Nitrogen pollution and source identification of urban ecosystem surface water in Beijing

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Abstract Nitrogen contamination of surface water is a worldwide environmental problem with intensive agriculture and high population densities. We assessed the spatial and seasonal variation in concentrations of total nitrogen and different nitrogen species present in surface-water in Beijing, China. Also, chemical (NO_3^- -N/ Cl^-) and isotopic ($\delta^{15}\text{N}_{\text{nitrate}}$) indicators were used to identify nitrate sources. The results showed that, during 2009 and 2010, nitrate nitrogen concentrations ranged from 0.7 to 7.6 $\text{mg} \cdot \text{L}^{-1}$, ammonium nitrogen from 0.1 to 3.4 $\text{mg} \cdot \text{L}^{-1}$, and total nitrogen from 2.4 to 17.0 $\text{mg} \cdot \text{L}^{-1}$. Inorganic nitrogen accounted for between 60 and 100% of total nitrogen at the ten monitoring sites. Nitrate nitrogen, ammonium nitrogen, and total nitrogen concentrations at the 2 downstream monitoring sites in south-eastern Beijing were significantly higher than those at the other eight upstream monitoring sites ($P < 0.01$). Examination of seasonal variation showed that there was a significant inverse relationship between nitrate nitrogen concentrations and precipitation, and that nitrate nitrogen concentrations peaked in the dry seasons. The information given by the $\delta^{15}\text{N}_{\text{nitrate}}$ values and nitrate nitrogen concentrations, combined with the NO_3^- -N/ Cl^- ratio distribution, showed that domestic sewage was the major source of nitrate in Beijing. Methods to control and reduce sewage pollution are urgently needed to help manage surface water quality in Beijing.

Keywords nitrogen concentration, spatial and seasonal variation, stable nitrogen isotope, urban ecosystem, source

1 Introduction

Nitrogen (N) pollution poses a serious threat to fresh water supplies and promotes eutrophication [1,2]. Possible sources of nitrogen contamination in surface water include manure applied to land, agricultural fertilizer, industrial effluent, domestic sewage, septic systems, human waste lagoons, animal feedlots, and native soil organic matter [3], as well as elevated atmospheric N deposition [4]. Urban environments are of great concern because of the high population densities and the immediate proximity of typical urban nitrogen sources, for example, wastewater disposal (onsite systems and leaky sewers) and solid waste disposal (landfills and waste tips) [5]. Sources of nitrogen in urban surface water must be identified before an efficient remediation plan can be devised.

With the growth of urban and suburban areas, urban surface water has become increasingly seriously polluted. A survey of streams and rivers [6] in Washington found that nitrate concentrations were significantly higher in urban watersheds than in partially developed and undeveloped watersheds.

It has also been reported that concentrations of dissolved organic nitrogen (from septic systems) in tributaries with residential development peaked during spring snow melt, and that between 19 and 23% of the annual N export from developed tributaries was derived from septic systems, as estimated from the $\delta^{15}\text{N}$ of algae [7]. Groffman et al. [8] reported that urban and suburban watersheds had much

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higher N losses than did completely forested watersheds (less than $1 \text{ kg N} \cdot \text{ha}^{-1} \cdot \text{a}^{-1}$), with N yields ranging from 2.9 to $7.9 \text{ kg N} \cdot \text{ha}^{-1} \cdot \text{a}^{-1}$. Research has shown that the NO_3^- -N concentrations in most rivers in populated regions could reach levels that are seven times higher than the $10 \text{ mg} \cdot \text{L}^{-1}$ guideline of the Global Environment Monitoring System (GEMS) database [9]. In China, surface water in urban areas such as Shanghai, Tianjin, Changshu, Xi'an, Guangzhou and Hangzhou is polluted to different degrees, and nitrate and total nitrogen are among the major pollutants [10–15].

In 2006 it was reported that about 60% of the rivers, lakes and reservoirs in Beijing, China were seriously polluted [16], with large areas of algal blooms present in surface water in Beijing [17]. Until now however, few studies have investigated or identified sources of nitrogen in surface water in Beijing. In this study, to address this gap in knowledge, an isotope tracing method has been combined with chemical indicators to examine the sources of nitrogen in surface water in Beijing. The objectives of this study were to (i) assess the spatial and seasonal variation of nitrogen contamination, and (ii) identify the main sources of anthropogenic nitrogen pollution in surface water in Beijing. Findings from this study will

provide key information that will be useful in controlling nitrogen pollution in surface water in Beijing, and in promoting sustainable water management in urban Beijing.

2 Methods

2.1 Study area descriptions

The study area ($39^\circ 53'$ to $39^\circ 59'$ N, $116^\circ 11'$ to $116^\circ 35'$ E) has a temperate territorial semi-humid climate. The annual average temperature is 12.7°C , and annual mean precipitation is about 562 mm, most of which occurs during the summer monsoon season from July to August. The annual mean evaporation is 1833 mm. The urban area of Beijing is about 1000 km^2 , which is almost 17 times what it was in 1949. In 2010, the permanent population was approximately 20 million people [18].

Rivers mostly flow from the north-west to the south-east in Beijing. The surface water monitoring sites chosen for this study are shown in Fig. 1, and were located on the Kunminghu Lake, Chang, Zhuan, Beihucheng River, Qianhai Lake, Changpu, Donghucheng and Tonghui Rivers, and covered a drainage area of 250 km^2 . The

Fig. 1 Surface water sampling sites in the Beijing urban area. “1–10” represent “Kunminghu, Changchunqiao, Library, Zoo, Zhuanhe, Huchenghe, Qianhai, Changpuhe, Dongbianmen and Tonghuihe, respectively. “☆” in the figure represent Gaobeidian Sewage Treatment Plant

land around the Kunminghu Lake and Changchunqiao Bridge sampling sites is largely greenbelt, but from Library to Tonghuihe River, land use is mainly residential or commercial.

The Gaobeidian wastewater treatment plant is situated near the Tonghuihe monitoring site on the Tonghui River. It is the biggest wastewater treatment plant in China, collecting most of the domestic sewage and industrial wastewater from southern Beijing. Because of the effect of sluice gate of Gaobeidian reservoir, most of the processed wastewater flow to the upstream of the treatment plant. Upstream of the treatment plant, the average DO values are all above $10 \text{ mg} \cdot \text{L}^{-1}$, but fall to $7 \text{ mg} \cdot \text{L}^{-1}$ downstream of the treatment plant (at Dongbianmen and Tonghuihe). The average COD value upstream of the plant (from Kunminghu to Qianhai) was $30 \text{ mg} \cdot \text{L}^{-1}$ but increased to an average of $104 \text{ mg} \cdot \text{L}^{-1}$ and $72 \text{ mg} \cdot \text{L}^{-1}$ at the Dongbianmen and Tonghuihe monitoring sites respectively (unpublished data from the CERN Beijing urban station collected from 2009 to 2010). When compared to the National Environmental Quality Standards for Surface Waters in China [19], COD values recorded at the Dongbianmen and Tonghuihe monitoring sites far exceed the class five guideline values ($\text{COD} \leq 40 \text{ mg} \cdot \text{L}^{-1}$), indicating severely polluted conditions.

2.2 Monitoring and analysis methods

Bi-monthly samples were collected from 2009 to 2011. Nitrate nitrogen ($\text{NO}_3^- \text{-N}$) and chloride (Cl^-) concentrations were measured using a Shimadzu Ion Chromatograph meter. Ammonium (NH_4^+) was analyzed by spectrophotometer. Concentrations of total nitrogen (TN) were determined by potassium persulfate digestion and measured by spectrophotometer. Dissolved organic nitrogen (DON) concentrations were calculated by subtraction as follows: $\text{TN} - (\text{NO}_3^- \text{-N} + \text{NH}_4^+ \text{-N})$.

The stable isotopic composition of nitrate ($\delta^{15}\text{N}_{\text{nitrate}}$) was measured using an anion exchange resin method [20]. The $\delta^{15}\text{N}_{\text{nitrate}}$ values were determined using a Finnigan MAT253 mass spectrometer with an online Flash Elemental Analyzer, and reported in the δ notation relative to N_2 (air) and Standard Mean Ocean Water (SMOW) in permil (‰). USGS-32 (Potassium nitrate) was used as a standard to check the anion exchange method and analysis accuracy. The isotope results are given in δ units defined as Equation 1:

$$\delta(\text{‰}) = \left((R_{\text{sample}}/R_{\text{standard}}) - 1 \right) \times 1000, \quad (1)$$

where R represents the $^{15}\text{N}/^{14}\text{N}$ ratio.

2.3 Identification of nitrate sources

The stable isotope method can provide effective informa-

tion on nitrate sources due to the distinctive nitrogen ratio of the main nitrate sources, such as precipitation, sewage, organic fertilizer, chemical fertilizer and nitrate from nitrification [21,22]. Inorganic fertilizers are produced by fixation of atmospheric N_2 and show small differences in $\delta^{15}\text{N}$ content as a result of the small fractionation during processing of the fixed N [23]. These fertilizers show a typical $\delta^{15}\text{N}$ value range of between -6 ‰ and $+6 \text{ ‰}$ [24]. Typical $\delta^{15}\text{N}$ values of atmospheric N deposition lie between -13 ‰ and $+13 \text{ ‰}$ [22]. Manure and sewage are rich in $\delta^{15}\text{N}$ relative to other N sources. During storage, treatment and application of sewage and animal wastes, ammonia (NH_3) volatilization causes a large enrichment of ^{15}N in the residual NH_4^+ . This NH_4^+ is subsequently converted into ^{15}N -enriched NO_3^- . Thus, $\delta^{15}\text{N}$ values of NH_3^- originating from manure are between $+5 \text{ ‰}$ and $+25 \text{ ‰}$ and sewage between $+4 \text{ ‰}$ and $+19 \text{ ‰}$ [24]. The typical $\delta^{15}\text{N}$ values of soil N range from 0 ‰ to $+8 \text{ ‰}$ [24]. Finally, $\delta^{15}\text{N}$ values of NO_3^- in industrial wastewater vary between 11 ‰ and 23 ‰ [25].

2.4 Statistical analysis

A one-way analysis of variance (ANOVA) (using a least significant difference (LSD) post-hoc test) was used to analyze the spatial variations in concentrations of N and N fractions between the surface water sampling sites in Beijing. Correlation analyses were conducted to explore the relationships between nitrogen and monthly mean rainfall. All statistics were analyzed by SPSS 17.0 software.

3 Results

3.1 Spatial variation of different species of nitrogen concentrations

The average nitrate nitrogen concentrations at the Dongbianmen and Tonghuihe River monitoring sites ranged from 7.0 to $7.6 \text{ mg} \cdot \text{L}^{-1}$, while those from the Kunminghu Lake to the Changpuhe River ranged from 0.7 to $3.4 \text{ mg} \cdot \text{L}^{-1}$ (Fig. 2(a)). Ammonium nitrogen concentrations were also significantly higher in the lower reaches at the Dongbianmen and Tonghuihe monitoring sites (3.3 and $3.4 \text{ mg} \cdot \text{L}^{-1}$, respectively) than those at the other 8 monitoring sites in the upper reaches (where they ranged from 0.1 to $0.5 \text{ mg} \cdot \text{L}^{-1}$) ($P < 0.01$) (Fig. 2(b)). Dissolved organic nitrogen concentrations ranged from 0.3 to $2.4 \text{ mg} \cdot \text{L}^{-1}$, with the highest values found at the Qianhai, Dongbianmen and Tonghuihe monitoring sites (Fig. 2(c)). Total nitrogen concentrations from the Kunminghu Lake to the Changpuhe River were from 2.4 to $4.5 \text{ mg} \cdot \text{L}^{-1}$, but increased to $17 \text{ mg} \cdot \text{L}^{-1}$ in the Dongbianmen and the Tonghuihe Rivers (Fig. 2(d)). Nitrate nitrogen, ammonium

Fig. 2 Spatial variation in NO_3^- -N, NH_4^+ -N, DON, TN concentrations and nitrogen composition (labeled with different letters (a, b, c, d, e, f, g), respectively) in surface water in Beijing from 2009 to 2010. Columns followed by different letters (a,b,c) are significantly different at 99% level and — denotes Class V guideline of surface water quality according to GB3838-2002. Boxplots illustrate the 25th, 50th, and 75th percentiles; the whiskers indicate the lowest and highest values

nitrogen, and total nitrogen concentrations at the Dongbianmen and Tonghuihe monitoring sites were significantly higher than those at the other eight monitoring sites ($P < 0.01$) (Figs. 2(a), 2(b), and 2(d)). The ammonium nitrogen and total nitrogen concentrations at sites Dongbianmen and Tonghuihe exceeded the Class V guideline for ammonium nitrogen ($2.0 \text{ mg} \cdot \text{L}^{-1}$) and total nitrogen ($2.0 \text{ mg} \cdot \text{L}^{-1}$) according to the national quality standards for surface waters of China [19] (Figs. 2(b), and 2(d)). In general, downstream river water in the south-east of Beijing was more heavily polluted by nitrogen than the upstream river water in the north of Beijing.

Inorganic nitrogen (DIN) was the major nitrogen species in surface water in Beijing. At the 7 monitoring sites from Kunminghu Lake to Qianhai Lake, nitrate nitrogen accounted for about 65 % to 80% of total nitrogen (Fig. 2(e)), while for the Dongbianmen and Tonghuihe monitoring sites, nitrate nitrogen accounted for about 47% to 56% of total nitrogen. The NH_4^+ -N/TN ratios for the 7 monitoring sites from Kunminghu to Qianhai ranged from 4% to 19%, but exceeded 30% in the Changpuhe, Dongbianmen and Tonghuihe monitoring sites (Fig. 2(f)). Although the NO_3^- -N/TN ratio tended to decline at the downstream monitoring sites, DIN was still the major nitrogen form, and ranged from 76% to 87%. The DIN/TN ratio fell between 60% to 100% for all 10 monitoring sites (Fig. 2(g)).

3.2 Seasonal variation of different species of nitrogen concentrations

There were obvious seasonal variations in surface water N

concentrations. (Fig. 3). Analysis showed that NO_3^- -N and TN concentrations were lowest in the wet season from June to August, with the lowest concentrations corresponding with peak rainfall values (Figs. 3(a) and 3(d)). Highest NO_3^- -N and TN concentrations occurred in the dry season during early spring and late autumn (Figs. 3(a) and 3(d)). At the Dongbianmen monitoring site, peak values of NO_3^- -N and TN reached $26 \text{ mg} \cdot \text{L}^{-1}$ and $45 \text{ mg} \cdot \text{L}^{-1}$, respectively, in November and April.

NO_3^- -N and TN concentrations were negatively correlated with rainfall. At the Library, Zoo, Zhuanhe, Huchenghe, Qianhai and Dongbianmen monitoring sites, NO_3^- -N concentrations were significantly and negatively correlated with mean monthly rainfall ($P < 0.05$) (Table 1). At the Changchunqiao and Qianhai monitoring sites, total N concentrations were significantly and negatively correlated with mean monthly rainfall ($P < 0.05$) (Table 1). However, the NH_4^+ -N concentrations were higher in the summer monsoon season, resulting in a significant positive correlation between rainfall and NH_4^+ -N in the Zhuanhe and Huchenghe Rivers ($P < 0.01$) (Table 1). There were no significant correlations between rainfall and DON.

3.3 The relationship of NO_3^- -N to Cl^-

Cl^- concentrations ranged from 14.8 to $86.0 \text{ mg} \cdot \text{L}^{-1}$ (Fig. 4 (a)), and, as with NO_3^- -N concentrations (Fig. 4(a)), increased from upstream to downstream, with the Cl^- concentrations at the Dongbianmen and Tonghuihe downstream monitoring sites significantly higher than those at the upstream sites ($P < 0.01$). The average NO_3^- -N/ Cl^- ratio was 0.08 for the Dongbianmen and Tonghuihe

Fig. 3 Seasonal variation in NO_3^- -N, NH_4^+ -N, DON and TN concentrations (labeled with a, b, c, d, respectively) in surface water in Beijing from 2009 to 2010. Seasonal variation in NO_3^- -N concentrations was assessed from 2009 to 2011, NH_4^+ -N and DON from March to December in 2009, and TN from 2009 to 2010

monitoring sites, but was 0.12 from Kunminghu to Zhuanhe. Values for the NO_3^- -N/ Cl^- ratios were widely scattered at the Dongbianmen and Tonghuihe monitoring sites, but fell within a relatively restricted range at the upper sites (Fig. 4(b)). For all 10 monitoring sites NO_3^- -N and Cl^- concentrations were significantly positively correlated ($R^2 = 0.424$, $P < 0.001$) (Fig. 4(b)).

3.4 Nitrate nitrogen isotopic characteristics

Overall, the $\delta^{15}\text{N}_{\text{nitrate}}$ values surface water in urban

Beijing ranged from -1.3‰ to 28.9‰ . The average value was 11.5‰ ($n = 54$), and the highest $\delta^{15}\text{N}_{\text{nitrate}}$ values found at the Dongbianmen monitoring site (from 16.6‰ to 26.3‰) (Fig. 5 (a)). The $\delta^{15}\text{N}_{\text{nitrate}}$ values at Dongbianmmen were significantly higher than those at the other sites ($P < 0.05$) (Fig. 5 (b)). The mean $\delta^{15}\text{N}_{\text{nitrate}}$ values for the Changchunqiao and Tonghuihe monitoring sites were close to the median value for all sites, and ranged from 9.1‰ to 14.3‰ (Fig. 5 (b)). The average $\delta^{15}\text{N}_{\text{nitrate}}$ values for the Qianhai, Zhuanhe and Changpuhe monitoring sites ranged from 8.0‰ to 8.5‰ (Fig. 5 (b)),

Table 1 Correlation coefficients between mean monthly rainfall and concentrations of different species of nitrogen in surface water in Beijing

monitoring site	NO ₃ ⁻ -N (n = 38)	NH ₄ ⁺ -N (n = 19)	DON (n = 19)	TN (n = 38)
Kunminghu	0.082	-0.004	-0.206	-0.133
Changchunqiao	-0.262	0.009	-0.379	-0.342*
Library	-0.345*	0.492	0.196	-0.292
Zoo	-0.366*	0.535	0.641	-0.283
Zhuanhe	-0.484**	0.849**	0.126	-0.236
Huchenghe	-0.415*	0.812**	-0.193	-0.239
Qianhai	-0.504**	0.397	0.181	-0.44**
Changpuhe	-0.355	-0.023	-0.145	-0.154
Dongbianmen	-0.602**	0.362	0.242	-0.335
Tonghuihe	-0.336	0.291	0.244	-0.007

Note: * and ** represent statistically significant correlation at the 95% and 99% levels respectively

Fig. 4 Spatial variation in Cl⁻ concentrations (a) and Plot of NO₃⁻-N versus Cl⁻ (b) in surface water in Beijing City from 2009 to 2010. Columns followed by different letters (a, b, c) are significantly different at the 99% level. Boxplots illustrate the 25th, 50th, and 75th percentiles; the whiskers indicate the lowest and highest values

and were significantly lower than those at the other sites ($P < 0.05$) (Fig. 5 (b)).

4 Discussion

4.1 Characteristics of nitrogen pollution

Surface water in urban Beijing is seriously polluted by nitrogen which indicates that surface water in urban Beijing is very obviously affected by human activities. Surface water functioning is impaired by the high NH₄⁺-N and TN concentrations, both of which exceeded the Class V guideline of the Chinese National Quality Standards for Surface Waters [19]. When compared with the TN

concentrations of rivers and lakes in the Beijing metropolitan area in 2003, at which point they were all below 2 mg · L⁻¹ [17], TN concentrations showed an increasing trend. The TN concentrations reported in this study are higher than those in the Taihu lake region [26], in the Haicheng river basin [27] and in the Beijiang river in south China [28], but close to the TN level of the Thames river in the UK [29], and of stream water in Pennsylvania, USA [30]. These increasing TN concentrations may be due to intensification of human activities caused by urbanization, and agrees with other studies which have shown that urbanization results in elevated TN and NO₃⁻-N concentrations in watersheds in developing areas [31,32], and that urbanization soon takes over as the major source of nitrogen in urban freshwater ecosystems [27].

Fig. 5 Cross-plot of the $\delta^{15}\text{N}$ composition of nitrate versus $\text{NO}_3^- \text{-N}$ concentrations (a) and the $\delta^{15}\text{N}$ composition of nitrate versus different sites (b) for surface water in Beijing. The isotope values relate to samples collected in October 2010 and from April to August 2011. Columns followed by different letters (a,b) are significantly different at 95% level

There were significant spatial variations in nitrogen concentrations in Beijing. Generally speaking, nitrogen pollution was mainly confined to the downstream areas in the south-east of the Beijing urban area. The higher values of the different nitrogen forms at the Dongbianmen and Tonghuihe monitoring sites suggest the presence of obvious inputs of pollutants in the vicinity of the monitoring sites. Indeed, the higher population density around the Dongbianmen and Tonghuihe Rivers compared to the other monitoring sites may have resulted in a higher input of municipal sewage to the surface water. In contrast, concentrations of the different nitrogen forms were low in the upstream region due to few anthropogenic inputs. Results from this study are comparable to those for the Shiyang River, which, downstream of Wuwei City, was reported to be seriously polluted by nitrogen [33]. Perona et al. [34] reported that high surface water nitrogen concentrations were consistent with high population densities, mainly due to the increasing discharges of domestic sewage.

The increase in the $\text{NH}_4^+ \text{-N}/\text{TN}$ ratio from upstream to downstream in Beijing's rivers may be due to the increasing residential development, and agrees with what has been found in other studies, for example, Chen et al. [26] found that the $\text{NH}_4^+ \text{-N}$ concentrations in surface water near residential areas were higher than those for the other areas. Results from this study show that, as population and residential density increased from the north-west to the south-east of Beijing, there was a corresponding increase in nitrogen pollution.

Examination of seasonal patterns in nitrogen concentrations showed that $\text{NO}_3^- \text{-N}$ and TN concentrations were high in the dry season and low in wet season, which is

consistent with the results of other similar studies. For example, Chen et al. [35] observed seasonal variations in surface water nitrogen concentrations in the Beijing Yuqiao reservoir, as did Zhang and Schilling [36], in their study of the Raccoon River in the USA. Withers and Lord [37] also reported that, in environments with low permeability surfaces (such as are found in urban areas), $\text{NO}_3^- \text{-N}$ concentrations in surface water tended to fall during high flow periods. Further, Mulliss et al. [38] reported that pollutant concentrations decreased as storm discharges increased. In-river processes may play a role in controlling river $\text{NO}_3^- \text{-N}$ and TN concentrations. For example, the lower $\text{NO}_3^- \text{-N}$ and TN values observed in summer may be attributable to biologic uptake of nitrogen in the river [36,39]; while higher values of $\text{NO}_3^- \text{-N}$ and TN in winter may be due to reduced plant and microbial uptake of nitrogen [40]. $\text{NO}_3^- \text{-N}$ pollution in surface water in Beijing is mainly from point sources, and, where point sources are important, river water $\text{NO}_3^- \text{-N}$ concentrations may be high during baseflow conditions [29].

Seasonal variation in $\text{NH}_4^+ \text{-N}$ concentrations is probably mainly due to inputs of surface runoff with high $\text{NH}_4^+ \text{-N}$ contents. Rainfall and DON were not significantly correlated, which may be due to the intense nitrification in summer which is known to promote biologic activities [41].

4.2 Source identification of nitrogen pollution

Potential sources of $\text{NO}_3^- \text{-N}$ in surface water in urban areas are sewage, fertilizer, manure, soil nitrogen and atmospheric deposition [42]. Cl^- is a good indicator of sewage impacts because it is not subject to physical, chemical, and

biologic processes [43] and as such, the $\text{NO}_3^- \text{-N}/\text{Cl}^-$ ratio, combined with the isotopic method, has proved to be a useful hydro-chemical indicator to detect sources of $\text{NO}_3^- \text{-N}$ in different ecosystems [44–46]. Values of the $\text{NO}_3^- \text{-N}/\text{Cl}^-$ ratio for this study were consistent with those reported by Wakida and Lerner [5]. Also the $\text{NO}_3^- \text{-N}/\text{Cl}^-$ ratios at Dongbianmen and Tonghuihe (0.08) are similar to the $\text{NO}_3^- \text{-N}/\text{Cl}^-$ ratios of the city sewage, which averaged 0.06 [47]. The close relationship of $\text{NO}_3^- \text{-N}/\text{Cl}^-$ may be due to anthropogenic sources of Cl^- , possibly related to municipal sewage [48,49]. The domestic sewage discharge from Beijing was about 0.9 billion tons in 2009, which accounted for 90% of the city's wastewater discharge, and this figure continues to increase year by year in line with the continuing growth in population.

The $\delta^{15}\text{N}_{\text{nitrate}}$ values for the 10 monitoring sites mainly ranged between 4‰–19‰, which are characteristic of manure and sewage (Fig. 5 (a)). Since there was little manure application to the urban soil and very few manure inputs to the surface water, this result indicates that the most likely source of $\text{NO}_3^- \text{-N}$ in the surface water of Beijing was domestic sewage, with only a minor contribution from soil organic matter or atmospheric deposition.

In the upstream region, from the Kunminghu to Changpuhe monitoring sites, mean $\delta^{15}\text{N}_{\text{nitrate}}$ values for surface water were close to the upper limit for atmospheric deposition and the lower limit for sewage, and were low when compared with those for the Dongbianmen and Tonghuihe monitoring sites. Nitrogen deposition is dominated by $\text{NO}_3^- \text{-N}$, with a $\text{NH}_4^+ \text{-N}/\text{NO}_3^- \text{-N}$ ratio of 0.79 [50]. Atmospheric nitrogen deposition rates for Beijing have been estimated at $75.13 \text{ mg} \cdot \text{m}^{-2}$, and, from June to September 2009, showed a significantly increasing trend [51]. Other authors have reported that direct runoff of atmospheric $\text{NO}_3^- \text{-N}$, mobilized from impervious surfaces, is an important source of $\text{NO}_3^- \text{-N}$ in urban watersheds during storm events [1,30,52]. In Beijing, atmospheric nitrogen deposition may account for a larger proportion of nitrogen pollution in the upper stream region relative to the downstream reaches, where the contribution from sewage was higher.

In general, $\delta^{15}\text{N}_{\text{nitrate}}$ values at the downstream monitoring sites (Dongbianmen and Tonghuihe) fell within the range of sewage with relatively high $\text{NO}_3^- \text{-N}$ concentrations, and may be explained by the fact that the population density near the Dongbianmen and Tonghuihe monitoring sites was somewhat higher than that of the other eight monitoring sites from Kunminghu to Changpuhe [53]. The $\delta^{15}\text{N}_{\text{nitrate}}$ values for Dongbianmen and Tonghuihe (which ranged from 9.1‰ to 14.3‰) fell within the expected range for sewage (from 6‰ to 14‰) [54]. Results for this study showed that the main source of surface water $\text{NO}_3^- \text{-N}$ may be domestic sewage at the downstream monitoring sites, which agrees with the results of Xie et al. [55] and Townsend et al. [56]. Processed

wastewater from the Gaobeidian treatment plant is the main source of water to the Tonghui River. However, concentrations of nitrate and other forms of N were still high in this river, which may have been due to unidentified direct inputs of pollutants to the river in addition to the wastewater discharges. Alternatively the volume of wastewater may have exceeded the processing capacity of the wastewater treatment plant, which may have meant that partially treated waste water was discharged. In addition, the $\text{NH}_4^+ \text{-N}$ in directly discharged sewage may have been nitrified to $\text{NO}_3^- \text{-N}$, in the presence of high DO, which may have further contributed to the increased $\text{NO}_3^- \text{-N}$ concentrations [27]. The $\delta^{15}\text{N}_{\text{nitrate}}$ values of the surface water were in the expected range of $\delta^{15}\text{N}_{\text{nitrate}}$ values for animal wastes, and ranged from 3‰ to 13‰ [57]. The high $\delta^{15}\text{N}_{\text{nitrate}}$ values in Dongbianmen, which were greater than 25‰, may also be indicative of denitrification in surface water [58–60].

5 Conclusions

Surface water in Beijing is seriously polluted by inorganic nitrogen, with $\text{NH}_4^+ \text{-N}$ and TN concentrations all exceeding the Class V guidelines given by the Chinese National Quality Standards for Surface Waters (GB3838-2002). Significant spatial variations in nitrogen concentrations suggest that surface water is very seriously polluted in the south-east of Beijing City. Human activities mainly controlled the inorganic nitrogen distribution in surface water in Beijing, with higher $\text{NO}_3^- \text{-N}$ and ammonia concentrations near residential and commercial areas.

Examination of seasonal variation showed that $\text{NO}_3^- \text{-N}$ and TN concentrations were high in the dry season and low in the wet season, which may be the result of point-source pollution and rainfall dilution. $\text{NO}_3^- \text{-N}/\text{Cl}^-$ and $\delta^{15}\text{N}_{\text{nitrate}}$ values showed that the main $\text{NO}_3^- \text{-N}$ source in the downstream reaches of Beijing was domestic sewage, while in the upper reaches, nitrate mainly derived from atmospheric deposition and, to a lesser degree, sewage.

The results from this study provide useful information for controlling sources of nitrogen to surface water in urban Beijing and eutrophication, and could contribute toward the implementation of sustainable environmental management in Beijing urban surface water. Results also suggest that investment into increased wastewater treatment facilities should be focused in the south-east part of Beijing. Further, the processing capacity of existing treatment plants should be increased, and the sewage treatment processes should be improved, so that wastewater treatment plant discharges are less polluting.

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