Assessment of sources and transformation of nitrate in the alluvial-pluvial fan region of north China using a multi-isotope approach

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ABSTRACT

A multi-isotope approach and mixing model were combined to identify spatial and seasonal variations of sources, and their proportional contribution to nitrate in the Hutuo River alluvial-pluvial fan region. The results showed that the NO_3^- concentration was significantly higher in the Hutuo River valley plain (178.7 mg/L) region than that in the upper and central pluvial fans of the Hutuo River (82.1 mg/L and 71.0 mg/L, respectively) and in the river (17.0 mg/L). Different land use types had no significant effect on the groundwater nitrate concentration. Based on a multi-isotope approach, we confirmed that the main sources of groundwater nitrate in different land use areas were domestic sewage and manure, followed by soil nitrogen, ammonia fertilizer, nitrate fertilizer and rainwater, and there were no significant spatial or seasonal variations. Combining $\delta^{15}N-NO_3^-$, $\delta^{18}O-NO_3^-$ and $\delta^{37}Cl$ results can increase the accuracy of traceability. Nitrification could be the most important nitrogen migration and transformation process, and denitrification did not significantly affected the isotopic composition of the nitrate. The SIAR model outputs revealed that the main nitrate pollution sources in groundwater and river water were domestic sewage and manure, accounting for 55.9%—61.0% and 22.6% (dry season), 50.3%—60.4% and 34.1% (transition season), 42.7%—47.6% and 35.6% (wet season 2016) and 45.9%—46.7% and 38.4% (wet season 2017), respectively. This work suggests that the random discharge and disposal of domestic sewage and manure should be the first target for control in order to prevent further nitrate contamination of the water environment.

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Introduction

Nitrate, is one of the most common pollutants in water environments, due to its stability, high solubility and mobility (Zhang et al., 2015a). In recent years, the problem of nitrate contamination has been widely reported, especially in the developing countries (Jin et al., 2015; Liu et al., 2006). High nitrate concentrations is often related to anthropogenic activities, mainly including wastewater discharge (Matiatos, 2016), overuse of nitrogen fertilizers and animal manures (Xue et al., 2012; Meghdadi and Javar, 2018), land fill seepage (Zhang et al., 2015a), and elevated atmospheric deposition (Ji et al., 2017).

Nitrate contamination affects human and environmental health. Previous studies have reported that excessive nitrate can cause not only deterioration in water quality, but also eutrophication, and toxic algal blooms (Nestler et al., 2011; Li et al., 2013). Furthermore, drinking water containing excessive levels of nitrate can increase the risk of diseases, such as methemoglobinemia, 'blue baby syndrome' and stomach cancer (Hord, 2011; Pastén-Zapata et al., 2014). Therefore, it is very important to take effective control measures to prevent the nitrate concentration from increasing further.

There are five main sources of nitrate pollution in water, namely sewage and manure (SAM), soil nitrogen (SN), NO_3^- fertilizer (NF), NO_3^- in precipitation (NP) and NH_4^+ in fertilizer and rain (NFAR) (Xue et al., 2009). Nitrate pollution in the water environment has often come from multiple sources, which makes it difficult to identify the sources by traditional methods (such as hydrochemical methods). Nowadays, the dual isotope approach ($\delta^{15}N-NO_3^-$ and $\delta^{18}O-NO_3^-$) is widely used because the different nitrate sources have distinct stable isotope signatures (Xue et al., 2009; Nestler et al., 2011; Ji et al., 2017). The $\delta^{15}N$ values from precipitation and soil nitrogen range from −13‰ to +13‰ and from −3‰ to +9‰ (Xue et al., 2009; Jin et al., 2015), respectively. The typical $\delta^{15}N$ values of chemical fertilizers vary from −6‰ to +6‰ (Kendall et al., 2008). Manure and sewage are enriched in ^{15}N relative to other sources, and display high $\delta^{15}N$ values between +4‰ and +25‰ (Xue et al., 2009; Ji et al., 2017). As can be seen from these ranges, the $\delta^{15}N$ values of some nitrate pollution sources overlap, so it is not possible to identify the sources accurately by using $\delta^{15}N$ alone. The $\delta^{18}O-NO_3^-$ signature can provide additional useful information because of its distinct isotopic characteristics. The $\delta^{18}O-NO_3^-$ values from nitrification, NO_3^- from fertilizers and precipitation range from −10‰ to +10‰, from +17‰ to +25‰, and from +25‰ to +75‰, respectively (Xue et al., 2009; Matiatos, 2016).

Although using the dual isotope approach ($\delta^{15}N-NO_3^-$ and $\delta^{18}O-NO_3^-$) can improve the accuracy of source identification, the ratio may be modified if a complex fractionation process (such as, nitrification, denitrification or assimilation) occurs during N transformation (Xue et al., 2009; Ji et al., 2017; Yu et al., 2018). In addition, due to the similar values range of nitrate isotopes in sewage and manure, they tend to be treated as a single source (Xue et al., 2009; Nestler et al., 2011). The above limiting factors have an impact on the accuracy of source identification. Previous researchers have tried to introduce other methods to improve this situation. Some studies, for example, combined the application of statistical tests (Correlation Analysis and Principal Component Analysis)

and with an isotopic approach ($\delta^{15}N-NO_3^-$ and $\delta^{18}O-NO_3^-$) to explain the variance in large inter-correlated hydrochemical and isotope datasets (Matiatos, 2016; Meghdadi and Javar, 2018). Other studies found that the combined application of $\delta^{15}N-NO_3^-$ and $\delta^{18}O-NO_3^-$ as well as isotopes from other elements, such as boron (David Widory et al., 2005; Tirez et al., 2010) and strontium (Nigro et al., 2017), can further increase the accuracy of nitrate traceability.

Chlorine is a common chemical element in nature. The fractionation of Cl^- is limited and its isotope ratio variation is low because it is neither adsorbed by clay nor involved in redox reactions. Therefore, it plays an important role in the research field of element migration and material origins (Sie and Frape, 2002). Plotting NO_3^- versus Cl^- is widely used to identify the sources of nitrate pollution (Li et al., 2010; Zhang et al., 2015a). Liu et al., 2006 used a plot of the NO_3^-/Cl^- molar ratio against Cl^- concentration to trace the sources of nitrate. In this study, we used a plot of the NO_3^-/Cl^- concentration ration against $\delta^{37}Cl$ in order to further improve the accuracy of the identification of nitrate sources.

The Hutuo River alluvial-pluvial fan is located in the western portion of the North China Plain. With rapid urbanization and industrialization in recent years, the chemical environment of shallow groundwater has been seriously affected by anthropogenic activities. The water chemistry is transforming from HCO_3^- -type water to HCO_3-Cl, HCO_3-SO_4 and SO_4-HCO_3 types (Zhang et al., 2017). Several studies have found that the concentrations of groundwater NO_3^- in this region exceeded the threshold for drinking water established by WHO (50 mg/L) and posed a serious threat to the safety of drinking water for the local population (Li et al., 2016; Zhang et al., 2017).

This study aims to (1) distinguish the characteristics of the spatial and seasonal variation of groundwater and river nitrate concentrations in the Hutuo River alluvial-pluvial fan; (2) identify the main NO_3^- sources in different hydrogeological units and land use areas by using the NO_3^- ($\delta^{15}N$ and $\delta^{18}O$), water (δ^2H and $\delta^{18}O$) and Cl^- ($\delta^{37}Cl$) isotopes; (3) reveal the main transformations of nitrogen in this study area by the combined use of NO_3^- ($\delta^{15}N$ and $\delta^{18}O$) and water (δ^2H and $\delta^{18}O$); (4) quantify the spatial and seasonal variation in the proportional apportionment of NO_3^- sources in different hydrogeological unit and land use areas by using a Bayesian isotopic mixing model.

1.   Materials and methods

1.1.   Description of study area

The Hutuo River alluvial-pluvial fan is located in the North China Plain. The study area is the Shijiazhuang segment of the fan, which starts at the western Gangnan reservoir (the upstream recharge area) and stretches to the western part of Gaocheng. The total area is approximately 2442 km^2.

The study area has a semi-humid and semi-arid monsoon climate. The terrain is higher in the west and lower in the east. The western landforms consist of medium and low hills, and the eastern part is the North China Plain. The main land use types include farmland (38.62%), bare land (including mountains and barren land) (34.34%), county land (13.09%), urban land (11.60%), and surface water (2.35%).

The main aquifer in the study area is part of the deep Quaternary multi-layer aquifer system in the Hebei Plain, where the lithology consists of gravel, pebbles, coarse sand and fine sand. There is abundant water in the aquifer, and the groundwater mainly occurs in the pores of the loose Quaternary sediments. The overall flow of groundwater is from northwest to southeast. In this research, the study area is divided into three hydrogeological sub-regions according to the characteristics of aquifers and the conditions of groundwater recharge, runoff, and discharge: namely the Hutuo River valley plain (HVP), upper pluvial fans of the Hutuo River (UPF), and central pluvial fans of the Hutuo River (CPF). The detailed description is as follows.

The HVP is between the Gangnan reservoir and the Huangbizhuang reservoir. It is located in the transitional zone between the mountainous and plain areas. The depth to water is shallow, the hydraulic conductivity is very good, and water is abundant. As a result, the aquifer is interconnected strongly with the rest of the region. The UPF includes Luquan, Shijiazhuang urban area, Lingshou and Zhengding County, and the aquifer lithology is mainly sand gravel. The type of groundwater is mainly pore water. Due to over-exploitation of groundwater, the upper first aquifer group is basically dried out and the second aquifer group is being mined. The CPF mainly includes Zhengding County as well as part of Luancheng, Gaocheng and Wuji. The depth to water is deeper (40−50 m) and the lithology of the aquifer is mainly composed of sandy gravel, boulder coarse sand and medium sand.

1.2. Sample collection and analysis

Water samples were obtained from four field campaigns carried out in January 2015 (dry season), October−November 2015 (transition from wet to dry season), August 2016 (wet season) and September 2017 (wet season), from the upstream to the downstream of the Hutuo River, respectively, and comprised 39 sampling sites (35 groundwater sites and four surface water sites (two reservoirs sites, one mainstream site and one major tributary)). Only two reservoir samples (Gangnan reservoir and Huangbizhuang reservoir) were collected in January 2015 due to the River being without water. The two reservoir sites are situated at the Hutuo River channel and are concentrated water sources for Shijiazhuang city. All sampling site positions are shown in Fig. 1. The rain sampling site was located on the rooftop of the Institute of Hydrogeology and Environmental Geology, Chinese Academy of Geological Sciences, and all sampling was conducted during June 2015−August 2016 (12 rain events monitored). All groundwater sampling wells are primarily used for domestic and/or agricultural purposes; the mean depth of these wells is 9.78 m (range from 4.0 to 50.0 m). The values of pH, dissolved oxygen (DO) and Electrical Conductivity (EC) were measured in the field using a WTW Multi 340i/SET multiparameter instrument (Germany).

Groundwater samples were collected by pumping from the wells. River water was taken as grab samples which were collected at a depth of 50 cm below the surface of the river. All samples were filtered through 0.45 μm membranes, and were collected by a high density polyethylene sampler and then stored in two 250-mL, two 1.5 L and one 4 L high-density polyethylene sampling bottles for analysis of the main ions (NO_3^-, NO_2^-, Cl^-, NH_4^+ and Mn) and the isotopes ($\delta^{15}N-NO_3^-$, $\delta^{18}O-NO_3^-$, δ^2H-H_2O,

$\delta^{18}O-H_2O$ and $\delta^{37}Cl$ (The Cl isotopic samples were collected only in August 2016)), respectively. Samples for cation tests were acidified with HNO_3 to a pH less than 2. Unpretreated (no HNO_3 addition) samples were used for anion and isotope analyses.

Hydrochemical parameters were analyzed at the laboratory of the Groundwater Mineral Water and Environmental Monitoring Center at the Institute of Hydrogeology and Environmental Geology, Chinese Academy of Geological Sciences. The ions, including nitrate (NO_3^-), nitrite (NO_2^-), chloride (Cl^-) and ammonia (NH_4^+) etc., were measured by spectrophotometry (PerkinElmer Lambda 35, USA), and Mn was determined by using inductively coupled plasma-mass spectrometry (Agilent 7500ce ICP-MS, Tokyo, Japan).

The $\delta^{15}N-NO_3^-$ and $\delta^{18}O-NO_3^-$ values were determined by ion-exchange methods (Silva et al., 2000) with a Finnigan MAT 253 mass spectrometer combined with an online Flash Elemental Analyzer in the Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences. The $\delta^{18}O-H_2O$ and $\delta D-H_2O$ values were analyzed by a Finnigan MAT 253 mass spectrometer at the Institute of Hydrogeology and Environmental Geology, Chinese Academy of Geological Sciences. The ratios of isotopic Cl were determined using a thermal ionization mass spectrometer (Thermo Fisher Triton) based on the Cs_2Cl^+ ion method (Xiao et al., 1995) in the Salt Lake Analytical and Test Department, Qinghai Institute of Salt Lakes (ISL) of the Chinese Academy of Sciences. The analytical precision of the $\delta^{15}N-NO_3^-$, $\delta^{18}O-NO_3^-$, $\delta^{18}O-H_2O$ and $\delta D-H_2O$ values was ±0.2‰, ±0.25‰, ±0.2‰ and ±1‰, respectively. In addition, the precision of the analysis based on the standard ISL 354 NaCl mean value (±2σ) was 0.319058 ± 0.000011 (Xiao et al., 1995).

The stable isotope ratios for NO_3^-, H_2O and Cl^- isotopic composition are expressed in delta (δ) units and as a per mil (‰) notation relative to international standards:

$$\delta_{sample} = \left(\frac{R_{sample}}{R_{standard}} - 1 \right) \times 1000‰ \qquad (1)$$

where R_{sample} and $R_{standard}$ are the $^{15}N/^{14}N$ for $\delta^{15}N$, D/H for δD, $^{37}Cl/^{35}Cl$ for $\delta^{37}Cl$ and $^{18}O/^{16}O$ for $\delta^{18}O$. The isotopic values are reported relative to N_2 in atmospheric air (AIR), Vienna Canyon Diablo Troilite (V-CDT), ISL 354 NaCl and Vienna Standard Mean Ocean Water (VSMOW) for $\delta^{15}N$, $\delta^{37}Cl$, and δD and $\delta^{18}O$, respectively.

1.3. Bayesian isotopic mixing model

The proportion of nitrate source contributions was quantified using the Bayesian isotopic mixing model (Parnell et al., 2010), implemented with the "SIAR" (Stable Isotope Analysis in R) software package. The model can be expressed as follows:

$$x_{ij} = \sum_{k=1}^{k} p_k \left(s_{jk} + c_{jk} \right) + \varepsilon_{jk}$$

$$s_{jk} \sim N \left(\mu_{jk}, \omega_{jk}^2 \right)$$

$$c_{jk} \sim N \left(\lambda jk, \tau_{jk}^2 \right) \qquad (2)$$

$$\varepsilon_{jk} \sim N \left(0, \sigma_j^2 \right)$$

where X_{ij} is the isotope value j of the mixture i, in which i = 1, 2, 3, ..., I and j = 1, 2.

3, ..., J; S_{jk} is the source value k of isotope j ($k = 1, 2, 3, ..., K$) and is normally distributed with a mean value μ_{jk} and a standard deviation ω_{jk}; P_k is the proportion of source k, which needs to be estimated by the SIAR model; C_{jk} is the fractionation factor for isotope j of source k and is normally distributed with a mean value λ_{jk} and a standard deviation τ_{jk}; and ε_{ij} is the residual error representing the additional unquantified variation between individual mixtures and is normally distributed with a mean value of 0 and standard deviation σ_j. A detailed description of this model can be found in Parnell et al. (2010).

1.4. Multivariate data analysis

The one-way analysis of variance (ANOVA) was used to analyze the differences in ground-water NO_3^- concentration, $\delta^{15}N$ and $\delta^{18}O-NO_3^-$, and δD and $\delta^{18}O-H_2O$ values in different hydrogeological subregions and land use. ANOVA was performed using SPSS software (version 21.0; SPSS Inc., Chicago, IL, USA).

2. Results

2.1. Spatial and temporal variations of nitrogenous species

The NH_4^+ concentrations in groundwater and the river in different seasons were below the detection limit (BDL; detection limit = 0.04 mg/L). The variations of NO_2^- and NO_3^- in groundwater and river water in different seasons are illustrated in Table 1 and Fig. 2. The NO_2^- concentrations in groundwater and river samples ranged from BDL (detection limit = 0.002 mg/L) to 0.980 mg/L and from BDL to 0.410 mg/L, respectively. The mean value of NO_2^- in the groundwater was clearly lower than the drinking water threshold of the WHO (3 mg/L).

The NO_3^- concentrations in groundwater and the river ranged from 1.76 to 509.0 mg/L and from 7.80 to 49.5 mg/L, with the mean values of 104.2 and 21.7 mg/L, respectively. The mean value in groundwater was higher than the drinking water threshold of the WHO (50 mg/L). The NO_3^- concentration was significantly higher than the values of NH_4^+ and NO_2^-, so NO_3^- was the main nitrogenous species in the Hutuo River alluvial-pluvial fan. As shown in Fig. 2(2-1), the spatial variation of the NO_3^- concentration was significant in all the seasons. It was higher in the HVP region (178.7 mg/L) than in UPC (82.1 mg/L), CPF (71.0 mg/L) and the river (17.0 mg/L), and the concentration fluctuations were larger in the HVP region than in UPC, CPF and the river. This may be due to the groundwater table being lower in the HVP which make the NO_3^- concentrations vulnerable to the rain and human activity.

As a whole, the groundwater NO_3^- concentrations were higher in the dry season than in the wet season and the transition season because of dilution by rainfall, but significantly higher levels ($p < 0.05$) were only shown in the UPC based on one-way ANOVA. By contrast, the NO_3^- concentration in the river was higher in the wet season than the dry and
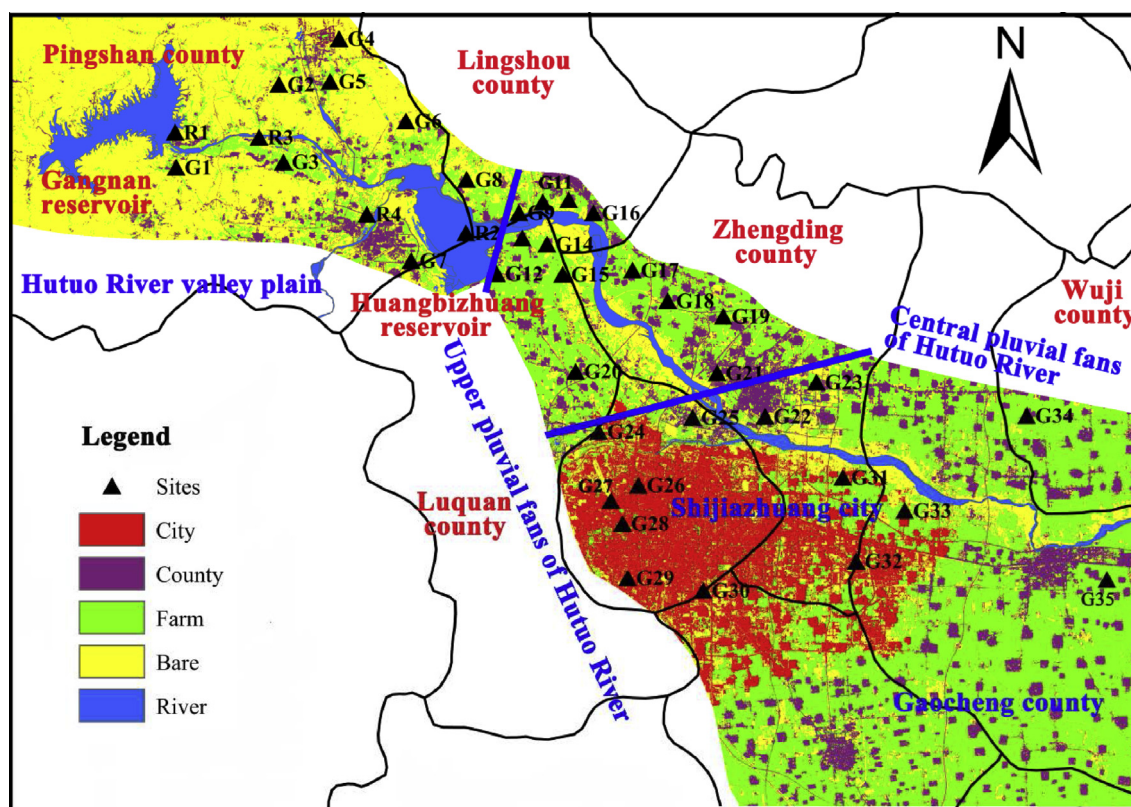

Fig. 1 — Land use and water quality monitor sites of Hutuo River alluvial-pluvial fan.

Table 1 – Summary of the NO_2^- values of groundwater and river in different season in the Hutuo River alluvial-pluvial fan.		Range (mg/L)	Mean (mg/L)	SD	Standard (mg/L)
Sampling time		Range (mg/L)	Mean (mg/L)	SD	Standard (mg/L)
Dry season	Groundwater ($n = 30$)	0.002–0.021	0.005	0.005	3.0
	River ($n = 2$)	0.002–0.002	0.002	0	
Transition season	Groundwater ($n = 34$)	0.002–0.980	0.031	0.168	
	River ($n = 4$)	0.002–0.128	0.009	0.012	
Wet season 2016	Groundwater ($n = 31$)	0.002–0.920	0.043	0.166	
	River ($n = 4$)	0.002–0.128	0.035	0.062	
Wet season 2017	Groundwater ($n = 32$)	0.002–0.048	0.013	0.016	
	River ($n = 4$)	0.047–0.410	0.157	0.171	

n = Number of samples; SD = Standard deviation; Standard is the threshold of drinking water by WHO (WHO, 2011).

transition season, which is mainly due to runoff carrying large amounts of pollutants from villages and farmland into rivers.

As shown in Fig. 2(2-2), the average concentrations of groundwater nitrate in the county (116.5 mg/L), agriculture (95.3 mg/L) and urban areas (86.1 mg/L) were significantly higher than in the river (21.7 mg/L). However, the different land use types had no significant effect on groundwater nitrate concentrations. It is worth noting that the highest NO_3^- concentrations in dry season (509 mg/L), wet season (495 mg/L) and transition season (465 mg/L) were found in the county regions, and the mean NO_3^- concentrations in county regions was higher than the drinking water threshold of the WHO (50 mg/L). Therefore, it poses a serious threat to the safety of drinking water for the local population.

2.2. Spatial and temporal variations of stable isotopes

2.2.1. Isotopic compositions and variations in groundwater, river and rainfall

The δD and $δ^{18}O$ values of groundwater and river water are summarized in Table 2. The mean values of the δD and $δ^{18}O$ were −58.9‰ and −8.09‰, −57.2‰ and −7.75‰ for groundwater and the river, respectively. The ranges of the δD and $δ^{18}O$ values of rainfall were from −100.0‰ to −38.1‰ and from −14.6‰ to −6.0‰, respectively, with a mean value of −63.1‰ and −9.4‰, respectively. As shown in Table 2, the

groundwater δD values were higher in the HVP region than in the UPC and CPF regions, and the mean was significantly higher in the HVP (−56.0‰) than in the UPC (−59.4‰) and CPF (−60.0‰) in the dry season (January, 2015). The groundwater $δ^{18}O$ values were higher in the HVP than in the UPC and CPF, and the $δ^{18}O$ value was significantly higher in the HVP (−7.66‰) than in the CPF (−8.19‰) in the wet season of 2016. For the river, the δD and $δ^{18}O$ values were higher than the groundwater in the dry and transition seasons, but the δD and $δ^{18}O$ values were lower than the groundwater in the wet season of 2016. There was no significant temporal variation of groundwater δD concentration in the three hydrogeological sub-regions (HVP, UPC and CPF). However, the groundwater $δ^{18}O$ value in the wet season of 2017 was significantly higher than in the dry season, transitional season and wet season of 2016. For the river, the $δ^{18}O$ value in the wet season was significantly higher than in the dry and transition season.

2.2.2. Isotopic compositions and variations in NO_3^-

The $δ^{15}N–NO_3^-$ values in the groundwater of the Hutuo River alluvial-pluvial fan were 1.86‰–16.03‰, with an average of 8.14‰, and the range in the river was 5.61‰–14.17‰, with an average of 10.29‰. As shown in Fig. 3, the $δ^{15}N–NO_3^-$ values of the groundwater did not show significant differences in the three hydrogeological units. The $δ^{15}N–NO_3^-$ value in river water was higher than that in the groundwater of the HVP and
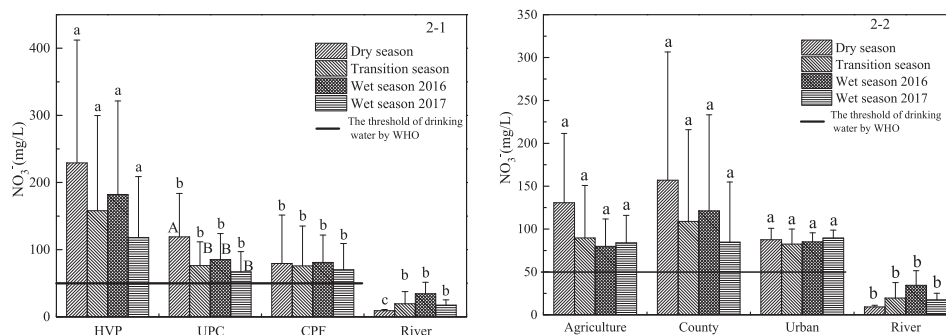

Fig. 2 – The spatial and temporal variations of the NO_3^- concentration in the Hutuo River alluvial-pluvial fan. The lines of the SD followed by different lowercase letters for different hydrogeological subregions (2-1) and land use (2-2) in same season designate significantly spatial variation at $p < 0.05$ level by one-way ANOVA; The lines of the SD followed by different capital letters for same hydrogeological subregions and riverin different season designate significantly temporal variation at $p < 0.05$ level by one-way ANOVA; The lines of the SD not followed by letters or different letters designate not significantly temporal and spatial variation.

Table 2 – Summary of the δ D‰-H$_2$O and δ^{18}O‰-H$_2$O values of groundwater and river in different season in the Hutuo River alluvial-pluvial fan.

Sampling time		δ D‰			δ^{18}O‰		
		Range	Mean	SD	Range	Mean	SD
Dry season	HVP (n = 8)	−60−−52^A	−56.0^a	2.39	−8.0−−6.8^A	−7.54^a	0.37
	UPC (n = 10)	−63−−57^A	−59.4^b	2.01	−8.6−−7.4^A	−7.89^a	0.35
	CPF (n = 10)	−65−−53^A	−60.0^b	3.80	−8.7−−6.7^A	−7.98^a	0.66
	River (n = 2)	−54−−50^A	−52.0^a	2.83	−6.8−−6.0^A	−6.40^b	0.57
Transition season	HVP (n = 8)	−60−−56^A	−57.6^{ab}	1.41	−8.2−−7.5^A	−7.81^a	0.24
	UPC (n = 14)	−63−−52^A	−58.1^a	2.91	−8.6−−6.7^A	−7.72^a	0.52
	CPF (n = 12)	−64−−50^A	−58.9^a	4.31	−8.8−−6.8^A	−7.97^a	0.66
	River (n = 4)	−62−−48^A	−53.8^b	5.91	−8.5−−6.2^A	−7.03^b	1.01
Wet season 2016	HVP (n = 8)	−60−−55^A	−56.5^a	1.77	−8.1−−7.3^A	−7.66^a	0.26
	UPC (n = 13)	−65−−53^A	−58.6^{ab}	3.71	−8.9−−6.7^A	−7.79^{ac}	0.64
	CPF (n = 10)	−65−−57^A	−60.7^b	3.09	−8.9− 0.7.5^A	−8.19^{bc}	0.51
	River (n = 4)	−66−−57^B	−62.3^b	4.11	−9.1−−7.7^B	−8.50^b	0.63
Wet season 2017	HVP (n = 8)	−70−−52^A	−58.6^a	5.63	−10.47−−7.8^B	−8.79^{ab}	0.82
	UPC (n = 14)	−67−−52^A	−59.0^a	5.62	−9.49−−7.7^B	−8.55^a	0.64
	CPF (n = 10)	−69−−56^A	−62.1^a	3.72	−9.66−−8.6^B	−9.07^b	0.34
	River (n = 4)	−63−−52^{AB}	−58.1^a	4.73	−8.94−−7.7^B	−8.41^{ab}	0.59
Total	GW (n = 125)	−70−−50	−58.9	3.85	−10.47−−6.7	−8.09	0.69
	River (n = 14)	−66−−48	−57.2	5.80	−9.1−−6.0	−7.75	1.09

GW: Groundwater; n: Number of samples; SD: Standard deviation.
The values followed by different lowercase letters within a row for different hydrogeological subregions and river in same season designate significantly spatial variation at $p < 0.05$ level by one-way ANOVA.
The values followed by different capital letters within a row for same hydrogeological subregions and river in different season designate significantly temporal variation at $p < 0.05$ level by one-way ANOVA.

UPF region. During the wet season, the δ^{15}N−NO$_3^-$ value in the groundwater of the HVP and UPF region was higher than that in the groundwater of the CPF. The range of δ^{18}O−NO$_3^-$ values in groundwater of the Hutuo River alluvial-pluvial fan was −1.91‰ to 25.3‰, with a mean of 6.48‰, and in surface water it was 6.70‰−24.74‰, with an average of 13.20‰. Similar to the statistical results of δ^{15}N−NO$_3^-$, the δ^{18}O−NO$_3^-$ values in groundwater showed no significant differences in the three hydrogeological units. The δ^{18}O−NO$_3^-$ values in surface water were higher than that in the groundwater of the UPF and CPF (Fig. 3). Due to the influence of precipitation, the groundwater δ^{18}O−NO$_3^-$ during the dry season was significantly higher than during the wet season and the transitional season. The δ^{18}O−NO$_3^-$ value in river water had no significant seasonal differences.

2.2.3. Isotopic compositions and variations in Cl$^-$

The δ^{37}Cl values of groundwater and river water are summarized in Table 3. The ranges of the δ^{37}Cl value were from 0.78‰ to 2.38‰ and from 0.73‰ to 1.50‰ for groundwater and the river, respectively. As shown in Table 3, the mean values of the δ^{37}Cl were higher in the UPC region (1.73‰) than in the HVP (1.41‰), CPF (1.37‰) and river (1.17‰) regions. However, the δ^{37}Cl values in groundwater of the three hydrogeological units and river did not show significant differences.

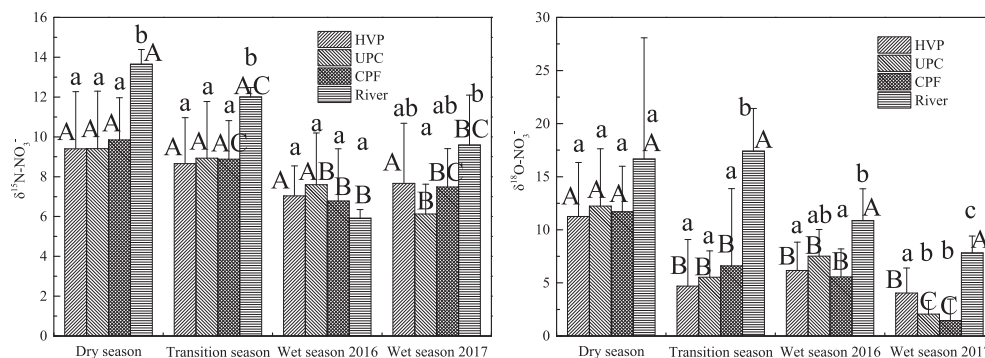**Fig. 3 – The spatial and temporal variations of the δ^{15}N−NO$_3^-$ and δ^{18}O−NO$_3^-$ value in the Hutuo River alluvial-pluvial fan. The lines of the SD followed by different lowercase letters for different hydrogeological subregions and riverin same season designate significantly spatial variation at $p < 0.05$ level by one-way ANOVA; The lines of the SD followed by different capital letters for same hydrogeological subregions and riverin different season designate significantly temporal variation at $p < 0.05$ level by one-way ANOVA; The lines of the SD not followed by letters or different letters designate not significantly temporal and spatial variation.**

3. Discussion

3.1. Groundwater origin and recharge

Stable water isotopes (δD and $\delta^{18}O$) can provide a fingerprint for the origin of water and hydrological processes (Pastén-Zapata et al., 2014; Ji et al., 2017), and can sometimes provide valuable information about likely nitrate pollution sources (Brooks et al., 2012; Ji et al., 2017). In addition, the δD and $\delta^{18}O$ values of the river and groundwater can be used to clarify their conversion relationship (Zhang et al., 2014), which is important for further analysis of the nitrate sources. We compare groundwater and river water with global and regional (Hutuo river alluvial-pluvial fan region) meteoric water lines (GMWL and LMWL, respectively) in Fig. 4. The global meteoric water lines, defined as $\delta D = 8\ \delta^{18}O + 10$. The regional meteoric water lines were obtained from local rainfall samples ($\delta D = 7.25\ \delta^{18}O + 4.85$).

As shown in Fig. 4, the compositions of the δD and $\delta^{18}O$ in river water and groundwater samples were close to the GMWL and LMWL, suggesting that precipitation was the primary recharge source of river and groundwater in the study regions. Fig. 4 indicated that the most of the points fall below the GMWL and LMWL, and the slopes of the regression lines for the river (5.00) and groundwater (the slopes were 5.72, 6.01, 6.00, for the dry season, transition season and wet season 2016, respectively), were lower than that of the GMWL (8) and LMWL (7.25), which may due to the rain having undergone intense evaporation during the recharge process. It is worth noting that the slope of the regression line in wet season 2017 was higher than in wet season 2016, perhaps because the rainfall in wet season 2016 (August) was not subjected to intense evaporation, and had yet to seep into the aquifer. By wet season 2017 (September), after three months of infiltration it had entered the aquifer, and the slope of the regression lines in the two months therefore showed significant differences.

The δD and $\delta^{18}O$ values in the river were higher than in the groundwater (Table 2), indicating that the river had undergone more intense evaporation than the groundwater. On the other hand, there was a strong hydraulic connection between the river and the groundwater, indicated by their similar regression line slopes. In the study region, the conversion relationship between river and groundwater was that the river
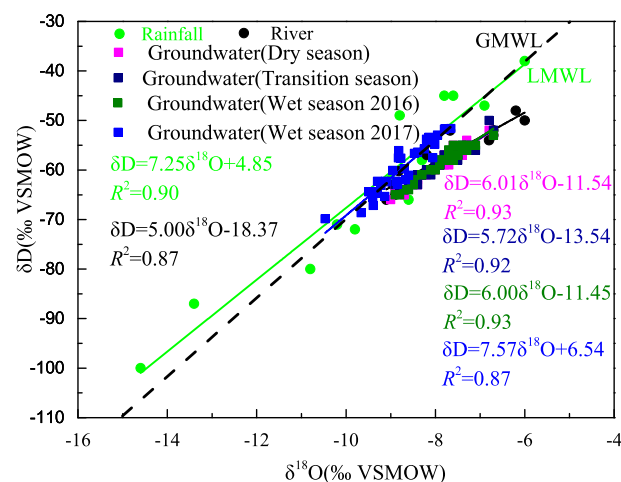

Fig. 4 – Relationship between δD and $\delta^{18}O$ with respect to Global Meteoric Water Line(GMWL) and Regional Meteoric Water Line(LMWL) in different season in the Hutuo River alluvial-pluvial fan.

recharged the groundwater, which due to the water table being deeper (the water tables were 2—21 m, 20—35 m and 25—60 m in HVP, UPF and CPF regions, respectively). Therefore, the pollutants in the river would increase the nitrogen concentration of the groundwater.

3.2. Identification of sources of nitrate

3.2.1. Identification of nitrate sources using $\delta^{15}N-NO_3^-$ and $\delta^{18}O-NO_3^-$

Nitrate in the water environment comes from various pollution sources, such as precipitation, fertilizer, soil nitrogen, sewage and manure (Xue et al., 2009; Zhang et al., 2018). In this study, we identified the nitrate sources in the river and groundwater of the Hutuo River alluvial-pluvial fan by using $\delta^{15}N-NO_3^-$ and $\delta^{18}O-NO_3^-$ isotopes. Fig. 5 shows that, in general, the $\delta^{18}O-NO_3^-$ value in the rainy season was more concentrated than that in the dry season, probably due to the strong evaporation in the dry season, which caused the fractional distillation of oxygen isotopes (Yue et al., 2014). In different seasons and different hydrogeological units, most of the water samples did not fall within the range of potential pollution sources. Therefore, the nitrates in the study area may have multiple sources, such as nitrate fertilizer, soil N, sewage and manure.

In the groundwater sampling sites, except for $\delta^{18}O$ in September 2017, the average $\delta^{15}N$ and $\delta^{18}O$ values of the three hydrogeological units did not show significant variation (Fig. 3). Therefore, we suggest that the nitrate may all come from the same pollution sources. According to previous studies, the $\delta^{15}N-NO_3^-$ and $\delta^{18}O-NO_3^-$ values for sewage and manure, soil N and ammonia fertilizers from +4‰ to +25‰, −3‰ to +9‰, −4‰ to +6‰ and −10‰ to +10‰, −10‰ to +10‰, −10‰ to +10‰, respectively (Xue et al., 2009; Nestler et al., 2011; Jin et al., 2015; Kim et al., 2015). The $\delta^{15}N-NO_3^-$ and $\delta^{18}O-NO_3^-$ values in most of the groundwater samples in this

Table 3 – Summary of the δ 37Cl‰ values of groundwater and river in the Hutuo River alluvial-pluvial fan.

Sampling time		$\delta^{37}Cl$‰		
		Range	Mean	SD
Wet season 2016	HVP ($n = 7$)	0.78–2.01	1.41[a]	0.50
	UPC ($n = 11$)	1.04–2.38	1.73[a]	0.42
	CPF ($n = 9$)	0.86–2.07	1.37[a]	0.36
	River ($n = 3$)	0.73–1.50	1.17[a]	0.40

n: Number of samples; SD: Standard deviation.
The values followed by different lowercase letters within a row for different hydrogeological subregions and river designate significantly spatial variation at $p < 0.05$ level by one-way ANOVA.
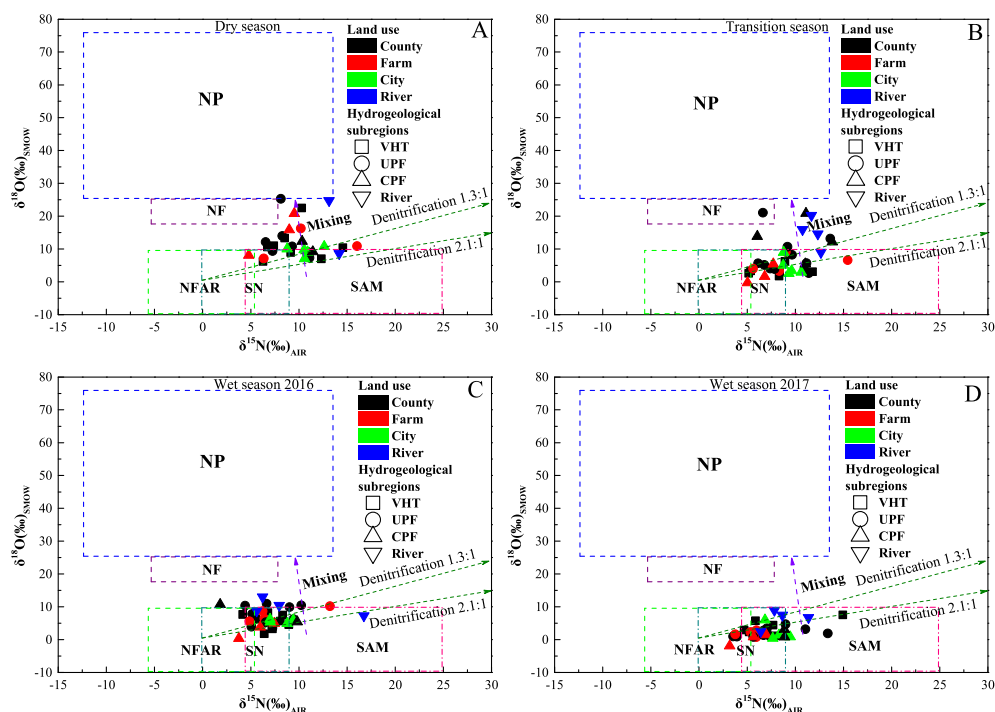
Fig. 5 — $\delta^{15}N-NO_3^-$ versus $\delta^{18}O-NO_3^-$ value in different seasons in three hydrogeological subregions and River from the Hutuo River alluvial-pluvial fan. SAM: sewage and manure; SN: soil nitrogen; NF: NO_3^- fertilizer; NP: NO_3^- in precipitation; NFAR: NH_4^+ in fertilizer and rain.

study area (60%, 76%, 87% and 100% of water samples in dry season and transition season, wet season in 2016, and wet season in 2017, respectively) were within the range of the above three potential pollution sources. As a result, the nitrate contamination of groundwater in the Hutuo River alluvial-pluvial fan area may result from a mixture of domestic sewage and manure, soil nitrogen and ammonia fertilizers.

The main land use type in the Hutuo River alluvial-pluvial fan region is farmland (38.62%), and the use of nitrogen fertilizers may also be a source of groundwater contamination by nitrate. Previous studies have found that if nitrate in the water was derived from nitrate fertilizers, the $\delta^{18}O$ values were between +17‰ and +25‰ (Fang et al., 2012; Liu et al., 2006). In our study area, 20% and 9% of the water samples in January 2015 and October 2015 were probably contaminated by nitrate fertilizers.

In the Hutuo River alluvial-pluvial fan region, the groundwater $\delta^{15}N-NO_3^-$ and $\delta^{18}O-NO_3^-$ values were not within the range of published nitrate values for precipitation ($\delta^{15}N-NO_3^-$: −13‰ to +13‰, $\delta^{18}O-NO_3^-$: +25‰ to +75‰) (Saccon et al., 2013; Xue et al., 2013). During the study period, we collected 12 precipitation samples. The average NO_3^- concentration of rainfall was 8.94 mg/L, which had relatively little impact on groundwater nitrate contamination. As a result, we can be confident that precipitation was not the main source of nitrate in the groundwater.

Only two river water samples (Gangnan reservoir and Huangbizhuang reservoir) were collected in dry season, and in both cases the nitrate concentrations were low (7.80 and

10.48 mg/L). The $\delta^{15}N-NO_3^-$ and $\delta^{18}O-NO_3^-$ values of Gangnan reservoir were +13.17‰ and +24.74‰, respectively, and not within the theoretical value ranges of the sewage and manure, soil N and ammonia fertilizers. In addition, the Gangnan reservoir is in the water conservation region of Shijiazhuang city, and there are protective walls around it; thus, it is less affected by human activities. Therefore, the NO_3^- in Gangnan reservoir may mainly come from rainfall and nitrate fertilizer. The $\delta^{15}N-NO_3^-$ and $\delta^{18}O-NO_3^-$ values of Huangbizhuang reservoir were +14.17‰ and +8.60‰, respectively, which was within the range of sewage and manure. During the research, it was found that the villages surrounding the reservoir discharged sewage directly into it, while garbage and animal manure were piled up everywhere and entered the Huangbizhuang reservoir directly as a result of the scouring effect of the runoff in the rainy season. Thus, the nitrate in the Huangbizhuang reservoir mainly came from sewage and manure. In the transition season, the $\delta^{15}N-NO_3^-$ and $\delta^{18}O-NO_3^-$ values of the four water samples were in the range of mixing values for sewage, manure and nitrate fertilizer, therefore resulting from a mixture of these nitrate sources. In the wet season in 2016 and 2017, the $\delta^{15}N-NO_3^-$ and $\delta^{18}O-NO_3^-$ values of the four water samples were within the ranges of the sewage, manure and soil N, indicating that the nitrate was probably a mixture from these three contamination sources.

3.2.2. Identification of sources of nitrate by using $\delta^{37}Cl$

As shown in Fig. 6, there was a positive relationship between Cl^- and NO_3^- in different seasons ($p < 0.001$), which indicated

that the Cl^- and NO_3^- have the same pollution sources in the region. Previous research showed that the $\delta^{37}Cl$ range of sewage was between +0.0‰ and +1.0‰ (Lang et al., 2008; Fang, 2014), and the $\delta^{37}Cl$ of rainfall was positive in Hebei province, China (Fang, 2014). In our study region, rainfall may not be the primary contamination source of the Cl^-, due to the concentration of Cl^- in rainfall being lower (mean value is 2.28 mg/L, $n = 12$). A scatter plot of $\delta^{37}Cl$ vs. NO_3^-/Cl was produced, based on the characteristic $\delta^{37}Cl$ and NO_3^-/Cl values for different pollution sources. As shown in Fig. 7, the Cl^- of groundwater mainly originated from the mixing of sewage, manure and fertilizer, further confirming this as the main groundwater nitrate source for the Hutuo River alluvial-pluvial fan.

3.3. Effects of land use types on nitrate sources

Land use type is a direct reflection of human activity and is closely related to groundwater pollution (Lockhart et al., 2013). Previous researchers found that land use types had a significant effect on groundwater nitrate levels (Zhang et al.,2015a). In the Hutuo River alluvial-pluvial fan area, due to the fact that the construction of the sewage network and garbage treatment facilities in rural areas was backward, and villagers had poor awareness of environmental protection, the groundwater pollution was very serious (The mean concentration was 116.5 mg/L in county areas and in excess of the drinking water threshold of the WHO (50 mg/L)). During the whole investigation and sampling period, we recorded that more than 20 villages in the HVP region did not have a sewage network, and their domestic sewage was directly discharged into the Hutuo River. In addition, large numbers of livestock and poultry were kept in the nearby villages. As shown in Fig. 5, the $\delta^{15}N$ and $\delta^{18}O$ values in county areas are relatively dispersed, and they are mainly located above the range of values of the domestic sewage and manure. Therefore, the main nitrate sources of groundwater in this region were probably domestic sewage and manure.

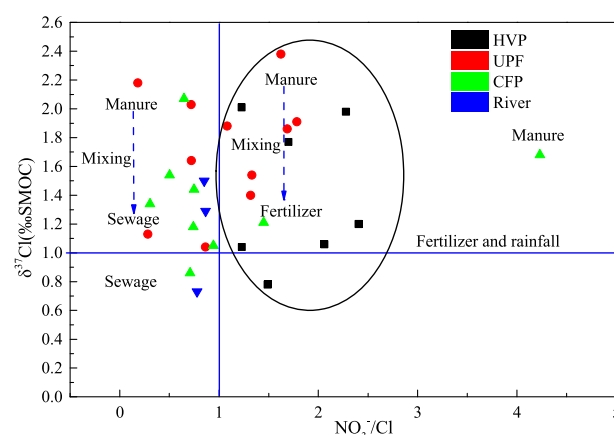It is worth noting that the mean concentration of groundwater nitrate in agricultural areas was 95.3 mg/L, above the

Fig. 7 – The combined biplot of $\delta^{37}Cl$ and NO_3^-/Cl^- in wet season 2016 from the Hutuo River alluvial-pluvial fan.

threshold for drinking water set by WHO (50 mg/L). As a result, groundwater in agricultural areas is also heavily contaminated with nitrates. As shown in Fig. 5, the $\delta^{15}N$ and $\delta^{18}O$ values in agricultural area are also relatively dispersed; thus, it can be inferred that nitrate in this area may come from mixed sources. In this study, the sampling sites in the agricultural area were close to the village and were located within 5 km of the Hutuo River. Therefore, the sources of groundwater nitrate in agricultural areas may be agricultural fertilizers, domestic sewage and manure.

In urban areas, the mean concentration of groundwater nitrate was 86.1 mg/L, and it was in excess of the threshold for drinking water set by WHO (50 mg/L). As shown in Fig. 5, the $\delta^{15}N$ and $\delta^{18}O$ values in urban areas are more concentrated, and mainly within the range of domestic sewage and manure. Due to the lack of livestock or poultry farming in urban areas, the main source of nitrate was domestic sewage. In addition, fertilizer may also be another important source of groundwater nitrate in urban areas, as the daily maintenance of green belts and park lawns requires fertilization.

3.4. Identification of transformation of nitrate

3.4.1. Nitrification
Theoretically, the $\delta^{18}O-NO_3^-$ values of nitrate produced by microbial nitrification could be calculated, because approximately one-third of the oxygen in NO_3^- should be derived from oxygen in the air, while two-thirds should be derived from ambient water at the site of nitrate formation (Li et al., 2010; Zhang et al., 2018). As a result, the $\delta^{18}O-NO_3^-$ values derived from microbial nitrification can be calculated by measuring the groundwater $\delta^{18}O-H_2O$ values and assuming that the $\delta^{18}O-O_2$ is from atmospheric O_2 (+23.5‰). As shown in Fig. 8, in the dry season, the $\delta^{18}O-NO_3^-$ values were all higher than the theoretical values, which may have resulted from higher $\delta^{18}O-H_2O$ values due to the evaporation of soil water, or by bacterial respiration generating higher$\delta^{18}O$ values in the O_2 (Kendall et al., 2008; Yue et al., 2014). The evaporation of soil water in the alluvial-pluvial fan region is very strong, which is due to the sediment being mainly composed of coarse-grained conglomerates and sands. Compared with the dry season, the
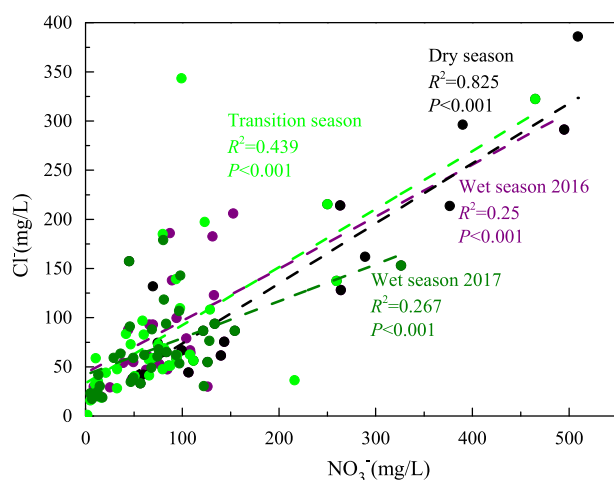
Fig. 6 – Relationship between the Cl^- and NO_3^- concentration in different seasons from the Hutuo River alluvial-pluvial fan.
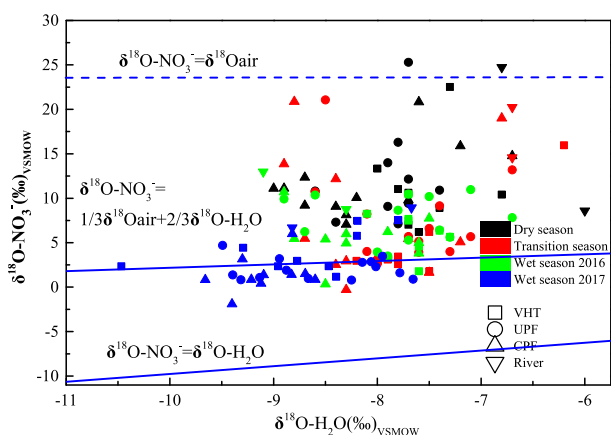
Fig. 8 – $\delta^{18}O$–H_2O versus $\delta^{18}O$–NO_3^- value in different seasons in three hydrogeological subregions and River from the Hutuo River alluvial-pluvial fan.

$\delta^{18}O$–NO_3^- values of water samples in the wet and wet–dry transition season were closer to theoretical values due to the lower evaporation of soil water. In our study region, the $\delta^{18}O$–NO_3^- values of 99.3% of water samples were lower than those in rainwater (+25‰ to +75‰) and 94.3% of water samples had values lower than in the fertilizers (+17‰ to +25‰); in addition, the NH_4^+ concentration in all the groundwater samples was lower than the detection limit (0.04 mg/L). Therefore, nitrification could be the most important nitrogen migration and transformation process in this region. In recent years, groundwater in the area has been heavily exploited, and two large reservoirs have been built upstream, which blocked the groundwater recharge sources. This, in turn, has led to a continuous decline in the groundwater level and created an artificially oxidizing environment, so that the vadose zone was also conducive to nitrification.

3.4.2.   Denitrification

Another process that caused changes in the nitrate isotope value was microbial denitrification. Denitrification is prone to occur when there is sufficient organic carbon and the oxygen content in groundwater is very low (Xue et al., 2009). In this study area, denitrification may not be a major process, as the aquifer system had an oxidizing environment (the average DO in groundwater was 6.82 mg/L and the average Mn concentration was below 8 µg/L). Research has shown that microbial denitrification will increase the $\delta^{15}N$–NO_3^- and $\delta^{18}O$–NO_3^- values of water samples, reduce the nitrate concentration and produce $\delta^{15}N$–NO_3^- and $\delta^{18}O$–NO_3^- ratios of 1.3–2.1:1 (Panno et al., 2006). As shown in Fig. 5, most water samples were not within these ratios; only five in the dry season, nine in the transition season, nine in wet season 2016, and six in wet season 2017 were within the ratios. For these sites, the concentration of DO was higher (4.87–8.88 mg/L in the dry season, 3.34–7.85 mg/L in transition season, 5.67–10.01 mg/L in wet season 2016 and 2.65–9.16 mg/L in wet season 2017) which was not within the appropriate denitrification oxygen level (<2.0 mg/L) (Zhang et al., 2018), while the nitrate concentration was higher (103.5–390 mg/L in dry season, 50.6–128.6 mg/L in transition season, 44.11–495 mg/L in wet season 2016 and

36.09–154.31 mg/L in wet season 2017). As a result, these sites did not show denitrification, or had only slight denitrification. In summary, denitrification did not significantly affect the isotopic composition of nitrate in the Hutuo River alluvial-pluvial fan region.

3.5.   Estimates of proportional contributions of the dominant nitrate sources

After determining the potential pollution sources and transformation of NO_3^- in the Hutuo River alluvial-pluvial fan by both hydrochemical and multi-isotope approaches, SIAR, based on the Bayesian Isotope mixing model (Eq. (2)), was applied in order to evaluate the proportional contributions of the possible nitrate source. We collected the five potential nitrate sources values from the literature (reviewed in Zhang et al., 2015b). We assumed the fractionation factor $C_{jk} = 0$ in Eq. (2) due to denitrification not having a great impact on the isotope composition. The results of the SIAR model showed high seasonal and spatial variation in the contributions of five potential sources of nitrate (Fig. 9).

3.5.1.   Estimates of proportional contributions of nitrate sources in different hydrogeological units

As shown in Fig. 9, the main groundwater nitrate pollution sources in different hydrogeological units of the Hutuo River alluvial-pluvial fan were domestic sewage and manure. In the dry season, domestic sewage and manure accounted for a large proportion, ranging from 55.9% to 61.0%. In the rainy-dry transitional season and rainy season, due to the impact of precipitation, the proportion of domestic sewage and manure decreased to 50.3%–60.4% (transition season), 42.7%–47.6% (wet season 2016) and 45.9%–46.7% (wet season 2017), respectively. In different seasons, the contribution of NO_3^- in rainwater to groundwater nitrate pollution was very low, at 2.9%–4.2% in the dry season, 1.6%–2.9% in the transitional season, and 1.1%–2.9% in wet season 2016 and 2017, respectively. This was mainly due to the low NO_3^- content in rainwater in this region. The contribution rates of NH_4^+ (NFAR) and soil nitrogen (SN) in NH_4^+ fertilizer and rainwater showed the following trend: wet season 2016 and 2017 (17.1%–21.4% and 23.6%–26.4%) > transitional season (13.9%–16.1% and 18.8%–22.6%) > dry season (10.7%–13.2% and 16.8%–18.2%) which was due to the erosion of residual fertilizer and soil nitrogen in the aerated zone by rainfall. The contribution rate of NO_3^- fertilizer to groundwater nitrate pollution did not change significantly in different seasons; it was 8.5%–9.6% in the dry season, 5.2%–8.2% in the transitional season, and 3.8%–8.7% in the wet season 2016 and 2017.

The contribution rate of nitrate pollution sources in the river showed that NO_3^- in rainwater contributed the least, with a value of 17.7% in the dry season (Only two reservoir samples (Gangnan reservoir and Huangbizhuang reservoir) were collected, and these two reservoirs are the surface water sources of Shijiazhuang city, with relatively good pollution protection measures, less impact from human activities, and the recharge source is mainly rainwater. Therefore, for the two samples, the contribution rate of NO_3^- in rainwater is relatively high), 8.9% in the rainy-dry transitional season, 4.56% in the wet season 2016 and 6.4% in the wet season 2017,
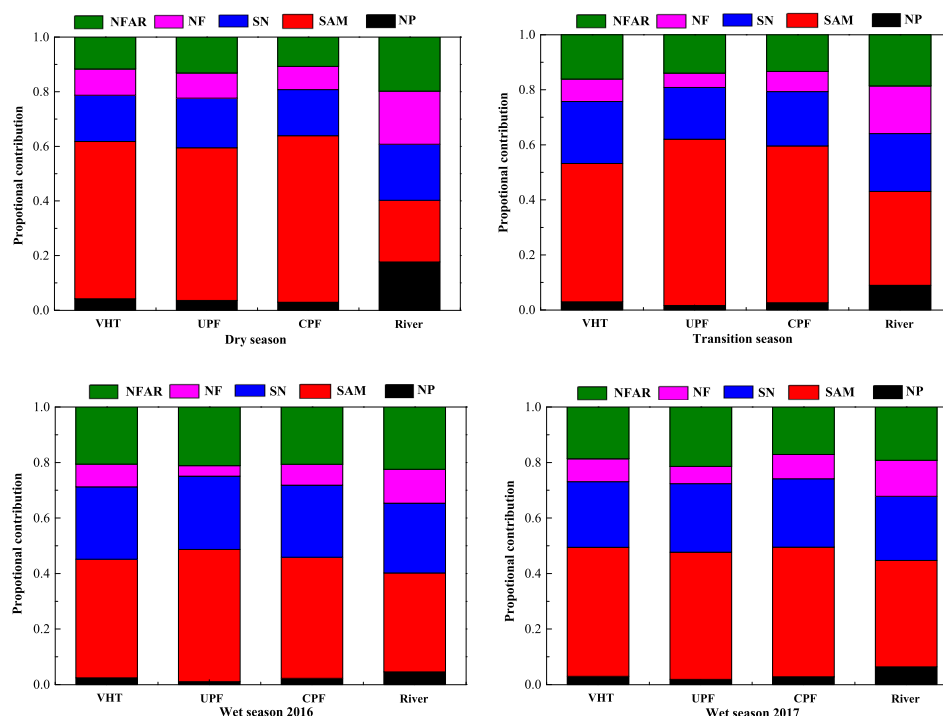
Fig. 9 – **Proportional contribution of five potential nitrate sources in groundwater and River in different seasons from the Hutuo River alluvial-pluvial fan. SAM: sewage and manure; SN: soil nitrogen; NF: NO_3^- fertilizer; NP: NO_3^- in precipitation; NFAR: NH_4^+ in fertilizer and rain.**

respectively, while it was also higher than the contribution rate to groundwater of 1.1%–4.2%. The contribution rate of domestic sewage and manure was the opposite to that of groundwater, and showed the trend of wet season (35.6% in wet season 2016 and 38.4% in wet season 2017) > transitional season (34.1%) > dry season (22.6%). This phenomenon is mainly due to the fact that domestic sewage and manure do not easily enter the river water in the dry season. However, in the rainy season, under the erosive effect of rainstorm runoff, the manure that has accumulated in the villages around the Hutuo River and has been applied to the farmland can easily be washed into the rivers and reservoirs. The contribution rate of ammonia fertilizer and ammonia in rainwater (NFAR) and soil nitrogen (SN) to nitrate in river water did not show much seasonal change, but it did show that there was a higher contribution in the wet season than the dry season and the transitional season, namely, accounting for 22.5% and 19.2% for wet season 2016, 25.2% and 23.0% for wet season 2017, 18.6% and 21.0% for transitional season, 19.8% and 20.5% for dry season. The contribution rate of nitrate fertilizer to river nitrate pollution did not change significantly in different seasons, namely 19.5% in the dry season, 17.3% in the rainy-dry transitional period, and 12.2% in the wet season of 2016 and 13.0% in the wet season of 2017.

3.5.2. Estimates of proportional contributions of nitrate sources in different land use

As shown in Fig. 10, the contribution ratio of different pollution sources to groundwater nitrate showed similar results in county, urban and agriculture areas; that is, the main sources of groundwater nitrate in different seasons are domestic

sewage and manure, followed by soil nitrogen, ammonia fertilizer, nitrate fertilizer and rainwater. The contribution rate of domestic sewage and manure to groundwater nitrate was the highest in rural areas, reaching 50.4%–66.0%, followed by 41.8%–49.5% in urban areas and 35.5%–41.7% in agriculture areas. Due to the diluting effect of rainfall, the contribution rate of domestic sewage was the lowest in the wet season and the highest in the dry season. The contribution rate of rainwater to groundwater nitrate in county areas (0.8%–2.9%),
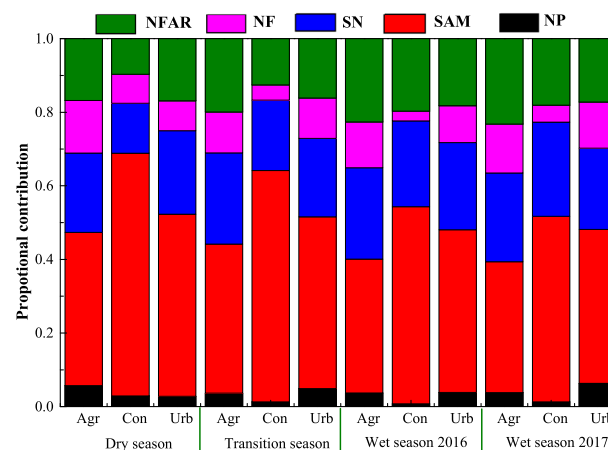

Fig. 10 – **Proportional contribution of five potential nitrate sources in different land use in different seasons from the Hutuo River alluvial-pluvial fan. Note: SAM: sewage and manure; SN: soil nitrogen; NF: NO_3^- fertilizer; NP: NO_3^- in precipitation; NFAR: NH_4^+ in fertilizer and rain.**

urban areas (2.8%–6.3%) and agriculture areas (3.7%–5.7%) was low and did not show significant seasonal variations.

The contribution rate of soil nitrogen and ammonia fertilizer to groundwater nitrate was the greatest in the rainy season and the smallest in the dry season (Fig. 10). The contribution rate of soil nitrogen and ammonia fertilizer to groundwater nitrate in county, urban and agriculture areas was 13.6%–25.6% and 9.7%–19.7%, 21.3%–23.7% and 16.2%–18.2%, 21.5%–24.8% and 16.8%–23.2%, respectively. The contribution of ammonia fertilizer to the groundwater nitrate in agriculture areas was higher than that in county and urban areas.

The contribution rate of nitrate fertilizer to groundwater nitrate did not show a significant seasonal change. Similar to ammonia fertilizer, the contribution rate of nitrate fertilizer to groundwater nitrate in the agriculture area was higher (11.1%–14.3%) than in county areas (2.7%-7.8%) and urban areas (8.1%–12.5%). The contribution rate of nitrate fertilizer to groundwater nitrate in urban areas was higher than in rural areas, which may be related to the green belt and park lawn fertilization in urban areas.

3.6.   *Management implication*

Nitrate pollution in water has become an environmental problem of widespread concern (Xue et al., 2009; Zhang et al., 2018). Our study indicated that the pollution sources of NO_3^- were mainly domestic sewage and manure for groundwater and river water in different seasons in the Hutuo River alluvial-pluvial fan region of north China. These results could provide technical support for the governmental agencies to implement targeted regional strategies for the prevention and control of water contamination by nitrates. The most important control measure would be stopping the random discharge and disposal of sewage and manure. To facilitate this, local government could build sewage pipelines and treatment plants in villages for collecting and processing domestic waste and use waste storage tanks for collecting and disposing of the manure before application. If domestic sewage were controlled, nitrate pollution could be reduced by about 50% and 30% for groundwater and river water, respectively.

The other important nitrate source was fertilizers (The mean contribution of fertilizer (i.e., $NH_4^+ + NO_3^-$ fertilizer) to groundwater nitrate accounted for 20.9%–30.1%, 19.1%–24.3% and 19.2%–22.8% for wet season, wet-dry transition season and dry season, respectively, and to surface water accounted for 36.1%, 36.9% and 39.3% for wet season, wet-dry transition season and dry season, respectively). Therefore, the state ministries and research institutions should promote fertilizer application based on soil testing, timed according to crop characteristics and nutrient demand, in order to improve the efficiency of nitrogen use. In addition, in the Hutuo River alluvial-pluvial fan region, nitrification could be the most important nitrogen migration and transformation process, and excessive groundwater exploitation is a factor inducing nitrate pollution. Thus, local government should develop strict laws to prohibit over-exploitation of groundwater and enforce groundwater recharge programs, such as water-saving irrigation technology and rainwater recycling technology, which could raise groundwater levels, change the groundwater environment, and then reduce nitrate pollution.

4.   Conclusions

Spatial and seasonal variations of sources and their proportional contribution to nitrate in the Hutuo River alluvial-pluvial fan region of north China were evaluated using a multi-isotope approach and the SIAR mixing model. We found that the NO_3^- concentration showed significant spatial variation in all seasons and was significantly higher in the HVP (178.7 mg/L) region than in UPC (82.1 mg/L), CPF (71.0 mg/L) and the river (17.0 mg/L). However, the different land use types had no significant effect on groundwater nitrate concentration. There was a strong hydraulic connection between the river and the groundwater and its conversion relationship was mainly the river recharging the groundwater.

We identified the nitrate sources by using a multi-isotope approach ($\delta^{15}N–NO_3^-$, $\delta^{18}O–NO_3^-$ and $\delta^{37}Cl$). The results showed that the groundwater nitrate sources mainly came from mixed pollution of domestic sewage and manure, soil nitrogen and ammonia fertilizers in this region. The nitrification could be the most important nitrogen migration and transformation process, while denitrification had not significantly affected the isotopic composition of nitrate in this region.

The proportional contribution of different sources to nitrate groundwater and river water was identified by using an SIAR model. The results showed that the main groundwater nitrate pollution sources in the different hydrogeological units of the Hutuo River alluvial-pluvial fan were domestic sewage and manure, accounting for 55.9%–61.0% (in dry season), 50.3%–60.4% (in transition season), 42.7%–47.6% (in wet season 2016) and 45.9%–46.7% (in wet season 2017). The main sources of groundwater nitrate in different land use types were domestic sewage and manure, followed by soil nitrogen, ammonia fertilizer, nitrate fertilizer and rainwater.

All in all, combined use of NO_3^- ($\delta^{15}N$ and $\delta^{18}O$), water (δ^2H and $\delta^{18}O$) and Cl^- ($\delta^{37}Cl$) isotope could exactly identify the nitrate pollution sources and transformation process in water environment. In addition, based on the results of this study, decision makers may propose more remediation strategies in order to improve the nitrate contamination of the water environment.

Declaration of interests

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgments

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