

Characteristics of Nitrogen Distribution and Influencing Factors in A Reservoir of Henan Province

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ABSTRACT

In order to reveal the spatial and temporal distribution characteristics of nitrogen and its influencing factors in a reservoir in Henan Province, a study on the changing characteristics of nitrogen in the water body was carried out in the fall of 2019 and the summer and fall of 2020 to identify the main sources of pollution in the water body in the reservoir area. The results showed that the total nitrogen concentration in the water body ranged from 1.65 to 3.53 mg/L, which exceeded the eutrophication threshold of the water body. Among them, the nitrogen component was dominated by nitrate nitrogen, which accounted for 62.63% of the total nitrogen, mainly from runoff pollution and endogenous release. On a seasonal scale, nitrogen concentrations exhibited higher concentrations in the fall than in the summer. At the spatial scale, total nitrogen, nitrate nitrogen and organic nitrogen concentrations showed similar trends, with a gradual decrease from the upstream to the front of the dam, and an increase after the dam, which was related to the dilution of the water body and the effect of the reservoir's water storage on sand retention. Principal component analysis showed that the key factors affecting water quality in the reservoir were pH, water temperature and ammonia. Pearson correlation analysis showed that the spatial and temporal characteristics of reservoir nitrogen were related to environmental factors, material transport transformations and anthropogenic influences.

KEYWORDS

Nitrogen; spatial and temporal characteristics; environmental factor; principal component analysis (PCA).

1. INTRODUCTION

Nitrogen is an important nutrient element in aquatic ecosystems and participates in physical, chemical and biological processes in water bodies in various forms, and is a key nutrient element in controlling eutrophication of water bodies^[1,2]. At present, eutrophication of water bodies is one of the important environmental problems in China, which seriously affects the ecological function of water bodies and water safety, and is an important factor restricting the quality of the ecological environment^[3-5]. Therefore, it is of great significance to study the spatial and temporal patterns of nitrogen change in water bodies and the factors affecting them to effectively guarantee the security of water resources.

The intercepting and storing effect of reservoirs can change the original hydrodynamic conditions of rivers, affecting the migration and diffusion of nitrogen and phosphorus nutrients, and causing nutrient accumulation in localized waters^[6,7]. The study of spatial and temporal variation characteristics of nitrogen and phosphorus nutrient salts, pollution sources and influencing factors in reservoir water bodies has become a hot issue^[8]. Currently, studies on reservoirs mainly focus on the overall quality of the water environment and nitrogen content, with less research on the spatial and

temporal distribution characteristics of nitrogen and the correlation between it and environmental factors. Therefore, this paper takes a reservoir water body in Henan Province as a research object, studies the spatial and temporal distribution pattern of the main nitrogen forms in the surface water body, analyzes the correlation between different nitrogen forms and their correlation with the water environment factors, and provides a reference for the study of water quality evaluation and nitrogen pollution management in the reservoir, and provides a scientific basis for the protection of water resources.

2. MATERIALS AND METHODS

2.1. Sample collection

A reservoir water body in Henan Province was used as the study object, and four sampling points were set up along the flow direction, which were upstream, midstream, in front of the dam, and behind the dam. The sampling time was in the fall of 2019, summer and fall of 2020, and the samples were collected at the end of each month. Water samples were taken at a depth of 0.5 m, and the samples were placed in 500 mL brown glass bottles for on-site determination of basic water quality parameters, stored at -20 °C away from light, and analyzed for other indicators within one week.

2.2. Experimental methods

The SX800 series of portable electrochemical water quality parameter meters are used for on-site determination of basic water quality parameters such as water temperature (WT), dissolved oxygen (DO), pH and electrical conductivity (EC). The appropriate amount of raw water was filtered through 0.45 μm mixed membrane, and the filtrate was used to determine the concentrations of total nitrogen (TN), ammonia nitrogen ($\text{NH}_4^+\text{-N}$), and nitrate nitrogen ($\text{NO}_3^-\text{-N}$). Among them, alkaline potassium persulfate spectrophotometry (HJ636-2012) was used to determine TN, phenol disulfonic acid spectrophotometry (HJ/T346-2007) was used for $\text{NO}_3^-\text{-N}$ content, and $\text{NH}_4^+\text{-N}$ was determined by Nano reagent spectrophotometry (HJ525-2009); solubility was found by the difference between TN and inorganic nitrogen ($\text{NH}_4^+\text{-N}$ and $\text{NO}_3^-\text{-N}$) concentrations Organic nitrogen (DON).

2.3. Data analysis

IBM SPSS Statistics 26.0 was used to analyze the water quality indicators of the water body by principal component analysis to extract the main factors that cause changes in water quality. Pearson correlation analysis and one-way ANOVA for nitrogen were performed on the environmental factors using Origin 2021 to determine the correlation between the different factors and the spatial and temporal variability of nitrogen.

3. RESULTS AND ANALYSIS

3.1. Basic parameters of water quality in the reservoir area

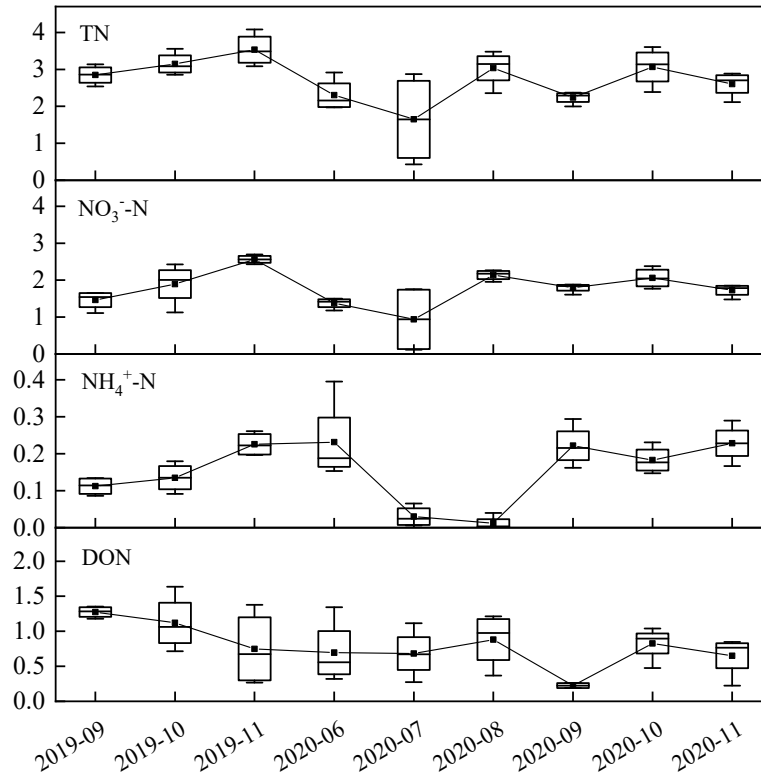
The basic physical and chemical parameters of the water samples collected from the reservoir area are shown in Table 1. It can be seen that the WT range of the reservoir area is between 16.33~27.23 °C, showing high in summer and low in fall, with obvious seasonal variability. The pH range of the water body was 7.45~8.15, and the water quality was weakly alkaline. The range of EC variation was 75.55~108.70 ms/m, and the mean values of EC in the fall of 2019, summer and fall of 2020 were 94.88, 95.48 and 96.67 ms/m, respectively, and the seasonal differences in the mean values of EC of the water body were not significant. DO concentration varies from 6.78 to 9.24 mg/L, the average value is more than 6 mg/L, which is in line with the Environmental Quality Standard for Surface Water (GB3838-2002) Class II water standard.

Table 1. Changes of basic physical and chemical parameters of samples

date	WT/(°C)	pH	EC/(ms·m ⁻¹)	DO/(mg·L ⁻¹)
2019.09	27.23±0.23	7.87±0.06	95.48±1.70	6.78±0.33
2019.10	19.15±1.20	7.91±0.33	86.68±11.44	7.50±0.46
2019.11	16.33±0.22	8.11±0.35	102.48±14.17	8.48±1.05
2020.06	22.80±2.95	8.15±0.33	89.83±6.28	7.71±0.62
2020.07	25.10±1.06	7.45±0.35	96.23±2.54	7.30±1.16
2020.08	24.28±0.15	7.71±0.18	100.38±10.21	8.48±0.44
2020.09	24.28±0.92	7.97±0.13	108.70±26.16	9.24±1.68
2020.10	19.45±0.44	7.87±0.19	105.75±19.94	8.08±0.33
2020.11	16.40±0.16	7.89±0.11	75.55±4.53	8.29±0.25

3.2. Spatial and temporal characterization of nitrogen nutrient salts

The characteristics of temporal variation of nitrogen in the water bodies of the study area are shown in Fig. 1, from which it can be seen that the TN concentration in the reservoir ranged from 1.65 to 3.53 mg/L, with a mean value of 2.71 mg/L. TN concentrations show an increasing trend in the fall of 2019, followed by decreasing and then increasing summer concentrations and increasing and then slightly decreasing fall concentrations in 2020. NO₃⁻-N concentration was 0.94~2.56 mg/L, the mean value was 1.77 mg/L, accounting for 62.63% of TN, and the trend was consistent with TN. NH₄⁺-N concentration was 0.01~0.23 mg/L, the mean value was 0.16 mg/L, accounting for 5.70% of TN. The seasonal variation trend of NH₄⁺-N concentration was contrary to that of DON, which showed a gradual increase and slow decrease. slowly decreasing and basically showing a smooth trend. The concentration of DON was 0.22~1.27 mg/L, with a mean value of 0.79 mg/L, accounting for 28.11% of TN. The concentration of DON showed a trend of gradual decrease, small increase, rise and then fall in three seasons, and the lowest concentration was found in September 2020.

**Figure 1.** Time variation characteristics of nitrogen nutrient salt concentration

The spatial variation of nitrogen in the water bodies of the study area is characterized in Figure 2. Water body TN concentration from the upstream to the dam after the overall trend of first decline and then rise, the concentration of changes in the range of 1.93 ~ 3.40 mg / L, the lowest concentration in the middle reaches of the highest value appeared in the upper reaches of the dam and after the TN concentration in line with the Class V water quality standards. NO_3^- -N concentrations were less variable overall in spatial distribution and did not differ significantly, with lower concentrations in the midstream and in front of the dam. The NH_4^+ -N concentration was higher in the upstream than in the midstream, but there was no significant difference in spatial distribution, and the highest value (0.22 mg/L) appeared in the upstream, and the NH_4^+ -N concentration complied with the Class II water quality standard. The DON concentration was similar to the trend of TN, with the concentration varying from 0.43 to 1.14 mg/L. The overall fluctuation was small, with the highest and lowest values occurring behind the dam and in the middle reaches, respectively.

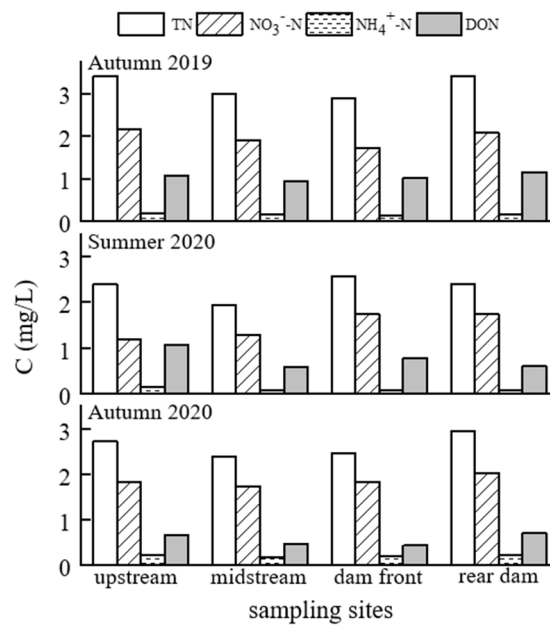


Figure 2. Spatial variation characteristics of nitrogen nutrient salt concentration

3.3. Correlation between nitrogen nutrients and environmental factors

The results of correlation analysis between nitrogen and environmental factors in the water bodies of the study area are shown in Figure 3. From the figure, it can be seen that DON concentration showed a significant negative correlation with DO ($P < 0.05$), NH_4^+ -N concentration showed a significant positive correlation with pH ($P < 0.01$), and there was a significant positive correlation between TN and NO_3^- -N ($P < 0.01$), which indicated that TN was homologous to NO_3^- -N, whereas nitrogen was weakly correlated with WT and EC.

3.4. PCA

SPSS software was used to reduce the dimensions of the water body indicator variables and extract the main components, and the analysis results are shown in Table 2. The results showed that there were three principal components (PC1, PC2 and PC3) with eigenvalues > 1 , with a cumulative contribution rate of 85.97%, which could better reflect the reservoir water environment information. Among them, PC1 has the largest contribution (31.20%), PC2 is the second largest (28.02%), and PC3 is the smallest (26.75%). The environmental factors significantly correlated with the first principal component PC1 were NH_4^+ -N, WT and pH, those significantly correlated with the second

principal component PC2 were TN and NO_3^- -N, and those significantly correlated with the third principal component PC3 were DO, DON and EC.

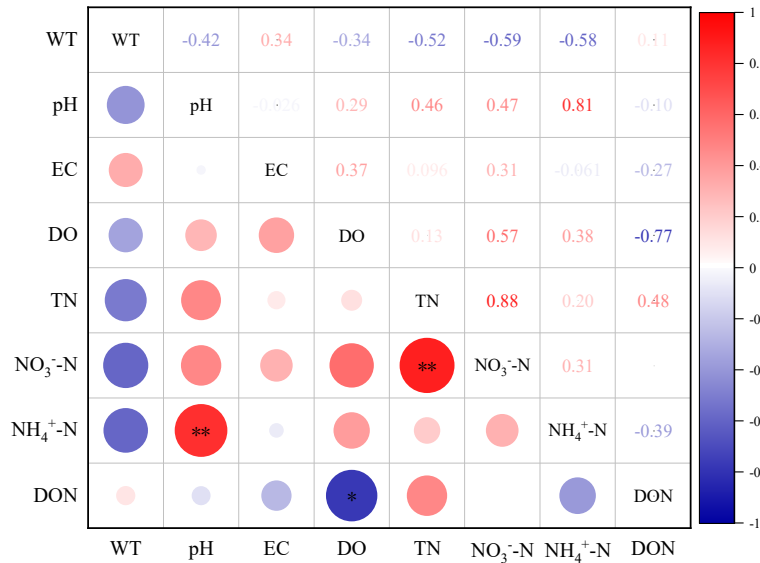


Figure 3. Correlation analysis

Table 2. Identification of main influence factors of nutritional changes in surface water of the reservoir

environmental indicators	principal component		
	PC1	PC2	PC3
WT	-0.783*	-0.340	0.024
pH	0.752*	0.308	0.119
EC	-0.457	0.348	0.695
DO	0.315	0.176	0.865*
TN	0.254	0.953*	-0.152
NO_3^- -N	0.314	0.883*	0.304
NH_4^+ -N	0.879*	0.024	0.255
DON	-0.270	0.435	-0.845*
eigenvalue	2.496	2.242	2.140
contribution rate (%)	31.204	28.024	26.746
cumulative contribution rate (%)	31.204	59.228	85.973

Note: * is the value of the environmental factor contributing more than 0.7 to the different principal components.

4. DISCUSSION

4.1. Spatial and temporal distribution of nitrogen in the water

Nitrogen nutrient salt concentrations in water bodies are temporally high in fall and low in summer, and some studies have shown that increased human activities and agricultural surface pollution in the fall result in higher nitrogen concentrations in water bodies than in summer^[9]. Summer rainfall in the study area is high, and rainfall generates surface runoff that carries a large number of pollutants

into the water body, while rainfall leads to an increase in the flow rate of the water body, which dilutes the nitrogen nutrient concentrations in the water body^[10]. Reservoir nitrogen concentrations in the water column decrease with decreasing sand content during sand regulation (summer)^[11]. Nitrogen in the waters of the study area was dominated by NO_3^- -N followed by DON. NO_3^- -N is the most stable form of all types of nitrogen-containing compounds and a decomposition product of the final stage of inorganic action of nitrogen-containing organic matter^[12]. DON is an important link in the nutrient cycle of the reservoir water, and the inorganic nitrogen absorbed by phytoplankton is released in the form of organic nitrogen^[13].

Nitrogen nutrient concentrations in the water column varied spatially, with an overall trend of decreasing and then increasing, with the lowest pollutant concentrations in the middle reaches, and higher pollutant concentrations behind the dams than in front of the dams. One-way ANOVA showed that there were no significant differences in the spatial variation of nitrogen nutrients in the water column. Changes in nitrogen nutrient salt concentrations at different sampling points are mainly affected by the dam interception effect, the reservoir water body has poor mobility and long retention time, the particles suspended in the reservoir after entering the reservoir by gravity continues to settle, resulting in a decrease in nitrogen concentration along the direction of water flow. And when the water body passes through the dam, the hydrodynamic conditions change, and the bottom suspended particulate matter appears to be re-suspended in the region, resulting in higher nitrogen nutrient salt concentrations^[14]. Consequently, concentrations are higher behind the dam than in front of it. The main sources of nitrogen nutrients in the reservoirs of the study area are upstream water, runoff from agricultural drainage and rainfall, and animal feces^[15]. The dam's water storage and sand retention effect causes a large amount of siltation of sediment, and the pollutants in the sediment will re-enter the water body under the strong disturbance of water and sand regulation to cause secondary pollution^[16].

4.2. Factors affecting nitrogen

The retention effect of reservoirs and changes in environmental factors are the main reasons for the uneven spatial and temporal distribution of nitrogen^[17]. The water body of the reservoir contains sediment from the Loess Plateau, where the loess is alkaline, resulting in an overall weak alkalinity. Correlation analysis among environmental factors showed that there was a significant correlation between pH and reservoir nitrogen. Under weak alkaline conditions, it is favorable to increase the rate of biodegradation of organic matter in the water body and affects the transformation of ammonia nitrogen and nitrogen forms in reservoir sediments^[18]. EC has no significant correlation with nitrogen concentration, and its variation is mainly related to precipitation and agricultural activities. The dilution effect of precipitation on water bodies decreases water body EC, while the increase in the intensity of agricultural activities promotes nitrogen inputs, resulting in higher EC. DO is related to factors such as the organic matter content of the water body, the biological community, the way the water body flows, and the water temperature, and is one of the sensitive indicators reflecting the changes in the water ecosystem^[19]. It was found that the reservoir water body is mildly eutrophic and DO is in a saturated state, which is favorable for pollutant degradation^[20]. DO was negatively correlated with WT, with higher WT resulting in lower DO concentrations. The phenomenon of stratification of water temperature affects the diffusive transport of nitrogen, the rate of biochemical reactions in the water column, alters the biomass and distribution characteristics, and affects water quality^[21]. The significant negative correlation between DO and DON concentration is mainly related to the fact that microbial ammonification-nitrification consumes DO in water^[22].

4.3. Source identification

The contribution of PC1 was the highest among the three principal components of the reservoirs in the study area, where WT, pH and NH_4^+ -N accounted for the higher loadings of the factors and were strongly correlated with PC1. NH_4^+ -N is an oxygen depletion and toxicity indicator of the water body,

which can reflect the degree of organic pollution in the reservoir area^[23], indicating that changes in the physical and chemical factors of the water environment have a certain impact on the water quality of the reservoir area. The contribution rate of PC2 was 28.02%, which showed strong positive correlation with TN and NO₃⁻-N. Among them, TN is one of the important indicators of water quality, which can reflect the degree of pollution of the water body; NO₃⁻-N is the decomposition product of nitrification of nitrogenous organic matter, with the most stable form. PC2 reflects the change of nitrogen in the water body dominates the change of water quality in the reservoir area. PC3 with a contribution rate of 26.74%, has a strong positive correlation with DO and a strong negative correlation with DON, which is an indicator of organic pollution.

5. CONCLUSION

(1) A reservoir in Henan Province, the overall water quality is in good condition, in line with the "surface water environmental quality standards" (GB 3838-2002) II water standards, but the TN single indicator for the inferior V water quality standards, the reservoir water body nitrogen is dominated by NO₃⁻-N, followed by DON.

(2) Temporally, the water body TN, NO₃⁻-N and NH₄⁺-N concentrations in the reservoir area had similar trends over time, showing that they were higher in fall than in summer, and the DON concentrations were fall 2019 > summer 2020 > fall 2020, and environmental factors such as WT and DO had an effect on the water body nitrogen concentrations. Spatially, the nitrogen concentration of the water body in the upstream and behind the dam was overall higher than that in the midstream and in front of the dam, and the spatial difference was not significant ($P > 0.05$), indicating that the self-purification of the water body and hydrological conditions were the main reasons affecting the changes in the spatial distribution of nitrogen.

(3) PCA showed that the water quality in the reservoir area depended on the 1st principal component water environment physicochemical factor characteristic index, and the key factors were pH, WT, and NH₄⁺-N. Pearson correlation analysis showed that there was a significant negative correlation between DO and DON, and a significant positive correlation between TN and NO₃⁻-N, pH, and NH₄⁺-N, which indicated that spatial and temporal characteristics of the reservoir nitrogen were affected by multiple factors such as environmental factors, anthropogenic impacts, and substance migration and transformation.

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