



Using nitrogen and oxygen isotopes to access sources and transformations of nitrogen in the Qinhe Basin, North China

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Abstract

Nitrate pollution in water is a common environmental problem worldwide. The Qinhe Basin (QHB) faces with the risk of eutrophication. To clarify nitrate pollution of river water, water chemical data, water isotope values (δD and $\delta^{18}O-H_2O$), and dual nitrate isotope values ($\delta^{15}N-NO_3^-$ and $\delta^{18}O-NO_3^-$) were used to discern sources and transformation mechanisms of nitrogen in the QHB. The nitrate concentrations of river water ranged from 0.71 to 20.81 mg L⁻¹. The δD and $\delta^{18}O-H_2O$ values of river water varied from -74 to -52‰ and from -10.8 to -7.2‰, with an average value of -60‰ and -8.2‰, respectively. The $\delta^{15}N-NO_3^-$ and $\delta^{18}O-NO_3^-$ values of nitrate ranged from -6.7 to +14.8‰ and from -6.0 to +5.6‰, with a mean value of +4.6‰ and -0.6‰, respectively. Assimilation by algae and the mixing of soil nitrogen, chemical fertilizer, sewage, and industrial wastewater could account for increasing $\delta^{15}N-NO_3^-$ values. There was neither significantly positive nor negative correlation between $\delta^{15}N-NO_3^-$ and $\delta^{18}O-NO_3^-$ in river water, indicating that no obvious denitrification shifted isotopic values of nitrate in the QHB. Based on the dual isotopic values of nitrate and land use change in the watershed, it could be concluded that intensive nitrification dominated in the QHB, and dissolved nitrate was mainly derived from nitrification of ammonium in fertilizer, soil nitrogen, and domestic sewage. As the primary nitrate sources identified in the QHB, effective fertilization and afforestation can be taken to protect water resource from nitrate pollution.

Keywords Qinhe Basin · Nitrate source · Dual nitrate isotopes · Assimilation · Denitrification · Nitrification

Introduction

The nitrate contamination of water, which is associated with anthropogenic activities including fossil fuel burning, agricultural fertilization, and discharge of manure and sewage (Barnes and Raymond 2010; Xue et al. 2012), is a pervasive

environmental problem in the world (Fukada et al. 2004; Zhang et al. 2014). Excess nitrate in water can cause myriad environmental and ecological problems, such as eutrophication of lakes and reservoirs, toxic algal blooms, and water acidification (Curtis et al. 2011; Li et al. 2019; Li et al. 2013). Furthermore, nitrate with a high concentration in drinking water is also harmful to human health and can cause methemoglobinemia in infants (Fan and Steinberg 1996; Fewtrell 2004). Therefore, to identify nitrate sources and elucidate the processes affecting local nitrate concentrations are imperative to effectively control nitrate pollution in freshwater ecosystems. Traditional methods of identifying nitrate sources can be accomplished by a combination of nitrate concentration, flux data, land use, and the hydrological characteristic of the study areas (Chang et al. 2002; Li et al. 2015b; Xing et al. 2013). However, the nitrate concentration is influenced by assimilation, mixing, ammonification (reaction 1), nitrification (reactions 2–4 (Kool et al. 2007)), and denitrification (reaction 5 (Tesoriero et al. 2000)) processes. As a result, traditional methods cannot well access sources and transformations of nitrogen.

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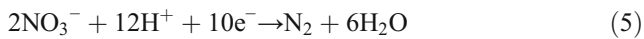
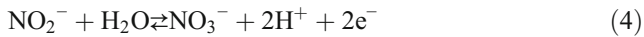
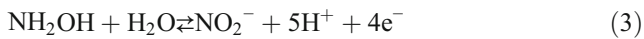
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The nitrogen and oxygen isotopic compositions of nitrate have been proved to be an effective tool to elucidate nitrate sources and decipher main nitrogen cycle processes (Deutsch et al. 2009; Kelley et al. 2013; Liu et al. 2006; Vrzel et al. 2016; Xing and Liu 2016). The dual-isotope approach is based on the fact that different sources of nitrate have distinct isotopic compositions. Nitrate in the fresh water system is mainly derived from chemical fertilizer, soil organic nitrogen, atmospheric precipitation, livestock waste, and sewage effluent (Chen et al. 2014; Kendall et al. 2007; Ohte 2013). The typical $\delta^{15}\text{N}$ values of chemical fertilizer, which is produced by fixation of atmospheric N_2 , range from -6 to $+6\text{‰}$ (Xue et al. 2009). The $\delta^{18}\text{O}-\text{NO}_3^-$ values of synthetic nitrate fertilizer vary between $+17$ and $+25\text{‰}$ (Kendall et al. 2007). The $\delta^{15}\text{N}$ values of soil nitrogen affected by the rate of ammonification and nitrification range from 0 to $+8\text{‰}$ (Ding et al. 2014; Xue et al. 2009). The $\delta^{18}\text{O}$ values of nitrate derived from nitrification originating from ammonia fertilizer and mineralized soil organic nitrogen vary from -10 to $+10\text{‰}$ (Kelley et al. 2013). The $\delta^{15}\text{N}$ and $\delta^{18}\text{O}$ signatures of nitrate from atmospheric precipitation range from -13 to $+13\text{‰}$ and from $+25$ to $+94\text{‰}$, respectively (Kendall et al. 2007; Xue et al. 2009; Yue et al. 2017). Compared with other nitrogen sources, nitrate from manure and sewage has high $\delta^{15}\text{N}$ values from $+7$ to more than $+20\text{‰}$ and low $\delta^{18}\text{O}$ values from -5 to $+10\text{‰}$ (Ding et al. 2014; El Gaouzi et al. 2013; Lee et al. 2008). Meanwhile, denitrification results in $\delta^{15}\text{N}$ and $\delta^{18}\text{O}$ values of the remaining nitrate increasing with a relationship of 1.3:1 to 2.1:1 (Wexler et al. 2014; Xu et al. 2016; Xue et al. 2009). The $\delta^{18}\text{O}$ values of water combining with $\delta^{18}\text{O}$ values of atmospheric O_2 can determine whether nitrification happened (Hollocher 1984; Kelley et al. 2013).

Qinhe is the second largest river of Shanxi province, China, which provides water resources for industrial, agricultural, and domestic uses along the river. However, the water quality of Qinhe Basin (QHB) deteriorated owing to the increasing discharge of industrial wastewater, agricultural, and domestic sewage (Fu et al. 2013). Recently, the water pollution problem of QHB has attracted concerns of numerous researchers (Feng et al. 2010; Fu 2012; Qin et al. 2016; Wang et al. 2013a; Zhang et al. 2012). The river water in QHB faces with the risk of eutrophication (Fu 2012). The nitrate of the river water in this area ranged from 4.93 to 43.24 mg/L (Qin et al. 2016), and the water bodies were polluted by urban point sources, agricultural, and rural non-point sources (Wang et al. 2012). In

order to prevent nitrate contamination, it is necessary to evaluate the nitrate sources of river water in the QHB. The purpose of this study was to identify the sources and transformations of nitrate in the QHB using isotopic compositions of nitrate and river water. The results of this study should be useful to improve the management measures of water quality and control nitrate pollution in the QHB.

Materials and methods

Study area description

The QHB, located in the north China between $35^\circ 03'$ to $36^\circ 48'$ N latitude and $112^\circ 03'$ to $113^\circ 30'$ E longitude, is the main tributary of the Yellow River, with a drainage area of $1.35 \times 10^4 \text{ km}^2$ and length of 485 km. It, originating from Erlangshen ditch south of Taiyue Mountain in Shanxi province, flows through Shanxi and Henan provinces, and finally empties into the Yellow River at Nanjia Village in Wuzhi County. The climate of QHB is mainly dominated by the temperate continental monsoon, and the annual mean temperature ranges from 10 to 14.4°C . The annual average precipitation is about 550–700 mm, mainly occurring from June to September when approximately 70% of the total annual precipitation falls (Bai et al. 2014). The terrain of the study area is high in the south and low in the north. The landforms of the region are divided into two large units, that is, Taiyue Mountain and Southeast Plateau of Shanxi province (Hu et al. 2012). The study area consists of four landscape types, including stony Mountain area, earth-rock hilly region, valley area, and alluvial plain region. The main strata of the headstream of QHB in Taiyue Mountain and the downstream of QHB in Taihang Mountain are Ordovician limestone, Cambro-Ordovician limestone, Lime sandstone, and Permian sandstone (Zhang et al. 2015). The sedimentary rocks widely exposed in the upper and middle stream of QHB are Triassic sandstone and sandy mudstone (Qin et al. 2016). There are mainly mountain areas and few human activities in the upstream. The midstream of the study area is characterized by high population density, developed industry, and frequent anthropogenic activities. The downstream of QHB is mainly agricultural area, intensive residential, and industrial areas. The Dan River is the biggest tributary of Qinhe Basin, originating from Danzhuling at Zhao village in Shanxi province. It loads wastewater of industrial enterprises in Gaoping and Jincheng cities and urban domestic sewage (Ma et al. 2010; Wang et al. 2012), which causes water quality to deteriorate severely.

Sampling and analysis

The sampling sites of surface water are shown in Fig. 1. A total of 24 surface water samples from Qinhe Basin were

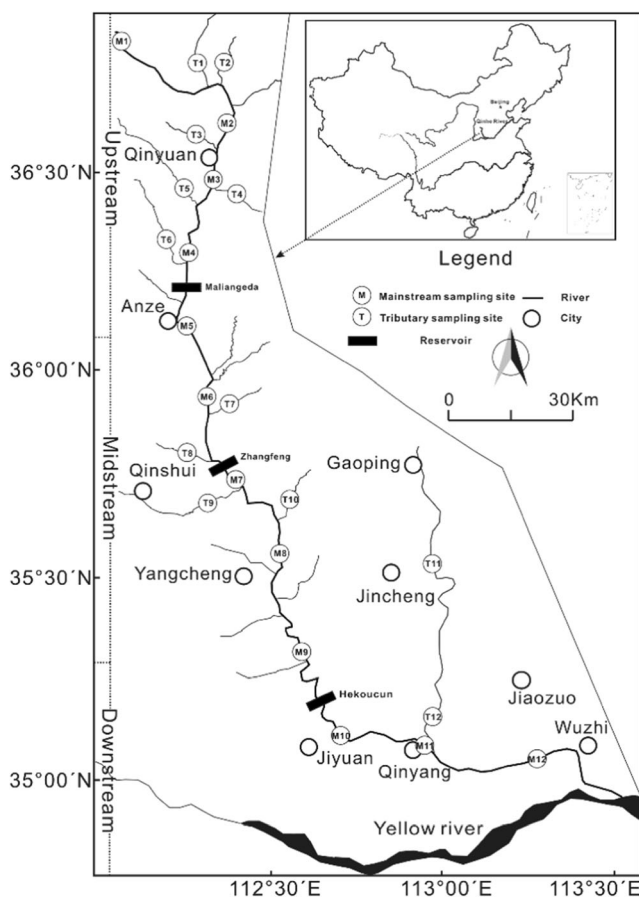


Fig. 1 Sampling sites of QHB (modified from Zhang et al. 2015)

collected in August (wet season) 2015. Water parameters, such as temperature, pH, electrical conductivity (EC), and dissolved oxygen (DO), were measured using field meters (SX716 and SX731, Sanxin, China). Then, the water samples were collected in 5-L pre-cleaned plastic bags and filtered through 0.22 μm cellulose acetate membrane within 24 h and then stored in 4 $^{\circ}\text{C}$ environment before analysis.

The concentrations of anions (NO_3^- and Cl^-) were determined by ionic chromatography (ICS90, Dionex) at the State Key Laboratory of Environmental Geochemistry in Guiyang City, China. The hydrogen and oxygen isotopic compositions of water were analyzed with an elemental analyzer (Flash 2000 HT) isotope ratio mass spectrometer (IRMS, MAT-253, Thermo Fisher Scientific) at the Provincial Key Laboratory of Henan Polytechnic University in Jiaozuo City, China. The analytical precisions of δD and $\delta^{18}\text{O}-\text{H}_2\text{O}$ were better than 2‰ and 0.2‰, respectively. The international standard VSMOW was used to calibrate δD and $\delta^{18}\text{O}-\text{H}_2\text{O}$ values.

The isotopic compositions of nitrate in river water were determined at the State Key Laboratory of Subtropical Mountain Ecology in Fuzhou City, China, with an IRMS (MAT-253, Thermo Fisher Scientific) attached Precon using the cadmium reduction method (McIlvin and Altabet 2005;

Xue et al. 2009). Analytical precision for $\delta^{15}\text{N}-\text{NO}_3^-$ and $\delta^{18}\text{O}-\text{NO}_3^-$ were 0.31‰ and 0.55‰, respectively. The international standard USGS34, USGS35, and IAEA-N3 were used to calibrate the ratios of $\delta^{15}\text{N}-\text{NO}_3^-$ and $\delta^{18}\text{O}-\text{NO}_3^-$.

The stable isotope ratios are reported using the delta (δ) per thousand (‰) notation relative to an international standard.

$$\delta (\text{‰}) = \left(\frac{R_{\text{sample}} - R_{\text{standard}}}{R_{\text{standard}}} \right) \times 1000 \quad (6)$$

Where R represents D/H, $^{15}\text{N}/^{14}\text{N}$, or $^{18}\text{O}/^{16}\text{O}$. The value of $^{15}\text{N}/^{14}\text{N}$ reference standard is N_2 in atmospheric air; the value of D/H and $^{18}\text{O}/^{16}\text{O}$ reference standard is the international Vienna Standard Mean Ocean Water (VSMOW).

Results

Chemical compositions of river water

The hydrochemical compositions of water samples collected in August 2015 were summarized in Table 1. The pH of river water ranged from 7.19 to 9.28 with an average value of 8.27, and DO varied from 0 to 24.92 mg L^{-1} with an average value of 9.95 mg L^{-1} . The EC value of river water in upstream, midstream, and downstream of QHB varied from 361 to 1002 $\mu\text{S cm}^{-1}$, from 425 to 781 $\mu\text{S cm}^{-1}$ and from 719 to 1305 $\mu\text{S cm}^{-1}$, with an average value of 564 $\mu\text{S cm}^{-1}$, 526 $\mu\text{S cm}^{-1}$, and 928 $\mu\text{S cm}^{-1}$, respectively. The EC value of river water in the mainstream and tributaries varied from 382 to 846 $\mu\text{S cm}^{-1}$ and from 361 to 1305 $\mu\text{S cm}^{-1}$, with an average value of 572 $\mu\text{S cm}^{-1}$ and 683 $\mu\text{S cm}^{-1}$, respectively. The concentrations of NO_3^- in the upstream, midstream, and downstream of QHB ranged from 3.21 to 20.81 mg L^{-1} , from 2.32 to 16.99 mg L^{-1} and from 0.71 to 16.32 mg L^{-1} , with a mean value of 7.37 mg L^{-1} , 7.88 mg L^{-1} , and 8.33 mg L^{-1} , respectively. The range of nitrate concentrations of river water in the mainstream was from 2.19 to 16.99 mg L^{-1} , with a mean value of 7.16 mg L^{-1} , while the nitrate concentrations of river water in the tributaries varied from 0.71 to 20.81 mg L^{-1} , with an average of 8.32 mg L^{-1} . The average value of NO_3^- (7.16 mg L^{-1}) in the mainstream of QHB was lower than that of the Yellow River (11.07 mg L^{-1}) in the high flow season (Yue et al. 2017). The Cl^- of river water in the upstream, midstream, and downstream of QHB ranged from 2.33 to 43.21 mg L^{-1} , from 8.32 to 33.79 mg L^{-1} , and from 27.08 to 112.29 mg L^{-1} , with an average value of 17.83 mg L^{-1} , 19.51 mg L^{-1} , and 55.58 mg L^{-1} , respectively. The Cl^- contents of river water in the mainstream varied from 2.33 to 50.98 mg L^{-1} with an average value of 21.23 mg L^{-1} , while the Cl^- contents in the tributaries ranged from 6.97 to 112.29 mg L^{-1} with average values of 31.28 mg L^{-1} .

Table 1 Hydrochemical parameters and isotopic analysis of water samples in the QHB

| Sample | pH | EC ($\mu\text{S cm}^{-1}$) | DO (mg L^{-1}) | NO_3^- (mg L^{-1}) | Cl^- (mg L^{-1}) | $\delta\text{D-H}_2\text{O}$ (‰) | $\delta^{18}\text{O-H}_2\text{O}$ (‰) | $\delta^{15}\text{N-NO}_3^-$ (‰) | $\delta^{18}\text{O-NO}_3^-$ (‰) |
|--------|------|------------------------------|---------------------------|--|--------------------------------------|----------------------------------|---------------------------------------|----------------------------------|----------------------------------|
| M1 | 9.28 | 382 | 9.50 | 5.33 | 2.33 | -74 | -10.8 | -6.7 | -3.9 |
| M2 | 7.19 | 524 | 7.86 | 6.17 | 11.23 | -62 | -8.4 | 1.8 | -1.9 |
| M3 | 8.43 | 487 | 10.28 | 4.90 | 13.93 | -62 | -8.2 | 9.0 | 5.5 |
| M4 | 8.15 | 442 | 7.34 | 5.53 | 12.21 | -57 | -7.7 | 2.6 | 1.8 |
| M5 | 8.31 | 468 | 8.34 | 5.60 | 17.43 | -56 | -7.2 | 3.8 | -1.2 |
| M6 | 8.22 | 483 | 6.91 | 3.76 | 16.11 | -56 | -7.3 | 4.5 | -1.0 |
| M7 | 8.76 | 435 | 14.19 | 4.49 | 14.55 | -58 | -7.9 | 3.7 | -0.1 |
| M8 | 9.12 | 522 | 24.92 | 2.32 | 24.69 | -56 | -7.2 | 10.9 | 5.6 |
| M9 | 7.84 | 781 | 11.43 | 16.99 | 29.67 | -61 | -8.3 | 5.8 | -6.0 |
| M10 | 8.57 | 719 | 12.41 | 16.32 | 27.08 | -61 | -8.2 | 6.0 | -5.8 |
| M11 | 8.25 | 772 | 10.58 | 12.26 | 34.60 | -60 | -8.1 | 6.2 | -1.7 |
| M12 | 8.25 | 846 | 9.97 | 2.19 | 50.98 | -59 | -8.0 | 14.8 | -1.9 |
| T1 | 8.28 | 764 | 9.17 | 8.38 | 22.64 | -63 | -8.7 | 7.6 | -3.4 |
| T2 | 8.08 | 361 | 7.99 | 3.21 | 6.97 | -61 | -8.4 | 9.6 | 3.2 |
| T3 | 8.36 | 1002 | 10.59 | 8.35 | 36.76 | -61 | -8.2 | 5.3 | -0.3 |
| T4 | 7.58 | 386 | 9.93 | 5.36 | 11.11 | -63 | -8.5 | 3.8 | 1.1 |
| T5 | 8.53 | 581 | 11.25 | 7.45 | 18.35 | -63 | -8.8 | -0.6 | 5.3 |
| T6 | 8.46 | 810 | 8.63 | 20.81 | 43.21 | -61 | -8.3 | -4.1 | -5.2 |
| T7 | 8.10 | 425 | 7.16 | 3.86 | 8.32 | -61 | -8.1 | nd | nd |
| T8 | 8.36 | 448 | 9.49 | 3.03 | 9.24 | -60 | -8.1 | 1.9 | 0.9 |
| T9 | 8.34 | 600 | 10.28 | 16.64 | 33.79 | -58 | -7.8 | 5.3 | -2.8 |
| T10 | 8.11 | 518 | 9.48 | 11.91 | 19.71 | -61 | -8.2 | nd | nd |
| T11 | 8.22 | 1305 | 11.07 | 10.20 | 112.29 | -52 | -7.2 | nd | nd |
| T12 | 7.79 | 1000 | 0 | 0.71 | 52.96 | -63 | -8.8 | nd | nd |

nd not determined

Isotopic compositions of river water

As shown in Table 1, the δD and $\delta^{18}\text{O-H}_2\text{O}$ values of river water varied from -74 to -52‰ and from -10.8 to -7.2‰, with a mean value of -60‰ and -8.2‰, respectively. As indicated in Fig. 2a, the water sample with the most negative δD and $\delta^{18}\text{O-H}_2\text{O}$ values was located in the headstream (M1), and the water sample with positive values exhibited in the downstream (T11).

The $\delta^{15}\text{N-NO}_3^-$ and $\delta^{18}\text{O-NO}_3^-$ values of river water ranged from -6.7 to +14.8‰ and from -6.0 to +5.6‰, with an average of +4.6 and -0.6‰, respectively (Table 1). The $\delta^{15}\text{N-NO}_3^-$ value of river water in the upstream, midstream, and downstream of QHB varied from -6.7 to +9.6‰, from +1.9 to +10.9‰, and from +6.0 to +14.8‰, with a mean value of +2.9‰, +5.4‰, and +9.0‰, respectively. The average of $\delta^{15}\text{N-NO}_3^-$ value in the upstream was lower than those in the midstream and downstream. The $\delta^{18}\text{O-NO}_3^-$ value of river water in the upstream, midstream, and downstream of QHB ranged from -5.2 to +5.5‰, from -6.0 to +5.6‰, and from -5.8 to -1.7‰, with a mean value of +0.1‰, -0.6‰, and -3.1‰, respectively. As shown in Fig. 3a, the $\delta^{15}\text{N-NO}_3^-$ values increased slowly with abruptly high values in M3, M8, and M12; however, the oxygen isotope values increased

slowly with high values in M3 and M8 and decreased in M9 and then increase slowly to the downstream.

Discussion

The source of river water and controlling factors of water isotopes

The local meteoric water line (LMWL), which was reported as $\delta\text{D} = 6.42\delta^{18}\text{O} - 4.66$ (Jia et al. 2015). In addition, the global meteoric water line (GMWL) was defined as $\delta\text{D} = 8\delta^{18}\text{O} + 10$ (Craig 1961). As indicated in Fig. 2a, the hydrogen and oxygen isotopic compositions of river water in the QHB distributed below GMWL and LMWL, suggesting that atmospheric precipitation was the major source of river water.

The δD and $\delta^{18}\text{O-H}_2\text{O}$ values of samples (M5, M6, M8, and T11) located below the lower right of LMWL, which was caused by evaporation of river water enriching hydrogen and oxygen isotope values of the residual water. The M5 was sampled in the downstream of the Maliangeda reservoir with relatively slow velocity where evaporation caused the enrichment of δD and $\delta^{18}\text{O-H}_2\text{O}$ values. M6 and M8 were also sampled in reaches

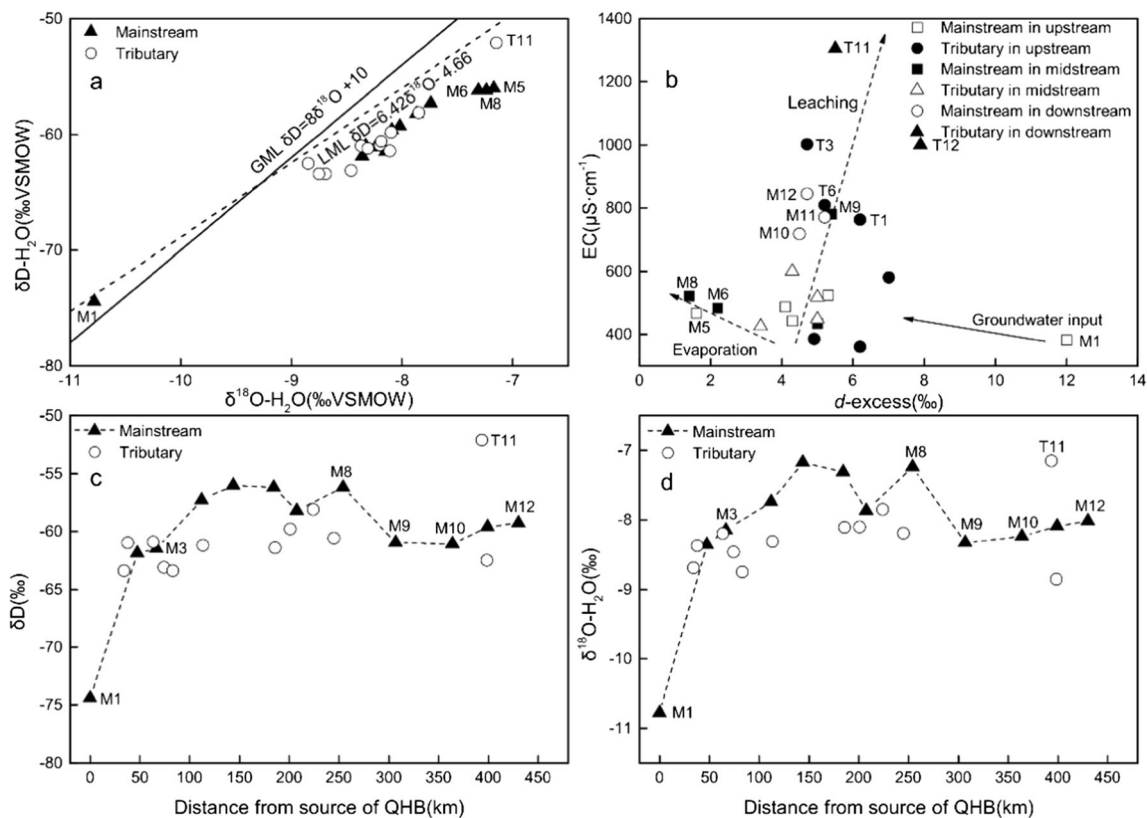


Fig. 2 Hydrogen and oxygen isotopic compositions (a), EC versus d excess (b), spatial variations of hydrogen isotopic values (c), and spatial distributions of oxygen isotope values (d) of river water in the QHB

with slow water speed where evaporation dominated the water isotopes of river water. T11 and T12 were sampled in tributary Danhe River where the river received much wastewater from sewage, agriculture, and industrial enterprises (Ma et al. 2010; Wang et al. 2012). Industrial and agriculture water induced runoff reduction, and water recycling caused further evaporation (Gao et al. 2011) with increasing hydrogen and oxygen values of river water in these sites.

Groundwater recharge occurred in the headwater (M1) and downstream (M9 and M10) where river water has relatively negative water isotope values (Fig. 2c, d). The most negative water isotope values of M1 was due to the direct recharge from spring water undergoing no obvious evaporation and keeping water isotope values of local wet precipitation. The reach from M9 to M10 was located in the Taihang Mountain where river flew through the mountain in deep valley receiving much spring water. Tributary water had more negative water isotope values than those in most mainstream water indicating groundwater was dominated water source in these tributaries due to tributaries sourced from mountain area (Li et al. 2015a). The residual samples did not experience obvious groundwater recharge (Fig. 2c, d).

The relationship between d excess ($d = \delta D - 8\delta^{18}O$) and total dissolved solid (TDS) value was often used to identify the controlling factors of dissolved components in

groundwater due to evaporation process resulted in increasing of TDS values together with decreasing of d excess values; however, leaching process of minerals only resulted in increasing of TDS values but not change of d excess values (Huang and Pang 2012; Qin et al. 2016). The EC values of river water were significantly associated with TDS; therefore, we use the plot between d excess and EC to discern the controlling processes of dissolved components in the river water. As indicated in Fig. 2b, the increase of EC values and the decrease of d excess values of river water were mainly found in M5, M6, and M8 where evaporation was responsible for the increase of EC values in these water samples. Water leaching process was responsible for the increase of EC values of most river water. It was worth to note that dissolved components in groundwater mostly derived from the water-rock reaction along the flow path. Groundwater infiltration and groundwater direct input into river water as spring were important factors to control the riverine components in the QHB. This conclusion was supported by the fact that the water exchange between surface water and groundwater was 1.03×10^9 m³ in 1988 in the QHB (Wang et al. 2006). The average EC value of river water in the midstream ($526 \mu S \cdot cm^{-1}$) was lower than that of river water in the upstream ($564 \mu S \cdot cm^{-1}$) was due to groundwater input

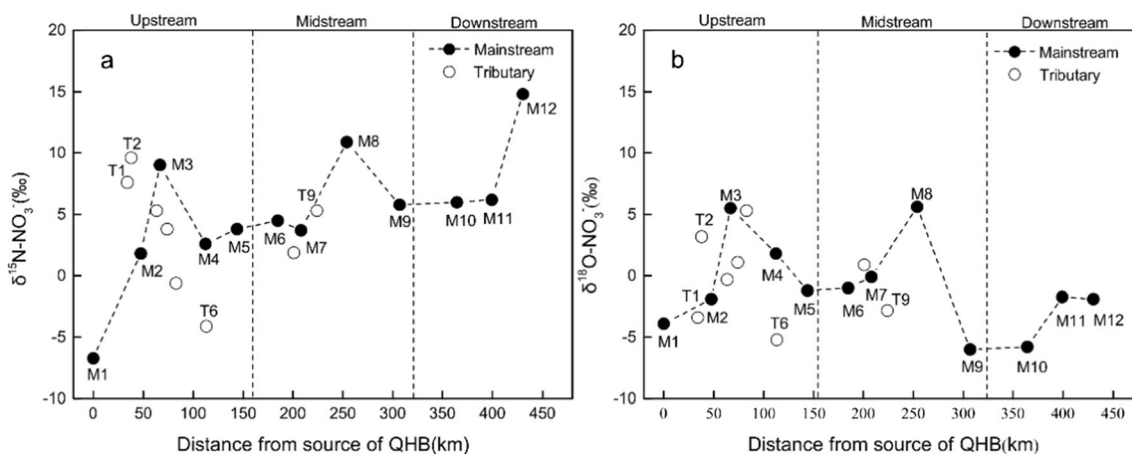


Fig. 3 Spatial distribution of nitrogen (a) and oxygen (b) isotopic values of nitrate in the QHB

from sandstone aquifer with low EC value (Zhang et al. 2015). The increase of EC values in the downstream (M10, M11, M12, T11, and T12) was not only due to groundwater input from karst aquifer with high dissolved components but also due to direct wastewater input from sewage, agriculture, and industrial enterprises.

Sources of dissolved nitrate in the river water

Spatial variations of nitrate contents in river water were due to different nitrate sources and variable nitrogen transforming paths. As shown in Fig. 4a, the nitrate concentrations of the river water were variable in the different reaches of the QHB with nitrate contents less than 8 mg/L from M1 to M8, but larger than 10 mg/L from M9 to the mouth except M12. The enhancement of NO₃⁻ and Cl⁻ concentrations from M9 to M11 was related to the input of sewage water, industrial wastewater, and agricultural fertilizer (Han 2008). The decreasing NO₃⁻ concentrations (Fig. 4a) but increasing Cl⁻ contents (Fig. 4b) in M3, M8, and M12 were possibly due to

input of groundwater and/or assimilation by algae at these sampling sites with DO contents of 10.28 mg/L, 24.92 mg/L, and 9.97 mg/L (Table 1). However, positive oxygen isotope values of M3, M8, and M12 indicated no obvious groundwater input (Fig. 2c, d); internal algae assimilation could be responsible for the decreasing of nitrate concentrations in these sites due to relatively steady conditions. The high NO₃⁻ and Cl⁻ concentration in T6 (Fig. 4) was probably related to the input of industrial wastewater from coking plant and coal preparation plant. The nitrate concentration of T9 was larger than 16 mg/L possibly owing to coal mining activities and wastewater from chemical enterprises (Fu et al. 2013). The DO concentration of T12 was 0 mg/L (Table 1), which was suitable for denitrification (Rivett et al. 2008).

The δ¹⁵N-NO₃⁻ and δ¹⁸O-NO₃⁻ values of river water in the source (M1) of the QHB were -6.7‰ and -3.9‰, which suggested that nitrate was mainly sourced from NH₄⁺ in the rainwater and subsequent nitrification. The δ¹⁵N-NO₃⁻ values of sites (M3, M8, and M12) were more than +7‰ (Fig. 3a), as mentioned above, indicating that nitrate assimilation by algae

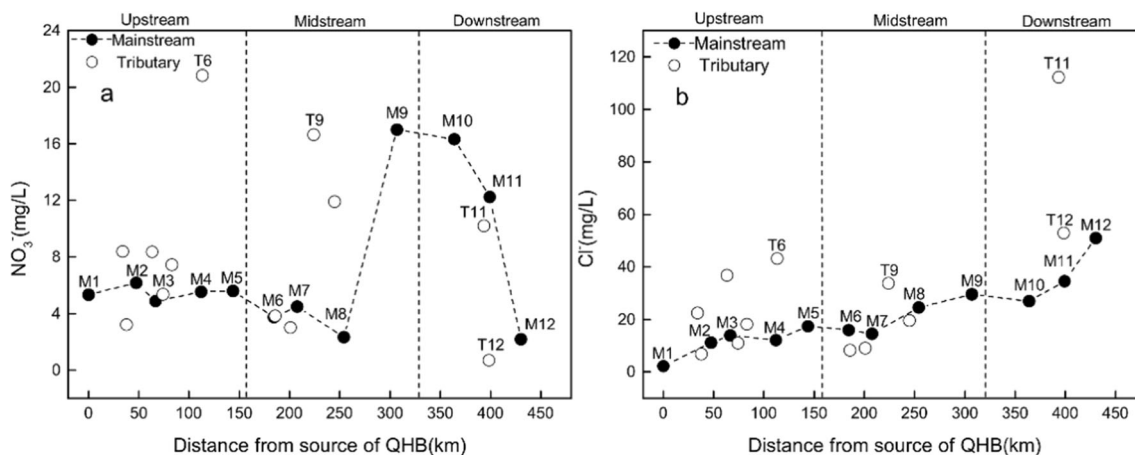


Fig. 4 Spatial variation of NO₃⁻ (a) and Cl⁻ (b) concentrations in the QHB

was responsible for the nitrogen and oxygen isotope enrichment of residual nitrate in water. Wang et al. (2006) proved that the percentage of exchange between surface water and groundwater in the area located from the source of QHB to Wuzhi hydrological station was more than 80% of total groundwater resources in 1 year. As shown in Fig. 3b, the $\delta^{18}\text{O}-\text{NO}_3^-$ values of sites (M9 and M10) were close to that of the headstream (M1), which was probably due to groundwater input corresponding to negative hydrogen and oxygen isotope values in M9 and M10 (Fig. 2c, d). However, the $\delta^{15}\text{N}-\text{NO}_3^-$ values of these sites (+ 5.8‰ and + 6.0‰) were significantly different from the source of QHB (− 6.7‰), which indicated that except groundwater nitrate input, there must be another important nitrate sources. Negative oxygen isotope values of nitrate could be formed from nitrification of ammonium, and nitrate in M1 was mainly controlled by nitrification of ammonium from rainwater with small Cl^- content (Table 1). However, nitrate in M9 and M10 was mainly affected by nitrification from sewage and industrial wastewater with high Cl^- contents (Table 1). As indicated in Fig. 3a, the $\delta^{15}\text{N}-\text{NO}_3^-$ values of tributaries (T1 and T2) were larger than + 7‰, indicating that domestic sewage from town residential area had an important effect on nitrate isotopic compositions. The nitrogen isotopic value of T6 was close to − 5‰ (Fig. 3a), which was mainly attributed to the input of ammonium in the fertilizer and industrial wastewater with high Cl^- content (Table 1) from coal mining company (Wang et al. 2013b). The $\delta^{15}\text{N}-\text{NO}_3^-$ value of T9 increased also due to wastewater from coal mining and chemical enterprises (Fu et al. 2013).

Transformations of nitrogen in the QHB

Mixing of different sources and assimilation by algae

The isotopic compositions of nitrate are usually modified by physical and biogeochemical processes. The nitrate derived from various potential sources seldom kept constant isotopic values, which was probably changed by diverse isotope fractionation in different periods of mixing (Kendall et al. 2007). The cross plot between $\delta^{15}\text{N}-\text{NO}_3^-$ and the inverse of nitrate was often used to elucidate the mixing processes. If two different nitrate sources mixed, the $\delta^{15}\text{N}-\text{NO}_3^-$ is linearly positively correlated with $1/[\text{NO}_3^-]$ (Kendall et al. 2007; Xu et al. 2016). There was a significantly positive relationship between $\delta^{15}\text{N}-\text{NO}_3^-$ and $1/[\text{NO}_3^-]$ (Fig. 5a), which indicated that the mixing processes could account for the shifting of $\delta^{15}\text{N}-\text{NO}_3^-$ values. As shown in Fig. 5a, the nitrate of river water was originated from at least two different sources: one with $\delta^{15}\text{N}-\text{NO}_3^-$ values below + 5‰, another with $\delta^{15}\text{N}-\text{NO}_3^-$ values above + 7‰. The $\delta^{15}\text{N}-\text{NO}_3^-$ values of river water in the QHB less than + 5‰ indicated that nitrate was primarily derived from soil nitrogen and chemical fertilizer. It was worth to note that nitrate from rain ammonium was one of the

important components in soil nitrogen. Although $\delta^{15}\text{N}-\text{NO}_3^-$ values of nitrate from rainwater and fertilizer and industrial wastewater were within a similar range, NO_3^- and Cl^- concentrations were quite different (Fig. 5a, b). Some river water with $\delta^{15}\text{N}-\text{NO}_3^-$ values larger than + 7‰ had potential nitrate from sewage and manure, and increasing of $\delta^{15}\text{N}-\text{NO}_3^-$ values with a decreasing of NO_3^- concentration but relatively constant or increased Cl^- contents may be due to occurrence of assimilation of nitrate by algae in water samples with DO contents more than 3 mg/L, e.g., M3, M8, and M12 (Fig. 5a).

Therefore, the nitrate in headwater was mainly derived from nitrification of ammonium from rainwater and soil organic nitrogen oxidation. Sewage and industrial wastewater were important nitrate sources in the domestic area, e.g., M3, M8, M12, T6, and T9. Algae assimilation was dominated in M3, M8, and M12 due to the relatively steady station and rich organic nutrition from sewage water.

Denitrification

Denitrification was an important process to remove nitrogen by the reduction of nitrate to gaseous nitrogen (Kendall et al. 2007; Wang et al. 2017; Xu et al. 2016). The denitrification causes nitrate concentrations to decrease and an enrichment of isotopic values of the remaining nitrate (Xue et al. 2009). In the denitrification process, nitrogen isotopic enrichment factors vary from − 40 to − 5‰ (Panno et al. 2006; Xue et al. 2009), and oxygen isotopic enrichment factors vary from − 18 to − 8‰ (Xue et al. 2009). The linear relationship between $\delta^{15}\text{N}-\text{NO}_3^-$ and $\delta^{18}\text{O}-\text{NO}_3^-$ (1.3:1 to 2.1:1) can provide evidence for denitrification (Xu et al. 2016; Xue et al. 2009). As indicated in Fig. 6, there was no significant relationship between $\delta^{15}\text{N}-\text{NO}_3^-$ and $\delta^{18}\text{O}-\text{NO}_3^-$ in river water ($P > 0.05$). Meanwhile, most water samples in the QHB had DO concentrations more than 2 mg/L (Table 1), which was not beneficial for denitrification (Rivett et al. 2008). Therefore, the relationship between $\delta^{15}\text{N}-\text{NO}_3^-$ and $\delta^{18}\text{O}-\text{NO}_3^-$ indicated that no obvious denitrification occurred in the QHB.

Nitrification

Nitrification was a process that ammonium was oxidized to nitrate mediated by a few different sorts of autotrophic bacteria or archaea (Kendall et al. 2007; Xu et al. 2016). Nitrogen enrichment factors in the nitrification process range from − 38 to − 14‰ (Casciotti et al. 2003; Xu et al. 2016). It is reported that the oxygen atoms derived from nitrification gain two thirds of oxygen from water and one third from atmospheric oxygen (Andersson and Hooper 1983). The $\delta^{18}\text{O}-\text{H}_2\text{O}$ values of river water in QHB ranged from − 10.8 to − 7.2‰ (Table 1), and the $\delta^{18}\text{O}$ value of atmospheric O_2 is 23.5‰ (Durka et al. 1994; Hollocher 1984). If there had been no isotope

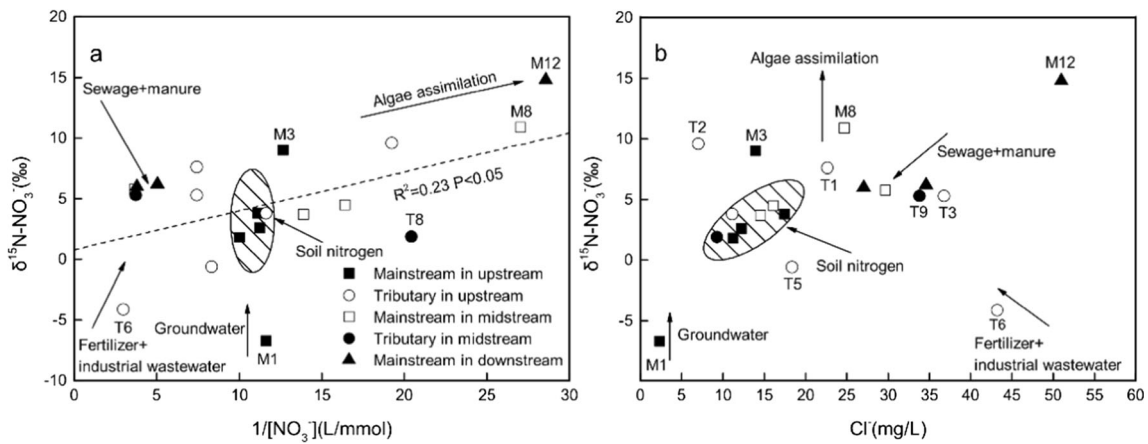


Fig. 5 $\delta^{15}\text{N}-\text{NO}_3^-$ versus $1/[\text{NO}_3^-]$ (a) and Cl^- (b) in river water of the QHB. The legends in Fig. 5b are same as Fig. 5a

fractionation, the theoretical values of $\delta^{18}\text{O}-\text{NO}_3^-$ originated from nitrification would have ranged from + 0.6‰ to + 3.0‰. Several $\delta^{18}\text{O}-\text{NO}_3^-$ values of river water from upstream and midstream were higher than theoretical values (Fig. 7), which probably caused by the variable proportion of oxygen from water and O_2 , oxygen isotope fractionation, and different biological processes (Kendall et al. 2007; Mayer et al. 2001). Kool et al. (2011) found that oxygen changes in water affect $\delta^{18}\text{O}$ values of nitrate in soil ecosystems. It may be the primary reason that some $\delta^{18}\text{O}-\text{NO}_3^-$ values were lower than theoretical values (Fig. 7), which possibly suggested that more oxygen from the water was transformed into nitrate in the nitrification process. As shown in Fig. 7, the $\delta^{18}\text{O}-\text{NO}_3^-$ values of river water were distributed around theoretical nitrification line and were in the range of - 10 to + 10‰ in which $\delta^{18}\text{O}-\text{NO}_3^-$ signatures derived from nitrification (Kendall et al. 2007). Thus, the oxygen isotopic compositions of nitrate indicated that the nitrate in river water of QHB would be affected by nitrification.

Identification of nitrate sources based on dual isotope approach

In the riverine ecosystem, the nitrate possibly originates from atmospheric deposition, agricultural fertilizer input, soil nitrogen, manure, urban domestic sewage, and industrial wastewater (Xu et al. 2016). The dual-isotope approach is used to access the nitrate sources of the QHB due to different nitrate sources having distinct isotopic compositions. As shown in Fig. 8, the $\delta^{15}\text{N}-\text{NO}_3^-$ and $\delta^{18}\text{O}-\text{NO}_3^-$ values fell into three sections, suggesting that NH_4^+ in fertilizer and rain, soil nitrogen, manure, and urban domestic sewage might be the nitrate sources of river water in the QHB. The $\delta^{18}\text{O}-\text{NO}_3^-$ values of nitrate in precipitation (+ 25 to + 94‰) and nitrate fertilizer (+ 17‰ and + 25‰) are higher than that of nitrate from manure and sewage, and higher than that of nitrate from nitrification of soil nitrogen and ammonium in rain and fertilizer (Kendall et al. 2007; Xue et al. 2009; Yue et al. 2017). The $\delta^{18}\text{O}-\text{NO}_3^-$ signatures of nitrate indicated that nitrate in atmospheric

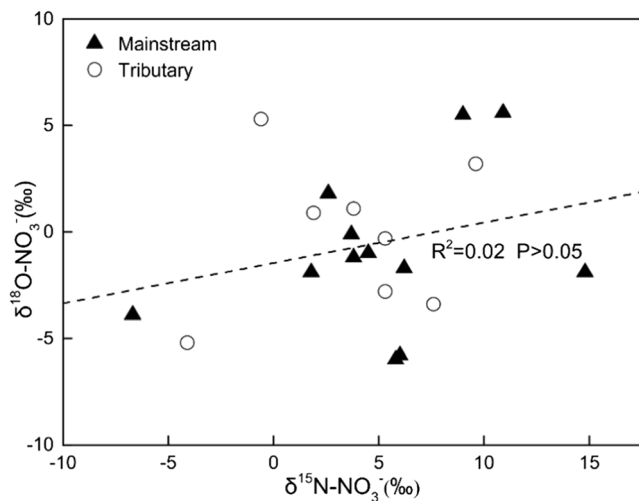


Fig. 6 The relationship between $\delta^{15}\text{N}-\text{NO}_3^-$ and $\delta^{18}\text{O}-\text{NO}_3^-$ in river water of the QHB

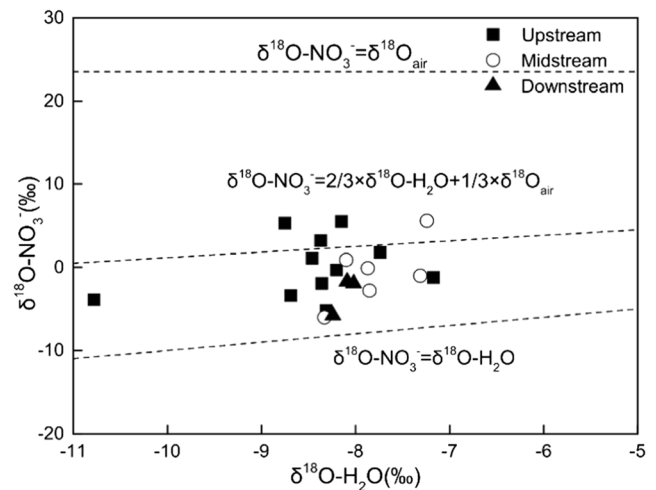


Fig. 7 Relationship between $\delta^{15}\text{N}-\text{NO}_3^-$ and $\delta^{18}\text{O}-\text{H}_2\text{O}$ in river water of QHB

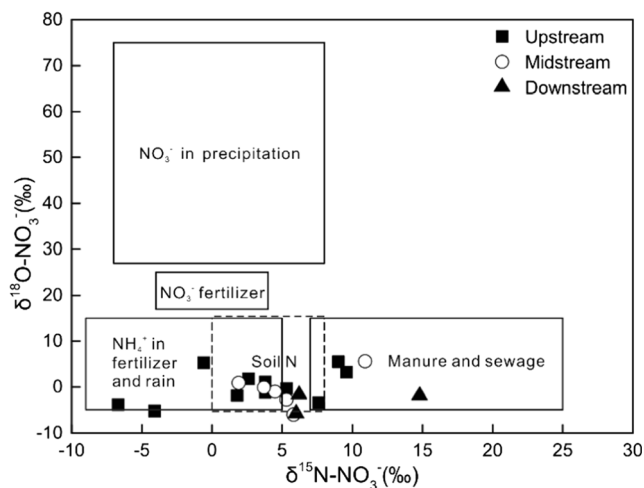


Fig. 8 Nitrogen and oxygen isotopic compositions of river water in the QHB. The box diagram shows the values of $\delta^{15}\text{N}$ and $\delta^{18}\text{O}$ of nitrate sources modified from Xue et al. (2009) and Nestler et al. (2011)

deposition and nitrate fertilizer contributed a minor proportion of nitrate to the river water.

Some researchers reported that the concentrations and isotopic compositions of nitrate in river water probably influenced by land use and human activities in the watershed (Ohte et al. 2010; Xing and Liu 2016; Yue et al. 2014). As shown in Fig. 8, the nitrate isotopic values ($\delta^{15}\text{N}-\text{NO}_3^-$, -6.7 to $+9.6\text{‰}$; $\delta^{18}\text{O}-\text{NO}_3^-$, -5.2 to $+5.5\text{‰}$) in the upstream indicated that nitrate was mainly derived from NH_4^+ in the rain and soil nitrogen, which was corresponding to the river flowing through dense forest and regions with few human activities. There were many coal mining plants, coking plants, and power plants distributed along the riverside of midstream in the QHB, and large amounts of industrial wastewater and urban domestic sewage discharged into the river. Meanwhile, the $\delta^{15}\text{N}-\text{NO}_3^-$ of river water receiving industrial wastewater were smaller than $+5\text{‰}$ (Xu et al. 2016). Therefore, the isotopic compositions of nitrate ($\delta^{15}\text{N}-\text{NO}_3^-$, $+1.9$ to $+10.9\text{‰}$; $\delta^{18}\text{O}-\text{NO}_3^-$, -6.0 to $+5.6\text{‰}$) in the midstream suggested that nitrate was primarily derived from industrial wastewater, soil nitrogen, ammonium fertilizer, and domestic sewage, which suggested that the main nitrate sources of river water agreed with pollution sources distribution in the midstream of QHB. The higher $\delta^{15}\text{N}-\text{NO}_3^-$ values of nitrate were observed in the downstream of QHB where it is characterized as dense agricultural and industrial activities and high population density. The $\delta^{15}\text{N}-\text{NO}_3^-$ values in the downstream ranged from $+6.0$ to $+14.8\text{‰}$, which was close to the $\delta^{15}\text{N}-\text{NO}_3^-$ values of nitrate (from $+5.5$ to $+11.6\text{‰}$) reported by Zhang et al. (2012). The isotopic values of nitrate in the downstream indicated that nitrate mainly originated from soil nitrogen, manure, and sewage. In summary, the nitrate isotopic compositions of river water in the QHB indicated that the nitrate mainly derived from soil nitrogen, ammonium in fertilizer, and domestic sewage.

Conclusions

This study evaluated sources and transformations of nitrogen in the QHB by combining isotopic compositions of nitrate and H_2O with water chemistry data. The hydrogen and oxygen isotopic compositions of water indicated that atmospheric precipitation was the main source of river water. The nitrogen and oxygen isotopic values were mainly affected by the mixing process and nitrification process. No obvious denitrification shifted nitrate isotopic values of the QHB. The mixing process and assimilation by algae would be responsible for $\delta^{15}\text{N}-\text{NO}_3^-$ values increasing. The $\delta^{15}\text{N}$ and $\delta^{18}\text{O}$ values of nitrate in river water of the QHB demonstrated that nitrate sources were mainly derived from nitrification of ammonia fertilizer, soil nitrogen, and domestic sewage. Some measures should be taken to alleviate nitrate pollution, such as effective fertilization and planting trees to prevent soil erosion. In the future study, different end members of isotopic compositions of nitrate should be determined to evaluate the contribution proportions of potential nitrate sources.

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