

A dual isotopic framework for identifying nitrate sources in surface runoff in a small agricultural watershed, northeast China

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ABSTRACT

The northeast black soil region of China, an important area of grain production, currently faces serious diffuse pollution issues. In this study, a dual isotopic ($\delta^{15}\text{N}$ and $\delta^{18}\text{O}$) framework was used to determine nitrate sources in runoff of a small agricultural watershed of this region. The results indicated that the ranges of $\delta^{15}\text{N}$ and $\delta^{18}\text{O}$ values of NO_3 -sources were significantly affected by natural geographic features and human activities. Nitrate in cropland runoff was mainly derived from soil, fertilizer and precipitation. Meanwhile, natural inputs, including those of soil and precipitation, represented the main nitrate sources in forest runoff. Domestic sewage, manure and precipitation contributed to most of the nitrate in runoff from villages. In addition, based on runoff export from different land uses and results from a stable isotope mixing model, soil and chemical fertilizer were identified as the main NO_3 -source in the whole watershed; suggesting that soil erosion could lead to serious diffuse pollution in the study area. Over all, this study not only provided suggestions to the optimal selection of Best Management Practices (BMPs) in Northeast China, but also could contribute to the identification and quantification of NO_3 -sources in agricultural watersheds of the black soil regions worldwide.

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1. Introduction

Excessive nitrate inputs can lead to eutrophication of surface water bodies and as a consequence seriously threaten drinking water safety (Mayer et al., 2002). As reported in the literature, dissolved organic nitrogen (DON) can account for nearly 70% of total nitrogen (TN) in rivers worldwide, but its bioavailability proportion is only 2%–16% (Collins and McGonigle, 2008; Deutsch et al., 2006). On the other end, nitrate, the main inorganic nitrogen found in aquatic environment, is readily bioavailable (Liang et al., 2013). Although a lot of diffuse pollution control projects have been imple-

mented in many regions of the world, such as the EU's detailed reduction directive of agricultural nitrate pollution (Collins and McGonigle, 2008), nitrate concentrations in water are still rising (Bourroui and Grizzetti, 2011; Edwards and Withers, 2008). Not surprisingly, nitrate pollution has become one of the major global water environmental problems (Collins et al., 2014; Huang et al., 2017; Nestler et al., 2011).

To mitigate nitrate pollution in water, identification of the sources and corresponding pollution loads has been identified as the first step towards implementing control measures (Li et al., 2010; Zhang et al., 2018). Statistical methods, using information derived from land use types (i.e., export coefficients) and physicochemical characteristics of water body (i.e., concentration and flow), have been widely used to single out nitrate sources from land to water (Yang and Toor, 2016). However, it is well known that nitrate migration and transformation processes are very complicated and that nitrate

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sources are affected by many factors such as topography and hydrometeorological conditions; leading to uncertainty when interpreting results related to “land-to-water” pollutant sources and loads (Jiang et al., 2018; Kaushal et al., 2011).

Since Kohl et al. (1973) first used nitrogen isotopes ($\delta^{15}\text{N}$) to assess the impact of chemical fertilizers on pollution in rivers, stable isotopes have been widely used as an effective tracer technique to identify nitrate sources and migration processes in surface waters (Kellman and Hillaire-Marcel, 2003). Due to overlap between ranges of $^{15}\text{N}\text{-NO}_3^-$ values of different sources and distinct isotope ratios of nitrogen and oxygen in diverse sources, scholars have begun to identify nitrate sources using coupled $^{18}\text{O}\text{-NO}_3^-$ isotope tracers (Table 1) (Soonthornnonda and Christensen, 2008; Xue et al., 2012). So far, use of $^{15}\text{N}\text{-NO}_3^-$ and $^{18}\text{O}\text{-NO}_3^-$ values (i.e., dual isotopic approach) combined with NO_3^- concentration and land use data have been successfully used to distinguish NO_3^- sources. Wassenaar (1995) evaluated nitrate sources in the Abbotsford aquifer in the Fraser Lowlands of southwestern British Columbia, Canada, by monitoring $\delta^{15}\text{N}$ and $\delta^{18}\text{O}$. Their results revealed that NO_3^- was mainly derived from poultry manure; the rest being from chemical fertilizers. Pardo et al. (2004) applied the dual isotopic approach to determine sources of nitrate in stream water in New Hampshire, USA, and suggested nitrification as the primary source. Similarly, Yue et al. (2013) indicated that wastewater and soil organic N were the main NO_3^- sources in the Liao River, northeast China. In addition, some scholars indicated that the benefit of combining $\delta^{15}\text{N}$ and $\delta^{18}\text{O}\text{-NO}_3^-$ with $\delta^{11}\text{B}$ to distinguish fertilizer from domestic sewage (Biddau et al., 2019). However, as shown in Table 1, the dual isotopic ($\delta^{15}\text{N}\text{-NO}_3^-$ and $\delta^{18}\text{O}\text{-NO}_3^-$) method has remained the most widely applied framework mostly because the associated benefits and limitations are well known (Xue et al., 2009).

Kendall et al. (2007) and Xue et al. (2009) comprehensively summarized the ranges of $\delta^{15}\text{N}$ and $\delta^{18}\text{O}$ values of organic and inorganic fertilizers, atmospheric deposition, animal waste, sewage and other nitrate sources based on findings in Europe and United States of America. It is noteworthy that most of the studies conducted in Asia have also referred to the aforementioned ranges of values for identifying nitrate sources (Li et al., 2010; Liang et al., 2013; Xing et al., 2010). These ranges provided a basis, although spatial heterogeneity in natural geography, vegetation and human distur-

Table 1
Benefits and limitations of isotope methods for the identification of nitrogen sources.

Identification methods	Benefits	Limitations
$\delta^{15}\text{N}\text{-NO}_3^-$	Simple to analyze; Low cost	Difficult to differentiate nitrate sources due to the overlap in $\delta^{15}\text{N}\text{-NO}_3^-$ values
$\delta^{15}\text{N}\text{-NO}_3^-$ and $\delta^{18}\text{O}\text{-NO}_3^-$	Sensitivity to microbially produced NO_3^- from fertilizer	Influence of denitrification on accuracy of the results
$\delta^{15}\text{N}\text{-NO}_3^-$ and $\delta^{18}\text{O}\text{-NO}_3^-$ combined with $\delta^{11}\text{B}$	Insensitive to biogeochemical transformation processes	Expensive and slow analysis

bances would inevitably lead to differences in the $\delta^{15}\text{N}$ and $\delta^{18}\text{O}$ values of similar nitrate sources among regions (Kendall et al., 2007). Nevertheless, using only one set of reference values in different study regions would in all likelihood reduce the reliability of inferring pollution sources. The black soil regions accounted for 7% of the world's ice-free land area, mainly distributed in America and Eurasia (Liu et al., 2012). It was usually recognized that Mollisols were fertile and productive soils, so they have been largely reclaimed for agriculture and pasture, and the original ecosystem strongly disturbed by human activities. Thus, soil erosion and agricultural diffuse pollution have been recognized as common environmental problems in black soil areas worldwide. All countries hope to carry out more targeted BMPs according to the identification of pollution sources. So, by establishing $\delta^{15}\text{N}$ and $\delta^{18}\text{O}$ values of NO_3^- sources in Northeast China, we believe it would provide a valuable contribution to build a complete isotopic finger-prints database of $\delta^{15}\text{N}\text{-NO}_3^-$ of the worldwide black soil regions, and thus, improve the identification accuracy of NO_3^- sources.

Meanwhile, few studies have attempted to assess the contribution rates of identified sources (Liu et al., 2006; Xue et al., 2012). Some of them used stable isotope models to quantitatively estimate the contributions of potential nitrate sources. Indeed, the mass-balance mixing model has been widely applied (Kaushal et al., 2011; Voss et al., 2006). For example, Deutsch et al. (2006) indicated that drainage water, groundwater and atmospheric deposition contributed 86%, 11% and 3% to river nitrates found in rivers. Using the same method, Liu et al. (2013) identified the contribution (7%) of atmospheric precipitation to nitrate loads in the Yellow River, China. However, isotope fractionation and additional sources could lead to some uncertainty in the results obtained with a mass-balance mixing model (Deutsch et al., 2006; Johannsen et al., 2008). On the other end, a Bayesian stable isotope mixing model, named SIAR (Stable isotope analysis in R), has been applied in some studies. This modeling approach could overcome the shortcomings of the standard mass balance model. (Xue et al., 2009, 2012). However, compared with the mass-balance mixing model, there are few application cases of SIAR, and its applicability still needs to be further tested (Xue et al., 2012). If the SIAR model was verified based on nitrogen isotope values of surface runoff sampled in the black soil region, Northeast China, which and then it would promote the application of advanced Bayesian modeling for estimating the proportional contributions of nitrate sources in the Mollisol areas worldwide. Meanwhile, the research results were might also be conducive to the improvement of SIAR.

Most studies focusing on the identification of nitrate sources and their contribution rates through collecting river water samples took place in mixed land-use watersheds (Burns et al., 2009; Burns and Kendall, 2002; Kaushal et al., 2011). However, during the transport process from land to rivers in a highly heterogeneous landscape watershed, isotope fractionation might substantially alter the $\delta^{15}\text{N}$ and $\delta^{18}\text{O}$ values of NO_3^- sources, causing bias in the interpretation of the results (Johannsen et al., 2008; Kendall, 1998). Thus, sampling surface runoff and selecting a highly homogeneous landscape watershed as study area could improve the accuracy of the isotope tracing method.

The Northeast black soil region plays a very important role in China's food security (Ou et al., 2017). The rapid growth of grain production depends on large input of chemical fertilizers. According to statistics, the annual input of chemical fertilizers in Northeast China has reached more than 6 million met-

ric tons, and has shown an increasing annual trend (Ongley et al., 2010). At the same time, since a large portion of rainfall occur during summer and given the spatial extent of sloping farmland, agricultural diffuse pollution has been identified as a great threat to surface waters (Sui et al., 2016). Existing research has essentially focused on qualitatively identifying nitrate sources and export loads of different land-use types in the Northeast black soil region (Ouyang et al., 2012; Yang et al., 2010). So, there is a need to apply a dual isotope ($\delta^{15}\text{N}$ and $\delta^{18}\text{O}$) framework to both identify nitrate sources in surface runoff and quantitatively assess the corresponding contribution rates in a typical agricultural watershed. The objectives of this study were to: (i) evaluate the ranges of $\delta^{15}\text{N}$ and $\delta^{18}\text{O}$ values of NO_3^- sources in the Northeast black soil region; (ii) identify nitrate sources in surface runoff from different land uses; and (iii) determine the contribution rates of each nitrate source.

2. Materials and methods

2.1. Study area

This study was conducted in a typical agricultural watershed of the black soil region, Northeast China (Fig. 1). The main soil types were dark brown and meadow. The 5.97-km² study watershed was covered by cropland, natural forest and villages; accounting for 55%, 42% and 2% of the total area, respectively. The region is in a cold temperate zone with a semi-humid and continental monsoon climate characterized as follows: (i) annual mean temperature of 5.2 °C with average highest temperature reaching 36 °C in July and average lowest temperature of -41 °C in January (Sui et al., 2016). The average annual rainfall in the study area is 563 mm, summer (June–September) precipitation accounting for 68% of the annual rainfall. In 2013, 2014, summer rainfall was 400 mm and 179 mm, respectively. Compared with the annual average, the rainfall in 2014 was relatively low. Based on Soil Conservation Service Curve Number (SCS–CN) method, annual surface runoff was 91 mm and 50 mm during the two years, of which 66% and 69% were from cropland, 29% and 23% from forest, 5% and 7% from villages (Sui, 2016). About 1800 people lived in the watershed at the time the study was conducted; mostly located in five villages. Agriculture was the main source of income. Annual application of nitrogen fertilizer was 200 kg/ha.

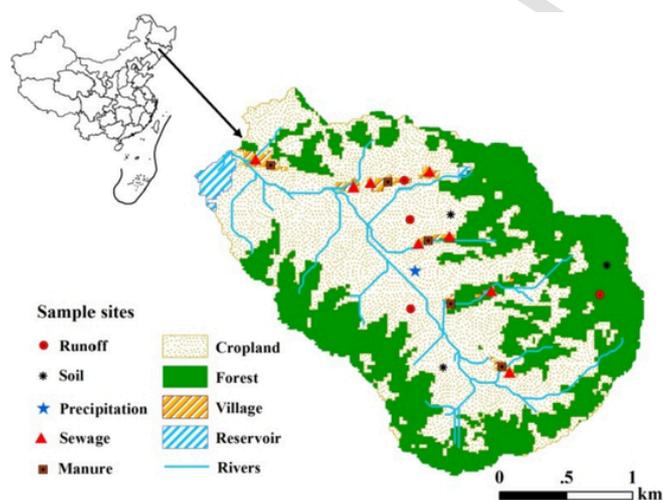


Fig. 1. Locations of the study watershed and distributions of sampling sites.

2.2. Sampling and chemical analysis

Most of the village surface was impermeable in the study area, so there was almost no subsurface flow. Due to high soil permeability rate, infiltration-excess runoff was the dominant mode in the forested area of the study watershed. However, average rainfall intensity was less than 4.21 mm/h in 2013–2014, the probability of subsurface flow was very low in the forest. Meanwhile, it was well known that natural forest was also not a high risk area of non-point source pollution (Zhang et al., 2019). Therefore, forest subsurface flow was not sampled in this study. Long-term cultivation resulted in subsoil compaction, thus, a plow sole was found at a depth of 20 cm in the Northeast black soil area, directly increasing surface and subsurface flow (Kong et al., 2017; Verbist et al., 2007). However, long series of monitoring data from HaiLun Experimental Station of Agricultural Ecology, Chinese Academy of Sciences (E126° 55' N47° 27'), located in the core of the Northeast black soil area, showed that subsurface flow accounted for less than 20% of total runoff during a wet year (An, 2012). Kong et al. (2017) indicated that above the plow sole in the black soil area, the soil saturated hydraulic conductivity varied between 10 and -16.8 mm/h. While the rainfall intensity range of the study area was 0.87–11.48 mm/h and 1.26–7.62 mm/h in 2013 and 2014 (Sui, 2016), respectively, below aforementioned range of saturated hydraulic conductivity, it was difficult for the soil layer above the plow sole to reach saturation and generate subsurface flow. In fact, in the study area, only for two rainfall events, cropland subsurface flow was observed during the two years using the standard soil plot with 5° slope. The ensuing flow accounted for about 10% of the total runoff from each rainfall event. Therefore, no cropland subsurface flow samples were collected in this study.

According to field surveys and related research results, nitrates in surface runoff are considered to be from atmospheric deposition (precipitation), rural domestic sewage, soil, fertilizer, and manure. Surface runoff samples were collected during eight rainfall-runoff events in 2013 and 2014. There were four sampling sites, two located in cropland (maize, slopes of 5° and 7°), and others in forest (*Quercus mongolica*) and country road settings. Precipitation samples were collected using 10-cm diameter plastic buckets during each event in 2013 and 2014. Rural domestic sewage was randomly sampled from 10 nearby rural households. Soil samples were taken from cropland abandoned for over five years and forest land without human disturbance. Urea and diammonium phosphate were collected from mainstream chemical fertilizer factories in Northeast China. Manure samples were mainly from cow dung heap scattered throughout the villages. All samples were kept at 4 °C in a cooler and transported to laboratory within 24 h. All runoff was gathered and mixed as a composite sample collected during each rainfall-runoff event, sealed in 300-ml plastic bottles, stored in a cooler at 4 °C and then transported to laboratory. TN, NO_3^- and NH_4^+ in runoff, precipitation and rural domestic sewage were determined using an Auto Analyzer (Smartchem 200, Italy). Soil, fertilizer, and manure samples were first dissolved in distilled water, extracted at constant temperature in a shaker for 1 h, and finally vacuum-filtered using a 0.45- μm mixed cellulose ester membrane for subsequent analysis (NO_3^- measurement and isotopic analysis).

2.3. Isotopic analysis

The cadmium (Cd) powder reduction method was used to analyze $\delta^{15}\text{N-NO}_3^-$ and $\delta^{18}\text{O-NO}_3^-$ by reducing nitrate to NO_2^- first, and then to N_2O (McIlvin and Altabet, 2005; Tu et al., 2016). The isotopic signature of the produced N_2O was identified using an Isoprime 100 automated continuous flow isotope ratio mass spectrometer (Isoprime Ltd, Stockport, UK). Results of the isotopic analysis were presented in the form of δ values based on atmospheric N_2 and VSMOW (Vienna Standard Mean Ocean Water) for $\delta^{15}\text{N}$ and $\delta^{18}\text{O}$ (Yang and Toor, 2016). International standards (IAEA- NO_3^- , USGS32, USGS34 and USGS35) were applied to calibrate the $\delta^{15}\text{N-NO}_3^-$ and $\delta^{18}\text{O-NO}_3^-$ values. The analytical precision for $\delta^{15}\text{N}$ and $\delta^{18}\text{O}$ was less than 0.5‰ and 1‰, respectively.

2.4. Statistical analysis

All statistical analyses were performed using SPSS 22.0 (SPSS, Chicago, IL). Multivariate analysis of variance (MANOVA) was applied to identify differences in isotopic values of runoff at a p -value of 0.05. According to existing research (Kendall et al., 2007; Xue et al., 2009) and isotopic analysis results in the study area, ranges of $\delta^{15}\text{N-NO}_3^-$ and $\delta^{18}\text{O-NO}_3^-$ values of five potential nitrate sources was mapped on a graph referred to as the isotopic finger-print (Fig. 3). SIAR, a stable isotope mixing model, was chosen to calculate the proportional contribution of each nitrate source to the mixture (Yang et al., 2013). The model was developed based on isotope mass balance and run using the R language statistical software. Based on Dirichlet prior distribution, SIAR evaluated the range of proportional contribution of each source to mixtures using a Bayesian framework (Xue et al., 2012). The model can be expressed as follows:

$$\begin{aligned} X_{ij} &= \sum_{k=1}^K P_k (S_{jk} + C_{jk}) + \varepsilon_{jk} \\ S_{jk} &\sim N(\mu_{jk}, \omega_{jk}^2) \\ C_{jk} &\sim N(\lambda_{jk}, \tau_{jk}^2) \\ \varepsilon_{jk} &\sim N(0, \sigma_j^2) \end{aligned} \quad (1)$$

where X_{ij} was the isotope value j of the mixed sample i ($i = 1, 2, 3 \dots, N$; $j = 1, 2, 3, \dots, J$); S_{jk} was the isotope value j of source k ($k = 1, 2, 3 \dots, K$) and followed a normal distribution with mean μ_{jk} and standard deviation ω_{jk}^2 ; P_k was the proportional contribution of source k , which was calculated using SIAR; C_{jk} was the fractionation factor of isotope j in source k and followed a normal distribution with mean λ_{jk} and standard deviation τ_{jk}^2 ; ε_{jk} was the residual error for isotope value j in mixed sample i and followed a normal distribution with mean = 0 and standard deviation σ^2 . Because denitrification was not identified in nitrate of surface runoff as described in Section 3.3., the fractionation factor C_{jk} for each source was set to be zero (Xue et al., 2009).

3. Results and discussion

3.1. Nitrogen composition in runoff from different land uses

As shown in Fig. 2, in general, TN in runoff decreased with increasing rainfall, probably due to dilution effects. However, TN in village runoff was not related to rainfall. In all likelihood, pollutant loads from impermeable land was mainly governed by surface accumulation.

There was significant differences in TN concentration in runoff from three land use types ($p < 0.05$), with the highest average concentration (5.9 mg/L) occurring in village runoff and the lowest average concentration (3.2 mg/L) occurring in forest runoff. TN in village runoff had the widest range of values (3.7–9.3 mg/L), while forest runoff had the narrow-

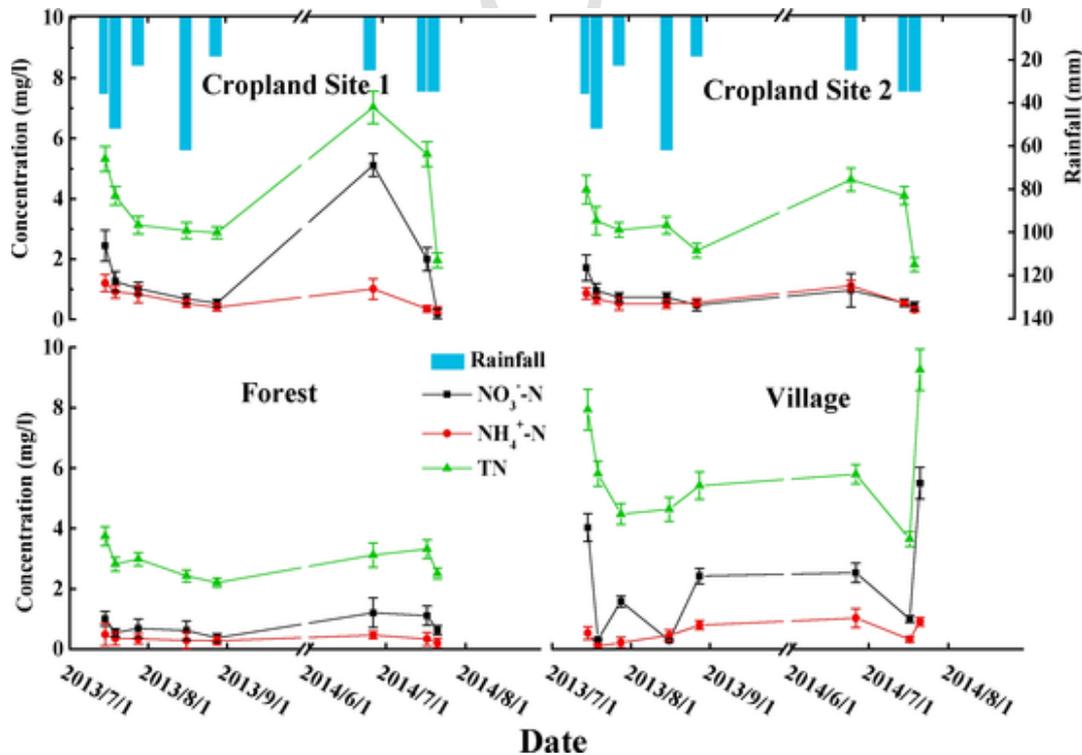


Fig. 2. Nitrogen concentration in runoff sampled in 2013–2014.

est range (2.2–3.8 mg/L). It can be seen from the above results that the TN concentrations in surface runoff from different land uses in the study area were all worse than that of Class V (2.0 mg/L, minimum standard) of the surface water environmental quality standard in China (GB3838-2002) (Bu et al., 2011). In addition, TN levels in surface runoff in other areas of Northeast China were also similar to those of this study (Bu et al., 2017). At present, most water reservoirs in Northeast China are in a moderate eutrophication state (Yang et al., 2010). Therefore, if nitrate sources in surface runoff cannot be accurately identified and then effectively mitigated, a large amount of nitrogen will keep on discharging into these water bodies. Thus, algae growth will be accelerated, increasing the risk of water quality deterioration.

Compared to TN, nitrate and ammonia in runoff did not vary significantly with rainfall, but maximum and minimum values were found in village and forest runoff, respectively. In fact, it suggests that there was significant difference in intensity of human activities among the three land use types. Due to the lack of treatment facilities (Wang et al., 2008), the random discharge of rural domestic sewage and livestock manure in villages had the highest nitrogen concentrations in runoff and the largest range of values; illustrating inherent fluctuations. Forests were generally considered to be least disturbed by human activity, and thus nitrogen level in runoff was the lowest.

The ratio of NO_3^- : TN in runoff was also different among the three land use types. The maximum average value (0.34) was associated with villages, and the minimum average value (0.26) with forest land. Compared to river water (Liang et al., 2013), NO_3^- in surface runoff accounted for a relatively low proportion of TN in this study, which was probably related to the short nitrification time during the runoff migration process. However, NO_3^- still accounted for a high proportion of TN in runoff, almost twice as much as NH_4^+ . It could be deduced that nitrate was the main form of nitrogen pollutants in the study area.

3.2. Isotopic compositions of nitrate sources

Nitrate sources could be distinguished based on differences in $\delta^{15}\text{N}$ content. Furthermore, $\delta^{18}\text{O}$ content was used for differentiating sources (Liu et al., 2013). However, ranges of $\delta^{15}\text{N}$ and $\delta^{18}\text{O}$ values of different nitrate sources varied according to regions (Burns and Kendall, 2002). For comparison purposes, there were more $\delta^{15}\text{N}-\text{NO}_3^-$ and $\delta^{15}\text{N}-\text{NH}_4^+$ data availability than $\delta^{18}\text{O}-\text{NO}_3^-$.

Nitrogen oxides in the atmosphere were mainly derived from combustion of fossil fuel and natural processes. Nitric acid was the main speciation of nitrogen oxides in the atmosphere and deposited on the surface as nitrate during wet precipitation (Driscoll et al., 2001). Gas emitted from vehicle exhausts and power plants, as anthropogenic sources, contributed most of $\delta^{15}\text{N}-\text{NO}_x$ to the atmosphere (Jaworski et al., 1997). In general, the range of $\delta^{15}\text{N}$ values characterizing natural sources was difficult to identify. Some studies have shown that the $\delta^{15}\text{N}$ value of precipitation in pristine environment was lower, usually negative, compared to regions with intense transport activity or heavily polluted areas (Ammann et al., 1999). The negative $\delta^{15}\text{N}$ value (mean -1.9%) of precipitation indicated that atmospheric pollution in the study area was mainly from natural processes. Indeed, in the study region, a small agricultural watershed, traffic was not developed, and industrial and mining activities were even less de-

veloped. In the study area, the above results were consistent to weak transportation infrastructure and large agricultural land.

Ammonia was the main fertilizer ingredient in the study area, and the range of $\delta^{15}\text{N}$ values of fertilizer samples was also consistent with existing research results (Xue et al., 2009). However, in this study, $\delta^{15}\text{N}$ and $\delta^{18}\text{O}$ values of nitrate in ammonium fertilizer were similar to those produced by nitrification (Kendall et al., 2007). It suggested that manufacturing processes, transportation and storage conditions inevitably had a negative effect on the purity of the ammonia fertilizer. Therefore, nitrate fertilizer from the oxidation of ammonia fertilizer was also an important source of nitrate in the study area.

Nitrate only accounted for a small part of soil total nitrogen, but its content reflected features of natural conditions or anthropogenic pollution sources in different regions (Liu et al., 2017). Although the range of soil $\delta^{15}\text{N}-\text{NO}_3^-$ values ($-2.4\% \sim +0.06\%$) in the study area was similar lower than that reported by Kendall (1998) ($2\% \sim 5\%$), their values were smaller. Some research indicated that $\delta^{15}\text{N}-\text{NO}_3^-$ values of soils in flat region or valley floor were larger, related to the strong denitrification rate or nitrate fixation rate in valley bottom soils (Karamanos et al., 1981). However, soil samples were collected from sloping cropland in this study, so the enrichment in soil $\delta^{15}\text{N}-\text{NO}_3^-$ was poor.

In general, the $\delta^{15}\text{N}-\text{NO}_3^-$ values of domestic sewage and manure were larger than other sources due to the continuous evaporation during storage, transport and application (Xue et al., 2009). These values were consistent with the aforementioned research conclusions (Table 2).

The $\delta^{18}\text{O}-\text{NO}_3^-$ from nitrification, precipitation, and fertilizer was impacted by different processes. The $\delta^{18}\text{O}-\text{NO}_3^-$ values of soils were between -5% and 15% , and mainly derived from surface and atmospheric water, closely related to evapotranspiration, respiration and nitrification processes (Kendall, 1998). In this study, the range of soil $\delta^{18}\text{O}-\text{NO}_3^-$ values was relatively wide, probably due to the higher summer evaporation and respiration rates of sloping cropland.

These results suggested that ranges of $\delta^{15}\text{N}$ and $\delta^{18}\text{O}$ values of NO_3^- sources were different from published research results. Therefore, the mapping of $\delta^{15}\text{N}$ and $\delta^{18}\text{O}$ signatures (Fig. 3) needed to be drawn according to the monitoring results of this study, along with other reference values (Kendall et al., 2007).

3.3. Identification of nitrate sources

The $\delta^{15}\text{N}-\text{NO}_3^-$ and $\delta^{18}\text{O}-\text{NO}_3^-$ values of three land use runoff were significantly different (Table 3), which was proba-

Table 2
Isotopic signature of nitrate sources in black soil region, Northeast China.

Nitrate sources	$\delta^{15}\text{N}-\text{NO}_3^-$ (‰)	$\delta^{18}\text{O}-\text{NO}_3^-$ (‰)
Precipitation (n = 8)	$-3.9 \sim +0.59$	$+42.0 \sim +82.4$
Fertilizer-Nitrate (n = 3)	$+7.0 \sim +13.7$	$+15.9 \sim +16.9$
Fertilizer- Ammonia (n = 3)	$-1.8 \sim +1.6$	-
Soil (n = 3)	$-2.4 \sim +0.06$	$+3.8 \sim +10.5$
Sewage (n = 10)	$+10.9 \sim +15.1$	$-7.7 \sim +7.4$
Manure (n = 5)	$+5.6 \sim +8.1$	$-0.40 \sim +1.6$

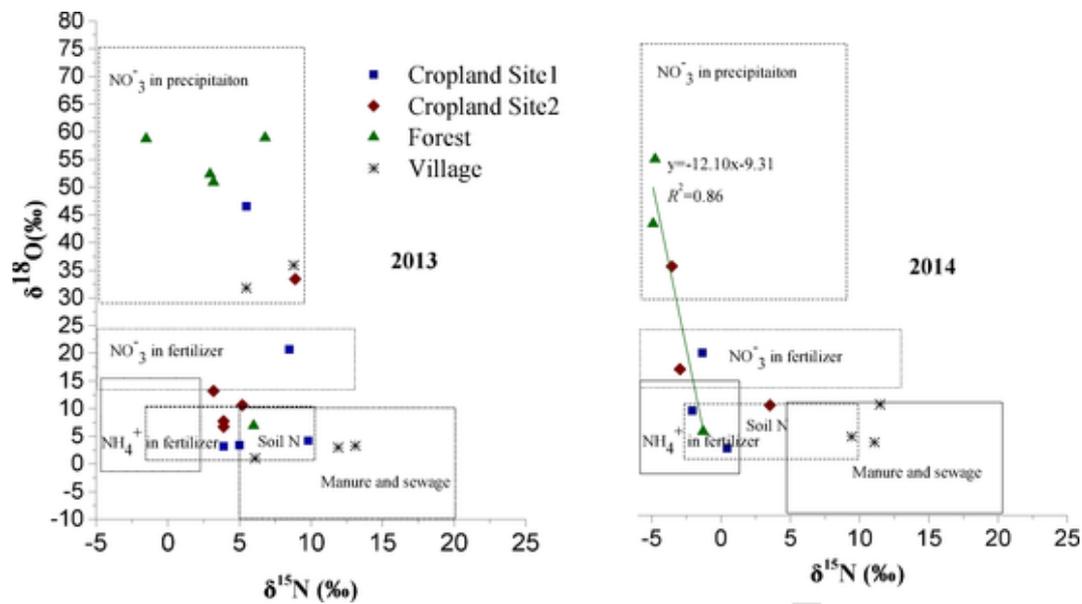


Fig. 3. Cross-plot of $\delta^{15}\text{N-NO}_3^-$ and $\delta^{18}\text{O-NO}_3^-$ values in runoff.

Table 3
Isotopic values in runoff sampled from three land use types.

	Cropland Runoff ^a		Forest Runoff ^b		Village Runoff ^c			
	$\delta^{15}\text{N-NO}_3^-$ (‰)	$\delta^{18}\text{O-NO}_3^-$ (‰)	$\delta^{15}\text{N-NO}_3^-$ (‰)	$\delta^{18}\text{O-NO}_3^-$ (‰)	$\delta^{15}\text{N-NO}_3^-$ (‰)	$\delta^{18}\text{O-NO}_3^-$ (‰)		
	Site 1	Site 2	Site 1	Site 2				
7/15/2013	8.5	3.9	20.7	6.7	6	6.9	6.1	1
7/19/2013	5.5	3.2	46.5	13.2	3	52.3	13.1	3.3
7/28/2013	9.8	3.9	4.2	7.7	3.2	50.9	11.9	3
8/16/2013	5.0	5.2	3.4	10.6	6.8	58.9	8.8	35.9
8/28/2013	3.9	8.9	3.2	33.4	-1.5	58.7	5.5	31.8
6/26/2014	-2.1	-3.6	9.6	35.7	-4.75	55	11.5	10.8
7/17/2014	0.4	3.5	2.9	10.6	-4.9	43.4	9.4	4.9
7/21/2014	-1.3	-3.0	20.1	17.1	-1.3	5.9	11.1	3.9

The different letters (a,b,c) mean significant difference (p -value < 0.05) among the runoff samples.

bly caused by the different nitrate pollution sources. As seen in Fig. 3, in 2013, the $\delta^{15}\text{N-NO}_3^-$ and $\delta^{18}\text{O-NO}_3^-$ values of runoff from cropland sampling site 1 (slope = 5°) were dispersed within the range of those from precipitation, fertilizer, soil and manure samples. However, the $\delta^{15}\text{N-NO}_3^-$ and $\delta^{18}\text{O-NO}_3^-$ values of two runoff samples fell in the overlapped areas of soil and manure values. Because compost products were not applied on cropland, it could be inferred that the soil was the dominant NO_3^- source in cropland runoff rather than manure. Compared with cropland sampling site 1, the $\delta^{15}\text{N-NO}_3^-$ and $\delta^{18}\text{O-NO}_3^-$ values of runoff from cropland sampling site 2 (slope = 7°) were close and concentrated, mainly derived from fertilizer and soil. Differences in pollutant sources in runoff from the two sampling sites may be due to differences in microtopography, soil types and vegetation cover of each watershed site. Flat terrain lead to longer runoff generation and concentration time at sampling site 1, NO_3^- level of overland flow could be affected by multiple pollution sources and $\delta^{15}\text{N-NO}_3^-$ and $\delta^{18}\text{O-NO}_3^-$ values of runoff would change accordingly. The large concentration of nitrogen in runoff of cropland sampling site 1 (Fig. 2) can be taken as evidence. The aver-

age rainfall intensity in 2013 and 2014 was only 3.2 mm/h and 6.0 mm/h (Sui, 2016), obviously below the saturated hydraulic conductivity (16.0 mm/h) in this study area, so the topographic characteristics had larger influence on surface runoff. Meanwhile, compared with sampling site 1 located on a sunny slope, sampling site 2 located on a shady slope had poor crop development, so the vegetation coverage in catchment area was low. Thus, combination of large slope and poor vegetation cover could have contributed to short runoff generation time and induced soil erosion within the drainage area of sampling site 2 (slope = 7°), so the ranges of values of $\delta^{15}\text{N-NO}_3^-$ and $\delta^{18}\text{O-NO}_3^-$ were small (Table 3). Meanwhile, the higher sediment content of runoff from soil and fertilizer represented major sources of nitrogen pollution. In 2014, the $\delta^{15}\text{N-NO}_3^-$ and $\delta^{18}\text{O-NO}_3^-$ values of runoff from the two cropland sampling sites were dispersed (Fig. 3). At sampling site 1, due to the significant reduction in rainfall, the soil moisture content was very low (less than 20%) increasing in all likelihood the surface runoff generation time, thus making chemical fertilizer and soil as the main NO_3^- sources because of the associated soil and water intensive mixing. In 2014, nitrate concentra-

tion in cropland runoff was significantly larger than that in 2013, providing additional support to the above finding. Furthermore, based on the aforementioned soil hydrological conditions and the excessively low concentrations of nitrogen pollutants in rainfall, the $\delta^{15}\text{N}\text{-NO}_3^-$ and $\delta^{18}\text{O}\text{-NO}_3^-$ characteristic values for precipitation in runoff were not detected. Within the drainage area of sampling site 2, the steep slope was more conducive to runoff generation, so more pollution sources had significant influence on the NO_3^- level of overland flow during the transport process.

The $\delta^{15}\text{N}$ and $\delta^{18}\text{O}$ values of forest runoff were mainly distributed within the range of those for precipitation. Some were located in the overlapped areas of fertilizer, manure and soil. However, because trees in the study area were all located in natural forests without chemical fertilizer application, soil was the only source of nitrate in runoff. The $\delta^{15}\text{N}$ and $\delta^{18}\text{O}$ values of village runoff were mainly distributed within the ranges of manure, domestic sewage and soil. In 2013, $\delta^{15}\text{N}$ and $\delta^{18}\text{O}$ values of village runoff were partly similar to those of precipitation. In the study area, because almost all land covers of the villages were impermeable, the soil could not export nitrogen pollutants into runoff. However, due to the lack of sewage and waste collection and treatment facilities in the study area (Wang et al., 2008), manure from small-scale farms and untreated domestic sewage became the main pollution sources of nitrate in village runoff. In 2014, due to severe drought, precipitation did not represent a nitrate source in village runoff. In general, both natural (precipitation, soil) and anthropogenic (chemical fertilizer, domestic sewage and manure) sources contributed to nitrate pollution in the study area.

Some studies suggested that a positive correlation between $\delta^{15}\text{N}\text{-NO}_3^-$ and $\delta^{18}\text{O}\text{-NO}_3^-$, with a slope of 0.5–1, is indicative of denitrification of a nitrate source (Hu et al., 2019). As seen in Fig. 3, nitrate in runoff did not undergo fractionation caused by denitrification. During the dry 2014 year, there was a significant negative correlation between $\delta^{15}\text{N}\text{-NO}_3^-$ and $\delta^{18}\text{O}\text{-NO}_3^-$ in forest runoff, probably due to mixing between nitrates from both soil and precipitation. Compared to 2013, the larger nitrate concentration in runoff provided evidence for the above phenomenon (Fig. 2). Similar results were found elsewhere. For example, in Northern China drought inhibited microbial activity, leading to the accumulation of nitrate in soils, thus $\delta^{15}\text{N}\text{-NO}_3^-$ values were negatively related to $\delta^{18}\text{O}\text{-NO}_3^-$ values (Liu et al., 2017).

3.4. Contributions of each nitrate source

Although the proportional contribution of ammonia fertilizer and nitrate fertilizer were calculated separately (Fig. 4), the content of nitrate mixed with ammonia fertilizers was very low, so in this study the two were combined into one source (fertilizer). As seen in Fig. 4, the rainfall amount had a large impact on the contribution of N sources to forest and village runoff. However, their contributions to cropland runoff were little related to rainfall. Over the two years of study, the NO_3^- contribution rates of soil, fertilizer and rainfall sources remained at about 52%, 38% and 10%, respectively. Similarly, $\delta^{15}\text{N}\text{-NO}_3^-$ and $\delta^{18}\text{O}\text{-NO}_3^-$ values in cropland runoff (Fig. 3) were primarily within the range of those from soils and fertilizers, while some fell within the range of those of precipitation. Chemical fertilizer was generally considered to be the main source of NO_3^- in upland (Ongley et al., 2010), but in this study, the soil contribution was even more than that of fertilizer, which reflected the features of agricultural diffuse pollution in the black soil area. The cropland was mainly sloping land, and conservation tillage measures were rarely implemented. In addition, with most of the rainfall occurring from July to September, soil erosion was substantial, leading to a large amount of organic nitrogen and nitrate transported in runoff with sediments. Contrary to cropland, although the $\delta^{15}\text{N}\text{-NO}_3^-$ and $\delta^{18}\text{O}\text{-NO}_3^-$ values found in forest runoff mostly fell within the range of those of precipitation, the results of the SIAR model suggested that the main pollution source was the soil. For the two-year study, NO_3^- contribution rates of soil to forest runoff were 62.1% (2013) and 50.8% (2014). Erosion was minimal for forest land (Sui et al., 2015) and a significant decline in rainfall in 2014 directly lowered the sediment content of forest runoff (less than 4.6 g/L), further increasing the contribution rate of precipitation. The contribution rates to village runoff varied greatly. In 2013, the NO_3^- contribution rates of sewage, precipitation and manure were 47.3%, 37.0%, and 15.7%, respectively and in 2014, they were 46.7%, 3.70% and 49.6%, respectively. Number of residents in villages and local socio-economic level did not change significantly during these two years, so the discharge of domestic sewage was relatively stable, thus NO_3^- contribution rates did not vary much (Sui et al., 2016). Since the surface of villages was impermeable, the rainfall amount directly deter-

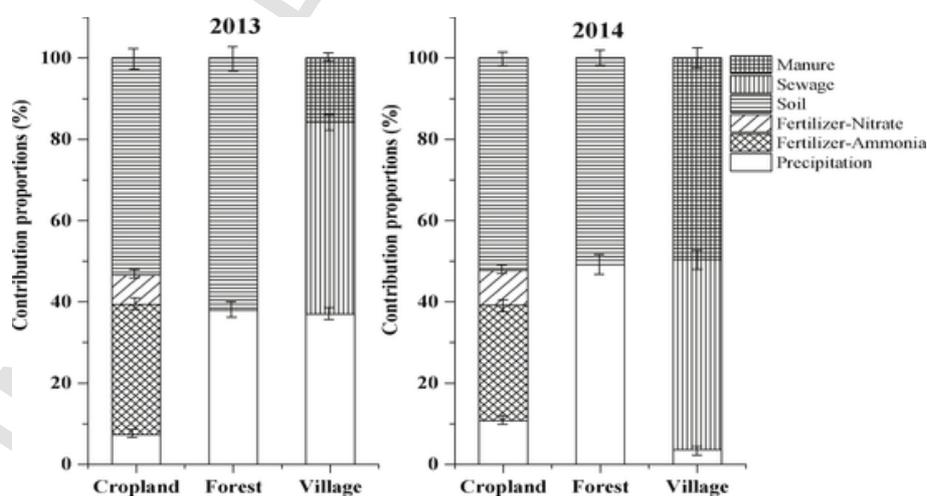


Fig. 4. Contributions of nitrate sources to surface runoff of different land uses.

mined the surface runoff. And the drought in 2014 resulted in the almost negligible contribution rate of precipitation. In the study area, most of the domestic farmyard poultry production was small-scale, and the manure production and emissions were random, so there was great uncertainty in the NO_3^- contribution rate of manure. Some studies suggested that anthropogenic sources were the main causes of nitrate pollution. For example, using the dual stable isotope method, fertilizer and rural domestic sewage were identified as the main NO_3^- sources in an agricultural region of south China (Liang et al., 2013). Kellman and Hillaire-Marcel (2003) indicated that manure was the dominant nitrate source in an agricultural watershed of eastern Canada. However, except for the village runoff, the nitrate contribution rate of soil to the runoff from cropland and forest was very high. Meanwhile, since cropland runoff accounted for more than 60% of the whole watershed land cover, it can be said that soil erosion was a vital NO_3^- source in the study area. It suggested that diffuse pollution mitigation in black soil region should not only focus on fertilizer management, but also on soil erosion control.

4. Conclusions

A framework based on a combination of dual isotope and water quality analyses was applied to determine nitrate diffuse pollution in a small agricultural watershed of the black soil region, Northeast China. Nitrogen concentration in runoff in the study area was greatly affected by land use and rainfall. The range of $\delta^{15}\text{N}$ and $\delta^{18}\text{O}$ values of NO_3^- sources reflected environmental characteristics of an agricultural watershed, which were different from published results. This indicated that our results could represent a valuable contribution towards building a database of isotopic signature of NO_3^- sources in black soil region, Northeast China. Therefore, it would be wise to monitor the isotopic signature of nitrate sources in the different black soil regions around the world for improving the determination and quantification NO_3^- sources. Based on isotopic finger-prints, $\delta^{15}\text{N}$ and $\delta^{18}\text{O}$ values of runoff could be used to highlight the importance of NO_3^- sources to some extent, but it was still different from results obtained with a mass balance mixing model. It was generally believed that anthropogenic sources had a greater influence on nitrate in runoff. However, according to land use area and runoff, soil and fertilizer could be considered as the major NO_3^- sources in the study watershed, contrary to existing research results indicating that the largest source of diffuse pollution was fertilizer in the black soil region. Hence, in order to effectively reduce diffuse pollution load in the black soil region, not only balanced fertilization practices should be implemented, but also development and application of soil erosion control measures should be further strengthened.

Although the estimation results of the SIAR model in our this study were reasonable, there were still had some shortcomings with it. For example, small changes in $\delta^{15}\text{N}$ and $\delta^{18}\text{O}$ levels of nitrate in water samples might cause large uncertainty in the interpretation of the results obtained with the SIAR model (Xue et al., 2012). In addition, the temporal variation of isotopic composition of NO_3^- in runoff, coupled with the large standard deviations of the $\delta^{15}\text{N}$ and $\delta^{18}\text{O}$ values of NO_3^- sources, would lead to a wide range of NO_3^- sources and associated proportional contributions proportion as calculated by the SIAR model. Therefore, in order to improve estimation of proportional source contribution, the $\delta^{15}\text{N}$ - and $\delta^{18}\text{O}$ - NO_3^- should be combined with boron stable isotopes, on the one hand, nevertheless more precise and efficient ad-

vanced isotope techniques need to be explored.

Declaration of competing interest

The authors declared no potential conflicts of interest with respect to the research, authorship, and/or publication of this article.

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