	125.3 ± 0.3	149.6 ± 0.9	193.9 ± 0.2	159.3 ± 0.7	171.4 ± 0.8	147.9 ± 0.4	164.3 ± 0.6	186.3 ± 0.4	163.24 ± 0.9	161.21 ± 0.56
Fe/Al-P	50.01 ± 0.47	30.12 ± 1.11	70.15 ± 1.28	83.85 ± 0.86	55.52 ± 0.97	44.63 ± 0.78	66.43 ± 1.20	80.65 ± 2.42	70.56 ± 0.68	88.15 ± 1.37	64.01 ± 1.11

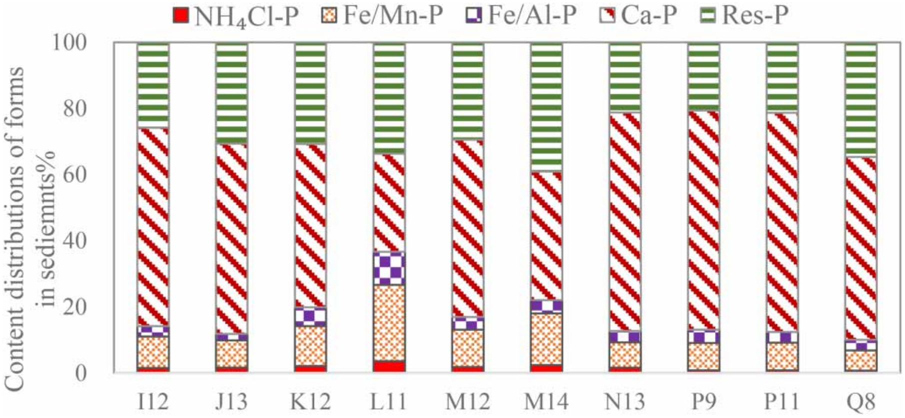

Figure 4 | The relative contribution of different phosphorus forms in surface sediments of Wuliangsuhai Lake.

Table 2 | Average contents (M ± SE) of BAP and proportion of BAP in TP ($n = 10$)

	BAP/(mg/kg)	Proportion of BAP in TP/%	Fe/Mn-P/(mg/kg)	Proportion of Fe/Mn-P in BAP/%
I12	225.01 ± 0.11	14.19	150.9 ± 0.35	67.06
J13	179.12 ± 1.95	11.78	125.3 ± 0.3	69.95
K12	245.15 ± 0.1	19.88	149.6 ± 0.90	61.02
L11	307.85 ± 1.18	36.64	193.9 ± 0.20	62.99
M12	240.52 ± 2.38	16.93	159.3 ± 0.70	66.23
M14	241.63 ± 0.57	22.02	171.4 ± 0.80	70.93
N13	245.43 ± 0.14	12.66	147.9 ± 0.40	60.26
P9	260.65 ± 1.63	13.1	164.3 ± 0.60	63.03
P11	275.56 ± 1.30	12.34	186.3 ± 0.40	67.61
Q8	270.75 ± 1.65	9.99	163.24 ± 0.96	60.29
Mean	249.167 ± 0.62	16.953	161.21 ± 0.56	64.93
P	0.2	0.118	0.2	0.2
Type	N	N	N	N

Note: p is Asymp. Sig. (2-tailed), $p > 0.05$ shows that data are normally distributed. N is normal distribution.

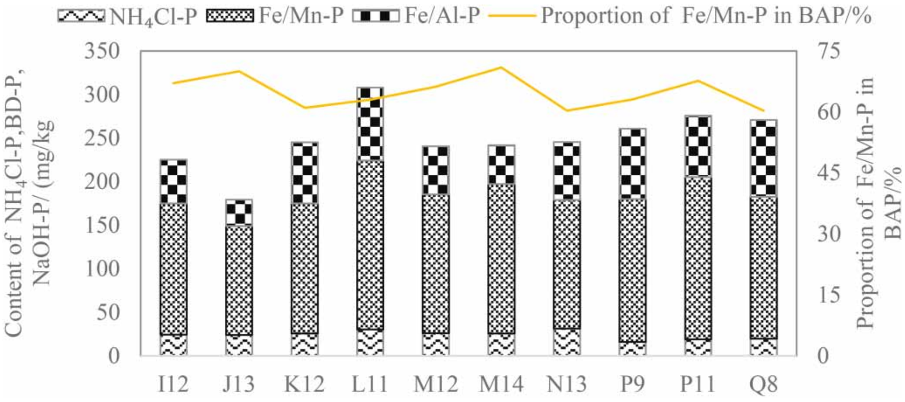

Figure 5 | The content distribution of bioavailable available phosphorus in surface sediments of Wuliangsuhai Lake.

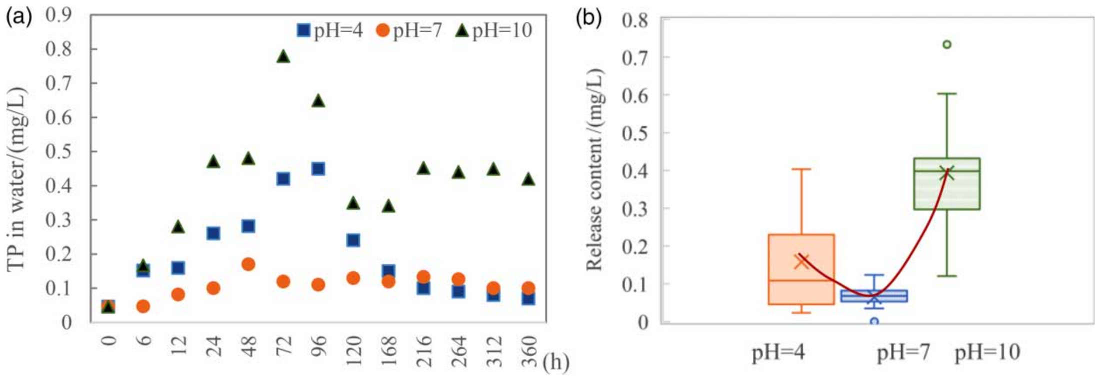

Figure 6 | Release of phosphorus from sediments at different pH values. *Note:* Figure 6(a) shows the total phosphorus content in water under different pH values as time changes. Figure 6(b) shows the amount of total phosphorus released from sediments to overlying water under different pH values. Under the condition of pH = 4, 7, 10, experiments were carried out respectively, and data of 13 overlying water bodies were obtained in each experiment (as shown in Figure 6 (a)). The concentration values of overlying water bodies at different release times were used to subtract the initial concentration values (t = 0) to obtain the release amounts at different times, and then the statistics of box diagram were obtained as shown in Figure 6(b).

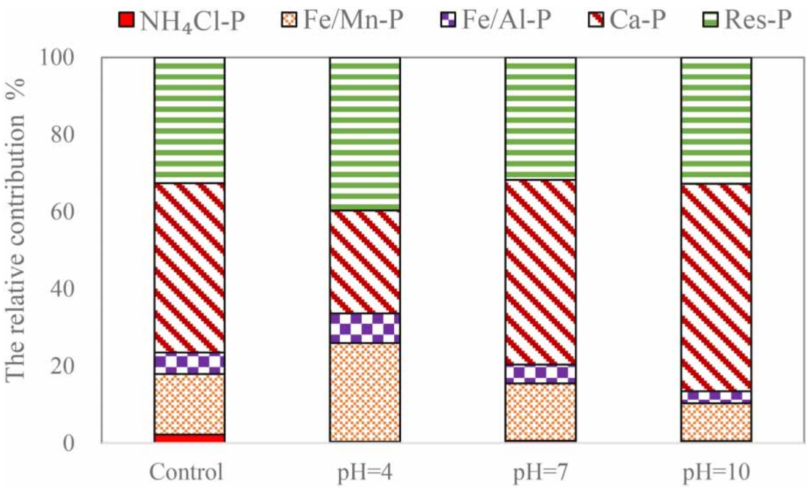

Figure 7 | Content changes of different forms of phosphorus in sediments under different pH conditions.

under the conditions of pH = 4, pH = 7, and pH = 10, respectively (Figure 8). The NH_4Cl-P in the sediments was released and converted into a portion of the soluble phosphorus in the overlying water. The weakly adsorbed phosphorus (NH_4Cl-P) primarily included loose adsorbed phosphorus on the surface of the sediment minerals, dissolved active phosphorus in the interstitial water, and phosphorus released from dead biological cell residues containing carbon (Zhou *et al.* 2005).

The content changes of Fe/Mn-P and Fe/Al-P were similar under the different pH conditions. The proportion of Fe/Mn-P and Fe/Al-P in the TP decreased with an increase in pH. When the pH value was 4.0, Fe/Mn-P and Fe/Al-P accounted for 25.5% and 7.69% of the TP, respectively. When the pH value was 7.0, it accounted for 14.8% and 4.8% of the TP, respectively. When the pH value was 10.0, it accounted for 9.8% and 3.1% of the TP, respectively (Figure 7). The Fe/Mn-P in the original sediment samples was 152.7 mg/kg, and the Fe/Al-P was 54.6 mg/kg. After the release experiment, under the condition of pH = 4, the Fe/Mn-P and Fe/Al-P increased significantly and were 206.4 and 62.1 mg/kg, respectively (Figure 9). Due to an increase in H^+, Fe^{3+}, and $A1^{3+}$ combined with PO_4^{3-}, HPO_4^{2-}, and $H_2PO_4^-$ in the water, they were re-adsorbed into the sediments. Under the condition of pH = 7, the Fe/Mn-P and Fe/Al-P were slightly reduced. This was because in a neutral environment, the primary forms of phosphate are HPO_4^{2-} and $H_2PO_4^-$, which are easily combined with some metal elements and then adsorbed in sediments, and thus the amount of release is minimal. Under the condition of pH = 10, Fe/Mn-P and

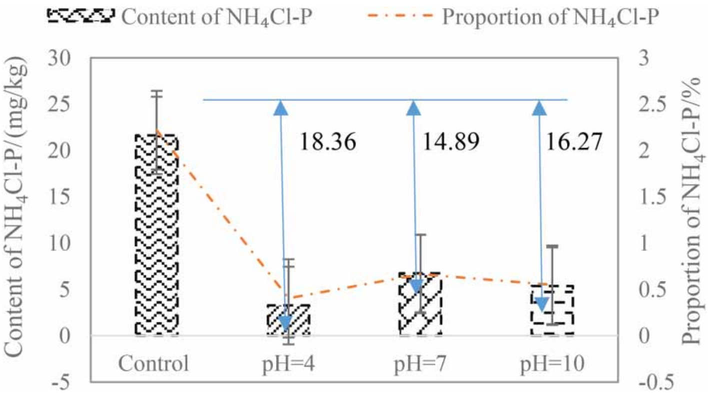

Figure 8 | Content and proportion of NH_4Cl-P changes of different forms of phosphorus in sediments under different pH conditions. *Note:* The numbers with the arrows in the figure panel refer to the left *y*-axis. The blue arrows represents the difference of NH_4Cl-P content between the control experiment and the experimental condition of pH = 4, 7, 10.

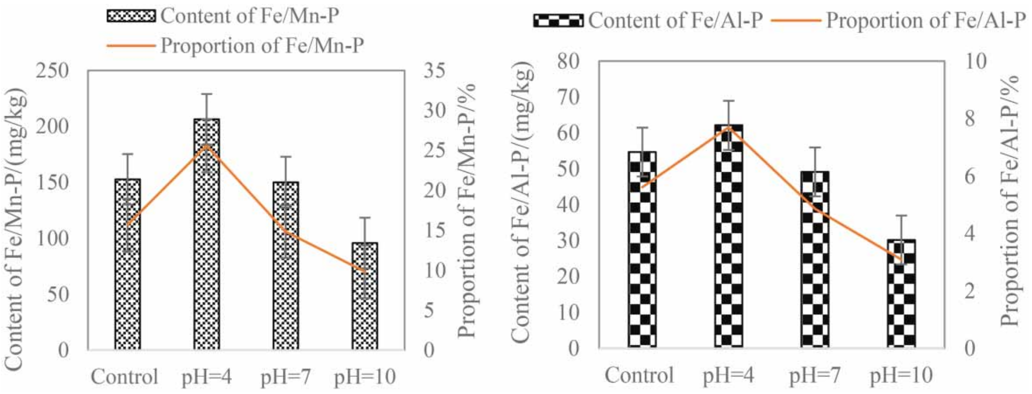

Figure 9 | Content and proportion of Fe/Mn-P and Fe/Al-P changes of different forms of phosphorus in sediments under different pH conditions.

Fe/Al-P decreased significantly by 95.6 and 30.1 mg/kg, respectively, before and after release. Under alkaline conditions, phosphate is primarily ion exchanged, that is, OH^- can be exchanged with a phosphate radical in Fe^{3+} and Al^{3+} cements, resulting in a large solution of iron- and aluminum-bound phosphorus in sediments. Phosphorus combined with Fe^{3+} and Al^{3+} was re-released into the water due to ion exchange. Fe/Mn-P plays an important role in the fixation and release of phosphorus at the sediment–water interface of the lake and is a significant component of potentially active phosphorus in sediments. Fe/Mn-P and Fe/Al-P are sensitive to pH. Under high pH conditions, the adsorbed phosphorus combined with amorphous or weakly crystalline iron and aluminum salts, such as ferrohydrate (FeOOH), blue iron ore ($Fe_3(PO_4)_2{\cdot}(H_2O)_8$), diaspore ($Al_2O_3{\cdot}H_2O$), and other molecules begin to be released to the overlying water continually. Under alkaline conditions, the surface of the variable charge body in the sediment carries a negative charge, which reduces the absorbability of $H_2PO_4^-$ in water. In addition, OH^- exists in large quantities in water and competes with the anions in the colloid in the sediment. Additionally, it exchanges with $H_2PO_4^-$ in the Fe/Al-P and increases the phosphorus content in the overlying water. This is consistent with the research results of Huang *et al.* (2003) and Jin *et al.* (2004).

The proportion of Ca-P in the TP increased with an increase in pH. The Ca-P content was 215.5 mg/kg, and Ca-P accounted for 26.7% of the TP in the sediment when the pH value was 4.0. The Ca-P accounted for 47.7% of the TP in the sediment when the pH value was 7.0. The Ca-P accounted for 53.7% of the TP in the sediment when pH value was 10.0. Under the alkaline condition of pH = 10, the Ca-P in the sediment samples increased significantly after the release experiment (Figure 9). The ratio of Ca-P to TP in the sediment under a low pH condition was lower than that under a high pH condition, indicating that acidic conditions were more conducive to the release of Ca-P in the sediment than neutral and alkaline conditions. Ca-P is highly stable in sediments and difficult to be dissolved. It is susceptible to low pH (Xin *et al.* 2020). Under acidic conditions, H^+ has a dissolution effect on Ca-P, which promotes the release of Ca-P in the sediment, resulting in an increase in $H_2PO_4^-$ in the water. This is consistent with the research results of Jin *et al.* (2004, 2006). Under alkaline conditions, Ca-P would produce deposits with certain substances in the sediments, causing an increase in its content. The release of some Fe/Mn-P in sediments might precipitate again and be converted to Ca-P, thereby increasing the amount of Ca-P.

Res-P is the most stable form of phosphorus, and it is not sensitive to pH changes and has difficulty participating in a short-time phosphorus cycle. The residual phosphorus content remains basically the same under the different pH conditions before and after the release experiment (Figure 10). In this experiment, one-way analysis of variance (ANOVA) was used to analyze the significance of Res-P content at different pH. It is found that all the data satisfy the normal distribution by using the Shapiro–Wilk normality test. According to the homogeneity of variance test, the significance of Res-P was all greater than 0.05, and the variance was homogeneity. Therefore, multiple comparison was used to analyze the significance of each treatment, and there was no significant difference in Res-P content among all groups ($P > 0.05$). Before the release experiment, the Res-P is 318.1 mg/kg, and after the release experiment the Res-P is 320.4, 321.4 and 319.8 mg/kg. Relatively speaking, after the release experiment, the residual phosphorus content in the sediment samples slightly increased compared with the original.

In general, pH was a factor that affected the release of phosphorus in sediments. Under neutral conditions, the phosphorus in the sediments was stable and not easily released. Acidic or alkaline conditions were favorable for the release of phosphorus in the sediments, with a larger release amount under alkaline conditions. Acidic conditions were conducive to the dissolution and release of Ca-P, and alkaline conditions were more conducive to the release of Fe/Mn-P and Fe/Al-P. As an important bioavailable phosphorus source in the surface sediments of Wuliangsuhai Lake, Fe/Mn-P accounted for the largest proportion. During the ice-free period, the water in Wuliangsuhai Lake exhibited weak alkaline characteristics. This occurs particularly from June to September, when algae and other phytoplankton grow in large quantities through intense photosynthesis, causing an increase in the lake water pH (Quan *et al.* 2019). This is beneficial to the release of iron–manganese chelated phosphorus in sediments to the overlying body, leading to an increase in the phosphorus content of the water. In addition, the phosphorus form is also affected by water redox characteristics under alkaline conditions. Fe^{3+} is lower and dissolved under a reduced oxidation–reduction potential, and phosphorus is released into the interstitial water. When the sediment–water interface is under anaerobic conditions, Fe/Al-P dissolves and is released into the overlying water. It is then taken up by algae and other aquatic plants. Located in the Mongolian Plateau Lakes, Wuliangsuhai Lake has obvious seasonal characteristics and undergoes an alternating process of ice-free season and an icebound season. Winter is a long period of the annual cycle for many lakes in the northern hemisphere. Low irradiance, ice, and snow cover lead to poor light penetration into the water column of these lakes. Therefore, in northern lakes, respiration often exceeds primary production leading to low dissolved oxygen concentrations (Song *et al.* 2019). The content of Fe/Mn-P and Fe/Al-P in the sediments of Wuliangsuhai Lake was 9.91%–28.56%. When the redox potential of Wuliangsuhai Lake changed, that is, during the icebound season, these two types of phosphorus could dissolve and be released into the overlying water, resulting in increases in the TP content in the water.

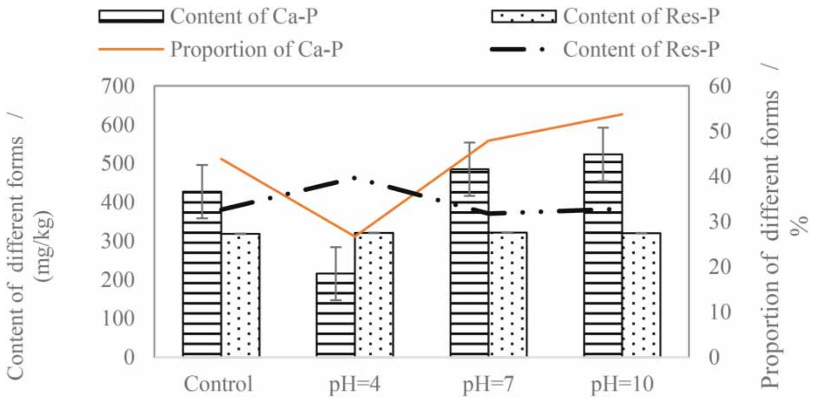

Figure 10 | Content and proportion of Ca-P, Res-P changes of different forms of phosphorus in sediments under different pH conditions.

4. CONCLUSION

The TP content in surface sediments of Wuliangsuhai Lake ranged from 840.16 to 2,709.03 mg/kg, with an average of 1,656.75 mg/kg. The order of the different inorganic phosphorus in the sediments was: Ca-P > Res-P > Fe/Mn-P > Fe/Al-P > NH_4Cl-P. The BAP in surface sediments accounted for 9.99–36.64%.

The pH alters the distribution of phosphorus types in sediments (NH_4Cl-P, Fe/Mn-P, Fe/Al-P, and Ca-P) and, hence, influences the content of phosphorus in lake water. Phosphorus release from the sediments occurred under both acidic and alkaline conditions, and the alkaline condition was more favorable. However, the least amount of phosphorus was released under the neutral condition. The effect of pH on phosphorus release was primarily reflected by the existing forms of phosphorus. A low pH promoted the release of Ca-P, and a high pH promoted the release of Fe/Mn-P and Fe/Al-P. Fe/Mn-P was an important bioavailable phosphorus in the surface sediments of Wuliangsuhai Lake, accounting for the largest proportion of easily transferable and converted phosphorus.

Wuliangsuhai Lake is characterized by weak alkaline characteristics throughout the year with high pH values. The iron–manganese chelated phosphorus in the sediments was found to be easily released into the overlying water. Therefore, water pH should be more accurately monitored and it is necessary to control the pH value of the water during the environmental treatment of Wuliangsuhai Lake. In addition, the changes of phosphorus form should be analyzed from the important factors affecting the release of phosphorus. Compared with subtropical and tropical lakes, lakes in cold regions have thicker ice sheets during the freezing period, which block the material exchange between the atmosphere and water. The existence of ice sheet changes the transmission of light to water and affects the light field environment of water. The organic matter content, salinity, eutrophication and other physical and chemical properties of the subglacial water changed greatly, especially the dissolved oxygen content of the bottom water. Due to the barrier of the ice sheet, the re-oxygenation process formed by natural aeration changes greatly, and the concentration of dissolved oxygen is at the lowest value. In particular, when snowfall occurs during the frozen period, the content of dissolved oxygen will be zero (extreme anaerobic conditions) (Song *et al.* 2019). The change of dissolved oxygen must have a great influence on the occurrence form of phosphorus, so we should analyze how the change of dissolved oxygen affects the occurrence form of phosphorus in the future.

The work was supported by the National Natural Science Foundation of China (52060022; 51779118; 51869020; 51909123). Ministry of Science and Technology of the Peoples' Republic of China (2017YFE0114800); The Inner Mongolia Autonomous Region Science and Technology Department (2019MS05032); The National Key Research and Development Program of China (2019YFC0409201;2019YFC0409204).

DATA AVAILABILITY STATEMENT

All relevant data are included in the paper or its Supplementary Information.

REFERENCES

Bao, Y. F., Wang, Y. H., Hu, M. M. & Wang, Q. W. 2017 Phosphorus fractions and its summer flux from sediments of deep reservoirs located at a phosphate-rock watershed, Central China. *Water Science & Technology: Water Supply* **18** (2), 688–697.

Bostrom, B. 1988 Relations between chemistry, microbial biomass and activity in sediments of a polluted vs. a nonpolluted eutrophic lake. *Verhandlungen International Verein Limnologie* **23** (1), 451–459.

Daneshgar, S., Callegari, A., Capodaglio, A. G. & Vaccari, D. 2018 The potential phosphorus crisis: resource conservation and possible escape technologies: a review. *Resources* **7**, 37.

Hao, W. C., Wang, C. F., Yang, Z. J., Liu, D. F., Ping, D. B., Yong, Z. & Long, D. Z. 2019 Speciation and transformation of phosphorus in sediments during the redox cycle. *Environmental Science* **40** (2), 640–648.

He, L. W., Zhou, X. J., Ji, L. & Li, B. 2017 Analysis of phosphorus form distribution and influence by pH and DO in the surface sediment of Erhai Lake. *Environmental Protection Science* **43** (3), 106–111.

Huang, Q. H., Wang, D. H., Wang, C. X., Ma, M. & Wang, Z. J. 2003 Relation between phosphorus forms in the sediments and lake eutrophication. *Environmental Science* **23** (6), 583–586.

Ja, B. M., Yuan, X. Y., Zhu, H., Nooni, I. K. & Khaing, Z. M. 2020 Spatial distribution and environmental significance of phosphorus fractions in river sediments and Its influencing factor from Hongze and Tiaoxi Watersheds, Eastern China. *International Journal of Environmental Research and Public Health* **17**, 5787.

Jin, X. C., Wang, S. R. & Pang, Y. 2004 The influence of phosphorus forms and pH on release of phosphorus from sediments in Taihu Lake. *China Environmental Science* **24** (6), 707–711 (in Chinese).

Jin, X. C., Wang, S. R. & Pang, Y. 2006 Phosphorus fractions and the effect of pH on the phosphorus release of the sediments from different trophic areas in Taihu Lake, China. *Environmental Pollution* **139** (2), 280–295.

Kaiserli, A., Voutsa, D. & Samara, C. 2002 Phosphorus fractionation in lake sediments-Lakes Volvi and Koronia, N. Greece. *Chemosphere* **46**, 1147–1155.

Kong, M., Liu, F. F., Zhang, W. J., Xu, X. T., Chao, J. Y., Wang, P. F., Wang, C. & Gao, Y. X. 2021 High resolution investigation of pH on control of mobile and organic phosphorus and associated release kinetics following lanthanum modified bentonite (LMB) amendment at the water-sediment interface. *Journal of Cleaner Production* **295**, 126–148.

Lane, C. R. & Autrey, B. C. 2016 Phosphorus retention of forested and emergent marsh depressional wetlands in differing land uses in Florida, USA. *Wetlands Ecology and Management* **24**, 45–60.

Liu, Y., Li, C. Y. & Anderson, B. 2017 A modified QWASI model for fate and transport modeling of mercury between the water-ice-sediment in Lake Ulansuhai. *Chemosphere* **176** (2), 117–124.

Ma, S. N., Wang, H. J. & Wang, H. Z. 2021 Effects of nitrate on phosphorus release from lake sediments. *Water Research* **194** (15), 116894.

Mudroch, A. & Azcue, D. J. M. 1995 *Manual of Aquatic Sediment Sampling*. Lewis Publishers, Boca Raton.

Norgbey, E., Li, Y., Ya, Z., Li, R., Nwankwegu, A. S., Takyi-Annan, G. E., Luo, F., Jin, W., Huang, Y. & Linda Sarpong, L. 2020 High resolution evidence of iron-phosphorus-sulfur mobility at hypoxic sediment water interface: an insight to phosphorus remobilization using DGT-induced fluxes in sediments model. *Science of the Total Environment* **724**, 138204.

Parsons, C. T., Rezanezhad, F., O'Connell, D. W. & Cappellen, P. V. 2017 Sediment phosphorus speciation and mobility under dynamic redox conditions. *Biogeosciences* **14** (14), 3585–3602.

Psenner, R. 1988 Fractionation of phosphorus in suspended matter and sediment. *Arch. Hydrobiol. Beih.* **30**, 98–110.

Quan, D., Shi, X. H., Zhao, S. N., Zhang, S. & Liu, J. J. 2019 Eutrophication of Lake Ulansuhai in 2006–2017 and its main impact factors. *Journal of Lake Sciences* **31** (5), 1259–1267.

Ruban, V., Lopez-Sanchez, J. F., Pardo, P., Rauret, G., Muntau, H. & Quevauviller, P. 2001 Harmonized protocol and certified reference material for the determination of extractable contents of phosphorus in freshwater sediments: a synthesis of recent works. *Fresenius Journal of Analytical Chemistry* **370**, 224–228.

Song, S., Li, C. Y., Shi, X. H., Zhao, S. N., Tian, W. D., Li, Z. J., Bai, Y. L., Cao, X. W., Wang, Q. K., Jussi, H., Tiina, T., Sari, U., Matti, L., John, Loehr & Lauri, A. 2019 Under-ice metabolism in a shallow lake in a cold and arid climate. *Freshwater Biology* **64** (10), 1710–1720.

Temporetti, P., Beamud, G., Nichela, D., Baffico, G. & Pedrozo, F. 2019 The effect of pH on phosphorus sorbed from sediments in a river with a natural pH gradient. *Chemosphere* **228**, 287–299.

Tian, W. D., Pei, G. X., Zhao, S. N., Shi, X. H. & Ma, H. 2020 Seasonal varieties and influential factors of heavy metals in sediments of Wuliangsuhai Lake. *Water Supply* **20** (15), 1–25.

Wang, S. R., Jin, X. C., Zhao, H. C. & Wu, F. C. 2009 Phosphorus release characteristics of different trophic lake sediments under simulative disturbing conditions. *Journal of Hazardous Materials* **161** (2–3), 1551–1559.

Wu, Y., Wen, Y., Zhou, J. & Wu, Y. 2014 Phosphorus release from Lake sediments: effects of pH, temperature and dissolved oxygen. *KSCE Journal of Civil Engineering* **18** (1), 323–329.

Xin, Y., Liu, B. Z., Pan, L. X. Song., Yang, Z. J., Ji, D. B., Cui, Y. J., Su & Q, Q. 2020 Study on the mechanism of the influence of flood storage at the end of the Three Gorges Reservoir on the phosphorus forms in the sediments of the tributary reservoir bay. *Aquatic Sciences* **82** (9), 617–629.

Yang, W. Q., Xiao, H., Li, Y. & Miao, D. R. 2018 Vertical distribution and release characteristics of phosphorus forms in the sediments from the river inflow area of Dianchi lake, China. *Chemical Speciation and Bioavailability* **30**, 14–22.

Yang, S. H., Peng, Z. H., Jiao, H. Z., Xu, J. & Wang, Y. G. 2020 External pollution source load and contribution of urban eutrophic Lakes-Taking Lake Houguanhu of Wuhan as an example. *Journal of Lake Science* **32** (4), 941–951.

Zhou, A. M., Wang, D. S. & Tang, H. X. 2005 Phosphorus fractionation and bioavailability in Taihu Lake (China) sediments. *Journal of Environmental Science* **17** (3), 384–388.

First received 21 April 2021; accepted in revised form 6 October 2021. Available online 19 October 2021