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Seasonal Variation and Driving Factors of Nitrate in Rivers of Miyun Reservoir Watershed, North China

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Abstract: In order to identify the seasonal variations and dominant driving factors of NO_3-N in rivers, investigations of five consecutive years were conducted in seven rivers of the Miyun Reservoir Watershed. Significant seasonal variation of NO_3-N in rivers was separately found in the dormant season (non-growing season) and the growing season. Furtherly, the V-shaped, W-shaped, and indistinct seasonal patterns of NO_3-N accounted for 53.0%, 38.7%, and 8.3%, respectively. They were remarkably affected by stream flow, and their significant quadratic function was discovered. The annual maxima and minima of NO_3-N corresponded to medium flow in the dormant season and low flow or flood in the growing season, respectively. On one hand, flood mainly played a role in the diluent for the Chao River with high NO_3-N, and on the other hand, it acted as a nitrogen source for the Bai River with low NO_3-N. The NO_3-N was closely correlated with human activities, and this correlation had obvious seasonal change trend. In the dormant season, significant and mostly extremely significant high correlation coefficient (R) values were determined, while partly non-significant with low R values were found in July, August, September, and October. Increasing seasonal variation index of NO_3-N from upstream to downstream was found that was gentle for large rivers and sharp for small tributaries. The seasonality of NO_3-N was more affected by natural factors, especially flood, than human factors.

Keywords: seasonality; nitrate nitrogen; flow; human activities; watershed

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1. Introduction

The input of large amounts of anthropogenic nitrogen (fertilizer, manure, domestic sewage, and other nitrogen sources closely related to human activities) to water bodies has resulted in enhanced concentrations of nitrate (NO_3-N), nitrite (NO_2-N), ammonium (NH_4^+-N), and organic nitrogen [1]. Meanwhile, a series of water environmental problems has appeared, such as the eutrophication of lakes/coastal seas [2,3], acidification of freshwater lakes/streams [4,5], and high nitrate in groundwater [6–8]. Furthermore, these nitrogen contaminations have posed adverse effects on aquatic ecosystems and human health [9,10]. For the development of human, agriculture, and industry, rivers are vital sources of fresh water [11–13]. However, they are facing multiple threats including natural factors (precipitation, erosion, and weathering) and anthropogenic activities (agriculture, industry, and urban activities) [14–20]. Over the last century, river water quality has gradually changed as a result of human activities, especially for riverine nitrogen [15,21–23]. Presently, more than half of severe environmental problems are related to nitrogen cycles, which is caused by excessive nitrogen from intensified anthropogenic activities

[18,24]. Generally, the temporal variations of nitrogen in river water are driven by some key processes including nitrogen sources, mobilization, transformation, and delivery [17,25,26]. Specifically, the key influencing factors include topography [27], precipitation or runoff [28,29], land use [27,28,30], the oxidation-reduction environment of water/sediment [31–34], and so on. Meanwhile, nitrogen retention by adsorption and degradation varies greatly from upstream to downstream, which also differs from one river to another [35–37]. Detailed and different factors may play an important role, such as river flow conditions, river channel characteristics, temperature, and sunshine hours [22,24,30,38,39].

Obvious temporal variations of nitrogen species have been observed among different rivers [7,40–45]. Furthermore, the strong increasing and decreasing seasonal variation of nitrogen species were discovered in winter and summer, respectively. That could be attributed to higher nitrogen uptake in rivers and denitrification rates during summer compared with winter [1,46,47]. Simultaneously, the highest values of nitrate in streams are clearly related to their hydrological conditions [48], such as summer storms in temperate regions [49] and snowmelt runoff in cold regions [50–52]. Additionally, fertilizer application in agricultural fields for enhancing the productivity of crops leads to the increase of nitrate in rivers [53], but it does not fully coincide with the nitrogen seasonality [54]. Nevertheless, significant seasonality of nitrate has not been found in some rivers [55] and well understood [56].

The control of river nitrogen pollution is one of the vital issues for sustainable watershed management [13]. However, the realization of successful results is based on the understanding of detailed temporal variations and the influencing factors. Past studies have focused on annual river nitrogen concentration and the export [3,15,56,57]. Detailed temporal variations in watersheds have not yet been investigated; meanwhile, the watershed scale is a very important scale for nitrogen in river [58,59]. Moreover, evaluating and understanding the temporal variation in the watershed scale could attribute to nitrogen transformation, and provide important information for regional water pollution control [29,60,61]. However, identifying the seasonal variation of nitrogen in rivers is still of insufficient understanding. We lack a comprehensive understanding of the whole watershed for a continuous long time series. Furthermore, we urgently need to determine the main driving mechanism of temporal variations of riverine nitrogen.

The Miyun Reservoir, with a maximum water area of 188 km^2, depth of 43.5 m, and storage capacity of 4.375×10^9 m^3, is the most important surface drinking water source for Beijing, the capital city of China [62]. In recent years, it has been at risk of eutrophication [63,64], although good water quality has long been retained [65]. Moreover, many key measures have been taken to fend off pollution sources, such as forestation for soil and water conservation, limitation of industrial development, treatment of rural living waste in the surrounding area, and cancellation of cage-fishing inside its water [66,67]. However, an upward trend of NO_3-N and total nitrogen (TN) in the rivers and Miyun Reservoir is still being observed [62,68,69]. Simultaneously, algal blooms broke out in the Miyun Reservoir [70], and this may be caused by the continuous input of nutrients from the upper rivers to the Miyun Reservoir [71,72]. Spatial patterns of NO_3-N in rivers of the Miyun Reservoir watershed were studied [66], but available data are poor for addressing seasonality of NO_3-N in rivers [66,73,74]. A better understanding of river nitrogen influenced by human activities and natural factors (hydrology and temperature) is important for reducing nitrogen pollution in rivers [23,75,76].

Many authors reported the temporal variation of nitrogen forms in rivers. However, it is rare to study seasonal variations in a multi-year time series on a monthly timescale. Moreover, understanding the seasonal changes and identifying driving factors (especially for river flow) are important to better understand the mechanisms underlying nitrogen transformation and decrease nitrogen pollution in rivers. The goals of our study are to: (1) elucidate the seasonal patterns of NO_3-N, (2) determine the key factors influencing the seasonality of NO_3-N, and (3) explore the longitudinal seasonality of NO_3-N in different rivers of the Miyun Reservoir watershed. The results will provide deep insights into the seasonal variation of riverine nitrogen and their driving factors in order to manage water quality in this watershed.

2. Materials and Methods

2.1. Study Area

The Miyun Reservoir watershed (from 40°19′~41°31′ N to 115°25′~117°33′ E) has a drainage area of 15,788 km[2] and is located in Yanshan Mountain, northern Beijing and Hebei Province, China. It consists of two river basins, Bai River in the west and Chao River in the east. Firstly, the Bai River flows through 4 counties including Chicheng, Yanqing, Huairou, and Miyun, and is joined by the Hei River, Tang River, and Baimaguan River. Secondly, the Chao River runs through 3 counties including Fengning, Luanping, and Miyun, and is fed by the Gangzi River and Qingshui River (Figure 1). The watershed belongs to the temperate semi-humid monsoon climate, which is dominated by woodland, accounting for 40.9%, and scattered with small amounts of farmland, accounting for 5.0%. The regional economy is dominated by agriculture production with a one-year cropping system [77].

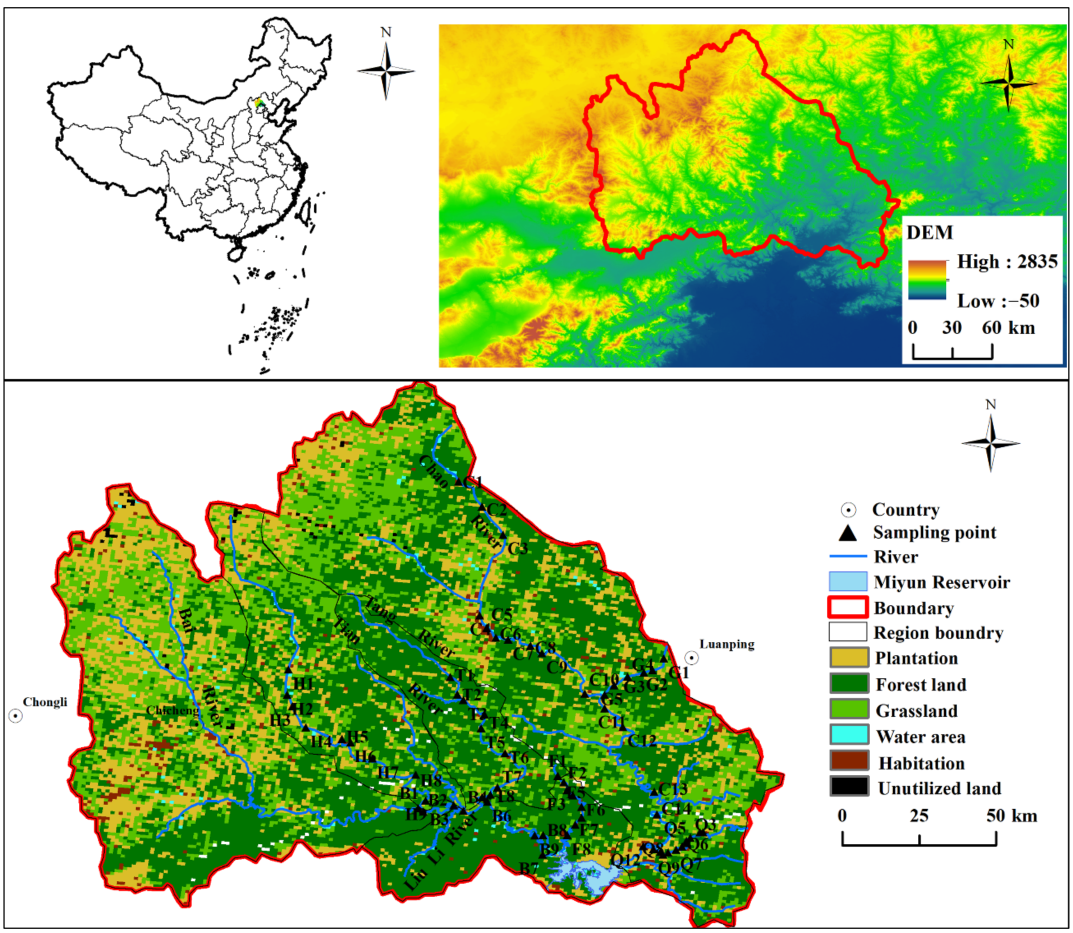


Figure 1. Overview map and in-stream sampling stations for Miyun Reservoir watershed.

2.2. Sampling and NO_3-N Analysis

In order to study the monthly variation of NO_3-N, sampling trips through the Miyun Reservoir watershed were conducted monthly from January 2006 to December 2010 (Figure 1). Sampling stations for monitoring NO_3-N were chosen where the rivers flow all the year round and positioned with GPS. In 2006, 45 sampling points were selected, among which 14 were on the Chao River, 12 on the Qingshui River, 6 on the Gangzi River, 5 on the Bai River, and 8 on the Tang River. From 2007 to 2010, 21 additional sampling points were selected, among which 4 were on the Bai River, 9 on the Hei River, and 8 on the Baimaguan River. No samples were collected in the Hei River in May, June, and July 2008 due to road construction.

The samples were stored in bottles under 4 °C in insulation boxes to inhibit biological activity. In the laboratory, samples were filtered through 0.45 um filters to remove suspended and particulate matter and frozen in freezers before further analysis. NO_3-N was analyzed using flow injection instrument (Lachat QuikChem 8000, Lachat Instrument, Milwaukee, WI, USA), and according to Lachat QuikChem Method 12-107-04-1-B released in 2003, with a detection limit of 0.005 mg/L.

2.3. Data and Statistical Analysis

In order to identify the influencing factors of seasonal variation of river nitrogen, some important data (fertilizer application, land use, population, and daily river flow) are separately collected as follows. Fertilizer application data were surveyed by asking local farmers throughout the whole watershed in 2007 (Jul.) and 2008 (Aug., Nov., and Dec.), which covered 4 types of chemical fertilizers including urea, ammonium phosphate, ammonium bicarbonate, and compound fertilizer, and 5 kinds of crops including maize, vegetables, potato, millet, and soybean. Land use and population data were collected from statistical yearbooks of the counties in the watershed. Daily flow data from 2006 to 2010 were from 3 hydrological stations, i.e., Zhangjiafen Hydrological Station (B8) in the lower reaches of the Bai River, Dage Hydrological Station (C7) in the middle reaches, and Gubeikou Hydrological Station (C13) in the lower reaches of the Chao River.

Nitrogen conversion factors of urea, ammonium phosphate, ammonium bicarbonate, and compound fertilizer are 46%, 18%, 17%, and 10%, respectively [78]. The average fertilizer nitrogen application rate of each crop is calculated according to amount and nitrogen conversion factor of each fertilizer. Fertilizer nitrogen load is calculated by summing all products of the area and fertilizer nitrogen application rate of each crop in the basin. Fertilizer application rate (kg N/km^2) is equal to the fertilizer nitrogen load divided by the basin area. Farmland percentage and population density (persons/km^2) are equal to farmland area and population size divided by the basin area, respectively. Regression analysis between NO_3-N and river flow, and statistical correlations between NO_3-N and human activity variables such as the fertilizer nitrogen application rate, population density, and farmland percentage were conducted using SAS 6.12 software (Cary, NC, USA).

2.4. Seasonal Variation Index

To express the degree of seasonal change of NO_3-N, the seasonal variation index (SVI) is established, and calculated by the equation as follows:

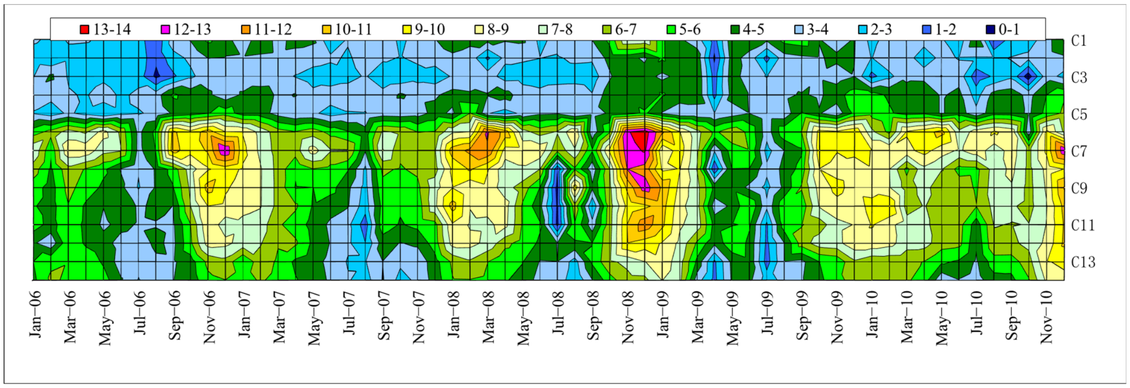
$$SVI(\%) = \left(N_{\mathrm{d}} - N_g\right) / N_d \times 100\%$$

where, SVI is the seasonal variation index; N_{d} is the average concentration of NO_3-N during the dormant season (no-growing season) including November, December, January, February, March, and April; N_g is the average concentration of NO_3-N during the growing season including May, June, July, August, September, and October. The seasonality of NO_3-N in the rivers is weak or unclear if the SVI is small. Otherwise, it is strong or clear.

3. Results

3.1. General Characteristics of NO_3-N

Generally, NO_3-N at all stations in the rivers varied greatly, with an average of 3.73 mg/L (0.10~18.60 mg/L) and the coefficient of variation (CV) of 81.5% (Figure 2). High average value of NO_3-N was separately observed in the Chao River (4.85 mg/L), Gangzi River (4.64 mg/L), Hei River (3.04 mg/L), and Baimaguan River (3.00 mg/L), whereas, low average NO_3-N was found at the outlets of the Tang River (2.33 mg/L), Bai River (1.84 mg/L), and Qingshui River (1.62 mg/L), respectively.



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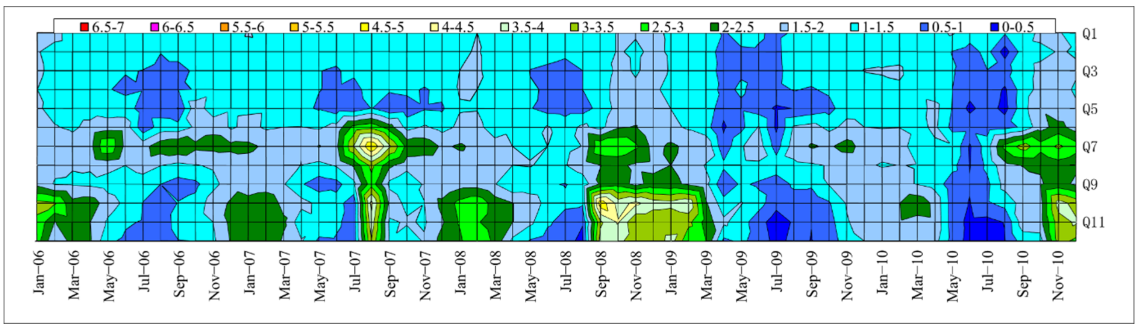

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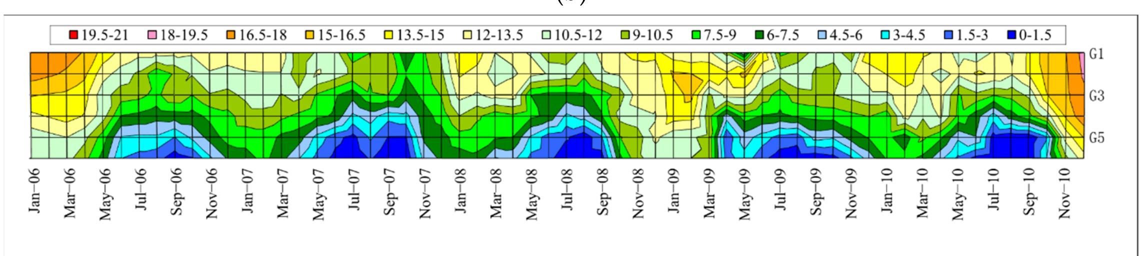

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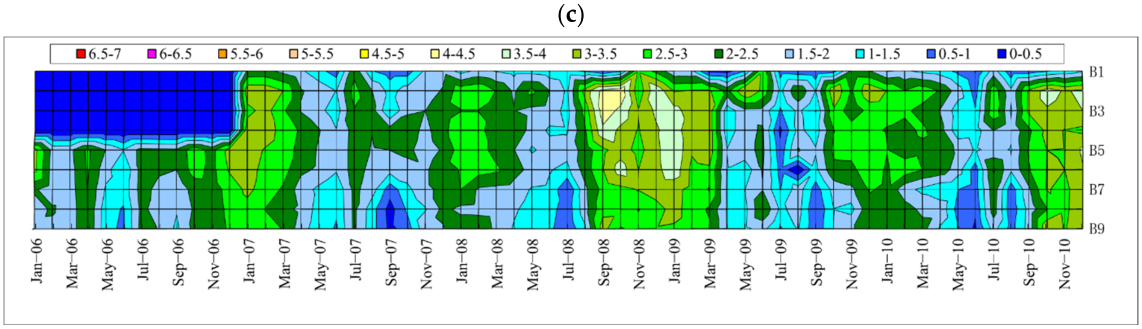

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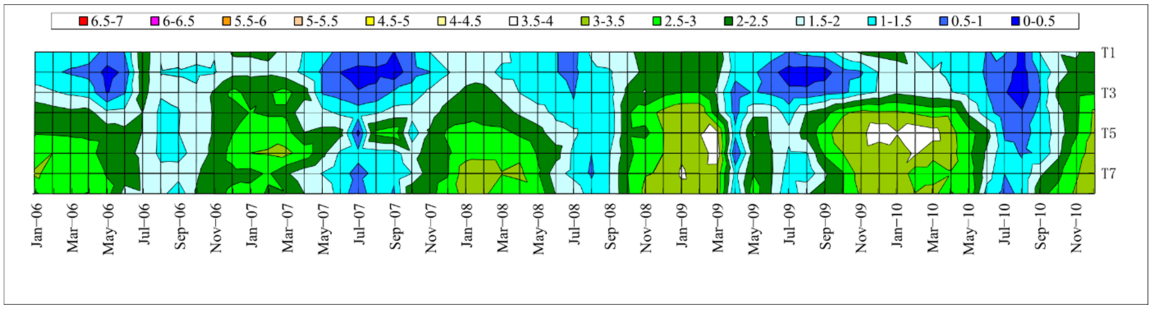

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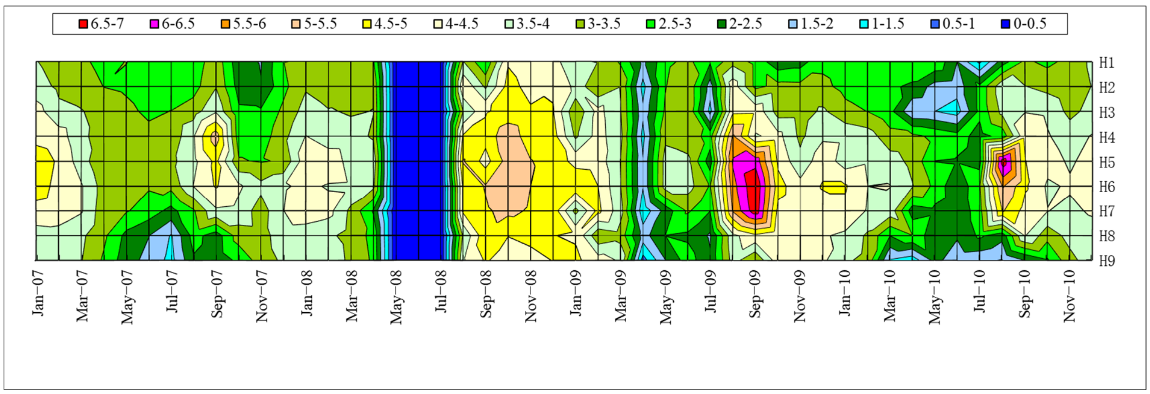

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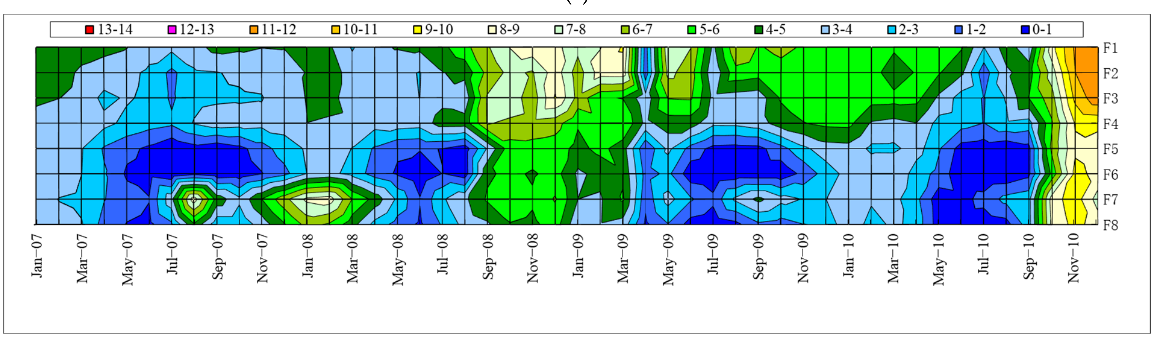


(**g**)

Figure 2. Seasonal change of NO_3-N in the Chao River (**a**), Qingshui River (**b**), Gangzi River (**c**), Bai River (**d**), and Tang River (**e**) from 2006 to 2010, and Hei River (**f**) and Baimaguan River (**g**) from 2007 to 2010.

In the Gangzi River, maximum NO_3-N (18.6 mg/L) was found at G1 in December 2010; that is the headwater station surrounded by a large area of crop land. Moreover, peak value (13.5 mg/L) in the Chao River was observed at C6 in December 2008, which was caused by wastewater discharge from Fengning town (the largest one in this study region), while, minimum NO_3-N (0.1 mg/L) was observed at the outlet of (G6) the Gangzi River in Autumn 2010.

The increasing trend of NO_3-N was observed in the downstream, as the rivers flowed through a large area of farmland or settlements. Firstly, the average value increased from H1 (2.91 mg/L) to H6 (4.08 mg/L) in the Hei River. Secondly, it increased from C5 (upstream of the town, 3.85 mg/L) to C6 (downstream of the town, 7.56 mg/L) in the Chao River. In addition, the decreasing trend of NO_3-N also happened in the downstream, as the streams passed though canyons. The average decreased from H6 (4.08 mg/L) to H9 (3.04 mg/L) on the Hei River, and from B6 (2.2 mg/L) to B9 (1.84 mg/L) in the Bai River.

On the whole, NO_3-N increased in the dormant season and decreased in the growing season, and that was the common seasonal variation in all rivers (Figure 2). Although the annual maxima of NO_3-N at all stations appeared every month, that accounted for 81.0% in the dormant season, especially 64.7% in winter. In contrast, the annual minima of NO_3-N accounted for 96.7% in the growing season, especially 79.0% in summer, but it did not appear in the dormant season, e.g., November, December, January, and February (Table 1).

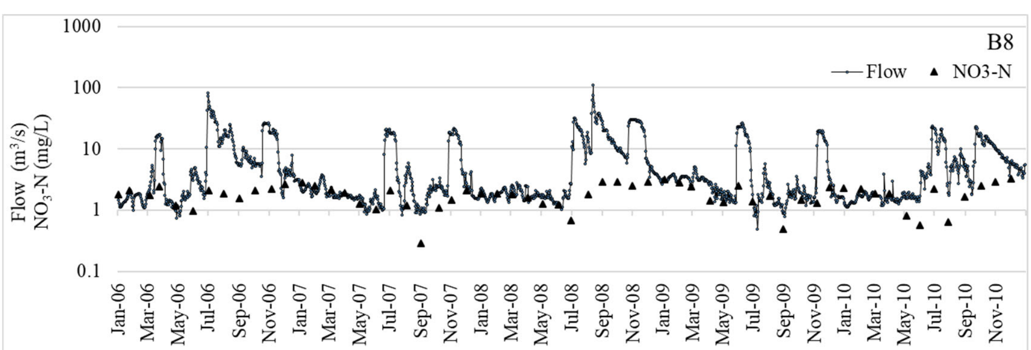
Table 1. Frequency of maximum and minimum of the NO_3-N.

Time	Jan.	Feb.	Mar.	Apr.	May.	Jun.	Jul.	Aug.	Sep.	Oct.	Nov.	Dec.
Maximum (%)	29.0	10.3	5.0	0.3	1.3	0.3	1.3	5.3	5.7	5.0	11.3	25.0
Minimum (%)	0.0	0.0	0.7	2.7	4.3	14.7	44.7	19.7	10.7	2.7	0.0	0.0

Three apparent seasonal patterns of NO_3-N were found. Firstly, the V-shaped pattern highlighted that the annual maxima and minima of NO_3-N dominated in two different periods (winter or late autumn, summer, or early autumn). Meanwhile, this prominent pattern accounted for 53.0% for all the stations. The V-shaped pattern in the Tang River, Baimaguan River, Gangzi River, Qingshui River, and Chao River accounted for 87.5%, 78.1%, 63.3%, 61.7%, and 48.6% for their own stations, respectively. Moreover, three stations on the lower Tang River all highlighted the V-shaped pattern in five consecutive years. Secondly, the prominent W-shaped pattern (accounting for 38.7%) of NO_3-N showed a great increase in summer and autumn rather than a decline in the trend, compared with the V-shaped pattern. One peak was in summer or autumn, and the other was in winter or late autumn, as mentioned above. W-shaped patterns in the Hei River and Bai River accounted for 92.6% and 80.5% for their own stations, respectively. Thirdly, the indistinct seasonal pattern, only accounting for 8.3%, mainly occurred at the stations in river headwater, such as G1 and G2 (Gangzi River), Q1 (Qingshui River), F1 (Baimaguan River), C1 and C2 (Chao River), and downstream of the large settlements, such as F7 (Baimaguan River).

3.2. Seasonal Variability of NO_3-N and Flow

In general, the rivers' flow was mostly low all year round, except during flooding caused by heavy precipitation or water discharge from reservoirs (Figure 3). Median flow in the study period was only 37.7%, 77.5%, and 83.8% of the average, which was 6.53 m^3/s at B8, 1.35 m^3/s at C7, and 2.58 m^3/s at C13, respectively. Moreover, maximum flow was 108.0 m^3/s observed at B8 on 13 August 2008, 24.7 m^3/s at C7 on 31 July 2010, and 30.1 m^3/s at C13 on 8 August 2008, while minimum flow was 0.48 m^3/s recorded at B8 on 10 July 2009, 0.147 m^3/s at C7 on 7 March 2010, and 0.206 m^3/s at C13 on 4 July 2009.



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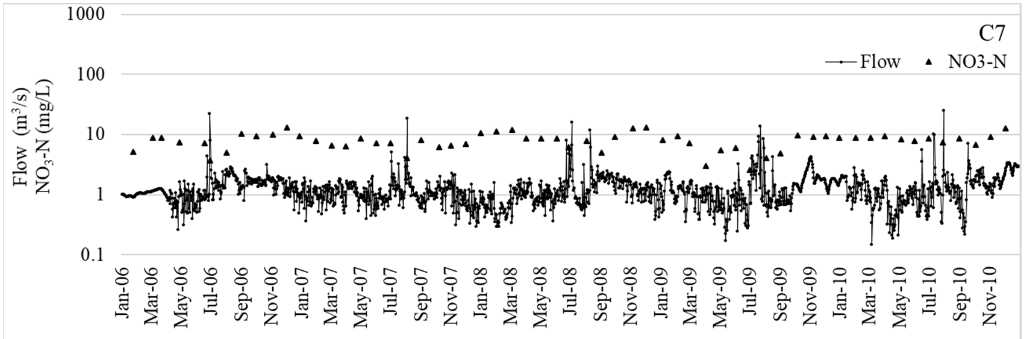

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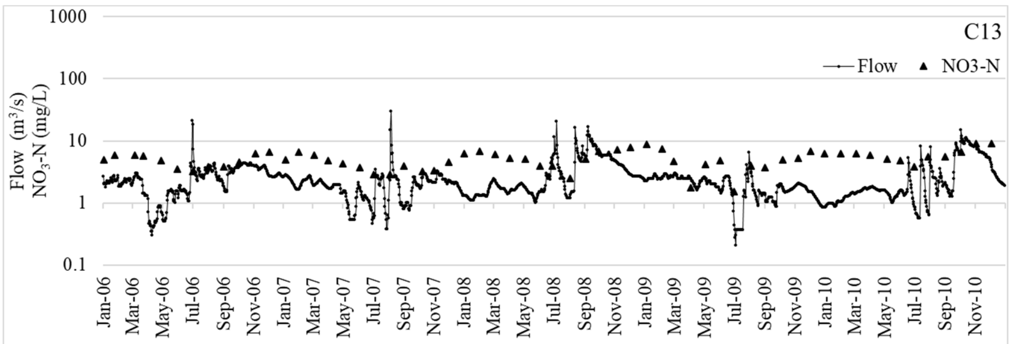

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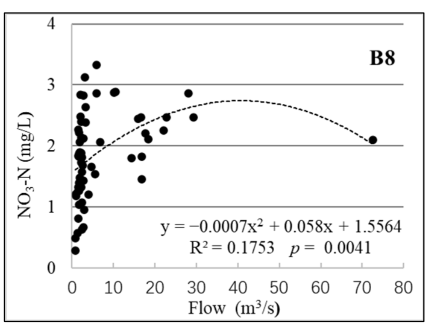
Figure 3. Seasonal variation of NO3-N and flow at B8 (**a**) on the Bai River, C7 (**b**) and C13 (**c**) on the Chao River.

The seasonal variability of NO3-N in the rives was closely related to the flow. Annual maxima of NO3-N corresponded to medium flow in the dormant season, which at three stations (B8, C7, and C13) varied yearly from 2.06 m^3/s to 5.98 m^3/s, from 1.22 m^3/s to 2.23 m^3/s, and from 1.65 m^3/s to 4.53 m^3/s. Nevertheless, annual minima of NO3-N were related to low flow or flood in the growing season. Therefore, flood mainly plays two roles in controlling NO3-N. On one hand, it acted as the diluent for the Chao River with high NO3-N, which reduced NO3-N and often led to the extremely low value. On the other hand, it also could carry the nitrogen source for the Bai River with low NO3-N, causing the increasing high value in the growing season. The flood contributed to the seasonal variation (W-shaped pattern) of NO3-N in the Bai River. Significant quadratic function between NO3-N and flow was identified ($p < 0.05$). At low concentrations, NO3-N tended to increase with the increase of flow, then decrease as flow went up at high concentrations (Figure 4).



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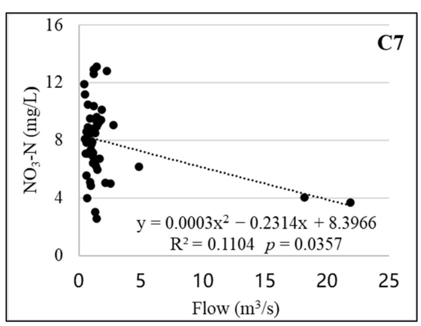

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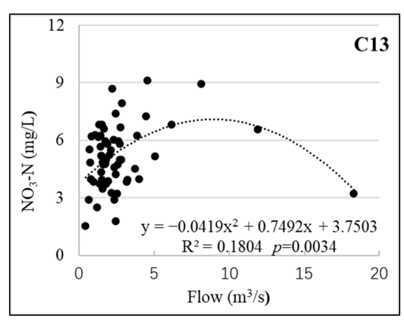

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Figure 4. Relationship between NO3-N and flow at B8 (**a**) on the Bai River, C7 (**b**) and C13 (**c**) on the Chao River.

3.3. Seasonal Variability of Correlation between NO_3-N and Human Factors

NO_3-N in rivers was strongly influenced by human activities, e.g., fertilizer application, population, and farmland [64,79–81]. At the same time, the correlations between them also have the obvious seasonal variation trend (Figure 5). Pearson's correlation coefficient (R) was high in the dormant season, with average values of 0.809, 0.744, and 0.745 for fertilizer application, population density, and farmland percentage, respectively, whereas the R was low in the growing season, with the average values of separately 0.570, 0.468, and 0.703. Annual maxima of R values separately accounted for 66.7% and 33.3% in the dormant and growing season, while annual minima of R values accounted for 93.3% from July to October (growing season), and 6.7% in February (dormant season).

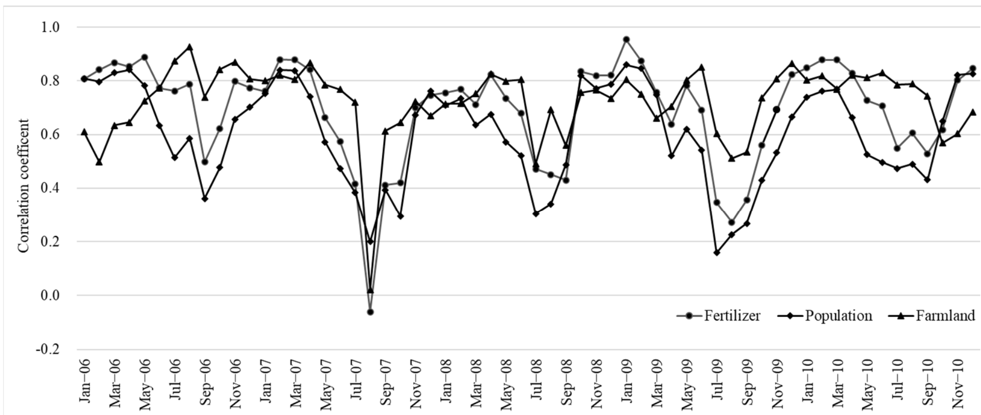

Figure 5. Seasonal variation of correlation coefficient (R) between NO_3-N and human activities.

Significant correlations occurred in the dormant season, and even in May and June, in which extremely significant correlations reached 73.3~100.0%; non-significant correlations only happened in July, August, September, and October, accounting for 40%, 46.7%, 46.7%, and 26.7%, respectively (Table 2).

Table 2. Seasonal variation of correlation between NO_3-N and human activities.

Degree of Significant	Jan.	Feb.	Mar.	Apr.	May.	Jun.	Jul.	Aug.	Sep.	Oct.	Nov.	Dec.
Non-significant (%)	0.0	0.0	0.0	0.0	0.0	0.0	40.0	46.7	46.7	26.7	0.0	0.0
Significant (%)	6.7	6.7	0.0	6.7	13.3	26.7	26.7	20.0	33.3	6.7	6.7	0.0
Extremely significant (%)	93.3	93.3	100.0	93.3	86.7	73.3	33.3	33.3	20.0	66.7	93.3	100.0

3.4. SVI of NO_3-N

An increasing trend of average SVI of NO_3-N was observed from upstream to downstream, that was less than 0.15 in the headwater and higher than 0.3 in the downstream (Figure 6). It became more and more prominent, except where the obvious nitrogen sources occurred, such as F7 where wastewater from Fengjiayu Town inputs into the Baimaguan River. A gentle increasing trend of the average SVI from upstream to downstream was observed in two large rivers that included the Bai River (0.1–0.35) and Chao River (0.14–0.37). Furthermore, a sharp one was found in the small tributaries, such as the Gangzi River (0.12–0.77) and the Baimaguan River (0.10–0.67).

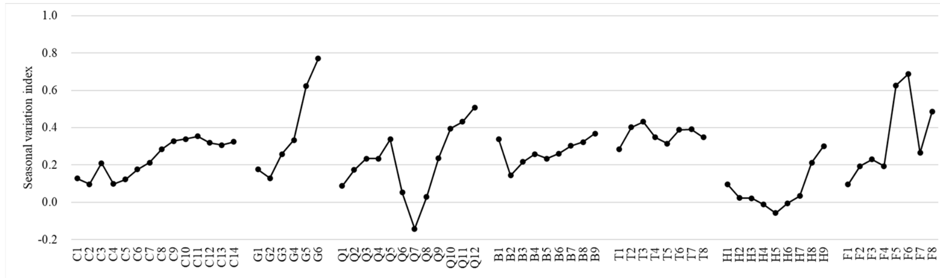

Figure 6. Seasonal variation index of NO_3-N in the rivers from upstream to downstream.

4. Discussion

4.1. Seasonal Variability and SVI of NO_3-N

Three seasonal patterns of NO_3-N are discovered in the rivers, i.e., V-shaped, W-shaped, and an indistinct one. The prominent V-shaped pattern was observed in the Tang River, Baimaguan River, Gangzi River, Qingshui River, and Chao River. It was characterized by the highest values mainly in winter or late autumn with cold weather, and the lowest values in summer or early autumn with warm weather and floods. Similar results could be confirmed by many previous studies [40–44,55,79,82–85].

The decline of NO_3-N in summer or early autumn was caused by strong denitrification in-stream [86], biological uptake [50,87], and flood dilution [88]. In addition, a similar seasonal pattern with a spring peak of nitrate during the dormant period (non-growing season) was highlighted in lakes of New York [89,90] and Vermont [91], and in streams of the Turkey Lakes watershed, Ontario [92], and the Catskill Mountains, New York [93]. In contrast, it was attributed to snowmelt flushing. The peak and trough values of dissolved inorganic nitrogen (DIN) or nitrate were separately found in April or May or June, and in October or November in the Yangtze River mainstream, in the periods of 1955–1985 [94], 1985–1990 [95], and 2004–2005 [96]. It was caused by agricultural fertilizer applied in spring, strong flood dilution, and biological uptake in summer, respectively. The W-shaped pattern in the Hei River and Bai River was also prominent. It highlighted the great increase of NO_3-N in summer or autumn rather than a decline trend compared with the V-shaped pattern, so another peak in summer or autumn was formed in addition to one peak in winter or late autumn mentioned above in Chaobai River [71] and the upper Mississippi River [80]. Some prairie streams highlighted two peak values of TN in the Red River Basin (Southern Manitoba), which was related to snowmelt in spring and wastewater discharge in summer, respectively [51].

The indistinct pattern of NO_3-N was also found in the headwater regions, this result was similar to Forge Valley of the River Derwent in UK [55]. It was caused by flashy precipitation and less biological uptake of NO_3-N [55]. Meanwhile, it showed the key effect of precipitation. Moreover, the peak after residential area was mainly related to the irregular wastewater discharge [97].

In addition, the reversed V-shaped seasonal pattern of TN was observed in Taojiang River, the small tributary of Yangtze River in the mountainous region of Jiangxi Province [98] i.e., the peak value occurred in the growing season rather than in the dormant season. This was attributed to substantial reactive nitrogen in soil particles and biological residues carried by heavy rain and overland flow. Autumn (October) peaks of NO_3-N occurred in a small southern British river, running through open heathland without agriculture activity. The nitrate response simply reflected an autumn flushing of nitrate as soils wet up [99]. Nevertheless, the reversed V-shaped pattern was not found in this study.

The increasing SVI trend was ascertained from upstream to downstream. In the headwater regions, nitrogen in-stream was mainly affected by flashy hydrology and nitrogen sources. The short residence time was not conducive to biochemical reactions, resulting in the inconspicuous seasonal variation [55]. In the downstream, the longer hydraulic retention time was beneficial to the chemical and biological processes of nitrogen in-stream [87], which was primarily controlled by temperature and vegetation. As a result, the seasonal variation was significant.

The increasing trend of SVI from upstream to downstream was gentle for two large rivers (the Bai River and Chao River), and sharp for the small tributaries. The adequate water flow in the large rivers was the dominant factor, while the impact of seasons related to the dynamics of temperature and vegetation on the total solute concentration could be minimal [54].

4.2. Factors Influencing the Seasonal Variability of NO_3-N

Overall, significant seasonal variability of NO_3-N increased in the dormant season and decreased in the growing season, respectively. We also observed that the V-shaped pattern was almost opposite to that of temperature [100]. Denitrification and growth of vegetation in streams played an important role in nitrogen reduction, however they were both controlled by temperature [101]. The microbial and plant uptake of nitrate in upland rivers of Northern Scotland was separately strong and weak in the warmer and colder months [102]. Meanwhile, the seasonal autotrophic uptake of NO_3-N was found in the reach of River Fischa in Austria [87]. Therefore, temperature has often been used as a predictor of nitrate variation [90,102–104].

Besides temperature, stream flow played different roles influencing the seasonal variability of NO_3-N. The annual maxima and minima of NO_3-N corresponded to medium flow in the dormant season and low flow or flood in the growing season, respectively. Significant quadratic function was found between NO_3-N and flow [43,105]. A strong positive relationship between NO_3-N and low flow was found, e.g., in the Humber Rivers [105], several rivers in the upper Thames basin [43], a few streams in lowland [42] in the UK, and a stream in an Austrian headwater agricultural catchment [54]. Nevertheless, the logarithmic or exponential increase trend of nitrate with high flows was found in the Salaca River and Daugava River in Latvia [82], which reflects the flow as nitrogen sources. However, more variable and complex relationships between nitrogen species and flow were also found in some rivers [43,82].

Furthermore, human activities (fertilizer application, population, and farmland) were also crucial factors influencing NO_3-N in rivers [66].

During the dormant season, surface runoff is rare due to little precipitation, and the river base flow are mainly recharged from groundwater with stable water quality. Moreover, there is little biochemical reaction of NO_3-N due to low temperature. Therefore, the spatial pattern of NO_3-N is marked by human activities, leading to the significant and extremely significant correlations between NO_3-N and human activity variables [106]. During the growing season, frequent floods (from July to October) could reduce the difference of NO_3-N from upstream to downstream, due to less biochemical reactions of NO_3-N resulting from its large water flow and fast flow rate.

During the flood period (July 2006), the CV of NO_3-N in the Bai River (1.5%) and Chao River (15.2%) was much lower than the average CV of 22.8% and 35.1%. Therefore, the flood dampened the impact of human activities on the spatial distribution of NO_3-N, resulting in the weak significant or even non-significant correlations between NO_3-N and human activity variables [106,107]. Population density, related to the wastewater discharge from the large settlements such as Fenjiayu Town, often caused the indistinct seasonality of NO_3-N. Fertilizer application did not directly affect the seasonal variation because the application time (April), due to an annual single cropping system, was not consistent with the seasonal variability of NO_3-N. Similarly, Exner-Kittrige et al., 2016 [54] also found that fertilizer application time was not the significant factor affecting the seasonality of nitrogen in the surface water. The fertilizer application supplied the long-term nitrogen load into the streams, while only multi-year reducing use of fertilizer would gradually reduce the concentrations of nitrogen species rather than the changes of the seasonal application rates.

5. Conclusions

The seasonal variation of NO_3-N was significant in different rivers, and increased and decreased in the dormant and the growing season, respectively. Furthermore, the V-shaped, W-shaped, and indistinct seasonal patterns separately accounted for 53.0%, 38.7%, and 8.3%. The river flow plays different roles that affects nitrogen concentration in different rivers. For example, river flow not only played a diluting role, e.g., Chao River (high NO_3-N), but also added nitrogen sources carried by surface runoff, e.g., Bai River (low NO_3-N). Then, it resulted in the W-shaped (Bai River) and V-shaped patterns (Chao River), respectively.

NO_3-N was closely correlated with human activities, such as fertilizer application, population, and farmland. Significant seasonality of these correlations was found in the dormant season, while partly non-significant ones were ascertained in July, August, September, and October. The former was attributed to low temperature and the little biochemical reaction of NO_3-N, while the latter was caused by flooding that alleviated the impact of human activities on NO_3-N. The increasing trend in SVI of NO_3-N from upstream to downstream was also discovered, which was gentle for large rivers and sharp for small tributaries. The hydraulic retention time, river flow, seasonality of temperature, and vegetation all played key roles. Generally, the effect of natural factors on the seasonal variation of NO_3-N was higher than that of human factors.

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