

Nitrogen pollution characteristics and source analysis using the stable isotope tracing method in Ashi River, northeast China

Guangwen Ma · Yeyao Wang · Xiang Bao ·
Yu Hu · Yuping Liu · Lihuan He · Taiming Wang ·
Fansheng Meng

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Abstract This study examined nitrogen (N) pollution characteristics based on water quality monitoring of the Ashi River and analyzed N sources by stable isotope tracer (SIT) techniques during a hydrological year in 2011. Twenty-two evenly distributed sites were sampled in the mainstream and tributaries of Ashi River during the temperate, wet, and dry seasons. The results showed that the concentrations of ammoniacal nitrogen ($\text{NH}_4^+\text{-N}$), nitrate nitrogen ($\text{NO}_3^-\text{-N}$), and total nitrogen (TN) were lower in the upstream section of Ashi River, while the concentrations were higher in most other sections of Ashi River. Different forms of N had significant seasonal variations. The range of $\delta^{15}\text{N-NO}_3^-$ values indicated different N pollution sources. The upstream headwater area of Ashi River was mainly polluted by atmospheric N deposition and soil organic N. In the midstream and downstream areas of Ashi River, some sampling sites were affected by water released from cropland and rural domestic sewage, while

other sites were polluted due to wastewater from livestock and poultry production. In addition, pollution in the downstream section of Ashi River was mainly caused by industrial wastewater. The city zone located in the basin had a greater impact on the variations of $\text{NH}_4^+\text{-N}$ concentrations, and less impact on $\text{NO}_3^-\text{-N}$. N pollution characteristics of $\text{NH}_4^+\text{-N}$, $\text{NO}_3^-\text{-N}$, and TN, as well as $\text{NO}_3^-\text{-N}$ analysis to identify sources, reflected the profound impact of non-point source pollution during the temperate and wet seasons and point source pollution during the dry season in Ashi River.

Keywords Non-point source · Nitrogen pollution · Isotope tracers · $\delta^{15}\text{N-NO}_3^-$ · Natural abundance · Water quality

Introduction

Due to the specific mode of economic development in China, as well as the process for environmental pollution control, the main rivers show obvious impacts from point source pollution. Non-point source (NPS) pollution is becoming an important source of water pollution, with growing impacts from the loss of nitrogen (N) and phosphorus (P) from the land on the water quality of the river. NPS pollution is random, intermittent, complex, hidden, and dispersed; therefore, it is very difficult to monitor. NPS pollutants are transferred by two processes during precipitation conditions. Under less intense precipitation, pollutants transfer with the infiltration of water to deep soil. When the precipitation intensity is greater than the soil infiltration capacity, it results in surface runoff, runoff erosion, and sediment migration (Zhang et al. 2007). NPS pollution tracing, identification, and classification studies

G. Ma · Y. Wang (✉) · L. He · T. Wang
China National Environmental Monitoring Centre,
Beijing 100012, People's Republic of China
e-mail: yeyaowang@163.com

G. Ma
e-mail: guangwenm@163.com

X. Bao · F. Meng
Chinese Research Academy of Environmental Sciences,
Beijing 100012, People's Republic of China

Y. Hu
College of Water Sciences, Beijing Normal University,
Beijing 100875, People's Republic of China

Y. Liu
Heilongjiang Research Institute of Environmental Protection
Science, Harbin 150056, People's Republic of China

aim to determine the source and amount of NPS pollution. Wu et al. (2012) assessed the impact of climate change on hydrological behavior, considering future land-use types and rural residential area and their propagation to NPS pollution loads. SIT techniques and water chemistry analysis methods can be used to trace the source of pollutants in water, in order to understand the migration law and exchange of contaminants over time. Minet et al. (2012) evaluated the utility of using SIT for NO_3^- -N source tracking through the determination of $\delta^{15}\text{N}$ - NO_3^- and $\delta^{18}\text{O}$ - NO_3^- in the unsaturated zone from varying N source types (artificial fertilizer, dairy wastewater, and cow slurry) and rates with contrasting isotopic compositions. The Dillon and Chanton (2008) study showed that stormwater N inputs need to be considered in N budgets for aquatic systems that show anthropogenic ^{15}N enrichment. The Bu et al. (2011) study measured the concentrations of different forms of N, revealed the characteristics of N pollution and water chemistry, and identified the sources of N pollution due to anthropogenic impacts in the waters of the Haicheng River in northeast China. There are two commonly used stable N isotope tracer (SNIT) methods: one that differentiates N sources and sinks under natural ^{15}N abundance conditions, and another isotope dilution method that utilizes the artificial enrichment of ^{15}N sources (Bedard-Haughn et al. 2003).

Many research results have shown that different sources of N have different compositions of two stable isotope (SI), ^{14}N and ^{15}N , reflected as $^{15}\text{N}/^{14}\text{N}$ values (Yue et al. 2010). Generally, little change in δ values is necessary to represent the isotope content of the elemental N isotope fractionation caused by significant differences in $\delta^{15}\text{N}$ in natural nitrogenous substances (Xing et al. 2010). The study of river nitrate $\delta^{15}\text{N}$ is an effective means to directly identify the sources of river N pollution (Xue et al. 2009). N SI is widely used to study all kinds of inorganic N sources, transport, and transformations in the water environment (Kameda et al. 2006; Zeng et al. 2012). Despite single use of SNIT, the N source cannot effectively distinguish between soil organic N and atmospheric precipitation N (Liu et al. 2006; Anisfeld et al. 2007; Ohte 2013), but the combination of land use and pollutant source distribution can be used to identify sources of NO_3^- -N in water bodies (Chen et al. 2008; Xing et al. 2010).

While Ashi River has serious NPS pollution of N (Chen et al. 2010), there is no direct research on the pollution in different seasons and sources of NPS pollutants. Using conventional monitoring and SNIT techniques, combined with land use, the objectives of this study were to: (1) measure the concentrations of different forms of N at different sampling points in Ashi River; (2) reveal the characteristics of N pollution and water chemistry; and (3) identify the main factors and sources of N pollution in Ashi

River. Ashi River sampling, analysis, and study on pollution characteristics and sources of N was conducted in order to focus on polluted rivers and different sources of NPS pollution, and provide managers with the basis for more effective river management. The results from this study will be meaningful to control N pollution in Ashi River and Songhua River for sustainable environmental management.

Materials and methods

Study area

Ashi River Basin is located in the Heilongjiang Province, northeast China, between latitude $45^\circ 05' - 45^\circ 49' \text{N}$ and longitude $126^\circ 40' - 127^\circ 42' \text{E}$, with a drainage area of $3,545 \text{ km}^2$ (Fig. 1). The whole territory of the Ashi River Basin is located within the Harbin city. Ashi River is an important tributary of the Songhua River, which originates in the southern Daqing Mountains and then flows through the Shangzhi, Wuchang, Acheng, and Xiangfang districts of Harbin city from southeast to northwest (Wang et al. 2012).

The Ashi River Basin is in the middle temperate zone with a continental monsoon climate consisting of a long winter and short summer. The river is frozen every year from mid-November until early April of the subsequent year. During the growing season from April–September each year, maize and rice comprise the main farm crops along the river. Water characteristics vary significantly between the wet and dry seasons. The wet season (also called the high-flow period) occurs in July–August; the temperate season (also called the mean-flow period) occurs in April–June and September–October; and the dry season (also called the rainless period) occurs in January–March and November–December each year (Yang 2007). Ashi River has two flood seasons: one in April due to melting snow and spring floods, and one in July–August due to the impact from southeast monsoons that bring a large amount of precipitation. The spring flood season is less intense than the summer flood season, as the summer season accounts for 60–70 % of the annual precipitation. The high amount of rainfall could easily lead to more serious NPS pollution in the summer. The terrain of the northwest Ashi River Basin is flat, while the southeast has low-lying mountainous and hilly vegetation cover, as shown in Fig. 1. The main types of land use include forest, grassland, farmland, water body, building land, and unused land. Farmland, forest and building land are the three largest land-use types that cover 46.25, 44.51 and 6.55 % of the total drainage area, respectively. Land-use types of grassland, water body and unused land are 1.33, 0.70 and 0.66 % of the total drainage area, respectively (Fig. 2).

Fig. 1 Sample locations and topography of Ashi River Basin

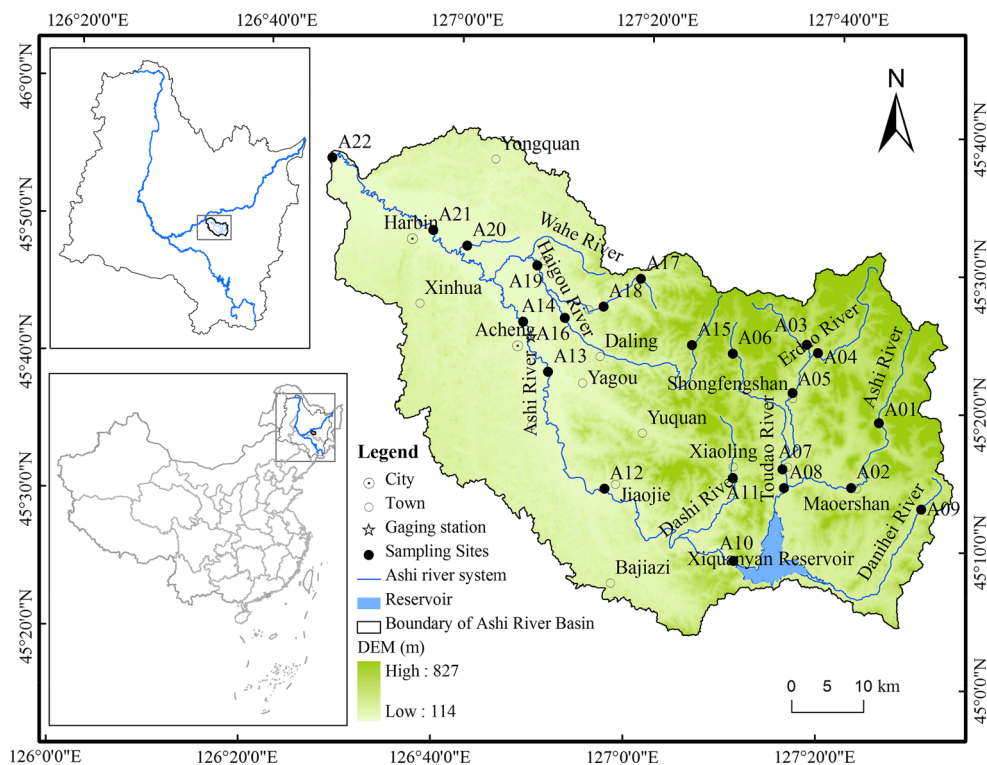
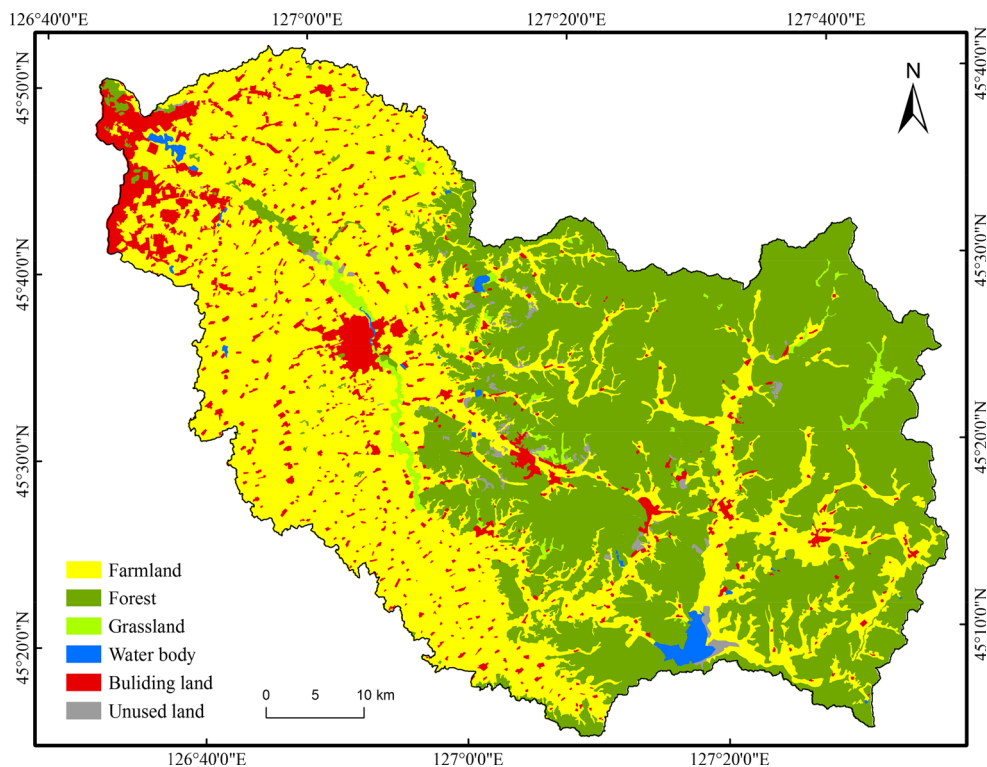


Fig. 2 Land use and land cover in the Ashi River basin in 2010



Water sampling and analytical methods

The water samples were collected seasonally during May 24–25, July 25–26, and November 2–3 in 2011. The

mainstream and tributaries were divided into 22 monitoring sections, each containing a sampling point so as to provide a representative sampling scheme in Ashi River. Each sampling point was recorded by GPS in the field and then

combined with ArcGIS10 software to map the sampling point distribution in Fig. 1. Of the 22 sampling sites, nine were situated along the mainstream (sites A01, A02, A08, A10, A12–A14, A21, and A22) and the others were spread in the main tributaries. Sites A03–A07 were located along Erdao River, sites A09 and A11 were located in Danihei River, and sites A15–A19 were located along Haigou River. Sites A02, A05, A07, A11, and A12 were located near Maoershan, Shongfengshan, Pingshan, Xiaoling, and Jiaojie towns, respectively. While sites A13 and A14 were in the upper and lower Acheng District, respectively, sites A21 and A22 were in the upper and lower Harbin urban area, respectively. Sites A01–A12 were located upstream, sites A13–A18 midstream, and sites A19–A22 downstream within Ashi River.

River water at each site was sampled in polyethylene plastic bottles pre-rinsed three times with distilled water and kept below 4 °C for laboratory analysis of dissolved inorganic nitrogen (DIN), including NH_4^+ -N, NO_3^- -N, and TN. Pretreatment and determination for these parameters analyzed in the laboratory were all conducted following national standard methods (NEPB 2002).

The river discharge data were obtained from the Acheng gauging station. In the laboratory, NH_4^+ -N was measured with the Nessler's reagent spectrophotometry method (HJ535-2009); NO_3^- -N was quantified by the UV spectrophotometry method (HJ/T 346-2007); and TN was determined through the alkaline potassium persulfate oxidation–UV spectrophotometric method (GB11894-89). Detection limits were 0.025, 0.02, and 0.05 mg/L for NH_4^+ -N, NO_3^- -N, and TN, respectively. The NH_4^+ -N of Ashi River was evaluated according to levels set in the Surface Water Quality Standards (GB3838-2002). TN and NO_3^- -N were evaluated according to their absolute concentrations.

For the isotope sample pretreatment, the water samples were first filtered through a 0.45- μm membrane, then through an anion exchange resin column and subjected to ion exchange. A quantity of 8 mL of 3 mol/L hydrochloric acid elution adsorption of NO_3^- was added to the resin column, with about 3.3 g Ag_2O added successively to the eluate for about 1 g reaction. Finally, a pH meter inspection was used, which recorded pH values between 5.5 and 6.0. The precipitated AgCl was removed with disposable syringe filters, then a filtrate containing 50 mL AgNO_3 in an injection tinfoil package was placed in a beaker, freeze-dried, and further processed with an isotope mass spectrometer analysis to obtain AgNO_3 crystals from the samples (Silva et al. 2000; Zhou et al. 2001). The mass spectrometry tests were conducted by the Isotope Laboratory, Institute of Earth Environment, Chinese Academy of Sciences. Delta Plus SI gas mass spectrometry through ConFlo III devices and Flash EA 1112 elemental analyzer

coupled with automatic continuous analysis were used to determine the $\delta^{15}\text{N}$ values with standard deviation ± 0.2 ‰. The δ value was used to represent the isotope ratio of the sample relative to a standard substance isotope ratio per thousand (Chang et al. 2002); $\delta^{15}\text{N}$ was calculated according to the following Eq. (1):

$$\delta^{15}\text{N}(\text{‰}) = \frac{R_{\text{sample}} - R_{\text{standard}}}{R_{\text{standard}}} \times 1000 \quad (1)$$

In the formula, $\delta^{15}\text{N}$ (‰) represents the N isotope ratios of samples, R_{sample} , and air quality standards, R_{standard} , measured by isotope mass spectrometer as the $^{15}\text{N}/^{14}\text{N}$ mass ratio (Liu et al. 2012).

Statistical analysis

In order to determine if the observation values in each sample site were independent of one another in the water of Ashi River, temporal and spatial autocorrelations of N pollution data were detected using time series analysis and spatial analysis, respectively. Two-way analysis of variance (ANOVA) was performed to estimate the temporal and spatial variability of N pollution in the river (Mendiguchía et al. 2007).

Hierarchical cluster analysis (HCA) using the squared Euclidean distance with Ward's method was also performed to assess the similarity among sampling sites for N pollution (Kazi et al. 2009). Prior to the cluster analysis, the raw water chemistry data were initially standardized by z-scale transformation in order to avoid misclassification due to wide differences in data units and dimensionality. Using raw data, discriminant analysis (DA) was also applied to determine the variables that could discriminate different groups, by building up a discriminant function that shared common properties among groups. All statistics were analyzed using SPSS19.

Results

Nitrogen pollution analysis

The concentrations of NH_4^+ -N ranged from 0.03 to 17.40 mg/L (Table 1); the maximum occurred at site A14 in the dry season (Fig. 3). According to the national quality standards for surface waters in China (GB3838-2002), NH_4^+ -N concentrations during the temperate season reached Class III guidelines (≤ 1.0 mg/L) at sites A01–A08, A10–A14, A16–A18, A20, and A21; reached Class IV guidelines (≤ 1.5 mg/L) at site A19; and exceeded Class V guidelines (≤ 2.0 mg/L) at sites A09 and A22. During the wet season, NH_4^+ -N concentrations achieved Class III guidelines at sites A01–A21, and Class IV guidelines at site

Table 1 $\text{NH}_4^+\text{-N}$, $\text{NO}_3^-\text{-N}$, and TN concentration ranges at monitoring sites in the three seasons

	Concentration ranges (mg/L)			
	Hydrological year	Temperate season	Wet season	Dry season
$\text{NH}_4^+\text{-N}$	0.03–17.40	0.06–6.31	0.03–1.30	0.04–17.40
$\text{NO}_3^-\text{-N}$	0.15–5.28	0.15–5.28	0.22–4.01	0.25–4.83
TN	0.38–19.40	0.38–12.89	0.90–5.61	0.42–19.40

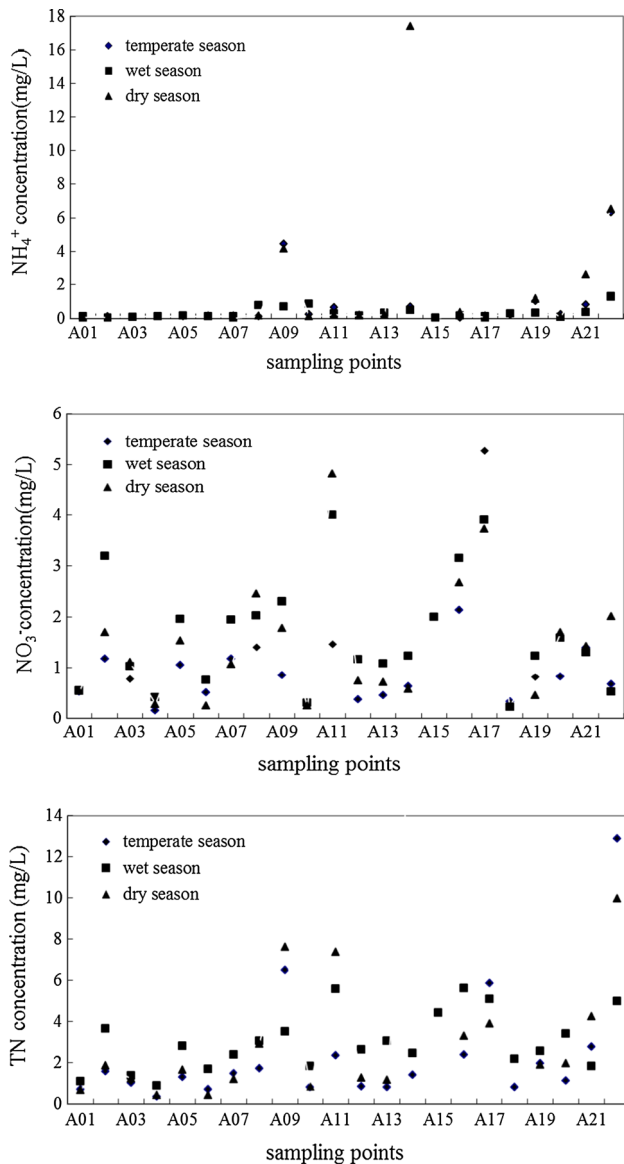


Fig. 3 $\text{NH}_4^+\text{-N}$, $\text{NO}_3^-\text{-N}$, and TN concentrations in Ashi River

A22. During the dry season, $\text{NH}_4^+\text{-N}$ concentrations reached Class III guidelines at sites A01–A08, A10–A13, A15–A17, and A20; reached Class IV guidelines at site A19; and exceeded Class V at sites A09, A14, A21, and

A22. The $\text{NH}_4^+\text{-N}$ concentrations of A14 and A22 were higher, indicating that the city zones had greater impact on them, because A14 and A22 were located further downstream in the two city zones.

The concentrations of $\text{NO}_3^-\text{-N}$ ranged from 0.15 to 5.28 mg/L (Table 1); the maximum occurred at site A17 in the temperate season (Fig. 3). During the temperate season, $\text{NO}_3^-\text{-N}$ concentrations at sites A02, A05, A07, A08, A11, and A21 ranged from 1.00 to 1.50 mg/L; sites A16 and A17 were from 2.00 to 5.28 mg/L; and the concentrations at the 14 other sampling sites were less than 1.00 mg/L. During the wet season, $\text{NO}_3^-\text{-N}$ concentrations at sites A03, A05, A07, A12–A14, and A19–A21 were from 1.00 to 2.00 mg/L; sites A02, A08, A09, A11, and A15–A17 were from 2.00 to 3.91 mg/L; and the concentrations at the six other sampling sites were less than 1.00 mg/L. During the dry season, $\text{NO}_3^-\text{-N}$ concentrations at sites A02, A03, A05, A07, A09, A20, and A21 were from 1.00 to 2.00 mg/L; sites A08, A11, A16, A17, and A22 were from 2.00 to 4.83 mg/L; and the concentrations of the remaining 10 samples were less than 1.00 mg/L. The city zones had a less impact on $\text{NO}_3^-\text{-N}$ concentration.

The concentrations of TN ranged from 0.38 to 19.40 mg/L (Table 1), with the maximum at site A14 in the dry season (Fig. 3). During the temperate season, TN concentrations were less than 1.0 mg/L at sites A01, A04, A06, A10, A12, A13, and A18; from 1.0 to 1.5 mg/L at sites A03, A05, A07, A14, A19, and A20; from 1.5 to 2.0 mg/L at sites A02 and A08; and greater than 2.0 mg/L at sites A09, A11, A16, A17, A21, and A22. During the wet season, TN concentrations were less than 1.0 mg/L at site A04; 1.0–1.5 mg/L at sites A01 and A03; 1.5–2.0 mg/L at sites A06, A10, and A21; and greater than 2.0 mg/L at sites A02, A05, A07–A09, A11–A20, and A22. During the dry season, TN concentrations were less than 1.0 mg/L at sites A01, A04, A06, and A10; 1.0–1.5 mg/L at sites A03, A07, A12, and A13; 1.5–2.0 mg/L at sites A02, A05, A19, and A20; and greater than 2.0 mg/L at sites A08, A09, A11, A14, A16, A17, A21, and A22.

Based on the concentrations of $\text{NH}_4^+\text{-N}$, $\text{NO}_3^-\text{-N}$, and TN during the temperate, wet, and dry seasons, the 22 sampling sites were classified into four distinct clusters at $(D_{\text{link}}/D_{\text{max}}) \times 25 < 5$ by HCA and then illustrated as a dendrogram (Fig. 4). Cluster 2 was formed by sampling sites A02, A08, A16, A21, A11, and A17; Cluster 3 by sites A09 and A22; and Cluster 4 by site A14. The 13 other sampling sites were included in Cluster 1. According to one-way ANOVA, there were significant differences ($p < 0.001$) in parameter concentrations of $\text{NH}_4^+\text{-N}$, $\text{NO}_3^-\text{-N}$, and TN among the four clusters (Fig. 4).

Accordingly, Clusters 1–4 were recognized to have low, moderate, high, and very high N pollution, respectively. In Cluster 1, all sites displayed the smallest concentrations of

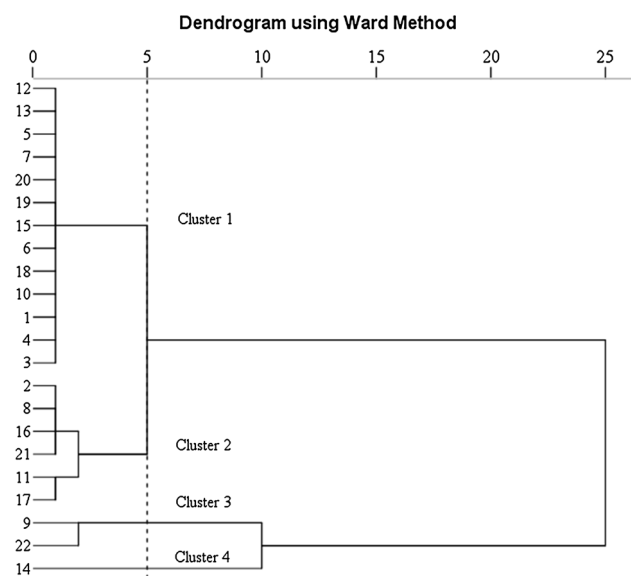


Fig. 4 Cluster dendrogram showing the groupings based on the concentrations of $\text{NH}_4^+\text{-N}$, $\text{NO}_3^-\text{-N}$, and TN during a hydrological year

each parameter, which represented the background values. Sites A01, A03, and A04 were all located in the source area of the river, where anthropogenic impacts were the lowest. Other sites in Cluster 1 had less N pollution, mostly due to fewer disturbances by human activities. Sampling sites in Cluster 2 were mostly located along agricultural areas, where N pollution was thought to be primarily derived from N fertilizer. The N fertilizer utilization rate in China is 30–35 %, as reported by Bu et al. (2010). According to the Harbin Statistical Yearbook 2010, more than 10.41×10^3 tons of N fertilizers are annually applied to crops in Ashi River Basin, the unused parts of which are finally discharged into the river. In Cluster 3, sites A09 and A22 were affected by sewage from livestock and poultry production, and the effluent from sewage treatment plants, respectively. In Cluster 4, site A14 was affected by urban sewage discharge from Acheng district.

Ashi River water quality showed lower concentrations of $\text{NH}_4^+\text{-N}$ at most sampling sites. Since $\text{NH}_4^+\text{-N}$ is subject to influence from agricultural and industrial production, most of the region remained within Class III guidelines (GB3838-2002). The number of sampling sites that reached Class III for $\text{NH}_4^+\text{-N}$ concentrations gradually increased from the wet season to the temperate season to the dry season. Sampling sites A01–A12 were located in upstream sections, A13–A19 midstream, and A20–A22 downstream in Ashi River. The experimental results of $\text{NO}_3^-\text{-N}$ and TN concentrations can be seen as water quality gradually deteriorated from upstream to midstream and downstream sites. The city zone had little effect on $\text{NO}_3^-\text{-N}$ concentrations during the temperate and wet

seasons, but had a greater impact during the dry season in Ashi River.

Source identification of nitrogen pollution

The range of $\delta^{15}\text{N-NO}_3^-$ values in this study can be used to effectively trace and identify different sources of N pollution in Ashi River. Different sources of N pollution were identified for each season. N isotope composition $\delta^{15}\text{N}$ values for different sources of N are generally as follows: 0 ± 3 ‰ for most synthetic fertilizers (Gormly and Spalding 1979; Heaton 1986), 8–20 ‰ for human and animal excreta (Kreitler 1979; Heaton 1986), 2–8 ‰ for atmospheric deposition, 4–9 ‰ for soil organic N (Heaton 1986; Mariotti et al. 1988), >10 ‰ for urban sewage, <10 ‰ for industrial wastewater (Li et al. 2005), and –20 to 30 ‰ for most terrestrial substances. Figure 5 has been mapped according to the range of $\delta^{15}\text{N-NO}_3^-$ values of the scholars' research results. N pollution sources have been determined on the basis of the range of $\delta^{15}\text{N-NO}_3^-$ values and land use of Ashi River Basin.

During the temperate season of Ashi River, $\delta^{15}\text{N-NO}_3^-$ values ranged from 3.68 to 6.09 ‰ in the upstream area (sites A01, A03, and A04), indicating that the main cause of organic N pollution was soil erosion (Fig. 5), due to sparser vegetation in the season, steeper topography and the black earth and dark brown soil in the area, all of which are conditions favorable to soil erosion. In the midstream and downstream sections, values ranging from 5.32 to 7.72 ‰ at sites A05–A10, A12, A13, and A18–A21 were affected by water released from cropland and sewage from villages; values from 8.45 to 11.86 ‰ at sites A02, A11, A16, and A17 were affected by effluent from livestock and poultry production, especially at site A11 with $\delta^{15}\text{N-NO}_3^-$ values up to 11.86 ‰. Sites A14 and A22 had lower $\delta^{15}\text{N-NO}_3^-$ values from 3.25 to 4.15 ‰ in midstream and downstream sections, which were mainly affected by municipal sewage and industrial wastewater, especially at site A22, which had a $\delta^{15}\text{N-NO}_3^-$ value of 3.25 ‰. Although the effluent from a sewage treatment plant was present in the upstream area, the region of the basin outlet is characterized by flat and wide, the main stream of Songhua River backwater caused slow-flowing rivers, which may account for the occurrence of ^{15}N isotope fractionation.

During the wet season, sites A01, A04, A10, and A18 had $\delta^{15}\text{N-NO}_3^-$ values less than 1.94–3.27 ‰ (Fig. 5), the main land-use type is forest in the upstream, indicating that they were mainly affected by atmospheric wet deposition, with individual sampling sites affected by artificial fertilizers, because the main land-use types are farmland and building land in the midstream and downstream. Sites A03, A05, A06, A12–A15, and A19–A22 with $\delta^{15}\text{N-NO}_3^-$ values of 4.62–7.80 ‰, as well as sites A02, A07, A08,

A16, and A17 with $\delta^{15}\text{N-NO}_3^-$ values of 8.38–9.89 ‰, were mainly affected by soil organic N and industrial effluent. Sites A09 and A11 with $\delta^{15}\text{N-NO}_3^-$ values from 15.17 to 15.35 ‰ were affected by effluent from livestock and poultry production and domestic sewage.

During the dry season, $\delta^{15}\text{N-NO}_3^-$ values at sites A01, A04, A06, A10, A14, and A19 were 1.11–2.07 ‰, indicating that they were mainly affected by artificial fertilizers. Sites A02, A03, A05, A07, A12, and A21 had $\delta^{15}\text{N-NO}_3^-$ values from 4.16 to 7.77 ‰, affected mainly by soil organic N. Sites A08, A09, A13, A15, and A20 had $\delta^{15}\text{N-NO}_3^-$ values of 8.36–9.89 ‰, mainly affected by domestic sewage. Sites A11, A16, A17, and A22 with $\delta^{15}\text{N-NO}_3^-$ values of 10.22–12.61 ‰ were distributed mainly in areas affected by livestock and poultry production and domestic sewage (Fig. 5).

Fig. 5 Concentrations of $\delta^{15}\text{N}$ at sampling sites in Ashi River

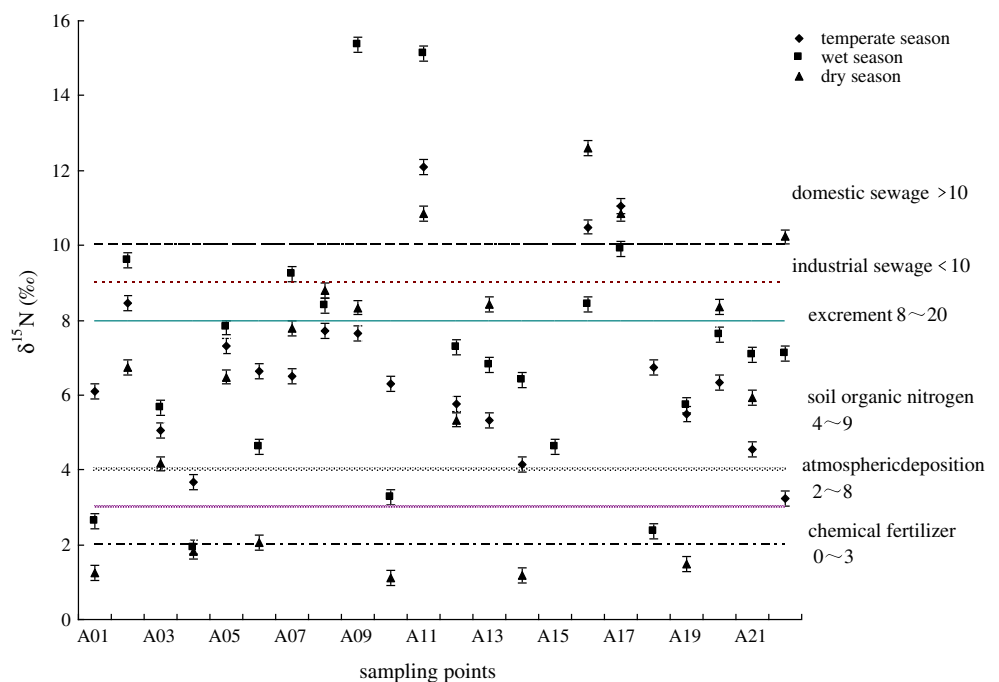
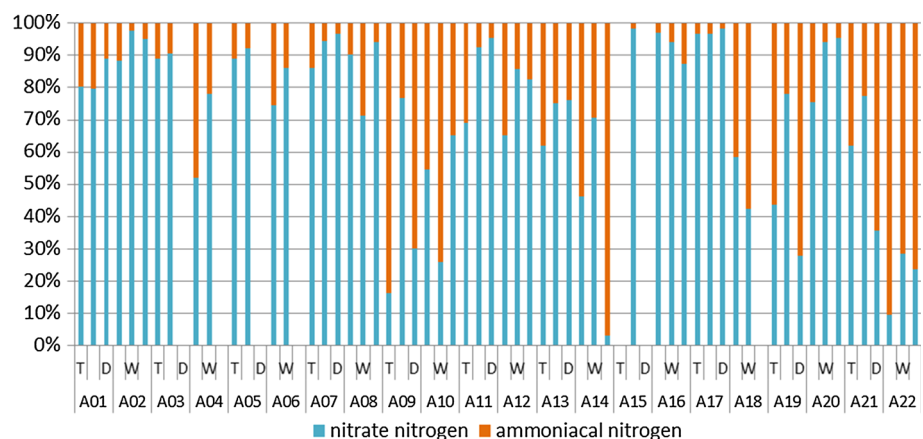


Fig. 6 Comparison of $\text{NH}_4^+\text{-N}$ and $\text{NO}_3^-\text{-N}$ concentrations in Ashi River



Discussion

Spatial and temporal variations of nitrogen pollution

By comparison of $\text{NH}_4^+\text{-N}$ and $\text{NO}_3^-\text{-N}$ content (Fig. 6), midstream and downstream pollution of Ashi River was more greatly impacted by $\text{NH}_4^+\text{-N}$, which was more closely associated with human activities and land-use relationships. $\text{NH}_4^+\text{-N}$ was much lower in mountainous and vegetated areas (A01–A08, A10–A13 and A16–A17) than in urban land-use areas (A14, A21 and A22). In addition, concentrations of $\text{NO}_3^-\text{-N}$ were the primary driver that led TN concentrations to change in the river water.

The nutrient variables displayed significant spatial differences in the watershed during the study period. The

concentrations of N ($\text{NH}_4^+\text{-N}$, $\text{NO}_3^-\text{-N}$, and TN) tended to increase in areas with higher density of urban and agricultural land uses, indicating that these high levels may be ascribed to the input of wastewater in industrial areas and the application of N fertilizers in arable areas (Bu et al. 2011; Wan et al. 2013).

There were clear seasonal variations showing an increase in the concentrations of nutrients during the rainy season. The results show impairment of the water quality of the river by anthropogenic activities in the catchment (Ngoye and Machiwa 2004).

Nitrogen pollution stable isotope tracing

Although the higher amount of water dilutes the point source pollution, the impact of NPS pollution runoff from the farmland was widely distributed in the midstream section of Ashi River Basin, as evidenced by higher TN concentrations during the wet season. In the upstream section, the water quality was better, with good vegetation cover limiting the amount of NPS pollution runoff caused by rainstorms. As the volume of river water increased from upstream to downstream, the TN concentration gradually decreased, but the impact of effluent from the sewage treatment plant showed increased TN concentrations in the basin outlet during the wet season. There were some areas affected by artificial fertilizer as the main source of N pollution during the dry season, which may be due to infiltration of nitrate from artificial fertilizer into the groundwater during the wet season, after which the $\text{NO}_3^-\text{-N}$ contamination is then stranded on the Ashi River.

In the N cycle, biological N fixation is one of the main ways for gaseous N input to the ecosystems. N isotope fractionation is small for the process of biological N fixation, during which the $\delta^{15}\text{N}$ values of biological N fixation and atmospheric N are similar (Shearer and Kohl 1986). The main soil N conversion is accomplished with the participation of microorganisms, through the series of transformations of mineralization (from organic form into inorganic form), nitrification (conversion from $\text{NH}_4^+\text{-N}$ to $\text{NO}_3^-\text{-N}$), and denitrification ($\text{NO}_3^-\text{-N}$ through microbial respiration into NO , N_2O , and N_2). Isotope fractionation leads to higher ^{15}N content of the product as compared with the substrate, which is reduced to a certain extent (Lin 2013). This study only tested $\delta^{15}\text{N}$ natural abundance in $\text{NO}_3^-\text{-N}$; therefore, it cannot explain the impact of N biogeochemical processes on research findings.

Multiple sources may exist, depending on the $\delta^{15}\text{N}$ of nitrogenous substances, since different sources of nitrate $\delta^{15}\text{N}$ sometimes have a certain degree of overlap. Different sources of $\delta^{18}\text{O}$ can also make up for the lack of $\delta^{15}\text{N}$. Although an increase in $\delta^{18}\text{O}$ analysis would double the cost of the study, using dual $\delta^{15}\text{N}$ and $\delta^{18}\text{O}$ isotope tracer

methods would help to more accurately determine the source of nitrate.

Conclusions

During the temperate season, concentrations of $\text{NH}_4^+\text{-N}$, $\text{NO}_3^-\text{-N}$, and TN were lower in the upstream section, while concentrations were higher in the other sections of Ashi River. The city zone had greater impact on the concentrations of $\text{NH}_4^+\text{-N}$ and less impact on $\text{NO}_3^-\text{-N}$. The upstream area of Ashi River was mainly affected by soil organic N from natural soil erosion, as well as atmospheric deposition pollution; the midstream water quality was affected by water released from cropland, village sewage, and livestock and poultry production sewage; and the downstream section was subject to pollution from municipal sewage and industrial wastewater in the temperate season.

During the wet season, the higher water volume, overall lower $\text{NH}_4^+\text{-N}$ concentrations, and higher TN concentrations, with dissolved $\text{NO}_3^-\text{-N}$ concentrations higher than those of TN, indicated that NPS pollution was primarily from stormwater runoff. The upstream sites were more influenced by atmospheric N wet deposition and artificial fertilizers, while other sites were more influenced by livestock and poultry production and domestic sewage impacts; the midstream water quality was mainly influenced by artificial fertilizers, while downstream water quality was affected mainly by soil organic N and industrial wastewater in the wet season.

During the dry season, the quantity of the river water was smaller, some sampling sites concentrations of $\text{NH}_4^+\text{-N}$ were higher, the maximum concentrations of $\text{NH}_4^+\text{-N}$ and TN occurred at site A14. The upstream section of Ashi River was affected mainly by soil organic N; the midstream influenced mainly by artificial fertilizers, livestock and poultry production, and domestic sewage; and the downstream affected primarily by industrial wastewater in the dry season.

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