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Nitrate sources and nitrogen biogeochemical processes in the Feng River in West China inferred from the nitrogen and oxygen dual isotope measurements of nitrate

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ABSTRACT

A portion of the nitrogen from watersheds entering river networks, which degrades river water quality and causes subsequent eutrophication of the downstream river. Identifying the source of nitrate in rivers is the primary method of controlling excessive nitrogen input into rivers. In this paper, nitrate sources in the Feng River were inferred from nitrate dual isotopes ($\delta^{15}N_{nitrate}$ and $\delta^{18}O_{nitrate}$) combined with the water quality data, and nitrogen biogeochemical processes were further explored. The results indicated that NO_3^--N is the dominant form of nitrogen in the Feng River system. The annual average content of nitrate was 3.21 mg/L, representing approximately 83% of the total nitrogen content. In September of 2012, the $\delta^{15}N_{nitrate}$ and $\delta^{18}O_{nitrate}$ values suggested that the atmospheric deposition and soil organic nitrogen were the main sources of nitrate in the upstream region, and that the atmospheric deposition, chemical fertilizers, sewage, and manure inputs were the sources in the downstream region, with average contribution ratios of 68.4, 19, and 12.6%, respectively. In December of 2011, the $\delta^{15}N_{nitrate}$ and $\delta^{18}O_{nitrate}$ values suggested that the nitrate upstream was mainly derived from soil organic nitrogen and that the nitrate downstream was derived mainly from sewage and manure inputs, with a contribution ratio of 68%. The $\delta^{18}O_{nitrate}$ data indicated that most of the nitrate from microbial nitrification could make a remarkable contribution to the Feng River system. The variations in the isotopic nitrate values suggested that denitrification enriched the heavier isotopes of nitrate in the upstream and midstream Feng River in the summer. The isotopic characteristics of the phytoplankton uptake of nitrogen were obvious in the downstream Feng River in April 2012. Nitrogen biogeochemical processes of the Feng River water system are the results of a mixture of denitrification and phytoplankton uptake and other processes.

Keywords: Nitrate sources; Nitrogen and oxygen dual isotopes; Nitrogen biogeochemical processes; Denitrification; Feng River

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1. Introduction

Nitrate (NO_3^-) contamination in the water is an environmental problem worldwide. Nitrogen (N) enters river networks, degrading river water quality and increasing the nutrient input and subsequent eutrophication of the downstream river and coastal marine ecosystems. The increased input of reactive N is attributed to intensive land use, increased use of N-containing organic and inorganic fertilizers [1], animal manure, discharge of human sewage, and elevated atmospheric N deposition [2]. The World Health Organization has set a limit of 10 mg/L NO_3^- for drinking water. However, to effectively control the NO_3^- contamination in water, the NO_3^- source inputs should be better understood. Subsequently, dedicated measures could be applied to prevent or minimize contamination. The stable N isotope data of NO_3^- ($\delta^{15}N_{nitrate}$) have been frequently used to estimate the origin of NO_3^- in the water [3–5] because the isotopic composition of N in NO_3^- is generally different among various nitrate sources, such as atmospheric precipitation, soil, chemical fertilizers, and manure. In recent years, a dual isotope approach (combination of ^{15}N and ^{18}O) has been widely used, which provides more conclusive information for tracing the sources of NO_3^- in water [6–9]. However, to date, there are no studies on the N biogeochemical cycling occurring in the Feng River system. To the best of our knowledge, few N isotope studies have been conducted for warm temperate rivers to investigate N processing in watershed ecosystems, especially under monsoon climate conditions. In this study, we report $\delta^{15}N_{nitrate}$ and $\delta^{18}O_{nitrate}$ from the Feng River. The objectives of our investigation are to identify the major sources contributing to the total dissolved NO_3^- in the river and to assess the possible occurrence and degree of denitrification in the context of the monsoon climate.

2. Samples collection and analysis

2.1. Background

The Feng River (N33.82° ~ 34.3°, E108.57° ~ 109.12°) originates from the north side of the Qinling Mountains, located south of the Jiwozi in the Weiziping township of the Chang'an district in Xi'an province, and flows through the Chang'an district of Xi'an, Huxian, Qindu town, and more than 10 towns and the Qindu district, feeding into the Wei River. Its total length is 78 km, and its watershed area is 1,460 km^2. The Feng River has three major tributaries: the Taipingyu, Gaoguanyu, and Jue Rivers.

Located in the northern foot of the Qinling Mountains to the Guanzhong plain, the Feng River basin belongs to a warm temperate, semi-arid, and sub-humid continental monsoon climate zone, with four distinct seasons. The weather is cold and dry in winter, summer is hot, and rainy. The annual precipitation in the Feng River basin is 575–1,000 mm, with a contribution of more than 60% from July to October.

The land-use types include farmland, woodland, grassland, waters, towns, and rural settlements, with woodland, arable land, and grassland dominating with proportions of 41, 36, and 16%, respectively. There are mainly woodland and grassland in the upstream region, and farmland, towns, and rural settlements in the midstream and downstream regions. The amount of chemical fertilizer used in the agricultural planting is high, with nitrogen-based fertilizer accounting for nearly 50% of the total amount, a large amount of nitrogen fertilizer in the pure discount being approximately 180 kg/ha nitrogen.

2.2. Feng River system classification and monitoring sections set

In this article, in accordance with the method of the Strahler division, the rivers of the Feng River basin were divided into three orders. Among these rivers, nine rivers are classified as first-order rivers, six as second-order rivers, and two as third-order rivers (Fig. 1).

2.3. Sampling and analysis

There were a total of 30 sampling points in the Feng River system, with 10 sites in the mainstream region of the Feng River from the upper reach to the lower reach and the remaining 20 sites in tributaries (Fig. 2).

The surface water in the middle of the river was collected three times during the hydrological year: December 2011 (dry season), April 2012, and September 2012 (wet season). In the mainstream Feng River, the sampling was accomplished by the Lagrangian approach, which can provide some detailed information about the location and transformation processes. In the tributaries, the sampling was also sequentially performed to collect the same water parcel as it moved downstream.

The water samples (the volume of the water samples normally required 1–10 L) were filtered through 0.45 μm polycarbonate membranes into precleaned polyethylene bottles on site and were then sealed and saved at 4 ℃. The samples were brought to the laboratory for the further analysis. The nitrate in the filtered water samples was concentrated on an anion-exchange

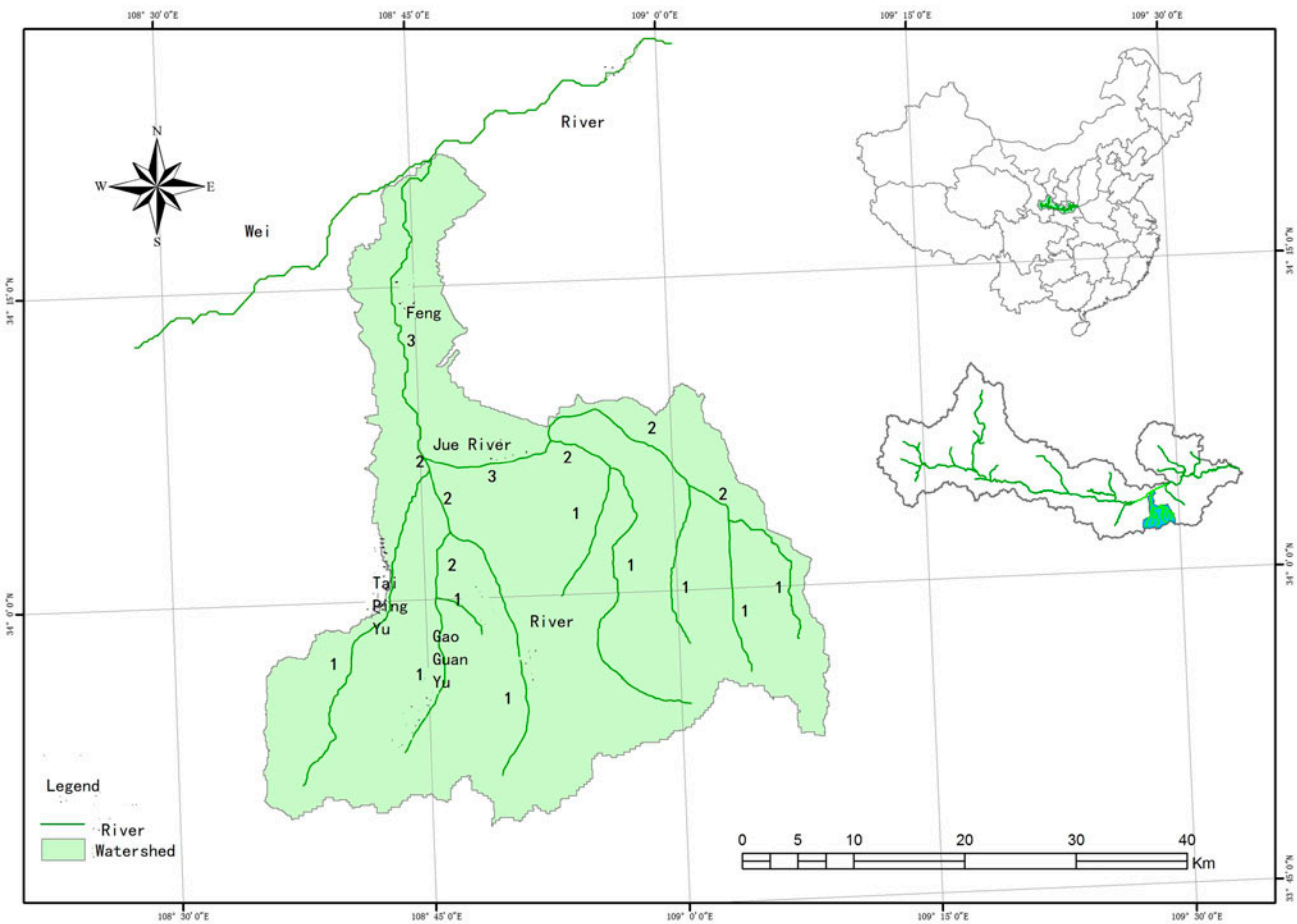

Fig. 1. Diagram of river classification by the method of Strahler.

resin column (201 × 7 [717] styrene-based strong base). The purification of the nitrate ions in the natural water nitrate used the $AgNO_3$-ion exchange method. According to the method presented by Silver et al. (2000), the dissolved nitrate was converted to solid $AgNO_3$. The $AgNO_3$ was then analyzed for $\delta^{15}N$ using a MAT DELTA (Thermo Finnigan) plus XP isotope-ratio mass spectrometer connected to a Flash EA1112 C/N analyzer, and for $\delta^{18}O$ using a MAT253 mass spectrometer connected to a high-temperature conversion elemental analyzer. Oxygen-bearing ions other than NO_3^- and dissolved organic matter were removed carefully during the preparation of $AgNO_3$ for the $\delta^{18}O$ analysis. The reproducibility of duplicate analyses was <0.4‰ for $\delta^{18}O$ ($n = 5$) and <0.2‰ for $\delta^{15}N$ ($n = 5$).

In addition, filtered water samples of approximately 20 mL were used for the anion and cation concentration determinations within, at most, 24 h. In the laboratory, the anion and cation concentrations in the water samples were determined by using ion chromatography, including NO_3^-, Cl^-, SO_4^{2-}, NO_2^-, and NH_4^+. The total nitrogen was determined by alkaline potassium persulfate digestion and ultraviolet spectrophotometry.

3. Results and discussions

3.1. Anion concentration analysis of the nitrate sources and nitrogen removal

Due to its inert chemical and biological nature, Cl^- is generally a good marker of sewage and manure. Using the NO_3^-/Cl^- method, whether the nitrogen removal process is the result of denitrification can be accurately estimated [8]. Herein, the NO_3^- and Cl^- concentration changes were analyzed (Fig. 3). The NO_3^- and Cl^- concentrations were significantly positively correlated ($R = 0.9216$) in the mainstream Feng River in December 2011, indicating that mixing may control the nitrate distribution in the winter. The NO_3^- and Cl^- concentration relationship in the Feng River

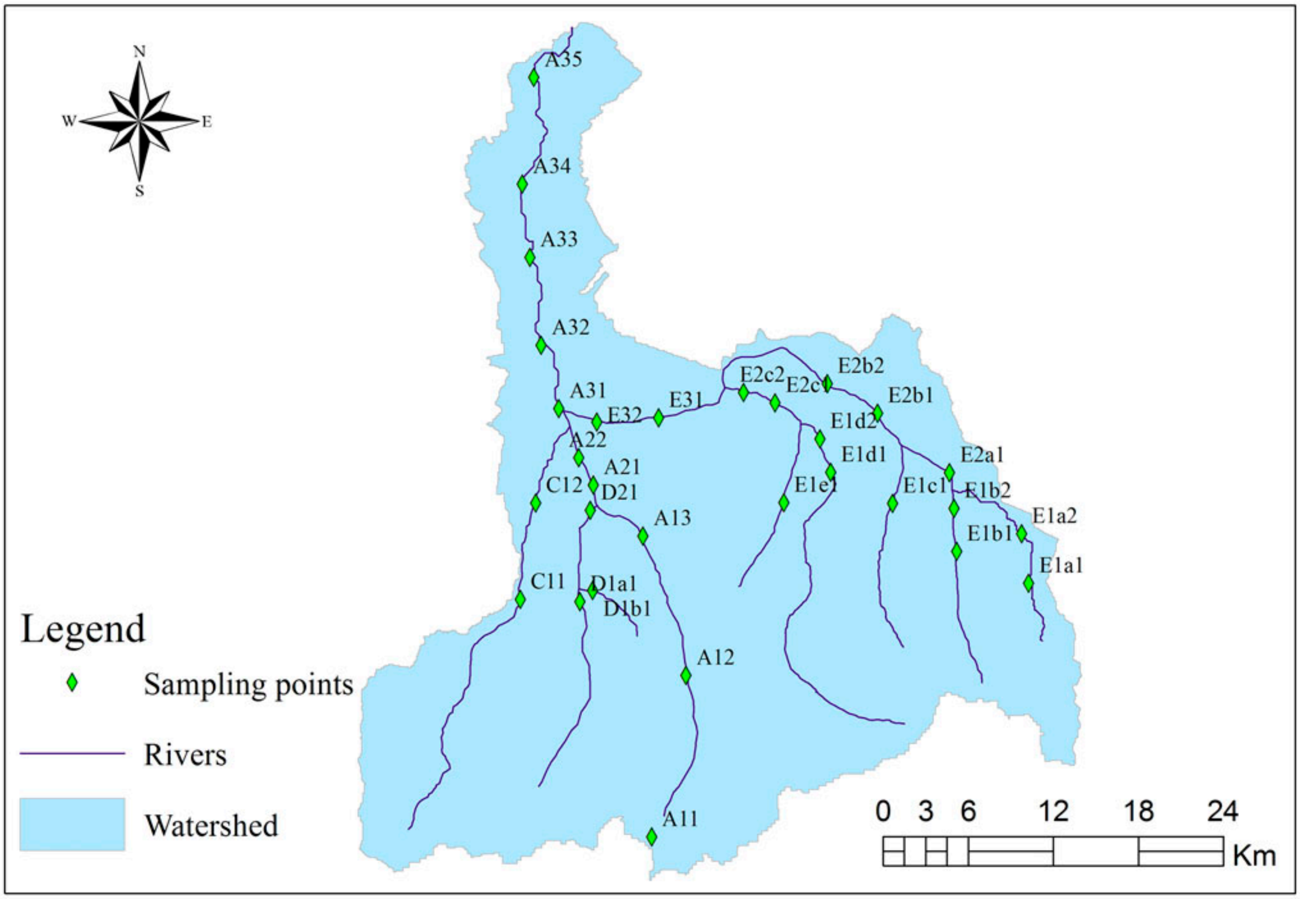

Fig. 2. Distribution of the Feng River system sampling points.

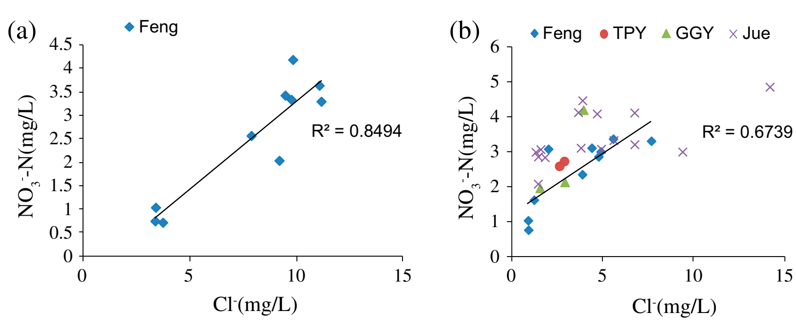

Fig. 3. Relationship between the NO_3^- and Cl^- concentrations (a) in wet season (b) in dry season.

in September 2012 was also positively correlated ($R = 0.8209$), but not as prominent as that in the winter. The relationship between the NO_3^-/Cl^- molar ratio and Cl^- molar concentration is shown in Fig. 4. Overall, most of the samples from the study area had high SO_4^{2-} and Cl^- concentrations and a low NO_3^-/Cl^- molar ratio in December 2011, and the sewage and manure input focused and overlapped within that region. Chen et al. [10] explained that this nitrogen form was ammonium that had not yet been transformed into nitrate. Sewage and manure inputs can be used to predict the most important source of nitrate in the winter in the Feng River. The source of nitrate in these sampling points in September 2012 showed that some of the central tendency in this direction was the fertilizer input and the other part

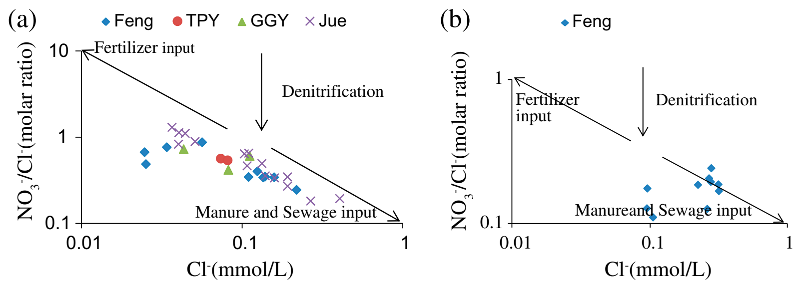

Fig. 4. Relationship between the molar ratio of NO_3^-/Cl^- and the molar concentration of Cl^- (a) in wet season (b) in dry season.

was focused on sewage and manure inputs. The sources of nitrate in the summer may be fertilizer and sewage inputs. According to Fig. 4, the nitrate from the denitrification process was not shown.

3.2. The $\delta^{15}N_{nitrate}$ analysis of nitrate sources and nitrogen removal

There are different types of nitrate sources with distinctive ranges of $\delta^{15}N_{nitrate}$ values in freshwater systems. The dominant sources of nitrate in freshwater systems are atmospheric deposition, N-bearing fertilizers, sewage and manure, and soil organic N. There is a large variation in the N isotopic composition of atmospheric deposition, which usually falls within the range of $\delta^{15}N_{nitrate}$ values from −15 to +15‰. Nitrate sources derived from manure ranged from +5 to +25‰, whereas those from sewage ranged from +4 to 19‰ [11]. In practical studies, high levels of $\delta^{15}N_{nitrate}$ in sewage and manure can be taken to signify anthropogenic contamination sources. The range of the $\delta^{15}N_{nitrate}$ values of these artificial fertilizers generally extends from −6 to +6‰. The N isotopic ratios of organic fertilizers (such as cover crops, plant compost liquid, and solid manure with a wide range of values from +2 to +30‰) are mostly higher than those of inorganic fertilizers. N isotopic ratios are between 0 and 8‰ for soil organic N.

The $\delta^{15}N_{nitrate}$ ranged from +3.218 to +11.607‰, −0.82 to 6.45‰, +4.308 ~ +12. 206‰ in the Feng River in the dry period, wet period, and spring rain period, respectively, with averages of (+6.54 ± 2.55)‰ (n = 26), (+2.44 ± 1.92)‰ (n = 26), and (+7.55 ± 2.47)‰ (n = 26) (Fig. 5). These data suggested that the $\delta^{15}N_{nitrate}$ was higher in the winter than in the summer, and highest in the spring rain period. These results showed a dilution effect of rainstorms on the sources of nitrogen pollution in the river. In the spring rain period, however, $\delta^{15}N_{nitrate}$ was even higher than in the winter, which indicated that nonpoint source pollution was serious in the Feng River watershed. This period represented the first rainstorm after the dry period. After rain erosion, not only the proportion of the rural sewage emissions and livestock feeding, but also the loss of fertilizer into the river increased.

Spatially, $\delta^{15}N_{nitrate}$ in the different periods in the Feng River gradually increased from upstream to downstream, from the headstreams to the agricultural areas or urban regions.

The relationship between $\delta^{15}N_{nitrate}$ and some important anions could provide a valuable reference to distinguish the sources of the nitrate. Fig. 6 draws the relationship between the $\delta^{15}N_{nitrate}$ and NO_3^--N concentration, and compares the $\delta^{15}N_{nitrate}$ of the Feng River with the $\delta^{15}N_{nitrate}$ distribution range of different sources of nitrate. The $\delta^{15}N_{nitrate}$ of the

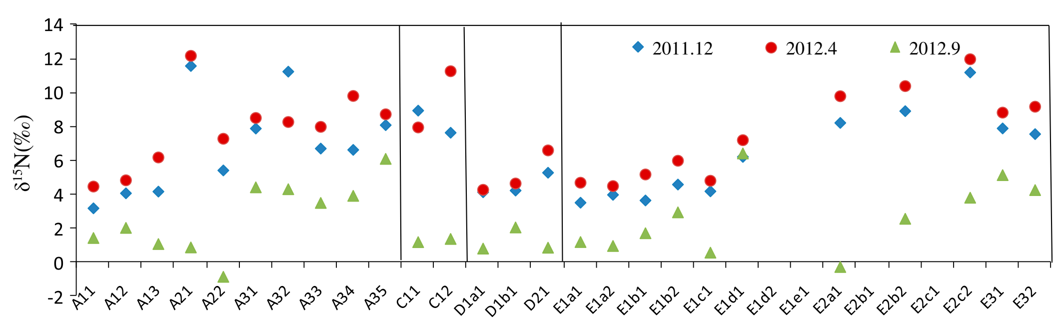

Fig. 5. The spatial and temporal distribution of $\delta^{15}N_{nitrate}$ in the Feng River System.

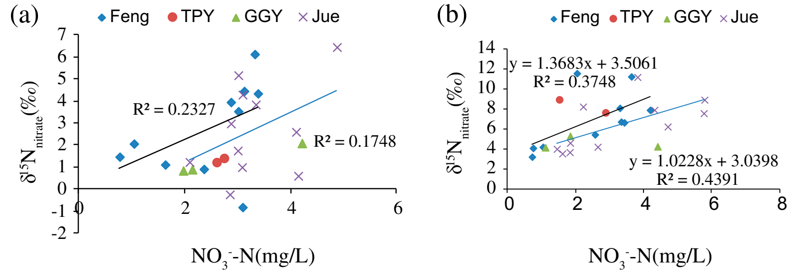

Fig. 6. Relationship between the molar ratio of $\delta^{15}N_{nitrate}$ and the concentration of NO_3^--N in the wet and dry seasons (a) in wet season (b) in dry season.

samples from the Feng River had a wide range and increased from upstream to downstream with the nitrate concentrations. We can initially estimate that this effect was the result of the mixing of two or more sources of nitrate.

3.3. The $\delta^{18}O_{nitrate}$ analysis of the nitrate sources and nitrogen removal

The $\delta^{18}O_{nitrate}$ value of dissolved nitrate has been extensively used to provide an additional, comprehensive, and precise means of identifying nitrate sources in fresh water systems. The O isotopic ratio of atmospheric nitrate deposition exhibits a wide range, from +25 to +75‰. The $\delta^{18}O$ values of many different types of anthropogenic nitrate and synthetic nitrate fertilizers typically range from +17 to +25‰. The range of values in the nitrate produced from the nitrification process was calculated to be from −10 to +15‰.

The $\delta^{18}O_{nitrate}$ ranged from +2.91 to +16.63‰ and +1.63 to +11.76‰ in the Feng River in September 2012 and December 2011, respectively, with averages of +13.57 and +9.09‰ ($n = 30$) (Fig. 7). The $\delta^{18}O_{nitrate}$ ranged from +2.33 to +16.29‰ and averaged 12.99‰ ($n = 30$) in April 2012. Overall, the $\delta^{18}O_{nitrate}$ in September 2012 was higher than that in December 2011, and the $\delta^{18}O_{nitrate}$ in April 2012 was close to that in September 2012. High $\delta^{18}O_{nitrate}$ values at some points indicated that nitrification was important in the atmospheric deposition as a nitrate source for the Feng River before the nitrate entered the river (Fig. 8).

3.4. Nitrate source identification and nitrogen removal analysis by combined $\delta^{15}N_{nitrate}$ and $\delta^{18}O_{nitrate}$

After using the $\delta^{15}N_{nitrate}$ and $\delta^{18}O_{nitrate}$ two-dimensional graph of the nitrogen sources in the study area, the nitrate source of the river system can be accurately determined and the nitrogen removal during this process can be analyzed. From the graph of the $\delta^{15}N_{nitrate}$ and $\delta^{18}O_{nitrate}$ distribution of the samples from the Feng River in September 2012 and December 2011 (Figs. 9–11), some conclusions were obtained and the mass balance mixing mode was used [12–14] to evaluate the nitrate contribution rates from the main sources (Fig. 12). Firstly, three main sources in the downstream region were determined by $\delta^{15}N_{nitrate}$ and $\delta^{18}O_{nitrate}$ distribution of the samples from the Feng River in September 2012 and December 2011. Then, according to nitrogen and oxygen isotope characteristics values of the three main nitrate sources in local area (Table 1), combining the measured nitrogen and oxygen isotope characteristic values of samples from the Feng River, simultaneous equations model of three variables (contribution ratios) was established. Finally, contribution ratios of the nitrate

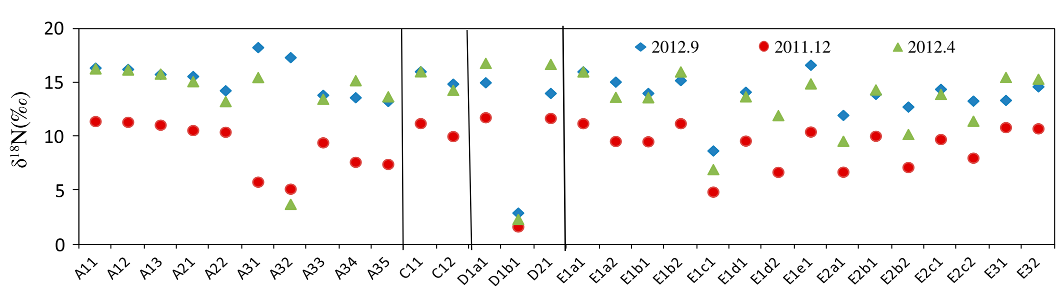

Fig. 7. The spatial and temporal distribution of $\delta^{18}O_{nitrate}$ in the Feng River system.

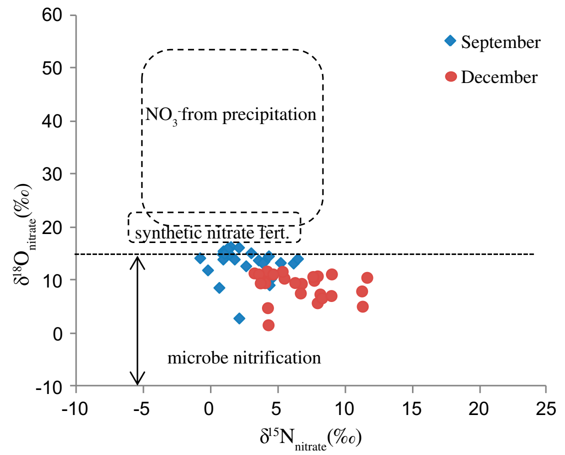

Fig. 8. Relationship between the $\delta^{15}N_{nitrate}$ and $\delta^{18}O_{nitrate}$ distributions.

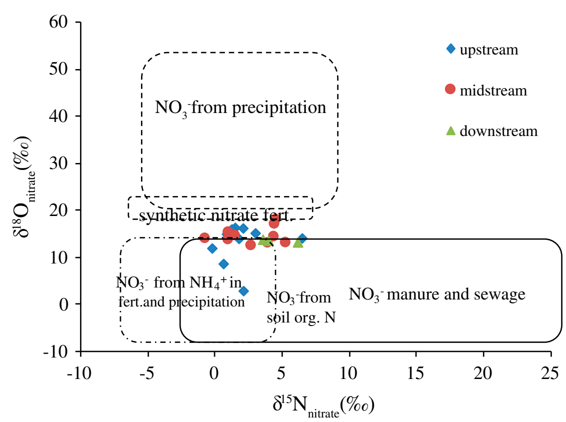

Fig. 9. The $\delta^{15}N_{nitrate}$ and $\delta^{18}O_{nitrate}$ of the Feng River water samples in September 2012.

sources in the downstream region were quantified by solving these three simultaneous equations.

In September 2012, the $\delta^{15}N_{nitrate}$ and $\delta^{18}O_{nitrate}$ values suggested that atmospheric deposition and soil organic nitrogen were the main sources in the upstream region, and atmospheric deposition, chemical fertilizers and sewage and manure inputs were the sources in the downstream region, with average contribution ratios of (68.4 ± 21.1), (19.0 ± 17.3), (12.6 ± 10.5)%, respectively. In December 2011, the $\delta^{15}N_{nitrate}$ and $\delta^{18}O_{nitrate}$ values suggested that the nitrate sources in the upstream region were derived mainly from soil organic nitrogen and that the nitrate sources in the downstream region were derived mainly from sewage and manure inputs. For the sewage and manure inputs, soil organic nitrogen and chemical fertilizer, the average contribution ratios

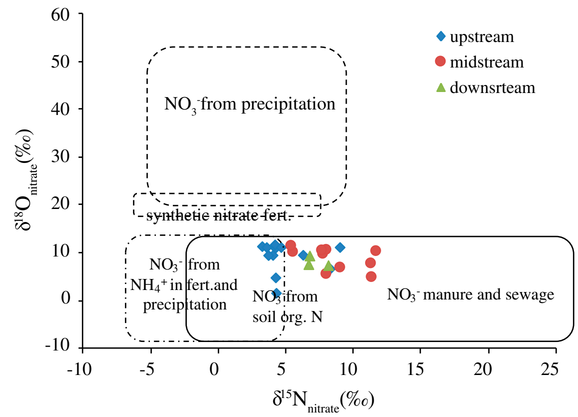

Fig. 10. The $\delta^{15}N_{nitrate}$ and $\delta^{18}O_{nitrate}$ of the Feng River water samples in December 2011.

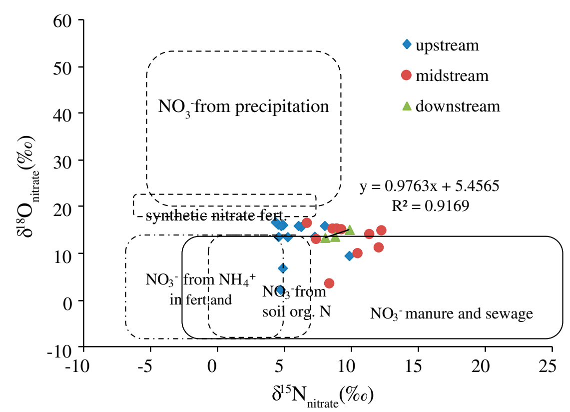

Fig. 11. The $\delta^{15}N_{nitrate}$ and $\delta^{18}O_{nitrate}$ of the Feng River water samples in April 2012.

were (67.2 ± 19.7), (19.8 ± 19.7), and (13.0 ± 12.3)%, respectively. In April 2012, atmospheric deposition and soil organic nitrogen appeared to play an important role in controlling the distribution of the nitrate in the upstream region. The nitrate sources in the downstream region were influenced by sewage and manure inputs, atmospheric deposition, and chemical fertilizer, with average contribution ratios of (66.4 ± 17.4), (25.4 ± 23.3), and (8.2 ± 8.0)%, respectively. Microbial nitrification was inevitable for the sources of nitrate.

In this study, whether in the wet or dry season, a negative correlation between the $\delta^{15}N_{nitrate}$ and NO_3^- concentration overall in the Feng River System were not be found (Fig. 6). A significant positive correlation of $\delta^{15}N_{nitrate}$ and $\delta^{18}O_{nitrate}$ were also not found (Fig. 8). Therefore, the data showed that the denitrification isotope characteristics in the wet and

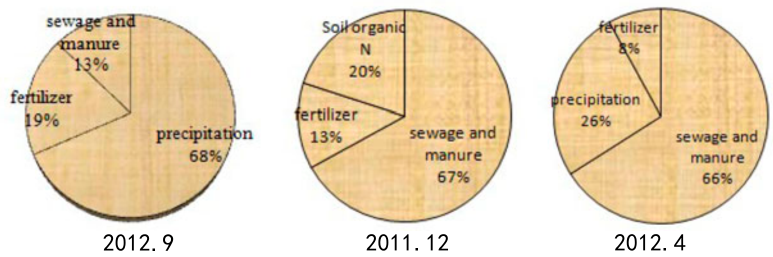

Fig. 12. The average contribution ratio of each source of nitrate in the three sampling periods for the Feng River.

Table 1
Nitrogen and oxygen isotope characteristics values of the nitrate sources in local area

	Atmospheric deposition	Chemical fertilizers	Sewage and manure	Soil organic nitrogen
$\delta^{15}N_{nitrate}$ (‰)	+3.8	+2.01 (September 2012) −0.45 (December 2011\April 2012)	+11.50	+4.20
$\delta^{18}O_{nitrate}$ (‰)	+15	+4 (September 2012\December 2011) +10.4 (April 2012)	+7.80	+8.96

dry seasons in the overall Feng River System were not obvious. However, the $\delta^{18}O_{nitrate}$ and $\delta^{15}N_{nitrate}$ in the upstream sampling points of mainstream Feng River during the wet period corresponded to a 1:2–1:1.3 linear correlation were found (Fig. 13, upstream $y = 0.4259x + 15.461$, $R = 0.6472$; midstream $y = 0.6701x + 14.868$, $R = 0.98$), indicating that the denitrification isotope characteristics were significant during the wet period in the upstream and midstream segments of the Feng River. The $\delta^{18}O_{nitrate}$ and $\delta^{15}N_{nitrate}$ of the downstream sampling points in April 2012 in the mainstream Feng River showed an approximate 1:1 linear relationship (Fig. 11) and accompanied with an increase in the Chla concentration (9.87, 10.06, 10.93 μg/L, respectively). Thus, the absorption of nitrate by phytoplankton was the main reason for the removal of river nitrogen in the downstream segments of the Feng River.

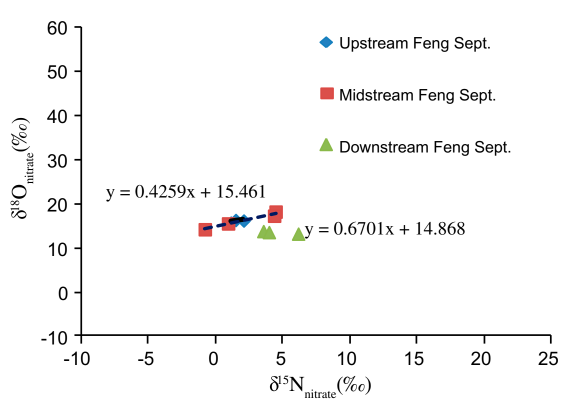

Fig. 13. The relationship between the nitrogen and oxygen isotopic values of the Feng River samples in September 2012.

4. Conclusion

The Feng River basin is a warm temperate forest and agricultural area influenced by the monsoon climate. Seasonal changes in precipitation and hydrology play important roles in modulating the river nitrate sources and watershed N processing. In September, during the rainy hot summertime, strong denitrification in the upstream and midstream regions of the Feng River occurred, as indicated by the 1:2 increase in $\delta^{18}O_{nitrate}$ and $\delta^{15}N_{nitrate}$. In addition to precipitation, fertilizer application from a few months ago was the main source of nitrate in the river. In December, during the dry wintertime, high Cl^- and SO_4^{2-} concentrations and low NO_3^-/Cl^- ratios, as well as the departure from the denitrification vector, suggested a significant nitrate input from manure and sewage. In April prior to the start of fertilizer application, the water was sampled after the first rainstorm after the dry season, and the abrupt increase in monsoon precipitation and runoff caused an enhancement of non-point source pollution (mainly rural sewage and manure). Consequently, the results demonstrate that the dominant controlling factors for watershed-scale N processing are highly variable overtime and that the sampling of N species in river water at one point in time is clearly not sufficient to assess the origins or predominant processes occurring in the watershed.

Acknowledgments

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