Quantitative identification of nitrate pollution sources and uncertainty analysis based on dual isotope approach in an agricultural watershed ☆

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ABSTRACT

Quantitative identification of nitrate (NO_3^--N) sources is critical to the control of nonpoint source nitrogen pollution in an agricultural watershed. Combined with water quality monitoring, we adopted the environmental isotope (δD-H_2O, δ^{18}O-H_2O, δ^{15}N-NO_3^-, and δ^{18}O-NO_3^-) analysis and the Markov Chain Monte Carlo (MCMC) mixing model to determine the proportions of riverine NO_3^--N inputs from four potential NO_3^--N sources, namely, atmospheric deposition (AD), chemical nitrogen fertilizer (NF), soil nitrogen (SN), and manure and sewage (M&S), in the ChangLe River watershed of eastern China. Results showed that NO_3^--N was the main form of nitrogen in this watershed, accounting for approximately 74% of the total nitrogen concentration. A strong hydraulic interaction existed between the surface and groundwater for NO_3^--N pollution. The variations of the isotopic composition in NO_3^--N suggested that microbial nitrification was the dominant nitrogen transformation process in surface water, whereas significant denitrification was observed in groundwater. MCMC mixing model outputs revealed that M&S was the predominant contributor to riverine NO_3^--N pollution (contributing 41.8% on average), followed by SN (34.0%), NF (21.9%), and AD (2.3%) sources. Finally, we constructed an uncertainty index, UI_{90}, to quantitatively characterize the uncertainties inherent in NO_3^--N source apportionment and discussed the reasons behind the uncertainties.

1. Introduction

Nitrate (NO_3^--N) contamination in waters has become a crucial global environmental issue. NO_3^--N arises from several point and nonpoint sources (NPS), including municipal wastewater discharge, agricultural runoff with significant amount of chemical fertilizer, and atmospheric deposition (AD) (Bordeleau et al., 2008; Holloway et al., 1998; Xue et al., 2012). Increased NO_3^--N loads within surface and groundwater seriously influence on aquatic ecosystems and have given rise to health considerations in humans and livestock. NO_3^--N contamination induces deterioration of water quality, resulting in eutrophication, toxic algal blooms, and hypoxia (Carey et al., 2011; Nestler et al., 2011; Paerl et al., 2010). Furthermore, excessively high NO_3^--N levels in drinking water can increase the risk of diseases, such as methemoglobinemia, diabetes,

spontaneous abortions, thyroid disorders, and stomach cancer (Burow et al., 2010; Hord, 2011; World Health Organization, 2011). Thus, the identification of NO_3^--N sources is vitally important for developing effective nitrogen pollution mitigation strategies and achieving water resources sustainability.

Different NO_3^--N sources exhibit their own distinct stable isotope signatures; thus, the dual isotope approach (δ^{15}N-NO_3^- and δ^{18}O-NO_3^-) can be used to differentiate the NO_3^--N sources (Nestler et al., 2011). The δ^{15}N values from the AD range from $-13‰$ to $+13‰$ (Kendall and McDonnell, 1998). The typical δ^{15}N values of soil nitrogen (SN) range from 0‰ to $+8‰$ (Kendall and McDonnell, 1998). The δ^{15}N values of chemical nitrogen fertilizer (NF), which originate from the fixation of atmospheric N_2, vary from $-6‰$ to $+6‰$ (Flipse and Bonner, 1985). Manure and sewage (M&S), which are enriched in ^{15}N relative to other sources, display high δ^{15}N values at $+4‰$ to $+25‰$ (Xue et al., 2009). Although some NO_3^--N sources are indistinguishable by ^{15}N alone because of the overlap of their distribution ranges, these sources may be identified once ^{18}O is incorporated. The δ^{18}O of precipitation is affected by complex atmospheric processes, indicating a wide range

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from +25‰ to +75‰ (Flipse and Bonner, 1985; Xue et al., 2009). The $\delta^{18}O$ in NO_3^--N fertilizer is within +17‰ to +25‰ (Amberger and Schmidt, 1987). The $\delta^{18}O$ in the NO_3^--N derived from nitrification often ranges from −5‰ to +15‰, which is quite different from the $\delta^{18}O$ in the NO_3^--N from precipitation and NO_3^--N fertilizer (Kendall and McDonnell, 1998; Mayer et al., 2001). Obviously, some specific value ranges exist for both $\delta^{15}N$ and $\delta^{18}O$ in different NO_3^--N inputs. However, they are not changeless among various watersheds. Therefore, the site-specific $\delta^{15}N$ and $\delta^{18}O$ values in NO_3^--N sources should be determined for improving the identification accuracy.

During the past decade, a growing number of studies have reported successful applications of the dual isotope approach for understanding the sources and transformations of NO_3^--N in rivers and groundwater. For example, Li et al. (2010) investigated the $\delta^{15}N$-NO_3^- and $\delta^{18}O$-NO_3^- in Yangtze River (China), and their results suggested that nitrification and urban sewage effluent were the major NO_3^--N sources in this river. Based on $\delta^{15}N$-NO_3^- and $\delta^{18}O$-NO_3^- values obtained from the shallow groundwater and stream water at Hubbard Brook Experimental Forest in New Hampshire of USA, Wexler et al. (2014) reported that extensive denitrification occurred during midsummer, when transient, perched patches of saturation developed in hill slopes, whereas stream water exhibited no isotopic evidence of denitrification. Similarly, Liu et al. (2006) employed the dual isotope approach to assess NO_3^--N sources in the karst groundwater of Guiyang (China), and found that the chemical fertilizer and nitrification of nitrogen-containing organic materials were responsible for the NO_3^--N contamination in suburban groundwater. In addition, NO_3^--N distribution in urban groundwater was mainly controlled by sewage effluents and denitrification.

With the aim of quantifying the NO_3^--N inputs into waters, researchers developed and implemented a linear mass-balance mixing model to track NO_3^--N sources and estimate the proportional contribution of each NO_3^--N source (Phillips and Koch, 2002; Voss et al., 2006). Given the considerable variations in the NO_3^--N sources apportionment caused by (1) spatial-temporal variations in $\delta^{15}N$-NO_3^- and $\delta^{18}O$-NO_3^-, (2) isotope fractionation during microbial denitrification process and (3) too many sources (number of sources > number of isotopes +1) contribute to NO_3^--N contamination (Moore and Semmens, 2008; Xue et al., 2009), the Markov Chain Monte Carlo (MCMC) method was utilized to solve the mixing model (Parnell et al., 2010). Xue et al. (2012) discussed the contributions of five potential NO_3^--N sources in surface water in Flanders (Belgium) through the MCMC mixing model, and the results showed that M&S contributed most of the NO_3^--N contamination. Divers et al. (2014) used the MCMC mixing model to estimate the contributions of NO_3^--N quantitatively from AD and sewage to urban stream water, indicating that 94% of the in-stream NO_3^--N originated from sewage sources during baseflow conditions and an average of 67% during storm flow conditions. As an intrinsic nature, the uncertainty in the proportional contribution of each source is an indispensable part associated with the quantitative identification of NO_3^--N sources. Unfortunately, due to the complexity of the uncertainty and the difficulties of its formulation, uncertainty assessment is often neglected, which might lead to serious misunderstanding of the "quantitative identification".

In eastern China, NPS pollution is of great importance due to its prevalence on water quality impairment with excessive chemical fertilizer application and rapid economic development in recent years. In the present study, we adopted the dual isotope approach and the MCMC mixing model to quantitatively identify the sources of NO_3^--N contamination in the ChangLe River watershed, a typical agricultural watershed of eastern China. Specifically, this study aims to (1) assess the temporal and spatial variations of nitrogen in the study watershed, (2) determine the significant sources and their quantitative contributions to riverine NO_3^--N pollution, and (3) develop an uncertainty assessment formulation for a better understanding of the NO_3^--N source contributions. We expect that the results can provide valuable information for controlling nitrogen pollution and prioritizing water quality remediation actions in areas with multiple pollution sources.

2. Materials and methods

2.1. Study area

The ChangLe River watershed (120°35′–120°49′ E and 29°27′–29°35′ N), located in Zhejiang Province of the eastern China, has a drainage area of 864 km² with a population of ~0.26 million (Fig. 1). The river is one of the main tributaries of the Cao-E River, which ultimately flows into the QianTang Estuary and East China Sea. The mainstream originates from Nanshan Reservoir, and has a length of ~31 km. The region has a subtropical monsoon climate with an average annual rainfall of 1228 mm, approximately 70% falls in April to September (He et al., 2016). The monthly precipitation and temperature of the ChangLe River watershed in 2014 are provided in Fig. 2. The watershed is a typical agricultural watershed in eastern China (Chen et al., 2011, 2013). The dominant land use categories are woodland, farmland and garden plots, which account for 48%, 22%, and 18% of the entire watershed, respectively. Point source pollution is negligible because only ~0.3 ton of N is discharged into the river each year from industrial waste water outlets and sewage water treatment plants (Liu and Lu, 2013).

2.2. Sample collection and analysis

Water samples were obtained from field campaigns carried out monthly in 2014 from upstream to downstream of the ChangLe River, comprising ten sampling sites (four mainstream sites, three major tributary sites, and three groundwater sites) (Fig. 1). The water samples collected from April to September were selected for the isotopic analysis of H_2O (i.e., δD and $\delta^{18}O$-H_2O). The water samples collected in June (wet season) and December (dry season) were chosen for the isotopic analysis of NO_3^--N (i.e., $\delta^{15}N$-NO_3^- and $\delta^{18}O$-NO_3^-). Precipitation sampling was conducted during April–September on an event basis using a 2.5 L high-density polyethylene container attached with a rubber hose to a ~300 cm² funnel. Evaporation was prevented by placing 80 mL of paraffin oil in the polyethylene container and a ping-pong ball inside the funnel. After a precipitation event, the plastic sample bottles containing the rainwater were immediately sealed. The top soil (0–10 cm), rainwater, chemical fertilizer (i.e., urea, and ammonium), domestic sewage and manure (i.e., cow dung, pig dung, human excrement, and poultry droppings) were also sampled within the ChangLe River watershed in June and December to obtain the site-specific isotopic characteristics of potential NO_3^--N sources. All sampling equipment were precleaned with deionized water. Samples were immediately chilled (but not frozen) by placing dry ice in the cold closet and kept dark until required for further treatments in laboratory. In addition to total nitrogen (TN) analysis, all water samples were filtered through sterile 0.45 μm Millipore polycarbonate membrane before their measurements.

The concentrations of TN, ammonium-nitrogen (NH_4^+-N), and NO_3^--N in water samples were determined using the alkaline potassium persulfate, the spectrophotometric salicylic acid, and the spectrophotometric phenol disulfonic acid methods, respectively. Water samples for isotope analysis were frozen at −20 °C, and