Study on spatial-temporal distribution of different forms of phosphorus in wetland sediments

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Abstract. As an important factor for controlling phosphorus adsorption and release in wetland system, the forms of phosphorus in sediment has a decisive effect on phosphorus retention and release. Four different wetland systems were selected to study the phosphorus status and its environmental effects in wetland sediment. Phosphorus forms in sediments were related to aquatic plant characteristics. In the Vallisneria Linn. wetland system, the content of Ca-P of sediment was higher than the other systems because of its higher pH of the water. The maximum phosphorus adsorption capacity is 766.82-840.27 mg/kg. The content of Ca-P and TP have very good correlation with Smax. When the phosphorus concentration in the water is lower than 0.1 mg/L, the surface sediment is no longer a "sink" of phosphorus but a "source" of phosphorus. The changes of TP in four wetland sediments basically follow a similar trend. The phosphorus content in the sediment decreased during the growth period of aquatic plants, and the wetland sediment as the phosphorus "source" provided the biomass for the growth of the aquatic plants. In autumn and winter, phosphorus in plants is released into wetland again with the decay of plants, resulting in the increase of phosphorus content in sediment.

1. Introduction

The amount of available phosphorus and the process of water-sludge-bio-interface exchange in wetland sediment depend on the form of phosphorus in the sediment. Total phosphorus (TP) in sediment is composed of organic phosphorus (OP) and inorganic phosphorus (IP), which can be divided into soluble and insoluble forms [1-2]. The cycling and absorption process of various forms of phosphorus in wetland is affected by many factors. Study the forms of inorganic phosphate in sediment by using the method of classification is very important. About 70% of TP in wetland sediment is absorbed or dissolved inorganic forms of phosphorus. OP in wetland sediment includes inositol phosphate, phospholipids, nucleic acids and a small amount of phosphoprotein, sugar phosphate and microbial phosphorus, generally accounting for about 30% of TP in the sediment. The amount of OP released from wetland sediment is very small (2%-4% per year) [3-4], so it is not as important as IP. The inorganic forms of phosphorus are mainly orthophosphates, including PO₄³⁻, HPO₄²⁻, and H₂PO₄⁻, which ions predominate depending on the pH. The IP in sediments is usually...
classified into calcium phosphorus (Ca-P), aluminum phosphorus (Al-P), iron phosphorus (Fe-P) and occluded phosphorus (O-P) [5]. This classification can describe the characteristics of major inorganic phosphorus. Ca-P predominate in the relatively neutral to alkaline environment, and convert to low soluble Al-P and Fe-P in the strongly acidic environment.

The chemical and microbial processes determine the fixation and release of phosphorus. The fixation of phosphorus in sediment refers to the conversion of available phosphorus into ineffective phosphorus. The fixation and release of phosphorus in wetland sediments are affected by many factors, such as the type and quantity of clay, the quantity and activity of Fe³⁺, aluminum, calcium, magnesium, pH and redox potential. There are several ways to react phosphorus with clay, one of which is mainly the substitution of hydroxide ions (OH⁻) in the surface layer of clay minerals. The pH of sediment is an important factor for affecting the effectiveness of phosphorus in sediment. The change of pH can promote the absorption or release of phosphorus. There is a negative correlation between pH and various forms of phosphorus [6]. The absorption of inorganic phosphorus by sediment microorganisms temporarily reduced the available phosphorus in the sediment, and the inorganic phosphorus was released again after the microorganisms died.

As an important factor for controlling phosphorus adsorption and release in wetland system, the forms of phosphorus in sediment has a decisive effect on phosphorus retention or release. Four different wetland systems were selected to study the phosphorus status and its environmental effects in wetland sediment, which will provide a scientific basis for further studying the internal mechanism of phosphorus control in wetland system.

2. Materials and methods

2.1. Sample collection and analysis

The experimental device consists four reinforced concrete pools arranged in parallel. The size of each pool is 4 m*2 m*1m. The plants are Phragmites australis, Acorus calamus Linn., Iris tectorum Maxim. and Vallisneria Linn. The sediment samples were collected by a self-made columnar mud collector from April to November of each month. The mud samples were divided into three layers: upper layer 0-5 cm, middle layer 5-15 cm and lower layer 15-30 cm. The mud samples were dried and classified by 100 mesh screen. Total phosphorus (TP) in sediment is composed of inorganic phosphorus (IP) and organic phosphorus (OP). Inorganic phosphorus (IP) is divided into soluble phosphorus (D-P), aluminum-bound phosphorus (Al-P), iron-bound phosphorus (Fe-P), calcium-bound phosphorus (Ca-P), occluded phosphorus (O-P), organic phosphorus (OP). The process of gradual extraction is summarized in Figure 1.

![Figure 1. Stepwise extraction flow pattern of phosphorus in sediment.](image-url)
2.2. Adsorption experiment

Soluble KH$_2$PO$_4$ in 0.01 mol/L KCl solution forms a standard series with phosphorus concentration gradients of 0, 0.05, 0.1, 0.5, 1.0, 5, 10, 50, 100 mg/L. Weighed about 2.5 g sediment from the four systems of *Phragmites australis*, *Acorus calamus* Linn., *Iris tectorum* Maxim. and *Vallisneria* Linn., and then added them to 9 centrifugal tubes (100 mL), and then added 20 mL phosphorus solution into every centrifugal tubes. Two drops of chloroform were added to each tube to prevent microbial action. The centrifuge pipes are sealed and oscillated for 24h. After equilibrium for one hour, the water was centrifuged at 3500 rpm for 10 minutes, then filtered by 0.45 m microporous membrane and determined by ammonium molybdate-ascorbic acid method. Phosphorus dissolved in solution can be regarded as phosphorus adsorbed by sediment.

2.3. Calculation of adsorption parameters

The adsorption characteristics of phosphorus in sediment can be well described by Langmuir or Freundlich equation[7-8]. In order to study the characteristics of phosphorus adsorption on sediment, the adsorption characteristics of phosphorus on surface sediment of four wetland systems were fitted by Langmuir and Freundlich isotherms. Origin and Excel software were used for curve fitting and statistical analysis.

1) Langmuir Isothermal Equation:
\[
\frac{C}{S} = \frac{1}{(K*S_{max})} + \frac{C_t}{S_{max}}
\]
S$_{max}$—— phosphorus adsorption maximum (mg/kg);
K—— bond energy constant (L/mg);
C$_t$——solution phosphorus concentration (mg/L);
S—— phosphorus adsorption capacity (mg/kg).

2) Freundlich Isothermal Equation:
\[
S = K_f*C_t^{1/n}
\]
K$_f$——phosphorus adsorption energy parameter (L/kg);
N——correlation factor.

3. Results & discussion

3.1. Distribution of different forms of phosphorus in wetland sediments

The phosphorus content in sediments of *Phragmites australis*, *Acorus calamus* Linn., *Iris tectorum* Maxim. and *Vallisneria* Linn. wetland systems at different depths is shown in Table 1 and Figure 2. According to table 1, the total phosphorus (TP) content in the four wetland systems is between 518.5 and 650.1mg/kg. The average content is in the order of *Vallisneria* Linn. > *Iris tectorum* Maxim. > *Acorus calamus* Linn. > *Phragmites australis*. The content of IP in sediment of four wetland systems accounts for 60.36% ~ 94.94% of TP.

\[
TP=IP+OP= D-P+ Al-P+ Fe-P+ O-P+ Ca-P+ OP
\]

The soluble phosphorus (D-P) extracted by NH$_4$Cl represents the easily desorbed components of inorganic phosphorus in sediment, which has strong phosphorus activity which can play an important influence on plant growth [9-10]. It can be seen from Table 1 that D-P content only accounts for about 1% of total phosphorus in wetland sediments. The content of D-P in the surface layer was higher than that in the middle and lower layers in all the three systems except the *Vallisneria* Linn. system. The content of DP in sediment of *Vallisneria* Linn. system was lower than that of the other three systems on average, the reason is that the pH of *Vallisneria* Linn. system was higher than that of the other three systems, and the content of Ca-P was higher. However, Ca-P was generally stable and could not be easily desorbed. The dissolved oxygen of the *Vallisneria* Linn. system is higher than that of the other three systems. In the relatively anoxic environment, the iron phosphate in the surface sediment is easily reduced to ferrous phosphate and releases phosphate ions.
Table 1. Contents of different forms of phosphorus in wetland sediment (mg/kg).

| type                | depth  | D-P | Al-P | Fe-P | O-P  | Ca-P | TP   | IP   | OP   |
|---------------------|--------|-----|------|------|------|------|------|------|------|
| Phragmites australis| 0-5cm  | 5.43| 39.47| 18.02| 28.42| 419.85| 539.68| 511.20| 28.48|
|                     | 5-15cm | 2.64| 33.88| 18.43| 30.30| 429.42| 563.43| 514.67| 48.76|
|                     | 15-30cm| 3.46| 28.86| 19.89| 31.68| 404.06| 518.54| 487.95| 30.59|
| Iris tectorum Maxim.| 0-5cm  | 5.89| 43.22| 14.22| 34.34| 445.51| 595.71| 543.17| 52.54|
|                     | 5-15cm | 6.28| 42.45| 19.67| 38.35| 451.04| 607.16| 557.78| 49.37|
|                     | 15-30cm| 6.95| 40.46| 13.67| 37.48| 422.15| 623.30| 520.71| 102.58|
| Acorus calamus Linn.| 0-5cm  | 8.06| 27.64| 19.98| 28.97| 431.41| 608.90| 516.05| 92.85|
|                     | 5-15cm | 7.12| 31.14| 22.12| 30.51| 335.84| 592.40| 426.74| 165.66|
|                     | 15-30cm| 4.94| 39.68| 13.19| 31.73| 306.12| 578.90| 395.67| 183.23|
| Vallisneria Linn.   | 0-5cm  | 2.64| 44.85| 9.77 | 31.83| 461.97| 650.11| 551.05| 99.06|
|                     | 5-15cm | 2.95| 38.99| 34.22| 33.39| 476.00| 635.90| 585.54| 50.36|
|                     | 15-30cm| 3.71| 29.81| 19.71| 36.33| 506.53| 627.79| 596.08| 31.71|

Iron-bound phosphorus (Fe-P) extracted by NaOH and aluminum-bound phosphorus (Al-P) extracted by NH₄F generally represent phosphorus bound to hydroxides by amorphous or weakly crystalline Fe/Al hydrates. The Fe-P content in the sediments of the four wetland systems accounts for about 3% of TP, while the Al-P content is not high, accounting for only about 7% of TP, and the sum of the two accounts for about 10% of TP. Because the rapid adsorption and desorption of phosphorus by Fe/Al oxides control the main forms of phosphate in interstitial water, it can be inferred that the diffusion and exchange capacity of phosphorus in the four wetland systems is weak at the water/soil interface.

Calcium-bound phosphorus (Ca-P) extracted by H₂SO₄ represents phosphorus in sediment which is stable bound with Ca and Mg, such as hydroxyapatite, and is difficult to be assimilated by organisms[11]. Ca-P accounted for 52.88%-80.68% of TP in the Four Wetland systems, with an average of 66.78%. Compared with other forms of IP, Ca-P accounted for the largest proportion. The content of Ca-P in sediment depends on the geological background of the system and the pH of the water. The sediments of the four wetland systems constructed in this experiment are all sand and soil mixtures of river floodplain, so the background value of Ca-P is higher. The Ca-P in the Vallisneria Linn. system was higher than that in the other three systems, mainly because the pH was higher than 8, which was alkaline. Under alkaline conditions, the sediment with high calcium and phosphorus accelerated the adsorption of phosphorus at the water/soil interface.

The O-P extracted by Na₂S₂O₄ and sodium citrate represents the mineral bound phosphorus which is covered by iron oxide film and can not be extracted by acid-base. O-P is generally considered to be phosphorus in silicate lattices, sometimes called insoluble phosphorus, which cannot be released from sediments to water by general environmental changes. The content of O-P in four wetland systems is not high, which accounts for about 5% of total phosphorus.

Phosphorus remaining through all extraction generally represents highly inert organic phosphorus (OP) in sediments. This part of phosphorus varies widely in the four Wetland systems, accounting for 5.06-31.64% of TP. Among them, the content of OP in Acorus calamus Linn. sediment is the highest, accounting for about 35% of TP, which indicates that the content of organic matter in Acorus calamus Linn. sediment is higher than that in other systems. The content of OP in sediment is controlled by many factors, such as input, sedimentary characteristics, early diagenesis and biological processes.

The distribution of phosphorus forms in sediments of each system is determined by the habitat conditions of water bodies/sediments formed by different aquatic plants, the characteristics of phosphorus forms and the formation process. Ca-P in sediment coexists mainly in the form of Ca₃(PO₄)₂ and Ca₃(PO₄)₃OH. Its formation rate is mainly controlled by pH. The formation rate of Ca-P
change with the pH[12]. In *Vallisneria Linn.* wetland, *Vallisneria Linn.* as a submerged plant, the whole plant body sinks below the water surface. Therefore, its photosynthesis consumes a large amount of CO$_2$ in the water and improves the pH. Phosphate is easy to combine with calcium ions to form calcium carbonate under alkaline conditions, thus reducing the phosphorus concentration in water. The phosphorus concentration in the water will decrease with the precipitation of calcium phosphate.

As can be seen from Figure 2, the phosphorus contents in the upper, middle and lower sediments of the four wetland systems changed little except OP and Ca-P contents. This may be mainly due to the fact that the background value of the initial sediment is the same, but the background values of DP, Al-P, Fe-P and O-P are not high, and their accumulation or release are not obvious. Therefore, the vertical distribution of the sediment can not be observed. Nevertheless, from Figure 2, we can still see the vertical changes of D-P and Fe-P, which are more active phosphorus, such as Fe-P in sediment of *Vallisneria Linn.* wetland. The content of Ca-P in *Vallisneria Linn.* wetland was higher than that of the other three systems, but the content of Ca-P is the lowest.

**Figure 2.** Distribution of different forms of phosphorus in the four wetland systems.
3.2. Relationship between phosphorus adsorption capacity and phosphorus removal in surface sediments

As shown in Figure 3, the results show that phosphorus adsorption play an important role in the phosphorus biogeochemical cycle, and it is an important internal mechanism of phosphorus retention in wetland. Studies have shown that phosphorus adsorption is mainly affected by the physical and chemical properties of sediment [13]. In acidic wetland sediment, phosphorus adsorption capacity is mainly controlled by iron and aluminum hydrate hydroxide, while in alkaline wetland sediment, phosphorus adsorption capacity may be mainly affected by calcium salt. Different forms of phosphorus in the wetland system were extracted by stages. The results showed that the main form of phosphorus in the wetland system was Ca-P, and the content of phosphorus was about 70%. Figure 3 clearly shows that the phosphorus adsorption on the surface sediments of the four wetland systems has a good correlation. The correlation coefficients fitted by Freundlich isotherm and Langmuir isotherm are all above 0.9, and the correlation of Langmuir isotherm fitting is better than Freundlich isotherm.

![Figure 3. Adsorption isotherms of phosphorus in wetland surface sediments.](image)

We can see that the maximum adsorption of phosphorus $S_{\text{max}}$ was about 766.82-840.27 mg/kg from Figure 3. The order of $S_{\text{max}}$ of the four systems was *Vallisneria Linn.* > *Acorus calamus Linn.* > *Iris tectorum Maxim.* > *Phragmites australis.* The maximum phosphorus adsorption capacity of the surface sediment of the *Vallisneria Linn.* system is obviously larger than that of the other three plant systems. There is a common point in the four systems. When the phosphorus concentration in the water is lower than 0.1mg/L, the phosphorus concentration in the water increases after 24 hours of adsorption equilibrium, which indicates that the surface sediment is not the "sink" of phosphorus but the "source" of phosphorus at lower concentrations. When the concentration of phosphorus in water is greater than 0.1mg/L, the surface sediments show good adsorption performance.

3.3. Analysis of seasonal variation trend of phosphorus content in sediment at different depths

From April 13 to November 15, 2017, sediment samples from each wetland system were collected and tested for a total of 215 days. The results are shown in Figure 4. From the figure 4, it can be seen that
the change of total phosphorus content in the sediments of the four wetland systems follows the same trend and can be divided into four stages.

The first stage is from April 13th to July 15th (that is, the 0~92 day). At this stage, aquatic plants are in the stage from germination to rapid growth, plant growth needs to absorb a large number of nutrients from the sediment. Phosphorus is an important component of the cytoplasm, nucleus and nucleotide of aquatic plants. At the same time, phosphorus also controls the metabolism of carbohydrates, proteins and fats and their mutual transformation. Therefore, plant growth needs a large supply of phosphorus. In order to meet their own growth, aquatic plants extract a large amount of phosphorus from sediment through the root system, resulting in a significant reduction in phosphorus content in sediment. At this stage, the decrease of total phosphorus concentration in the middle and lower layers was greater than that in the upper layers, mainly because the roots of plants were mainly rooted in the middle and lower layers of sediment. When the phosphorus content in the middle and lower sediments decreases, a phosphorus concentration gradient is formed between the upper and lower sediments, which is beneficial to the phosphorus transport from the upper to the lower sediments, and leads to the phosphorus reduction in the upper sediments to a certain extent.

The second stage is from July 15th to August 12th (that is, 92~120 days). At this stage, the content of total phosphorus in the upper, middle and lower layers of sediment has different degrees of rising trend. At this stage, the growth of plants tends to be stable, and the phosphorus required for the growth of plants is reduced to a certain extent compared with the previous stage. When exogenous phosphorus is added to the wetland system, the upper sediment absorbs phosphorus from the overlying water and transfers it into the middle layer. Some of the phosphorus is absorbed by the plants, and some of the phosphorus is transformed into stable phosphorus in the middle layer. Compared with the surface layer and the lower layer, the increase trend of phosphorus in the middle layer is smaller, which is mainly because the roots of aquatic plants mainly grow in the middle layer, and the plants mainly extract phosphorus from this layer.

Figure 4. TP content in the sediment of four wetland varies with seasons.
The third stage is from August 12th to September 19th (that is, 120~158 days). During the summer, the water temperature in is higher, bacteria, plankton, plants and algae multiply in large numbers, and consume a lot of phosphorus. In this process, the upper sediment is no longer the "sink" of phosphorus, but the "source" of phosphorus release from the overlying water.

The fourth stage is from September 19th to November 15th (that is, 158~215 days). At this stage, the aquatic plants died, and the phosphorus in the plants migrated from the above ground to the underground. This stage was the accumulation of phosphorus in the sediment. The phosphorus content in the upper, middle and lower sediments increased in varying degrees. At this stage, the decay of plankton and algae also releases a large amount of phosphorus into the water body. Through sedimentation and adsorption of upper sediment, phosphorus in upper sediment increases more than that in upper sediment and bottom sediment.

Generally speaking, wetland sediment serves as phosphorus source for aquatic plant growth in spring and summer. In autumn and winter, with the decay of plants, phosphorus in plants is re-released into the wetland, resulting in an increase in phosphorus content in the sediment, and the wetland sediment becomes a "sink" of phosphorus.

4. Conclusions

Through research, we can draw the following four conclusions:

1. Phosphorus forms in sediments are related to aquatic plant characteristics. Submerged macrophytes consume CO₂ due to photosynthesis during the daytime, which leads to the increase of pH in water [14]. In the Vallisneria Linn. wetland system, the respiration of Vallisneria Linn. increased the pH of the water, so the content of Ca-P in the sediment was higher than that in the other three wetland systems.

2. Adsorption of phosphorus by sediment is an important internal phosphorus retention mechanism in wetland system. The maximum adsorption capacity of \( S_{\text{max}} \) is about 766.82-840.27 mg/kg. In the wetland system with Ca-P as the main component, the content of Ca-P and TP have a very good correlation with \( S_{\text{max}} \).

3. There is a dynamic equilibrium of phosphorus adsorption in surface sediment. When the phosphorus concentration in the water is lower than 0.1mg/L, the surface sediment is no longer a "sink" of phosphorus but is a "source" of phosphorus.

4. The changes of total phosphorus content in four wetland sediments basically follow a similar trend. That is to say, the phosphorus content in the sediment decreased during the growth period of aquatic plants, and the wetland sediment as the phosphorus "source" provided the biomass for the growth of the aquatic plants. In autumn and winter, phosphorus in plants is released into Wetland again with the decay of plants, resulting in the increase of phosphorus content in sediment.

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