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## Phosphorus Release from the Sediments in Rongcheng Swan Lake under Different pH Conditions

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### Abstract

Rongcheng Swan Lake is a coastal lagoon in eastern Shandong Peninsula, China, whose water quality and ecological environment has deteriorated in recent years. The effect of pH on phosphorus (P) release from the sediments and the contribution of P fractions to release in Swan Lake were investigated. The results showed that the sediments released significant amount of P under the strong acidic (pH 3) and alkaline conditions (pH 9), especially at pH 3; whereas under the strong alkaline (pH 10) and neutral conditions, a low quantity of P was released in this lagoon. The sediments in northwestern lake (site 1) showed significantly higher P release than that in the west (site 2). Under the strong acidic condition, the maximum release rates at sites 1 and 2 were 204.49 and 159.12  $\mu\text{g}/\text{m}^2/\text{day}$ , respectively; while at pH 9, the maximum were 190.52 and 10.12  $\mu\text{g}/\text{m}^2/\text{day}$ , respectively. P fractions in the sediments indicated that P release was mainly from BD-P, HCl-P and NaOH-P fractions in Swan Lake. Under the strong acidic condition, the contribution of HCl-P to release was high; whereas under alkaline condition the release of NaOH-P was great. Due to the high proportions of mobile P (NaOH-P+BD-P) to total P in surface sediments, P release potential in northwestern sediments is large under the slightly alkaline environment of Swan Lake.

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*Keywords:* phosphorus release; pH; phosphorus fractions; Rongcheng Swan Lake

### 1. Introduction

Phosphorus (P) was one of the most important nutrients for lake eutrophication. P release from the sediments is often a significant component of the P budget of lakes, which can maintain a certain P level in the overlying water for a long time after reduction in external loading [1, 2]. Therefore, P release from the sediments has been a focus in lake research for several decades.

P release is affected by a multitude of factors, such as pH, redox potential, temperature, hydrological conditions, etc, and in various lakes different factors can be dominant [3–5]. Many investigations have shown that P release rate from the sediments increased markedly in the summer, and one of the reasons was the increase in pH caused by intense algal photosynthesis [6, 7]. pH can affect sorption-adsorption, precipitation-solubilization and oxidation-reduction reactions through its control over the concentrations of available iron, aluminum, and calcium [8]. At present, pH is believed to be an important regulating factor for P release from the sediments.

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However, the pH effect on P release differs between calcareous and non-calcareous sediments, freshwater and seawater system. In non-calcareous lakes, an increase in pH can free P from its binding with ferric complexes due to the competition between hydroxyl ions and phosphate ions [2, 3]. However, in calcareous lakes this P may be re-precipitated as hydroxyl apatite or adsorbed to CaCO<sub>3</sub>. In contrast to non-calcareous lakes, P immobilization may occur in calcareous lakes at higher pH levels due to co-precipitation or adsorption of P on calcite. This carbonate-bound P can be mobilized at lower pH value [8].

P remobilization from the sediments is probably controlled by its speciation, and it is important to know which part of the stock can be mobilized. According to Hieltjes and Lijklema [9], the extracted P fractions in lake sediments may be characterized as the loosely adsorbed P (NH<sub>4</sub>Cl-P), redox sensitive P (BD-P), metal oxide bound P (mainly of iron and aluminum, NaOH-P) and calcium bound P (HCl-P). The mobilizations of BD-P and NaOH-P fractions are the most important mechanism of P release under high pH values and anaerobic conditions [10–12]. The pH values for the maximum net liberation of P from lake sediments differ among different hydrological conditions.

Rongcheng Swan Lake is a small coastal lagoon in eastern Shandong Peninsula, China. The lake water is slightly alkaline, and the mean depth is less than 2.0 m. Water quality and ecological environment in this lake has deteriorated rapidly as a result of frequent human activities and inappropriate utilization in recent 30 years [13, 14]. Large amounts of *Enteromorpha prolifera* occur in the spring and summer, which caused the pH variations in the water column. However, few studies have been done concerning P release from the sediments in Swan Lake. The objective of this study was to understand the P release trend from the sediments when experiencing pH changes in a coastal lagoon. In present study, the effect of pH in the overlying water on P release from sediments, and the variability of P fractions in sediments before and after the release experiments were investigated in Swan Lake.

## 2. Materials and Methods

### 2.1. Study sites

Two sampling sites were chosen for collecting sediments in Swan Lake, where P pollution was relatively serious. Site 1 was in the northwest of the lake, near the entrance of some small rivers, through which large quantities of wastewater and sewage containing phosphorus came into the lake. Site 2 was at the west-tip of the lake, close to human habitation and the sixth middle school of Rongcheng City; this area receives domestic sewage from Chengshan Town, and water quality was most polluted throughout the lake. Some general characteristics of the sediments are summarized in Table 1.

### 2.2. Sediment and water sampling

The surface sediments (0–10 cm) were collected using a hand-driven stainless steel corer 50 cm long with an internal diameter of 6 cm (made in the Institute of Hydrobiology, Chinese Academy of Sciences) in May 2011. After homogenization, all the samples were kept in the portable refrigerator and delivered to the laboratory immediately. Upon return to the laboratory, moisture content and P fractions were analyzed, and the fresh sediments were tested for the rate of P release.

The overlying water was taken from the eastern Swan Lake, where the water quality was good. The pH of lake water was 8.1, total phosphorus (TP) was 0.013 mg/L, and soluble reactive phosphorus (SRP) was 0.002 mg/L. After being transported to the laboratory, the collected lake water was filtered immediately and stored at 4 °C for the release experiment.

### 2.3. Release experiment

The release experiments were performed in the 2.0 L glass beaker (24 cm in height, 13 cm in diameter), covered with dark cloth to avoid light. Each vessel contained 300 g of fresh sediment and 1.8 L of filtrated lake water. The pH of filtrated water was adjusted to desired pH levels with HCl or NaOH, respectively. Six treatments were conducted for each site: 3.0, 5.0, 7.0, 8.1 (CK), 9.0 and 10.0, and three repeats were conducted. All experiments were incubated for 20 days at ~22 °C, and SRP in the overlying water was monitored during the experimental period. Water sample (50 mL) was taken daily for the first 15 days and every other day thereafter in each vessel and analyzed for SRP. The

Table 1. Physical and chemical properties of the two studied fresh sediments

Parameters	Position	NH <sub>4</sub> Cl-P	BD-P	NaOH-P	HCl-P	pH
		mg/kg	mg/kg	mg/kg	mg/kg	
Site 1	N37°21.447' E122°34.301'	0.21	11.29	59.86	119.39	5.78
Site 2	N37°20.910' E122°33.482'	0.32	8.1	70.86	239.20	6.67

same volume of filtrated lake water were added to the vessel after sampling. During the incubation, the pH in overlying water was measured and validated every sampling time.

P fractions in the fresh sediments in each vessel were measured at the end of release experiment.

#### 2.4. Analytical methods

The SRP concentration in overlying water was analyzed using the molybdenum blue method. TP concentration was determined by the molybdenum blue method after digestion with K<sub>2</sub>S<sub>2</sub>O<sub>8</sub>+NaOH to orthophosphate [15]. pH was measured with a S20P-K pH meter (METTLER).

P fractions in fresh sediments were determined using the sequential extraction scheme of Hieltjes [9], and our procedure was described previously [16]. Fresh sediment was subjected to sequential chemical extraction with 1.0 M NH<sub>4</sub>Cl (0.5 h), 0.11 M NaHCO<sub>3</sub>/Na<sub>2</sub>S<sub>2</sub>O<sub>4</sub> (40 °C, 1 h), 1.0 M NaOH (16 h) and 0.5 M HCl (16 h). The extracts were centrifuged and the supernatants were filtered through a 0.45 μm pore-size P-free membrane. The SRP concentration in each fraction was determined as described above. The moisture content in sediments was determined by drying at 105 °C (2 h).

Statistical analysis was performed using SPSS 17.0 software package.

### 3. Results

#### 3.1. SRP concentrations in the overlying water

Figure 1 shows the SRP concentrations in the overlying water during the release experiment at the two sites. At site 1 (in northwestern lake), significant differences in SRP concentration were observed among different pH (pH 3–10), ranging from 2.68 to 431.39 μg/L. At pH 3, SRP concentrations (ranged at 55.98–431.39 μg/L) were the highest throughout the 20-day incubation, the second at pH 9, followed by at pH 7 and pH 8.1 (CK), and lowest at pH 10 (4.27–19.61 μg/L) (Fig. 1a, 1b).

For the sediments in western lake (site 2), the P release trend at different pH values was different (Fig. 1c, 1d). The highest SRP concentrations in overlying water were also observed at pH 3, ranging from 22.46 to 318.90 μg/L; whereas at other pH treatments (pH 5–10), SRP concentration remained lower or was close to the detection limit (0–25 μg/L). The order of SRP concentration was pH 3 >> pH 9 > pH 10 > pH 5, pH 7, CK.

As a whole, P release from the sediments varied greatly as a function of overlying water pH (in the 3–10 range). The SRP concentrations at pH 3 were highest at the two studied sites, and above pH 3, SRP concentrations decreased with increasing pH (pH 5–8); while at alkaline condition, relatively high SRP concentrations were observed at pH 9, but very low at pH 10. These results suggest that P release from the surface sediments was significantly high under the strong acidic condition, followed by the alkaline condition (pH 9), and lowest under the strong alkaline (pH 10) and neutral conditions in Swan Lake.

#### 3.2. P release rate from the sediments at different pH

Table 2 indicates that the release rate of phosphorus from the sediments differed with pH value and sampling sites. At pH 3, SRP concentration in the overlying water at site 1 increased sharply during the first 10 days, and decreased

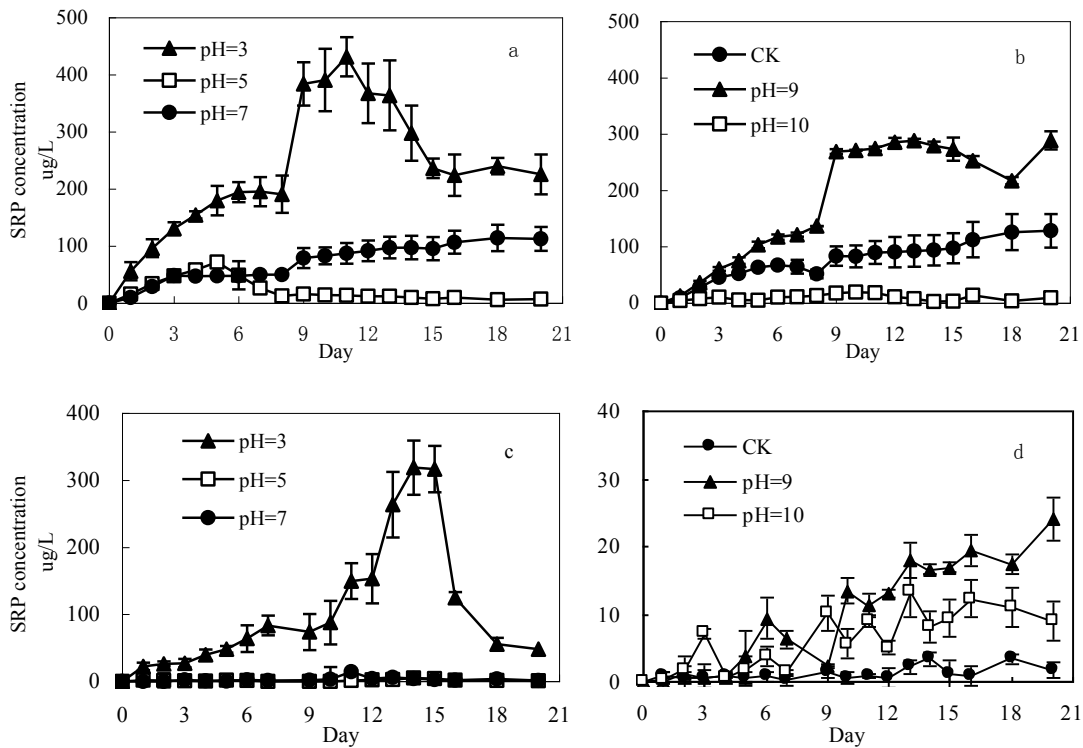


Fig. 1. The SRP concentrations with time in the overlying water during the incubation for site 1 (a, b) and site 2 (c, d)

Table 2. The release rate of phosphorus from the sediments during the experiment period ( $\mu\text{g}/\text{m}^2/\text{day}$ )

Treatments	5 days	10 days	15 days	20 days	
Site 1	pH=3	270.78±18.01	294.52±21.88	118.60±5.72	175.40±6.54
	pH=5	108.41±11.04	10.77±3.07	3.81±0.82	4.98±0.92
	pH=7	72.41±1.23	62.67±7.36	47.94±9.81	85.44±8.28
	pH=9	155.86±6.13	204.49±3.68	137.37±6.95	190.70±3.07
	pH=10	7.59±1.23	14.77±1.84	1.67±0.41	4.98±0.61
	CK	95.95±2.45	62.48±9.20	48.91±8.99	95.82±10.73
Site 2	pH=3	72.35±11.04	66.22±12.87	159.12±18.20	18.10±3.37
	pH=5	2.60±1.23	0.26±0.61	2.12±0.41	0.42±0.31
	pH=7	1.76±1.23	0.30±0.61	1.38±0.41	0.53±0.31
	pH=9	5.51±2.45	10.12±3.07	8.51±0.41	9.08±0.61
	pH=10	2.52±1.23	4.25±0.61	4.72±1.23	3.43±0.92
	CK	0.89±1.23	0.46±0.61	0.51±0.82	0.66±0.31

rapidly thereafter; for site 2, it increased rapidly during the first 15 days, and then decreased. The maximum release rates at sites 1 and 2 were 204.49 (0–10 days) and 159.12  $\mu\text{g}/\text{m}^2/\text{day}$  (0–15 days), respectively; which decreased to 175.40 and 18.10  $\mu\text{g}/\text{m}^2/\text{day}$  at the end of the incubation (Fig. 1, Table 2).

At pH 9, the SRP concentration in overlying water at site 1 increased rapidly with time during the first 10 days, remained stable at 10–15 days, and then decreased slightly; for site 2, it increased gradually throughout the experiment period. The maximum release rates at sites 1 and 2 at pH 9 were 190.52 and 10.12  $\mu\text{g}/\text{m}^2/\text{day}$ , respectively, which was

both observed during the first 10 days. At other pH treatments, SRP concentration remained at a low level, and the release rates were relatively low (Fig. 1, Table 2).

On the whole, P release increased rapidly with time at first, and then decreased sharply at the strong acidic conditions (pH 3). P adsorption capacity of the sediments enhanced as a result of the daily addition of  $H^+$  during the calibration of pH in the overlying water, which maybe one of reasons for the dramatic decrease in SRP concentration at the later period at pH 3. At neutral condition, P release increased with time at first, and then remain stable or decreased slightly; while at alkaline condition (pH 9), the release amount increased slightly or remain stable during the later period.

### 3.3. The difference in P release amount among different pH

The highest release amount at sites 1 and 2 were both observed at pH 3, which reached 5.30 and 3.99 mg/kg, respectively (Fig. 2). At alkaline condition, the maximum release amount at pH 9 was relatively high, but still lower than that at pH 3. The release amounts at pH 3 were 1.5 times and 13.1 times higher than that at pH 9 at sites 1 and 2, respectively. At circumneutral pH, a lower quantity of P was released.

For the sediments at site 1, there were significant differences in release amount among different pH treatments ( $P < 0.05$ ). However, the maximum release amounts at pH 3 were significantly higher than that at other pH at site 2, and no significant difference occurred in the 5–10 range. The maximum release amounts at site 1 were much higher than that at site 2 at the same pH. At pH 3, the release amount at site 1 was 1.3 times that at site 2; while at pH 9, the difference was much higher and reached up to 12 times (Fig. 2). The results indicate that the sediments from different areas in Swan Lake had different P release trend, which maybe connected with total P level, P fractions and physico-chemical characteristic of the sediments [3, 7].

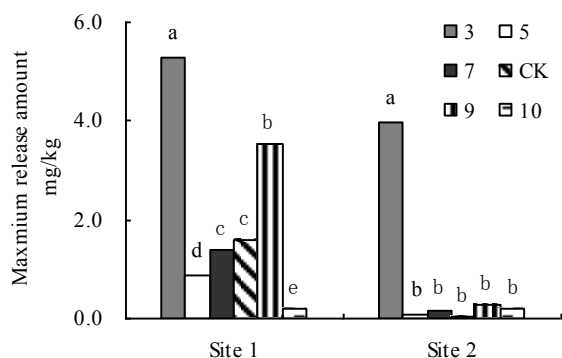


Fig. 2. The maximum release amount of phosphorus at different pH. LSD test,  $P < 0.05$ ,  $n = 3$

### 3.4. P fractions in the sediments

Figure 3 shows the concentrations of P fractions ( $NH_4Cl$ -P, BD-P, NaOH-P, HCl-P) in the sediments after the release experiment.  $NH_4Cl$ -P represents the loosely adsorbed phosphorus in the sediments, whose concentration was very low (ranged at 0.01–0.25 mg/kg) in Swan Lake (Fig. 3a). Due to the least proportion to TP in the sediments, the contribution of  $NH_4Cl$ -P to P release was minor.

BD-P represents the redox-sensitive P forms, which has been known to be a source for internal P loading [1]. BD-P concentrations ranged from 3.60 to 10.06 mg/kg, and large concentration differences were found among different pH, especially at site 2 (Fig. 3b). As the pH increased from 3 to 10, BD-P concentrations in the sediments changed as a U shape. Compared with other pH, it was relatively lower at pH 8 and pH 9.

NaOH-P represents P mainly bound to metal oxide, which is exchangeable again with  $OH^-$ . NaOH-P was the secondary inorganic P in the sediments of Swan Lake, varying at the range of 45.14–67.47 mg/kg (Fig. 3c). The lowest concentrations at two sites were both observed at pH 9, at which P release were relatively high. These results

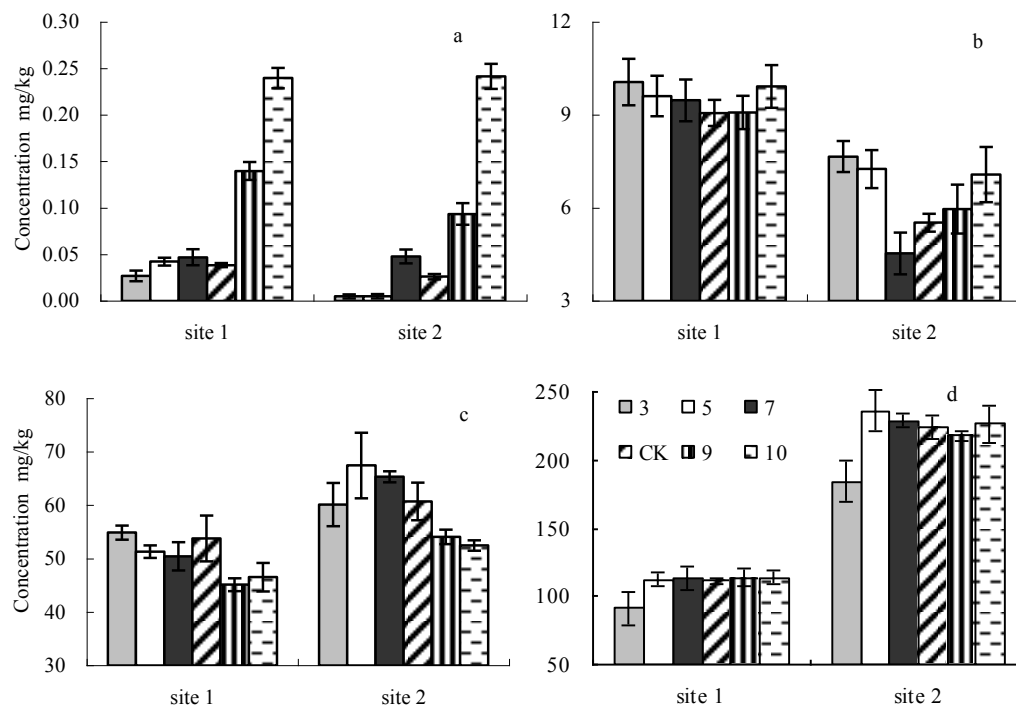


Fig. 3. The concentrations of P fractions in the sediments after the release experiment. NH<sub>4</sub>Cl-P (a), BD-P (b), NaOH-P (c) and HCl-P (d).

suggest that the contribution of NaOH-P to release was great at high pH.

HCl-P consists mainly of apatite P, P bound to carbonates and traces of hydrolysable organic P. In Swan Lake, HCl-P was the major component of inorganic P in the sediments, whose concentrations ranged from 91.25 to 236.24 mg/kg (Fig. 3d). The largest concentration difference before and after the release experiment were both observed at pH 3, at which the P release at the two sites were highest. No significance difference occurred among other pH values (pH 5–10), especially for site 1. These observations indicate that at strong acidic condition the released P was mainly from the dissolution of HCl-P in the sediments.

#### 4. Discussion

The pH in the overlying water can affect the phosphate adsorption, and ion exchange between OH<sup>-</sup> and PO<sub>4</sub><sup>3-</sup>, thus changes the P solubility in the sediments [17, 18]. In present study, the pH in overlying water had a significant effect on P release from the sediments during the 20-day incubation, and the release tendency differed with sites due to their difference in P fractions and physico-chemical characteristics of the sediments from different trophic areas. As a whole, the highest P release occurred at strong acidic condition (pH 3), followed by the alkaline condition (pH 9), and lowest at strong alkaline (pH 10) and neutral conditions. The high BD-P concentrations in the sediments maybe one of the reasons for larger P release at site 1.

The pH values for the maximum net liberation of P from lake sediments differ among different hydrological conditions. Lijklema (1980) argued that above pH 8.5 probably no positive binding sites remain on iron hydroxyl complexes, greatly reducing the phosphorus adsorption capacity of the sediments [19]. Seitzinger found that the release rate increased markedly when the pH was 9.5–10 [20]. However, the rate of P release in Taihu Lake decreased as pH increased from 2 to 6, but increased as pH increased from 8 to 12 [21]. Swan Lake was a coastal lagoon, whose salinity (32.04) and Ca<sup>2+</sup> concentration (0.44 g/L) in lake water were very high. The relatively low release at pH 10

maybe the result of the re-precipitation of the released P with Ca carbonates [2, 18]. The certain pH value at which P release begin to decrease at alkaline condition needs further investigation.

P remobilization from the sediments is probably controlled by its speciation, and the metal oxide bound P and calcium bound P are particularly sensitive to redox and pH variations of the system [10–12]. P fractions in the sediments showed that large concentration differences before and after the release experiment were observed in HCl-P at strong acidic condition (pH 3) and in NaOH-P at alkaline condition (pH 9). It suggests that the increase in pH promoted the release of NaOH-P, and the drop of pH promoted the release of HCl-P. BD-P has been known to be a source for internal P loading [9, 10], which can be released at slightly alkaline condition in Swan Lake.

Rydin (2000) reported that mobile P comprises BD-P and NaOH-P, whose concentrations in sediments can be used to estimate the potential release of sediment P to the overlying water [1]. In Swan Lake, there was large spatial variability of P fractions in the surface sediments. The potentially mobile P (NaOH-P+BD-P) constituted a considerable proportion of TP in the sediments from northwestern lake; whereas in the southeastern sediments HCl-P comprised a large proportion in the TP [22]. On the other hand, large amounts of *Enteromorpha prolifera* occur in northwestern lake. In the summer, due to the intense photosynthesis and the degradation of fresh organic matter, the pH value would increase and Eh decrease at the sediment-water interface, upon which NaOH-P and BD-P can be dissolved and released to the lake water [6, 20]. At present, pH values in Swan Lake varied at the range of 7.9–8.7. Therefore, it can be inferred that the sediments in northwestern area had greater release potential in Swan Lake.

## 5. Conclusions

P release from the surface sediments in Swan Lake varied greatly as effected by the pH in overlying water, and different sediments had different release trend. P release from the sediments occurred at the strong acidic (pH 3) and alkaline conditions (pH 9), and strong acidic condition was more favorable. However, the strong alkaline (pH 10) and neutral conditions were not favorable in this lagoon. During the 20-day incubation, the SRP concentrations in the overlying water increased rapidly with time at first, and then decreased sharply at strong acidic conditions; while at alkaline condition, SRP concentrations increased slightly or remain stable during the later period. The release rate from the sediments in the northwest lake was significantly higher than that in the west. P fractions in the sediments showed that high pH promoted the release of NaOH-P, and low pH promoted the release of HCl-P. It can be inferred that the sediments in northwest area had greater release potential at the slightly alkaline condition in Swan Lake.

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