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

Qingsuo Wang 1,*,†, Dongbao Sun 1,†, Yilei Yu 2,†, Zhiyang Tang 3 and Yongxin Lu 4

1 Institute of Environment and Sustainable Development in Agriculture, Chinese Academy of Agricultural Sciences/Key Laboratory of Dryland Agriculture, Ministry of Agriculture and Rural Affairs, Beijing 100081, China
2 Xiongan Institute of Innovation, Chinese Academy of Sciences, Xiong’an, Baoding 071899, China
3 Chengde City Water Resources Bureau, Chengde 067000, China
4 Chengde Hydrological and Water Resources Survey Bureau of Hebei Province, Chengde 067000, China
* Correspondence: wangqingsuo@163.com
† These authors contributed equally to this work.

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. Furthermore, 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

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]. For the development of human, agriculture, and industry, rivers are vital sources of fresh water [10–12]. However, they are facing multiple threats including natural factors (precipitation, erosion, and weathering) and anthropogenic activities (agriculture, industry, and urban activities) [13–19]. Over the last century, river water quality has gradually changed as a result of human activities, especially for riverine nitrogen [14,20–22]. Presently, more than half of severe environmental problems are related to nitrogen cycles, which is caused by excessive nitrogen from intensified anthropogenic activities [17,23]. Generally, the temporal variations of nitrogen in river water are driven by some key processes including nitrogen...
sources, mobilization, transformation, and delivery [16,24,25]. Specifically, the key influencing factors include topography [26], precipitation or runoff [27,28], land use [26,27,29], the oxidation-reduction environment of water/sediment [30–33], and so on. Meanwhile, nitrogen retention by adsorption and degradation varies greatly from upstream to downstream, which also differs from one river to another [34–36]. Detailed and different factors may play an important role, such as river flow conditions, river channel characteristics, temperature, and sunshine hours [21,23,29,37,38].

Obvious temporal variations of nitrogen species have been observed among different rivers [7,39–43]. 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 [1,44,45]. Simultaneously, the highest values of nitrate in streams are clearly related to their hydrological conditions [46], such as summer storms in temperate regions [47] and snowmelt runoff in cold regions [48–50]. Additionally, fertilizer application in agricultural fields for enhancing the productivity of crops leads to the increase of nitrate in rivers [51], but it does not fully coincide with the nitrogen seasonality [52]. Nevertheless, significant seasonality of nitrate has not been found in some rivers [53] and well understood [54].

The control of river nitrogen pollution is one of the vital issues for sustainable watershed management [12]. 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 [3,14,54,55]. Detailed temporal variations in watersheds have not yet been investigated; meanwhile, the watershed scale is a very important scale for nitrogen in river [56,57]. 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 [28,58,59]. 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 $4.375 \times 10^9$ m$^3$, is the most important surface drinking water source for Beijing, the capital city of China [60]. In recent years, it has been at risk of eutrophication [61,62], although good water quality has long been retained [63]. 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 [64,65]. However, an upward trend of NO$_3^-$-N and total nitrogen (TN) in the rivers and Miyun Reservoir is still being observed [60,66,67]. Simultaneously, algal blooms broke out in the Miyun Reservoir [68], and this may be caused by the continuous input of nutrients from the upper rivers to the Miyun Reservoir [69,70]. Spatial patterns of NO$_3^-$-N in rivers of the Miyun Reservoir watershed were studied [64], but available data are poor for addressing seasonality of NO$_3^-$-N in rivers [64,71,72]. A better understanding of river nitrogen influenced by human activities and natural factors (hydrology and temperature) is important for reducing nitrogen pollution in rivers [22,73,74].

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 km² 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 [75].

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 [76]. 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:

$$SVI(\%) = \frac{(N_d - N_g)}{N_d} \times 100\%$$

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.
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.

(a) 

(b) 

(c) 

(d) 

Figure 2. Cont.
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.

The seasonal variability of NO$_3$-N in the rivers was closely related to the flow. Annual maxima of NO$_3$-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 NO$_3$-N were related to low flow or flood in the growing season. Therefore, flood mainly plays two roles in controlling NO$_3$-N. On one hand, it acted as the diluent for the Chao River with high NO$_3$-N, which reduced NO$_3$-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 NO$_3$-N, causing the increasing high value in the growing season. The flood contributed to the seasonal variation (W-shaped pattern) of NO$_3$-N in the Bai River. Significant quadratic function between NO$_3$-N and flow was identified ($p < 0.05$). At low concentrations, NO$_3$-N tended to increase with the increase of flow, then decrease as flow went up at high concentrations (Figure 4).
On the whole, NO$_3$-N increased in the dormant season and decreased in the growing season. The flood contributed also could carry the nitrogen source for the Bai River with low NO$_3$-N at B8, 1.35 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.

Figure 3. Seasonal variation of NO$_3$-N and flow at B8 (a) on the Bai River, C7 (b) and C13 (c) on the Chao River.

Figure 4. Relationship between NO$_3$-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 [62,77–79]. 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](image-url)  
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).

| 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 |

Table 2. Seasonal variation of correlation between NO$_3$-N and human activities.

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 [39–43,53,77,80–83].

The decline of NO$_3$-N in summer or early autumn was caused by strong denitrification in-stream [84], biological uptake [48,85], and flood dilution [86]. 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 [87,88] and Vermont [89], and in streams of the Turkey Lakes watershed, Ontario [90], and the Catskill Mountains, New York [91]. 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 [92], 1985–1990 [93], and 2004–2005 [94]. 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 [69] and the upper Mississippi River [78]. 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 [49].

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 [53]. It was caused by flashy precipitation and less biological uptake of NO$_3$-N [53]. Meanwhile, it showed the key effect of precipitation. Moreover, the peak after residential area was mainly related to the irregular wastewater discharge [95].

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 [96] 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 [97]. 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 [53]. In the downstream, the longer hydraulic retention time was beneficial to the chemical and biological processes of nitrogen in-stream [85],
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 [52].

4.2. Factors Influencing the Seasonal Variability of NO\textsubscript{3}-N

Overall, significant seasonal variability of NO\textsubscript{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 [98]. Denitrification and growth of vegetation in streams played an important role in nitrogen reduction, however they were both controlled by temperature [99]. The microbial and plant uptake of nitrate in upland rivers of Northern Scotland was separately strong and weak in the warmer and colder months [100]. Meanwhile, the seasonal autotrophic uptake of NO\textsubscript{3}-N was found in the reach of River Fischa in Austria [85]. Therefore, temperature has often been used as a predictor of nitrate variation [88,100,101].

Besides temperature, stream flow played different roles influencing the seasonal variability of NO\textsubscript{3}-N. The annual maxima and minima of NO\textsubscript{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\textsubscript{3}-N and flow [42,102]. A strong positive relationship between NO\textsubscript{3}-N and low flow was found, e.g., in the Humber Rivers [102], several rivers in the upper Thames basin [42], a few streams in lowland [41] in the UK, and a stream in an Austrian headwater agricultural catchment [52]. Nevertheless, the logarithmic or exponential increase trend of nitrate with high flows was found in the Salaca River and Daugava River in Latvia [80], which reflects the flow as nitrogen sources. However, more variable and complex relationships between nitrogen species and flow were also found in some rivers [42,80].

Furthermore, human activities (fertilizer application, population, and farmland) were also crucial factors influencing NO\textsubscript{3}-N in rivers [64].

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\textsubscript{3}-N due to low temperature. Therefore, the spatial pattern of NO\textsubscript{3}-N is marked by human activities, leading to the significant and extremely significant correlations between NO\textsubscript{3}-N and human activity variables [103]. During the growing season, frequent floods (from July to October) could reduce the difference of NO\textsubscript{3}-N from upstream to downstream, due to less biochemical reactions of NO\textsubscript{3}-N from its large water flow and fast flow rate.

During the flood period (July 2006), the CV of NO\textsubscript{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\textsubscript{3}-N, resulting in the weak significant or even non-significant correlations between NO\textsubscript{3}-N and human activity variables [103,104]. Population density, related to the wastewater discharge from the large settlements such as Fenjiayu Town, often caused the indistinct seasonality of NO\textsubscript{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\textsubscript{3}-N. Similarly, Exner-Kittrige et al., 2016 [52] 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.

Author Contributions: Q.W.: Conceptualization, Funding acquisition, Methodology, Investigation, Formal analysis, Writing—original draft; Writing—review & editing. D.S.: Conceptualization, Methodology, Investigation, Data curation, Writing—review & editing. Y.Y.: Conceptualization, Methodology, Investigation, Data curation, Writing—review & editing. Z.T.: Data curation. Q.W., D.S. and Y.Y. contributed equally to this work. All authors have read and agreed to the published version of the manuscript.

Funding: This work was financially supported by Beijing Municipal Science & Technology Commission (D0705045040391), Ministry of Science and Technology of China (2006BAD29B05) and Chinese Academy of Agricultural Sciences (Y2021LM03).

Data Availability Statement: The data that support the findings of this study are available on request from the corresponding author.

Conflicts of Interest: The authors declare no conflict of interest.

References

1. Mekonnen, M.M.; Hoekstra, A.Y. Global gray water footprint and water pollution levels related to anthropogenic nitrogen loads to fresh water. Environ. Sci. Technol. 2015, 49, 12860–12868. [CrossRef] [PubMed]
2. Bechmann, M.E.; Berge, D.; Eggestad, H.O.; Vandsemb, S.M. Phosphorus transfer from agricultural areas and its impact on the eutrophication of lakes—Two long-term integrated studies from Norway. J. Hydrol. 2005, 304, 238–250. [CrossRef]
3. Strokal, M.; Yang, H.; Zhang, Y.; Kroeze, C.; Li, L.; Luan, S.; Wang, H.; Yang, S. Increasing eutrophication in the coastal seas of China from 1970 to 2050. Mar. Pollut. Bull. 2014, 85, 123–140. [CrossRef]
4. Burton, E. Acidification of freshwater ecosystems: Implications for the future. Geochim. Cosmochim. Acta 1997, 61, 2150. [CrossRef]
5. Chen, C.; Lin, J.; Liu, Y.; Ren, X. Effects of freshwater acidification and countermeasures. IOP Conf. Ser. Earth Environ. Sci. 2022, 1011, 012035. [CrossRef]
6. Strebel, O.; Duynisveld, W.; Btcher, J. Nitrate pollution of groundwater in western Europe. Agric. Ecosyst. Environ. 1989, 26, 189–214. [CrossRef]
7. Wang, Q.S.; Sun, D.B.; Hao, W.P.; Li, Y.Z.; Mei, X.R.; Zhang, Y.Q. Human activities and nitrogen in waters. Acta Ecol. Sin. 2012, 32, 174–179. (In Chinese) [CrossRef]
8. Miller, M.P.; Tesoriero, A.J.; Capel, P.D.; Pellerin, B.A.; Burns, D.A. Quantifying watershed-scale groundwater loading and in-stream fate of nitrate using high-frequency water quality data. Water Resour. Res. 2015, 52, 330–347. [CrossRef]
9. Camargo, J.A.; Alonso, A. Ecological and toxicological effects of inorganic nitrogen pollution in aquatic ecosystems: A global assessment. Environ. Int. 2006, 32, 831–849. [CrossRef]
10. Gupta, N.; Pandey, P.; Hussain, J. Effect of physicochemical and biological parameters on the quality of river water of Narmada, Madhya Pradesh, India. Water Sci. 2017, 31, 11–23. [CrossRef]
11. Kamboj, N.; Kamboj, V. Water quality assessment using overall index of pollution in riverbed-mining area of Ganga-River Haridwar, India. Water Sci. 2019, 33, 65–74. [CrossRef]
12. Srinivas, R.; Singh, A.P.; Dhadse, K.; Garg, C. An evidence based integrated watershed modelling system to assess the impact of non-point source pollution in the riverine ecosystem. *J. Clean. Prod.* 2020, 246, 118963. [CrossRef]

13. Bhat, S.U.; Bhat, A.A.; Jehangir, A.; Hamid, A.; Sabha, I.; Qayoom, U. Water quality characterization of Marusudar River in Chenab Sub-Basin of North-Western Himalaya using multivariate statistical methods. *Water Air Soil Pollut.* 2021, 232, 449. [CrossRef]

14. Cui, M.; Guo, Q.; Wei, Y.; Yu, X.; Hu, J.; Tian, L.; Kong, J. Variations and its driven factors of anthropogenic nitrogen loads in the Yangtze River Economic Belt during 2000–2019. *Environ. Sci. Pollut. Res. Int.* 2022. [CrossRef][PubMed]

15. Pinardi, M.; Soana, E.; Severini, E.; Racchetti, E.; Celico, F.; Bartoli, M. Agricultural practices regulate the seasonality of groundwater-river nitrogen exchanges. *Agric. Water Manag.* 2022, 273, 107904. [CrossRef]

16. Shi, W.; Zhang, Y.; Zhang, C.; Zhang, W. Sources and health risks of nitrate pollution in surface water in the Weihe River watershed, China. *J. Mt. Sci.* 2022, 19, 2226–2240. [CrossRef]

17. Sun, X.; Dong, Z.; Zhang, W.; Hou, C.; Liu, Y.; Zhang, C.; Wang, L.; Wang, Y.; Zhao, J.; Chen, L. Seasonal and spatial variations in nutrients under the influence of natural and anthropogenic factors in coastal waters of the northern Yellow Sea, China. *Mar. Pollut. Bull.* 2022, 175, 113171. [CrossRef]

18. Wang, X.; Xu, Y.J.; Zhang, L. Watershed scale spatiotemporal nitrogen transport and source tracing using dual isotopes among surface water, sediments and groundwater in the Yiluo River Watershed, Middle of China. *Sci. Total Environ.* 2022, 833, 155180. [CrossRef]

19. Zhang, A.; Lei, K.; Lang, Q.; Li, Y. Identification of nitrogen sources and cycling along freshwater river to estuarine water continuum using multiple stable isotopes. *Sci. Total Environ.* 2022, 851, 158136. [CrossRef]

20. Zhang, X.; Zhang, Y.; Shi, P.; Bi, Z.; Shan, Z.; Ren, L. The deep challenge of nitrate pollution in river water of China. *Sci. Total Environ.* 2021, 770, 144674. [CrossRef]

21. Zhou, J.; Luo, X.; Xiao, J.; Wei, H.; Zhao, W.; Zheng, Z. Modeling the seasonal and interannual variations in nitrate flux through Bering Strait. *J. Mar. Syst.* 2021, 218, 103527. [CrossRef]

22. Liu, S.; Fu, R.; Liu, Y.; Suo, C. Spatiotemporal variations of water quality and their driving forces in the Yangtze River Basin, China, from 2008 to 2020 based on multi-statistical analyses. *Environ. Sci. Pollut. Res. Int.* 2022, 29, 69388–69401. [CrossRef]

23. Vitousek, P.M.; Menge, D.; Reed, S.C.; Cleveland, C.C. Biological nitrogen fixation: Rates, patterns and ecological controls in terrestrial ecosystems. *Philos. Trans. R. Soc. Lond.* 2013, 368, 20130119. [CrossRef] [PubMed]

24. Guo, D.; Lintern, A.; Webb, J.A.; Ryu, D.; Liu, S.; BendeMichl, U. Key factors affecting temporal variability in stream water quality. *Water Resour. Res.* 2019, 55, 112–129. [CrossRef]

25. Shi, J.; Jin, R.; Zhu, W. Quantification of effects of natural geographical factors and landscape patterns on non-point source pollution in watershed based on geodetector: Burhatong River Basin, Northeast China as an example. *Chin. Geogr. Sci.* 2022, 32, 707–723. [CrossRef]

26. Jabbar, F.K.; Grote, K. Statistical assessment of nonpoint source pollution in agricultural watersheds in the Lower Grand River watershed, MO, USA. *Environ. Sci. Pollut. Res.* 2019, 26, 1487–1506. [CrossRef] [PubMed]

27. Nobre, R.; Caliman, A.; Cabral, C.R.; Araujo, F.; Carneiro, L.S. Precipitation, landscape properties and land use interactively affect water quality of tropical freshwaters. *Sci. Total Environ.* 2020, 716, 137044. [CrossRef] [PubMed]

28. Wu, Z.; Jiang, M.; Wang, H.; Di, D.; Guo, X. Management implications of spatial-temporal variations of net anthropogenic nitrogen inputs (NANI) in the Yellow River Basin. *Environ. Sci. Pollut. Res. Int.* 2022, 29, 52317–52335. [CrossRef]

29. Xu, G.; Li, P.; Lu, K.; Tantai, Z.; Zhang, J.; Ren, Z.; Wang, X.; Yu, K.; Shi, P.; Cheng, Y. Seasonal changes in water quality and its main influencing factors in the Dan River basin. *Catena* 2019, 173, 131–140. [CrossRef]

30. Qin, X.; Li, Y.; Goldberg, S.; Wan, Y.; Fan, M.; Liao, Y.; Wang, B.; Gao, Q.; Li, Y. Assessment of indirect N2O emission factors from agricultural river networks based on long-term study at high temporal resolution. *Environ. Sci. Technol.* 2019, 53, 10781–10791. [CrossRef]

31. Salk, K.R.; Ostrom, N.E. Nitrous oxide in the Great Lakes: Insights from two trophic extremes. *Biogeochemistry* 2019, 144, 223–243. [CrossRef]

32. Soto, D.X.; Koehler, G.; Hobson, K.A. Combining denitrifying bacteria and laser spectroscopy for isotopic analyses (δ15N, δ18O) of dissolved nitrate. *Anal. Chem.* 2015, 70, 7000–7005. [CrossRef] [PubMed]

33. Wang, J.; Chen, N.; Yan, W.; Wang, B.; Yang, L. Effect of dissolved oxygen and nitrogen on emission of N2O from rivers in China. *Atmos. Environ.* 2015, 103, 347–356. [CrossRef]

34. Canela, P.; Clements, T.L.S.; Sobolev, D. High nitrogen to phosphorus ratio in a Texas coastal river: Origins and implications for nutrient pollution sources and exports. *J. Coast. Conserv.* 2020, 24, 46. [CrossRef]

35. Li, C.; Zhang, H.; Hao, Y.; Zhang, M. Characterizing the heterogeneous correlations between the landscape patterns and seasonal variations of total nitrogen and total phosphorus in a peri-urban watershed. *Environ. Sci. Pollut. Res. Int.* 2020, 27, 34067–34077. [CrossRef]

36. Bi, Z.; Zhang, Y.; Shi, P.; Zhang, X.; Shan, Z.; Ren, L. The impact of land use and socio-economic factors on ammonia nitrogen pollution in Weihe River watershed, China. *Environ. Sci. Pollut. Res. Int.* 2021, 28, 17659–17674. [CrossRef]

37. Varol, M. Temporal and spatial dynamics of nitrogen and phosphorus in surface water and sediments of a transboundary river located in the semi-arid region of Turkey. *Catena* 2013, 100, 1–9. [CrossRef]
38. Zhou, W.; Zhang, Y.; Yin, J.; Zhou, J.; Wu, Z. Evaluation of polluted urban river water quality: A case study of the Xunsi River watershed, China. Environ. Sci. Pollut. Res. Int. 2022, 29, 68035–68050. [CrossRef]

39. Hunt, C.W.; Ilii, T.L.; Vörösmarty, C. Spatial and temporal patterns of inorganic nutrient concentrations in the Androscooggin and Kennebec rivers, Maine. Water Air Soil Pollut. 2005, 163, 303–323. [CrossRef]

40. Smart, R.P.; Cresser, M.S.; Calver, L.J.; Clark, M.; Chapman, P.J. A novel modelling approach for spatial and temporal variations in nutrient concentrations in an impacted UK small upland river basin. Environ. Pollut. 2008, 153, 65–72. [CrossRef]

41. Jarvie, H.P.; Withers, P.; Bowes, M.J.A.; Palmer-Felgate, E.J.; Armstrong, L.K. Streamwater phosphorus and nitrogen across a gradient in rural-agricultural land use intensity. Agric. Ecosyst. Environ. 2010, 135, 238–252. [CrossRef]

42. Neal, C.; Jarvie, H.P.; Neal, M.; Hill, L.; Wickham, H. Nitrate concentrations in river waters of the upper Thames and its tributaries. Sci. Total Environ. 2006, 365, 15–32. [CrossRef] [PubMed]

43. Tipping, E.; Thacker, S.A.; Wilson, D.; Hall, J.R. Long-term nitrate increases in two oligotrophic lakes, due to the leaching of atmospherically-deposited N from moorland ranker soils. Environ. Pollut. 2008, 152, 41–49. [CrossRef] [PubMed]

44. Mulholland, P.J.; Helton, A.M.; Poole, G.C.; Hall, R.O.; Hamilton, S.K.; Peterson, B.J.; Tank, J.L.; Ashkenas, L.R.; Cooper, L.W.; Dahm, C.N. Stream denitrification across biomes and its response to anthropogenic nitrate loading. Nature 2008, 452, 202–205. [CrossRef]

45. Alexander, R.B.; Böhlke, J.K.; Boyer, E.W.; David, M.B.; Harvey, J.W.; Mulholland, P.J.; Seitzinger, S.P.; Tobias, C.R.; Tonitto, C.; Wollheim, W.M. Dynamic modeling of nitrogen losses in river networks unravels the coupled effects of hydrological and biogeochemical processes. Biogeochemistry 2009, 93, 91–116. [CrossRef]

46. Basu, N.B.; Destouni, G.; Jawitz, J.W.; Thompson, S.E.; Rao, P.S.C. Nutrient loads exported from managed catchments reveal emergent biogeochemical stationarity. Geophys. Res. Lett. 2010, 37, 23404–23405. [CrossRef]

47. Fang, X.; Pomeroy, J.W.; Westbrook, C.J.; Guo, X.; Brown, T. Prediction of snowmelt derived streamflow in a wetland dominated prairie basin. Hydrol. Earth Syst. Sci. 2010, 14, 991–1006. [CrossRef]

48. Corriuveau, J.; Chambers, P.A.; Yates, A.G.; Culp, J.M. Snowmelt and its role in the hydrologic and nutrient budgets of prairie streams. Water Sci. Technol. 2011, 64, 1590–1596. [CrossRef] [PubMed]

49. Rattan, K.J.; Corriuveau, J.C.; Brua, R.B.; Culp, J.M.; Yates, A.G.; Chambers, P.A. Quantifying seasonal variation in total phosphorus and nitrogen from prairie streams in the Red River Basin, Manitoba Canada. Sci. Total Environ. 2017, 575, 649–659. [CrossRef]

50. Cade-Menun, B.J.; Bell, G.; Baker-Ismail, S.; Pouli, Y.; Wu, K. Nutrient loss from Saskatchewan cropland and pasture in spring snowmelt runoff. Can. J. Soil Sci. 2013, 93, 445–458. [CrossRef]

51. David, M.B.; Gentry, L.E. Anthropogenic inputs of nitrogen and phosphorus and riverine export for Illinois, USA. J. Environ. Qual. 2000, 29, 494–508. [CrossRef]

52. Exner-Kitrtridge, M.; Strauss, P.; Bloeschl, G.; Eder, A.; Saracevic, E.; Zessner, M. The seasonal dynamics of the stream sources and input flow paths of water and nitrogen of an Austrian headwater agricultural catchment. Sci. Total Environ. 2016, 542, 935–945. [CrossRef] [PubMed]

53. Mian, I.A.; Begum, S.; Riaz, M.; Ridealgh, M.; Mclean, C.J.; Cresser, M.S. Spatial and temporal trends in nitrate concentrations in the River Derwent, North Yorkshire, and its need for NVZ status. Sci. Total Environ. 2010, 408, 702–712. [CrossRef]

54. Chen, X.; Strokal, M.; Kroze, C.; Ma, L.; Shen, Z.; Wu, J.; Shi, X. Seasonality in river export of nitrogen: A modelling approach for the Yangtze River. Sci. Total Environ. 2017, 617, 1282–1292. [CrossRef]

55. Frossard, V.; Aleya, L.; Vallet, A.; Henry, P.; Charlier, J.B. Impacts of nitrogen loads on the water and biota in a karst river (Loue River, France). Hydrobiologia 2020, 847, 2343–2448. [CrossRef]

56. Memon, Y.I.; Sundus, S.; Qureshi, A.; Kandhar, A.; Saleh. Statistical analysis and physicochemical characteristics of groundwater quality parameters: A case study. Int. J. Environ. Anal. Chem. 2021, 101, 1–22. [CrossRef]

57. Qureshi, S.S.; Channa, A.; Memon, S.A.; Khan, Q.; Saleh. T.A. Assessment of physicochemical characteristics in groundwater quality parameters. Environ. Technol. Innov. 2021, 24, 101877. [CrossRef]

58. Ba, W.; Du, P.; Liu, T.; Bao, A.; Chen, X.; Liu, J.; Qin, C. Impacts of climate change and agricultural activities on water quality in the Lower Kaidu River Basin, China. J. Geogr. Sci. 2020, 30, 164–176. [CrossRef]

59. Mendivil-Garcia, K.; Amabilis-Sosa, L.E.; Rodriguez-Mata, A.E.; Rangel-Peraza, J.G.; Gonzalez-Huitrón, V.; Cedillo-Herrera, C.I.G. Assessment of intensive agriculture on water quality in the Culiacaín River Basin, Sinaloa, Mexico. Environ. Sci. Pollut. Res. Int. 2020, 27, 28636–28648. [CrossRef]

60. Wang, Q.; Mei, X.; Zhang, Y.; Sun, D.; Yu, Y. Review of water quality of Miyun Reservoir. J. Agric. Sci. Technol. Chin. 2009, 11, 45–50. [CrossRef]

61. Meng, D.; Xi, G.E. Assessment and control of water eutrophication in Miyun Reservoir J. Hebei Acad. Sci. 2011, 28, 1–5. (In Chinese)

62. Xu, E.; Zhang, H. Aggregating land use quantity and intensity to link water quality in upper catchment of Miyun Reservoir. Ecol. Indic. 2016, 66, 329–339. [CrossRef]

63. Jia, H.; Cheng, S. Spatial and dynamic simulation for Miyun Reservoir waters in Beijing. Water Sci. Technol. 2002, 46, 473–479. [CrossRef] [PubMed]

64. Wang, Q.; Sun, D.; Tang, Z.; Lu, Y. Nitrate nitrogen concentrations in the upstream of Miyun Reservoir: Spatial distribution pattern. J. Agric. 2020, 10, 50–55. (In Chinese)

65. Qiu, J.; Shen, Z.; Chen, L.; Hou, X. Quantifying effects of conservation practices on non-point source pollution in the Miyun Reservoir Watershed, China. Environ. Monit. Assess. 2019, 191, 582. [CrossRef] [PubMed]
66. Xue, J.; Wang, J.; Chen, C. Preliminary study on the influence of inflow streams on water quality of Miyun Reservoir. *Beijing Water* 2022, 4, 11–14. (In Chinese)

67. Zhang, X.; Zhao, L.; Li, Y.; Wang, J.; Li, L. Current situation analysis of nitrogen and phosphorus nutrient input in main inflow rivers of Miyun Reservoir. *Beijing Water* 2021, 2, 21–25. (In Chinese)

68. Wang, L.; Yang, M.; Guo, Z.H.; Zhang, Y.; Jiang, Y.; Fan, K.P. Study on water quality transformation in Miyun Reservoir. *China Water Wastewater* 2006, 22, 432–435

69. Yu, Y.; Wang, Q. Analysis of seasonal changes of water quality in Miyun Reservoir and reaches of its main influents. (In Chinese) *Chin. J. Agronometrol.* 2008, 29, 432–435.

70. Yang, D.; Xu, X.; Liu, X.; Xu, Q.; Ding, G.; Cheng, X.; Chen, H.; Zhou, H.; Wang, Z.; Wang, W. Complex sources of air-soil-water pollution processes in the Miyun reservoir region. *Sci. China Earth Sci.* 2005, 16, 230–245

71. Jiao, J.; Liu, B.Y.; Du, P.F.; Yang, Y.; Duan, X.W.; Lang, C. Seasonal variation of nutrients in rivers of the upper-river basin of miyun reservoir. *J. Soil Water Conserv.* 2013, 4, 12–17

72. Wei, J.; Zheng, X.; Zhang, G.; Zhang, Y.; Wang, C.; Wang, R. Nitrogen and phosphorus content of surface water in the upstream basin of Guanting Reservoir and Miyun Reservoir. *Environ. Eng.* 2020, 38, 101–144. (In Chinese)

73. Wang, A.; Yang, D.; Tang, L. Spatiotemporal variation in nitrogen loads and their impacts on river water quality in the upper Yangtze River basin. *J. Hydrol.* 2020, 590, 125487. [CrossRef]

74. Freire, L.L.; Costa, A.C.; Lima Neto, I.E. Spatio-temporal patterns of river water quality in the semiarid northeastern Brazil. *Water Air Soil Pollut.* 2021, 232, 452. [CrossRef]

75. Wang, Q.; Sun, D.; Hao, W.; Gu, Y.; Li, Y.; Mei, X.; Zhang, Y. Nitrate concentration distribution in groundwater of the Miyun Reservoir Watershed (In Chinese). *Acta Pedol. Sin.* 2011, 48, 141–150.

76. Zhang, F.; Wang, J.; Zhang, W.; Cui, Z.; Ma, W.; Chen, X.; Jiang, R. Nutrient use efficiencies of major cereal crops in China and their impacts on river water quality. *Environ. Sci. China Earth Sci.* 2020, 29, 11–14. (In Chinese)

77. Monaghan, R.M.; Wilcock, R.J.; Smith, L.C.; Tikkisetty, B.; Thorrold, B.S. Linkages between land management activities and water quality in an intensively farmed catchment in southern New Zealand. *Agric. Ecosyst. Environ.* 2007, 118, 211–222. [CrossRef]

78. Schilling, K.E.; Jones, C.S.; Seeman, A.; Bader, E.; Filipiak, J. Nitrate-nitrogen patterns in engineered catchments in the upper Mississippi River Basin. *Ecol. Eng.* 2012, 42, 1–9. [CrossRef]

79. Ulrich, K.U.; Paul, L.; Meybohm, A. Response of drinking-water reservoir ecosystems to decreased acidic atmospheric deposition in SE Germany: Trends of chemical reversal. *Environ. Pollut.* 2006, 141, 42–53. [CrossRef]

80. Stalnacke, P.; Grimvall, A.; Libiseller, C.; Laznik, M.; Kokorite, I. Trends in nutrient concentrations in Latvian rivers and the response to the dramatic change in agriculture. *J. Hydrol. Amst.* 2003, 283, 184–205. [CrossRef]

81. Laane, R. Applying the critical load concept to the nitrogen load of the river Rhine to the Dutch coastal zone. *Estuar. Coast. Shelf Sci.* 2005, 62, 487–493. [CrossRef]

82. Angeli, N.; Dambrine, E.; Boudot, J.P.; Nedeltcheva, T.; Guérolod, F.; Tixier, G.; Bourrie, G. Evaluation of streamwater composition changes in the Vosges Mountains (NE France): 1955–2005. *Sci. Total Environ.* 2009, 407, 4378–4386. [CrossRef] [PubMed]

83. Bowes, M.J.; Smith, J.T.; Neal, C.; Leach, D.V.; Scarlett, P.M.; Wickham, H.; Armstrong, L.K.; Davy-Bowker, J.; Haft, M. Changes in water quality of the River Frome (UK) from 1965 to 2009: Is phosphorus mitigation finally working? *Sci. Total Environ.* 2011, 409, 3418–3430. [CrossRef]

84. Hester, E.T.; Brooks, K.E.; Scott, D.T. Comparing reach scale hyporheic exchange and denitrification induced by instream restoration structures and natural streambed morphology. *Ecol. Eng.* 2018, 115, 105–121. [CrossRef]

85. Preiner, S.; Dai, Y.; Pucher, M.; Reitsema, R.E.; Hein, T. Effects of macrophytes on ecosystem metabolism and net nutrient uptake in a groundwater fed lowland river. *Sci. Total Environ.* 2020, 721, 137620. [CrossRef]

86. Prior, K. *In-Stream Nitrogen Processing and Dilution in An Agricultural Stream Network;* The University of Iowa: Iowa City, IA, USA, 2015.

87. Driscoll, C.T.; Dreason, R. Seasonal and long-term temporal patterns in the chemistry of Adirondack lakes. *Water Air Soil Pollut.* 1993, 67, 319–344. [CrossRef]

88. Mitchell, M.J.; Driscoll, C.T.; Kahil, J.S.; Likens, G.E.; Murdoch, P.S.; Pardo, L.H. Climatic control of nitrate loss from forested watersheds in the Northeast United States. *Environ. Sci. Technol.* 1996, 30, 2609–2612. [CrossRef]

89. Stoddard, J.L.; Kellogg, J.H. Trends and patterns in lake acidification in the State of Vermont: Evidence from the Long-Term Monitoring Project. *Water Air Soil Pollut.* 1993, 67, 301–317. [CrossRef]

90. Foster, N.W.; Nicholson, J.A.; Hazlett, P.W. Temporal variation in nitrate and nutrient cations in drainage waters from a deciduous forest. *J. Environ. Qual.* 1989, 18, 238–244. [CrossRef]

91. Murdoch, P.S.; Stoddard, J.L. Chemical characteristics and temporal trends in eight streams of the Catskill Mountains, New York. *Water Air Soil Pollut.* 1993, 67, 367–395. [CrossRef]

92. Li, M.; Xu, K.; Watanabe, M.; Chen, Z. Long-term variations in dissolved silicate, nitrogen, and phosphorus flux from the Yangtze River into the East China Sea and impacts on estuarine ecosystem. *Estuar. Coast. Shelf Sci.* 2007, 71, 3–12. [CrossRef]

93. Duan, S.; Liang, T.; Zhang, S.; Wang, L.; Chen, X. Seasonal changes in nitrogen and phosphorus transport in the lower Changjiang River before the construction of the Three Gorges Dam. *Estuar. Coast. Shelf Sci.* 2008, 79, 239–250. [CrossRef]

94. Zheng, B.H.; Cao, C.J.; Qin, Y.W.; Huang, M.S. Analysis of nitrogen distribution characters and their sources of the major input rivers of Three Gorges Reservoir. *Environ. Sci.* 2008, 29, 1–6. (In Chinese)
95. King, K.W.; Hanrahan, B.R.; Stinner, J.; Shedekar, V.S. Field scale discharge and water quality response, to drainage water management. *Agric. Water Manag.* 2022, 264, 107421. [CrossRef]

96. Chen, J.; Gao, X.; He, D.; Xia, X. Nitrogen contamination in the Yangtze River system, China. *J. Hazard. Mater.* 2000, 73, 107–113.

97. Howden, N.; Burt, T.P. Temporal and spatial analysis of nitrate concentrations from the Frome and Piddle catchments in Dorset (UK) for water years 1978 to 2007: Evidence for nitrate breakthrough? *Sci. Total Environ.* 2008, 407, 507–526. [CrossRef]

98. Rusjan, S.; Miko, M. Seasonal variability of diurnal in-stream nitrate concentration oscillations under hydrologically stable conditions. *Biogeochemistry* 2010, 97, 123–140. [CrossRef]

99. Seitzinger, S.P. Denitrification in freshwater and coastal marine ecosystems: Ecological and geochemical significance. *Limnol. Oceanogr.* 1988, 33, 702–724. [CrossRef]

100. Clark, M.J.; Cresser, M.S.; Smart, R.; Chapman, P.J.; Edwards, A.C. The influence of catchment characteristics on the seasonality of carbon and nitrogen species concentrations in upland rivers of Northern Scotland. *Biogeochemistry* 2004, 68, 1–19. [CrossRef]

101. Arheimer, B.; Andersson, L.; Lepist, A. Variation of nitrogen concentration in forest streams—Influences of flow, seasonality and catchment characteristics. *J. Hydrol.* 1996, 179, 281–304. [CrossRef]

102. Neal, C.; Davies, H.; Neal, M. Water quality, nutrients and the water framework directive in an agricultural region: The lower Humber Rivers, northern England. *J. Hydrol.* 2008, 350, 232–245. [CrossRef]

103. Liu, H.; Meng, C.; Wang, Y.; Li, Y.; Wu, J. From landscape perspective to determine joint effect of land use, soil, and topography on seasonal stream water quality in subtropical agricultural catchments. *Sci. Total Environ.* 2021, 783, 147047. [CrossRef] [PubMed]

104. Wu, J.; Lu, J. Spatial scale effects of landscape metrics on stream water quality and their seasonal changes. *Water Res.* 2021, 191, 116811. [CrossRef] [PubMed]