Dynamic characteristics of nitrogen and phosphorus in the representative input tributaries of Miyun Reservoir

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Abstract. The study analyzed dynamic characteristic of nitrogen and phosphorus and influencing variables in three representative input tributaries of Miyun Reservoir from 2012 to 2016. The results showed that Chaohe River in the study period had relatively high TN, NO₃⁻-N and NH₄⁺-N concentrations. While high phosphorus content was found in Qinghe River. Basing on environmental quality standard for surface water, NO₃⁻-N, NH₄⁺-N and TP met the drinking water criterion in most samples. However, TN content met the drinking water criterion only in less than 15% samples. In Qingshuihe River, pH and TSS were significantly variable due to nitrogen variations and TOC was significantly variable for phosphorus variations. However, water parameters (BOD, COD, TSS, TOC, EC and pH) had no significant effects on nitrogen and phosphorus dynamics in Chaohe River and Baihe River.

1. Introduction

Miyun reservoir is the only surface drinking water source for Beijing, which dedicates to control the floods and provides water for hydraulic electrogenerating and supply industrial and agricultural water and offer recreation. Its main input tributaries are Chaohe River, Baihe River and Qingshui River. Before 1990s, the water quality of Miyun Reservoir belonged to the middle nutritional status [1-4]. After 1990s, the total nitrogen (TN) and COD index were within eutrophication standards. In 2002, cyanobacteria formed blooms [2, 5]. The nutrient inflow load in Miyun Reservoir is mainly from the flood season, and the inorganic nitrogen and phosphorus pollutants are mainly from Chaohe River, Baihe River and Qingshui River.

Water quality monitoring in Miyun Reservoir began in 1975 [6]. The former researches mainly focus on the water quality of Miyun Reservoir. And most of the water quality parameters reported in the literature, such as TN and total phosphorus (TP), are the average values measured in the two periods or periods of the year. However, there are few reports about the continuous variation of water quality parameters in Miyun Reservoir Basin.

In this study, almost 4 years’ field observation was conducted in three input tributaries in Miyun Reservoir basin. The objectives of this study were to (a) investigate dynamic characteristics of nitrogen and phosphorus, (b) study their influence factors and discuss the relationship among them in these three tributaries. This study should be helpful for understanding the biogeochemical cycling and environmental effects of nitrogen and phosphorus in Miyun Reservoir Basin.

2. Materials and methods
2.1. Study sites and sampling
Chaohe River, Baihe River and Qingshui River are the main input tributaries of Miyun Reservoir. According to on-the-spot investigation and literatures, twelve representative sampling sites were selected for this study, including five sites in Chaohe River (Bakeshiying, Gubeikou Bridge, Beidianzi Bridge, Xiaohui hydrometrical station and Xinzhuang Bridge), three in Baihe River (Sihefang Bridge, Zhangjiajie hydrometrical station and Old Daguan Bridge) and four in Qingshuihe River (Huangyankou, Dongzhuangkou, Dongzhuang and Taishidun Bridge). The field survey and sample collection were conducted in every month from October 2012 to June 2016. Water samples about 1000 ml were collected from 0.3 meters below the water surface. All samples were transported in an ice-cooled cabinet to the laboratory and stored in a cooler before analysis.

2.2. Analytical methods

2.2.1. Determination of nitrogen and phosphorus characteristics and other variables. All parameters analyzed in study are based on national standards or industry standards. TN was determined by alkaline potassium persulfate digestion with UV Spectrophotometry (GB11894-198) [7], ammonium nitrogen (NH$_4^+$-N) was determined by colorimetric method and nitrate (NO$_3^-$-N) analyzed by UV Spectrophotometry. TP content was determined by ammonium molybdate spectrophotometric method (GB11893-1989) [8].

Additionally, some water variables, such as BOD, COD, TSS, TOC, EC and pH were analyzed using the national standard analysis. BOD was determined with water quality automatic analyzer (HJ/T 99-2003) [9], COD with potassium dichromate method (GB11914-89) [10], TSS with gravimetric determination (GB11901-89) [11], TOC by total organic carbon analyzer (HJ 501-2009) [12], EC with water quality automatic analyzer of conductivity (HJ/T 97-2003) [13], pH with glass electrode method (GB/T 6920-86) [14].

2.2.2. Statistical analyses. All statistical analyses in study were all conducted with software R (version 3.0.2). Among these, analysis for the least significant difference (LSD) has been done with “agricolae” packages in R [15], and constrained ordination analysis with “GPArotation” [16] and “Vegan” [17] packages in R.

Before constrained ordination analysis, we carried out initial de-trended correspondence analyses for the most appropriate ordination method with the gradient length [18]. Results of de-trended correspondence analyses showed that gradient in nitrogen and phosphorus data among sites was short (<3) [19], which means we should use redundancy analysis (RDA) to determine the relationship between nitrogen and phosphorus characteristics and explainable water variables. Additionally, 999 permutation test was used to test statistical significance of each analysis. And forward selection by residuals permutation at the 5% significance level was conducted for determining significant variables. Variation partitioning was performed with these significant variables and results are presented in an ordination diagram. In ordination diagram, all of the variables are represented with arrows. Additionally, smaller angle between arrows representing high correlation between variables, and the direction and the length of the arrows meaning positive or negative correlations and their importance in explaining the variation of nitrogen and phosphorus.

3. Results and analysis

3.1. Nitrogen and phosphorus characteristics in three tributaries
In this study, there are 1260 samples for 105 sampling times from October 2012 to June 2016. TN, NO$_3^-$-N, NH$_4^+$-N and TP concentration in three input tributaries of Miyun Reservoir (Baihe River, Chaohe River and Qingshuihe River) are shown in figure 1.
3.1.1. TN characteristics. TN concentration in Chaohe River was significantly higher than in Baihe and Qingshuihe River with ANOVA analysis (p<0.05), while there are no difference between Baihe and Qingshuihe Rivers. Mean concentration of TN in Chaohe River is 7.66 mg/L with the highest content in 230 samplers 21.2 mg/L and the lowest 0.081 mg/L (table 1). According to environmental quality standard for surface water (GB 3838-2002) [20], TN contents in about 99.57% samples is above the V criterion (>2 mg/L) and only about 0.43% samples meet the drinking water criterion. Additionally, among five sampling sites in Chaohe River, there was no significant difference.

Mean TN content in Baihe River and Qingshuihe River was 2.74 and 2.56 mg/L, respectively. In Baihe River, TN contents in about 60.99% samples are above the V criterion and only about 12.06% samples meet the drinking water criterion. In Qingshuihe River, about 52.15% samples above the V criterion and 14.52% samples meet the drinking water (figure 2).

Comparing the variation of TN from 2012 to 2016, results showed TN content in 2013 was
significantly higher than in 2015 in Qingshuihe River, TN content in 2012 and 2014 significantly higher than those in other years, while there was no significant difference in Baihe River.

Table 1. Overall monitoring results of three of Miyun reservoir.

| River        | Parameter | Num. of sample | Mean (mg/L) | Max (mg/L) | Min (mg/L) | CV (%) |
|--------------|-----------|----------------|-------------|------------|------------|--------|
| Baihe River  | TN        | 139            | 2.74        | 15.6       | 0.01       | 91.05  |
|              | NO3-N     | 139            | 1.87        | 9.45       | 0.05       | 71.47  |
|              | NH4-N     | 139            | 0.17        | 1.04       | 0.002      | 108.22 |
|              | TP        | 139            | 0.03        | 0.141      | 0.001      | 87.94  |
| Chaohe River | TN        | 230            | 7.66        | 21.2       | 0.081      | 46.87  |
|              | NO3-N     | 230            | 6.21        | 19.2       | 0.252      | 45.91  |
|              | NH4-N     | 224            | 0.23        | 2.76       | 0.01       | 141.77 |
|              | TP        | 220            | 0.04        | 0.543      | 0.0008     | 112.57 |
| Qingshuihe   | TN        | 185            | 2.56        | 22         | 0.09       | 104.14 |
| River        | NO3-N     | 185            | 1.56        | 6.996      | 0.041      | 73.05  |
|              | NH4-N     | 185            | 0.21        | 1.32       | 0.01       | 109.73 |
|              | TP        | 185            | 0.06        | 0.787      | 0.0008     | 177.76 |

Figure 2. Frequency distribution for TN, NO3-N, NH4-N and TP concentration in three rivers from 2012 to 2016.

3.1.2. NO3-N characteristics. NO3-N concentration in Chaohe River was significantly higher than in Baihe and Qingshuihe River with ANOVA analysis (p<0.05), while there are no difference between Baihe and Qingshuihe River.

Mean concentration of NO3-N in Chaohe River is 6.21 mg/L with the highest content in 230 samplers 19.2 mg/L and the lowest 0.252 mg/L (table 1). According to environmental quality standard for the centralized drinking water sources (GB 3838-2002), NO3-N contents in Chaohe River in about
6.96% samples are beyond the drinking water criterion (< 10 mg/L), while all samples in Baihe and Qingshuihe River meet the drinking water criterion (figure 2). Additionally, there was no significant difference among five sampling sites in Chaohe River, while NO$_3^-$-N in Zhangjiafen hydrometrical station was higher than other two sites in Baihe River.

Comparing the variation of NO$_3^-$-N from 2012 to 2016, results showed NO$_3^-$-N content in 2012 and 2013 was significantly higher than in other year in Qingshuihe River, while there was no significant difference in Baihe River and Chaohe River.

3.1.3. NH$_4^+$-N characteristics. For NH$_4^+$-N contents, there were no significant difference among Chaohe River, Baihe and Qingshuihe River with ANOVA analysis (p>0.05). Mean concentration of NH$_4^+$-N in Chaohe River is 0.23 mg/L with the highest content in 224 samplers 2.76 mg/L and the lowest content 0.01mg/L (table 1). According to environmental quality standard for surface water (GB 3838-2002), NH$_4^+$-N contents in about 97.31% samples meet the drinking water criterion (<1 mg/L) and only about 0.90% samples are above the V criterion (>2mg/L) (figure 2).

Mean NH$_4^+$-N content in Baihe River and Qingshuihe River was 0.17 and 0.21 mg/L, respectively. NH$_4^+$-N contents in about 99.29% samples meet the drinking water criterion (<1 mg/L) in Baihe River, while 98.35% samples in Qingshuihe River (figure 2).

Comparing the variation of NH$_4^+$-N from 2012 to 2016, results showed NH$_4^+$-N content in 2016 was significantly higher than in 2012 and 2014 in Qingshuihe River, NH$_4^+$-N content in 2013 significantly higher than those in 2012 and 2014, while NH$_4^+$-N content in 2016 significantly higher than those in 2012 and 2014.

3.1.4. TP characteristics. TP concentration in Qingshuihe River was significantly higher than in Baihe and Chaohe River with ANOVA analysis (p<0.05), while there are no difference between Baihe and Chaohe River. Mean concentration of TP in Qingshuihe River is 0.06 mg/L with the highest content in 185 samplers 0.787 mg/L and the lowest 0.0008 mg/L (table 1). According to environmental quality standard for surface water (GB 3838-2002), TP contents in about 3.28% samples are above the V criterion (>0.4 mg/L) and about 94.54% samples meet the drinking water criterion (<0.2 mg/L) (figure 2). Additionally, among four sampling sites in Qingshuihe River, there was no significant difference.

Mean TP content in Baihe River and Chaohe River was 0.03 and 0.04 mg/L, respectively. About 99.09% samples in Chaohe River and 100% samples in Baihe River meet the TP criteria for drinking water (<0.2 mg/L) (figure 2). Comparing the variation of TP from 2012 to 2016, results showed TP content in 2013 was significantly higher than in 2012 in Baihe River and Chaohe River, while there are no significant differences in Qingshuihe River from 2012 to 2016.

3.2. Multivariate analysis for effecting variables

Redundancy analysis showed the relationship of nitrogen and phosphorus concentration with water variables in Chaohe River, Baihe River and Qingshuihe River, respectively. However, results showed there were significant correlations between nitrogen and phosphorus concentrations and water variables only in Qingshuihe River (p=0.017). Eigenvalues of the first two RDA axes accounted for 9.83% of the variance of nitrogen and phosphorus contents (figure 3). The permutation tests showed that three variables, such as pH (p=0.001), TOC (p=0.001) and TSS (p=0.004), had statistically significant effects on variation of nitrogen and phosphorus contents. Along RDA axis 1, NO$_3^-$-N and TN stand out with a positive RDA axis 1 and are thus negatively related with TSS and pH. Along RDA axis 2, TP stands out with a negative RDA axis 2 and is associated with TOC, while NH$_4^+$-N stands out with a positive RDA axis 2 and shows a positive score correlating with TSS and pH.
The results of this study were similar to those of previous studies, showing that nitrogen in Chaohe River was higher than in Baihe and Qingshuihe [21, 22]. The reason for higher nitrogen is probably related to intensive agriculture around Chaohe River basin, such as intensive croplands and aquaculture. The higher degree of intensive agriculture and the greater is the influence on water quality. Some reports showed that nitrate mainly come from runoff from fertilizer and manure applied to agricultural land [23, 24], and the contribution rate of nitrate nitrogen to TN is about 93%, which is the reason that TN in Chao River is significantly higher than ones in Baihe River and Qingshuihe River. Higher TP was found in Qingshuihe River. The reason for this is due to the increase of population density, which increases phosphorus load with domestic sewage. Baihe River has relative lower nitrogen and phosphorus load, which is related to its Mountainous Areas sources. Nevertheless, new tourist sites around the Baihe River may be nitrogen and phosphorus pollution sources. Additionally, it is worth noting that there are no significant differences among sampling site in every river, except for AJFWS sampling points in the Baihe River, which is significantly lower than the other 2 sampling points.

There are many variables effecting nitrogen and phosphorus contents in many study, including physical and chemical parameters in water body and ecological factors around river basins. In study, pH and TSS were significant variables for nitrogen variation and TOC was a significant variable for phosphorus variation in Qingshuihe River. However, water variables, such as BOD, COD, TSS, TOC, EC and pH, have no significant effects on variation of nitrogen and phosphorus in Chaohe and Baihe Rivers, which showed variables outside water body, such as landscape, agricultural planting, aquaculture, domestic sewage discharge and so they probably have effects on nitrogen and phosphorus variation.

Eutrophication has become the primary water quality issue for most of the freshwater in the world and Miyun reservoir is no exception. The present study analyzed dynamic characteristic of nitrogen and phosphorus and influencing variables in three representative input tributaries of Miyun Reservoir from 2012 to 2016. The results showed that Chaohe Rivers in the study period showed being with relatively high TN, NO$_3^-$-N and NH$_4^+$-N concentrations. An even higher phosphorus content was found in Qinghe River. According to environmental quality standard for surface water (GB 3838-
NO$_3^-$, NH$_4^+$-N and TP meet the drinking water criterion in most of the samples. However, TN content in less than 15% samples meets the drinking water criterion. In Qingshuie River, pH and TSS were significant variables for nitrogen variation and TOC was significant variables for phosphorus variation. However, water variables (BOD, COD, TSS, TOC, EC and pH) have no significant effects on nitrogen and phosphorus in Chaohe River and Baihe River.

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