Bull Environ Contam Toxicol (2010) 85:562–567
DOI 10.1007/s00128-010-0156-0

Using Nitrogen Isotopic Approach to Identify Nitrate Sources in Waters of Tianjin, China

Fujun Yue · Xiaolong Liu · Jun Li ·
Zhaozhou Zhu · Zhongliang Wang

Received: 22 July 2010 / Accepted: 10 November 2010 / Published online: 25 November 2010

Abstract To understand the nitrogen sources and fate in the surface water of Tianjin, the concentrations of nitrogen and δ^{15}N-NO_3^- were analyzed in different types of waters. Mostly, NO_3^- was the dominant species of DIN (Dissolved Inorganic Nitrogen), although NH_4^+ was the main species in certain samples, such as sewage. The δ^{15}N-NO_3^- values ranged from −5.5 to +28.6‰. The water chemical and isotopic results suggested that domestic sewage and agricultural activities were the two main sources of nitrate in surface waters. In addition, the nitrogen isotopic compositions were significantly influenced by nitrification, ammonia volatilization and denitrification.

Keywords Nitrogen isotope · Tianjin · Surface water · Nitrogen pollution

With the rapid economic growth and population increase that has occurred in metropolitans especially in industrial cities, increased levels of nitrogen have been input into aquatic systems via anthropogenic activities, including industrial wastewater discharges, agricultural N fertilizer application, urban domestic sewage, and human or animal excreta. In drinking water, high levels of NO_3^- may cause methemeoglobinemia in infants (Fewtrell 2004), and can induce cancer in a variety of organs, including the stomach, colon, bladder, lymphatics, and hematopoietic system in many different animal models (Gulis et al. 2002). High NH_4^+ level suggests the presence of more serious residential or agricultural contaminants, such as pathogens or pesticides. Furthermore, a high NH_4^+ concentration has the potential to increase the levels of NO_3^- via nitrification (Umezawa et al. 2008). Therefore, it is necessary to identify the sources of nitrogen pollution.

Nitrogen has two stable isotopes, ^{14}N and ^{15}N, which can be used to discriminate between sources (e.g., animal wastes, urban waste water, synthetic fertilizer, soil organic nitrogen, and atmospheric deposition) of NO_3^-. In many cases, NO_3^- originating from different sources produce with distinguishable ^{15}N/^{14}N ratios. Accordingly, the stable isotopic composition of the nitrogen has been used extensively to identify the sources and transformations of DIN in surface water (Sebilo et al. 2003; Townsend-Small et al. 2007; Xu et al. 2007; Li et al. 2010a) or groundwater (Widory et al. 2004; Liu et al. 2006; Li et al. 2010b). In recent years, many scientists have used water chemical and multi-isotopic methods to ascertain the nitrate sources and fate in the waters, including δ^{18}O-NO_3^-, δ^{11}B, and ^{87}Sr/^{86}Sr (Widory et al. 2004; Liu et al. 2006; Li et al. 2010a), with varying degrees of success.

The municipality is surrounded by Bohai Sea on the east and Yanshan mountain to the north. The study region is located in the warm temperate semi-humid monsoon climate and has a typical East Asia monsoon climate with an average annual temperature of 11.4–12.9°C. The annual precipitation is 520–660 mm, with 75% of the total

F. Yue · X. Liu (✉)
State Key Laboratory of Environmental Geochemistry, Institute of Geochemistry, Chinese Academy of Sciences, 550002 Guiyang, China
e-mail: liuxiaolong@inbox.com

F. Yue
Graduate School of the Chinese Academy of Sciences, 100049 Beijing, China
e-mail: yuefujun@mails.gyig.ac.cn

X. Liu · J. Li · Z. Zhu · Z. Wang
Key Laboratory of Aquatic Environment and Water Resource, Tianjin Normal University, 300384 Tianjin, China

precipitation occurring in June, July and August. Major rivers in the study area include the Haihe River, Yongdingxin River, Caobaixin River, and the Jiyun River. The Haihe River is fed by five major rivers (Beiyun River, Yongding River, Daqing River, Ziya River, Nanyun River) that flow into Tianjin from the north, west, and south and then out to the Bohai Sea. Another three rivers in the vicinity of the city (Yongdingxin River, Caobaixin River, Jiyun River) also flow into the Bohai Sea. The surface water is major water sources for the city. The water resources in Tianjin are limited. As the city continues to develop, the water resources will become increasingly important. In this study, we used nitrogen isotope technology to identify nitrogen sources and discuss the major factors that influenced the δ^{15}N-NO_3^- levels in surface water in Tianjin. Using nitrogen isotope analysis to assess the sources and fate of nitrate in Tianjin surface water will be useful for evaluation of the quality of water and pollution sources, which might improve the management practices with respect to water quality.

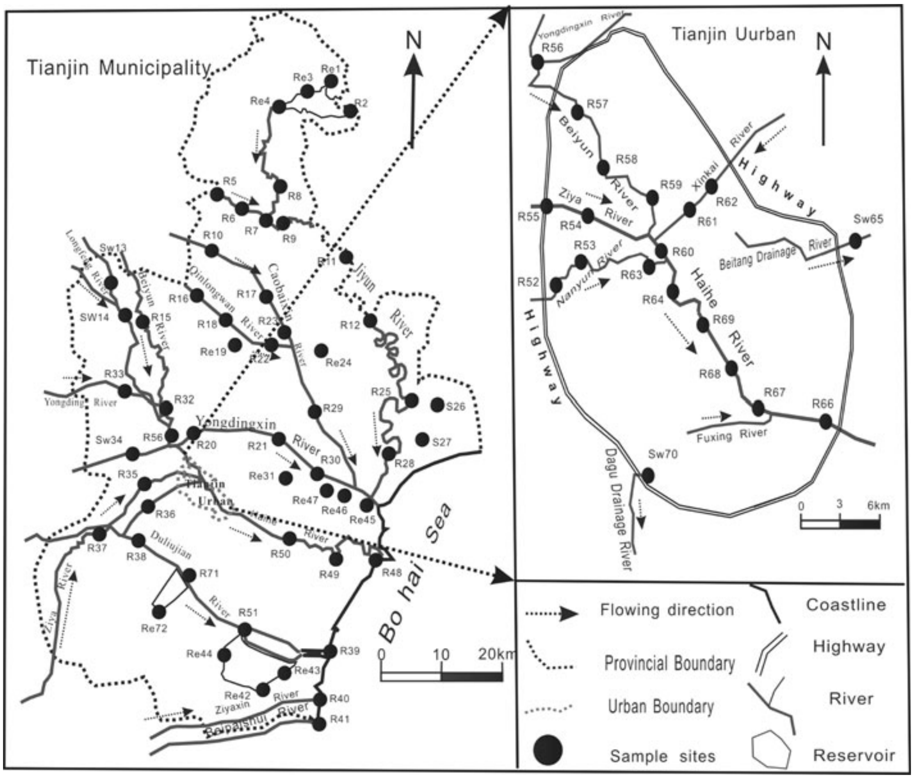
Materials and Methods

Seventy-two water samples were collected in January 2008 from rivers, reservoirs, sewage water with bad smell odors and color during sampling, salinized water and other sites. The sampling locations are shown in Fig. 1. At each sample site, the pH, temperature (T) and electrical conductivity (EC) were measured using a portable meter. The alkalinity was measured by titration with HCl within hours of sample collection using methyl orange as the indicator. Anions (Cl^-, SO_4^{2-}, NO_3^-) were analyzed by ionic chromatography using a Dionex ICS-90 after diluting to a suitable concentration. The NH_4^+-N content was determined by spectrophotometry after distillation and treatment using nessler's reagent. To determine the concentration of NO_2^--N, we used N-(1-naphthyl)-ethylene diamine spectrophotometry. Another samples for analyzing nitrogen isotopic compositions were preserved in plastic bottles added with pure HCl so as to prevent biological activity. The Devarda's alloy diffusion protocol developed by Sigman et al. (1997) was used for pretreatment in NO_3^--N isotope analysis. For δ^{15}N-NH_4^+ pre-treatment, we used ammonium diffusion methods described by Holmes et al. (1998). The acid traps were freeze dried, after which EA-MS was used to determine the isotopic compositions. The isotopic composition of nitrogen in a sample was expressed in terms of its δ^{15}N-value and the value of $^{15}N/^{14}N$ in atmospheric N_2 was used as a standard. The δ^{15}N can be expressed as follows:

$$\delta^{15}N(\text{‰}) = \left\{\left[\left(^{15}N/^{14}N_{\text{sample}}\right)/\left(^{15}N/^{14}N_{\text{standard}}\right)\right] - 1\right\} \times 1000$$

where δ^{15}N-NO_3^- has a precision of 0.2‰.

Fig. 1 The location of sampling sites



Results and Discussion

The NO_3^- concentrations of the samples (Table 1) ranged from 0.04 to 73.12 mg L^{-1}, with a mean value of 9.96 mg/L. The NH_4^+-N ranged from BDL (below the detection limit) to 10.60 mg L^{-1}, with a mean value of 1.15 mg L^{-1}. The NO_2^--N contents ranged from BDL to 0.53 mg L^{-1}, with a mean value of 0.07 mg L^{-1}. As indicated by Fig. 2, NO_3^- was the dominant species of DIN, although NH_4^+ was the main nitrogen species in some waters, especially in sewage water collected from central and east of Tianjin. These findings suggest that these samples contain more organic nitrogen or ammonium derived from domestic sewage in which the NH_4^+ could not fully transform into NO_3^-. Moreover, four samples had NO_3^- concentrations (R1, Sw13, Sw14, S26) greater than 50 mg L^{-1}, which is the limit for drinking water set by the World Health Organization (WHO). Sample R1 was collected from a

Table 1 DIN concentration and nitrogen isotopic values in Tianjin surface water

No.	NO_3^- (mg L^{-1})	NH_4^+-N	NO_2^--N	$\delta^{15}N$-NO_3^- (‰)	No.	NO_3^- (mg L^{-1})	NH_4^+-N	NO_2^--N	$\delta^{15}N$-NO_3^- (‰)
R1	73.12	0.24	0.02	6.9	R37	0.49	0.04	0.02	–
R2	13.06	0.05	0.02	8.0	R38	4.21	2.54	0.01	−2.3
Re3	7.09	BDL	0.02	7.8	R39	33.75	0.04	0.04	–
Re4	7.53	BDL	0.02	–	R40	2.70	10.33	0.02	–
R5	12.40	1.79	0.01	−5.5	R41	22.23	0.19	0.02	8.2
R6	18.38	BDL	0.03	5.9	Re42	18.07	0.34	0.02	–
R7	0.04	0.06	BDL	–	Re43	0.58	0.14	0.06	3.8
R8	8.15	0.06	0.04	6.2	Re44	2.66	BDL	BDL	−2.4
R9	4.07	0.05	0.02	1.2	Re45	0.58	BDL	BDL	–
R10	43.93	1.47	0.53	6.0	Re46	0.40	0.03	BDL	–
R11	0.22	0.03	BDL	–	Re47	0.58	BDL	BDL	–
R12	1.82	0.08	0.01	11.4	R48	8.24	1.06	0.20	−0.5
Sw13	56.38	1.70	0.43	11.7	R49	17.14	0.45	0.16	−4.1
Sw14	57.70	2.69	0.41	8.4	R50	3.23	0.05	0.03	16.6
R15	39.77	1.90	0.49	8.0	R51	1.28	0.03	0.03	8.7
R16	23.03	2.46	0.22	13.2	R52	0.58	5.70	BDL	13.3
R17	2.08	0.20	0.02	19.1	R53	5.71	0.04	0.01	9.6
R18	3.19	0.11	0.02	17.7	R54	4.38	0.15	0.03	8.5
Re19	0.93	0.02	BDL	2.9	R55	3.94	0.27	0.03	3.9
R20	2.13	5.72	0.18	9.1	R56	25.64	1.52	0.17	–
R21	1.99	3.72	0.10	28.6	R57	0.22	1.12	0.08	–
R22	7.31	0.19	0.12	12.3	R58	0.31	2.43	0.06	–
R23	4.03	1.10	0.07	13.7	R59	14.39	0.20	0.04	–
Re24	0.84	0.25	0.06	15.7	R60	5.49	0.14	0.05	25.0
R25	0.27	0.55	BDL	22.7	R61	6.16	0.09	0.01	–
S26	50.62	0.08	0.01	1.4	R62	4.56	0.50	0.03	6.5
S27	18.69	0.03	0.01	–	R63	1.11	0.11	0.02	−4.7
R28	0.80	1.31	0.02	−1.3	R64	5.49	0.24	0.03	–
R29	2.17	0.94	0.04	13.6	Sw65	1.28	10.60	0.17	–
R30	1.37	5.84	0.01	–	R66	5.71	0.12	0.03	16.1
Re31	1.68	0.03	BDL	9.0	R67	4.69	0.09	0.05	−4.6
R32	1.55	2.03	BDL	14.1	R68	6.38	0.11	0.06	–
R33	19.80	2.37	0.17	12.3	R69	8.50	0.12	0.06	8.4
Sw34	0.31	1.14	0.01	–	Sw70	0.27	2.75	BDL	–
R35	0.71	0.03	BDL	8.7	R71	3.19	1.52	0.18	15.5
R36	6.60	1.37	0.14	25.6	Re72	1.15	0.09	0.01	–

[a] Re, R, Sw, S stands for reservoir, river, sewage water, salinized water

[b] BDL stands for below detection limit of 0.02 mg/L of NH_4^+-N and 0.003 mg/L of NO_2^--N

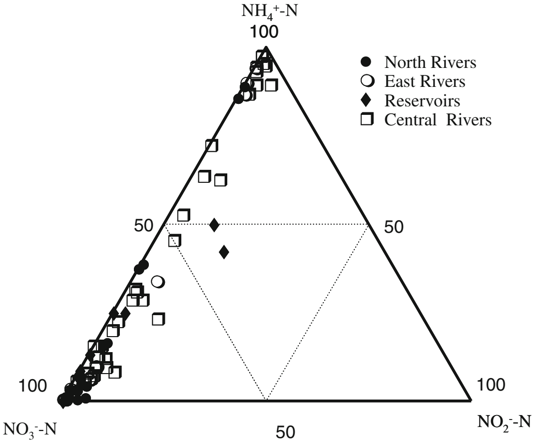


Fig. 2 Triangular diagram of DIN in Tianjin surface water

stagnant water body that flowed into domestic water, while samples Sw13 and Sw14 were affected by a drainage river and sample S26 was influenced by sewage water from salt field. The Environmental Quality Standards for Surface Water (GB3838-2002, China) divide surface water into four classes based on the concentration of NH_4^+-N, I $\leq$ 0.15 mg L^{-1}; II $\leq$ 0.5 mg L^{-1}; III $\leq$ 1.0 mg L^{-1}; IV $\leq$ 1.5 mg L^{-1}. In the present study, 17 samples (25% of the total sample set) had concentrations of NH_4^+-N higher than 1.5 mg L^{-1}. As shown in Fig. 3, NH_4^+ was the typical nitrogen pollutant in Tianjin surface waters, and two samples (R40, Sw65) had particularly high concentrations of NH_4^+-N greater than 10 mg L^{-1}. The concentration of NO_2^--N was very low and below the detection limit in many samples. However, six samples still contained levels of NO_2^--N greater than the WHO recommended value of 0.2 mg L^{-1} for long-term drinking water. In addition, the concentrations of NH_4^+-N and NO_3^- in these six samples were also high, indicating serious pollution and high toxicity.

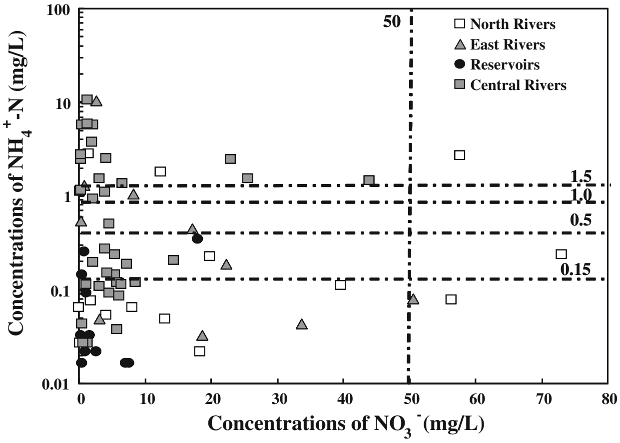


Fig. 3 Variations of NH_4^+-N and NO_3^- in the Tianjin surface water

The concentrations of NO_3^- and NH_4^+-N were high in Longfeng River, the upper reach of Yongding River and Beiyun River, which indicates that these rivers may have received more sewage from factories. After these three rivers crossed the sampling site (sample R56), they flowed into the Beiyun River and the Yongdingxin River. In sample R56, the concentration of NO_3^- and NH_4^+-N were high; however, the NO_3^- concentration in Haihe river decreased after crossing the Tianjin urban area. There were also two rivers that received sewage in the urban portion of Tianjin, the Tanggu Drainage River and Dagu Drainage River. Indeed, it has been reported that these two sewage rivers accept 80% of the urban sewage for Tianjin (Qin et al. 2009); therefore, it is not surprising that these rivers were found to have high levels of NH_4^+-N in the present study, with one having levels of 10.60 mg L^{-1}. The Haihe River in the urban portion of the study site did not have a high concentration of NO_3^- and NH_4^+-N, which was likely because sewage effluent from the city was not directly discharged into the river. The water that flowed into Yongdingxin River had a low level of NO_3^- and a high level of NH_4^+-N at the beginning of the stretch, but this decreased moving in the downstream direction. After the Beitang Drainage River, which contained high levels of sewage, flowed into Yongdingxin River, the concentration of NH_4^+-N in the Yongdingxin increased. In southern Tianjin, the Duliujian River had a very low flow rate, and samples collected from the upstream portion of this river had high NH_4^+-N concentrations. Another sample collected from the estuary had a high concentration of NO_3^-. Finally, the Ziyaxin River had high concentrations of NH_4^+-N and the Beipaishui River had high concentrations of NO_3^-, which may have been related to sewage and industrial waste in this region.

Most samples collected from north Tianjin had low contents of NH_4^+-N (Fig. 3). This may have been because this portion of the study site is an agriculture area. In such areas, nitrogen fertilizer used for crops is generally the primary source of nitrogen to water. In addition, the nitrification of soil organic matter contributes NO_3^- to water in these areas. However, soil colloids are generally negatively charged so that they strongly adsorb NH_4^+ and weakly adsorb NO_3^-. As a result, easily leached NO_3^- in soil will accumulate in groundwater and surface water (Fig. 3). Twelve samples in the reservoir had low concentrations of nitrogen except for one sample (Re42) in the Shajingzi Reservoir, which had a high concentration of NO_3^-.

The NO_3^- in surface water had many sources, including soil organic nitrogen, fertilizers, human and animal excreta, industrial wastewater, domestic sewage and rain. Stable isotopic compositions of NO_3^- can provide useful information that can be used to trace the source of NO_3^- in surface water due to the distinct isotopic characteristics of the main sources of NO_3^- (Kendall 1998; Sebilo et al. 2003; Liu et al. 2006; Li et al. 2010a, b). It has been reported that NO_3^- and NH_4^+ in fertilizers have δ^{15}N-values close to zero. Studies have also indicated that δ^{15}N-values of soil organic nitrogen are typically in the range of +2.0 to +8.0‰. Under normal conditions, most soil organic nitrogen is slowly converted into NH_4^+, which is then converted into NO_3^- by nitrification bacteria. The δ^{15}N-values of NH_4^+ and NO_3^- in the product are similar to those of soil organic nitrogen. The δ^{15}N -values of animal excreta are typically in the range +8.0 to +20.0‰. Therefore, if the sewage waste is derived from animal excreta, the δ^{15}N-values should be more than +10.0‰. However, if the sewage waste is derived from industrial waste, the δ^{15}N-values should be below +10.0‰ (Kendall 1998; Liu et al. 2006).

The N isotopic compositions of NO_3^- are listed in Table 1. The δ^{15}N of NO_3^- in surface water ranged from −5.5 to +28.6‰ (n = 49, mean + 9.0‰, median + 8.5‰). The δ^{15}N-NH_4^+ ranged from −8.8 to +34.3‰ (n = 11, mean + 11.6‰, median + 13.6‰). As indicated by Fig. 4, 51% of the samples had δ^{15}N-values between +8.0 and +20.0‰ and 20% of the samples had δ^{15}N-values below +2.0‰. Both the DIN and δ^{15}N-NO_3^- data indicated that domestic sewage and agricultural activity are the two main sources of nitrogen in the study area. In addition, these nitrogen pollution sources had wide ranging isotopic values and were seriously influenced by complex artificial pollution sources. For example, the δ^{15}N-values of NO_3^- in the Qinglongwan River and Caobaixin River ranged from +12.3 to +19.1‰, except for one sample that was below +10.0‰. In the suburban area of Tianjin, the δ^{15}N-values of NO_3^- were above +14.0‰. These findings indicate that aquatic systems in the suburban areas were more heavily influenced by domestic waste. The δ^{15}N-values of NO_3^- in the northern portion of the study region were below +8.0‰ and two samples had δ^{15}N-values of NO_3^- below +2.0‰.

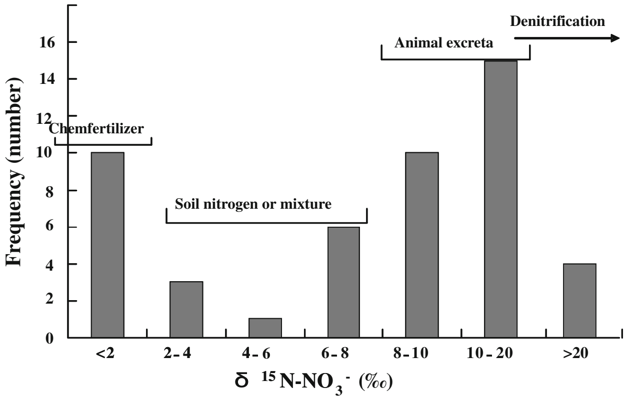


Fig. 4 Histograms of δ^{15}N-NO_3^- in Tianjin surface water

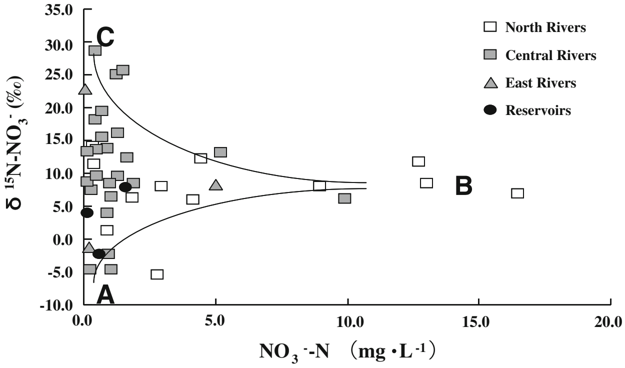


Fig. 5 Relationship between NO_3^--N and δ^{15}N-NO_3^- in Tianjin surface water

The wide range of δ^{15}N-values of NO_3^- was also related to the processes involved in nitrogen biogeochemistry, such as nitrification and volatilization (Kendall, 1998). In the present study, some samples had high δ^{15}N-NH_4^+ values above +10.0‰, indicating that the high δ^{15}N-values of NH_4^+ were related to these processes. Therefore, NH_4^+ was enriched with ^{15}N due to nitrification. For example, sample R20 had δ^{15}N-NO_3^- of +9.1‰ and δ^{15}N-NH_4^+ of +13.5‰, which indicated that nitrification affected the isotope of NH_4^+. Additionally, the results obtained for sample R10 also indicated that this process was occurring in the water, with a δ^{15}N-NO_3^- value of +6.0‰ and δ^{15}N-NH_4^+ value of +13.1‰.

For this study, samples with low contents of NO_3^- with δ^{15}N-values lower than +2.0‰ were designated as being from source A (Fig. 5), which might have been affected by chemical fertilizer from the suburbs and nitrification of organic pollution. When domestic water flowed into surface water, organic materials were oxidized to NO_3^-. ^{14}N was easily enriched in nitrate during the nitrification process; therefore, the δ^{15}N-values of NO_3^- were low. Additionally, there were some waters with high contents of NO_3^- and δ^{15}N-values near +8.0‰, which may have been influenced directly by sewage effluent. These water bodies were defined as source B. Some samples also had low contents of NO_3^-, but high δ^{15}N-values, indicating that the water sources that they were taken from were highly influenced by denitrification. In the denitrification process, NO_3^- is reduced to NO_x or N_2 by bacteria, which results in significant isotopic fractionation ranging from −40.0 to +5.0‰ (Kendall 1998). As a result, the residual NO_3^- in these samples was enriched with ^{15}N. Thus, waters with low contents of NO_3^- having high δ^{15}N-NO_3^- levels near +25.0‰ were designated as source C. As indicated by Fig. 5, the NO_3^- in waters of Tianjin should be mainly affected by mixing between the three sources. In addition, different nitrogen sources not only had different δ^{15}N-values, but were also influenced by biological effects

(Waser et al. 1998). The biological effects were another factor that influenced δ^{15}N-values of nitrate in the surface water in Tianjin.

The results of this study indicated that NO_3^- was the dominant species of inorganic nitrogen in the surface water in Tianjin. However, in some of the samples, NH_4^+ was the main nitrogen species and the NH_4^+ pollution was very serious. Indeed, approximately 25% of the samples were unable to achieve the Class IV Environmental Quality Standards for Surface Water in China. There was also little correlation among nitrogen species, which might indicate that pollution was affected by many factors. Water close to the suburbs and sewage drainage in urban areas had high concentrations of NO_3^-. Conversely, all samples have low concentrations of NO_2^--N, but several samples have high concentrations of NO_2^--N greater than 0.2 mg L^{-1}. These findings indicated that the samples were directly influenced by domestic wastewater. The high δ^{15}N-NO_3^- values in samples collected near the suburban areas and sewage drainage in urban areas suggested that domestic sewage was the main factor affecting the water in these areas. Additionally, 51% of the samples had δ^{15}N-values between +8.0 and +20.0‰ and 20% of the samples had δ^{15}N-values below +2.0‰ based on frequency analysis of δ^{15}N-NO_3^-. The water chemical and nitrogen isotopic results suggested that there were at least three end members influencing the nitrate distribution. Additionally, in some samples, denitrification and nitrification were the major factors involved in shifting of the nitrogen isotopes. However, additional studies are needed to distinguish the nitrate sources and the extent of the impact of the biological process due to the various sources of nitrate and complicated biological processes in the aquatic systems in the study area.

Acknowledgments The authors thank Dr. Congqiang Liu and Siliang Li for their valuable comments and suggestions. This study was financially supported by National Natural Science Foundation of China through Grants (40721002) and the Natural Science Foundation of Tianjin (10JCZDJC24800, 09JCZDJC25900).

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