

Article

Environmental Impacts of Nitrogen and Phosphorus Nutrient Diffusion Fluxes at a Sediment-Water Interface: The Case of the Yitong River, China

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Abstract: Under the premise of controlling the external input of nitrogen and phosphorus, endogenous release is the main cause of eutrophication in lakes. To investigate the characteristics of endogenous nitrogen and phosphorus release from urban rivers, the Yitong River, an urban river in northern China, was used as an experimental object. Eight sampling sites were set up in the upstream, urban, and downstream regions of an urban section. The nitrogen and phosphorus nutrient exchange fluxes at the sediment-water interface of the Yitong River were assessed by analyzing the sediment and overlying water, and the effects of environmental factors on nitrogen and phosphorus release were investigated using static release experiments. The results showed that the diffusive fluxes of endogenous total nitrogen (TN), ammonia nitrogen ($\text{NH}_4^+\text{-N}$), and total phosphorus (TP) in the urban section of the Yitong River ranged from -1.571 to $19.365 \text{ mg}\cdot(\text{m}^2\cdot\text{d})^{-1}$, -0.171 to $9.227 \text{ mg}\cdot(\text{m}^2\cdot\text{d})^{-1}$, and -0.052 to $0.595 \text{ mg}\cdot(\text{m}^2\cdot\text{d})^{-1}$, respectively. The diffusive fluxes of nitrogen and phosphorus nutrients were all greater under anaerobic conditions than under aerobic conditions. The diffusive fluxes of nitrogen and phosphorus were influenced by changes in pH, DO, and temperature of the overlying water, and the release of phosphorus from the sediment was accelerated by high temperatures in the range of $5\text{--}25\text{ }^\circ\text{C}$. Acidic conditions favored the release of TN, whereas alkaline conditions favored the release of TP from the sediment. Furthermore, during the control of nitrogen and phosphorus pollution, it should be noted that fluxes are higher in spring and autumn. Thus, when appropriate techniques should be implemented to achieve better control. These findings are intended to provide a reference for the study of nitrogen and phosphorus diffusion fluxes at the sediment-water interface in urban rivers and other surface waters around the world.

Keywords: urban rivers; sediment-water interface; nitrogen and phosphorus nutrients; diffusive fluxes; release pattern



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1. Introduction

Eutrophication of water bodies is a water pollution problem occurring worldwide [1]. It is problematic because the discharge of excess nutrients, such as nitrogen and phosphorus, into rivers not only leads to eutrophication of the water column, but the nutrients also accumulate in sediments and become an endogenous pollution load [2,3]. However, when external inputs are controlled, the release of endogenous N and P from sediments becomes the dominant factor in water column eutrophication [4,5]. River water quality and habitats are degraded by pollution from urban areas caused by surface runoff and lack of riparian forests that block subsurface flows [6]. The input of municipal sewage seriously damages the chemical characteristics of rivers and has a complex effect on the function of

ecosystems [7]. In the process of urbanization, human activities caused serious pollution to the sediment surface, which caused the interaction between surface water and pore water [8]. Particularly in highly polluted urban rivers, such as the Thames in the UK [9] and the Jepara estuary in Indonesia [10], sediments in urban rivers have proven to be a source of nitrogen and phosphorus nutrients. Large amounts of municipal wastewater, agricultural irrigation drainage, and farming wastewater are discharged directly into urban rivers, leading to a continuous accumulation of nitrogen and phosphorus in water. When external nitrogen and phosphorus decrease, only the release of primitive internal pollutants leads to eutrophication in water bodies. Therefore, it is important to study the migration and diffusion processes of nitrogen and phosphorus at the overlying water interface of sediments for the treatment of eutrophication in lakes [11].

Environmental change is a major factor influencing the dispersal of endogenous pollutants [12]. Sediment nitrogen release is mainly driven by microbial activity, and a complex network of microorganisms linking nitrogen transformation reactions can exacerbate human-induced global changes, which promote sediment nitrogen release and lead to eutrophication in aquatic systems [13], whereas phosphorus release is driven by abiotic factors such as the dissolved oxygen (DO) content, redox conditions, temperature, pH, and hydrodynamics [14–17]. Notably, the pH of a water column affects metal precipitation, resulting in different sediment P distributions at different pH values [18]. In a study on environmental factors affecting nitrogen and phosphorus release from Gunston Cove, Virginia, Cerco et al. found that high temperatures and low DO contents promoted the release of endogenous $\text{NH}_4^+\text{-N}$ [19]. Kieseckamp et al. found that high temperatures and low DO contents promoted the release of endogenous $\text{NH}_4^+\text{-N}$ from the Wadden Sea in the Netherlands [20]. Changes in environmental factors can affect the release of nitrogen and phosphorus to varying degrees [21–23].

Urban rivers are shallow and characterized by a blurred boundary layer, pronounced acoustic-wind flow, and strong material and energy exchange in the vertical plane, exacerbating the impact of sediments on the water quality of the overlying water bodies [24]. The Yitong River, the largest secondary tributary on the left bank of the Songhua River in northern China, is an urban river in Changchun, Jilin Province, with a low natural volume of water, weak self-purification capacity, and flow that is influenced by seasons and precipitation. The Yitong River flows through a densely populated area, agricultural production areas, and livestock breeding areas, resulting in a constant accumulation of N and P in the water. Prior to this study, tests revealed that this water body was already polluted to some extent, with the total nitrogen (TN) and total phosphorus (TP) in the water body already being well above the internationally defined thresholds determining the occurrence of eutrophication [25] (TN was $0.2\text{ mg}\cdot\text{L}^{-1}$, TP was $0.02\text{ mg}\cdot\text{L}^{-1}$). Few studies have been conducted on the endogenous pollution of the Yitong River, and the current state of pollution cannot be ignored. The main objectives of this study were: (a) To investigate the temporal distribution of water quality indicators and nitrogen and phosphorus nutrients in the Yitong River, (b) to estimate the nitrogen and phosphorus exchange fluxes at the sediment-water interface of the Yitong River using Fick's first law, and to investigate the temporal source-sink characteristics of nitrogen and phosphorus nutrients at the sediment-water interface of the Yitong River, (c) and to investigate the effects of environmental factors, such as temperature, pH, and DO, on nitrogen and phosphorus in sediment on a single-factor basis. The results of this study aim to provide data support for the prevention and control of eutrophication in urban water bodies, enrich theories on the influence of environmental factors on the release of endogenous nitrogen and phosphorus from water bodies, and provide references for the prevention and control of eutrophication in other urban rivers and surface waters.

2. Materials and Methods

2.1. Placement of Sampling Sites

The Yitong River basin belongs to the temperate continental monsoon climate with seasonal rainfall changes. The regional average annual rainfall is 400–900 mm, and 80% of annual rainfall is in summer. The total length of the Yitong River is 343.5 km, while the catchment area is 7515 km². The annual runoff is 3.5×10^8 – 6×10^8 m³. To obtain the exchange characteristics of nitrogen and phosphorus nutrients at the sediment–water interface, water and sediment samples were collected along the Yitong River every two months from April 2021 to December 2021. Based on water quality characteristics, river topography, and distribution of pollution levels, eight sites were established: The upstream of the urban section of the Yitong River (Xingguang section (S1)), the urban section (Xinlizheng Reservoir Dam (S2), South Barrage of South Third Ring Road (S3), Free Barrage (S4), Yangjia Waizi (S5), and Beihu Bridge (S6)), and the downstream of the urban section of the Yitong River (Baolong Bridge section (S7), and Leishan Bridge section (S8)). The sampling sites were also set up with reference to China's national and provincial control cross-sections (S1, S2, S5, S7, and S8). The sampling site layout is shown in Figure 1.

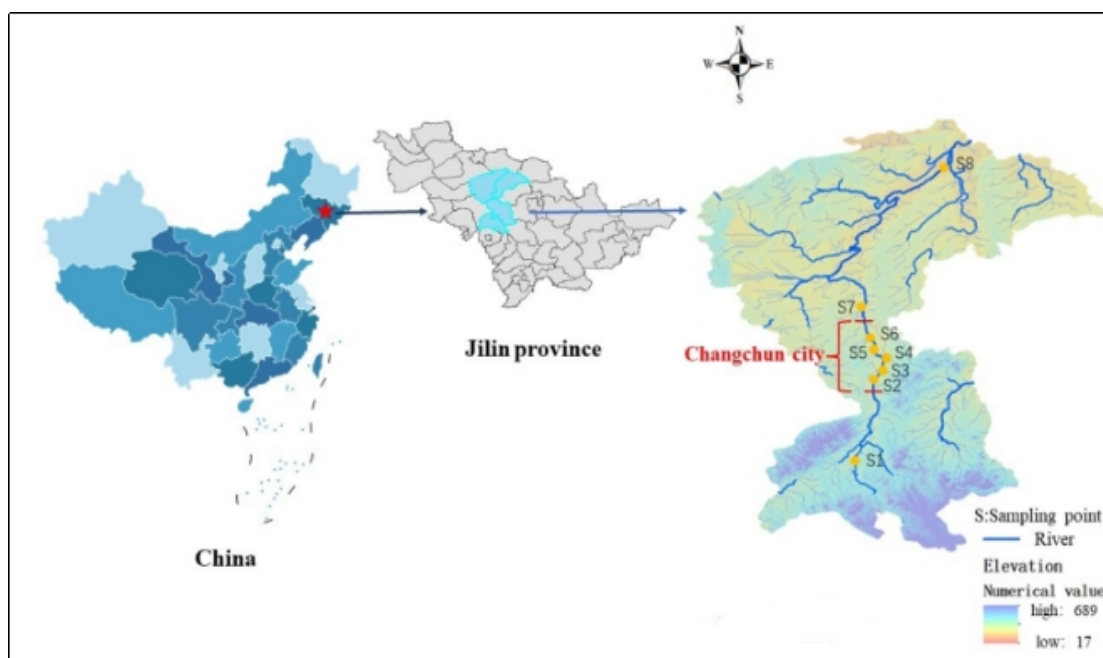


Figure 1. Distribution of the experimental sampling (research) sites in the Changchun section of the Yitong River.

2.2. Sample Collection and Testing Methods

Owing to the low temperatures and presence of thick ice on the water surface in December in Northeast China, sediment samples were only collected at points S1, S2, and S7. The DO, pH, and depth of the water bodies were measured on-site during sampling. Overlying water was collected using a stainless-steel water collector in polyethylene sampling bottles, and sediment samples from 0–10 cm of the river surface were collected using a Peterson mud collector and stored in sealed polyethylene bags. The water and sediment samples were transported back to the laboratory and maintained at a low temperature. The sediment samples were partly centrifuged to collect interstitial water, partly dried, ground, and sieved through a 100-mesh sieve to determine the TN and TP contents in the sediment. The overlying and interstitial waters were filtered through a 0.45 µm glass fiber membrane before the determination of TN, NH₄⁺-N, and TP in the water column, and all water quality indicators were determined within 24 h [26,27].

2.3. Simulation Experimental Program

To study the effects of different environmental factors on nitrogen and phosphorus exchange fluxes in the Yitong River, sediment and overlying water samples with high sediment pollution contents in the urban area and faster endogenous nitrogen and phosphorus diffusion (S3) were selected for simulation experiments for the influencing factors, and three factors, namely temperature, pH, and DO, were selected based on the single-influence-factor method and simulated independently in different batches. To simulate the underwater environment, sediment samples were rapidly transferred to Plexiglas columns without disturbing the sediment interlayer structure, and the sediment sample height was adjusted to approximately 10 cm. Three parallel samples and one blank sample were set up for each group of experiments, and the entire experimental cycle lasted for 7 d, totaling 168 h. Temperature effects: To approximate the actual temperature range. The samples were incubated in incubators at 5 °C, 15 °C, and 25 °C, protected from light, with the pH adjusted to 7.5, and left open. pH impact test: The Yitong River water body was considered neutral to slightly alkaline. To account for the margin of error, three pH conditions were set: Slightly acidic, neutral, and slightly alkaline, and the pH of the overlying water for column incubation was adjusted to 5, 7, and 9 using 1 mol·L⁻¹ HCl and 0.5 mol·L⁻¹ Na₂CO₃ at room temperature (25 °C). The samples were then left open. Dissolved oxygen effects: One column was filled with a volume of nitrogen to create an oxygen-poor environment (DO less than 1 mg·L⁻¹), and another column was filled with an equal volume of air to create an oxygen-rich environment (DO greater than 5 mg·L⁻¹) at room temperature (25 °C) and pH 7.5. The overlying water (150 mL) was pipetted 2 cm from the sediment every 12 h, and an equal volume of the original overlying water was added.

2.4. Calculation Method for Nitrogen and Phosphorus Release Fluxes

2.4.1. Calculation Method for Nitrogen and Phosphorus Quantities in the Yitong River

The exchange of nitrogen and phosphorus nutrients at the sediment-water interface is mainly achieved by molecular diffusion due to concentration differences, and the net fluxes of TN, TP, and NH₄⁺-N were calculated using Fick's first law, as follows [28,29]:

$$F = \frac{\varnothing \times D_s \times \partial C}{\partial x} \quad (1)$$

where F is the diffusion flux of a substance at the sediment-water interface (mg·m⁻²·d⁻¹), $\varnothing$ is the sediment porosity, is the concentration gradient of nutrient salts at the sediment-water interface (mg·m⁻⁴), and D_s is the diffusion coefficient of nutrient salts at the sediment-water interface (cm²·s⁻¹). Although the bending effect of the sediment is included in equation, measuring the bending of the sediment is difficult to achieve in practical studies. The porosity $\varnothing$ of the sediment and the diffusion coefficient of the ideal solution are commonly used to derive the following relationship [30]:

$$D_s = \varnothing D_0 \quad (\varnothing < 0.7) \quad (2)$$

$$D_s = \varnothing^2 D_0 \quad (\varnothing \geq 0.7) \quad (3)$$

where D_s is the diffusion coefficient of the ideal solution. The ideal diffusion coefficient for NH₄⁺-N = 9.8 × 10⁻⁶ cm²·s⁻¹, ideal diffusion coefficient for TN D_0 = 14.21 × 10⁻⁶ cm²·s⁻¹, and ideal diffusion coefficient for TP = 6.12 × 10⁻⁶ cm²·s⁻¹. The porosity was calculated as follows [31]:

$$\varnothing = \frac{(W_w - W_d) \times 100\%}{(W_w - W_d) + \frac{W_d}{\rho}} \quad (4)$$

where W_w is the fresh weight of the sediment (g), W_d is the dry weight of the sediment (g) and is the ratio of the average density of the sediment to the density of the water, which is usually taken as 2.5.

2.4.2. Nitrogen and Phosphorus Flux Calculation Method for Simulation Experiments

Nitrogen and phosphorus exchange fluxes at the sediment-water interface were estimated from the mean value of the net change in nitrogen and phosphorus nutrient concentrations in the overlying water at each sampling interval during the experiment and were calculated as follows [32]:

$$F = M_t \cdot A^{-1} \cdot t^{-1} \quad (5)$$

where F is the nutrient exchange flux at the sediment-water interface ($\text{mg} \cdot \text{m}^{-2} \cdot \text{d}^{-1}$), A is the surface area of material exchange at the sediment-water interface (m^2), and Mt is the mass change of nutrients (mg) over time period t , calculated as follows:

$$M_t = V \cdot [C_t - D_{t-1}] \quad (6)$$

where V is the total volume of overlying water in the culture column (L), C_t is the concentration of nutrients in the overlying water at time t ($\text{mg} \cdot \text{L}^{-1}$), and D_{t-1} is the actual nutrient concentration in the overlying water at time $t-1$ ($\text{mg} \cdot \text{L}^{-1}$) and is calculated as follows:

$$D_{t-1} = \frac{[(V - V_0) \cdot C_{t-1} + V_0 \cdot C_0]}{V} \quad (7)$$

where V_0 is the volume of overlying water collected at each sampling (L), C_0 is the concentration of nutrients in the original overlying water ($\text{mg} \cdot \text{L}^{-1}$), and C_{t-1} is the concentration of nutrients in the overlying water at time $t-1$ ($\text{mg} \cdot \text{L}^{-1}$).

3. Results and Discussion

3.1. Overlying Water—Interstitial Water Quality Characteristics

The variation in the nitrogen and phosphorus nutrient contents in the overlying and interstitial water of the Yitong River is shown in Figure 2, and the variation in the TN content in the overlying and interstitial water is shown in Figure 2a,b, ranging from 0.28 to $9.07 \text{ mg} \cdot \text{L}^{-1}$ and 0.35 to $15.51 \text{ mg} \cdot \text{L}^{-1}$, respectively. The levels were consistently the highest at these points, mainly because these two points are located in the urban section, and the excessive discharge of domestic sewage not only seriously affected the water quality of the overlying water but also that collected in the sediment, resulting in serious endogenous nitrogen pollution. The variation of NH_4^+ -N in the overlying water is shown in Figure 2c. It ranged from 0.06 to $3.17 \text{ mg} \cdot \text{L}^{-1}$, with a mean value of $0.63 \text{ mg} \cdot \text{L}^{-1}$ and showed the same trend as that of TN with the maximum value occurring at point S3 in the urban section in October and the minimum value at point S7 in December. The NH_4^+ -N content in the interstitial water varied, as shown in Figure 2d, ranging from 0.31 to $9.05 \text{ mg} \cdot \text{L}^{-1}$, which was approximately five times the NH_4^+ -N concentration in the overlying water. The variation in TP in the overlying water is shown in Figure 2e, ranging from 0.01 to $0.78 \text{ mg} \cdot \text{L}^{-1}$, with the maximum value occurring at point S1 in June. Because the surrounding area of this point is agricultural land, and the remaining pesticides and fertilizers in the soil flow into the river through rainwater, the phosphorus content of the water body exceeds the standard. Point S8 is near agricultural land, and in addition to the influence of pesticides, fertilizers, and livestock manure, the TP content of the interstitial water is also shown in Figure 2f, ranging from 0.09 to $1.51 \text{ mg} \cdot \text{L}^{-1}$, of which the contents at points S3 and S5 are too high. The TN and TP in the Yitong River water body far exceeded the internationally defined threshold determining the occurrence of eutrophication [25]. The river body is at risk of eutrophication. According to China's surface water environmental quality standards, TN content of 70% data of Yitong River water exceeds the surface water Class V standard, TP content of all points meets the limit of the surface water Class III standard, and some points, such as S3, S5, and S8, exceed the surface water Class V standard in August. Compared with other studies, the TN and TP contents in the Yitong River water body are 5.3 times and 8.8 times the average TN and TP contents in watershed landscape river bodies [33]. Compared with the Three Gorges Reservoir, the contents of TN and TP in the water of Yitong River are 2.6 times and 4.8 times of the contents [34]. It can be seen that the Yitong River water body is heavily polluted with eutrophication.

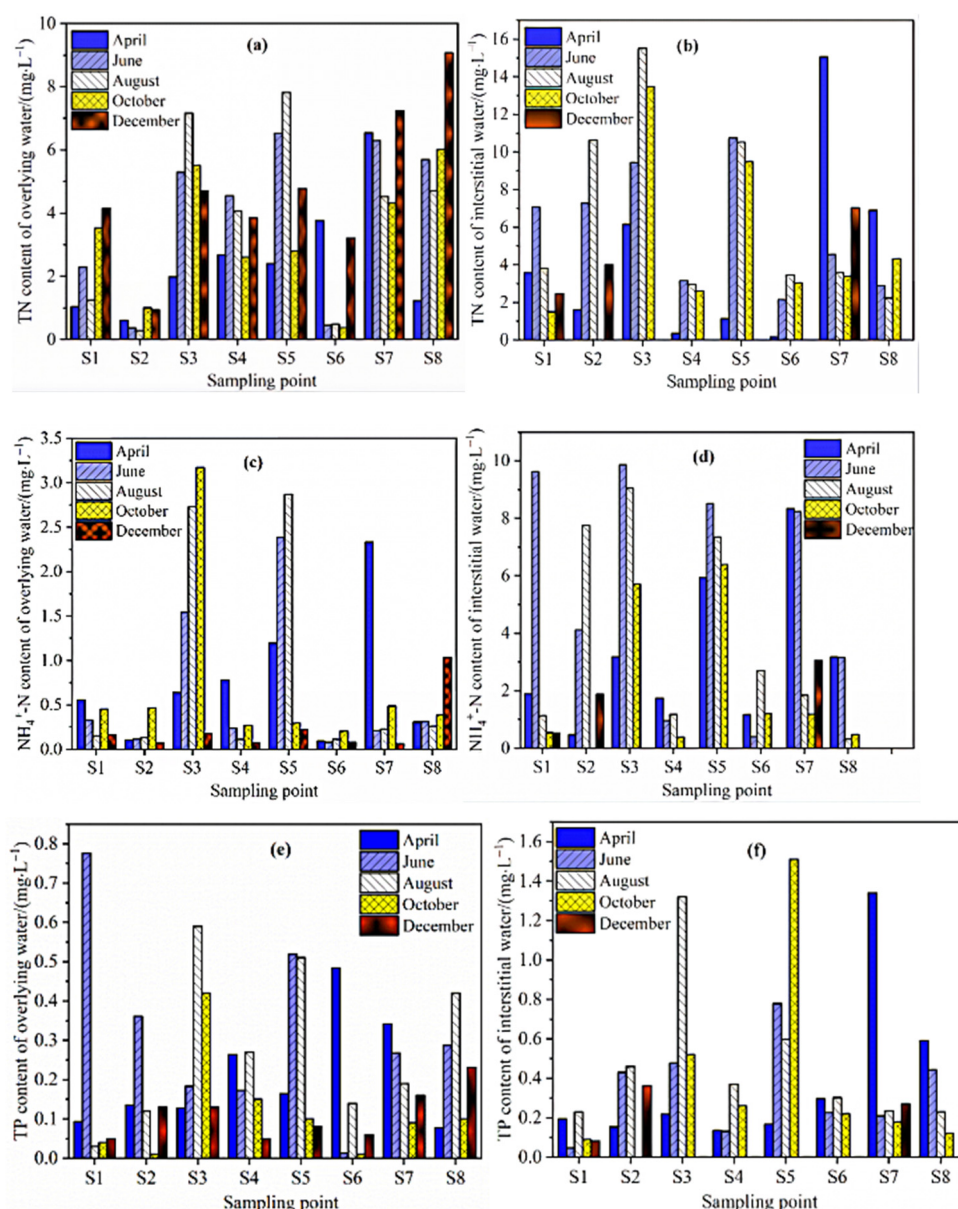


Figure 2. Distribution of nitrogen and phosphorus nutrients in the overlying and interstitial waters of the Yitong River (TN, $\text{NH}_4^+\text{-N}$, TP overlying and interstitial water content measured at each site in April, June, August, October, and December, where (a,c,e) represent TN, $\text{NH}_4^+\text{-N}$, TP overlying water content and (b,d,f) represent TN, $\text{NH}_4^+\text{-N}$, TP interstitial water content, respectively.).

Overall, the water in the middle and lower reaches of the Yitong River is more seriously polluted, mainly because there are more residents near the middle reaches, and the excessive discharge of domestic sewage is the main factor for the deterioration of the water quality. Water bodies in the lower reaches are affected by the confluence of pollutants in the middle reaches and agricultural surface pollution sources, leading to the deterioration of the water quality. Many foreign scholars have found similar patterns. For example, Cheng et al. investigated the water quality characteristics of four typical urban rivers in Tanzania, Africa, and found that serious pollution of water bodies was more prevalent in large cities, and there was a tendency for pollution to increase with rapid population growth [35]. Haghnazar et al. studied the water quality conditions of the Zarjoub River in northern Iran before and after the blockade and found that, during the blockade, the contribution of urban sewage to water pollution increased from 23% to 50% [36]. In addition, river

nitrogen and phosphorus nutrients were significantly higher as endogenous pollutants than as pollutants in the overlying water, with a tendency to spread to the overlying water bodies.

3.2. Analysis of Sediment Nitrogen and Phosphorus Release Fluxes

The above water quality analysis results show that there was a distinct concentration gradient between the nitrogen and phosphorus nutrient contents of the overlying water and interstitial water in the Yitong River. The average nitrogen and phosphorus diffusion fluxes at the sediment-water interface from April to December 2021 are shown in Figure 3. The TN diffusion fluxes range from 0.02 to $6.24 \text{ mg} \cdot (\text{m}^2 \cdot \text{d})^{-1}$, and the order of diffusion fluxes is urban section > downstream > upstream ($p = 0.031$). The river diffusion fluxes in the artificially polluted urban section through the city are larger. The diffusion flux of $\text{NH}_4^+\text{-N}$ ranges from 0.28 to $3.03 \text{ mg} \cdot (\text{m}^2 \cdot \text{d})^{-1}$, and the trend of diffusion flux at each point is consistent with TN. The order of diffusion flux is urban section > downstream > upstream ($p < 0.001$). The diffusion flux of TP was $0.02\text{--}0.27 \text{ mg} \cdot (\text{m}^2 \cdot \text{d})^{-1}$, and the order of diffusion flux was urban section > downstream > upstream ($p < 0.001$). When the diffusion flux is positive, nutrients are diffused from the sediment to the overlying water, and when it is negative, nutrients are pooled from the overlying water to the sediment. The TN diffusion flux at each point in the Yitong River from April to December is shown in Table 1, with a range of -1.571 to $19.365 \text{ mg} \cdot (\text{m}^2 \cdot \text{d})^{-1}$ and an annual mean value of $2.879 \text{ mg} \cdot (\text{m}^2 \cdot \text{d})^{-1}$. The diffusion flux of TN reaches its maximum in August and October, the TN diffusion flux at point S1 in the upper reaches was small ($p < 0.05$), whereas the mean TN diffusion flux at point S2 was the largest and positive, mainly because the high temperatures in August and October increased microbial activity and accelerated the mineralization of organic N. Enhanced mineralization led to microbial decomposition of organic matter in the sediment, resulting in the accumulation and release of $\text{NH}_4^+\text{-N}$ into the sediment pore water [37]. In addition, the poor connectivity and mobility of the water column due to the abundance of water plants at this site, which, in turn, led to lower DO levels, and the lack of oxygen in the deep sediment due to dissolved oxygen penetrating only a few millimeters into the sediment facilitate the desorption of $\text{NH}_4^+\text{-N}$ from the sediment and the accumulation of $\text{NH}_4^+\text{-N}$ in the pore water, enhancing denitrification and contributing to the release of endogenous nitrogen pollutants into the overlying water column [38]. The TN diffusion rate to the overlying water at site S7 was the fastest throughout the year, reaching $19.365 \text{ mg} \cdot (\text{m}^2 \cdot \text{d})^{-1}$ in April, after which the TN diffusion fluxes were all negative, mainly due to fertilizer nitrogen input leading to increased nitrogen pollutant levels in the overlying water at this site and the diffusion of nitrogen pollutants from the sediment to the overlying water. It can be seen that agricultural surface pollution sources are a key factor in the eutrophication of river water bodies [39].

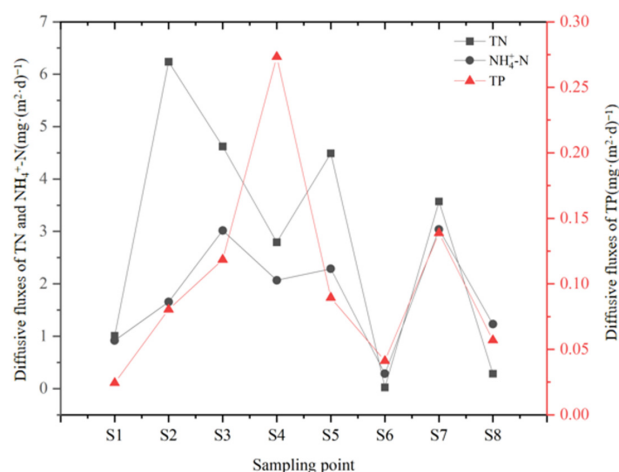


Figure 3. Monthly average nitrogen and phosphorus diffusion fluxes at the sediment-water interface of Yitong River.

Table 1. Diffusive fluxes of nitrogen and phosphorus nutrients at the sediment-water interface. Indicator Unit: $\text{mg} \cdot (\text{m}^2 \cdot \text{d})^{-1}$.

Nutritional Salts	Points	April	June	August	October	December
TN	S1	2.398 ± 0.281	2.381 ± 0.241	1.813 ± 0.194	-0.878 ± 0.009	-0.661 ± 0.051
	S2	1.477 ± 0.181	4.001 ± 0.372	6.075 ± 0.302	16.239 ± 1.324	3.391 ± 0.296
	S3	2.213 ± 0.246	4.681 ± 0.391	11.593 ± 0.719	-0.004 ± 0.001	—
	S4	0.596 ± 0.076	-0.087 ± 0.010	-0.646 ± 0.077	11.311 ± 0.994	—
	S5	9.120 ± 0.995	5.823 ± 0.613	1.697 ± 0.185	1.317 ± 0.085	—
	S6	-2.177 ± 0.213	1.021 ± 0.122	1.667 ± 0.153	-0.418 ± 0.037	—
	S7	19.365 ± 2.143	-0.500 ± 0.061	-0.398 ± 0.033	-0.729 ± 0.052	0.119 ± 0.010
	S8	5.082 ± 0.521	-1.495 ± 0.179	-1.571 ± 0.104	-0.878 ± 0.079	—
$\text{NH}_4^+\text{-N}$	S1	0.821 ± 0.093	3.146 ± 0.177	0.486 ± 0.025	0.026 ± 0.002	0.119 ± 0.009
	S2	0.075 ± 0.016	1.685 ± 0.159	3.991 ± 0.381	1.423 ± 0.101	1.100 ± 0.095
	S3	1.843 ± 0.203	3.613 ± 0.318	6.517 ± 0.529	0.101 ± 0.074	—
	S4	0.296 ± 0.332	0.445 ± 0.036	0.43 ± 0.048	7.098 ± 0.517	—
	S5	4.031 ± 0.398	2.827 ± 0.311	1.948 ± 0.205	0.339 ± 0.031	—
	S6	-0.171 ± 0.028	0.095 ± 0.011	0.998 ± 0.106	0.216 ± 0.019	—
	S7	9.227 ± 1.072	3.631 ± 0.257	0.473 ± 0.037	0.025 ± 0.002	1.835 ± 0.175
	S8	2.272 ± 0.219	2.599 ± 0.176	0.025 ± 0.003	0.026 ± 0.003	—
TP	S1	0.033 ± 0.003	0.002 ± 0.001	0.062 ± 0.005	0.009 ± 0.001	0.016 ± 0.001
	S2	0.031 ± 0.002	0.103 ± 0.009	0.113 ± 0.011	0.034 ± 0.002	0.121 ± 0.011
	S3	0.051 ± 0.006	0.141 ± 0.013	0.223 ± 0.019	0.059 ± 0.005	—
	S4	0.019 ± 0.002	0.03 ± 0.002	0.024 ± 0.002	1.020 ± 0.089	—
	S5	0.055 ± 0.006	0.230 ± 0.017	0.025 ± 0.002	0.048 ± 0.005	—
	S6	0.058 ± 0.005	0.050 ± 0.006	0.039 ± 0.003	0.018 ± 0.002	—
	S7	0.595 ± 0.071	0.001 ± 0.000	0.009 ± 0.001	0.004 ± 0.000	0.085 ± 0.010
	S8	0.127 ± 0.015	0.144 ± 0.012	-0.052 ± 0.005	0.009 ± 0.001	—

As can be seen from Table 1, the variation in $\text{NH}_4^+\text{-N}$ diffusive fluxes ranged from -0.171 to $9.227 \text{ mg} \cdot (\text{m}^2 \cdot \text{d})^{-1}$. The diffusion flux of $\text{NH}_4^+\text{-N}$ reached its maximum value in August and October, with the same trend as that of TN in general with positive values at all points except point S6 in April ($p < 0.05$), indicating that the sediment acted as a source of $\text{NH}_4^+\text{-N}$ nutrients, that is, $\text{NH}_4^+\text{-N}$ diffused from the sediment to the overlying water. April was the dry period of the Yitong River, and the effect of wind and wave disturbance on the river was. The mean value of the $\text{NH}_4^+\text{-N}$ diffusion flux at site S7 was the highest, indicating that $\text{NH}_4^+\text{-N}$ diffusion from sediment to overlying water was the fastest at this site. Overall, the diffusive flux values of $\text{NH}_4^+\text{-N}$ in the Yitong River followed the same trend as those of TN, with lower flux values in the upper reaches and larger $\text{NH}_4^+\text{-N}$ flux values in the middle and lower reaches.

The diffuse fluxes of TP in the Yitong River are shown in Table 1, with diffuse fluxes ranging from -0.052 to $0.595 \text{ mg} \cdot (\text{m}^2 \cdot \text{d})^{-1}$, with large variability in diffusion rates at each site. In general, the highest value is in January, the lowest value is in August, and the second lowest value is in October ($p < 0.05$). Many studies have shown that the diffusion flux of TP is negatively correlated with temperature and chlorophyll [40,41]. The highest temperature of the Yitong River in summer coincides with the rainy season, so the TP diffusion flux is lowest in August. At the same time, the increase in temperature leads to the proliferation of algae in the water and increases the content of chlorophyll, so the TP diffusion flux reaches its lowest value in October. The diffusive flux of TP at site S8 in August was negative, mainly because rural residents are not environmentally conscious and may have discharged domestic sewage directly into the river, as well as because August is a period of abundant water, and the rainy season leads to lower nutrient levels in the sediment [42]. In contrast, sediments with smaller particle sizes have a larger specific surface area, leading to more phosphorus adsorption by the sediments [43]. The sediments in the urban section of the Yitong River are mostly sediment with a larger particle size, which facilitates the desorption of phosphorus pollutants and ultimately leads to increased phosphorus release to the overlying water column. In the lower reaches, the TP diffusion flux at site S7 was larger in

April, reaching $0.595 \text{ mg} \cdot (\text{m}^2 \cdot \text{d})^{-1}$ because there were agricultural fields near site S7 and April was a critical period for planting crops. Therefore, disturbance and anthropogenic influence were the main reasons for the fastest diffusion rate of phosphorus pollutants at this site. The maximum TP diffusion flux was reached in October at site S4, probably because of the high algal abundance at this site and the decomposition of algae as a major source of phosphorus release from sediments [44].

3.3. Effects of Environmental Factors on Nitrogen and Phosphorus Release

The sediment can first release nitrogen and phosphorus attached to sediment particles into the gap water and then diffuse them into the overlying water through the concentration gradient in the water or external disturbance. This process is referred to as the free diffusion process. The free diffusion process is mainly affected by environmental factors and is the main way for nitrogen and phosphorus in sediments to diffuse into water. A large number of studies have shown that temperature, pH, and DO are considered to be the main factors of nitrogen and phosphorus release in sediments, so this paper compares the nitrogen and phosphorus release characteristics of temperature, pH, and DO under different conditions.

3.3.1. Influence of Environmental Factors on Nitrogen and Phosphorus Release

The variations in TN and $\text{NH}_4^+\text{-N}$ diffusion fluxes with temperature are shown in Figure 4a,b. The diffusion flux of TN was highest at 5°C , which was three and four times higher than those at 15°C and 25°C , respectively. The $\text{NH}_4^+\text{-N}$ fluxes were affected by temperature and showed the same trend as that of TN. The $\text{NH}_4^+\text{-N}$ fluxes were negative under all three temperature conditions from 60 to 72 h of the experiment, indicating that the sediment acted as a sink for nitrogen nutrients. The variation in TP flux with temperature is shown in Figure 4c. The TP fluxes decreased rapidly within 24 h and then stabilized, with values ranging from -0.0016 to $0.0435 \text{ mg} \cdot (\text{m}^2 \cdot \text{d})^{-1}$. TP fluxes increased with temperature and were highest at 25°C . Under the 5°C condition, the flux values were greater than 15°C for the first 60 h of the experiment and then remained the lowest. The main reason for this phenomenon is that high-temperature conditions lead to increased ionic activity and faster inter-ion exchange, which, in turn, increases phosphate migration and transformation [45]. Meanwhile, higher temperatures increase biological activity, which, in turn, creates anaerobic conditions at the sediment-water interface, a condition that favors the reduction of Fe^{3+} to Fe^{2+} and Mn^{4+} to Mn^{2+} [46], resulting in the release of Fe-Mn-bound phosphorus and ultimately an increase in TP content.

3.3.2. Effect of pH on the Release of Nitrogen and Phosphorus

The pH value mainly influences biochemical reactions in the system by affecting the activities of functional microorganisms and other physicochemical reactions, which, in turn, affects the nitrogen and phosphorus nutrient exchange fluxes at the interface. The variation in nitrogen and phosphorus fluxes with pH is shown in Figure 5, which shows that the fluxes of nitrogen and phosphorus released under weakly acidic and weakly alkaline conditions were higher than those under neutral conditions. $\text{NH}_4^+\text{-N}$ fluxes were the greatest under alkaline conditions and least under neutral conditions, with $\text{NH}_4^+\text{-N}$ fluxes at $\text{pH} = 9$ being approximately twice as high as those at $\text{pH} = 7$. The nitrogen fluxes were all more acidic or alkaline than neutral conditions, mainly because under acidic conditions, H^+ would compete with NH_4^+ in the system for adsorption on the colloid. The higher the acidity, the more H^+ adsorbed on the colloid, resulting in more nitrogen release [47]. Under alkaline conditions, the higher OH^- concentration together with the higher NH_4^+ content as NH_3 overflow in the overlying water caused the overlying water and interstitial water to increase the $\text{NH}_4^+\text{-N}$ concentration difference, which, in turn, promoted the release of endogenous nitrogen pollutants into the overlying water.

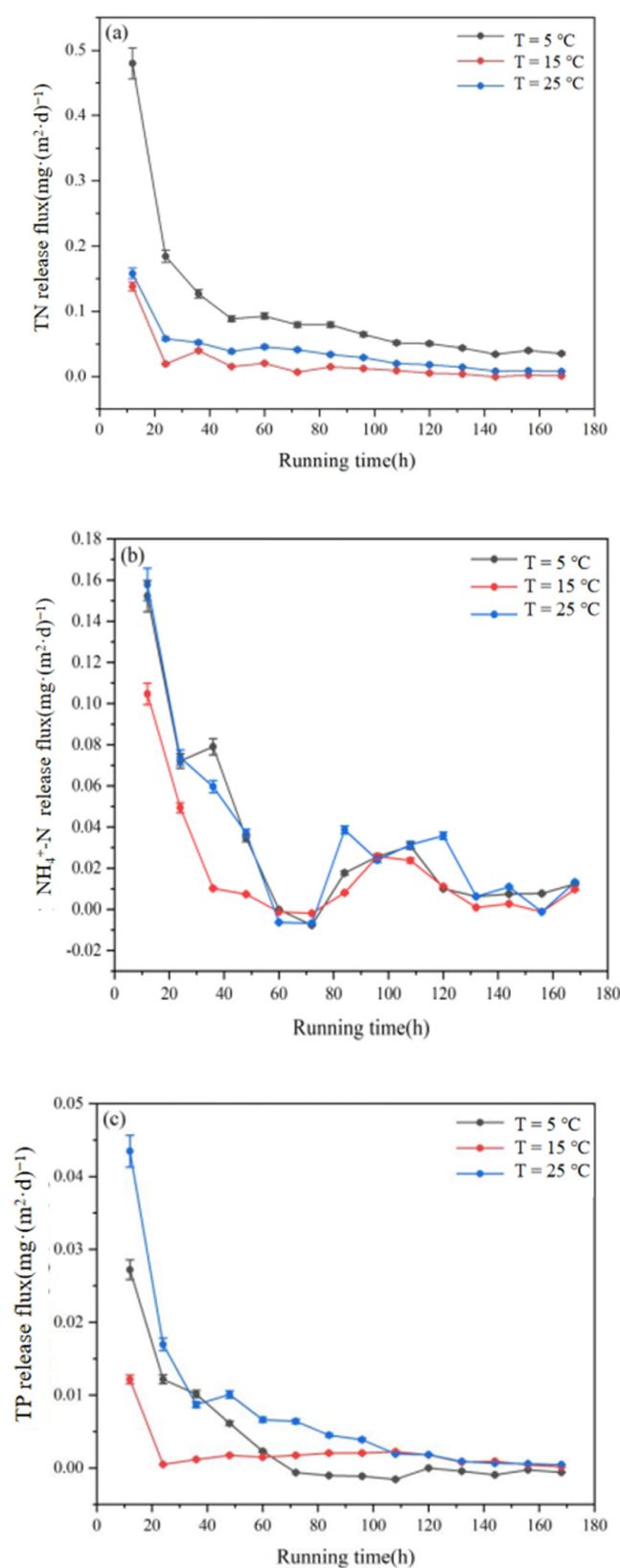


Figure 4. Effect of different temperature conditions on the flux of nitrogen and phosphorus nutrients released (DO and pH are kept constant, single-factor control of temperature changes. When the final values level off, the change in flux of nitrogen and phosphorus nutrients released can be seen).

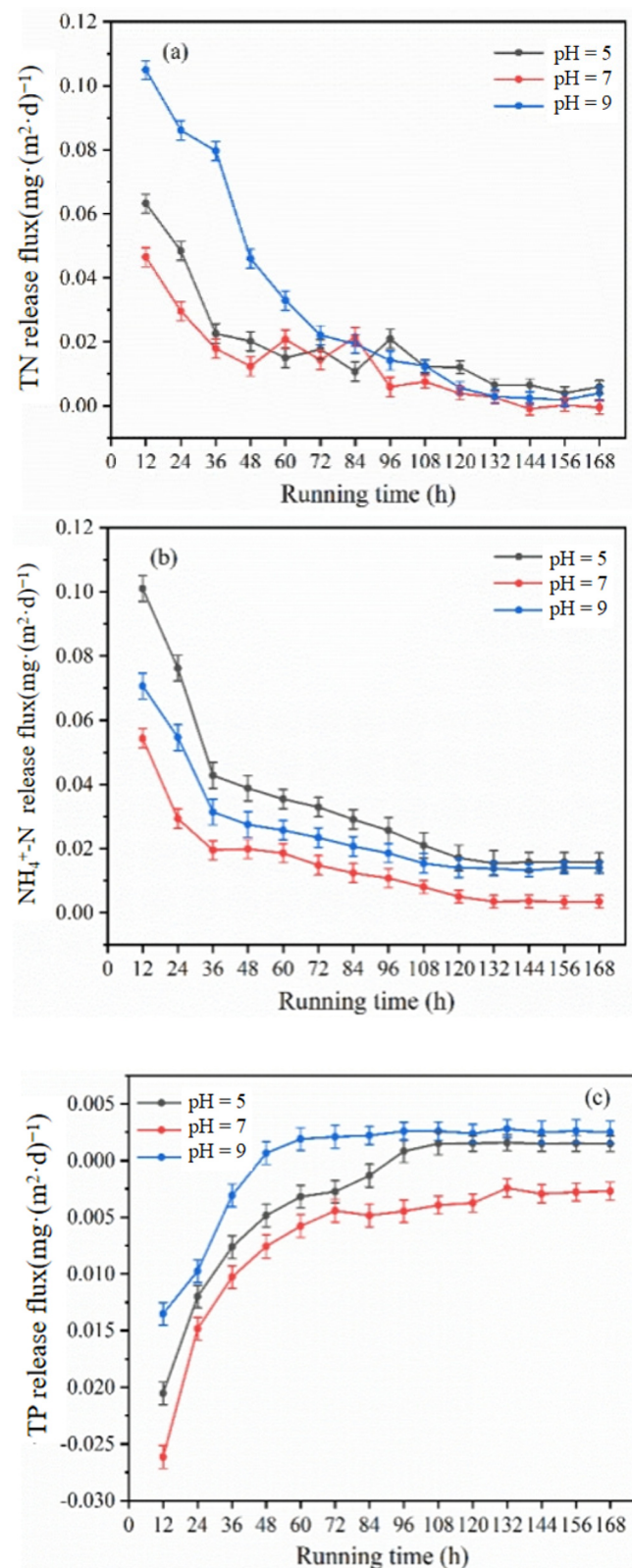


Figure 5. Effect of different pH conditions on nitrogen and phosphorus fluxes (constant DO and temperature conditions, single-factor control of pH, when the final values level off, the changes in nitrogen and phosphorus nutrient release fluxes can be seen).

The variation in the TP diffusion flux with pH is shown in Figure 5c, which shows that the highest TP diffusion flux values were found under alkaline conditions and the lowest under neutral conditions. The TP fluxes varied considerably during the first 24 h of the ex-

periment and then stabilized, with the highest values occurring at 12 h. The maximum value was $0.0135 \text{ mg} \cdot (\text{m}^2 \cdot \text{d})^{-1}$ (at pH = 9), and the minimum value was $-0.0305 \text{ mg} \cdot (\text{m}^2 \cdot \text{d})^{-1}$ (at pH = 5). pH affects the diffusion of phosphorus in sediments mainly through adsorption-dissociation and ion exchange. Zhang and Wu found that, under alkaline conditions, phosphate mainly underwent ion exchange with OH^- in the system, but the phosphorus flux did not increase with increasing pH [48]. Zhang found that phosphorus flux values were smaller at pH = 10, presumably due to higher Ca^{2+} concentrations in the water column, resulting in the re-adsorption of released phosphorus and the generation of sub-acidic conditions. Moreover, the dissolution of insoluble phosphate, as well as desorption of the hydroxide colloids that have adsorbed phosphorus, occurs, leading to more phosphorus release from the sediment to the overlying water. Under neutral conditions, the phosphorus in the system mainly exists in the form of HPO_4^{2-} and H_2PO_4^- , which are easily adsorbed by metal ions in the system, which, in turn, leads to a reduction in phosphorus release from the sediment.

3.3.3. Effect of Dissolved Oxygen on Nitrogen and Phosphorus Release

Research suggests that altered oxygen environments are a key factor influencing nutrient release [49], and the variation in the diffusive fluxes of TN and $\text{NH}_4^+\text{-N}$ at the interface with DO are shown in Figure 6a,b. The variation in the TN fluxes ranged from 0.013 to $0.277 \text{ mg} \cdot (\text{m}^2 \cdot \text{d})^{-1}$. Both values being positive indicates that the sediment acted as a source of TN. The $\text{NH}_4^+\text{-N}$ fluxes ranged from -0.0129 to $0.062 \text{ mg} \cdot (\text{m}^2 \cdot \text{d})^{-1}$, with negative values occurring during the first 12 h of the experiment under aerobic conditions and with sediment acting as a sink for $\text{NH}_4^+\text{-N}$. Under anaerobic conditions, the $\text{NH}_4^+\text{-N}$ fluxes decreased rapidly during the first 72 h of the experiment and then stabilized at $0.028 \text{ mg} \cdot (\text{m}^2 \cdot \text{d})^{-1}$, which is approximately 2.1 times higher than that under aerobic conditions. Among them, anaerobic environments accelerate the release of nitrogen and phosphorus from the substrate. Aerobic conditions inhibit denitrification and reduce $\text{NO}_3^-\text{-N}$ consumption and can simultaneously inhibit the reduction of $\text{NO}_3^-\text{-N}$ to $\text{NH}_4^+\text{-N}$ by allotropy, and inorganic nitrogen is released as $\text{NH}_4^+\text{-N}$ to promote nitrification, thus leading to an increase in the nitrogen flux [50]. On the other hand, it is possible that the increase in the DO content at the sediment-water interface leads to enhanced microbial activity and that the anaerobic environment accelerates the anaerobic ammonia-oxidation process, resulting in a reduced $\text{NH}_4^+\text{-N}$ flux. Thus, enhanced mineralization leads to microbial decomposition of organic matter in sediments, resulting in the accumulation and release of $\text{NH}_4^+\text{-N}$ into sediment pore water [51]. Beutel found that ammonia release from lake sediments usually occurs under anaerobic conditions and that high dissolved oxygen levels inhibit ammonia release from sediments [52]. Kang found that the TP and TN release rates in the anoxic environment of an estuary were approximately twice those in the aerobic environment, confirming that a low DO content promotes the release of nitrogen and phosphorus, which is consistent with the results of this study [53].

The variation in TP flux with DO is shown in Figure 6c. The TP fluxes ranged from -0.0107 to $0.0198 \text{ mg} \cdot (\text{m}^2 \cdot \text{d})^{-1}$ and were all negative under aerobic conditions, indicating that the sediment acted as a sink for phosphorus pollutants. Under anaerobic conditions, TP fluxes decreased rapidly during the first 36 h of the experiment and stabilized after 60 h, with TP fluxes remaining at approximately $\text{mg} \cdot (\text{m}^2 \cdot \text{d})^{-1}$. The flux value of TP under anaerobic conditions was significantly higher (approximately 2.4 times higher) than that under aerobic conditions because under anaerobic conditions, Fe^{3+} was reduced to Fe^{2+} , thus releasing phosphorus adsorbed by iron hydroxide colloids. On the contrary, at higher DO concentrations, Fe^{2+} in the system would be oxidized to Fe^{3+} , forming more iron hydroxide colloids that can adsorb phosphorus, leading to a decrease in the release of phosphorus from the substrate [54]. Meanwhile, Fe^{3+} also generates precipitation with some phosphates, which also reduces the exchange flux of phosphorus. Zhang studied the effects of different environmental factors on phosphorus release from sediments [55], and Ahlgren found that dissolved oxygen levels were the most important factor affecting

the rate of phosphorus release from sediments compared with other environmental factors such as temperature, which is the same as our findings [56].

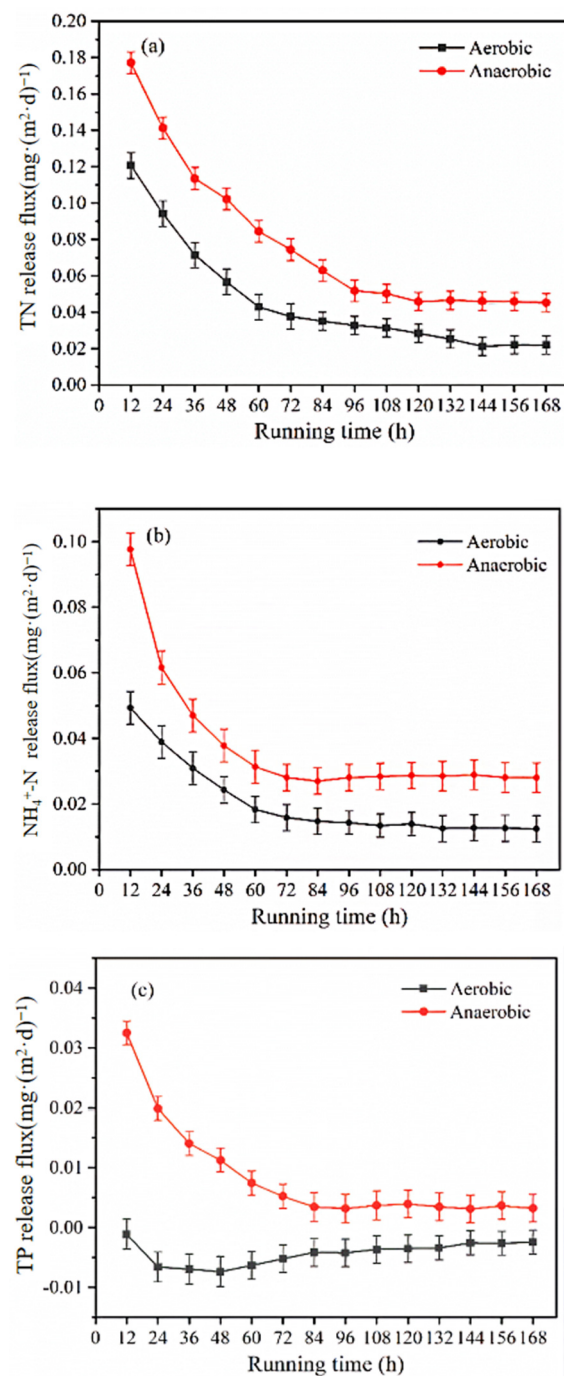


Figure 6. Effect of DO on nitrogen and phosphorus fluxes (the variation of dissolved oxygen is controlled unilaterally by keeping the pH and temperature conditions constant, and variations in the nitrogen and phosphorus nutrient-release fluxes can be observed when the final values level off).

4. Conclusions

The diffusion fluxes of nitrogen and phosphorus nutrients in urban rivers and their water quality indicators were studied. The results show that the Yitong River is generally eutrophic, with a clear concentration gradient between the overlying water and interstitial water and a potential trend of releasing nitrogen and phosphorus pollutants into the overlying water. The spatial and temporal distribution of nitrogen and phosphorus diffusion at

the sediment-water interface of the Yitong River varies as follows: The diffusion fluxes of TN, $\text{NH}_4^+\text{-N}$, and TP change with the direction of water flow, and the diffusion fluxes of nitrogen and phosphorus nutrients change with the seasons. The exchange fluxes of TN and $\text{NH}_4^+\text{-N}$ are larger in summer and autumn, and the diffusion rate of TP is the slowest in summer and autumn. Nitrogen and phosphorus diffusive fluxes were influenced by the pH, DO, and temperature of the overlying water, according to profile analysis, with endogenous TN and $\text{NH}_4^+\text{-N}$ diffusing at the fastest rate at 5 °C and the slowest at 15 °C ($p < 0.05$). It is believed that temperature affects microbial activity and thus, nitrogen diffusion. The diffusive flux values of TP, on the other hand, became larger with increasing temperature ($p < 0.01$). pH significantly influenced the release of nitrogen and phosphorus from the sediment, with the release of nitrogen and phosphorus under alkaline conditions being greater than that under acidic conditions, and the release of nitrogen and phosphorus under neutral conditions being the smallest ($p < 0.05$). The DO supply levels significantly influenced the release of nitrogen and phosphorus from the sediment. The release of nitrogen and phosphorus under anaerobic conditions was much greater than that under aerobic conditions, and the release of nitrogen and phosphorus was much greater under anaerobic conditions than under aerobic conditions ($p < 0.01$). Therefore, seasonal variations in nitrogen and phosphorus nutrient fluxes and concentrations should be considered for the control of endogenous pollutants during the early stages of lake eutrophication.

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