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The contribution of nitrate sources in Liao Rivers, China, based on isotopic fractionation and Bayesian mixing model

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Abstract

The riverine nitrate stable isotopic compositions characterize its fate and reflect its sources. In this study, the proportional contribution of riverine nitrate was calculated by Bayesian mixing model based on the dual nitrate isotopes in Liao Rivers, Northeast of China after considering the isotopic fractionation of nitrogen transformation. The results show the contribution of nitrogen sources has large variations in different section of rivers. The proportional contribution from synthetic fertilizer increases after considering impacting for isotopic compositions of nitrate by the key processes at the high flow season. Thus, the main transformations and isotopic fractionations should be identify when calculate the contribution of sources accurate using the Bayesian model.

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1. Introduction

Nitrogen is an essential element for organisms that plays an important role in the ecological status of aquatic systems. High nitrogen level is considered to be harmful to human health in drinking water, it is also considered as one of significant signal for eutrophication of aquatic ecosystems^[1]. Recognizing the sources and dynamics of biologically available, dissolved nitrogen in surface water is important for nutrient management and protection^[2,3].

Dual isotopes of nitrate (N and O) have been successfully used to identify the sources of nitrate in aquatic systems^[2,4]. To track the contribution of the different sources, stable isotope analysis in R (SIAR) based on the Bayesian model was developed and used to quantitative the contributions of different sources to nitrate in aquatic systems^[5]. The model can apportion more than three sources when only two isotopes are used. It also considers the ranges and distributions of the sources instead of using a single signature to represent one source as in the previous works. In addition, the deviation of stable isotopes caused by fractionation, which may significantly change the

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original signature of the isotopes during transport and transformation processes, can be easily incorporated into this model [6].

Several researches had been carried out on quantitative the contribution of nitrogen source using stable isotope analysis in R [7, 8, 9, 10, 11]. However, few studies considered the isotopic fractionation during nitrogen transformations. Here, a combination of isotopic fractionation of volatilization and denitrification was considered in the SIAR calculation in Liao River Basin.

2. Sample analysis and SIAR mixing model

Water samples were collected from the main stream and major tributaries of the Liao River Basin during high and low flow seasons [5]. Water samples were filtered through 0.22 μm cellulose-acetate filters and then placed into pre-washed polyethylene bottles. The filtrate for isotopic analysis and anions were cooled and kept frozen until analysis. The dual isotopes of nitrates were measured by an isotope ratio mass spectrometer via quantitative bacterial reduction of nitrates to nitrous oxide (N_2O) based on the denitrifier method [12]. The international nitrates were treated identically with the water samples were used to calibrate the measured sample data. Each sample was measured in duplicate and the standard error was 0.3‰ for $\delta^{15}\text{N}\text{-NO}_3^-$ and 0.5‰ for $\delta^{18}\text{O}\text{-NO}_3^-$.

The applied mixing model is described by the following equations:

$$X_{ij} = \frac{\sum_{k=1}^K p_k q_{jk} (S_{jk} + C_{jk})}{\sum_{k=1}^K p_k q_{jk}} + \varepsilon_{ij}$$

$$S_{jk} \sim N(\mu_{jk}, \omega_{jk}^2)$$

$$C_{jk} \sim N(\lambda_{jk}, \tau_{jk}^2)$$

$$\varepsilon_{jk} \sim N(0, \sigma_{jk}^2)$$

Where X_{ij} is the observed isotope value j ($\delta^{15}\text{N}$ and $\delta^{18}\text{O}$) of the mixture i , in which $i=1, 2, 3 \dots N$ and $j=1, 2, 3 \dots J$. S_{jk} is the source value k on isotope j ($k=1, 2, 3 \dots K$) and is normally distributed with mean μ_{jk} and variance ω_{jk}^2 . p_k is the proportion of source k estimated by the SIAR model; q_{jk} refers to concentration of isotope j in source k . C_{jk} is the fractionation factor for isotope j on source k and is normally distributed with mean λ_{jk} and variance τ_{jk}^2 . ε_{jk} is the residual error representing the additional inter-observation variance between individual mixtures and is normally distributed with mean 0 and variance σ_{jk}^2 . Detailed description of this model can be found in Parnell et al. (2010) [6].

3. Results based on the Bayesian mixing model

Nitrate sources in river basin include synthetic fertilizers, atmospheric deposition, soil organic nitrogen, manure, and sewage waste. To estimate the contribution of different NO_3^- sources, the nitrate isotopic composition ($\delta^{15}\text{N}$ and $\delta^{18}\text{O}$) from different sources should be chose. The isotopic values of nitrate in unfertilized soil (Table 1) were used to calculate the contribution of soil organic nitrogen (SON) [13]. The synthetic fertilizers (SF) in the study area were analysed with $\delta^{15}\text{N}\text{-NO}_3^-$ mean value of $0.0 \pm 0.8\%$ [5]. Considering the seasonal variation of atmospheric wet deposition (AT), the average nitrate isotopic values of rain water samples and snow samples collected in Liao River Basin and other river basin, Songhua River Basin [14], which close to Liao River Basin, were used for high flow and low flow season (Table 1), respectively. The $\delta^{18}\text{O}$ values of nitrate nitrified from manure and sewage related to the isotopic composition of water and O_2 in the surrounding environment [2, 15]. Thus the deviation of $\delta^{18}\text{O}_{\text{water}}$ values during two flow seasons can represent the deviation of $\delta^{18}\text{O}_{\text{nitrate}}$. The lowest $\delta^{18}\text{O}$ values in the river samples may indicate oxygen atom exchange occur between nitrite and water via the nitrification process and also can represent nitrate derived from the above two sources [16]. In the present study, these lowest $\delta^{18}\text{O}$ values can represent the original $\delta^{18}\text{O}$ values via nitrification from manure, fertilizers and sewage. Therefore, the isotope values of nitrate sources used for calculation were different between different flow seasons.

Table 1 Isotopes values of the nitrate reservoirs used in SIAR mixing model

Sources	Flow season	$\delta^{15}\text{N}$	$\delta^{15}\text{N}$	$\delta^{18}\text{O}$	$\delta^{18}\text{O}$
		mean	SD	mean	SD
SON ^[13]		+6.4	0.6	-6.2	0.4
Synthetic fertilizers ^[5]	high flow season	0.0	0.8	-5.7	1.7
	low flow season	0.0	0.8	-0.9	1.0
Atmospheric deposition ^[14]	high flow season	-4.8	1.6	+60.2	6.7
	low flow season	+10.2	4.3	+87.3	8.3
Manure ^[5, 17]	high flow season	+8.9	9.3	-5.7	1.7
	low flow season	+8.9	9.3	-0.9	1.0
Sewage ^[5, 17]	high flow season	+24.4	7.7	-5.7	1.7
	low flow season	+24.4	7.7	-0.9	1.0

Samples were divided by four groups, upstream of Liao River (G1, No.s 6-11)^[5], tributaries of Liao River (G2, No.s 12, 14, 18, 22, 23)^[5], main stream of Liao River (G3, No.s 13, 16, 17, 19, 20)^[5], Daliao River (G4, No.s 24-28)^[5]. The proportional contribution of nitrate sources in different section of rivers is listed in Table.2. The results shown the mean contribution of atmospheric wet deposition was approximately 10%, and slightly higher contribution in high flow season than low flow season. The main nitrate sources during high flow season are synthetic fertilizers in group 1 and sewage waste in other three groups. During low flow season, main nitrate source was sewage waste in group 1 and 4, SON in group 2 and 3, respectively.

Table 2 Mean values of source contributions using SIAR

Source	High flow season				low flow season			
	G 1	G 2	G 3	G 4	G 1	G 2	G 3	G 4
SON	0.24	0.23	0.24	0.19	0.20	0.24	0.26	0.25
SF	0.30	0.18	0.19	0.16	0.20	0.22	0.25	0.21
AT	0.10	0.17	0.09	0.12	0.19	0.12	0.08	0.09
M	0.24	0.16	0.19	0.22	0.20	0.19	0.20	0.18
SW	0.11	0.26	0.29	0.30	0.21	0.23	0.21	0.26

This result ignored the isotopic fractionation during nitrogen transformations. However, the nitrogen entrances into the river, its original signature may alter by volatilization, nitrification and denitrification^[2, 4, 18]. Thus, it's necessary to consider main transformations in terrestrial and aquatic environment. Although, our previous studies showed no intense denitrification occurs in the Liao Rivers according to the isotopic and chemical data^[5]. To accurately calculate the contribution of different sources using the Bayesian model, different extends of denitrification were taken into account for the estimation. In this study, we take an example to compare the result difference when considered the isotopic fractionation of volatilization and denitrification during high flow season.

4. Discussion

4.1. The calculated results after considering the volatilization

Previous studies shown volatilization process followed Rayleigh distillation equation with an overall fractionation effect of around -20% ^[19]. Xing and Zhu (2002) reported the loss N through volatilization for urea was 0.22 in the agriculture land, China^[20]. Based on the conversion factors and Rayleigh fractionation equation and $\delta^{15}\text{N}$ values of nitrogenous fertilizers collected within basin, nitrogen isotopic composition of the residual fertilizer would be about $+5.0\%$ after considering the volatilization fractionation. The results (Table 3) showed the contribution of synthetic fertilizers decreased in Group 1, which has the lowest mean average $\delta^{15}\text{N}$ values ($+4.2\pm 0.4\%$) than other groups, and increased in three groups. After considering the volatilization, the contribution of atmosphere wet deposition and manure sources shown less change than SON and sewage waste.

Table 3 Mean values of source contributions using SIAR after considering the isotopic fractionation of volatilization.

Source	G 1	G 2	G 3	G 4
SON	0.26	0.23	0.23	0.19

SF	0.28	0.22	0.23	0.19
AT	0.11	0.17	0.09	0.12
M	0.25	0.15	0.19	0.21
SW	0.10	0.23	0.26	0.28

4.2. The calculated results after considering the denitrification

The extent and isotopic fractionation of denitrification all can affect the isotopic compositions of nitrate sources. The isotopic enrichment factor for N during the microbial denitrification process can vary significantly, with ϵ values ranging from -5 to nearly -40‰³. For this calculation, -15.9‰ for ¹⁵N and -8‰ for ¹⁸O were used ϵ values [15]. The calculation result showed in Figure 1, which the extent of denitrification was 10%, 20%, 30%, respectively. After considering the denitrification, the variation of sources contribution was different for different groups. The contribution of SON was increased in group 1, 3 and 4 followed the increased extent of denitrification. However, the contribution of synthetic fertilizers was increased in group 2, 3 and 4 as the increased extent of denitrification. The contribution decreased in other three sources, especially atmosphere wet deposition and sewage waste. Large change for the sources contribution was observed in synthetic fertilizers and sewage waste, which has lightest and heaviest $\delta^{15}\text{N}$ values, respectively.

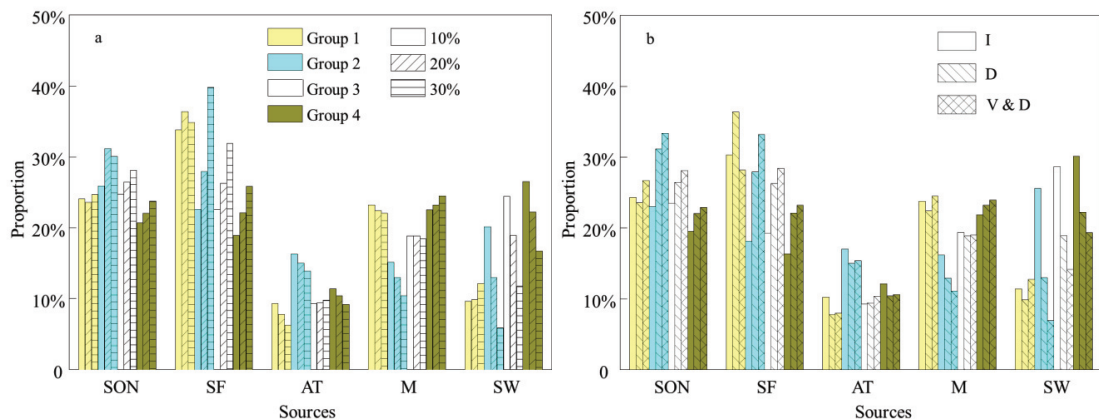


Figure 1 (a) the calculation of different extent of denitrification during high flow season; (b) the contrast of calculation of isotopic fractionation based on 20% denitrification; I stands for ignore volatilization and denitrification; D stands for the extent of 20% denitrification; V&D stands for considering the isotopic fractionation of volatilization and 20% denitrification.

Figure 1b showed the calculated results after considering the volatilization and denitrification with extent 20% in river basin. Large difference was also observed on the contribution from synthetic fertilizers and sewage waste. The increased contribution of synthetic fertilizers and decreased contribution of sewage waste were found in group 2, 3 and 4. The increased contribution of synthetic fertilizers between ignoring and considering the transformation was 15%, 9% and 7% for three groups, respectively. The decreased contributions of sewage waste between ignore and considering the transformation was 19%, 15% and 11% for three groups, respectively. These large change also resulted in different main sources. In the high flow seasons, the sewage waste water would contribute small part of nitrate sources to this large river due to more rain water discharging into rivers. Meanwhile, the monsoonal climate leads to high humidity and temperature in summer, which would increase the biological activities, such as denitrification. Thus, the calculated results after considering the key biogeochemical processes might be more reasonable. Of course, there are many processes under various environments effecting the calculations of nitrate sources contribution, producing the large uncertainty for the quantitative analysis of nitrate sources.

5. Summary

After considering the isotopic fractionation of nitrogen transformation, the contribution of nitrogen sources showed great change, especially for sources with the lightest and heaviest $\delta^{15}\text{N}$ values. Synthetic fertilizer was also the main nitrogen source in group 1. The SON and synthetic fertilizers were the main nitrogen sources instead of

sewage waste in group 2, 3 and 4. To calculate the contribution of sources accurate using the Bayesian model, the main transformation and isotopic fractionations should be taken into account for estimation. The calculated proportional contribution of nitrate sources after considering the key processes might stand much closer to nature and more accurate than just using isotope values.

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