

NITRATE SOURCE DISTRIBUTION IN RIVERS, ESTUARIES AND GROUNDWATER USING A DUAL ISOTOPE APPROACH AND A BAYESIAN ISOTOPE MIXING MODEL

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Abstract. Identification and quantification of nitrate (NO_3^-) sources in rivers, estuaries and shallow groundwater (SG) may help implementation in the water quality control measures. In this study, a dual isotope approach ($\delta^{15}\text{N}$ - and $\delta^{18}\text{O}$ - NO_3^-) and Bayesian isotope mixing model (SIAR) have applied to estimate the proportional contributions of NO_3^- from precipitation (NP), NO_3^- fertilizer (NF), ammonia nitrogen (NH_4^+) from fertilizer and rain (NF&R), soil N (Soil), and manure and sewage (M&S) for six rivers, two estuaries and SG in a coastal municipality in northern China. The combination of “M&S” (17-56%), “Soil” (21-37%), and “NF&R (14-25%)” contributions occupied more than 60% in total, and were considered as the dominant NO_3^- sources for the rivers and estuaries. The mean proportions of “NF” ranged from 6 to 20% and “NP” ranged from 2 to 11%, respectively. For SG, the mean proportions of “M&S” (27%), “Soil” (22%), and “NF&R” (21%) occupied about 70% in total, while the residual two NO_3^- sources occupied about 19% for “NF” and 11% for “NP”. We suggest that this approach can be easily modified determine NO_3^- sources and help to develop better N management practices in other environments where NO_3^- is a major N contributor.

Keywords: $\delta^{15}\text{N}$ - NO_3^- , $\delta^{18}\text{O}$ - NO_3^- , sources identification, SIAR, N contribution

Introduction

NO_3^- contamination in aquatic systems has become a serious environmental problem throughout the world. With the increasing population, extensive agricultural activities and rapid development of urbanization, the high NO_3^- levels of water impose a serious threat to drinking water and promote eutrophication, hypoxia, loss of biodiversity and habitat destruction both in riverine and coastal ecosystems (Galloway et al., 2003; Li et al., 2013; Umezawa et al., 2008; Villnäs et al., 2013). Monitoring NO_3^- concentrations alone cannot fully assess the sources and distribution of NO_3^- inputs in aquatic systems, which are the key factors in protecting water quality and reducing NO_3^- loadings.

Since NO_3^- from different sources (fertilizer, manure, human sewage, soil N and atmospheric deposition) have distinct isotopic compositions, it is possible to identify these different sources using N ($\delta^{15}\text{N}$) and O ($\delta^{18}\text{O}$) isotopic values (Xue et al., 2012; Wankel et al., 2015). Pardo et al. (2004) successfully used a dual isotope approach ($\delta^{15}\text{N}$ - and $\delta^{18}\text{O}$ - NO_3^-) to identify atmospheric deposition and microbial nitrification as the two main sources of NO_3^- in stream water at two forested watersheds. Chang et al. (2002) found that $\delta^{15}\text{N}$ and $\delta^{18}\text{O}$ values of NO_3^- indicated manure as the predominant source when discharge and NO_3^- concentrations were low (winter), and soil-derived NO_3^- as the predominant source when discharge and NO_3^- concentrations were high

(spring-summer) in Mississippi River Basin. For the second tributary Pearl River in southern China, Chen et al. (2009) and Jin et al. (2017) pointed out that the N and O isotopic values fell in the range of nitrification of reduced fertilizer N in soil zones. Li et al. (2010) found that the $\delta^{15}\text{N}$ - and $\delta^{18}\text{O}$ - NO_3^- values of the Yangtze River indicating a main source from urban sewage effluent.

In addition, to reduce NO_3^- loadings in aquatic systems, it is quite meaningful to quantify the contributions of different NO_3^- sources. Some researchers, Deutsch et al. (2006) and Yang et al. (2018) also applied $\delta^{15}\text{N}$ - and $\delta^{18}\text{O}$ - NO_3^- to quantify NO_3^- source distribution in water via a mass balance mixing model (Semmens et al., 2013). However, this method is limited to (1) temporal and spatial variability in $\delta^{15}\text{N}$ - and $\delta^{18}\text{O}$ - NO_3^- ; (2) isotope fractionation by denitrification; and (3) number of sources > number of isotopes + 1 (Moore et al., 2008; Xue et al., 2009). A mixing model for stable isotope analysis called SIAR (stable isotope analysis in R) under a Bayesian framework has been developed to solve source distribution problems (Parnell et al., 2010). The disadvantages of a mass balance mixing model mentioned above are overcome. Xue et al. (2012) successfully applied SIAR to estimate NO_3^- source distribution of surface waters of Flanders in Belgium. Thereafter, SIAR was also applied to evaluate contributions of NO_3^- sources in underground water (Gaouzi et al., 2013; Chen et al., 2015), rivers (Ding et al., 2014) and reservoir (Yang et al., 2013), respectively.

Tianjin is an important coastal municipality located in the Bohai Bay in northern China. An investigation of surface waters of Tianjin (Wang et al., 2009) reported that NO_3^- concentrations could highly reach up to 10.3 mg L^{-1} in rivers, and about 8.1% of agricultural drainages that NO_3^- concentrations were over 15 mg L^{-1} . Wang et al. (2011) concluded that NO_3^- was the dominant Dissolved inorganic nitrogen (DIN) species in coastal water of Tianjin, with water quality deteriorating. Thus, it is essential to specify predominant NO_3^- sources and assess potential NO_3^- source distribution, which is of great significance to control water contamination and protect coastal ecological system. The aim of this study is to: (1) apply a dual isotope bi-plot approach ($\delta^{15}\text{N}$ - and $\delta^{18}\text{O}$ - NO_3^-) combining with physicochemical properties to identify NO_3^- sources; and (2) apply the SIAR model to estimate the contributions of potential NO_3^- sources in rivers, estuaries and shallow groundwater (SG) in Tianjin.

Material and methods

Study area

The investigated rivers, estuaries and SG are located in Tianjin, a coastal municipality in northern China (Fig. 1). The study region is mainly influenced by a warm temperate semi-humid monsoon climate with an average annual temperature of $11.4\text{--}12.9 \text{ }^\circ\text{C}$, and the annual precipitation of $520\text{--}660 \text{ mm}$ (Yue et al., 2010; Wang et al., 2014). The geological structure is complex, and mostly covered by Cenozoic sediments. The terrain is dominated by plains and depressions, with low mountains and hills in the north, and the altitude gradually decreases from north to south. The highest and lowest altitude are 1052 m and 3.5 m in the north and southeast, respectively. The total area of Tianjin is 11919.7 km^2 and the coastline is about 153.0 km (Wang et al., 2013).

The six rivers distributed from north to south are Jiyun River (JY River), Chaobaixin River (CB River), Haihe River (HH River), Dagu sewage River (DG River), Duliujian River (DL River), and Ziyaxin River (ZY River), respectively. The properties of the river are shown in Table 1. The northern rivers, the JY River and the CB River flowing

through a rural area and are characterized by 144 km and 81 km in length, 300 m and 700 m in width, 7 m and 5-7 m in depth, and a watershed area of 2416 km² and 1387 km², respectively (Starks et al., 2014; Chen et al., 2000). Precipitation is the main water supply of the JY River so that the runoff seasonally changed. There is an important livestock breeding base in the watershed area of the CB River. Upper reaches are the main water supply of CB River. The rivers of HH and DG flow through the urban and industrial area in the middle of the municipality. The DG River is characterized by 71 km in length, 54-120 m in width, and a watershed area of 1000 km², which is an important river channel that holds industrial wastewater and domestic sewage (Guo et al., 2009). The HH River is characterized by 72 km in length, 100 m in width, 3-5 m in depth, and a watershed area of 2066 km², and water mainly come from the precipitation and upper reaches (Liu et al., 2010). The HH River is separated by a floodgate into two parts: the upstream of the HH River (HHup) flow through the center of the municipality, while the downstream of the HH River (HHdw) flow through the industrial area. The southern rivers DL and ZY flow through the agricultural and industrial area. The DL River is characterized by 70 km in length, and 400 m in width (Lai et al., 2001), where the upper reaches is the main water supply of DL River. The ZY River is characterized by 29 km in length and 100-300 m in width (Ding et al., 2016), and water mainly come from the precipitation and upper reaches. One of the studied estuaries is the confluence of the JY and the CB River (CJ Estuary) in north, and the design flow is 4640 m³/s (Dong et al., 2007). The other is the estuary of the HH River (HH Estuary) in middle, and the design flow is 800 m³/s (Dong et al., 2007).

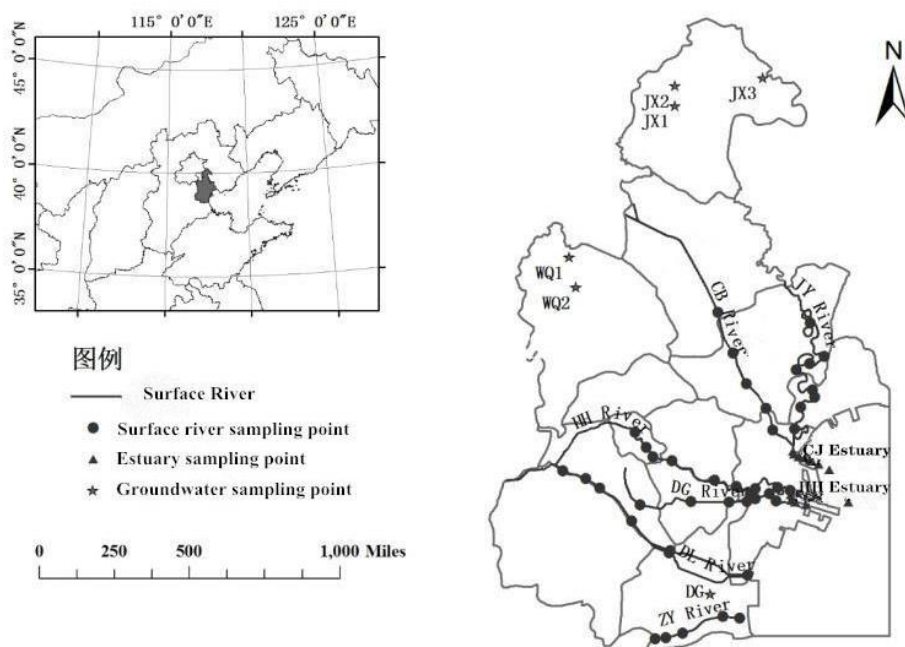


Figure 1. Sampling locations for six rivers, two estuaries and groundwater. JY, CB, HH, DG, DL and ZY River are the abbreviations of the Jiyun River, the Chaobaixin River, the Haihe River, the Dagang sewage River, the Duliujian River and the Ziyaxin River, respectively. CJ, HH are the abbreviations of the CJ Estuary (co-estuary of the JY and the CB River) and Haihe Estuary, respectively. DG, JX and WQ are the abbreviations of Dagang, Jixian and Wuqing, which are all located in the rural areas of Tianjin. Number represent different sampling locations and -May and -Nov represent samples were collected in mid-May and mid-November during dry and wet periods, respectively

Table 1. Properties of the rivers and the corresponding estuaries

Location	Longitude	Latitude	Length (km)	Width (m)	Depth (m)	Drainage area (km ²)	Design flow (m ³ /s)
JY River	117.83732 °E	39.34846 °N	144	300	7	2416	–
CB River	117.38531 °E	39.60658 °N	81	700	5~7	1387	–
CJ Estuary	117.48532 °E	39.03454 °N	–	–	–	–	4640
HH River	117.19165 °E	39.14954 °N	72	100	3~5	2066	–
HH Estuary	117.46202 °E	38.57143 °N	–	–	–	–	800
DG River	117.21497 °E	38.95831 °N	71	54~120	–	1000	–
DL River	116.94644 °E	39.04793 °N	70	400	–	–	–
ZY River	117.25816 °E	38.60085 °N	29	100~300	–	–	–

The water table of SG in the study area displays different spatial distribution: it is about 10 to 50 m in the northern piedmont plain, 30 to 80 m in the middle plain and 2 to 3 m in the southern littoral plain. Particularly, in recent 20 years, the SG table is steady in northwest and eastern plain of Tianjin, while it goes down yearly in the coastal areas (Wang et al., 2014). Most rivers in this study are artificial, where groundwater cannot compensate because of the relatively low groundwater table level. The flood seasons occurred in July and August, while from May to June and September to next February were dry seasons.

Sampling and analysis

Samples were collected along the rivers and estuaries in November 2012 and SG samples were sampled in mid-May 2014 and mid-November 2014, during dry and wet periods, respectively. Water samples were taken on a bridge using a bucket serially from upstream downwards for the rivers and on a ship for estuarine water. The bucket was put into the river/estuary water until it reached ~0.5 m below the surface to sample water. SG is extracted by pumping pump and collected after the water flow is stable (about 5 min). Then, the water samples were stored frozen in 1 L high-density polyethylene (HDPE) bottles for determination of physico-chemical properties and $\delta^{15}\text{N}$ - and $\delta^{18}\text{O}$ - NO_3^- . Salinity, pH and dissolved oxygen (DO) were determined in situ by a portable water quality probe (Thermo Orion, USA). Water samples were filtered through 0.45 μm membrane filters and stored at 4 °C until analysis. NO_3^- , nitrite (NO_2^-) and NH_4^+ concentrations were analyzed on a continuous flow analyzer (Auto Analyzer 3, Seal, Germany). Chloride (Cl^-) was determined by ion chromatography (ICS–2100, Dionex, USA). The $\delta^{15}\text{N}$ - and $\delta^{18}\text{O}$ - NO_3^- values were determined by “Bacterial denitrification method” (Mcilvin et al., 2011; Templer et al., 2011; Xue et al., 2010) in the UC Davis Stable Isotope Facility of California University.

Stable isotope data of ^{15}N and ^{18}O are expressed in delta (δ) units in per mill (‰) relative to their respective international standards: atmospheric air (AIR) and Vienna standard mean ocean water 2 (VSMOW 2):

$$\delta_{\text{sample}} (\text{‰}) = \left(\frac{R_{\text{sample}}}{R_{\text{standard}}} - 1 \right) * 1000 \quad (\text{Eq.1})$$

where R_{sample} and R_{standard} refer to the $^{15}\text{N}/^{14}\text{N}$ or $^{18}\text{O}/^{16}\text{O}$ ratio of the sample and standard for $\delta^{15}\text{N}$ and $\delta^{18}\text{O}$, respectively. The calibration standards are the nitrate salts USGS 32, USGS 34, and USGS 35, supplied by NIST (National Institute of Standards and Technology, Gaithersburg, MD).

Source distribution mixing model (SIAR)

The contribution proportions of NO_3^- sources to surface water samples were quantified using the SIAR model (Parnell et al., 2010) as follows:

$$X_{ij} = \sum_{k=1}^K p_k (s_{jk} + c_{jk}) + \varepsilon_{ij} \quad (\text{Eq.2})$$

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

$$c_{jk} \sim N(\lambda_{jk}, \tau_{jk}^2)$$

$$\varepsilon_{ij} \sim N(0, \sigma_j^2)$$

where X_{ij} is the observed isotope value j of the sample i ($i = 1, 2, 3, \dots, N$ and $j = 1, 2, 3, \dots, J$); s_{jk} is the source value k on isotope j ($k = 1, 2, 3, \dots, K$) and normally distributed with mean μ_{jk} and variance ω_{jk}^2 ; c_{jk} is the fractionation factor for isotope j on source k and normally distributed with mean λ_{jk} and variance τ_{jk}^2 ; ε_{ij} is the residual error which describes additional variation between sample measurements, and it is normally distributed with mean 0 and variance σ_j^2 ; p_k is the proportion of source k estimated by SIAR.

The fractionation factor, c_{jk} is relevant to denitrification. This process can result in an exponential increase of $\delta^{15}\text{N}$ - and $\delta^{18}\text{O}$ - NO_3^- as NO_3^- concentration decreases. An enrichment of ^{15}N relative to ^{18}O by a factor between 0.8 and 2.0 gives evidence for denitrification (Aravena and Robertson., 2010; Fukada et al., 2003; Xue et al., 2009). The enrichment factors (ε) of denitrification can be calculated via the relation between the isotopic values and the logarithm of residual NO_3^- and are expected to fall into the range from -40‰ to -5‰ for $\varepsilon^{15}\text{N}$ and from -18‰ to -8‰ for $\varepsilon^{18}\text{O}$ (Hubner, 1986; Bottcher et al., 1990; Smith et al., 1991; Mengis et al., 1999; Fukada et al., 2003; Sebiló et al., 2003; Knöller et al., 2011).

Statistical analysis

In this study, the principle coordinate analysis (PCoA) has been applied to evaluate the data sets of physicochemical properties of the six rivers and the corresponding estuaries and shallow groundwater samples.

Results and discussion

Physicochemical properties of the rivers and the corresponding estuaries

The physicochemical properties and isotopic values of the water samples were shown in *Table 2*. The mean pH of the rivers and their corresponding estuaries changed from 7.4 to 8.4, and the mean DO concentrations ranged from 4.1 to 11.2 mg L⁻¹. The mean salinity of the middle rivers (2.5-3.2) except the HHup (0.7) was higher than the northern (0.5-0.7) and southern rivers (1.9-2.5). The municipality had been suffering multiple seawater intrusion and regression, which results in the salinization of the rivers and soil (Wang, 2004).

Table 2. *Physicochemical properties and isotopic composition of NO₃⁻ for the rivers and the corresponding estuaries*

Location	pH	DO	Salinity	Cl ⁻	NO ₃ ⁻	NH ₄ ⁺	NO ₂ ⁻	δ ¹⁵ N- NO ₃ ⁻	δ ¹⁸ O- NO ₃ ⁻
				mg L ⁻¹				‰	
CB River	7.9	8.9	0.5	117.0	7.4	6.0	1.8	13.7	4.0
	8.6	10.5	0.5	138.5	8.3	3.0	0.5	14.0	4.8
	8.5	9.1	0.5	161.4	9.8	6.8	0.6	13.9	3.9
	8.5	9.9	0.5	180.6	10.6	2.6	0.5	12.2	4.3
	8.6	10.4	0.6	184.0	10.6	6.6	0.4	13.7	4.8
	8.2	10.0	0.6	195.0	9.4	3.8	0.3	14.1	5.6
Mean ± SD	8.4 ± 0.3	9.8 ± 0.7	0.5 ± 0.1	162.8 ± 30.0	9.4 ± 1.3	4.8 ± 1.9	0.7 ± 0.6	13.6 ± 0.7	4.6 ± 0.6
JY River	8.1	7.2	0.6	171.4	2.5	1.3	0.3	6.5	0.9
	8.2	8.7	0.7	194.9	2.6	1.2	0.3	6.3	2.0
	8.2	7.5	0.7	206.4	2.7	1.0	0.2	6.4	1.4
	8.4	9.3	0.7	215.6	2.9	0.9	0.2	5.8	0.8
	8.4	9.3	0.8	233.7	4.7	0.2	0.3	5.3	1.3
	8.4	9.7	0.8	251.1	4.8	0.5	0.2	5.3	1.1
	8.5	9.9	0.8	254.3	5.2	0.2	0.1	4.4	2.8
	8.5	9.9	0.8	254.5	5.1	0.6	0.1	4.4	5.3
Mean ± SD	8.3 ± 0.2	8.9 ± 1.1	0.7 ± 0.1	222.7 ± 30.8	3.8 ± 1.2	0.7 ± 0.4	0.2 ± 0.1	5.6 ± 0.8	2.0 ± 1.5
CJ Estuary	8.2	10.6	2.0	7028.2	9.5	5.9	0.2	13.6	5.9
	8.2	11.4	2.5	4973.9	7.4	5.5	0.2	15.0	6.1
	8.3	11.5	2.7	1201.1	6.8	5.1	0.4	14.7	6.4
	8.3	11.1	4.2	1216.8	8.1	5.2	0.3	13.6	6.4
	8.3	11.4	9.0	509.6	2.3	3.3	0.4	11.9	6.2
	8.3	11.3	13.7	2172.8	1.5	2.2	0.3	9.3	6.7
	8.3	11.2	20.0	9831.6	0.4	0.8	0.2	7.1	6.9
	Mean ± SD	8.3 ± 0.1	11.2 ± 0.3	7.7 ± 6.9	3847.7 ± 3537.1	5.1 ± 3.6	4.0 ± 1.9	0.3 ± 0.1	12.2 ± 3.0
HHup River	7.5	2.7	0.7	207.2	13.6	4.0	0.8	-0.2	-0.5
	7.7	4.0	0.7	184.6	9.0	6.0	0.8	0.5	0.2
	7.7	4.8	0.7	219.1	8.3	5.6	0.9	0.6	0.2
	7.9	5.0	0.8	275.8	6.5	5.9	1.0	1.1	0.5
Mean ± SD	7.7 ± 0.2	4.1 ± 1.0	0.7 ± 0.1	221.7 ± 38.8	9.4 ± 3.0	5.4 ± 0.9	0.9 ± 0.1	0.5 ± 0.5	0.1 ± 0.4
HHdw River	8.1	8.2	1.0	408.2	5.9	2.8	1.0	4.5	0.6
	8.4	10.4	2.3	1441.5	5.6	2.2	0.3	4.6	1.1
	8.5	10.5	2.4	1696.6	5.8	2.3	0.5	4.3	1.3
	8.3	10.4	3.7	1983.0	5.5	2.3	0.4	3.9	1.2
	8.3	9.9	4.6	2673.9	3.9	2.8	0.7	8.4	1.5
	8.2	9.4	4.9	3486.6	4.3	2.7	0.7	7.4	1.4
Mean ± SD	8.3 ± 0.1	9.8 ± 0.9	3.2 ± 1.5	1948.3 ± 1057.0	5.2 ± 0.8	2.5 ± 0.3	0.6 ± 0.3	5.5 ± 1.9	1.2 ± 0.3

HH Estuary	8.1	10.7	18.6	10225.6	1.6	1.6	0.3	8.0	5.4
	8.1	10.7	20.6	10519.7	1.1	1.4	0.3	7.9	5.6
	8.2	10.7	21.3	12202.2	0.9	1.4	0.3	8.1	5.7
	8.2	10.7	24.1	13270.0	0.4	1.2	0.3	8.3	5.8
Mean ± SD	8.2 ± 0.1	10.7 ± 0.0	21.2 ± 2.3	11554.4 ± 1437.5	1.0 ± 0.5	1.4 ± 0.2	0.3 ± 0.0	8.1 ± 0.2	5.6 ± 0.2
DG River	8.1	9.1	1.8	707.9	6.0	2.5	0.7	7.2	3.0
	7.0	5.7	1.7	699.8	5.3	14.5	0.4	8.4	2.9
	7.2	3.8	2.3	1050.9	0.2	16.7	0.0	11.6	5.1
	7.1	5.5	3.0	1397.3	3.9	14.2	0.6	7.7	0.5
	7.8	8.7	3.6	1804.1	6.9	10.6	0.5	6.2	1.5
Mean ± SD	7.4 ± 0.5	6.6 ± 2.3	2.5 ± 0.8	1132.0 ± 473.1	4.4 ± 2.6	11.7 ± 5.6	0.4 ± 0.3	8.2 ± 2.0	2.6 ± 1.7
DL River	8.2	10.8	1.8	723.7	9.6	2.7	0.4	4.0	2.5
	7.7	7.7	1.8	731.3	12.5	10.4	0.9	6.8	3.6
	7.7	8.3	2.0	791.4	11.2	9.0	1.0	6.5	7.2
	8.3	10.9	2.5	1043.5	12.5	1.2	0.3	4.3	2.5
	8.2	11.3	2.4	1105.3	11.1	0.1	0.1	4.2	3.0
	8.2	11.1	2.9	1410.1	11.2	2.0	0.0	6.4	7.7
Mean ± SD	8.1 ± 0.3	10.0 ± 1.6	2.2 ± 0.4	967.6 ± 270.9	11.4 ± 1.1	4.2 ± 4.3	0.5 ± 0.4	5.4 ± 1.3	4.4 ± 2.4
ZY River	7.3	9.1	1.8	736.7	5.5	34.3	2.2	8.2	7.7
	7.5	10.1	1.8	697.9	5.4	51.9	2.1	7.9	8.2
	7.3	9.1	1.7	701.4	4.9	52.4	1.9	8.7	9.2
	7.4	9.4	1.9	839.8	4.4	55.7	2.0	8.9	8.9
	7.4	9.3	2.1	929.3	2.4	61.2	1.8	14.1	13.4
Mean ± SD	7.4 ± 0.1	9.4 ± 0.4	1.9 ± 0.2	781.0 ± 100.8	4.5 ± 1.3	51.1 ± 10.1	2.0 ± 0.2	9.6 ± 2.6	9.5 ± 2.3

The mean Cl^- concentrations were relatively high, varying from 162.8 to 1948.3 mg L^{-1} for the rivers and from 3847.7 to 11554.4 mg L^{-1} for the estuaries. Both the salinization and anthropogenic activities, such as sewage and livestock effluent can cause relatively high Cl^- concentrations in the rivers (Yao et al., 2007). The relatively higher mean NO_3^- concentrations appeared in the rivers of DL (11.4 mg L^{-1}), CB (9.4 mg L^{-1}) and the HHup (9.4 mg L^{-1}); the relatively lower mean NO_3^- concentrations appeared in the rivers of JY (3.8 mg L^{-1}). The mean NO_3^- concentrations of the estuaries were 5.1 mg L^{-1} for the CJ Estuary and 1.0 mg L^{-1} for the HH Estuary. The mean NH_4^+ concentrations varied largely from 0.7 to 51.1 mg L^{-1} . The highest mean NH_4^+ concentration appeared in the ZY River because of intensive industry along the upstream of the river and large volume discharge of low treatment rate of sewage (He and Huang, 2013).

The mean NO_2^- concentrations of the rivers and their corresponding estuaries changed from 0.2 to 2.0 mg L^{-1} . The isotopic composition of NO_3^- varied spatially among the rivers and the corresponding estuaries (Table 2). The mean $\delta^{15}\text{N}-\text{NO}_3^-$ values varied from 0.5 to 13.6‰ and the mean $\delta^{18}\text{O}-\text{NO}_3^-$ values varied from 0.1 to 9.5‰. The relatively large isotopic range potentially indicates that the rivers and estuaries were influenced by complex NO_3^- sources.

The PCoA results revealed that the rivers and the corresponding estuaries were divided into three parts (Fig. 2). The rivers of CB, JY and HHup with low salinity located in the north of Tianjin were grouped together, while the rivers of HHdw, DG, DL and ZY with high salinity were grouped together. The residual two estuaries (CJ and HH) were grouped together with highest salinity.

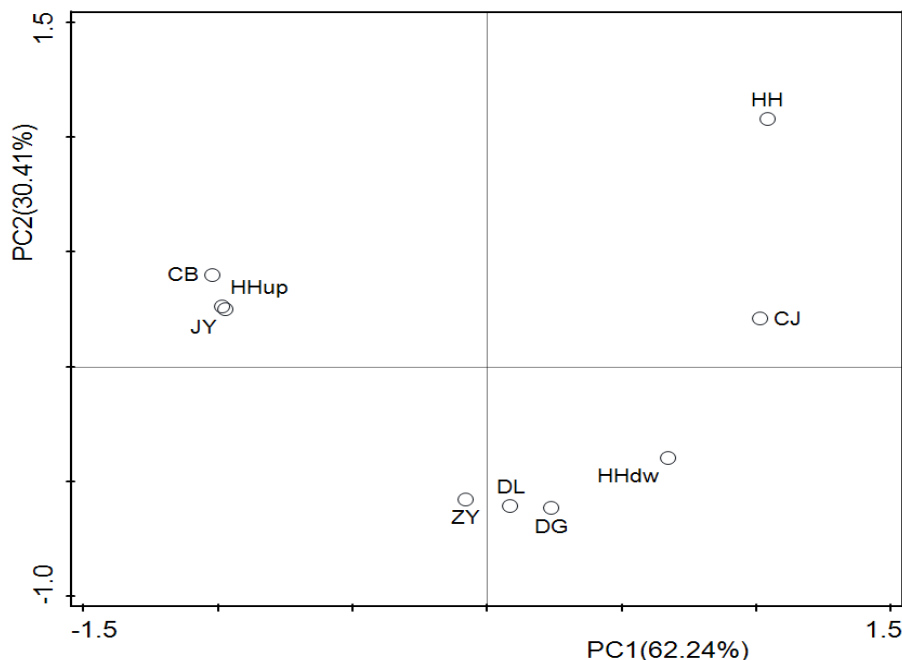


Figure 2. Principle coordinate analysis for physicochemical properties of the six Rivers and the corresponding Estuaries. CB, JY, HHup, HHdw, DL, ZY and DG River are the abbreviations of the Chaobaixin River, the Jiyun River, the upstream of the Haihe River, the downstream of the Haihe River, the Duliujian River, the Ziyaxin River and the Dagu sewage River, respectively. CJ, HH are the abbreviations of the CJ Estuary (co-estuary of the JY and the CB River) and Haihe Estuary, respectively

Physicochemical properties of the SG

The physicochemical properties and isotopic values of the SG were shown in Table 3. The average pH of SG in May and November was 7.1 and 7.4, with a range between 6.6 to 7.8 and 6.9 to 8.2, respectively. The mean DO was 4.6 mg L⁻¹ and 5.9 mg L⁻¹, and varied from 1.9 to 7.9 mg L⁻¹ and 1.7 to 8.4 mg L⁻¹, respectively. The average salinity and its variations ranged between 0.4 to 3.2 with a mean value of 1.1 in May and between 0.4 to 3.3 with a mean value of 1.2 in November, respectively.

The mean Cl⁻ concentrations in SG were higher in May (1085.2 mg L⁻¹) than that in November (420.1 mg L⁻¹), with a maximum Cl⁻ concentration achieved as high as 2704.3 mg L⁻¹. The average concentration of NO₃⁻ in May was 117.5 mg L⁻¹ lower than that of 159.8 mg L⁻¹ in November. The variation was in a large range, from 0.3 to 221.9 mg L⁻¹ and 6.7 to 360.3 mg L⁻¹ in May and November, respectively.

The average concentrations of NO₂⁻ in November and May were 0.06 mg L⁻¹ and 0.06 mg L⁻¹, with a range from 0.01 to 0.15 mg L⁻¹ and 0.01 to 0.21 mg L⁻¹, respectively. The average concentration of NH₄⁺ was 0.3 mg L⁻¹ and 0.2 mg L⁻¹ in May and November, with variations ranging from 0 to 0.9 mg L⁻¹ and 0 to 1.0 mg L⁻¹, respectively. The δ¹⁵N-NO₃⁻ values varied from +10.2 to +45.9‰ and +2.9 to +38.2‰ in May and November, with a mean δ¹⁵N-NO₃⁻ value of +22.5‰ and +13.5‰, respectively. The average value of δ¹⁸O-NO₃⁻ was relatively close in May (+9.9‰) and November (+10.8‰), ranging from -7.9 to +28.4‰ and +2.2 to +22.6‰.

The PCoA results revealed that groundwater sampling points of Jixian, Wuqing and Dagang were grouped into three parts (Fig. 3) based on their spatial locations.

Table 3. Physicochemical properties and isotopic composition of NO_3^- for the shallow groundwater

Season	Sampling point	pH	Salinity	DO	Cl ⁻	NO ₃ ⁻	NO ₂ ⁻	NH ₄ ⁺	$\delta^{15}\text{N} - \text{NO}_3^-$	$\delta^{18}\text{O} - \text{NO}_3^-$
			(ppt)	mg/L					‰	
May	JX1	6.6	0.5	7.9	640.6	238.0	0.04	0.0	19.6	7.5
	JX2	6.9	0.5	7.3	40.0	221.9	0.03	0.0	10.4	0.9
	JX3	6.6	0.4	4.4	551.0	128.1	0.02	0.0	10.2	-7.9
	WQ1	7.5	1.2	2.6	1291.6	0.3	0.01	0.9	31.0	28.4
	WQ2	7.2	0.9	1.9	1283.5	59.8	0.04	0.8	17.6	8.7
	DG	7.8	3.2	3.5	2704.3	56.9	0.21	0.0	45.9	21.9
	Mean ± S D	7.1 ± 0.4	1.1 ± 0.9	4.6 ± 2.3	1085.2 ± 844.5	117.5 ± 87.8	0.06 ± 0.07	0.3 ± 0.4	22.5 ± 12.6	9.9 ± 12.2
November	JX1	7.1	0.6	8.4	64.4	276.1	0.02	0.0	10.7	5.4
	JX2	7.2	0.6	7.7	62.0	360.3	0.03	0.0	3.2	7.1
	JX3	6.9	0.4	3.4	44.3	186.9	0.01	0.0	2.9	2.2
	WQ1	7.5	1.1	7.3	424.8	6.7	0.14	1.0	15.5	17.0
	WQ2	7.3	1.1	1.7	272.2	74.1	0.15	0.2	10.5	10.6
	DG	8.2	3.3	6.8	1652.7	54.7	0.03	0.1	38.2	22.6
	Mean ± S D	7.4 ± 0.4	1.2 ± 0.9	5.9 ± 2.5	420.1 ± 568.2	159.8 ± 126.7	0.06 ± 0.06	0.2 ± 0.3	13.5 ± 11.9	10.8 ± 7.0

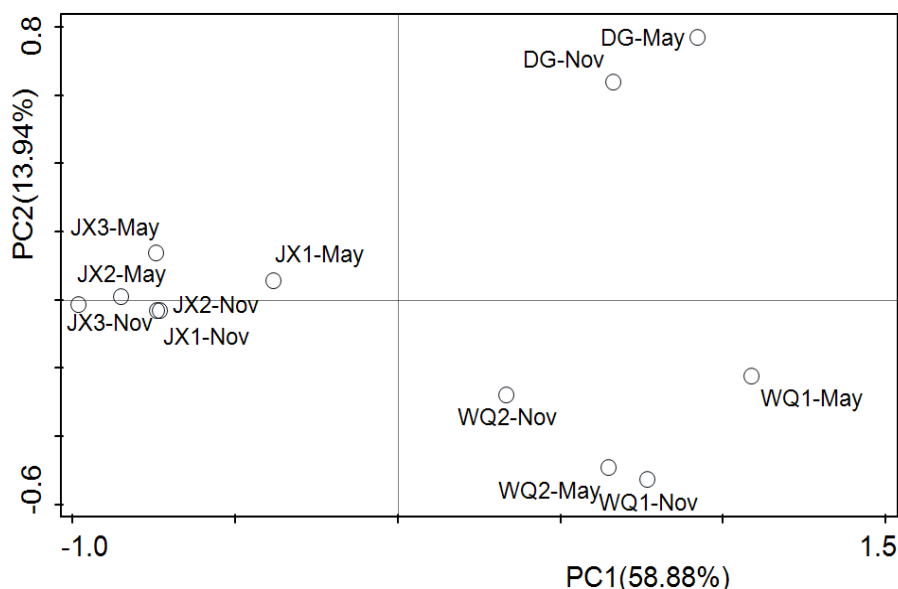


Figure 3. Principle coordination analysis for physicochemical properties of the shallow groundwater. DG, JX and WQ are the abbreviations of Dagang, Jixian and Wuqing, which are all located in the outskirts of Tianjin. Number represent different sampling locations and -May and -Nov represent samples were sampled in mid-May and mid-November, during dry and wet periods, respectively

Potential NO_3^- source identification for the rivers and the corresponding estuaries

A classical dual isotope bi-plot approach ($\delta^{15}\text{N}-\text{NO}_3^-$ vs. $\delta^{18}\text{O}-\text{NO}_3^-$) was applied to identify the potential dominant NO_3^- sources in different rivers and the corresponding estuaries (Fig. 4). It is clear that the predominant NO_3^- sources are “Soil” and/or “M&S” for the HH River, the CB River, the JY River, the CJ and the HH Estuary. The isotopic

signatures of the DL River were mainly concentrated in the “Soil” source box, indicating NO_3^- derived from soil organic, N. The $\delta^{15}\text{N}$ - and $\delta^{18}\text{O}$ - NO_3^- values of the DG River and the ZY River were distributed in the source box of “M&S”. In general, more than half of the sampling locations were mainly influenced by “manure” and/or sewage, but it is difficult to specify whether the predominant NO_3^- source is from only one or both two sources based on the bi-plot.

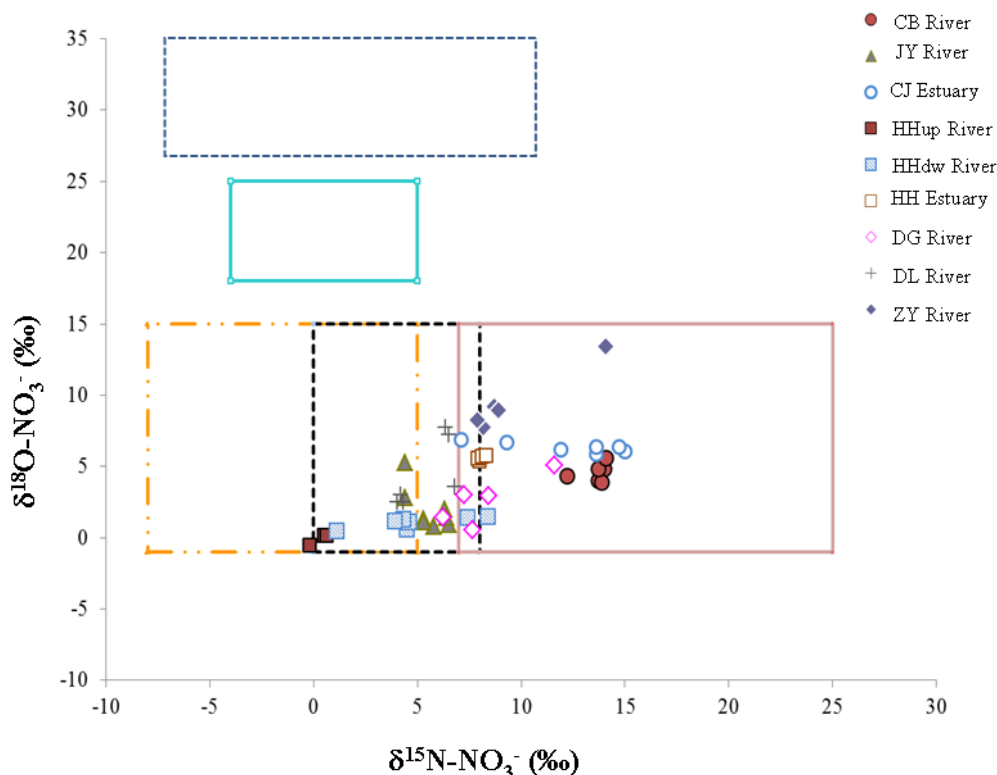


Figure 4. The $\delta^{15}\text{N}$ - and $\delta^{18}\text{O}$ - NO_3^- of the rivers and the corresponding estuaries. CB, JY, HHup, HHdw, DL, ZY and DG River are the abbreviations of the Chaobaixin River, the Jiyun River, the upstream of the Haihe River, the downstream of the Haihe River, the Duliujian River, the Ziyaxin River and the Dagu sewage River, respectively. CJ, HH are the abbreviations of the CJ Estuary (co-estuary of the JY and the CB River) and Haihe Estuary, respectively. Ranges of the isotopic composition for five potential NO_3^- sources are adapted from Kendall et al. (2007) and Xue et al. (2009) and indicated by boxes: NO_3^- in precipitation (NP), NO_3^- fertilizer (NF), NH_4^+ in fertilizer and rain (NF&R), soil N (Soil) and manure and sewage (M&S). To provide a wider and clear range of $\delta^{18}\text{O}$ - NO_3^- values, the upper limit of NP reaches 35‰

Cl^- is a useful indicator for contamination source tracking. High levels of Cl^- have been detected in sewage and livestock effluent (Yao et al., 2007). Thus, a plot of $\delta^{15}\text{N}$ - NO_3^- vs. $\text{NO}_3^-/\text{Cl}^-$ molar ratio might reveal further detailed information for source identification (Fig. 5). As shown in Figure 5, in the “M&S” source box, the majority of the rivers and estuaries were potentially influenced by four sources: (a) extremely low $\text{NO}_3^-/\text{Cl}^-$ molar ratio and relatively low $\delta^{15}\text{N}$ - NO_3^- values (mainly appeared in the HH Estuary, box A in Fig. 5); (b) relatively low $\text{NO}_3^-/\text{Cl}^-$ molar ratio and high $\delta^{15}\text{N}$ - NO_3^- values (mainly appeared in the CJ Estuary, box B in Fig. 5); (c) high $\text{NO}_3^-/\text{Cl}^-$ molar ratio and high $\delta^{15}\text{N}$ - NO_3^- values (mainly appeared in the CB River, box C in Fig. 5);

and (d) relatively low $\text{NO}_3^-/\text{Cl}^-$ molar ratio and relatively low $\delta^{15}\text{N}-\text{NO}_3^-$ values (mainly appeared in the ZY River, box D in Fig. 5). Since the HH River discharge was limited due to the floodgate at the end, the HH Estuary (box A) and the highest salinity sampling location of the CJ Estuary might be regarded as the coast end-member. The last two sampling locations of the HH River were obvious to be influenced by seawater from the HH Estuary not sewage. There are mooring ships in the vicinity of the CJ Estuary all year around, domestic sewage is the main NO_3^- source in this estuary. Thus, the CJ Estuary (box B) can be considered as domestic sewage end-member. Along with point-source contamination was diluted by estuarine water, the residual sampling locations of the CJ Estuary were close to the HH Estuary end-member (box A). The CB River (box C) was considered as the manure end-member, as this watershed plays the role of important livestock breeding base for the municipality (Shao et al., 2010). Furthermore, the $\delta^{15}\text{N}-\text{NO}_3^-$ values were enriched and varied around 14‰, indicating anthropogenic NO_3^- derived from manure (Kendall et al., 2007; Xue et al., 2009). The ZY River (box D) was considered as the industrial sewage end-member, as industry was intensively distributed along the upstream of the river and low treatment rate of sewage was largely discharged into the river. The data distribution of the DG River is quite scattered, possibly resulting from multiple NO_3^- source inputs.

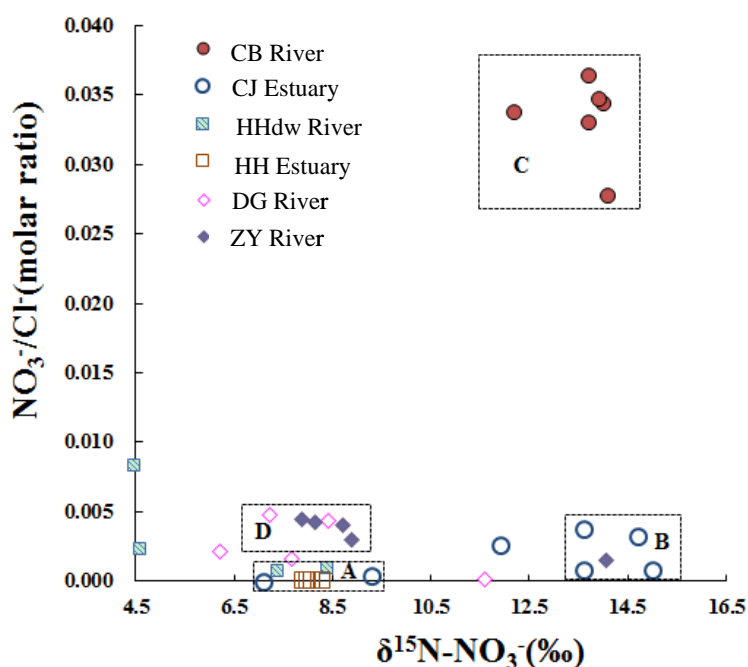


Figure 5. The $\text{NO}_3^-/\text{Cl}^-$ molar ratio versus the nitrogen isotope of NO_3^- in the rivers and the corresponding estuaries. Boxes A, B, C, and D represent different end-members. CB, HHdw, ZY and DG River are the abbreviations of the Chaobaixin River, the downstream of the Haihe River, the Ziyaxin River and the Dagu sewage River, respectively. CJ, HH are the abbreviations of the CJ Estuary (co-estuary of the JY and the CB River) and Haihe Estuary, respectively

Wide ranges of the $\delta^{15}\text{N}$ - and $\delta^{18}\text{O}-\text{NO}_3^-$ values of the rivers and corresponding estuaries showed that surface waters in Tianjin are mainly influenced by multiple NO_3^- sources, but dominated by one or two. To get more specific information, a more quantitative technique based on isotopic mixing model has been applied.

Potential NO_3^- source identification for the SG

As shown in *Figure 6*, the values of $\delta^{15}\text{N}$ - and $\delta^{18}\text{O}$ - NO_3^- seasonally varied in a wide range and increased from north to south (along the direction of groundwater flow), resulting in a linear positive correlation of 0.82 and 0.53, which indicated that significant denitrification occurred in SG (Xue et al., 2009; Aravena and Robertson, 2010; Fukada et al., 2003; Mengis et al., 2005). In the northern part of SG, the lower $\delta^{15}\text{N}$ - and $\delta^{18}\text{O}$ - NO_3^- values were mainly located in the “M&S” source box in May and in the “NF&R” and “Soil” in November.

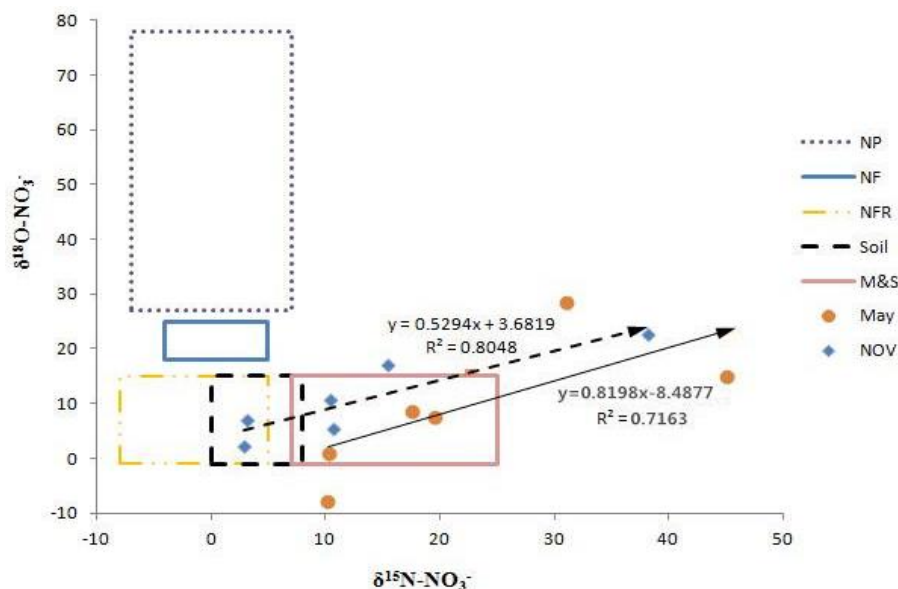


Figure 6. The $\delta^{15}\text{N}$ - and $\delta^{18}\text{O}$ - NO_3^- of the shallow ground. Orange dots and blue diamonds represent the distribution area of the $\delta^{15}\text{N}$ - NO_3^- and $\delta^{18}\text{O}$ - NO_3^- during May and November, respectively. NP, NF, NF&R, Soil, M&S are the abbreviations of NO_3^- in precipitation, NO_3^- fertilizer, NH_4^+ in fertilizer and rain, soil N and manure and sewage, respectively

Potential NO_3^- source contributions estimated from the rivers and the corresponding estuaries by SIAR

The SIAR mixing model was applied to estimate proportional contributions of five potential NO_3^- sources (NP, NF, NF&R, Soil and M&S). The observed linear relationship between the $\delta^{15}\text{N}$ - and $\delta^{18}\text{O}$ - NO_3^- values of the rivers and the corresponding estuaries indicated that no obvious denitrification occurred. The mean oxygen concentrations of all surface waters were above 4.1 mg L^{-1} , which is not ideal for denitrification (Piña-Ochoa et al., 2006). Thus, we assumed parameter $c_{jk} = 0$ in *Equation 2*.

The SIAR mixing model outputs revealed a high variability in contributions of the five potential NO_3^- sources to the rivers and the corresponding estuaries as shown in *Figure 7*. The overall mean contributions of each NO_3^- source to the study area are as follows: “M&S” contributed 35%, “Soil” contributed 27%, “NF&R” contributed 20%, “NF” contributed 12%, and “NP” contributed 6% (dash line in *Fig. 7*). The combination of “M&S” and “Soil” contributions occupied more than 60% in total, which are considered as the dominant NO_3^- sources for the rivers and the corresponding estuaries.

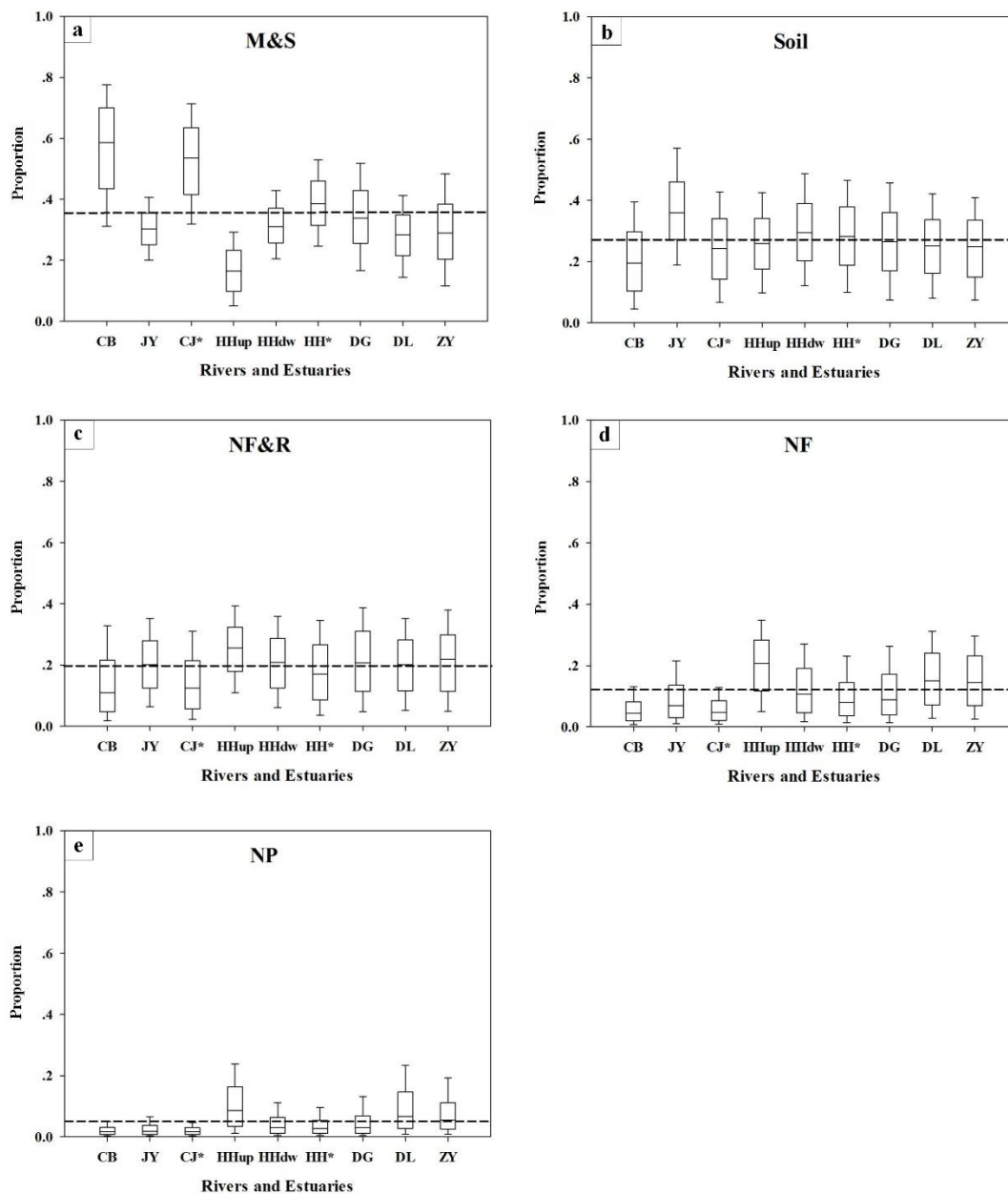


Figure 7. Contribution proportions of NO_3^- sources to the rivers and the corresponding estuaries estimated by SIAR. The dash line in each graph represents the overall mean proportional contribution of the corresponding NO_3^- source. CJ* represents the CJ Estuary, HH* represents the HH Estuary. NP, NF, NF&R, Soil, M&S are the abbreviations of NO_3^- in precipitation, NO_3^- fertilizer, NH_4^+ in fertilizer and rain, soil N and manure and sewage, respectively

The highest contribution source, the “M&S” demonstrated a wide range of proportional contributions for most of the rivers and estuaries, with mean proportions from 17 to 56%. In general, the “M&S” contributed more for the northern rivers and estuary than the rivers and estuary in the middle and southern area. Relatively high mean proportional contributions were observed for the CB River and the CJ Estuary, up to 56% and 52%, respectively. The reason could be that the watershed of the CB River

is the base of livestock breeding for the municipality. Thus, manure showed significant effect on NO_3^- of the river. Furthermore, the CJ Estuary is not only influenced by the CB River, but also greatly influenced by sewage because of the mooring ships in the vicinity of the estuary. For the middle and southern rivers of the municipality, the mean contributions of the “M&S” fluctuated in a narrow range between 28 and 39%, excluding the HHup (17%).

The source of “Soil” is another important potential source of NO_3^- for the rivers and the estuaries, which contributed with the mean proportions ranging from 21 to 37%. In addition, “Soil” is the highest contributing NO_3^- source to the rivers of JY and HHup, occupying 37% and 26% contribution, respectively. This finding revealed that the dominant NO_3^- source of the two rivers mainly originated from nitration of nitrogenous organic matter mineralization.

The mean contributions of the residual three NO_3^- sources occupied about 40% in total, and the mean contribution from high to low are as follows “NF&R” (14–25%) > “NF” (6–20%) > “NP” (2–11%). It has been observed that the contribution pattern of the three NO_3^- sources is quite similar for the rivers and estuaries, indicating spatial consistency of the source distribution.

Although the SIAR model overcome the questions, e.g. multiple NO_3^- sources, isotopic fractionation and spatial variability of $\delta^{15}\text{N}$ - and $\delta^{18}\text{O}$ - NO_3^- values, the limitation of the SIAR model cannot be neglected. The relatively wide ranges of $\delta^{15}\text{N}$ - and $\delta^{18}\text{O}$ - NO_3^- values of the five potential NO_3^- sources resulted in the contribution ranges estimated by SIAR are wide as well. Furthermore, the isotopic composition of NO_3^- in part of the samples appeared in the overlapping area of different NO_3^- source boxes, in which even small variations in isotopic values of NO_3^- might result in large changes in source distribution. To improve the SIAR outputs, it is essential to narrow the isotopic ranges of the potential NO_3^- sources.

Potential NO_3^- source contributions estimated from the SG by SIAR

According to the output of the SIAR mixed model, the NO_3^- contribution proportions of the potential NO_3^- sources to the SG in Tianjin demonstrated seasonal similarity (Fig. 8): “M&S” > “Soil” > “NF&R” > “NF” > “NP”.

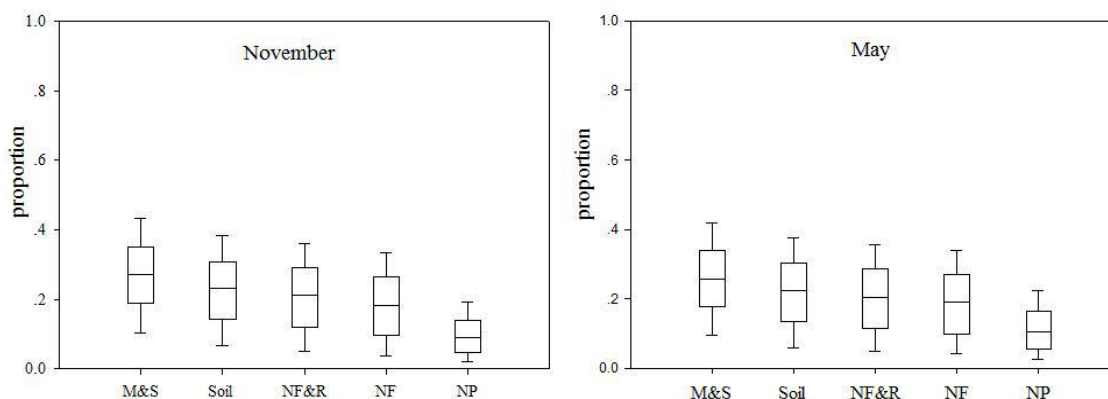


Figure 8. Contribution proportions of NO_3^- sources in May and November to the shallow groundwater estimated by SIAR. NP, NF, NF&R, Soil, M&S are the abbreviations of NO_3^- in precipitation, NO_3^- fertilizer, NH_4^+ in fertilizer and rain, soil N and manure and sewage, respectively

In November and May, “M&S” contributed an average proportion of 27.4% and 26.2%, respectively; “Soil” averagely contributed about 23.0% and 21.0%, respectively; “NF&R” mean contribution was 21.0% and 20.7%, respectively; “NF” mean contribution was 18.6% and 19.2%, respectively, and “NP” was 10.0% and 11.6%, respectively. Compared with rivers and estuaries, there was small difference in the contribution proportions among NO_3^- sources. The mean contribution proportions of “M&S”, “Soil” and “NF&R” occupied about 70% in total. The residual 30% contribution originated from “NF” and “NP”. Although atmospheric precipitation is an important water supply for SG, it is not the main NO_3^- source in this research area.

Conclusion

Extensive agricultural activity, increasing population and rapid development of urbanization resulted in high NO_3^- levels in the rivers, the corresponding estuaries and the shallow groundwater in the coastal municipality of Tianjin in China. Identification and quantification of different NO_3^- sources are imperative to control water quality in this area. By combining dual isotope data of NO_3^- ($\delta^{15}\text{N}-\text{NO}_3^-$ and $\delta^{18}\text{O}-\text{NO}_3^-$) with a Bayesian isotope mixing model (SIAR), we estimated the contribution of five potential NO_3^- sources for the rivers, estuaries and the SG. Despite of some uncertainties, SIAR performed reasonably well in estimating the contributions of potential NO_3^- sources. Future research required to improve the SIAR outputs by using original source material, which might provide more narrow ranges of the isotopic composition of NO_3^- sources. In addition, NO_3^- source apportionment should consider temporal variations. In general, the finding from this research may help to develop better nitrogen management practices in other environments where NO_3^- is a major N contributor.

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