Annual nitrate load patterns in an agricultural watershed in consecutive dry years

Shuai Chen a,b and Xiaohong Ruan a,b,*

a Key Laboratory for Surficial Geochemistry of the Ministry of Education, Nanjing University, Nanjing 210023, China
b School of Earth Sciences and Engineering, Nanjing University, Nanjing 210023, China
*Corresponding author. E-mail: ruanxh@nju.edu.cn

ABSTRACT

Nitrate (NO₃-N) load characteristics in consecutive dry years in the Huai River Basin (HRB), China, were examined using streamflow and NO₃-N concentration data. The data set spanned 12 years including three consecutive dry years. Baseflow separation, load estimation, and nonparametric linear regression were applied to separate point source (PS), baseflow, and surface runoff NO₃-N loads from the total load. The mean annual nonpoint source (NPS) load was 2.84 kg·ha⁻¹·yr⁻¹, accounting for 90.8% of the total load. Baseflow contributed approximately one-fourth of the natural runoff and half of the NPS load. The baseflow nitrate index (i.e., the ratio of baseflow NO₃-N load to total NPS NO₃-N load) was 25.4% higher in consecutive dry years than in individual dry years. This study demonstrated that baseflow is the preferential hydrological pathway for NO₃-N transport in the HRB and that baseflow delivers a higher NO₃-N percentage to streams under long-term drought than under short-term drought. This study highlights the alarming evidence that continuous drought caused by climate change may lead to a higher rate of nitrogen loss in agricultural watersheds.

Key words: agricultural watershed, baseflow, baseflow enrichment ratio, consecutive dry years, Huai River Basin, nitrate load

HIGHLIGHTS

• Baseflow is the preferential hydrological pathway for nitrate transport in the Huai River Basin.
• Baseflow delivers a higher percentage of nitrate to streams in consecutive dry years than in individual dry years.
• The combination of baseflow separation, load estimation, and nonparametric linear regression provides a convenient method to differentiate the nitrate load from different sources.

INTRODUCTION

The Huai River Basin (HRB), where the annual nitrogen fertilizer application rates amount to approximately 600 kg·N·ha⁻¹·yr⁻¹, is one of the major grain-producing areas in China. Nitrogen fertilizers have been identified as the main contributor to the increases in the nitrate-nitrogen (NO₃-N) concentration in groundwater in agricultural watersheds (Czekaj et al. 2016; Coskun et al. 2017; Paladino et al. 2020; Wu et al. 2021), and the HRB is no exception (Ju & Zhang 2017). The NO₃-N concentration in groundwater below agricultural fields is generally much higher than in surface waters (Almasri & Kaluarachchi 2004). This NO₃-N in groundwater may be primarily transferred to surface waters under baseflow conditions (He & Lu 2016; Richards et al. 2021). However, apart from Chen (2013) and Chen et al. (2017), who estimated the NO₃-N load in groundwater discharge in a small subbasin, few researchers have reported the long-term baseflow contributions to the nonpoint source (NPS) NO₃-N loads in streamflows in the HRB. Therefore, it is necessary to quantify the NPS NO₃-N loads and baseflow contribution for NPS NO₃-N assessment and management of the HRB.

Climate change is likely to make hydrological regimes more extreme, with wet seasons becoming wetter and dry seasons becoming drier. The runoff from the upper and middle HRB has decreased over the last 60 years because of regional climate change and human activities, implying that the risks and intensity of droughts have increased (An & Hao 2017). Consecutive dry years, such as those occurring from 2011 to 2013, will probably occur more frequently in the future. These changes may influence the temporal variations in NPS NO₃-N loads. Many researchers have reported that the NO₃-N loads transported from agricultural watersheds to surface
waters are low in low-flow periods, owing to the reduced runoff, but will increase after droughts end (Schilling & Zhang 2004). However, few studies focus on the impact of long-term droughts persisting over many years on base-flow NO$_3$-N loads. If carrying much NO$_3$-N, baseflow as the main source of environmental flow in dry periods (de Graaf et al. 2019) may threaten the health of riverine ecosystems under long-term drought. Within the context of climate change, to support the development of effective policies to manage the water quality, such as total maximum daily load programs and best management practices, the impact of consecutive dry years on baseflow NO$_3$-N loads needs to be evaluated.

Traditionally, constituent loads are calculated as the product of the discharge volume and constituent concentration in water. However, no direct approach exists at present to continuously measure baseflow and the constituent concentration in baseflow. One of the common methods is to estimate the baseflow NO$_3$-N load by assuming the streamflow NO$_3$-N concentration, with a baseflow index (BFI, i.e., the ratio of baseflow to total streamflow) $\geq 90$ or 80% as the real baseflow concentration combined with baseflow separating methods and load estimation programs (e.g., LOADEST; Runkel et al. 2004; He & Lu 2016). However, this method may be problematic when applied to regions where the point source (PS) NO$_3$-N load cannot be neglected, because the assumed baseflow NO$_3$-N concentration (i.e., streamflow NO$_3$-N concentration at BFI $\geq 90$ or 80%) consists of both PS and baseflow contributions. Therefore, the PS NO$_3$-N load needs to be quantified when applying this method to estimate the baseflow NO$_3$-N load. However, it is difficult to directly quantify the PS contributions for regions like the HRB, where the NO$_3$-N concentration is not a routine monitoring item of sewage outfalls, in addition to the influence of the chemical and biological transformations between the source and monitoring station (Albek 2003). Albek (2003) provided an indirect method – the Kendall–Theil robust line (KTRL) regression method (Helsel & Hirsch 1992) – to estimate the PS constituent load based on discharge and concentration data measured at monitoring stations. This approach assumes that the PS constituent load remains constant over a given period and is estimated as the slope of the KTRL. In this study, the NO$_3$-N loads consisting of PS, baseflow, and surface runoff contributions at the outlet of the upper and middle HRB were estimated via a combination of baseflow separation, load estimation, and KTRL regression, as described above.

The main objectives of this study are to (1) quantify the total NPS NO$_3$-N loads exported from the upper and middle HRB and quantify the baseflow contribution, (2) identify the preferential hydrological pathway of NO$_3$-N transport, and (3) evaluate the impact of consecutive dry years on the baseflow NO$_3$-N loads.

**STUDY AREA AND DATA**

**Watershed description**

The study site is the watershed above the Bengbu Hydrometric Station (Figure 1). The area of the watershed is 121,330 km$^2$. The study area mainly comprises hills and flatlands, which account for 71% of the watershed area. The quaternary layers have a thickness ranging from 50 to 200 m and mainly consist of fluvial and lacustrine loose sediments. The main aquifer is the quaternary unconsolidated rock, which is separated into shallow and deep aquifers by a thick layer of clayey soil. The thickness of shallow aquifer ranges from 50 to 60 m and the buried depth of shallow groundwater ranges from 2 to 6 m (Ge et al. 2006). The mean annual precipitation is 911 mm. The flood season lasts from June to September, and the dry season lasts from December to February. Rainfall accounts for 60% of the annual precipitation in the flood season (Figure 1(d)).

In general, most of the rivers are recharged by groundwater all year round (Pan 2014). Figure 2 shows the monthly river stages measured at four gauging stations (Figure 1(c)) from 2011 to 2012 and the nearby groundwater levels. It is evident that the groundwater levels are higher than surface water levels.

The agriculture, urban, and forest land account for 70.1, 14.2, and 6.8% of the watershed area, respectively. As a major grain-producing area in China, the study area is dominated by dry land crops and the application rate of chemical fertilizer (600 kg·ha$^{-1}$·yr$^{-1}$) ranks first in the country (Ju & Zhang 2017). Agricultural food processing, leather manufacturing, and papermaking are the main industries in this area.

**Data**

This study is based on daily stream discharge data collected from 2007 to 2018 at the Bengbu Station, which is operated by the Huai River Commission of the Water Resources Ministry of the P.R.C. The baseflow was extracted from the streamflow using the digital filter method. The wastewater discharge data originated from
the Huai River Water Resources Bulletin (http://www.hrc.gov.cn). The precipitation data were downloaded from the National Meteorological Information Center (http://data.cma.cn/site).

A total of 128 surface water samples were collected at the Bengbu Station from 2007 to 2018, either monthly or bimonthly. Groundwater quality samples were collected from 122 phreatic wells (Figure 1(c)) in both the flood and non-flood seasons between 2007 and 2018, excluding 2013. The NO$_3$-N concentrations were determined
in the laboratory by ultraviolet spectrophotometry (detection limit = 0.08 mg/L). The NO$_3$-N concentration in the surface water samples ranged from 0.31 to 4.45 mg/L, with an average of 2.05 mg/L (Figure 3(a)). It was generally the highest when the streamflow was low. The result of a seasonal Kendall test (Helsel & Hirsch 1992) suggests that from 2007 to 2018, the streamflow NO$_3$-N concentration exhibited no significant temporal trend ($p > 0.05$), indicating that the entire data set could be grouped together for analysis purposes. The streamflow NO$_3$-N concentration on days when BFI $> 90\%$ was assumed to be caused by the PS and baseflow NO$_3$-N loads. This NO$_3$-N concentration ranged from 1.52 to 4.45 mg/L with an average of 2.86 mg/L. The annual average groundwater NO$_3$-N concentration over the 122 monitoring wells (Figure 1(c)) ranged from 4.12 mg/L in 2017 to 9.34 mg/L in 2008 (Figure 3(b)). The maximum groundwater NO$_3$-N concentration reached 75.9 mg/L. This was much higher than the surface water NO$_3$-N concentration.

**METHODOLOGY**

**Overall procedures**

In this study, the total streamflow was assumed to be composed of discharge from sewage outfalls, baseflow, and surface runoff. The discharge from sewage outfalls was termed as anthropogenic PS discharge, and the total discharge subtracted by the anthropogenic PS discharge was termed as natural discharge (i.e., baseflow plus surface runoff). Anthropogenic PS discharge can obscure the contributions from surface runoff and baseflow to a streamflow hydrograph when using digital filter methods (Barlow et al. 2015). Therefore, the anthropogenic PS discharge was removed from the total flow before baseflow separation. Baseflow was separated from the natural streamflow using the recursive digital filter method proposed by Eckhardt (2005). The total NO$_3$-N load consisted of PS and NPS contributions (i.e., anthropogenic PS discharge and the natural streamflow, respectively). First, the total load and the PS and baseflow loads were estimated using regression estimator LOADEST (Runkel et al. 2004). This regression estimator assumes that the relationship between the logarithms of the constituent concentration and discharge is approximately linear (Cohn et al. 1989). Second, the PS load was estimated using the method proposed by Albek (2003) with confining conditions. Finally, the surface runoff load and baseflow load were extracted from the total load and the PS and baseflow loads, respectively. For the purpose of comparison, the annual discharges were converted into millimeter, and the annual loads were calculated as the average daily load multiplied by the number of days per year and divided by the drainage area, including the PS discharge and PS load.

![Figure 3](image)

**Figure 3** | (a) Time series of the daily baseflow and surface runoff and streamflow NO$_3$-N concentrations observed at the Bengbu Station from 2007 to 2018 and (b) annual variations in the spatially averaged (over all the groundwater monitoring sites) groundwater NO$_3$-N concentration. SEM, standard error of mean.
Baseflow separation

The natural flow was extracted from the total flow before baseflow separation:

\[ Q_{n,k} = Q_{t,k} - Q_b \]  

(1)

where \( Q_n \) is the natural streamflow, \( k \) is the time step, \( Q_t \) is the total streamflow, and \( Q_b \) is the PS discharge, which remains constant over a given period. Assuming that the outflow from an aquifer is linear to its storage (Eckhardt 2008), the recursive digital filter method divides the natural flow into surface runoff and baseflow. The filter is expressed as follows:

\[ Q_{b,k} = \frac{(1 - BFImax)\alpha Q_{b,k-1} + (1 - \alpha)BFImaxQ_{n,k}}{1 - \alpha BFImax} \]  

(2)

\[ Q_{s,k} = Q_{n,k} - Q_{b,k} \]  

(3)

The filter is subject to \( Q_{b,k} \leq Q_{n,k} \), where \( Q_b \) is the baseflow, \( Q_s \) is the surface runoff, \( BFImax \) and \( \alpha \) are filter parameters. The filter parameter \( BFImax \) was set to 0.8 in this study, which, according to Eckhardt (2005), is suitable for perennial streams and porous aquifers. Filter parameter \( \alpha \) was set to 0.9982, which was determined by recession analysis according to Eckhardt (2008).

\[ NO_3-N \text{ load estimation} \]

Two user-defined regression models were built in LOADEST to estimate the total \( NO_3-N \) load (Model 1) and the PS and baseflow \( NO_3-N \) loads (Model 2), as described in the following equations, respectively (Runkel et al. 2004):

\[ L_t = \exp(a_0 + a_1\ln(Q_t) + a_2 \ln(BFI) + a_3 \ln(P_L) + a_4 \sin(2\pi\bar{d}_{time}) + a_5 \cos(2\pi\bar{d}_{time}) + a_6 \bar{d}_{time})g_t \]  

(4)

\[ L_{pb} = \exp(b_0 + b_1\ln(Q_p + Q_b) + b_2 \ln(P_L) + b_3 \sin(2\pi\bar{d}_{time}) + b_4 \cos(2\pi\bar{d}_{time}) + b_5 \bar{d}_{time})g_{pb} \]  

(5)

where \( a_0 \) and \( b_0 \) are model coefficients, \( L_t \) is the estimated total \( NO_3-N \) load, \( L_{pb} \) is the estimated \( NO_3-N \) load consisting of PS and baseflow contributions, \( g_t \) and \( g_{pb} \) are bias correction factors, \( \ln(Q_t) \), \( \ln(BFI) \), \( \ln(P_L) \), and \( \sin(2\pi\bar{d}_{time}) \) are the centered values of the natural logarithms of the total streamflow, \( BFI \), annual precipitation in the last year, and summation of the PS discharge and baseflow, respectively. \( \bar{d}_{time} \) is the centered decimal time. The explanatory variables are centered to eliminate collinearity, and the center of a variable can be found in Runkel et al. (2004).

The explanatory variables in Model 1 (Equation (4)) are chosen to consider the influence of the total streamflow, \( BFI \), antecedent precipitation, and seasonal factors, such as agricultural activities and temperature, which are major drivers of biological, chemical, and physical processes. Model 2 (Equation (5)) considers the influence of baseflow, antecedent precipitation, and seasonal factors. The model coefficients (\( a_i \) and \( b_j \)) in Equations (4) and (5) were calculated using the maximum likelihood estimator (MLE) (Cohn et al. 1989). The MLE assumes that the model residuals follow a normal distribution with a constant variance. The calibration period ranged from 2007 to 2018. The coefficients in Model 1 were calibrated by the streamflow \( NO_3-N \) concentration (\( n = 128 \)). The coefficients in Model 2 were calibrated by the streamflow \( NO_3-N \) concentration on days when the \( BFI \) was between 90 and 100\% (\( n = 35 \)).

The PS \( NO_3-N \) load was estimated based on the mass balance (Albek 2003):

\[ C_t Q_t = C_p Q_p + C_n Q_n \]  

(6)

where \( C_t \), \( C_p \), and \( C_n \) are the \( NO_3-N \) concentrations in the total streamflow, PS discharge, and natural runoff, respectively. If the total streamflow is much greater than the PS discharge (i.e., \( Q_t \gg Q_p \)), \( Q_n \) can be replaced by \( Q_t \) and Equation (6) can be written as follows:

\[ C_t = L_{p,KTRL} / Q_t + C_n \]  

(7)
where \( L_{p,\text{KTRL}} = C_p Q_p \), which is the initially estimated PS NO\(_3\)-N load and is constant over a given period. This can be estimated by linear regression of \( C_t \) against \( 1/Q_t \). For nonparametric linear regression, the KTR has been recommended to eliminate the effects of data outliers and to avoid any restrictions posed by normality assumptions (Helsel & Hirsch 1992). In this study, \( L_{p,\text{KTRL}} \) was estimated in three time periods (2007–2010, 2011–2013, and 2014–2018) to account for the annual variations in the PS NO\(_3\)-N load.

Assuming that the PS NO\(_3\)-N load will remain constant over a given period and should be no higher than the NO\(_3\)-N loads consisting of PS and baseflow contributions (\( L_{pb} \)), the upper limit of the PS NO\(_3\)-N load for a given year can be written as follows:

\[
L_{p,u}(i) = \min \{ L_{pb}, j | 1 \leq j \leq 365 \text{ or } 366 \} \quad i = 2007, 2008, \ldots, 2018
\]

(8)

where \( L_{p,u} \) is the upper limit of the PS NO\(_3\)-N load, \( i \) is the year, and \( j \) is the \( j \)th day of year \( i \). Finally, the PS NO\(_3\)-N load in this study is estimated as follows:

\[
L_p(i) = \min \{ L_{p,\text{KTRL}}(i), L_{p,u} \} \quad i = 2007, 2008, \ldots, 2018
\]

(9)

where \( L_p \) is the final result of the PS NO\(_3\)-N load estimation.

The surface runoff, baseflow, and total NPS NO\(_3\)-N loads are estimated as follows:

\[
L_s = L_t/C_0
\]

\[
L_b = L_{pb}/C_0
\]

\[
L_n = L_s + L_b = L_t/C_0
\]

(10) (11) (12)

where \( L_s, L_b, \) and \( L_n \) are the estimated surface runoff, baseflow, and total NPS NO\(_3\)-N loads, respectively.

The baseflow nitrate index (BFNI, i.e., the ratio of baseflow NO\(_3\)-N load to total NPS NO3-N load) is calculated as follows:

\[
BFNI = \frac{L_b}{L_n} \times 100\%
\]

(13)

where BFNI represents the baseflow contribution to the total NPS NO\(_3\)-N load. The baseflow enrichment ratio (BER) is used to describe the preferential pathway of NO\(_3\)-N transport (Schilling & Zhang 2004). The BER is calculated as follows:

\[
BER = \frac{BFNI}{BFI}
\]

(14)

If NO\(_3\)-N essentially followed the water flow, then the BFNI would be equal to the BFI and the BER would equal 1. A BER value greater than 1 implies that NO\(_3\)-N is preferentially leached into groundwater and carried by the baseflow to streams.

**RESULTS**

**Parameters calibration**

The coefficients for Model 1 (Equation (4)) and Model 2 (Equation (5)) are presented in Table 1. The scatter plots of the observed load versus the estimated load are shown in Figure 4(a) and 4(b), and the correlation coefficients for Models 1 and 2 were all larger than 0.85. The scatter plots and normal probability plots for the model residuals (Figure 4(c)–4(f)) indicate that the residuals of the two models adhere to the normal distribution and constant variance assumptions of the MLE. The significance level \( (p > 0.05) \) of the independent-sample \( t \)-test for the model residuals in the consecutive dry years (2011–2013) versus the other years indicates that climate conditions exhibited no significant differences between the consecutive dry years and the other years to the models. Therefore, it is appropriate to fit only one model for the entire study period when estimating the total NO\(_3\)-N load or the PS and baseflow NO\(_3\)-N loads. The bias percentage (Bp), Nash–Sutcliffe efficiency (NSE), and ratio of the root mean square error to the standard deviation of the measured data (RSR) were –2.53, 0.773, and 0.428 for
Model 1, respectively, and 0.629, 0.755, and 0.443 for Model 2, respectively. The accuracy of the model simulations obtained in this study was satisfactory according to Moriasi et al. (2007), who recommended that model simulations could be considered satisfactory when NSE >0.50 and RSR ≤0.70.

Baseflow

The mean annual precipitation and runoff in the upper and middle reaches of the HRB were 932.7 and 237.2 mm, respectively, during our study period. The annual runoff series (1956–2018) were analyzed via frequency analysis based on the Pearson Type III distribution to identify the annual hydrological patterns in the study area. The results indicate that the period from 2011 to 2013 was continuously dry, 2009 was also dry, 2007 and 2017 were wet, and the other years were normal.

From 2007 to 2018, the annual PS discharge increased from 14.6 to 22.5 mm (Table 2). The mean annual PS discharge was 17.5 mm, accounting for 9.0% of the total discharge (194.6 mm). The mean annual baseflow and surface runoff were 47.1 and 130.0 mm, accounting for 19.5 and 71.5% of the total discharge, respectively. Because of the reduced precipitation, the baseflow and surface runoff were lower in the consecutive dry years (2011–2013) than in the individual dry year (2009) and the other normal or wet years (Figure 5(a)). The coefficient of variance (CV) of the daily baseflow and surface runoff was 1.25 and 1.80, respectively. This result suggests that the baseflow was less variant than the surface runoff. Over the study period, the annual BFI ranged from 20.3 to 34.6% with an average of 26.6%. The BFI was the highest in the consecutive dry years, with an average of 33.0%, which was higher than the BFI in the individual dry year (24.6%) and the mean annual BFI (Figure 5(c)). In general, the BFI tended to increase in drier years because less precipitation was routed to streams as surface runoff, while the baseflow remained relatively steady.

PS NO3-N load

The PS NO3-N loads estimated by KTRL regression ($L_{pKTRL}$) were 23.6, 10.5, and 4.1 t/d for the time periods of 2007–2010, 2011–2013, and 2014–2018, respectively (Figure 6). The upper limit of the PS NO3-N load is shown in Figure 7. It decreased from 17.5 t/d in 2007 to 11.1 t/d in 2018. The final PS load ($L_p$), estimated from Equation (9), ranged from 17.5 t/d (0.55 kg·ha$^{-1}$·yr$^{-1}$) to 4.1 t/d (0.12 kg·ha$^{-1}$·yr$^{-1}$), which also exhibited a decreasing trend (Table 2; Figure 5(b)). It decreased by 77% from 2007 to 2018. The mean annual PS load was 9.7 t/d (0.29 kg·ha$^{-1}$·yr$^{-1}$), which accounted for 9.2% of the total load, and the mean annual PS load in the consecutive dry years was 10.6 t/d (0.32 kg·ha$^{-1}$·yr$^{-1}$), which accounted for 22.2% of the total load. Because of the reduced natural runoff in the consecutive dry years, the NPS load decreased, but the proportion of the PS load increased.

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**Table 1** | Model coefficients, regression statistics, and bias diagnostics for Models 1 and 2

| Items         | Model 1                     | Model 2                     |
|---------------|-----------------------------|-----------------------------|
| Model coefficients | $a_0 = 9.651$; $a_1 = 0.908$; $a_2 = 0.006$; $a_3 = 0.243$; $a_4 = -0.256$; $a_5 = 0.409$; $a_6 = 0.017$ | $b_0 = 13.453$; $b_1 = 0.995$; $b_2 = -0.434$; $b_3 = 0.055$; $b_4 = -0.014$; $b_5 = 0.191$ |
| Regression statistics | $R^2 = 0.834$ | $R^2 = 0.839$ |
| $S^2$          | 0.166                       | 0.049                       |
| PPCC           | 0.991                       | 0.993                       |
| $p^a$          | 0.967                       | 0.907                       |
| $p^b$          | 0.421                       | 0.126                       |
| Bias diagnostics | $Bp = -2.53$                | $Bp = 0.629$                |
| $NSE$          | 0.773                       | 0.755                       |
| $RSR$          | 0.428                       | 0.443                       |

*aThe PPCC test is at a significance level of 0.05.

*bThe independent-sample t-test for the model residuals in the consecutive dry years versus the other years at a significance level of 0.05.

$R^2$, coefficient of determination; $S^2$, residual variance; PPCC, probability plot correlation coefficient; $Bp$, bias percentage; $NSE$, Nash–Sutcliffe efficiency index; $RSR$, ratio of the root mean square error to the standard deviation of the measured data.
Figure 4 | (a,b) Scatter plots of the observed load versus the estimated load; (c,d) model residuals versus estimates of the log load; and (e,f) normal probability plots for the model residuals.
Table 2 | Summary of the annual precipitation, PS discharge and NO₃-N load, natural runoff, and NPS NO₃-N load

| Year | Annual precipitation (mm) | PS discharge (mm) | Baseflow | Surface runoff | Total natural runoff | BFI (%) | PS nitrate load (kg·ha⁻¹ yr⁻¹) | Baseflow | Surface runoff | Total Nonpoint source | BFNI (%) | BFI (%) |
|------|---------------------------|-------------------|----------|----------------|----------------------|---------|-----------------------------|----------|----------------|----------------------|---------|---------|
| 2007 | 989.9                     | 14.6              | 87.4     | 219.2          | 306.6                | 28.5    | 0.53                        | 2.14     | 1.35           | 3.49                 | 61.2    | 2.15    |
| 2008 | 947.6                     | 14.6              | 63.9     | 152.4          | 216.2                | 29.5    | 0.51                        | 1.50     | 1.31           | 2.81                 | 53.3    | 1.81    |
| 2009 | 887.4                     | 16.0              | 27.9     | 85.5           | 113.4                | 24.6    | 0.47                        | 0.70     | 0.88           | 1.58                 | 44.2    | 1.80    |
| 2010 | 974.7                     | 16.5              | 59.5     | 190.4          | 250.0                | 23.8    | 0.45                        | 1.63     | 1.97           | 3.60                 | 45.2    | 1.90    |
| 2011 | 800.5                     | 16.6              | 22.0     | 43.4           | 65.3                 | 33.6    | 0.32                        | 0.71     | 0.40           | 1.12                 | 63.8    | 1.90    |
| 2012 | 769.6                     | 17.0              | 26.0     | 49.2           | 75.1                 | 34.6    | 0.32                        | 0.96     | 0.25           | 1.21                 | 79.2    | 2.29    |
| 2013 | 748.1                     | 16.8              | 16.3     | 38.1           | 54.4                 | 29.9    | 0.32                        | 0.67     | 0.36           | 1.03                 | 65.3    | 2.18    |
| 2014 | 939.6                     | 17.5              | 34.0     | 99.4           | 133.3                | 25.5    | 0.12                        | 1.26     | 0.93           | 2.19                 | 57.4    | 2.25    |
| 2015 | 934.4                     | 17.7              | 52.4     | 146.2          | 198.6                | 26.4    | 0.12                        | 1.70     | 1.80           | 3.50                 | 48.5    | 1.84    |
| 2016 | 1,114.7                   | 18.4              | 42.4     | 166.5          | 209.0                | 20.3    | 0.12                        | 1.39     | 2.32           | 3.71                 | 37.5    | 1.85    |
| 2017 | 997.4                     | 21.6              | 76.1     | 202.0          | 278.1                | 27.3    | 0.12                        | 1.97     | 3.08           | 5.05                 | 39.0    | 1.42    |
| 2018 | 1,053.0                   | 22.5              | 57.1     | 168.1          | 225.2                | 25.4    | 0.12                        | 1.86     | 2.98           | 4.84                 | 38.4    | 1.51    |

**Average over the consecutive dry years**

| Year | Annual precipitation (mm) | PS discharge (mm) | Baseflow | Surface runoff | Total natural runoff | BFI (%) | PS nitrate load (kg·ha⁻¹ yr⁻¹) | Baseflow | Surface runoff | Total Nonpoint source | BFNI (%) | BFI (%) |
|------|---------------------------|-------------------|----------|----------------|----------------------|---------|-----------------------------|----------|----------------|----------------------|---------|---------|
|      | **772.8**                 | **16.8**          | **21.4** | **43.5**       | **64.9**             | **33.0**| **0.32**                    | **0.78** | **0.54**       | **1.12**             | **69.8**| **2.12**|

**Mean annual average**

| Year | Annual precipitation (mm) | PS discharge (mm) | Baseflow | Surface runoff | Total natural runoff | BFI (%) | PS nitrate load (kg·ha⁻¹ yr⁻¹) | Baseflow | Surface runoff | Total Nonpoint source | BFNI (%) | BFI (%) |
|------|---------------------------|-------------------|----------|----------------|----------------------|---------|-----------------------------|----------|----------------|----------------------|---------|---------|
|      | **929.7**                 | **17.5**          | **47.1** | **130.0**      | **177.1**            | **26.6**| **0.29**                     | **1.37** | **1.47**       | **2.84**             | **48.3**| **1.82**|

Note: The bold and italic rows denote the consecutive dry years.
Figure 5 | (a) Annual discharge of PS ($Q_p$), baseflow ($Q_b$), and surface runoff ($Q_s$) in the study period (2007–2018), (b) annual NO$_3$-N loads contributions of PS ($L_p$), baseflow ($L_b$), and surface runoff ($L_s$), and (c) annual BFI. SEM, standard error of mean.

Figure 6 | KTRL regression between the streamflow NO$_3$-N concentration ($C_t$) and reciprocal of the total streamflow ($1/Q_t$) in the time periods of (a) 2007–2010, (b) 2011–2013, and (c) 2014–2018. The PS NO$_3$-N load ($L_p$, KTRL) was estimated as the slope of the KTRL, and $r$ is the Pearson correlation coefficient.
The total NPS NO$_3$-N loads ranged from 1.03 kg·ha$^{-1}$·yr$^{-1}$ in 2013 to 5.05 kg·ha$^{-1}$·yr$^{-1}$ in 2017 and averaged 2.84 kg·ha$^{-1}$·yr$^{-1}$ (Table 2). Over the study period, the NPS loads accounted for 90.8% of the total loads discharged from the study area. The temporal variations in the NPS loads were mainly controlled by the rainfall–runoff process, i.e., the NPS load often reached a maximum when the discharges were high (Figure 5(a) and 5(b)). The baseflow NO$_3$-N load ranged from 0.67 to 2.14 kg·ha$^{-1}$·yr$^{-1}$ and averaged 1.37 kg·ha$^{-1}$·yr$^{-1}$, while the surface runoff NO$_3$-N load ranged from 0.25 to 3.08 kg·ha$^{-1}$·yr$^{-1}$ and averaged 1.47 kg·ha$^{-1}$·yr$^{-1}$ (Table 2). Baseflow and surface runoff contributed 43.8 and 47.0%, respectively, to the total load. The CV was 0.38 and 0.66 for the baseflow and surface runoff loads, respectively. This implies that the baseflow loads were less variable than the surface runoff loads.

The BFNI represents the baseflow contribution to the NPS NO$_3$-N load. It ranged from 37.5 to 79.2% and averaged 48.3% over the study period (Table 2; Figure 8(a)). The BFNI was the highest in the consecutive dry years with an average of 69.8%, which was higher than the BFNI in the individual dry year (44.2%) and the average over the study period (48.3%). The annual BER in the study area ranged from 1.42 to 2.29 and averaged 1.82 (Table 2; Figure 8(b)).

**DISCUSSION**

**PS and NPS NO$_3$-N load patterns**

Averaged over the 12-year study period, the PS, baseflow, and surface runoff NO$_3$-N load contributions were 0.29, 1.37, and 1.47 kg·ha$^{-1}$·yr$^{-1}$, accounting for 9.2, 43.8, and 47.0% of the total load, respectively. The NO$_3$-N exported from the upper and middle HRB was mainly attributed to NPSs.

Leather, paper, and chemical fertilizer industries are the main sources of PS NO$_3$-N load in this area (Li et al. 2016), and the denitrification of ammonia nitrogen from domestic sewage is an important indirect source (Ding et al. 2018). With the improvement of PS pollution control measures, such as the increase of wastewater treatment plants, the improvement of sewage treatment process, and the upgrading of wastewater discharge standards (He et al. 2015), the PS NO$_3$-N load declined by 77% from 2007 to 2018. This can also be interpreted from Figures 6 and 7. As shown in Figure 6, the slope of the KTRL and the Pearson correlation coefficient ($r$) between $C_t$ and 1/$Q_t$ decreased from 2007 to 2018, and the upper limit of the PS NO$_3$-N load in Figure 7 also reveals a decreasing trend. Because the NO$_3$-N concentration is not routinely monitored from the sewage outfalls, the estimated PS NO$_3$-N load cannot be directly verified. According to the Huai River Water Resources Bulletin (http://www.hrc.gov.cn), both the chemical oxygen demand and ammonia nitrogen (NH$_3$-N) emissions declined by approximately 70% from 2007 to 2018, which is close to the estimated decline of PS NO$_3$-N load (77%). This provides indirect evidence for the correctness of the estimated PS NO$_3$-N loads. In this study, the PS NO$_3$-N load was estimated based on the data collected at the monitoring station. It represents the exported NO$_3$-N load attributed to PSs, which was the result of PS NO$_3$-N transportation and the chemical and biological transformations of PS nitrogen (e.g., nitrification and denitrification) between the source and monitoring station (Albeck 2003).

The annual NPS NO$_3$-N load ranged from 1.03 to 5.05 kg·ha$^{-1}$·yr$^{-1}$ and averaged 2.84 kg·ha$^{-1}$·yr$^{-1}$. The mean annual baseflow NO$_3$-N load was 1.37 kg·ha$^{-1}$·yr$^{-1}$ and accounted for 48.3% of the NPS load. This is similar to...
the result reported for a subbasin in the study area (0.95 kg·ha⁻¹·yr⁻¹ for the baseflow NO₃-N load (Chen et al. 2017) and 40% for the BFNI (Chen 2013)). N fertilizers have been identified as the main source of NPS NO₃-N pollution in this agricultural watershed (Chen 2013; Ma et al. 2019). According to Ju et al. (2010), soil residual N and nitrate leaching accounted for about 27 and 30% of the fertilizer N (approximately 600 kg·N·ha⁻¹·yr⁻¹), respectively. The large amount of NO₃-N retained in the soil and that leached to groundwater will be transported to surface waters through surface runoff and baseflow. However, the NPS NO₃-N load was much lower in this study area than that in other agricultural watersheds worldwide (Table 3). This may occur due to the high nitrogen uptake rate of crops (Ju & Zhang 2017) and the high denitrification rate in the subsoil zone (Li et al. 2020) in the study area. The denitrification in the groundwater (Kolbe et al. 2019) and hyporheic zones (Harvey et al. 2013) probably also imposes significant impacts and needs to be further investigated in this watershed.

**Preferential hydrological pathway of NO₃-N transport**

Hydrological processes could be the dominant factors affecting N loss, such as baseflow (Schilling & Zhang 2004), tile drainage (Schilling & Wolter 2001; Deelstra et al. 2014), and wet deposition (Povilaitis et al. 2014). Various reports have indicated that baseflow is one of the dominant hydrological pathways for NO₃-N migration toward streams (He & Lu 2016). For example, the percentages of total NO₃-N load contributed by baseflow were 66, 59, 52, and 62% for the Raccoon River watershed in the USA (Schilling & Zhang 2004), the Corberia

**Table 3 |** The annual NPS NO₃-N load in this and worldwide studies

| Region                      | Agricultural land (%) | Annual runoff (mm) | NPS NO₃-N load (kg·ha⁻¹·yr⁻¹) | Citation                  |
|-----------------------------|-----------------------|--------------------|--------------------------------|---------------------------|
| Walnut Creek, USA           | 86                    | 69-865             | 4-66                           | Jaynes et al. (1999)      |
| Raccoon River, USA          | 76.2                  | 223                | 26                             | Schilling & Zhang (2004)  |
| Upper Sangamon River, USA   | 87                    | 300                | 26.4                           | Guo et al. (2002)         |
| Central Germany             | 66.2                  | 117                | 18.5-41.2                      | Rode et al. (2009)        |
| Nordic and Baltic countries | 35-99                 | 130-1,246          | 1.7-102.8                      | Deelstra et al. (2014)    |
| Huai River, China           | 70.1                  | 237.2              | 2.84                           | This study                |
watershed in Spain (Rodríguez-Blanco et al. 2013), the Mulgrave River watershed in Australia (Rasiah et al. 2013), and the Changle River watershed in China (He et al. 2020), respectively. In the upper and middle HRB, the baseflow only accounted for one-fourth of the total natural runoff, while it contributed half of the total NPS NO$_3$-N load. This may result from the higher NO$_3$-N concentrations in the groundwater (Figure 3). The excessive use of nitrogen fertilizers has caused extremely high NO$_3$-N accumulation in the vadose zone of the study area (Ju 2017). Dominated by flatland, this area’s groundwater buried depth is generally smaller than 6 m (Ge et al. 2006), which makes it easier for the retained NO$_3$-N to leach to groundwater with the infiltration of rainfall. This results in much higher NO$_3$-N concentrations in groundwater.

The magnitude of BER (Table 2; Figure 8(b)) suggests that baseflow was the preferential hydrological pathway for NO$_3$-N transport in the upper and middle HRB. The BER in this study area was relatively higher than that in other agricultural watersheds. For example, the BER in the Raccoon River Watershed, USA, ranged from 0.23 to 1.61 and averaged 1.23 (Schilling & Zhang 2004); the BER in the Daejeon region, South Korea, ranged from 0.6 to 1.5 (Kim et al. 2010). These results suggest that controlling the baseflow NO$_3$-N concentration plays a key role in NPS NO$_3$-N management of the upper and middle HRB.

**Influences of the consecutive dry years on the baseflow NO$_3$-N load**

In the consecutive dry years, the reduced runoff resulted in a decrease in the NPS NO$_3$-N load (Figure 5(a) and 5(b)), while the proportions of the PS and baseflow NO$_3$-N loads increased. The PS, baseflow, and surface runoff contributions were 22.2, 54.2, and 23.6%, respectively, to the total load. The baseflow was the major contributor to the total load in the consecutive dry years. The BFNI was 25.4% higher in the consecutive dry years than that in the individual dry year (2009), and the BER was 0.32 higher in the consecutive dry years than that in the individual dry year (Table 2). Furthermore, both the BFNI and BER are positively related to the BFI in the study area, as shown in Figure 9. These results suggest that a higher percentage of NO$_3$-N will be delivered to streams through the baseflow in periods of long-term drought than in short-term drought. Climate change increases the probability of long-term drought (Paxian et al. 2019), during which more NO$_3$-N retained in agricultural soils would leach to groundwater and then transfer to surface waters through baseflow. As a result, the risk of severe NO$_3$-N pollution in this agricultural area may increase during the dry period. To minimize the NO$_3$-N pollution in baseflow, appropriate measures should be applied, such as setting the threshold of N fertilizer application rate, limiting N fertilizer application on risk areas, and targeting fertilizer application to periods

![Figure 9](http://iwaponline.com/hr/article-pdf/doi/10.2166/nh.2021.135/899853/nh2021135.pdf)
Table 4 | Comparison of the natural runoff and NPS NO$_3$-N load between the time periods before and after the consecutive dry years

| Time span      | Mean annual precipitation (mm) | Baseflow | Surface runoff | Total natural runoff |
|----------------|-------------------------------|----------|---------------|---------------------|
|                | Discharge (mm) | NO$_3$-N load (kg·ha$^{-1}$·yr$^{-1}$) | Discharge (mm) | NO$_3$-N load (kg·ha$^{-1}$·yr$^{-1}$) | Discharge (mm) | NO$_3$-N load (kg·ha$^{-1}$·yr$^{-1}$) |
| Period 1 (2007–2010) | 949.9 | 59.7 | 1.5 | 161.9 | 1.38 | 221.5 | 2.87 |
| Period 2 (2014–2018) | 1,007.8 | 52.4 | 1.6 | 156.4 | 2.22 | 208.5 | 3.66 |
| Change | 6.1% | –12.2% | 9.7% | –3.4% | 61.1% | –5.7% | 34.4% |

Impacts of the errors in PS NO$_3$-N load estimation

In this study, the PS, baseflow, and surface runoff NO$_3$-N loads were estimated using LOADEST and KTRL regression. Stenback et al. (2011) reported that LOADEST may overestimate the NO$_3$-N loads for certain rivers, while it performs well at sites with large drainage areas (>20,000 km$^2$). The drainage area of the upper and middle HRB is much larger than 20,000 km$^2$. Furthermore, Table 1 and Figure 4 reveal that LOADEST performed well in this area (i.e., $NSE >0.75$, $Bp < 3$, and $RSR < 0.45$).

Albek (2003) reported that for nonconservative substances, settling, chemical, and biological transformations between the source and monitoring station could induce uncertainty when estimating the PS NO$_3$-N load based on the linear regression between the concentration and the reciprocal of the discharge. Because the total NO$_3$-N load mainly stemmed from NPSs, we mainly analyzed the impacts of the errors in PS NO$_3$-N load estimation on BFNI and BER. According to Equations (11)–(14), the upper and lower limits of BFNI and BER were calculated, when the PS NO$_3$-N load ranged from 0 to its upper limit (Figure 7). A small influence interval (the difference between the upper and lower limits) indicates a nonsignificant impact of the PS NO$_3$-N load errors on the BFNI and BER. It is evident from Figure 8 that the influence intervals for the BFNI (4.3–14.0%) and BER (0.17–0.52) are relatively small, and the characteristics of the interannual variations in the BFNI and BER have little changes. For example, the mean BFNI was higher in the consecutive dry years (64.9–76.3%) than that in the individual dry year (44.2–56.9%), while the BER, ranging from 1.31 to 2.45, was higher than 1 in all years. Therefore, it is reasonable to conclude that the errors in PS NO$_3$-N load estimation imposed nonsignificant impacts on the BFNI and BER in this work.

Although a physical basis is lacking, the combined methods applied in this study could provide a rough estimation of the NO$_3$-N loads consisting of PS, baseflow, and surface runoff contributions for regions where the PS load cannot be neglected and wastewater monitoring is not performed. Compared to physically based hydrological process models (He & Lu 2016), the above-combined methods require less data (mainly concentration and discharge data measured at monitoring stations). It is a good choice to use the combined methods to separate the PS, baseflow, and surface runoff NO$_3$-N loads from the total load when few PS monitoring data are available.

CONCLUSIONS

Over a 12-year study period, the PS, baseflow, and surface runoff NO$_3$-N loads were quantified in the upper and middle HRB. The PS, baseflow, and surface runoff contributions were 9.2, 43.8, and 47.0%, respectively, to the...
mean annual total load (3.13 kg·ha⁻¹·yr⁻¹). The baseflow accounted for approximately one-fourth of the total natural runoff and contributed half of the total NPS NO₃-N load, and the mean annual BER was 1.82. The BFNI and BER were higher in the consecutive dry years (69.8% and 2.12, respectively) than those in the individual dry years (44.2% and 1.80, respectively). We have demonstrated that NPSs are the major contributors to the total NO₃-N load and that baseflow is the primary hydrological pathway for NO₃-N transport in this area. Compared to short-term drought, a higher percentage of NO₃-N will be delivered to streams through baseflow under long-term drought. This study highlights the alarming evidence that continuous drought caused by climate change may lead to a higher rate of nitrogen loss in agricultural watersheds. Therefore, controlling the baseflow NO₃-N load (e.g., fertilizer application rate control, vegetated buffer strips, straw return, and permeable reactive barrier) plays a key role in NPS NO₃-N management of the upper and middle HRB, especially in dry periods that span consecutive years.

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DATA AVAILABILITY STATEMENT

All relevant data are available from an online repository or repositories.

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