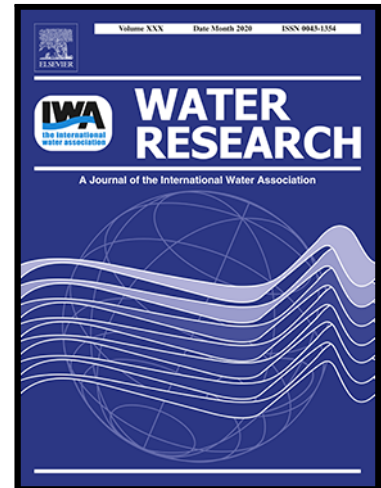


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The impact of a large sub-tropical reservoir on the cycling of nutrients in river

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Highlights

- Thermal stratification has different degrees of control over the concentration and form of nutrients in water;
- The thermal stratification of large reservoirs has obvious temporal and spatial heterogeneity;
- Thermal stratification and bottom drainage mode cause the longitudinal discontinuity of water quality of the river;

The impact of a large sub-tropical reservoir on the cycling of nutrients in river

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Abstract:

The quantity and composition of nutrients carried by rivers play an important role in maintaining the ecosystem of downstream rivers and marginal sea. In order to reveal the impact of damming on the composition and flux changes of nutrients in rivers, this study conducted a detailed survey of a large sub-tropical reservoir (the Xinanjiang Reservoir, XAJR) in eastern China from August 2013 to June 2014 according to the sampling frequency at bi-monthly intervals. Along the fluvial direction, the thermal stratification, water quality in situ parameters and the contents of nutrients in the water column of the river inflow, transition area, central reservoir area and the discharge water of the XAJR were analyzed in detail. The results show that the thermal stratification of the XAJR had

obvious characteristics of seasonal and spatial heterogeneity. Accordingly, pH and DO saturation degree in water also showed similar stratification phenomenon. The analysis of nutrient limitation for primary productivity indicated that in different seasons, varying degrees of the silicon or phosphorus limiting was developed in different locations along the XAJR- river system. Among them, the river area and transition area were more susceptible to silicon restriction in winter, while, phosphorus restriction mainly occurs during the warm seasons from April to October. The XAJR had obvious retention effect on nitrogen, phosphorus and silicon, among which, phosphorus was more easily retained by the reservoir than nitrogen and silicon. In addition, nitrogen had obvious transformation processes between different forms inside the reservoir. In the reservoir, the different degree of retention effect of nutrients also led to a significant increase in the ratio of silicon to phosphorus and nitrogen to phosphorus in the discharged water. This study confirmed that thermal stratification has important control over the contents and forms of nutrients in water, and this finding provides an idea for the restoration of the fluxes and stoichiometric ratios of the nutrients in the downstream river by using the reservoir's capacity of artificial regulation.

Keywords: nutrients; the Xinanjiang Reservoir; retention effects; thermal stratification

1.0 Introduction

Rivers are important channels connecting terrestrial and marine ecosystems. Annually, global rivers transport large amounts of biogenic materials to the ocean, which is of great significance for maintaining the health and sustainability of the ecosystem in marginal sea

(Friedl and Wüest 2002, Humborg et al. 1997, Jiao et al. 2007, Turner et al. 1998).

Therefore, monitoring the materials carried in rivers has always been an important scientific task. However, in the past few decades, strong human activities have greatly changed the fluvial flux and forms of river nutrients. Increasing industrial and agricultural activities, as well as large-scale river impounding, are considered to be the main factors causing changes in river material flux. Among them, the impact of dam retention on the transport of river nutrients has become a hot issue in academic circles in recent years (dos Santos et al. 2020, Pozdnyakov et al. 2019, Liu et al. 2019, Huang et al. 2019, Nemery et al. 2016, Lu et al. 2016, Wang et al. 2014, Maavara et al. 2014, Koiv et al. 2011, Wang et al. 2010, Humborg et al. 2008, Matzinger et al. 2007, Teodoru et al. 2006a, Humborg et al. 2006, Friedl et al. 2004).

After impounding, the flow velocity of river decreases, and the transparency of the water body of reservoir increases significantly. This is conducive to the development of phytoplankton, and the photosynthesis of water body has gradually enhanced (Friedl and Wüest 2002, Matzinger et al. 2007). Correspondingly, along the fluvial direction, aquatic ecosystems have gradually shifted from river heterotrophic to lake-autotrophic dominant (Huang et al. 2019, Han et al. 2018). In addition, with the rising of water level, seasonal thermal stratification often develops along the water column of reservoir. This phenomenon also led to the development of biological and chemical stratification on the water column (Wang et al. 2010, Matzinger et al. 2007, Teodoru et al. 2006b). For example, during the thermal stratification of reservoir, over-saturation of DO and high pH value are often observed in the epilimnion, due to the strong photosynthesis; on the

contrary, due to the barrier effect of thermal stratification, there is a lack of convection exchange between the upper and lower waters. This often leads to hypoxia and low pH in the deep water (Wang et al. 2015a, Taleb et al. 2004).

In reservoir-river system, the differences in the major biogeochemical processes in the direction of river flow and water column have an important impact on the absorption and transformation of river nutrients (Kelly 2001, Liu et al. 2019, Teodoru et al. 2006a, Maavara et al. 2015, Milliman 1997, Paul 2003, Putz and Benndorf 1998). Another important factor also has an important impact on the downstream transport of river nutrients, i.e. hydroelectric reservoirs usually use bottom drainage to generate electricity. This often leads to important differences in the concentrations and forms of nutrients in the inlet and outlet of reservoir. These factors, on the one hand, destroy the water quality continuity of river and bring about negative effects on the regional water environment quality; On the other hand, changes in the output fluxes and forms of river nutrients also have a potential impact on the primary productivity structure of estuaries and marginal sea areas (Humborg et al. 1997, Jiao et al. 2007, Latrubesse et al. 2017, Humborg et al. 2000).

Currently, approximately 70% of the world's rivers are intercepted by dams (Kummu and Varis 2007), and the global active storage capacity of reservoir grew from about 200 to over 5000 km³ during the past fifty years, which is over 70% of the total global reservoir capacity (7000-8000 km³) (Zhou et al. 2016, Vorosmarty et al. 1997). There is no doubt that this has a major impact on the fluvial flux of nutrients into the sea from global rivers. Estimates indicate that due to the retention of reservoirs, nutrients from rivers around the

world have been retained in large quantities. For example: at the global scale, the retention of DSI in lakes and reservoirs is 163 Gmol yr^{-1} (9.8 Tgyr^{-1}) (Maavara et al. 2014); Total P (TP) trapped in the global reservoirs was estimated as 42 Gmol yr^{-1} , and the retention of reactive P was 18 Gmol yr^{-1} in the year of 2000. It is expected that by 2030, as more dams are built, 17% of the TP load of global rivers will be trapped by reservoirs (Maavara et al. 2015). Therefore, the retention of nutrients and the transformation of their forms in reservoirs are important issues facing the current inland water environment and marginal sea ecosystems. Understanding the impact of large reservoirs on the nutrient cycle of rivers has important global significance and has practical significance for regional water environment quality protection.

Large reservoirs have a pivotal role in the development of water resources and hydropower in river basin. This type of reservoir is significantly different from small reservoirs in terms of hydrological retention time, storage capacity, and regulating capacity. As a result, the disturbance of large reservoir on riverine water environment may be more serious. In contrast, many studies in the past have paid more attention to the retention effect of dams on substances transported by river, and there is a lack of in-depth understanding of the conversion process of nutrients in reservoir, as well as the main controlling mechanism. The detailed study on the latter will help to improve the water quality of the downstream as well as reservoir itself by using the reservoir's regulating capacity.

In this study, a large reservoir in the Qiantang River Basin in eastern China, the Xinanjiang Reservoir (XAJR), was selected for detailed investigation. This reservoir has the

characteristics of long hydrological retention time, huge storage capacity and strong regulating capacity. It is a typical large-scale water conservancy project in the subtropical area. Through a detailed investigation of the cycling of nutrients in the XAJR-River System, this study focused on following objectives: (1) to reveal the transformation of nutrients contents and forms in rivers by large reservoir; (2) to elaborate the major controlling factors that affect the nutrients cycling in reservoir.

2.0 Studied area and Methodology

2.1 Studied reservoir and sampling

The Xinanjiang Reservoir (E118°42'~E118°59', N29°28'~N29°58'), located in the Wuyuan County, Zhejiang Province, was constructed in 1959, also known as the Qiandao Lake (Figure 1). It has a surface area of 567 km², with the mean and maximum water depths of 34m and 117m, respectively. The drainage area of the XAJR is 10442 km², and the recharge coefficient is 18.2. The normal water level of this reservoir is 108 m, corresponding to a reservoir volume of 17.84 billion cubic meters. The minimum water level is 86m, with the storage capacity of 7.57 billion cubic meters. The climate is typically subtropical monsoon climate with air temperature ranging from -5°C to 36°C (annual average value of 17°C) and the annual precipitation of 1429.9 mm on average. The air humidity here is about 76% and forest coverage rate of the drainage area reaches 83% (Wang et al. 2015b). The area around the XAJR is a hilly landform. The local geology is relatively complicated. In addition to a large amount of sedimentary rocks and shallow metamorphic rocks, it also includes some volcanic eruptive rocks and intrusive rocks. The soil in this area is mainly yellow earth and red earth.

In this study, from August 2013 to June 2014, water samples along the fluvial direction of the XAJR were collected at bimonthly sampling intervals (Figure 1). Due to the shallow depth in the incoming river area of the reservoir, only surface and bottom water samples were collected; along the water column in the central reservoir, the upper water (above 20m in depth) was sampled with an interval of 5 meters and the lower water (below 20m in depth) was sampled with an interval 10 meters; discharge from the dam was only collected 0.5 meters underwater because of the good mixing. Temperature (T), pH and dissolved oxygen (DO) were measured in situ with a portable pH and conductivity meter (YSI-6600v2). For dissolved nutrients determination, water samples were filtered through a 0.45 μm polycarbonate membrane immediately after sampling and stored in 100-ml plastic bottles on ice in a cooler until analysis. For TN and TP, water samples were directly stored in 100-ml plastic bottles and added little bit of H_2SO_4 for protection.

For TP and TN determination, water samples were first digested in a DRB200 digestion instrument (Hach Company), and then measured using a DR3900 spectrophotometer (Hach Company). The concentrations of dissolved silicon (DSi), dissolved inorganic phosphorus (DIP) and dissolved inorganic nitrogen (DIN), including NO_3^- , NO_2^- and NH_4^+ , were measured using an automated flow-injection analyzer (SKALAR Sans Plus Systems). Analytical errors were less than 5 %.

2.2 Calculation

$V = \frac{C_{in} - C_{out}}{C_{in} + C_{out}} \times 100\%$

between surface and bottom water; T_{average} : average temperature of the water column;

Variation rate of nutrient concentration in and out of the reservoir (V): $V\% = 100 \times$

$(C_{\text{inflow}} - C_{\text{outflow}}) / C_{\text{inflow}}$. Among them, C_{inflow} : the concentration of nutrients in the inflow of the reservoir; C_{outflow} : the concentration of nutrients in the discharge of the reservoir. If V value is positive, indicating that the reservoir has a retention effect on the nutrients; if V value is negative, indicating that the reservoir has increased the concentration of the nutrients in the its discharge.

3.0 Results

3.1 Longitudinal variations of water temperature, pH, DO and their seasonal stratification

After the impounding of reservoir, as the water level rises, seasonal stratification of varying degrees usually develops along the water column. Water temperature is the most direct indicator of water mixing. As shown in figure 2, the XAJR had obvious seasonal water quality stratification, especially in summer. But in winter, the upper and lower water bodies were well mixed. February is the coldest season in the studied area. Affected by the temperature drop, the water column of the reservoir is well mixed, with very small difference of water temperature between the upper and the bottom. On the contrary, along the direction of river flow, water temperature of the inflow river was low, but a relatively high water temperature was found in discharge from the dam. The difference between these two sites was nearly 5 degrees. Similar to the distribution pattern of water temperature, in February, pH and DO saturation did not show obvious stratification on the water column, indicating good mixing in the vertical direction; but along the direction of flow, the pH and DO saturation of the inflow river were slightly higher than that of

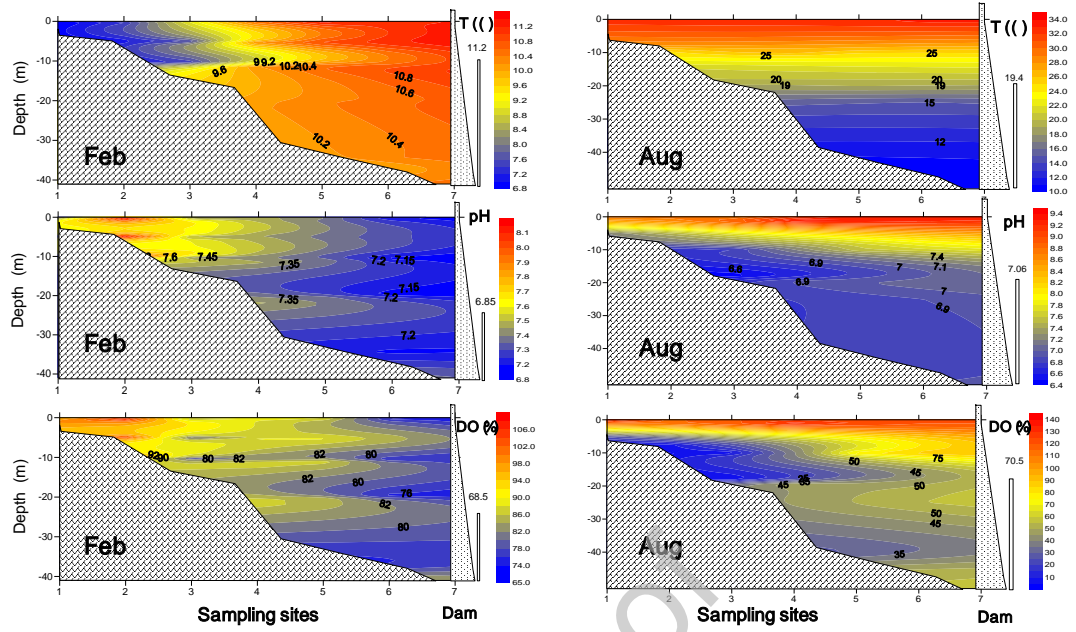


Figure 2. Longitudinal variations of water temperature (T), pH, and dissolved oxygen saturation degree (DO%) in the XAJR in February and August. (The vertical bar represents the value of parameters in downstream the dam)

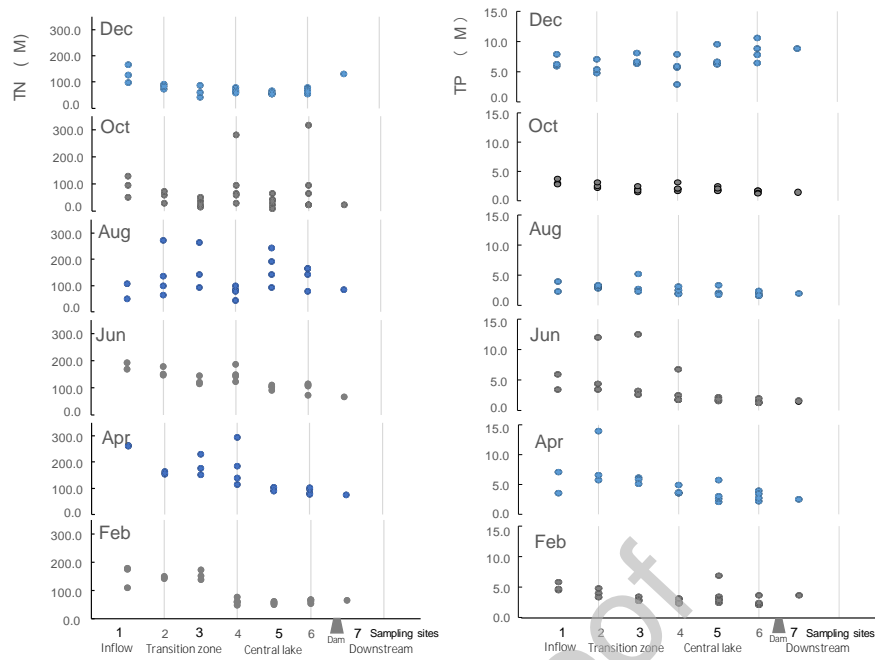


Figure 3. Longitudinal variations of TN and TP in the XAJR. (The data points on each sampling site represent the concentrations of TN or TP in the water column)

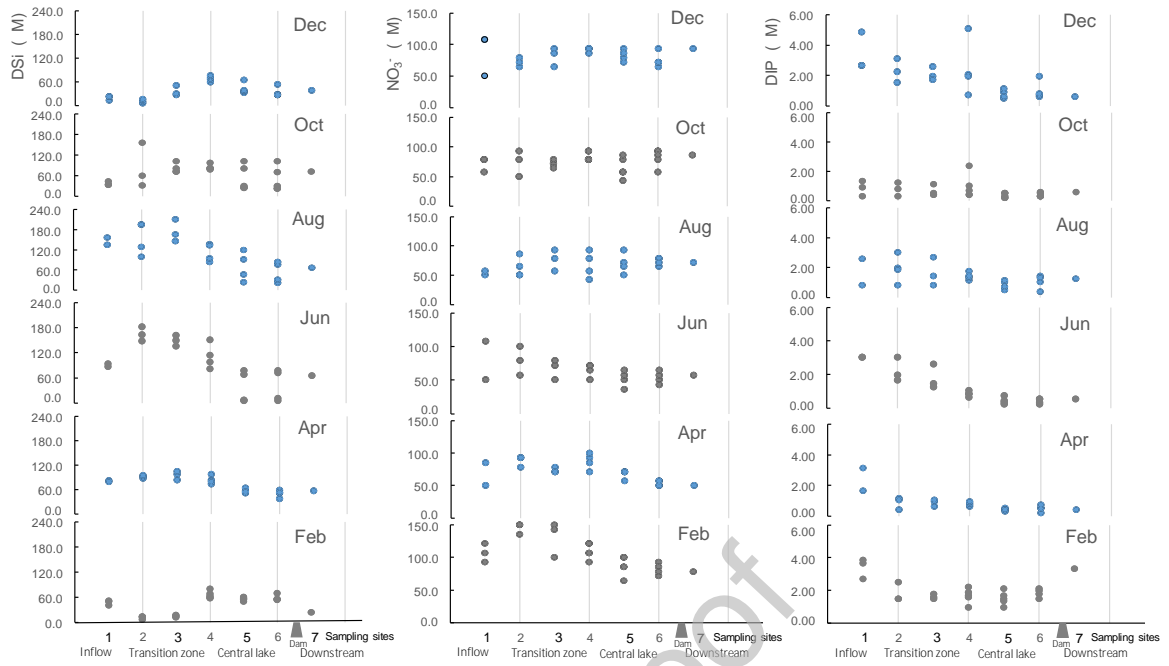


Figure 4. Longitudinal variations of dissolved nutrients in the XAJR. (The legend is the same as Figure 3)

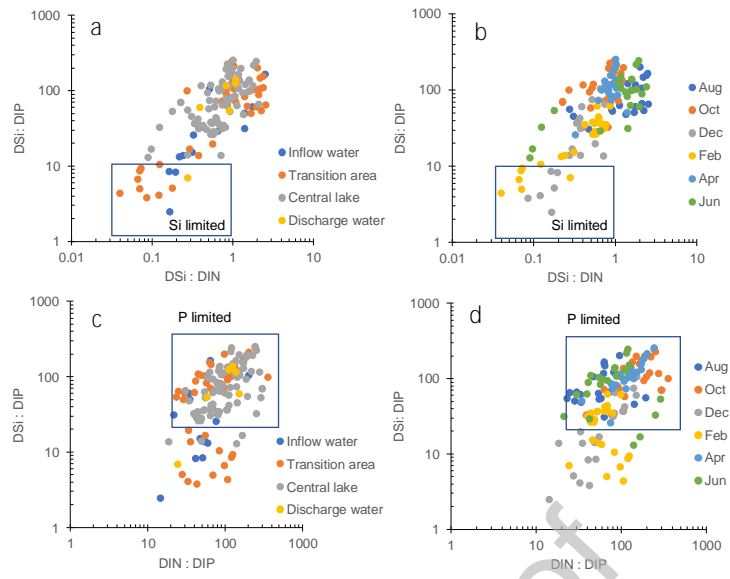


Figure 5. The stoichiometric restricting analysis of silicon and phosphorus in the XAJR. ($\text{Si:P} > 22$ and $\text{DIN:P} > 22$ for P limitation; $\text{Si:P} < 10$ and $\text{Si:DIN} < 1$ for Si limitation; The concentrations of $\text{DSi} = 2 \text{ M}$, $\text{DIN} = 1 \text{ M}$ and $\text{DP} = 0.1 \text{ M}$ were used as threshold values (Justic et al. 1995).

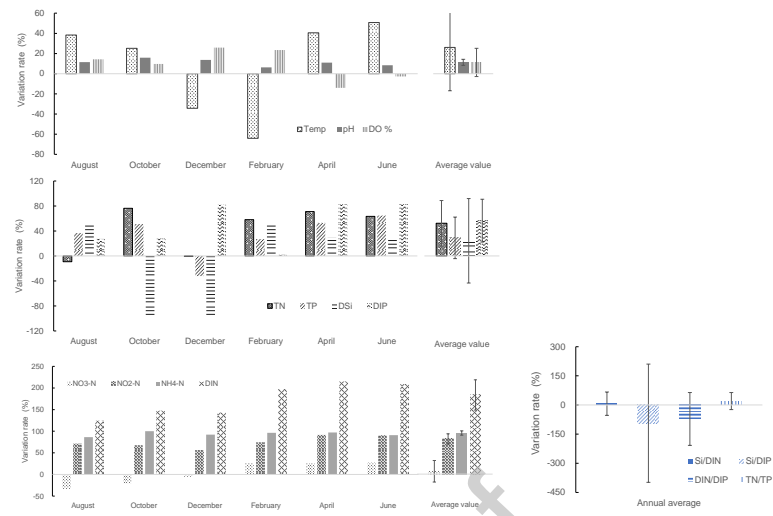


Figure 6. The variation rates of nutrients between inflow river and discharge water from the dam.

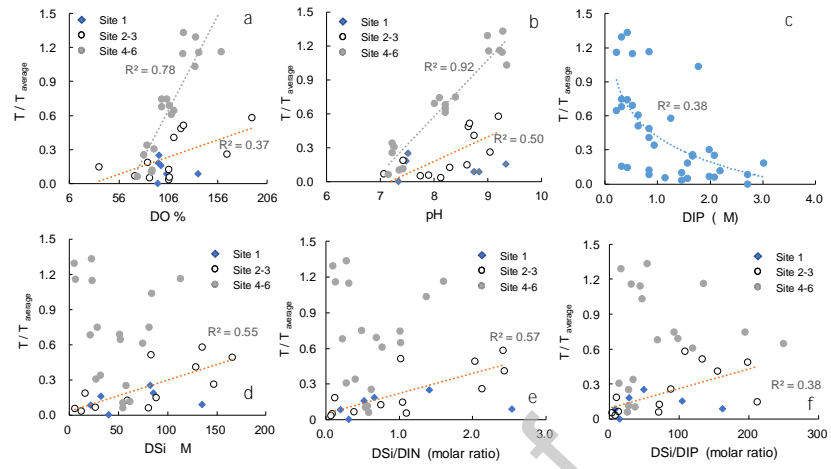


Figure 7. The influence of thermal stratification on water quality parameters of epilimnion.

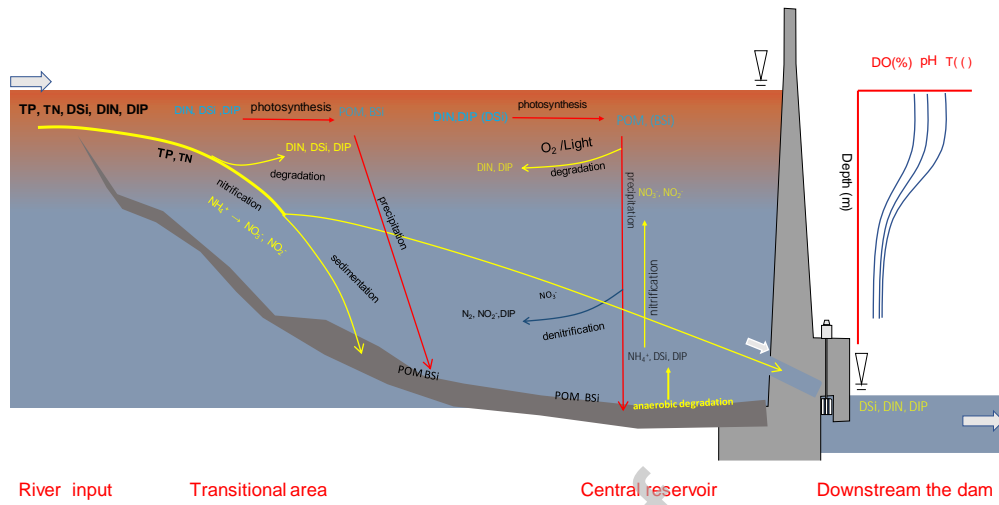


Figure 8. Schematic diagram of the major cycling processes of nutrients in the fluvial-reservoir system during thermal stratification.

Graphic abstract

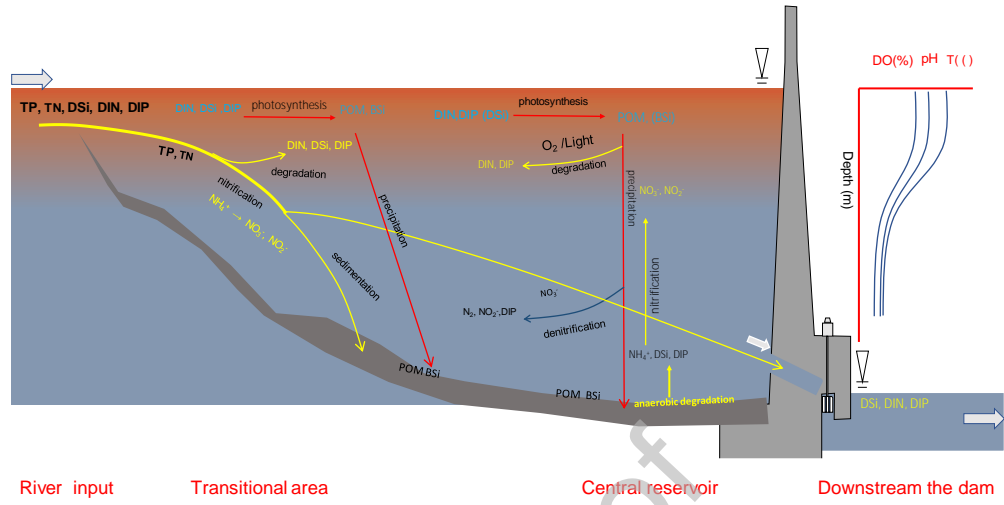


Table 1. Correlation analysis of the water quality parameters.

	Temper	pH	DO	TN	TP	DSi	NO ₃ ⁻	NO ₂ ⁻	NH ₄ ⁺	DIP	DSi:DIN	DSi:DIP	DIN:DIP	TN:TP
	°C		mg/L	μM	μM	μM	μM	μM	μM	μM	molar ratio			
Temper		.513**	-.141	.051	-.111	.316**	-.370**	.175	-.125	-.162	.335**	.260**	.238**	.160
pH	.513**		.603**	.028	-.010	-.301**	-.051	.072	-.094	-.079	-.212**	-.076	.269**	.059
DO	-.141	.603**		.032	.204	-.504**	.194	.079	-.061	.146	-.416**	-.328**	-.036	-.067
TN	.051	.028	.032		.114	.233**	.127	.428**	.326**	.209	.150	-.056	-.082	.664**
TP	-.111	-.010	.204	.114		.001	.163	.304**	.138	.379**	-.083	-.272**	-.287**	-.435**
DSi	.316**	-.301**	-.504**	.233**	.001		-.152	.200	.034	.080	.875**	.450**	-.270**	.089
NO ₃ ⁻	-.370**	-.051	.194	.127	.163	-.152		.287**	.256**	.320**	-.448**	-.357**	-.073	-.064
NO ₂ ⁻	.175	.072	.079	.428**	.304**	.200	.287**		.546**	.278**	-.025	-.109	-.069	-.022
NH ₄ ⁺	-.125	-.094	-.061	.326**	.138	.034	.256**	.546**		.247**	-.201	-.203	-.081	-.028
DIP	-.162	-.079	.146	.209	.379**	.080	.320**	.278**	.247**		-.071	-.489**	-.557**	-.160
Si:DIN	.335**	-.212**	-.416**	.150	-.083	.875**	-.448**	-.025	-.201	-.071		.532**	-.250**	.134
Si:DIP	.260**	-.076	-.328**	-.056	-.272**	.450**	-.357**	-.109	-.203	-.489**	.532**		.513**	.166
DIN:DIP	.238**	.269**	-.036	-.082	-.287**	-.270**	-.073	-.069	-.081	-.557**	-.250**	.513**		.242**
TN:TP	.160	.059	-.067	.664**	-.435**	.089	-.064	-.022	-.028	-.160	.134	.166	.242**	

** . The correlation was significant at the 0.01 level (double-tailed).

* . The correlation was significant at the 0.05 level (double-tailed).

N=149