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Identification of sources and transformations of nitrate in the Xijiang River using nitrate isotopes and Bayesian model

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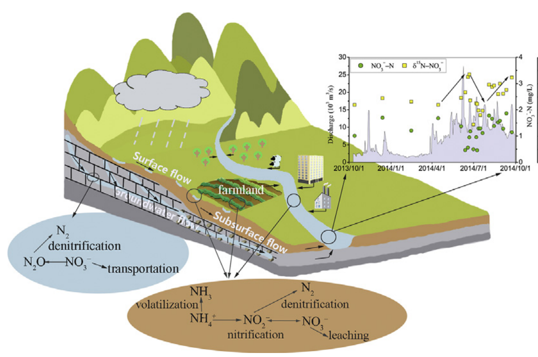
HIGHLIGHTS

- Evaluate spatio-temporal contributions of nitrate sources by Bayesian mixing model.
- Identify temporal nitrogen dynamics by high-frequency analysis of nitrate isotopes.
- Nitrate concentrations determine the long-term pattern of nitrate flux.

GRAPHICAL ABSTRACT



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ABSTRACT

Coupled nitrogen and oxygen isotopes of nitrate have proven useful in identifying nitrate sources and transformation in rivers. However, isotopic fractionation and low-resolution monitoring limit the accurate estimation of nitrate dynamics. In the present study, the spatio-temporal variations of nitrate isotopes (^{15}N and ^{18}O) and hydrochemical compositions (NO_3^- and Cl^-) of river water were examined to understand nitrate sources in the Xijiang River, China. High-frequency sampling campaigns and isotopic analysis were performed at the mouth of the Xijiang River to capture temporal nitrate variabilities. The overall values of $\delta^{15}N$-NO_3^- and $\delta^{18}O$-NO_3^- ranged from +4.4‰ to +14.1‰ and from −0.3‰ to +6.8‰, respectively. The results of nitrate isotopes indicated that NO_3^- mainly originated from soil organic nitrogen (SON), chemical fertilizer (CF), and manure and sewage wastes (M&S). The negative correlation of nitrate isotopic values with NO_3^-/Cl^- ratios suggested the importance of denitrification in NO_3^- loss. The results of Bayesian model with incorporation of isotopic fractionation during the denitrification showed that SON and CF contributed to the most (72–73%) nitrate in the wet season; whereas approximately 58% of nitrate was derived from anthropogenic inputs (M&S and CF) in the dry season. The nitrate flux was 2.08×10^5 tons N yr^{-1} during one hydrologic year between 2013 and 2014, with 86% occurring in the wet season. Long-term fluctuations in nitrate flux indicated that nitrate export increased significantly over the past 35 years, and was significantly correlated with nitrate concentrations. The seasonal pattern of nitrate dynamics indicated the mixing of nitrified NO_3^- and denitrified NO_3^- between surface flow and groundwater

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flow under different hydrological conditions. Overall, the present study quantitatively evaluates the spatio-temporal variations in nitrate sources in a subtropical watershed, and the high-frequency monitoring gives a better estimate of nitrate exports and proportional contributions of nitrate sources.

1. Introduction

Extensive human activities have resulted in increased delivery of nitrogen to rivers and streams from 34 Tg N yr^{-1} to 64 Tg N yr^{-1} over the 20th century (Beusen et al., 2016). Of all nitrogen species, nitrate is the dominant one and poses serious threats to aquatic ecosystems (e.g., eutrophication and water acidification) and human health (e.g., methemeoglobinemia in infants) (Comely, 1945; Kendall et al., 2007). Hence, it is crucial to identify the sources and transformations of nitrate for water quality management.

Nitrate potentially originates from soil organic nitrogen (SON), chemical fertilizer (CF), manure and sewage wastes (M&S) and atmospheric precipitation (AP) (Kendall et al., 2007). The nitrogen and oxygen isotope composition of nitrate is a powerful indicator for identifying nitrate sources because different sources have distinctive isotopic signatures (Kendall et al., 2007). The isotopic approach has been used to investigate the sources and fate of nitrate in many large rivers, such as the Mississippi (Panno et al., 2006), Seine (Sebilo et al., 2006), Yangtze (Li et al., 2010), and the Yellow River (Liu et al., 2013; Yue et al., 2017). However, nitrate sources may have overlapping isotopic values, which limit the applicability of nitrate isotopes alone to provide accurate estimation of nitrate origins. Moreover, isotopic fractionation during biogeochemical processes can alter the original isotope compositions of sources during nitrate transport (Kendall et al., 2007). The main processes modifying nitrate isotopic signatures include mineralization, ammonia volatilization, assimilation, nitrification, denitrification, anammox and dissimilatory nitrate reduction to ammonium (Kendall et al., 2007). Take denitrification as an example, $\delta^{15}N\text{-}NO_3^-$ and $\delta^{18}O\text{-}NO_3^-$ values tend to exhibit simultaneous increases with enrichment ratios ranging from 1:1 to 2:1 (Kendall et al., 2007; Li et al., 2010).

One potential solution to the above problem is to combine the isotopic signatures of nitrate with hydrochemical compositions (e.g., NO_3^-/Cl^-, discharge) (Xia et al., 2017; Yue et al., 2017), land use (Müller et al., 2018; Matiatos, 2016) and/or other isotopes (e.g., $^{18}O\text{-}H_2O$, ^{11}B, $^{87}Sr/^{86}Sr$) (Meghdadi and Javar, 2018; Kim et al., 2015; Vrzel et al., 2016) as well as statistical methodologies (e.g., Cluster Analysis, Principal Component Analysis) (Liu et al., 2013; Meghdadi and Javar, 2018).

The sources and transformations of nitrate display spatial and seasonal variations, which can be discerned in the large rivers. However, traditional low-resolution sampling may miss some key transformations, resulting in uncertainties in identification of nitrate sources. Recently, biweekly to monthly sampling campaigns have been performed in some rivers using the coupled nitrogen and oxygen isotope approach. Those field campaigns suggest that high-frequency monitoring can provide more insights into nitrate behaviors under different hydraulic conditions (BryantMason et al., 2013; Müller et al., 2018; Yue et al., 2017). For example, BryantMason et al. (2013) found that isotopic signals of nitrate suggested the nitrate removal during the extreme flood pulses in the lower Mississippi River and its tributaries.

To estimate the proportional contributions of nitrate sources, the dual isotopic mixing model based on mass balance has been successfully used (Kaown et al., 2009; Li and Ji, 2016). However, this method assumes no significant isotopic fractionations from biogeochemical processes and is limited to trace no more than three sources (Parnell et al., 2010; Xue et al., 2012). A Bayesian mixing model has been implemented in a software package SIAR (Stable Isotope Analysis in R) to estimate the probability distribution of the proportional contributions of nitrate sources (Parnell et al., 2010), which overcomes the aforementioned limitations of the linear isotopic mixing model. The SIAR model has proven useful for source apportionment of nitrate in surface water (Liu et al., 2018b; Matiatos, 2016; Xia et al., 2017; Xue et al., 2012). However, the denitrification process and related fractionation were rarely considered when using SIAR to estimate the nitrate sources in rivers (Xia et al., 2017; Yue et al., 2015a).

Xijiang River is the largest tributary of the Pearl River, which is the second largest river in China in terms of discharge. Previous studies showed that nitrate was the main species of dissolved inorganic nitrogen (DIN) at the river mouth of the Xijiang River, with the average annual molar ratios of NO_3^-/NH_4^+ ranging from 8 to 29 during 2000–2009 (Ye, 2010). However, few studies on the sources and fate of nitrate have been conducted in the Xijiang River. In this study, the spatio-temporal variations in nitrate sources and transformations were identified using the coupled nitrogen and oxygen isotopes of nitrate and hydrochemical compositions over one hydrological year. High-frequency sampling was conducted at the mouth of the Xijiang River to capture key transformations of nitrate based on the assumption that variations in nitrate isotopic signals during nitrate transformations were associated with different hydrologic conditions, which created different residence time and redox conditions. Proportional contributions of multiple nitrate sources were estimated using the Bayesian isotope mixing model by incorporating isotopic fractionation along the Xijiang River. Finally, interannual variations in nitrate flux were examined over the past 35 years at the mouth of the Xijiang River based on the assumption that long-term patterns of nitrate flux were associated with changes in land use and environmental policy.

2. Material and methods

2.1. Study area

The Xijiang River, located in Southern China, originates at the Maxiong Mountain in Yunnan Province and flows through Guizhou Province, Guangxi Zhuang Autonomous Region (GZAR) and Guangdong Province, draining an area of 353,120 km^2 before merging with the Beijiang River. The Xijiang watershed covers approximately 77.8% of the drainage basin area of the Pearl River watershed. The Xijiang River comprises five main sections, which are the Nanpanjiang River, the Beipanjiang River, the Hongshuihe River, the Yujiang River and the Qianjiang River. The upper reaches include the Nanpanjiang River, the Beipanjiang River and the Hongshui River (Fig. 1), and the rest sites after Hongshui River represent the mid-lower reaches.

The studied watershed belongs to a subtropical humid monsoon climate with annual air temperature changing from 14 °C to 22 °C. The mean annual precipitation ranges from 1200 mm to 2200 mm, which is mainly concentrated in the period from April to September (wet season) (Han et al., 2018; Liu, 2007). The Xijiang River has abundant water resources, with an average discharge of 2.30×10^{11} m^3 yr^{-1}. The Xijiang River is the major water source for about 30 million local population (Fig. 1). The Xijiang River is impacted by intense anthropogenic disturbance and provides important water resources for socio-economic development of southern China.

The landscapes of the Xijiang river basin are dominated by mountains and hills with significant topographic relief. The elevation of the watershed decreases from northwest (Yunnan-Guizhou Plateau) to southeast. Geologically, the mid-upper parts of the catchment are mostly Permian and Triassic carbonate rocks with intercalated coal-bearing formations. In contrast, the mid-lower part is dominated by