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Risk assessment and source identification of coastal groundwater nitrate in northern China using dual nitrate isotopes combined with Bayesian mixing model

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ABSTRACT

Due to the intensive and complicated human activities, the identification of nitrate pollution source of coastal aquifer is usually a challenge. This study firstly adopted stable isotope technique and stable isotope analysis in R (SIAR) model to identify the nitrate sources and contribution proportions of different sources in typical coastal groundwater of northern China. The results showed that about 91.5% of the groundwater samples illustrated significantly high nitrate concentrations exceeding the maximum WHO drinking water standard (50 mg/l), reflecting the high risk of groundwater nitrate pollution in the coastal area. A total of 57 sampling sites were classified into three groups according to hierarchical cluster analysis (HCA). The $\delta^{15}N\text{-}NO_3^-$ and $\delta^{18}O\text{-}NO_3^-$ values of groundwater samples from Group C (including nine samples) were much higher than those from Group A (including 40 samples) and Group B (including 8 samples). SIAR results showed that NH_4^+ fertilizer was the dominant nitrate source for groundwater samples of Groups A and B while manure and sewage (M&S) served as dominant source for Group C. This study provided essential information on the high risk and pollution sources of coastal groundwater nitrate of northern China.

Introduction

Known as an important earth's critical zone, the coastal zone is dramatically influenced by the anthropogenic activities. Therefore, groundwater in this area has shown various problems such as seawater intrusion (De Filippis *et al.* 2016), land subsidence due to overexploitation of the groundwater (Hu *et al.* 2004), and groundwater pollution (Re *et al.* 2013). Groundwater nitrate pollution has remarkable effects on coastal ecosystem and human health, which thus becomes an important issue for this area. Nitrate pollution of

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groundwater is a worldwide issue attracting extensive attention by the public (Gu *et al.* 2013; Hosono *et al.* 2013; Menció *et al.* 2016). Intensive anthropogenic activities have caused large amount of nitrogen matters that are discharged into the groundwater. Therefore, nitrate concentrations of the groundwater continuously increase to seriously disturb fate and transport of nitrate in the groundwater and extensively affect the human health and ecological stability (Gu *et al.* 2013; Miller *et al.* 2016; Musgrove *et al.* 2016). Identification of the groundwater nitrate sources has become an important issue for preventing and controlling groundwater nitrate pollution (Hosono *et al.* 2013; Matiatos 2016). However, it is usually difficult to identify groundwater nitrate pollution because of multiple factors including uncertainty of groundwater nitrate sources, complexity of nitrate transformation, and retardant effects of groundwater nitrate. Therefore, identification of nitrate sources in groundwater will not only lay the scientific basis on evaluating groundwater resources but also have important sense in theory and practice for prevention and control of groundwater pollution.

There are diverse groundwater nitrate sources such as fertilizer and manure, industrial and domestic sewage, atmospheric N deposition, and soil organic N (Kendall 1998). Various nitrate sources and complex physic-chemical reactions in nitrogen cycle have caused remarkable shortcoming using individual approach for source identification (Hosono *et al.* 2013). Stable isotope technique has been gradually employed to identify the nitrate sources along with the development of this technique (Kaown *et al.* 2009; Matiatos 2016). Generally, δ^{15}N-NO$_3^-$ values range from -6‰ to $+6$‰ for fertilizers, from -13‰ to $+13$‰ for atmospheric N deposition, from $+5$‰ to $+25$‰ for manure, from $+4$‰ to $+19$‰ for sewage, and from 0‰ to $+8$‰ for soil N while δ^{18}O-NO$_3^-$ values range from -10‰ to $+10$‰ for nitrate derived from nitrification, from $+25$‰ to $+75$‰ for atmospheric N deposition, and from $+17$‰ to $+25$‰ for fertilizers (Bateman and Kelly 2007; Finlay *et al.* 2007; Hales *et al.* 2007; Lee *et al.* 2008; Singleton *et al.* 2007; Xue *et al.* 2009). Individual isotope method shows limitations such as overlapping isotope value range and variance in isotope values of target groundwater and source sites due to isotope fractionation. Therefore, individual isotope approach cannot accurately identify the nitrate source of groundwater (Hosono *et al.* 2013). Quantitatively evaluating the contribution proportions of the different nitrate sources is important for prevention and control of groundwater nitrate pollution. Based on stable isotope technique, many models for identifying source contribution have been established (Moore and Semmens 2008; Parnell and Jackson 2008; Parnell *et al.* 2010; Matiatos 2016; Grimmeisen *et al.* 2017). SIAR (Stable Isotope Analysis In *R*) is a Bayesian mixing model based on Direchlet distribution (Jackson *et al.* 2009; Parnell and Jackson 2008), showing good ability of solving limits of mass-balance mixing models. SIAR model has been applied to evaluate the contribution of different nitrate sources (Yue *et al.* 2015a; Xue *et al.* 2012; Matiatos 2016), exhibiting good application potential.

Freshwater resources in coastal zones are limited while demands are high, resulting in strict water resource management and protection of coastal freshwater aquifers. In the face of growing water scarcity, groundwater is an important water supply in the coastal zone. Many attempts have been devoted to protecting the groundwater in coastal zone. Due to the rapid increase in population and remarkable economic development in the coastal zone in China, water demands have become greater and groundwater has been over-abstracted. Due to the intensive and complicated human activities in coastal area, the identification of nitrate source of coastal aquifer is usually a challenge. This study adopted stable isotope technique and SIAR model to identify the nitrate sources and contribution proportions of

different source in typical coastal groundwater in northern China. It aims at providing essential information on the coastal groundwater protection and pollution control in northern China.

Methods and materials

Study area

The study area is a typical coastal zone located in the eastern Laizhou Bay, northern China, bordering on Bohai Sea in the north (Figure 1). Laizhou Bay coastal area was affected by extremely intensive anthropogenic activities in China. Groundwater in this area has been over-abstracted for the last few decades. Therefore, seawater intrusion in coastal aquifer throughout this area has become the most serious in China (Yin 1992). The annual exploitation of groundwater in the eastern Laizhou Bay was 1.54×10^8 m^3 in 2003 (Li 2005), thus significantly decreasing groundwater levels. It is under continental monsoon climate with an average annual temperature of 12.4°C. The average annual precipitation is 640.3 mm, mainly (about 72.4%) distributing from June to September. The average annual
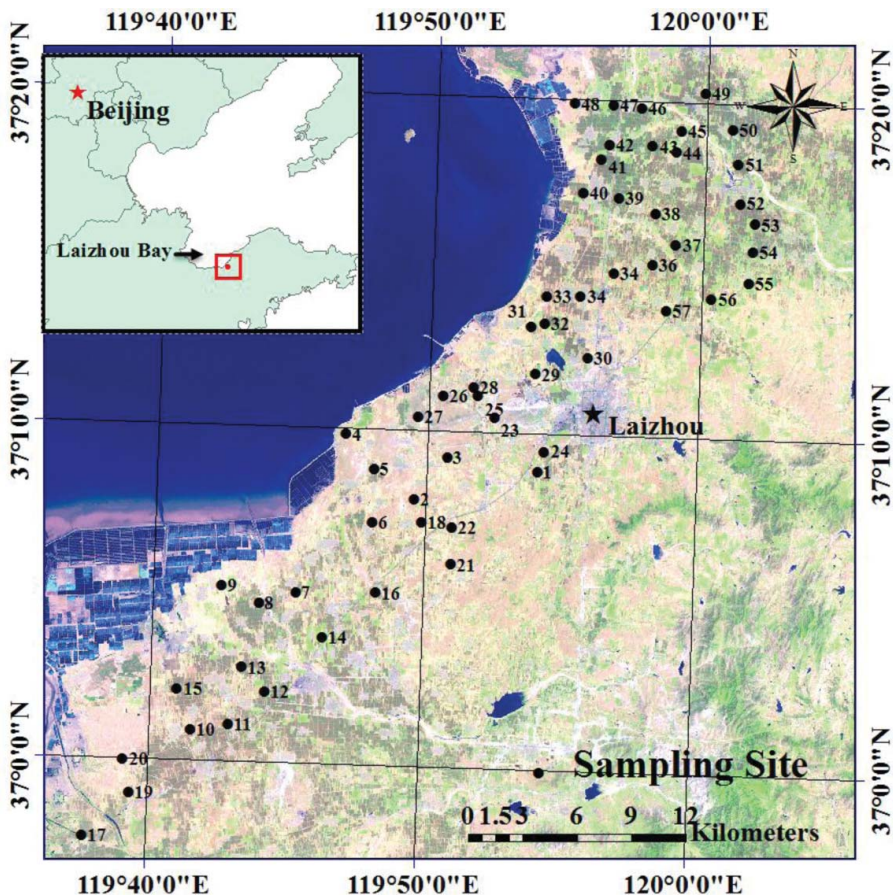

Figure 1. Study area and sampling sites.

potential evaporation is 2,118.7 mm (Fu *et al.* 1994). The study area shows five types of land-forms (*i.e.* marine deposits plain, alluvial plain, pluvial plain, and bedrock hills) spreading from coast to inland, being made up of sandbar, lagoon, and bedrock. With the width of 5–10 and 2–3 km in some parts, the plains distribute in the shape of belt in east-north direction. The study area possesses two types of water-bearing bodies including Quaternary loose beds and bedrock-fissured aquifer. The Quaternary water-bearing beds are made up of fluvial and pluvial sediments, sand layers, and talus strata, with the deposit thickness of 10–100 m in the west and 15–25 m in the east. There are 2–3 aquifers made up of different litho facies such as gravel sand, coarse sand, medium-granular sand, and small-granular sand, and then transiting to the sediments of marine phase or lagoon phase. Upper aquifers are in close hydraulic connection with lower aquifers due to a large amount of borehole withdrawal and "deposit windows." The detailed information on the hydrology of the study area refers to Wen *et al.* (2012).

Sampling and chemical analysis

Field sampling and investigation were carried out in June 2013 to evaluate groundwater nitrate pollution in the study area. Fifty-seven groundwater samples were collected from long-term groundwater observation wells and drinking wells with depths of 5–40 m (Figure 1). Water temperature (T), pH, dissolved oxygen (DO), and electrical conductivity (EC) of the groundwater samples were measured *in situ* using a portable water quality analyzer (HQd30, Hach, USA). Water samples were filtered through a 0.45-μm cellulose-acetate filter and stored at 4°C until chemical and isotope analysis. The concentrations of NO_3^-, Cl^-, SO_4^{2-}, Na^+, K^+, Mg^{2+}, and Ca^{2+} were analyzed using ion chromatography (ICS3000, Dionex, USA). The concentrations of HCO_3^- were determined using titration.

    The stable isotope $\delta^{18}O$-H_2O compositions of groundwater samples were analyzed using an isotope ratio mass spectrometer (MAT-253, Thermo Scientific, USA). The $\delta^{15}N$-NO_3^- and $\delta^{18}O$-NO_3^- compositions were analyzed using the denitrifier method at the Facility for Isotope Ratio Mass Spectrometry, University of California, Riverside. All stable isotope results are expressed in the delta (δ) units of per mil (‰) relative to a suitable standard. Vienna Standard Mean Ocean Water (VSMOW) standard was used for $\delta^{18}O$-H_2O and $\delta^{18}O$-NO_3^- while atmospheric nitrogen gas (N_2) was used for $\delta^{15}N$-NO_3^-. More detailed information on the determination procedure and main principles for $\delta^{15}N$-NO_3^- and $\delta^{18}O$-NO_3^- refers to Yang *et al.* (2013).

Data analysis

Since several chemical and isotopic sub-datasets did not follow a normal distribution, non-parametric tests (Mann–Whitney and Kruskal–Wallis) were used to evaluate these datasets by comparing the average values of two independent samples (subgroups). Data selection obeys the null hypothesis stating that two or more samples taken from a single population would have no consistent differences between two or more ranking sets. When the calculated *p*-value is less than 0.05, two groups are significantly different. Hierarchical cluster analysis (HCA) was adopted to classify Ward's linkage rule which iteratively linked nearby data through a similarity matrix. ANOVA was performed to evaluate the distance between different clusters. The squared Euclidian distance was selected for the similarity measurement.

δ^{15}N-NO$_3^-$ and δ^{18}O-NO$_3^-$ values were standardized based on z-scores. All statistical calculations were performed using SPSS 20.0.

Estimation of nitrate source contributions (SIAR)

To quantify the contributions of the NO$_3^-$ sources to groundwater, a Bayesian mixing model SIAR (Stable Isotope Analysis In R) was used (Parnell and Jackson 2008; Parnell *et al.* 2010). By defining a set of *N* measurements on *J* isotopes with contributions of *K* sources, the SIAR model can be expressed as follows (Parnell *et al.* 2010):

$$X_{ij} = \sum_{k=1}^{k} p_k(S_{jk} + c_{jk}) + \varepsilon_{ij}$$
$$S_{jk} \sim N(\mu_{jk}, \omega_{jk}^2)$$
$$c_{jk} \sim N(\lambda_{jk}, \tau_{jk}^2)$$
$$\varepsilon_{ij} \sim N(0, \sigma_j^2)$$

where X_{ij} is the observed isotope value *j* of mixture *i*, in which $i = 1, 2\ 3,\dots, I$ and $j = 1, 2, 3, \dots, J$; S_{jk} refers to the source value *k* on isotope *j* ($k = 1, 2\ 3,\dots, K$) that is normally distributed with mean μ_{jk} and variance ω_{jk}; p_k is the proportion of source *k*, which needs to be estimated by the SIAR model; c_{jk} is the isotope fractionation factor for isotope *j* on source *k*, being normally distributed with mean value λ_{jk} and standard deviation τ_{jk}; and ε_{ij} is the residual error representing the additional unquantified variation between individual mixtures and is normally distributed with mean 0 and standard deviation σ_j. Detailed information on SIAR model refers to Parnel *et al.* (2010).

Due to the lack of the information on the δ^{15}N-NO$_3^-$ and δ^{18}O-NO$_3^-$ isotope characteristic values for the potential nitrate sources in the study area, the mean value and standard deviation of each source nitrate isotope signature were cited from literatures (Kendall *et al.* 2007; Chae *et al.* 2009; Kaown *et al.* 2009; Xue *et al.* 2009; Urresti-Estala *et al.* 2015; Yue *et al.* 2015a; Yue *et al.* 2015b). The isotope fractionation factor c_{jk} for all sources was set as zero because no significant signs of nitrogen transformation occurred in the groundwater during the sampling periods.

Results and discussion

Risk assessment and isotope compositions of coastal groundwater nitrate

The statistical summary of water quality parameters was shown in Table 1. The nitrate concentrations ranged from 9.35 to 660.88 mg/l, with an average value of 190.65 mg/l. The nitrate concentration in groundwater is generally less than 10 mg/l under the natural condition (ECETOC 1988). Except one sample, the remaining 56 groundwater samples exhibited high nitrate concentrations (exceeding 10 mg/l), indicating that anthropogenic contamination has dramatically increased nitrate concentrations in the groundwater. In particular, about 91.5% of the groundwater samples showed remarkably high nitrate concentrations which exceeded the recommended maximum allowable value for nitrate in drinking water according to the WHO (50 mg/l), indicating the high risk of groundwater nitrate pollution

Table 1. Statistical summary of groundwater parameters.

	Minimum	Maximum	Mean	Standard deviation	Skewness
pH	7.00	7.68	7.38	0.15	−0.13
EC (μS/cm)	509.00	3650.00	1416.96	513.92	1.50
DO (mg/l)	3.42	10.22	7.21	1.49	−0.28
Na^+ (mg/l)	22.11	532.87	80.39	75.04	4.31
K^+ (mg/l)	0.11	18.56	1.96	2.67	4.73
Mg^{2+} (mg/l)	10.42	77.20	30.89	14.48	1.21
Ca^{2+} (mg/l)	37.84	383.53	192.11	73.65	0.25
Cl^- (mg/l)	34.45	1319.82	224.05	190.35	3.66
NO_3^- (mg/l)	9.35	660.88	196.87	131.54	1.36
SO_4^{2-} (mg/l)	35.66	271.40	108.77	56.29	0.95
HCO_3^- (mg/l)	124.56	500.96	282.74	75.65	0.49
TDS (mg/l)	258.09	2795.71	979.82	422.96	1.48
$\delta^{15}N$-NO_3^- (‰)	3.06	18.57	7.52	2.77	1.34
$\delta^{18}O$-NO_3^- (‰)	0.07	8.01	3.43	1.71	0.58
$\delta^{18}O$-H_2O (‰)	−8.35	−4.63	−7.19	0.73	1.19

in the coastal area. Nitrate concentrations reached 600 mg/l at some sampling sites, which reflected the extremely high risk of groundwater nitrate pollution in the coastal area.

Most of groundwater quality parameters varied in very wide ranges and high standard deviations (Table 1). The pH values ranged from 7.00 to 7.88 with an average of 7.40, indicating a slight tendency toward a basic composition. DO varied from 3.42 to 11.49 mg/l with an average of 7.29 mg/l to illustrate oxic conditions. Groundwater samples showed highly dispersed EC values, ranging from 490 to 3650 μS/cm. The Cl^- concentrations also had a wide range between 42.68 and 1319.82 mg/l with an average of 218.25 mg/l. Concentrations of Ca^{2+}, Mg^{2+}, K^+, HCO_3^-, and SO_4^{2-} also showed remarkable variations (Table 1), indicating that chemical composition was affected by diverse hydro-chemical processes (Park et al. 2005).

The $\delta^{15}N$-NO_3^- values in the groundwater ranged from +3.06‰ to +18.57‰, with an average value of +7.52‰. The $\delta^{18}O$-NO_3^- values in the groundwater varied between +0.07‰ to +8.01‰, with a mean value of +3.44‰. The wide distributions of $\delta^{15}N$-NO_3^- and $\delta^{18}O$-NO_3^- indicated that high nitrate concentrations in groundwater mainly originated from multiple nitrate sources (Xue et al. 2009). The $\delta^{18}O$ compositions of the groundwater samples ranged from −8.35 to −4.63‰ with an average of −7.19‰.

Distribution of water quality classification based on HCA

A total of 57 sampling sites were classified into three groups according to HCA (Figures 2 and 3). Furthermore, Kruskal-Wallis test results showed that the differences between each cluster were all significant at the 95% level ($p < 0.05$). As illustrated in Figure 2, the $\delta^{15}N$-NO_3^- and $\delta^{18}O$-NO_3^- values of groundwater samples from Group C were much higher than those from Groups A and B. Group B showed the lowest values of $\delta^{15}N$-NO_3^- and $\delta^{18}O$-NO_3^-.

Potential nitrate sources in groundwater include soil organic nitrogen, synthetic fertilizers, atmospheric nitrogen deposition, manure, and sewage waste (Kendall 1998). A classical dual isotope approach ($\delta^{15}N$-NO_3^- versus $\delta^{18}O$-NO_3^-) was applied to identify the predominant sources of NO_3^- in the groundwater samples (Figure 4). Due to the absence of nitrate isotope values for potential nitrate sources in the study area, the $\delta^{15}N$-NO_3^- and $\delta^{18}O$-NO_3^- isotopic composition results were compared to those obtained by Kendall et al.
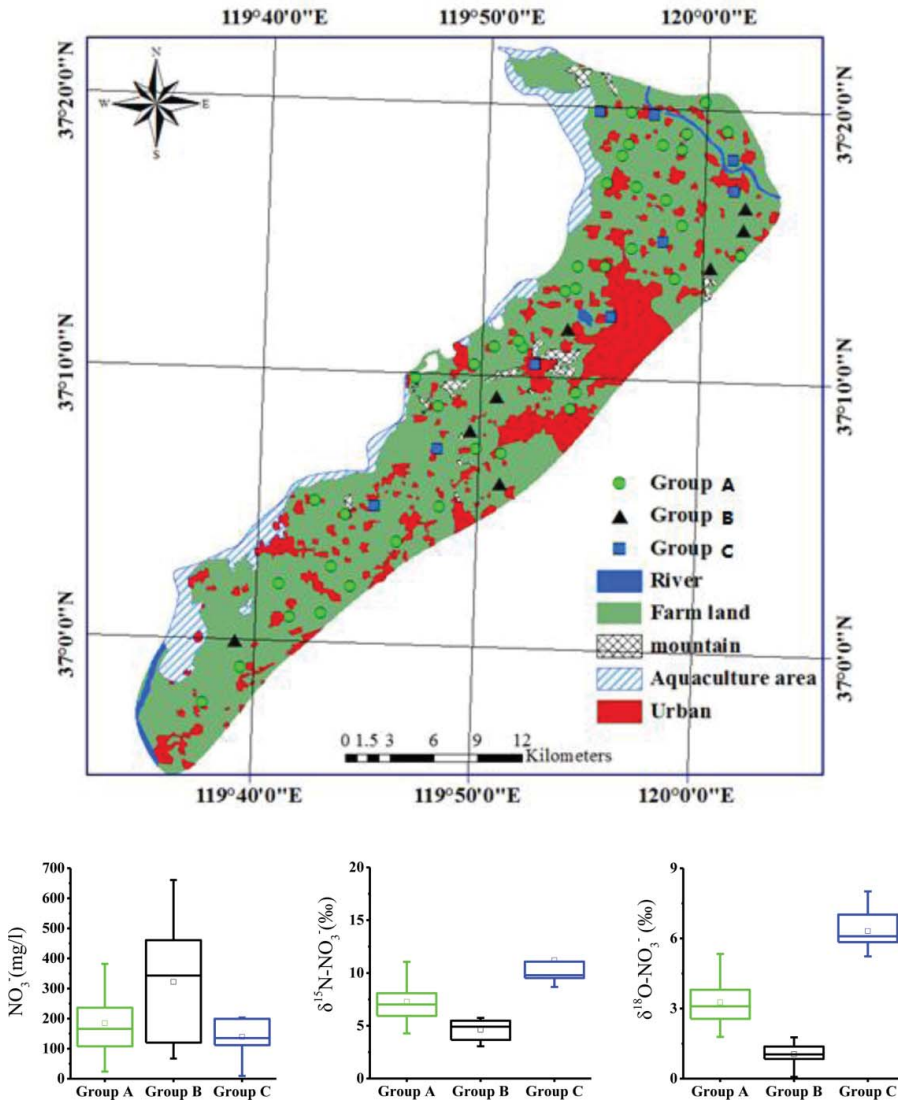
Figure 2. Distribution of water quality classification using HCA.

(2007) and Xue *et al.* (2009). Figure 4 illustrated that the isotopic signatures of the groundwater samples spread over the range of soil N, NH_4^+ fertilizer & soil N, soil N & manure and sewage (M&S).

Nitrate concentrations of Group A ranged from 23.85 to 484.76 mg/l with an average of 184.75 mg/l. The $\delta^{15}N\text{-}NO_3^-$ and $\delta^{18}O\text{-}NO_3^-$ values of groundwater samples which were classified into Group A ranged from +4.28 to +11.82‰ and from +1.76 to +5.31‰, respectively (Figure 2). It was observed visually that the samples did not fall into the ranges for a specific source (Figure 4), illustrating that these groundwater samples most likely possessed multiple nitrate source inputs. The isotopic signatures of nitrate were close to a mixture of nitrate in soil N, NH_4^+ fertilizer, and M&S (Figure 4), suggesting that nitrate was influenced by these nitrate sources. This is consistent with the land use pattern in the study area. The
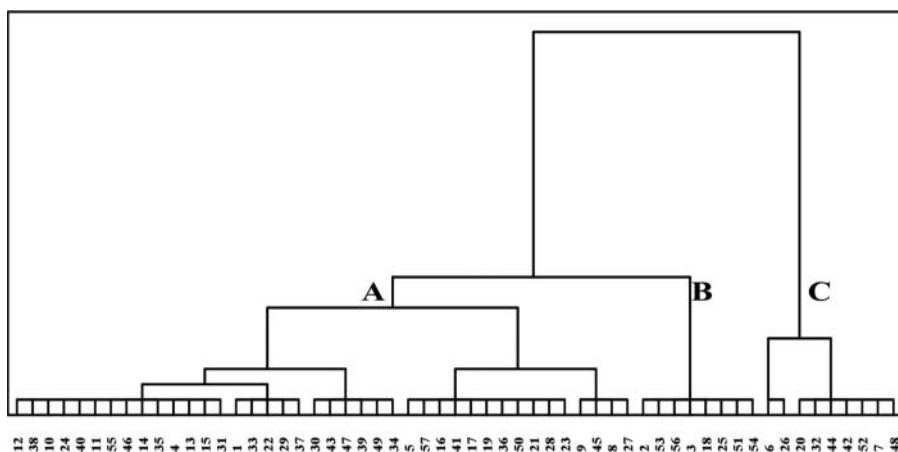
Figure 3. Water quality classification of different sampling sites using HCA.

most of Group A sampling sites are located in the agricultural areas. However, these sampling sites are not far from the residential areas where crops receive synthetic NH_4^+ fertilizer, manure, and sewage from the residential areas. Additionally, several sampling sites lay near the coastal aquaculture area where the aquaculture sewage was discharged. Therefore, groundwater in these sites is affected by multiple nitrate sources.

A total of eight samples were clustered into Group B with $\delta^{15}N\text{-}NO_3^-$ values between +3.06‰ and +5.74‰ and $\delta^{18}O\text{-}NO_3^-$ values between +0.07‰ and +1.77‰. It is clear that the isotopic values of the group B mainly fall into the range for NH_4^+ fertilizer and soil N sources (Figure 4). However, soil N cannot be considered as the significant nitrate source of the samples clustered into Group B because the concentrations of NO_3^- for group B ranging from 67.07 to 660.88 mg/l with an average 321.96 mg/l exceeded the NO_3^- concentrations produced by the mineralization of soil N (Puig *et al.* 2013). Groundwater samples of group B were collected from the agricultural areas which are far from the residential areas compared to Group A (Figure 2). NH_4^+ fertilizers are very commonly used in these areas,
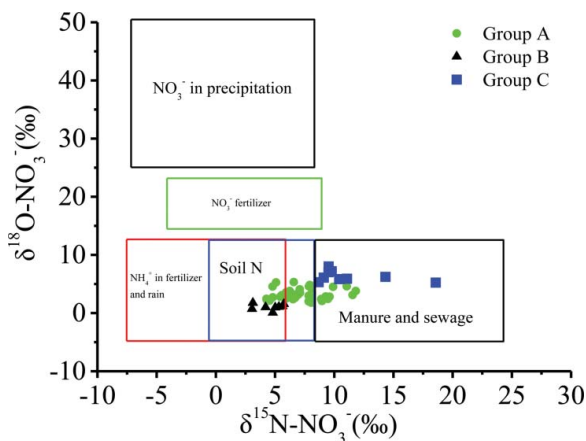

**Figure 4.** Identification of nitrate sources in the groundwater samples.

revealing that the dominant nitrate source of these groundwater samples might be NH_4^+ fertilizers that underwent processes such as volatilization and nitrification (Yuan *et al.* 2012; Matiatos 2016).

Nitrate concentrations of Group C that included nine groundwater samples ranged from 9.35 to 203.40 mg/l with an average of 139.58 mg/l. $\delta^{15}N$-NO_3^- and $\delta^{18}O$-NO_3^- values of Group C varied between +8.68‰ and +18.57‰ and +5.23‰ and +8.01‰. The isotopic signatures of group C mainly fell into the range for M&S sources (Figure 4), suggesting that nitrate in groundwater samples mainly derived from M&S. The sampling sites are located near the industrial and urban zones. A great deal of domestic sewage was directly discharged into the nearby ground or ditches without treatment due to the lack of wastewater treatment facilities in this study area. Therefore, nitrate in groundwater of group C might be attributed to leakage or disposal of untreated wastes from septic systems and industries. Moreover, a manure origin cannot be precluded because animal breeding frequently occurs at a small distance from the industrial and urban zones in this area. Since aquaculture is an important industry in coastal regions, coastal aquaculture might be an important nitrate source of the groundwater in group C near the aquaculture area due to the discharge of aquaculture wastewater.

Nitrogen transformations such as nitrification and denitrification are generally biogeochemical processes that may especially occur in shallow aquifers (Rivett *et al.* 2008; Xue *et al.* 2009; Hosono *et al.* 2013). Theoretically, NO_3^- derived from nitrification has $\delta^{18}O$-NO_3^- values ranging from -10‰ to $+10$‰ (Xue *et al.* 2009). The measured $\delta^{18}O$-NO_3^- values of the groundwater samples varied between +0.07‰ and +8.01‰ with a mean value of +3.43‰ (Figure 5). These relatively low values suggested that nitrification was the dominant process in the groundwater. Typically, it is considered that NO_3^- produced from autotrophic nitrification contains two-thirds of the O_2 from local water (*e.g.* soil water, groundwater, etc.) and one-third of the O_2 from atmospheric oxygen (+23.5‰) (Wassenaar 1995). Therefore, measured $\delta^{18}O$-H_2O values in the groundwater can be used to estimate the theoretically $\delta^{18}O$-NO_3^- of groundwater during nitrification. Measured $\delta^{18}O$-H_2O values of groundwater in the study area ranged from -8.35‰ to -4.63‰ with a mean value of
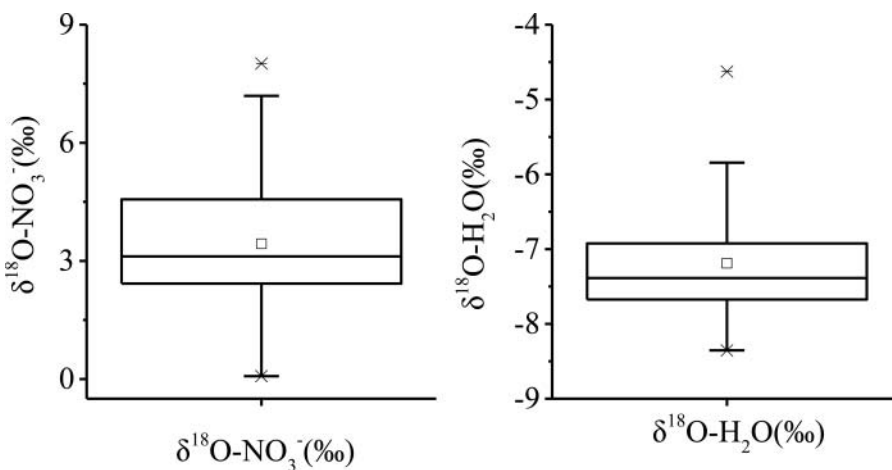
Figure 5. Box plots of $\delta^{18}O$-NO_3^- and $\delta^{18}O$-H_2O.
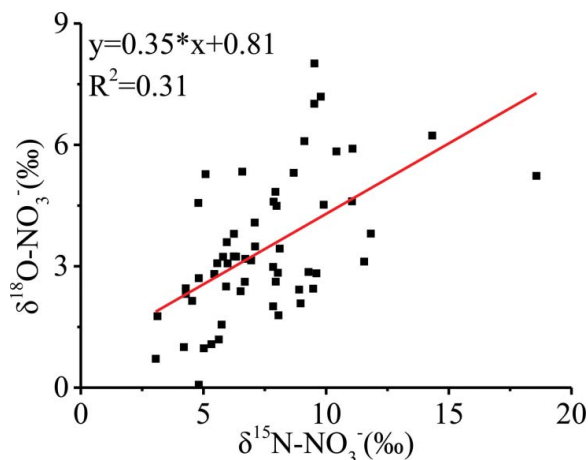
Figure 6. Relationship between $\delta^{15}N\text{-}NO_3^-$ and $\delta^{18}O\text{-}NO_3^-$ values of the groundwater samples.

−7.19‰ (Figure 5). Consequently, the expected $\delta^{18}O\text{-}NO_3^-$ values for groundwater nitrate derived from nitrification should be ranged from +2.26‰ to +4.75‰ with mean value of +3.04‰ according to the equation of $\delta^{18}O\text{-}NO_3^- = 2/3\ (\delta^{18}O\text{-}H_2O) + 1/3\ (\delta^{18}O\text{-}O_2)$ (Jakóbczyk-Karpierz *et al.* 2017). The theoretically expected value was close to but narrower than the measured $\delta^{18}O\text{-}NO_3^-$ values ($\delta^{18}O\text{-}NO_3^- = +3.43‰ \pm +1.71‰$), indicating that groundwater nitrate was derived from the nitrification of organic soil N, NH_4^+ fertilizer, and M&S.

In theory, a remarkably positive linear relationship between $\delta^{15}N\text{-}NO_3^-$ and $\delta^{18}O\text{-}NO_3^-$ will be observed if significant denitrification occurs (Singleton *et al.* 2007; Sacchi *et al.* 2013). No significant correlation of $\delta^{15}N\text{-}NO_3^-$ and $\delta^{18}O\text{-}NO_3^-$ was observed in the groundwater samples (Figures 4 and 6). Moreover, the DO concentrations in the groundwater samples illustrated in Table 1 were much higher than the O_2 concentration suitable for denitrification (Rivett *et al.* 2008). In consideration of the oxic groundwater conditions, denitrification was not a major process in groundwater.

Contribution of different nitrate sources determined by SIAR

Based on the previous analysis of $\delta^{15}N\text{-}NO_3^-$ and $\delta^{18}O\text{-}NO_3^-$ isotopic characteristic values for the groundwater samples, it is clear that nitrate in the groundwater originated from soil N, NH_4^+ fertilizer, and M&S. However, the contribution rate of the potential nitrate sources cannot be distinguished by the bi-plot approach. To quantify the contribution proportions of the each nitrate source, SIAR model that can only be applied with two or more values (El Gaouzi *et al.* 2013) was used to estimate the probability distribution for the relative contribution of each source in the study area. Contribution proportions of different nitrate sources including soil N, NH_4^+ fertilizer, and M&S for groundwater samples were determined by SIAR for Groups A, B, and C, respectively (Figure 7). The source contributions to groundwater nitrate were assessed by SIAR which incorporate the source uncertainty as the 25th and 75th confidence intervals, and the ranges of the mean values (Figure 7).

In this study, the mean values of contribution proportions were used for further analysis. The mean values revealed a high variability in contribution of the three potential NO_3^-
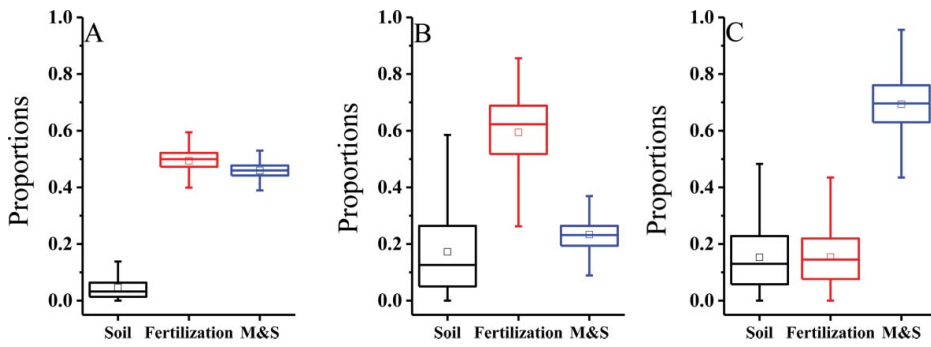
Figure 7. Contribution proportions of different nitrate sources for groundwater.

sources for different groups of the groundwater samples (Figure 7). The results demonstrated that NH_4^+ fertilizer was the dominant source for groundwater samples of Group A, with the mean contribution proportion of 50%. M&S also contributed significantly, with the mean proportion of 46%. The mean contribution proportion of soil N was only 4% for groundwater samples of Group A. NH_4^+ fertilizer contributed 60% of the NO_3^- in groundwater for Group B. M&S and soil N contributed to groundwater nitrate for Group B with average proportions of 23% and 17%, respectively. M&S served as dominant nitrate contribution source for the groundwater samples of group C, with the mean contribution proportion of 70%. NH_4^+ fertilizer and soil N showed similar contribution pattern, contributing to the groundwater nitrate with proportions of 15% and 15%, respectively.

On the whole, the nitrate source contributions determined by SIAR model were reasonable and in accordance with previous analysis by $\delta^{15}N$-NO_3^- and $\delta^{18}O$-NO_3^- isotope characteristics. Comparing the above findings with the specific NO_3^- pollution sources, it was found that the dominant nitrate pollution sources of groundwater NO_3^- in the study area were NH_4^+ fertilizer and M&S. This may be attributed to two reasons. Firstly, chemical fertilizer and manure are widely used to increase crop production in the study area where winter wheat, summer maize, and vegetable crops are widely cultivated. Excessive use of fertilizer in China is well known, with average farmland application amount per unit area of three times the world average (Ministry of Environmental Protection 2011). In the study area, fertilizers (300–600 kg/ha) are usually applied for better cultivation. Moreover, organic fertilizers such as pig and cattle manures (500–1000 kg/ha) are also generally used for crops. However, the efficiency of utilizing fertilizers in China is only 30%–40%, accompanying about half of the nitrogen lost by volatilization and another 5%–10% lost by leaching (Gu *et al.* 2013). Excessive use of agricultural fertilizers in the area has deteriorated groundwater nitrate pollution. Secondly, sewage waste and/or manure are important nitrate sources in the groundwater of the study area. Industrial and domestic sources produce more than 3.0×10^{10} m^3 untreated sewage in China every year, and the sewage discharge into rivers is used for irrigation of farmland (Zhang *et al.* 2014). It is assumed that the amount of sewage will dramatically increase in the study area in accordance with significant progression of economic developments and urbanization. Moreover, this sewage is usually under low-level or no treatment before discharge, resulting in the high nitrate concentration in the groundwater. In addition, mineralization of soil organic N was another nitrate

source of the groundwater. Due to the sea-water intrusion, soil salinization is serious in this region (Wen *et al.* 2012). In order to increase the soil organic matter content and control saline-alkali soil, straw and stalks of crops are widely reused in the study area (Jia *et al.* 2010) to cause increased soil organic N content. Soil organic N is an important source of NO_3^- pollution of groundwater, which is also corresponded by the findings of this study.

The results from SIAR outputs showed that NO_3^- in the groundwater mainly originated from NH_4^+ fertilizer and M&S. Although our results provide important information for controlling nitrate concentrations in the groundwater, it has some limitations. Firstly, only the spatial variation of nitrate sources in different groups was investigated in this study. Therefore, further research is necessary to understand the temporal variation of NO_3^- sources in the groundwater. Secondly, the mean and standard deviations of potential NO_3^- sources used in this study were mostly cited from literatures. Thus, the outputs obtained from SIAR model will become more precise if site-specific and more accurate isotope information on $\delta^{15}N$-NO_3^- and $\delta^{18}O$-NO_3^- values of sources from the study area can be obtained. Thirdly, the model gave large confidence intervals in this work, which might cause large uncertainty in the apportionment results. The outputs of Group A which had 40 samples showed smaller confidence intervals based on SIAR results, which illustrated that information derived from large number of samples could reduce the uncertainty and improve discrimination of nitrate source.

Conclusions

Stable isotope technique and SIAR model was firstly used to identify the nitrate sources and contribution proportions of different sources in typical coastal groundwater in northern China. About 91.5% of the groundwater samples collected from Laizhou Bay coastal area illustrated significantly high nitrate concentrations which exceeded WHO drinking water standard, reflecting the high risk of groundwater nitrate pollution in the study area. A total of 57 sampling sites were classified into three clusters according to HCA. The $\delta^{15}N$-NO_3^- and $\delta^{18}O$-NO_3^- values of groundwater samples from Group C were much higher than those from Groups A and B. SIAR results showed that NH_4^+ fertilizer was the dominant nitrate source for groundwater samples of Groups A and B while manure and sewage served as dominant source for Group C. The results obtained in this study will provide important information for groundwater management and nitrate pollution control in the coastal zone.

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