



Contribution of nitrate sources in surface water in multiple land use areas by combining isotopes and a Bayesian isotope mixing model

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ABSTRACT

Nitrate pollution is a worldwide problem in aquatic systems. Major ions and stable isotopes (δD_{H_2O} , $\delta^{18}O_{H_2O}$, $\delta^{15}N_{NO_3}$ and $\delta^{18}O_{NO_3}$) were applied to reveal the characteristics of nitrate and identify its sources in the East Tiaoxi River system, which is one of the most densely populated, rapidly developing and extensive crop-growing areas with multiple land uses in East China. The total nitrogen (TN) concentrations, which are dominated by nitrate (NO_3^-) in all of the water samples, exceed the Chinese surface water limit of 0.5 mg N L^{-1} . The NO_3^- concentrations, which ranged from 0.03 to 5.46 mg N L^{-1} , were spatially heterogeneous and were greatly affected by the hydrogeology and land uses. The temporal distribution of the NO_3^- concentrations (July, $1.38 \pm 0.63 \text{ mg N L}^{-1}$ and January, $2.77 \pm 0.77 \text{ mg N L}^{-1}$) was influenced by the temporal variations of precipitation. The $\delta^{15}N_{NO_3}$ values ranged from $+1.8\%$ to $+14.0\%$ and the $\delta^{18}O_{NO_3}$ values ranged from $+3.0\%$ to $+11.5\%$ in the East Tiaoxi River system. It was revealed that nitrification rather than denitrification acted as the primary N cycling process in the East Tiaoxi River system. The source apportionment results obtained by applying a Bayesian model (stable isotope analysis in R, SIAR) showed that there were no obvious differences in the source contributions between July and January. The source contributions differed significantly among the three reaches: soil nitrogen (68–73%) contributed more than precipitation in the upper reach, sewage/manure > chemical fertilizers > soil nitrogen contributed more than 85% of the NO_3^- to water in the middle reach, and chemical fertilizers > sewage/manure > soil nitrogen played the role of the major contributors (more than 85%) in the lower reach. The results indicated that nitrogen pollution causing by non-point source pollution has become a very serious problem, better nitrogen management practices should be adopted to meet safe drinking water demands and control the eutrophication in the East Tiaoxi River system.

1. Introduction

Nitrate (NO_3^-) has been well documented as the most wide spread contaminant in aquatic systems caused by anthropogenic activities. High NO_3^- concentrations in surface water threatens human health and results in eutrophication (Casciotti and McIlvin, 2007; Nanus et al., 2008; Zhou et al., 2017). The various NO_3^- sources in aquatic systems include precipitation, soil nitrogen, chemical fertilizers, sewage/manure and industrial wastewater. To control the NO_3^- concentrations and take effective water quality control measures, it is necessary to identify the sources of N.

Because different NO_3^- sources have different stable isotope signatures, dual isotopes of NO_3^- ($\delta^{15}N_{NO_3}$ and $\delta^{18}O_{NO_3}$) have been frequently and successfully used for NO_3^- source identification in aquatic systems (Mayer et al., 2011; Kendall et al., 2007; Xue et al., 2009; Archana et al., 2016; Sanchez et al., 2017). Additionally, the δD_{H_2O} and $\delta^{18}O_{H_2O}$ values have widely been used to survey the origin - of water, and hydrogeological processes (Kendall and Coplen, 2001; Chae et al., 2009; Yuan and Miyamoto, 2008; Hosono et al., 2011). Thus, researchers use stable isotope data for NO_3^- ($\delta^{15}N_{NO_3}$ and $\delta^{18}O_{NO_3}$) with help of water isotopes (δD_{H_2O} and $\delta^{18}O_{H_2O}$) to investigate the sources and possible transformations of NO_3^- in aquatic systems (Panno et al., 2001; Li et al., 2010; Yue et al., 2014; Archana et al., 2016; Lingle et al., 2017). To estimate the proportional contributions of different NO_3^- sources, a Bayesian steady isotope mixture model has been constructed for the stable isotope analysis in the R (SIAR), software package (Parnell et al., 2010). SIAR can distribute more than three sources when merely two isotopes are utilized. It has been demonstrated that the SIAR model output is able to recognize a “fingerprint” for a contributing source of NO_3^- (Xue et al., 2012; Yang et al., 2013; Davis et al., 2015; Kim et al., 2015; Matiatos, 2016; Xing and Liu, 2016; Xia et al., 2017).

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The East Tiaoxi River system provides more than 2.5 million residents in Hangzhou city with drinking water. The East Tiaoxi River basin represents the most densely populated, rapidly developing and extensive crop-growing areas in East China. Recent studies have revealed that due to human activities, the increasing NO_3^- concentration in the East Tiaoxi River causes great concern about its future usage as a drinking water source (Nie et al., 2012; Liang et al., 2013). Therefore, it is essential to identify the NO_3^- sources for meeting the drinking water demand and providing evidence and information for water quality control in the East Tiaoxi River system.

The objective of this study is to (1) compare nitrogen conditions in the East Tiaoxi River system with different land uses; (2) identify the NO_3^- sources and transformations by applying hydrochemicals and isotopes; and (3) use SIAR to quantitatively determine the proportional contributions of potential NO_3^- sources affected by the land uses in the East Tiaoxi River system. Thus, this study could provide new information for water quality management and should help with obtaining a sustainable clean water supply for drinking water purposes.

2. Material and methods

2.1. Description of the study area

The East Tiaoxi River system (N30°12'00"~N30°40'00", E119°35'00"~E120°04'00"), is 96 km long, is located to the southwest of Hangzhou City and mostly receives water from three main tributaries: the South Tiaoxi, Middle Tiaoxi, and North Tiaoxi (Fig. 1). The East Tiaoxi River system originates in the Tianmu Mountains, which are at an elevation of 1506 m, and provides 2.5 million residents in Hangzhou city with drinking water. The average discharge rate of the East Tiaoxi River system is $15.4 \times 10^8 \text{ m}^3 \text{ a}^{-1}$ ($13.4 \times 10^8 \text{ m}^3 \text{ a}^{-1}$ in the high flow season and $3.5 \times 10^8 \text{ m}^3 \text{ a}^{-1}$ in the low flow season), and it flows into Taihu Lake (Feng and Du, 2010). The terrain of the East Tiaoxi River basin is high in the west but low in the east. The dominant types of bedrock are limestone, sandstone and pyroclastics, and paddy soil is the major soil type. The East Tiaoxi River basin has a subtropical monsoon climate whose average annual temperature is approximately 15.7 °C, average annual precipitation is approximately 1454 mm, with nearly three quarters of the precipitation falling during April to September, and the annual evaporation is 1298 mm.

The East Tiaoxi River system is divided into three reaches (upper reach, middle reach and lower reach) based on the different land uses. The upper reach area is dominated by natural forestland. The middle reach area is covered by natural forestland, rural residential areas and agricultural lands with rice and vegetables. The lower reach area includes urban areas, rural residential areas, industrial areas sprinkled with food factories and bamboo processing enterprises and agricultural lands with rice and vegetables. Chemical fertilizers, such as urea and a NPK compound fertilizer, rather than nitrate fertilizer are typically applied at rates of approximately $550\text{--}650 \text{ kg N ha}^{-1} \text{ yr}^{-1}$ for planting rice and vegetables (Nie et al., 2012). Manure is also used for the growth of rice and vegetables (Xu et al., 2016). Sewage from rural residential areas usually flows into rivers directly, but sewage from urban areas is treated at domestic sewage treatment plants and then flows into rivers. Industrial wastewater, which may overflow to rivers when torrential rains occur and the wastewater treatment systems are working incorrectly, is treated in a wastewater treatment system at every factory.

2.2. Sampling

Surface water was sampled in July (high flow season, summer) 2015 and January (low flow season, winter) 2016. Thirty-four water samples were collected from the upper reach (T1 and T2), middle reach (T3–T8) and lower reach (T9–T34) in July 2015 and January 2016, corresponding to high and low flow seasons, respectively (Fig. 1). Surface

water samples from the 18 sites analyzed for stable isotopes were filtered through 0.22- μm membrane filters (Whatman) on the day of sampling and gathered in bottles (60 mL) of pre-cleaned polyethylene, then refrigerated until analysis. Rainwater (P1–P6) and industrial wastewater (I1–I3) were collected for isotope analysis and represented precipitation and industrial wastewater NO_3^- sources in the study area.

2.3. Chemical and isotope analysis

At the sample site, the electric conductivity (EC) and temperature were detected using an EC meter (Leici DDB-303A), and dissolved oxygen (DO) was measured using a DO meter (Leici JPB-607A). Samples that were collected for chemical analysis were filtered through 0.45- μm membrane filters on the day of sampling and were put into bottles (60 mL) of pre-cleaned polyethylene, and then frozen at -20°C before analysis. The concentrations of sodium (Na^+), potassium (K^+), calcium (Ca^{2+}), magnesium (Mg^{2+}), ammonium (NH_4^+), nitrate (NO_3^-), nitrite (NO_2^-), chloride (Cl^-), and sulfate (SO_4^{2-}) were detected by an ion chromatography system (ICS900, Dionex). The total nitrogen (TN) was determined by the alkaline potassium persulfate digestion UV spectrophotometric method (HJ636-2012). Bicarbonate (HCO_3^-) was determined by titration: HCl was used to titrate the samples with $\text{C}_{14}\text{H}_{14}\text{O}_3\text{N}_3\text{SNa}$ as an indicator (GB/T8538-1995). All data analyses were conducted by the Statistical Package for the Social Sciences Software-SPSS 16.0 (SPSS Inc., Chicago, USA) for Windows.

A Picarro L2140-i wavelength-scanned cavity ring-down spectroscopy instrument was applied to analyse the samples used for the stable isotopes of water ($\delta\text{D}_{\text{-H}_2\text{O}}$ and $\delta^{18}\text{O}_{\text{-H}_2\text{O}}$). $\delta\text{D}_{\text{-H}_2\text{O}}$ and $\delta^{18}\text{O}_{\text{-H}_2\text{O}}$ have a precision of 0.5‰ and 0.1‰, respectively. The $\delta^{15}\text{N}_{\text{-NO}_3}$ and $\delta^{18}\text{O}_{\text{-NO}_3}$ values were analyzed by the denitrifier method (Casciotti et al., 2002; Révész and Casciotti, 2007). The NO_3^- in samples was transformed to nitrous oxide (N_2O) by denitrifying bacteria (*Pseudomonas aureofaciens*) lacking N_2O -reductase activity. Then, the N_2O was removed by inletting helium carrier gas, cleaned by cryogenic trapping (Thermo Precon System), divided with chromatography (Thermo Gas Bench), and finally measured by mass spectrometry (Thermo Delta V Advantage). All samples were analyzed 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 isotopic values shown in terms of delta (δ) units were defined as:

$$\delta_{\text{sample}}(\text{‰}) = [(\text{R}_{\text{sample}} - \text{R}_{\text{standard}}) / \text{R}_{\text{standard}}] \times 1,000 \quad (1)$$

where $\text{R} = \text{D}/\text{H}$, $^{15}\text{N}/^{14}\text{N}$ or $^{18}\text{O}/^{16}\text{O}$. The $^{15}\text{N}/^{14}\text{N}$ values were reported relative to atmospheric air, and the D/H and $^{18}\text{O}/^{16}\text{O}$ values were reported relative to Vienna Standard Mean Ocean Water.

2.4. SIAR mixing model

By applying a Bayesian isotope mixing model (SIAR), the proportional contributions of potential NO_3^- sources to surface water can be quantified. The mixture model, by determining a series of N mixing measurements on J isotopes with K source contributors, can be defined as (Parnell et al., 2010):

$$X_{ij} = \sum_{k=1}^K p_k (S_{jk} + C_{jk}) + \varepsilon_{ij} \quad (2)$$

$$(1) S_{jk} \sim N(\mu_{jk}, \omega_{jk}^2)$$

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

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

where X_{ij} is the isotope value j of the mixture i , ($i = 1, 2, 3, \dots, N$ and $j = 1, 2, 3, \dots, J$); S_{jk} is the source value k of the isotope j ($k = 1, 2, 3, \dots, K$) and is normally distributed with mean μ_{jk} and standard deviation ω_{jk} ; p_k is the proportion of source k , which must be calculated by the

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