

## Research Article

# The Release of Endogenous Nitrogen and Phosphorus in the Danjiangkou Reservoir: A Double-Membrane Diffusion Model Analysis

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Endogenous contamination from the newly submerged sediment may have an impact on the water quality of the Danjiangkou Reservoir, the water source of the middle route of the South-to-North Water Diversion Project. In this study, in situ sediment samples were collected at different locations (Guojiashan (DJK1), Kongqueyuan (DJK2), Shijiagou (DJK3), Shiqiao Wharf (DJK4), and Songgang Wharf (DJK5) from the north to the south) of the Danjiangkou Reservoir and the upstream tributary using a columnar sediment sampler and statically cultured in laboratory, and the distribution and release of endogenous N and P from the sediment were investigated based on a double-membrane diffusion model. The results showed that the P contents in the main reservoir and the upstream tributary followed the order of inorganic phosphorus (IP) > organic phosphorus (OP) > calcium – phosphorus (Ca – P) > iron – phosphorus (Fe – P) > labile phosphorus (LP). IP accounted for the largest proportion (47.10-59.70%) of total phosphorus (TP), while LP accounted for only a small proportion (0.10-0.90%) of TP. There is a significant difference in the spatial distribution of P at different sampling points, especially for the OP content (226.90 mg·kg<sup>-1</sup>) with a coefficient of variation of 26.90%. The contents of different forms of P and NH<sub>4</sub><sup>+</sup>-N decreased from the upstream tributary to the main reservoir, which was mainly attributed to the land use type. In the vertical distribution, the contents of different forms of P in DJK4 and DJK5 decreased with the increase of sediment depth. The contents of NH<sub>4</sub><sup>+</sup>-N and PO<sub>4</sub><sup>3-</sup>-P in the sediment interstitial water of DJK4 and DJK5 were higher than those in the overlying water. In addition, the contents of NH<sub>4</sub><sup>+</sup>-N and PO<sub>4</sub><sup>3-</sup>-P were higher in DJK5 than that in DJK4. The static culture experiments showed that N and P were mainly released from the sediment-overlying water interface to the overlying water. The release rate of NH<sub>4</sub><sup>+</sup>-N and PO<sub>4</sub><sup>3-</sup>-P ranged from 13.08 mg·(m<sup>2</sup>·d)<sup>-1</sup> to 21.39 mg·(m<sup>2</sup>·d)<sup>-1</sup> and from 3.06 mg·(m<sup>2</sup>·d)<sup>-1</sup> to 6.02 mg·(m<sup>2</sup>·d)<sup>-1</sup>, and the release amount calculated based on the double-membrane diffusion model was 1.17 × 10<sup>3</sup> t·a<sup>-1</sup> and 0.53 × 10<sup>3</sup> t·a<sup>-1</sup>, respectively. Thus, endogenous contamination from the newly submerged land is an important factor affecting the water quality of the Danjiangkou Reservoir.

## 1. Introduction

Reservoir sediment is considered to be an important sink of various nutrients in the overlying water [1] and thus even a small change of reservoir sediment can have a substantial impact on the quality of the overlying water [2]. The nutrients accumulated in the sediment such as nitrogen (N) and phosphorus (P) can be released from the sediment back to the overlying water through the interstitial water as a result of convection, diffusion, and resuspension, causing secondary pollution of the overlying water [3]. For instance, the release rate of  $\text{NH}_4^+\text{-N}$  from the sediment is still as high as  $3.31 \times 10^3 \text{ t}\cdot\text{a}^{-1}$  in the Dianchi Lake of Yunnan Province, China, after dredging and sewage interception [4], and resuspension of nutrient-rich sediment causes eutrophication for several decades even when external nutrient loads are curtailed [5]. In this case, endogenous release of nutrients from the sediment is the main factor affecting the water quality [6]. Therefore, a better understanding of the distribution of nutrients in the sediment and their release fluxes is essential to take steps to reduce endogenous nutrient load and improve reservoir water quality [7].

The Danjiangkou Reservoir is the main water source of the middle route of the South-to-North Water Transfer Project of China, and thus the water quality has been maintained at a high level for years. However, evidence has emerged that there is an increasing risk of endogenous contamination that can seriously affect the water quality of the reservoir [8]. The overflow weir crest of the Danjiangkou Reservoir was heightened in 2012, resulting in an increase in the storage capacity from 17.45 billion  $\text{m}^3$  to 29.05 billion  $\text{m}^3$  [9] and consequently inundation of 17333 ha of farmland [10]. The newly formed sediments contain a higher amount of organic matter compared with the original sediments, which implies a higher risk of endogenous release and contamination. N is more likely to be released from the newly submerged farmland and orchard of the Danjiangkou Reservoir [11], and P loss is more prominent in the new riparian zone compared with that in the existing riparian zone [12]. Thus, endogenous release of nutrients such as N and P from the sediment in the newly submerged area may pose a threat to the water quality of the reservoir. A number of studies have been conducted to investigate the factors affecting the release of nutrients from the sediment, such as existing states and seasonal variations of nutrients, dissolved oxygen, and temperature [13], but little is known about the release of nutrients from the sediment in the newly submerged area.

A number of models have been proposed to describe the release of nutrients from the lake sediment, such as the permeation model, the double-membrane diffusion model, and the surface renewal model. Among them, the double-membrane diffusion model is particularly suitable to characterize the flux of endogenous nutrients from the kinetic perspective, as it uses mathematical conversion to obtain the double film thickness that is difficult to measure by other models and generalizes the actual complex release process. However, there are three theoretical premises: both water and sediment phases are single homogeneous phases, transmission takes place by means of molecular diffusion, and

the total amount of sediment nutrients remains unchanged. It avoids the influence of complicated environmental factors and allows for the estimation of the release of sediment nutrients in a large reservoir area. The  $K$  value is calculated from the data obtained from the simulated release experiment, which is the net release coefficient derived from the actual sediment adsorption, precipitation, and microbial action [14].

In this study, in situ sediment samples were collected at different locations of the Danjiangkou Reservoir and statically cultured in laboratory, and the distribution and release of endogenous N and P from sediments were investigated based on the double-membrane diffusion model. The results of this study may provide important insights into how to improve the water quality of the reservoir.

## 2. Materials and Methods

**2.1. Study Area and Sampling Sites.** The Danjiangkou Reservoir is located in the northwest of Hubei province and the southwest of Henan province and consists of Hanjiang and Danjiang reservoirs. The annual average inflow is about 39.48 billion  $\text{m}^3$  from the Hanjiang River and its tributary Danjiang River, and the terrain is high in the northwest but low in the southeast. The reservoir was put into operation in 1973, and the overflow weir crest was heightened in 2012. Now, it is the largest artificial freshwater lake in Asia, with a water area of about 102275 ha and a storage capacity of about 29.05 billion  $\text{m}^3$  [15].

In this study, five representative sampling sites were established at Guojiashan (DJK1;  $33^\circ 02' 39''\text{N}$  and  $111^\circ 28' 46''\text{E}$ ), Kongqueyuan (DJK2;  $33^\circ 0' 51''\text{N}$  and  $111^\circ 27' 11''\text{E}$ ), Shijiagou (DJK3;  $32^\circ 54' 42''\text{N}$  and  $111^\circ 30' 47''\text{E}$ ), Shiqiao Wharf (DJK4;  $32^\circ 49' 23''\text{N}$  and  $111^\circ 34' 28''\text{E}$ ), and Songgang Wharf (DJK5;  $32^\circ 46' 02''\text{N}$  and  $111^\circ 38' 50''\text{E}$ ), as shown in Figure 1. These sampling sites were about 0.5 km away from the reservoir shore with a water depth of about 2 m. The overlying water and sediment samples were collected in March and August, 2018. The longitude and latitude of the sampling sites were determined by GPS (see Table 1). AD, DJK 4, and DJK 5 were continuous farmland since 2012 where a large amount ( $188\text{-}356 \text{ kg}\cdot\text{ha}^{-1}$ ) of chemical fertilizers (mainly potash and phosphate fertilizers) were used with a maximum of  $646 \text{ kg}\cdot\text{ha}^{-1}$  [16]. Thus, the double-membrane diffusion model was used to investigate the effect of the release of endogenous N and P on the overlying water at these two sampling sites based on the data collected in March, 2018.

**2.2. Sample Collection and Analysis.** Columnar sediment samples were collected using a columnar sampler with an organic glass tube ( $90 \text{ mm} \times 500 \text{ mm}$ ), and three parallel samples were collected at each sampling site for static culture experiments. The overlying water samples were also collected at each sampling site without disturbing the sediment. A portion of water samples was encapsulated in 5 L plastic bottles to supplement the water in static culture experiments, while the rest was encapsulated in 500 ml polyethylene bottles for the measurement of N and P concentrations in the overlying

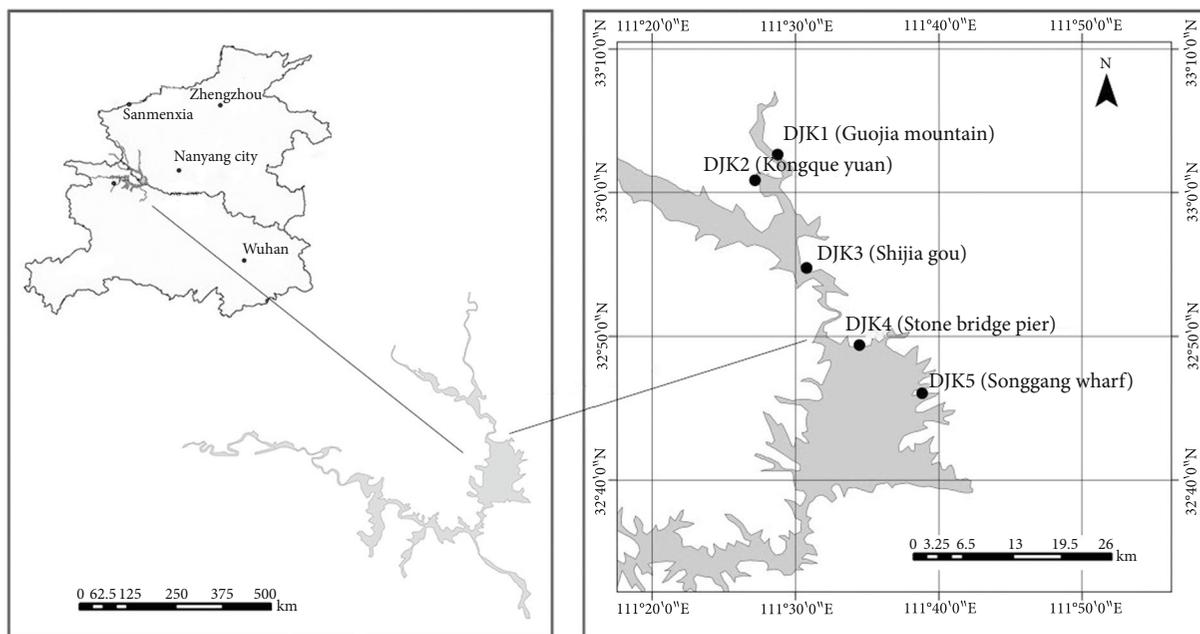


FIGURE 1: The sampling sites in the Danjiangkou Reservoir.

TABLE 1: N and P contents in the overlying water at each sampling site and the original land use type.

Sampling sites	Background concentration in the overlying water ( $\text{mg}\cdot\text{L}^{-1}$ )		Land use type	Longitude	Latitude
	$\text{NH}_4^+\text{-N}$	$\text{PO}_4^{3-}\text{-P}$			
DJK1	1.08	0.12	Farmland (corn field)	E $111^\circ28'46''$	N $33^\circ02'39''$
DJK2	0.59	0.08	Farmland	E $111^\circ27'11''$	N $33^\circ00'51''$
DJK3	0.56	0.06	Moving the topsoil to cultivate fertility	E $111^\circ30'47''$	N $32^\circ54'45''$
DJK4	0.35	0.02	Farmland and woodland	E $111^\circ34'27''$	N $32^\circ49'23''$
DJK5	0.53	0.02	Farmland	E $111^\circ38'50''$	N $32^\circ46'02''$

water, and several drops of concentrated sulfuric acid were added to reach a pH value of 2 and shaken uniformly in order to inhibit the microbial activity. Statically cultured samples were cut according to the depth (0-1 cm, 1-2 cm, 2-3 cm, 3-4 cm, 4-5 cm, 5-6 cm, 6-7 cm, 7-8 cm, 8-9 cm, and 9-10 cm) and centrifuged at 5000 r/min for 20 min. Sediment interstitial water was obtained and filtered using a  $0.45\ \mu\text{m}$  fiber filtration membrane for the measurement of  $\text{NH}_4^+\text{-N}$  and  $\text{PO}_4^{3-}\text{-P}$  concentrations in the sediment interstitial water.

**2.3. Static Culture Experiments.** The overlying water was removed from columnar sediment samples by siphonage, and then the original overlying water was filtered using the  $0.45\ \mu\text{m}$  fiber filtration membrane and carefully introduced into the columnar sediment samples along the wall by siphonage. In order to better simulate the field environment of the Danjiangkou Reservoir (the annual average temperature is about  $16^\circ\text{C}$ ), all columnar sediment samples were placed vertically in a culture vessel with a water depth of 0.40 m in dark at  $16^\circ\text{C}$  for 10 days. Water samples were collected at the middle of the sample at the beginning of the experiment and then

every 8 h during the culture. Prior to each sampling, the overlying water was stirred slowly using a slender glass rod in order to ensure uniform sampling and to avoid sediment resuspension. After sampling, an equal amount of original overlying water was supplemented. All samples were kept in a constant temperature incubator at  $4^\circ\text{C}$ .

**2.4. Analysis Methods.** The contents of  $\text{NH}_4^+\text{-N}$  in the overlying water, sediment, and sediment interstitial water were measured using Nessler's reagent colorimetric method (GB7479-87, National Standards of People's Republic of China), KCl extraction-distillation method [17], and Nessler's reagent colorimetric method [17], respectively, while those of  $\text{PO}_4^{3-}\text{-P}$  were measured using molybdenum-antimony anticolorimetry (GB11893-89, National Standards of People's Republic of China) and the molybdenum blue coloration method [17], respectively. The states of P were determined as described in using the Standards, Measurements, and Testing (SMT) method (Standards Measurements and Testing Program of the European Commission) [18] (see Figure 2). Labile phosphorus (LP) was extracted

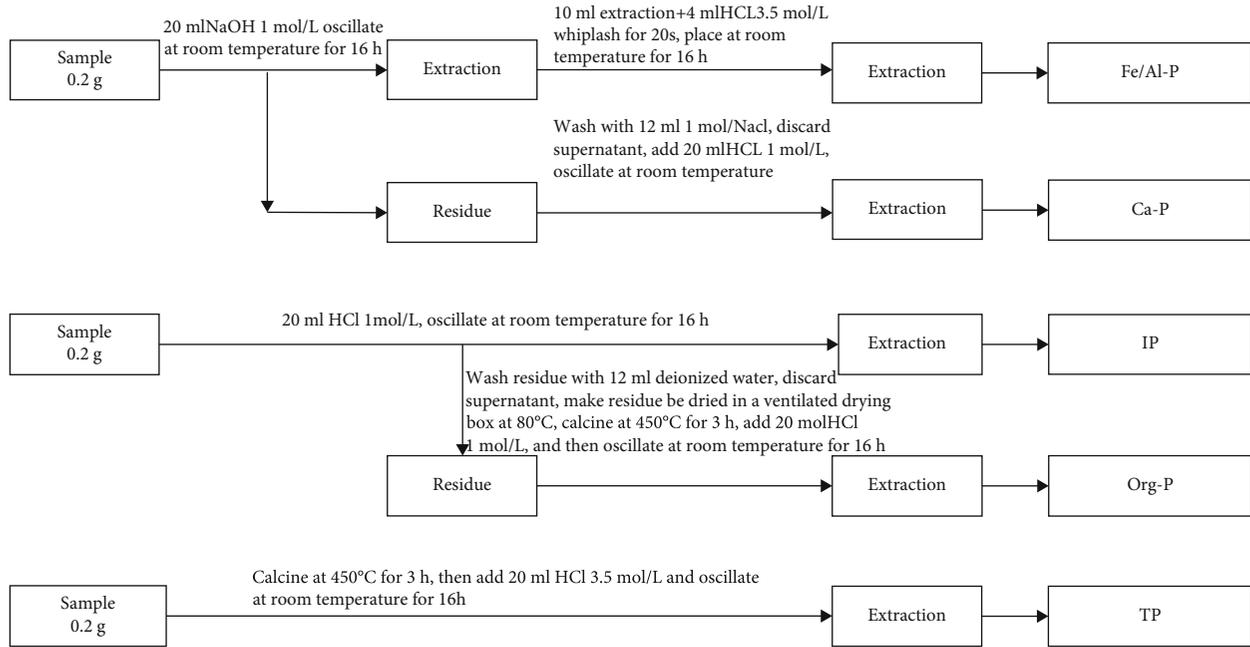


FIGURE 2: Extraction of P from the sediment by the SMT method.

using 1 mol/L  $\text{NH}_4\text{Cl}$  [19]: 1 g of sediment was placed in a centrifuge tube, and 25 ml of  $\text{NH}_4\text{Cl}$  (1 mol/L) was added, oscillated for 0.5 h, and centrifuged. The LP content in the supernatant was measured using molybdenum blue colorimetry. All measurements were repeated three times, and the average was reported (the error was within <5%). The significance of spatial difference was analyzed by one-way ANOVA using SPSS 19.0, and figures were plotted using Origin 9.0 and ArcGIS 10.2. Error bars represented the standard deviations (SD) throughout the paper.

## 2.5. Calculation of Experimental Results

**2.5.1. Double-Membrane Diffusion Model.** A number of models have been proposed to describe the release of contaminants from the lake sediment, such as the permeation model, the double-membrane diffusion model, and the surface renewal model. In this study, the double-membrane diffusion model is used, in which the molecular diffusion coefficient and the ratio of the thickness of double membranes ( $K$ ) are used instead of the thickness of double membranes that is difficult to determine [20]. Three assumptions are made in this model: (1) both the overlying water and sediment are single homogeneous phases, and the overlying water is well mixed, (2) the mass transfer between the sediment and the overlying water takes place only through molecular diffusion, and (3) the nutrient content is relatively high in the sediment compared with that in the overlying water, and thus nutrient loss due to sediment release is negligible throughout the study. The release processes of nutrients from the sediment into the overlying water consist of (1) migration of nutrients from the interior to the surface of the sediment, (2) interfacial transfer of nutrients to the water side, (3) diffusion through the liquid membrane, and

(4) uniform mixing in the overlying water. Given the above three assumptions, steps 1, 2, and 4 are assumed to occur instantaneously, and thus step 2 is the controlling step of the release processes [21].

According to the double-membrane diffusion model, the transfer flux  $N$  should be proportional to the molecular diffusion coefficient  $D$  and the concentration gradient in the double membrane, the latter of which is the concentration difference between the two sides of the membrane divided by the thickness of the double membrane  $\delta$ :

$$N = D \frac{(C_w - C)}{\delta}, \quad (1)$$

where  $C$  is the contaminant concentration on the water side ( $\text{mg}\cdot\text{L}^{-1}$ ), and  $C_w$  is the equilibrium concentration of contaminants in the water phase ( $\text{mg}\cdot\text{L}^{-1}$ ).

Let the transfer velocity constant be  $K = D/\delta$ . According to the double-membrane diffusion model and the dynamics theory,

$$KV(C_w - C) = V \times \frac{dc}{dt}. \quad (2)$$

Thus, the dynamics of contaminant concentration in the water phase can be described as follows:

$$C = C_w \left( 1 - e^{-\frac{KA}{V} \times t} \right), \quad (3)$$

where  $A$  is the release area ( $\text{m}^2$ ), and  $V$  is the volume of the overlying water ( $\text{m}^3$ ).

Eq. (3) can be transformed into

$$\frac{V}{A} \times \ln\left(\frac{Cw}{Cw-C}\right) = Kt, \quad (4)$$

where  $V/A$  is the depth of the overlying water in the experimental column [22].

The plot of  $(V/A) \times \ln(Cw/Cw - C)$  against time  $t$  is a straight line through the origin of coordinates, and the slope is the  $K$  value [21]. The  $K$  values calculated from experimental results are shown in Table 2.

According to the double-membrane diffusion model, the release flux of contaminants from the sediment is

$$N = K(Cw - C). \quad (5)$$

The release rate of contaminants is

$$\frac{dC}{dt} = KA(Cw - C), \quad (6)$$

where  $A$  is the sediment area ( $m^2$ ).

Thus, the annual diffusion amount  $W$  is

$$W = K(Cw - C) \times V \times t, \quad (7)$$

where  $V$  is the volume of the overlying water ( $m^3$ ),  $V = AH$ ,  $H$  is the depth of the overlying water (m), and  $t$  is the diffusion period [21].

**2.5.2. Release Rate of Nutrients in Statically Cultured Sediments.** The release rate of contaminants can be calculated according to the mass conservation principle:

$$R = \frac{[V(\rho_n - \rho_0) + \sum_{j=1}^n v_{j-1}(\rho_{j-1} - \rho_\alpha)]}{At}, \quad (8)$$

where  $R$  is the release rate of contaminants from sediment samples,  $mg/(m^2 \cdot d)$ ;  $V$  is the volume of the overlying water (L);  $\rho_0$ ,  $\rho_n$ , and  $\rho_{j-1}$  are the contents of contaminants collected at the beginning of the experiment, time  $n$  and  $j-1$ , respectively ( $mg/L$ );  $\rho_\alpha$  is the contaminant content in the added water ( $mg \cdot L^{-1}$ ),  $v_{j-1}$  is the volume of  $j-1$  samples (L);  $A$  is the contact area between the sediment and the overlying water ( $m^2$ ); and  $t$  is the release time ( $d$ ) [22].

### 3. Results and Discussion

**3.1. Distribution of Different Forms of P and N in the Sediment.** There is a significant difference in total phosphorus (TP) contents (402.40-560.30  $mg \cdot kg^{-1}$ ) among the five sampling sites (DJK 1-5) with a coefficient of variation of 14.4% ( $p < 0.01$ ), which is consistent with the previous finding in the Danjiangkou Reservoir (530  $mg \cdot kg^{-1}$ ) [15] but lower than that in the Three Gorges Reservoir (1189  $mg \cdot kg^{-1}$ ) [23]. In sampling sites from DJK1 to DJK5, a great amount of P in chemical fertilizers and crop residues can be fixed in the soil by adsorption, sedimentation, and microbial immo-

TABLE 2: Contaminant migration velocities ( $K$ ) in the sediment.

Sampling sites	$K$ values
DJK4-NH <sub>4</sub> <sup>+</sup> -N	0.06
DJK5-NH <sub>4</sub> <sup>+</sup> -N	0.06
DJK4-PO <sub>4</sub> <sup>3-</sup> -P	0.15
DJK5-PO <sub>4</sub> <sup>3-</sup> -P	0.12

bilization [24]. However, the TP contents in DJK 1-5 seem to be less affected by agricultural practices compared with that in the Three Gorges Reservoir. The highest TP content is found in DJK 1, which is 1.34 times that in DJK 4. In general, the TP content decreases from the upstream tributary to the main reservoir, which may be associated with the original land use type [25] and the amount of chemical fertilizers used (see Table 1).

The contents of different forms of P follow the order of IP > OP > Ca - P > Fe - P > LP. Thus, IP accounts for the largest proportion (47.10-59.70%) of TP in the five sampling sites, while the LP content is only 0.98-3.50  $mg \cdot kg^{-1}$ , accounting for a small proportion (0.10-0.90%) of TP (see Figure 3). However, it is noted that LP is a weakly bound phosphate on the sediment surface that is readily exploitable by aquatic organisms, and P is most easily released from the sediment in the form of LP [26]. The vertical distribution of various forms of P in DJK 4 shows a decreasing trend with sediment depth and the contents of Fe-P, which can also be easily utilized by aquatic organisms, range from 1.70  $mg \cdot kg^{-1}$  to 4.70  $mg \cdot kg^{-1}$ , while that in DJK 5 shows a W-shaped decreasing trend and the Ca-P contents range from 9.30 to 28.50  $mg \cdot kg^{-1}$ . The vertical distribution of P may be associated with the environment, sedimentation rate, and age. The greater the sediment depth is, the lower the contents of various forms of P will be [27]. Fertilizers containing P were not allowed in early years, thus resulting in less accumulation of nutrients in the sediment; whereas an increasing amount of P fertilizers are used in recent years, thus resulting in an increase in P contents in the sediment.

Inorganic N exists in the sediment and overlying water mainly in the form of NH<sub>4</sub><sup>+</sup>-N [28]. Table 3 shows that the NH<sub>4</sub><sup>+</sup>-N content ranges from 173.00  $mg \cdot kg^{-1}$  to 208.10  $mg \cdot kg^{-1}$  in the five sampling sites, which is slightly higher than that obtained in a previous study (142.30  $mg \cdot kg^{-1}$ ) [29]. In line with the study of the Yuqiao Reservoir [30], the NH<sub>4</sub><sup>+</sup>-N content also decreases from the upstream tributary to the main reservoir. Compared with the reservoir, the tributary river is characterized by smaller bed slopes and flow velocities, making it easier to accumulate organic matter [31]. The spatial distribution of P is also affected by agricultural practices at the five sampling sites due to extensive use of chemical fertilizers. In the vertical distribution, the NH<sub>4</sub><sup>+</sup>-N content increases as the sediment depth increases (see Figure 3), because NH<sub>4</sub><sup>+</sup>-N can be easily diffused from the sediment surface to the overlying water through complex physical, chemical, and biological exchanges [32]. However, the NH<sub>4</sub><sup>+</sup>-N content is increased at 4-12 cm. Organic N is mineralized at an increasing rate in the deep sediment under the effect of ammonifiers, and

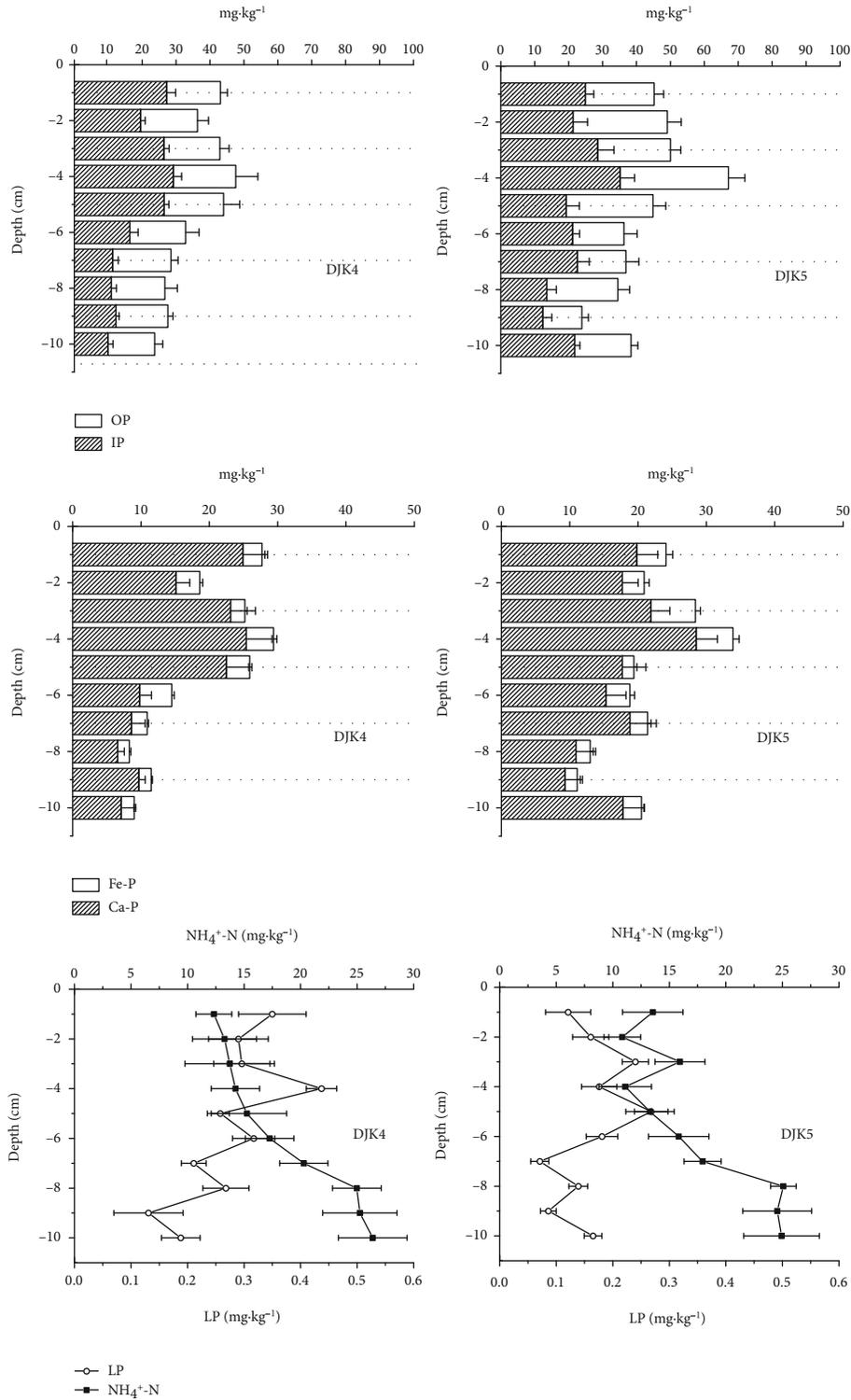


FIGURE 3: Vertical distribution of various forms of P and NH<sub>4</sub><sup>+</sup>-N in the sediments collected from sites DJK4 and DJK5.

more importantly, less oxygen is available as the sediment depth increases, resulting in inhibition of nitrification and thus transformation of less NH<sub>4</sub><sup>+</sup>-N into other forms of N. As a consequence, an increase in the NH<sub>4</sub><sup>+</sup>-N content is observed at 4-12 cm [33].

The contents of NH<sub>4</sub><sup>+</sup>-N and PO<sub>4</sub><sup>3-</sup>-P in the sediment interstitial water of DJK 4 and DJK 5 increase with increasing

depth (see Figure 4), and they are significantly higher in DJK4 than in DJK5 ( $p < 0.01$ ). The average NH<sub>4</sub><sup>+</sup>-N content in the interstitial water at a depth of 10 cm in samples from DJK4 and DJK5 is 16.00 mg·L<sup>-1</sup> and 3.50 mg·L<sup>-1</sup> with a coefficient of variation of 42.50% and 107.70%, respectively. Thus, the NH<sub>4</sub><sup>+</sup>-N content varies more dramatically in DJK5 [34]. In DJK5, the NH<sub>4</sub><sup>+</sup>-N content increases as the

TABLE 3: Average contents of P in the surface sediments of different sampling sites.

Sampling sites	LP/(mg·kg <sup>-1</sup> )	Fe-P/(mg·kg <sup>-1</sup> )	Ca-P/(mg·kg <sup>-1</sup> )	OP/(mg·kg <sup>-1</sup> )	IP/(mg·kg <sup>-1</sup> )	TP/(mg·kg <sup>-1</sup> )	NH <sub>4</sub> <sup>+</sup> -N/(mg·kg <sup>-1</sup> )
DJK1	3.50 ± 0.51a	59.40 ± 5.33a	265.50 ± 25.83a	226.90 ± 18.56a	334.60 ± 20.28a	560.30 ± 28.55a	208.10 ± 27.40a
DJK2	0.98 ± 0.14b	57.01 ± 4.37b	194.60 ± 14.00b	230.90 ± 21.06a	279.70 ± 18.13b	516.50 ± 24.71b	198.30 ± 24.50a
DJK3	2.94 ± 0.35ab	48.72 ± 3.47bc	180.30 ± 10.58b	165.20 ± 11.91b	245.50 ± 17.14b	452.90 ± 21.72b	186.40 ± 26.50b
DJK4	2.75 ± 0.42b	28.85 ± 4.67c	152.90 ± 9.42c	163.60 ± 14.58c	189.40 ± 11.45c	402.40 ± 16.72c	182.90 ± 23.80c
DJK5	1.61 ± 0.12b	33.99 ± 3.42bc	177.80 ± 7.96c	205.40 ± 11.23b	220.50 ± 9.33c	439.00 ± 16.73b	173.00 ± 22.90c

Note: different letters after the values indicate significant differences ( $p < 0.01$ ), means ± standard deviations.

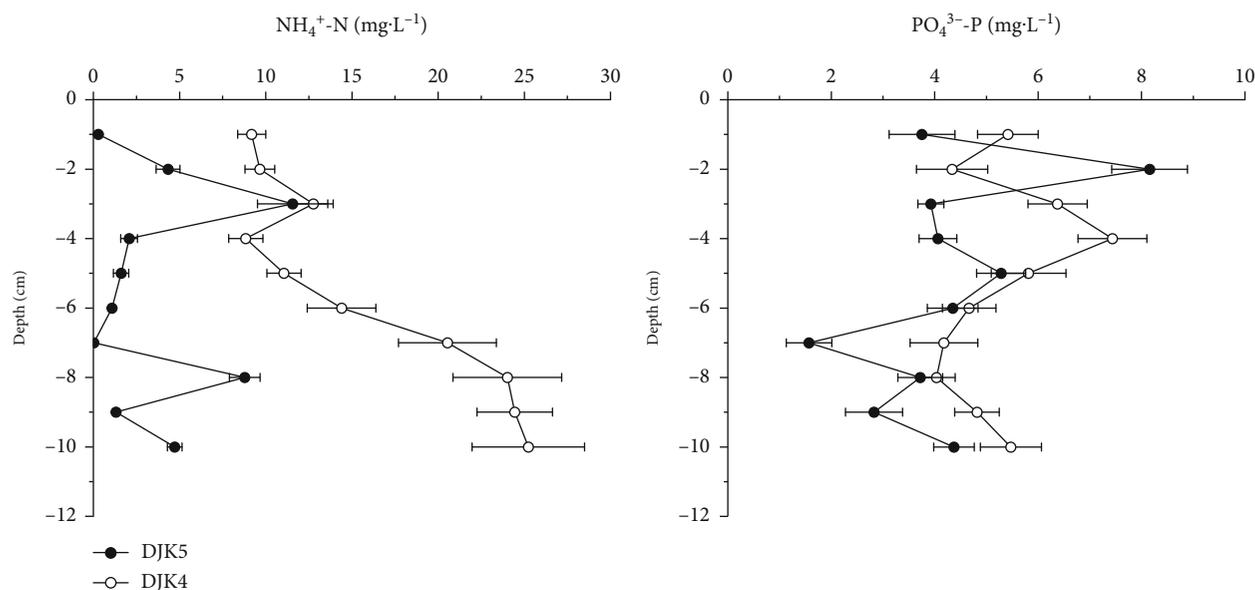


FIGURE 4: Variation of NH<sub>4</sub><sup>+</sup>-N and PO<sub>4</sub><sup>3-</sup>-P contents in the sediment interstitial water.

depth increases until a maximum of 12.75 mg·L<sup>-1</sup> is reached at 3 cm, after which it decreases with further increase of the depth. This agrees well with the study of Liu et al. about the Beili Lake of the Hangzhou West Lake [35] and the study of Wang et al. about the Nansi Lake [36]. The significant difference in the NH<sub>4</sub><sup>+</sup>-N content at 4–10 cm between DJK 4 and DJK 5 can be attributed to the presence of more iron and manganese oxides in DJK5, which act as electron acceptors of NH<sub>4</sub><sup>+</sup> for conversion of NH<sub>4</sub><sup>+</sup> into NH<sub>3</sub> gas under anaerobic conditions [37]. It is also noted that the higher NH<sub>4</sub><sup>+</sup>-N content in the interstitial water of DJK 4 is consistent with the NH<sub>4</sub><sup>+</sup>-N content in the sediment.

The average PO<sub>4</sub><sup>3-</sup>-P content in the interstitial water at a depth of 10 cm in samples from DJK4 and DJK5 is 5.26 mg·L<sup>-1</sup> and 4.30 mg·L<sup>-1</sup> with a coefficient of variation of 20.50% and 36.20%, respectively, which is related to the high P content in DJK 4. In DJK 5, the PO<sub>4</sub><sup>3-</sup>-P content first increases and then decreases with increasing depth, and the maximum of 8.16 mg·L<sup>-1</sup> is reached at 2 cm; while in DJK 4, the PO<sub>4</sub><sup>3-</sup>-P content is maximized at 4 cm (7.45 mg·L<sup>-1</sup>) and 10 cm (5.47 mg·L<sup>-1</sup>). This is because the PO<sub>4</sub><sup>3-</sup>-P in the surface interstitial water can be easily diffused into the overlying water, resulting in a lower PO<sub>4</sub><sup>3-</sup>-P content compared with that in the deep interstitial water [38]. In both DJK 4 and

DJK 5, the PO<sub>4</sub><sup>3-</sup>-P content is decreased at 4–7 cm, at which there is a transition from aerobic to anaerobic conditions that can inhibit the effect of aerobic microbes on the active organic detritus and increase the dissolution of iron and manganese oxides under anaerobic conditions, and consequently result in the release of adsorbed P.

### 3.2. Release of NH<sub>4</sub><sup>+</sup>-N from Statically Cultured Sediments.

NH<sub>4</sub><sup>+</sup>-N is released from the sediment-overlying water interface into the overlying water in March in DJK1–5 (see Figure 5), which is in good agreement with that of the Danjiangkou Reservoir in August [11]. The release rate ranges from 13.08 mg·(m<sup>2</sup>·d)<sup>-1</sup> to 21.39 mg·(m<sup>2</sup>·d)<sup>-1</sup>, and the maximum is observed in DJK3 (21.39 mg·(m<sup>2</sup>·d)<sup>-1</sup>), which is 1.32 times of the average. It is higher than that in the Meiliang Bay of the Tai Lake at 15°C (12.60 mg·(m<sup>2</sup>·d)<sup>-1</sup>) [39], but lower than that in the Fubao Bay of the Dianci Lake at 14–16°C (93.03 mg·(m<sup>2</sup>·d)<sup>-1</sup>) [40], because organic matter is released in a larger amount from the sediment to the overlying water in DJK3. In the spatial distribution, the coefficient of variation of the NH<sub>4</sub><sup>+</sup>-N content is 50.60% in DJK 4 and 74.30% in DJK 5, both of which are higher than that in DJK1–DJK3 (18.70%, 20.90%, and 20.10%, respectively) which were predominantly used for agricultural purposes.

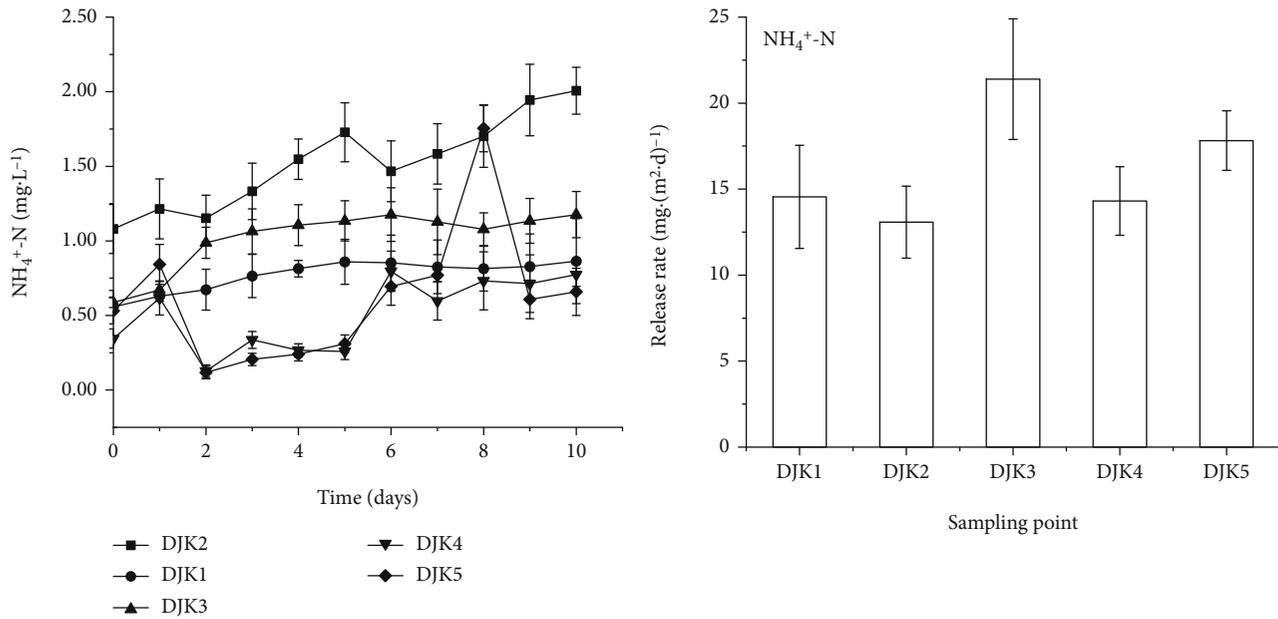


FIGURE 5: The content and release rate of  $\text{NH}_4^+\text{-N}$  in the overlying water.

The flow velocity is generally low at the bottom of the reservoir, making it difficult for nutrients to migrate to the overlying water through the sediment-interstitial water-overlying water interface. Under oxygen-rich conditions, the organic N in the sediment can be converted into inorganic ions such as  $\text{NH}_4^+$  and  $\text{NO}_3^-$  by nitrification, which in turn can be diffused to the interstitial water and then to the overlying water and, as a result, have an effect on the  $\text{NH}_4^+\text{-N}$  content in the overlying water [37]. It is also noted that more  $\text{NH}_4^+$  would be released under anaerobic conditions compared with that under aerobic conditions [41]. In addition, the decomposition of organic N results in the formation of  $\text{NH}_3$  under hypoxia conditions but  $\text{NH}_4^+\text{-N}$  under acidic conditions. The  $\text{NH}_4^+$  in the overlying water can also be diffused back to the sediment. The activities of microorganisms in the sediment and subsequent ammonification are reduced in an anoxic environment, and the reducing environment can also promote the denitrification, and finally, N is released into the atmosphere.

**3.3. Release of  $\text{PO}_4^{3-}\text{-P}$  from Statically Cultured Sediments.** The  $\text{PO}_4^{3-}\text{-P}$  concentration in the overlying water of five sampling points (DJK1-5) tends to increase over time in March, and the coefficient of variation in the reservoir (35.40% and 64.70% in DJK 4 and DJK 5, respectively) is significantly higher than that in the upstream tributary (21.40%, 15.80%, and 26.70% in DJK1-DJK3, respectively) (see Figure 6). The same phenomenon is also observed for the  $\text{NH}_4^+\text{-N}$  content in the overlying water. The release rate of  $\text{PO}_4^{3-}\text{-P}$  ranges from  $3.06 \text{ mg}\cdot(\text{m}^2\cdot\text{d})^{-1}$  to  $6.02 \text{ mg}\cdot(\text{m}^2\cdot\text{d})^{-1}$  with an average of  $4.65 \text{ mg}\cdot(\text{m}^2\cdot\text{d})^{-1}$ , which is lower than that in the Meiliang Bay of the Tai Lake in July ( $76.55 \text{ mg}\cdot(\text{m}^2\cdot\text{d})^{-1}$ ) [42], but slightly higher than that in the Wuli Lake of the Tai Lake ( $2.05 \text{ mg}\cdot(\text{m}^2\cdot\text{d})^{-1}$ ) [43]. The highest release rate is found in DJK1, which is 1.29 times the average. The release

rate of  $\text{PO}_4^{3-}\text{-P}$  decreases from the upstream tributary to the main reservoir, which is consistent with the contamination extent of the sediment. However, the release potential of P from the sediment is not entirely determined by the TP amount in the sediment. The release rate of P is high in water with severe organic contamination, which is related to the presence of a large amount of easily degradable matter [44]. At the beginning of the experiment when there is rich oxygen, the active organic debris in the sediment can release a large amount of  $\text{PO}_4^{3-}$  under the effect of microorganisms.  $\text{PO}_4^{3-}$  can be diffused to the interstitial water and then to the overlying water driven by the concentration gradient, forming the first release peak of  $\text{PO}_4^{3-}$ . On the other hand, an anaerobic environment would be formed under the effect of aerobic microbes, and iron and manganese oxides can be easily reduced to increase the solubility, resulting in the release of adsorbed P and thus the formation of the second release peak of  $\text{PO}_4^{3-}$ .

**3.4. Annual Release Amount of N and P from the Sediment and Risk Evaluation.** The increase of dam height in 2012 results in a total reservoir area of  $1023 \text{ km}^2$ , a storage capacity of 29.05 billion  $\text{m}^3$  and an average water depth of about 30 m. After interception of contaminants, the annual release amount of  $\text{PO}_4^{3-}\text{-P}$  and  $\text{NH}_4^+\text{-N}$  from the newly submerged sediment into the overlying water is calculated to be  $0.53 \times 10^3 \text{ t}$  and  $1.17 \times 10^3 \text{ t}$ , respectively, using formula (7) based on the migration coefficient ( $K$ ) obtained in experiments and the double-membrane diffusion model at an average temperature of  $16^\circ\text{C}$  for the Danjiangkou Reservoir. This differs substantially from the release amount of TP based on the SWAT model ( $1.86 \times 10^4 \text{ t}$ ) [45], probably because some management practices such as moving the topsoil to cultivate fertility can reduce the endogenous contaminants in the sediment and consequently the release amount of TP. The

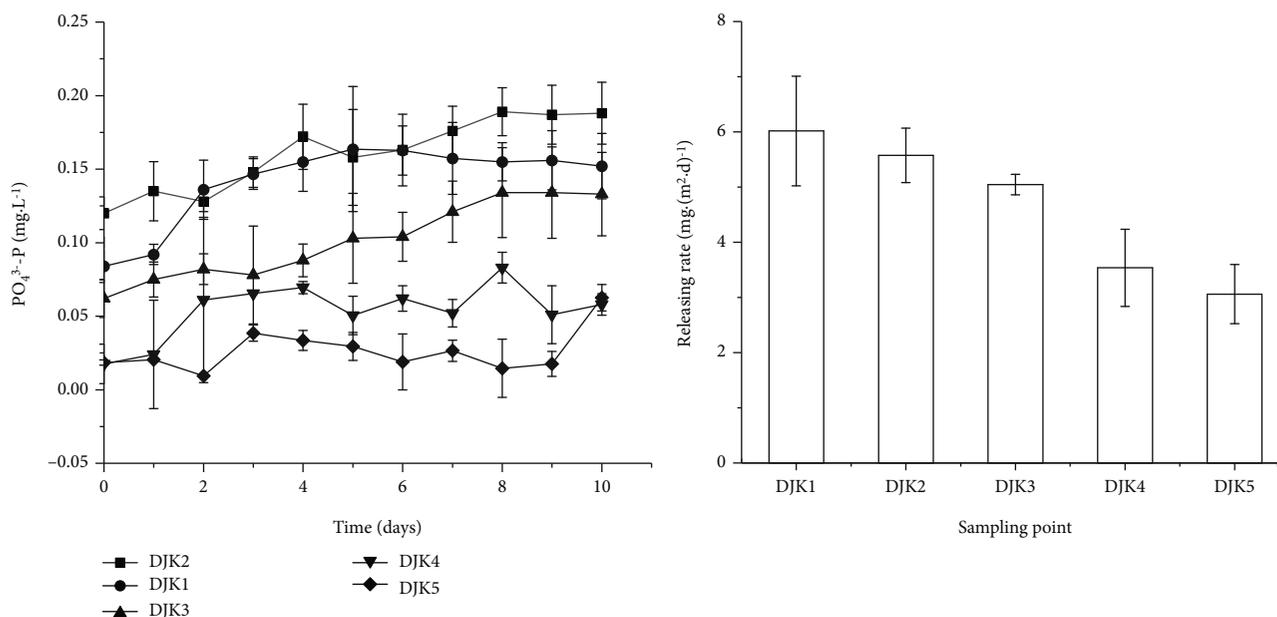


FIGURE 6: The content and release rate of  $PO_4^{3-}\text{-P}$  in the overlying water.

amounts of  $NH_4^+\text{-N}$  and  $PO_4^{3-}\text{-P}$  would be increased from  $0.44\text{ mg}\cdot L^{-1}$  and  $0.02\text{ mg}\cdot L^{-1}$  to  $0.57\text{ mg}\cdot L^{-1}$  and  $0.02\text{ mg}\cdot L^{-1}$  according to the average annual inflow (39.48 billion  $m^3$ ) and to  $0.62\text{ mg}\cdot L^{-1}$  and  $0.03\text{ mg}\cdot L^{-1}$  according to the total reservoir storage (29.05 billion  $m^3$ ), respectively. In theory, the water quality is between mesotrophy and eutrophication ( $0.03\text{--}0.05\text{ mg}\cdot L^{-1}$  for TP and  $0.31\text{--}0.65\text{ mg}\cdot L^{-1}$  for TN) [46]. The reservoir storage is increased in the wet season from May to October, and the increase of temperature leads to an increase in dissolved carbon and microbial activities in the soil. As a result, a large amount of N and P accumulated in the soil would migrate to the overlying water, which is now the main factor affecting the water quality of the Danjiangkou Reservoir. In addition, the newly submerged area is often in alternative submergence-dry states, and land is cultivated for agricultural production under dry conditions [16], thus resulting in an increase in the diffusion of P and N from the sediment into the overlying water.

#### 4. Conclusions

- (1) The TP contents in the 0-10 cm sediment samples collected in the Danjiangkou Reservoir and its upstream tributary range from  $402.40\text{ mg}\cdot kg^{-1}$  to  $560.30\text{ mg}\cdot kg^{-1}$ , and the contents of different forms of P follow the order of  $IP > OP > Ca - P > Fe - P > LP$ . The spatial difference in P contents among the five sampling points may be related to the original land use type
- (2) The average  $PO_4^{3-}\text{-P}$  and  $NH_4^+\text{-N}$  contents in the interstitial water of DJK 4 and DJK 5 are higher than those in the overlying water, and thus  $PO_4^{3-}\text{-P}$  and  $NH_4^+\text{-N}$  are likely to be released from the sediment to the overlying water

- (3) Both experimental and calculation results show that N and P are easily released from the sediment to the overlying water, and thus endogenous contamination from the newly submerged sediment is an important factor affecting the water quality of the Danjiangkou Reservoir

#### Data Availability

The data used to support the findings of this study are available from the corresponding author upon request.

#### Conflicts of Interest

The authors declare no conflict of interest.

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