by Ruyu Yuan^{1,2}, Tianyuan Zheng^{3*}, Xilai Zheng^{1,2}, Dongsheng Liu⁴, Jia Xin^{1,2}, Lu Yu^{1,2}, and Guanqun Liu^{1,2}

Identification of groundwater nitrate pollution sources in agricultural area using PCA and SIAR methods

¹ College of Environmental Science and Engineering, Ocean University of China, Qingdao 266100, China

² Key Laboratory of Marine Environment and Ecological Education, Ocean University of China, Qingdao 266100, China

³ College of Engineering, Ocean University of China, Qingdao 266100, China; *Corresponding author, E-mail: zhengtianyuan@ouc.edu.cn

⁴ Center for Eco-Environmental Research, Nanjing Hydraulic Research Institute, Nanjing 210098, China

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Groundwater nitrate sources are diverse and it is of great scientific significance to analyze the sources and respective contribution rates. However, the existed methods of source parsing have some shortcomings. Hence, this study compared principal component analysis (PCA) and Stable Isotope Analysis in R (SIAR), taking the Dagu River groundwater source in Qingdao as an example. The pollution sources analyzed by PCA are more comprehensive and more reliable than those of SIAR. For the contribution rate, the results of PCA can only provide the total contribution of the similar sources, while SIAR is able to capture the contribution rate of each pollution source. Here, we proposed a mixed method taking the advantage of the PCA and SIAR. The new approach can better determine the pollution sources and is capable of solving the contribution rate of each pollution source. Utilizing the combined method, the main sources of nitrate pollution in the Dagu River are found to be manure, NO_3^- fertilizer, sewage, soil N and NH_4^+ fertilizer, with average contribution rates 27.7, 27.3, 21.8, 13.0 and 10.2%, respectively. Through this case study, we are confirmed that this mixed method is preferred clearing pollution source and contribution rate.

Introduction

Groundwater is an essential and irreplaceable resource for economic and social development which is the major drinking water for more than 1.5 billion people worldwide (Lee et al., 2017; Wang et al., 2018). However, nitrate (NO_3^-) pollution in groundwater has become one of the most severe environmental issues of common concern to the international community (Rebolledo et al., 2016; Ghaeminia and Mokhtarani, 2018; Raza and Lee, 2019). The excessive intake of NO_3^- in the human body will be restored to toxic NO_3^- and further converted into nitrosamines, which can easily lead to digestive dis-

eases (Widory et al., 2004; Ma et al., 2016). Therefore, the World Health Organization (WHO) and some major countries have established corresponding drinking water standards stipulating that the maximum concentration of NO_3^- (in N) is 10–11.3 mg/L (Baily, 2011). Meanwhile, China's drinking water standards state that the maximum allowable concentration of NO_3^- (in N) is 10 mg/L. The rural small centralized and distributed water supply regulations are 20 mg/L. The highest concentration of NO_3^- in groundwater in the Shandong Peninsula from 2005 to 2012 reached 184.6 mg/L, and the rate of exceeding the standard was up to 48.3% (Zhao et al., 2007). Therefore, the study of NO_3^- pollution in groundwater has aroused widespread concern in the academic community and the analysis of pollution sources has become one of the current research hotspots.

Potential sources of NO_3^- contamination in groundwater include chemical fertilizers used in agricultural activities, manure, industrial and domestic sewage, atmospheric nitrogen deposition, nitrogen in the soil (Soil N) (Xue et al., 2009; Kaushal et al., 2011; Jin et al., 2012). The methods for recognizing and inferring the source of NO_3^- contamination in groundwater mainly include water quality analytical methods and stable nitrogen and oxygen isotope methods (Zhao et al., 2010). The water quality analysis method is to draw the analysis results into a six-component map and Piper map, which qualitatively analyze the sources of NO_3^- in the groundwater (Zhao et al., 2010). In addition, some scholars input the analytical data of groundwater quality into the models of chemical mass balance (CMB), positive matrix factorization (PMF) and principal component analysis (PCA) to quantitatively address the sources of NO_3^- pollution in groundwater (Matiatos et al., 2014; Xue et al., 2015). In recent years, PCA has widely applied to the sources analysis field (Kim et al., 2015; Matiats, 2016) which extracts the principal components (PCs) and calculates the contribution rate through “dimension reduction” and “multiple linear regression analysis”. It determines the sources of the PCs according to hydrogeological conditions. However, using this method, it is difficult to distinguish the contribution rates of each pollution source with similar pollution information (for example, sewage and manure are often treated as a single source) (Pastén-Zapata et al., 2014).

Recently, some scholars have inferred NO_3^- sources based on the

unique nitrogen and oxygen isotope values of various NO_3^- sources (Chang et al., 2002; Burns et al., 2009; Kaown et al., 2009; Xue et al., 2009), and combined with the Stable Isotope Analysis In R (SIAR) model to calculate contribution rate of each pollution source. The nitrogen and oxygen isotope values of different NO_3^- sources can provide a basis for predicting the sources of pollution. Xue et al. (2009) collected the ranges of nitrogen and oxygen isotopes of potential sources of NO_3^- contamination. For example, for NO_3^- precipitation, $\delta^{15}\text{N}-\text{NO}_3^-$ and $\delta^{18}\text{O}-\text{NO}_3^-$ range from -13 to 13‰ and 25 – 75‰ , respectively. The $\delta^{15}\text{N}-\text{NO}_3^-$ and $\delta^{18}\text{O}-\text{NO}_3^-$ of manure have characterized by ranges 5 – 25‰ , -10 to 10‰ , respectively. Soil has $\delta^{15}\text{N}-\text{NO}_3^-$ and $\delta^{18}\text{O}-\text{NO}_3^-$ values in the range of 0‰ to 8‰ , -10‰ to 10‰ , respectively. For example, in 2016, the main sources of NO_3^- pollution in the highly urbanized Beiyun River Basin in China were manure and sewage with the total contribution rates of 77.59 and 89.57% in the rainy and dry seasons, respectively (Liu et al., 2018). The main sources of NO_3^- pollution in Xijiang River for the rainy season are organic nitrogen and chemical fertilizer, with a contribution rate of 72 – 73% . While, the main sources of NO_3^- pollution for the dry season are manure and fertilizer, with 58% contribution rate (Li et al., 2019). However, the dual isotope method does not always accurately track the sources of pollution. The overlap and changes in isotopic values as a result of biogeochemical process can cause inaccurate identification of pollution sources (Wang et al., 2017).

In this study, taking the groundwater source of Dagu River in Qingdao as an example, we compared the analysis results of PCA and SIAR to clear the pros and cons of the both approaches, and then proposed a novel method that combines the advantages of the two approaches. Finally, using the combined method, we can accurately analyze the sources and contribution rate of NO_3^- pollution in the groundwater source of Dagu River. The main research purposes of this study are (1) to emphasize that the multivariate statistical method is slightly superior to the dual isotope method in determining the sources of NO_3^- contamination and the isotope method is superior to multivariate statistical method in calculating the contribution rate of pollution sources; (2) to prove that this mixed method can preferred clear pollution sources and contribution rate; (3) to provide theoretical support for reducing NO_3^- pollution and rationally distributing the load of each pollution source.

Materials and Methods

Study Area

The Dagu River is the largest river in the Shandong Peninsula, China. The length of the main stream is 179.9 km with the total drainage area of 6131.3 km². The Dagu River groundwater source is located in the middle and lower reaches belonging to Pingdu, Jimo, Laixi, Jiaozhou and other urban areas in the administrative division. The groundwater source area is around 421 km² and the geographical coordinates are $120^\circ04'48''$ – $120^\circ21'00''\text{E}$ and $36^\circ18'00''$ – $36^\circ45'45''\text{N}$ in Fig. 1a (Liu et al., 2017).

There is a temperate monsoon continental climate with typical marine climate characteristics within this area. It is hot and rainy in the summer, cold and dry in the winter, and pleasant in the spring and

autumn (Liu et al., 2017). The monthly precipitation distribution in this area is rather uneven and the precipitation from July to September accounts for approximately 70% of the annual precipitation.

The groundwater of the Dagu River mainly exists in the sand and gravel layers in the lower part of the Quaternary alluvial deposit, the water-bearing layer is a thin phreatic aquifer covered with a weakly permeable clay (e.g. sandy clay). Groundwater in the region is recharged from atmospheric precipitation, river infiltration and irrigation, and is drained for the industrial and agricultural usage (Fang et al., 2018). The groundwater level is 0.5 – 4 m to the surface. The variation of the groundwater level within a single year is generally 2 – 3 m (Liu et al., 2017). The direction of groundwater flow in the study area is consistent to the direction of the main stream of the Dagu River, from north to south (Fang et al., 2018).

The land use in this area can be classified as cultivated land, forestland and grassland, of which grain planting area accounts for 65 – 80% and vegetable planting area accounts for 10 – 20% . The amount of used pesticides is generally 4.5 – 13.5 kg/hm² and about 500 – 600 kg/hm² for the chemical fertilizer with the nitrogen fertilizer of approximate 50% .

Sampling

In April 2015, 29 sampling sites were selected in the Dagu River water source (Fig. 1b), and the concentrations of Ca^{2+} , Mg^{2+} , Na^+ , Cl^- and SO_4^{2-} in groundwater were determined by an ion chromatograph. The concentrations of NH_4^+-N , NO_2^--N and NO_3^--N were measured by the Nessler reagent, N -(1-naphthalene)-ethylenediamine hydrochloride and ultraviolet spectrophotometry, respectively. The concentration of HCO_3^- was identified by titration (Table 1).

$\delta^{15}\text{N}-\text{NO}_3^-$ and $\delta^{18}\text{O}-\text{NO}_3^-$ in groundwater samples were measured by the “denitrifying bacteria method” in the Isotope Laboratory of the Chinese Academy of Agricultural Sciences in 2015 (Liu et al., 2017) (Table 2). The stable isotope ratios can be expressed in relation to the international standard values as follows:

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

where R is the ratio of $^{15}\text{N}/^{14}\text{N}$ or $^{18}\text{O}/^{16}\text{O}$, respectively and R_{sample} and R_{standard} are the ratios of the sample and standard $^{15}\text{N}/^{14}\text{N}$ and $^{18}\text{O}/^{16}\text{O}$.

Analytical Methods

Multivariate Statistical Analysis

PCA is a statistical tool used to identify data and analyze the similarities and differences between data (Jain et al., 2017). Through the method of dimensionality reduction, PCA takes a small number of comprehensive indicators to characterize the research objective (not less than 80%) through dimensionality reduction and obtains the components of eigenvalues greater than 1, defined as the main components (PCs) (Bošnjak et al., 2012). The KMO value is greater than 0.5 , and Bartlett's test has a p -value less than 0.001 , indicating that the data is suitable for factor analysis (Liu et al., 2003). The Kaiser normalized orthogonal rotation were used to obtain the load of each component.

When using the PCA model, the raw data is first converted to a

Figure 1. (a) Location of Dagu River Groundwater Source, (b) Locations of monitored wells and land use in the study area.

dimensionless standardized form to eliminate the impact of different dimensions (Jain et al., 2018).

$$z_{ij} = \frac{c_{ij} - \bar{c}_i}{\sigma_i} \quad (2)$$

where z_{ij} is the normalized value; c_{ij} is the concentration of element i in sample j , $i=1,2,3,\dots,n$, $j=1,2,3,\dots,m$; $\bar{c}_i$ and σ_i are the mean concentration and standard deviation for element i , respectively.

Then, the PCA model can be expressed as (Li et al., 2000):

$$z_{ij} = \sum_{k=1}^p g_{ik} h_{kj} \quad (3)$$

where $k=1,\dots,p$, represents the different sources of pollution, g_{ik} represents the concentration of element i in the pollution source k , also known as the factor load and h_{kj} represents the contribution of the pollution source k to the sample j , called the factor score.

Bayesian Isotope Mixing Model

In 2010, SIAR model based on Bayesian equations began to be applied in the field of sources analysis (Parnell et al., 2010). It inputted the isotopic values measured from pollution sources and groundwater sample into the model. The Bayesian equation is used to calculate the contribution rate and posterior distribution characteristics of each pollution source.

The mathematical principle expression of the model is as follows:

$$X_{ij} = \frac{\sum_{k=1}^p p_k g_{jk} (s_{jk} + c_{jk})}{\sum_{k=1}^p p_k q_{jk}} + \varepsilon_{ij} \quad (4)$$

$$s_{ij} \sim N(\mu_{jk}, \omega_{ij}^2) \quad (5)$$

$$c_{jk} \sim N(\lambda_{jk}, \tau_{jk}^2) \quad (6)$$

$$\varepsilon_{ij} \sim N(0, \sigma_j^2) \quad (7)$$

where X_{ij} represents the value of the j isotope in the i water sample, $i=1, 2, 3, 4, \dots, n$, $j=1, 2, 3, \dots, p$, p_k is the k source of the pollution contribution rate which is the output of the SIAR model, q_{jk} is the concentration of the isotope j in the k source, s_{jk} represents the value of the j isotope in the k source, $k=1, 2, 3, \dots, k$, which obeys the mean μ_{jk} and the normal distribution of the variance ω_{jk}^2 , c_{jk} is the fractionation coefficient for the isotope j on the pollution source k and ε_{ij} is the residuals representing the remaining unquantified variations in each mixture.

Results and Discussion

Characteristics of Hydrogeochemistry

Nitrate Contamination

According to the monitoring results of the groundwater quality, this area is mainly low mineralized fresh water, the water type is HCO_3^- water, and a few locations are HCO_3^- - SO_4^{2-} water (Table 1). On the whole, the NO_3^- pollution in the study area is severe (Fig. 2), and 86.2% of the groundwater samples exceeds the standard (20 mg/L). This is because

Table 1. Monitoring results of the water quality of the Dagou River groundwater source

Sites	pH	DO (mg/L)	NO ₃ ⁻ (mg/L)	Na ⁺ (mg/L)	Ca ²⁺ (mg/L)	Mg ²⁺ (mg/L)	Cl ⁻ (mg/L)	HCO ₃ ⁻ (mg/L)	SO ₄ ²⁻ (mg/L)
A01	7.06	6.52	133.49	34.73	156.51	36.08	71.06	15.25	139.63
A02	7.18	3.17	52.31	32.45	124.06	22.33	41.91	213.56	133.33
A03	7.93	4.28	22.22	38.83	99.70	23.19	46.99	289.83	87.09
A04	7.61	10.17	160.74	46.24	205.87	34.80	91.37	106.78	140.78
A05	7.36	9.20	77.22	58.99	242.94	28.89	175.34	244.07	208.11
A06	7.17	3.39	43.07	68.81	135.96	29.07	106.73	366.10	94.61
A07	7.33	6.18	70.35	31.43	95.71	17.41	50.69	76.27	34.60
A08	6.69	8.36	127.51	48.60	157.99	41.00	76.36	144.92	121.45
A09	7.27	4.43	70.90	39.78	99.17	30.78	53.36	91.53	133.58
A10	7.46	9.03	115.65	35.09	189.10	21.52	62.01	137.29	138.80
A11	6.33	4.96	45.27	41.19	85.94	22.54	73.07	152.54	66.77
A12	7.49	8.39	108.31	38.62	137.82	33.47	58.91	228.81	81.07
A13	7.65	4.36	63.64	27.32	96.60	25.79	47.86	91.53	86.84
A14	6.68	7.46	99.53	31.19	188.44	25.58	120.87	152.54	118.90
A15	7.40	8.58	116.86	43.13	203.42	38.14	97.99	228.81	149.94
A16	7.33	9.42	100.12	42.83	180.49	35.35	84.96	251.70	88.51
A17	7.15	7.72	124.42	45.92	178.72	40.28	98.51	152.54	110.61
A18	7.12	6.41	105.80	46.08	153.01	20.76	86.86	198.31	74.36
A19	6.49	3.80	53.00	40.57	88.56	36.07	60.26	45.76	188.64
A20	6.55	4.41	72.04	46.46	113.89	38.34	59.19	122.03	165.40
A21	6.29	9.21	120.73	24.22	188.13	15.70	75.46	228.81	95.46
A22	7.23	3.75	59.29	36.04	130.80	27.34	58.92	289.83	68.15
A23	7.43	4.33	48.42	93.62	143.62	30.20	161.71	350.85	65.19
A24	--	--	78.96	26.02	132.06	17.59	55.15	221.19	79.67
A25	7.50	8.75	12.06	39.91	159.50	21.62	102.56	282.20	129.75
A26	--	--	0.15	23.89	31.27	12.05	34.94	114.41	58.33
A27	6.97	2.26	21.38	69.13	113.07	39.32	87.34	434.75	103.73
A28	7.52	2.36	37.10	48.11	119.88	23.45	90.96	289.83	63.50
A29	7.47	0.50	2.07	152.0	121.10	46.76	157.33	549.15	256.98

Table 2. Isotopic compositions of groundwater samples in the Dagou River Groundwater source

Sites	δ ¹⁵ N (‰)	δ ¹⁸ O (‰)	Sites	δ ¹⁵ N (‰)	δ ¹⁸ O (‰)
A01	10.26	4.92	A13	5.45	3.73
A02	12.69	7.46	A15	7.08	5.17
A03	9.35	6.90	A16	7.45	3.30
A04	40.98	39.19	A17	5.99	4.01
A05	11.24	6.75	A18	31.98	29.85
A07	6.24	5.47	A21	4.81	3.27
A09	6.93	4.86	A23	7.96	4.89
A10	4.93	2.08	A25	1.90	4.90
A11	15.00	6.95	A27	16.96	5.54
A12	7.74	4.37	A28	12.02	5.06
A13	5.45	3.73	A29	41.29	26.30

the entire study area is located in the agricultural vegetable base, and local residents apply large amounts of fertilizer to increase vegetable yield. Among them, sampling points with higher NO₃⁻ concentration (5 times above the standard level) are A01, A04, A08, A10, A12, A15, A16, A17, A18 and A21. Most of these sampling points are

located in the upstream of the study area. The reason for this phenomenon is the vegetable planting area in the upstream is larger than that in the downstream. However, A26 and A29 have a very low NO₃⁻ concentration (0.15 and 2.07 mg/L), because there are no crops and residents around the sample, A26 located around the forest and A29

Figure 2. Nitrate concentration interpolation map.

Figure 3. Crossplot of $\delta^{15}\text{N-NO}_3^-$ and $\delta^{18}\text{O-NO}_3^-$ values in the groundwater samples.

was around the abandoned wasteland.

Stable Isotope Compositions

The variation of $\delta^{15}\text{N-NO}_3^-$ and $\delta^{18}\text{O-NO}_3^-$ in groundwater samples in the study area are large (1.90–40.98‰ and 2.08–39.19‰) and the mean values are 2.04 and 1.97‰ respectively. It indicates the diverse sources of NO_3^- . The $\delta^{15}\text{N-NO}_3^-$ value of 61.9% sampling points is less than 10‰, the $\delta^{15}\text{N-NO}_3^-$ value of 23.8% sampling points is between 10–15‰, and the $\delta^{15}\text{N-NO}_3^-$ values of 14.3% sampling points (A04, A18 and A29) is relatively high (40.98, 31.98 and 41.29). The $\delta^{18}\text{O-NO}_3^-$ values of 18 sampling points ranged from 0 to 10‰, while the $\delta^{18}\text{O-NO}_3^-$ value are higher at the other three sampling points (A04, A18 and A29) in Table 2. Since the NO_3^- concentrations at the A04 and A08 are also high, it can be concluded that the abnormal values of the two points come from multiple sources of pollution. The extremely low NO_3^- concentration at the A29 shows that denitrification may have occurred at this point.

In general, the values of $\delta^{15}\text{N-NO}_3^-$ and $\delta^{18}\text{O-NO}_3^-$ in groundwater can reveal the sources of NO_3^- pollution and the denitrification process of the groundwater system in the study area (Kellman and Hillaire-Marcel, 1998; Pardo et al., 2004). The sources of NO_3^- is related to the nitrogen cycle and the isotope fractionation will bias the values of $\delta^{15}\text{N-NO}_3^-$ and $\delta^{18}\text{O-NO}_3^-$. Thus, the effect of denitrification becomes significant (Teppey et al., 2003; Xue et al., 2009), and it is important to identify the denitrification reaction for the analysis of the sources pollution. When the slope between $\delta^{15}\text{N-NO}_3^-$ and $\delta^{18}\text{O-NO}_3^-$ is between 1.3:1 and 2:1, the denitrification process occurs in the system (Araena and Robertson, 2010; Xue et al., 2012; Xing and Liu, 2016). According to the groundwater isotope data, the values of $\delta^{15}\text{N-NO}_3^-$ and $\delta^{18}\text{O-NO}_3^-$ in groundwater are linear with a slope of 0.827 (Fig. 3). It can be seen that there is no obvious denitrification reaction in the groundwater of the study area.

Sources Analysis

Principal Component Analysis

To study the sources of NO_3^- in the groundwater of the Dagu River, the principal component analysis was carried out on the original data of 10 hydrochemistry components (pH, DO, NO_3^- , NH_4^+ , Na^+ , Ca^{2+} , Mg^{2+} , Cl^- , HCO_3^- and SO_4^{2-}) from the sampling sites ($n=29$). The result shows that the contribution of the first four PCs is 32.6, 27.3, 13.1 and 11.7%, respectively, covering more than 84.7% of the total data (Fig. 4). Fig. 5 shows the relationship between 10 water chemistry parameters and 4 PCs. The larger the projection of the parameter on the axis, the greater the load of the parameter in the PC. The parameters on the same side of the x axis or y axis indicate a positive correlation between these parameters (e.g. Mg^{2+} , Cl^- and SO_4^{2-}) and a negative correlation for the other cases (e.g. HCO_3^- and NO_3^-). Fig. 6 shows the load of the 10 water chemistry param-

Figure 4. Principal component analysis results of 10 water chemical parameters at sampling points ($n=29$): principal component interpretation variance percentage Scree plot.

Figure 5. Principal component analysis results of 10 water chemical parameters at sampling points ($n=29$): (a) Correlation load map of 10 water chemical parameters on PC 1 and PC 2, respectively, (b) Correlation load map of 10 water chemical parameters on PC 3 and PC 4, respectively.

eters on the first 4 principal components. According to the principle that the load is not less than 0.5 (Bošnjak et al., 2012), the variables explained by each principal component are selected.

In PC 1, Na^+ , Mg^{2+} , Cl^- , SO_4^{2-} and HCO_3^- are large loads, and they are positively related to each other (Fig. 4). They are the main ionic components in groundwater and are related to the salt content of groundwater, which may come from mineral dissolution and cation exchange in the soil (Panno et al., 2001). Brink et al. (2007) indicated that the infiltration of domestic sewage is accompanied by the enrichment of solutes (Na^+ , Mg^{2+} , Cl^- and HCO_3^-). Cl^- is considered as a stable tracer

not subject to changes in NO_3^- content and its potential sources are industrial, domestic sewage and manure. The study area is mainly located at the place of agricultural activities, and the application of farm manure will increase the Cl^- content in the groundwater (Meghdadi and Javar, 2018). To conclude, the source of pollution may be manure or sewage.

In PC 2, DO , NO_3^- and Ca^{2+} have the greatest effect with loads of 0.7697, 0.8299 and 0.9076, respectively (Table 3). The strong correlation between DO and NO_3^- indicates that the concentration of NO_3^- in groundwater may be affected by the redox environment. These ions are closely related to solutes produced by anthropogenic activities,

Table 3. Loads of the 10 water chemical parameters on the first 4 principal components

	Dim1	Dim2	Dim3	Dim4
pH	0.3035	0.1528	0.5174	0.6824
DO	-0.4245	0.7697	-0.2722	0.1909
NO ₃ ⁻	-0.3922	0.8299	-0.0241	-0.1045
NH ₄ ⁺	-0.1483	0.3106	0.8440	0.0565
Na ⁺	0.9514	-0.0459	0.0116	-0.0505
Ca ²⁺	0.1460	0.9076	-0.2071	0.2252
Mg ²⁺	0.5959	0.3772	0.1804	-0.4634
Cl ⁻	0.7573	0.3798	-0.3201	0.1679
HCO ₃ ⁻	0.8000	-0.2267	-0.1635	0.3482
SO ₄ ²⁻	0.5646	0.4109	0.2270	-0.4838

such as domestic sewage and fertilizers (Ioannis et al., 2016; Wang et al., 2017). We took samples during the irrigation period (April). Thus the nitrogen in the soil may infiltrate into the groundwater through irrigation and leaching. In addition, the local farmers use chemical fertilizer (calcium nitrate) for a long time resulting in the acidification of soil and increase the content of Ca²⁺ in groundwater. Thus, it could come from soil N, sewage and NO₃⁻ fertilizer.

The pH loads in the PC 3 and PC 4 were large, 0.5174 and 0.6824, respectively. The load of NH₄⁺ in the main component 3 was 0.8440 (Table 3). The locations of Pingdu and Laixi in the upper and middle reaches of the Dagu River are known as the “hometowns of vegetables”. To enhance soil fertility and increase vegetable yield, the people used a large amount of nitrogen fertilizer, thereby increasing the pH and NH₄⁺ content of local groundwater. Thus, the source may be inorganic fertilizer (ammonium fertilizer).

In summary, the pollution sources analyzed by PCA mainly include sewage, inorganic fertilizer (NO₃⁻ fertilizer, ammonium fertilizer), manure and soil N. However, the contribution rate of each PC only represents the sum of all possible similar sources of pollution, not the contribution rate of a particular source.

Stable Isotope Analysis in R

From Fig. 6, it can be found that 33% of the sampling points (A01, A02, A03, A05, A11, A27 and A28) fall in the overlapping area of manure and sewage. The sampling period took place during a stage with the utilization of a large amount of fertilization and most villages in the study area have not effectively treat the sewage. Hence, manure and sewage are likely to be sources in those points. The sampling point (A25) falls at the overlap of the two sources, soil N and NH₄⁺ Fertilizer & Precipitation. Appelo and Postma (2006) declare that the concentration of NO₃⁻ from soil N ranges from 0.062 to 12.4 mg/L. Since the NO₃⁻ concentration in A25 is lower than 12.4 mg/L (Table 1), it is believed that the NO₃⁻ pollution in A25 may come from soil N. Besides, 47% of sampling points locate at the intersection of the four pollution sources (manure, sewage, soil N and NH₄⁺ Fertilizer & Precipitation). Besides A26 with NO₃⁻ concentration below 10 mg/L, other sampling points are enriched in the concentration of NO₃⁻. A26 is located close to town area, so its source of NO₃⁻ is likely to be sewage. However, other sampling points are difficult to distinguish for the main source of pollution. Because they are distributed

Figure 6. Principal component analysis results: load diagrams of 10 water chemical parameters on the 4 PCs.

throughout the study area and there is a mixtures of activities, which makes it difficult to specify a single source of NO₃⁻ pollution.

However, 14% of the sampling points (A04, A18 and A29) does not fall within the scope of any sources of pollution. Since the content of NO₃⁻ in A04 and A18 is high and the land use type in the study area is mainly arable land, the reason for the high values of δ¹⁵N-NO₃⁻ and δ¹⁸O-NO₃⁻ in these two points is that they may come from multiple pollution sources (Table 1 and 2). Kendall (1998) pointed out that the denitrification process is accompanied with a decrease in NO₃⁻ concentration, and the ratio of δ¹⁵N-NO₃⁻ and δ¹⁸O-NO₃⁻ is close to 1.3:1–2:1. Therefore, denitrification reaction may occur at A29 (1.57:1). In addition, there is no sampling points falling in NO₃⁻ fertilizer and NO₃⁻ precipitation. This may be due to isotope fractionation.

To summary, the potential sources of contamination by SIAR are

Table 4. SIAR result: contribution rates of nitrate pollution sources

Source	Min	Max	Mode	Mean
Manure	0	0.902	0.381	0.377
Sewage	0	0.991	0.330	0.329
Soil N	0	0.942	0.303	0.294

manure (37.7%), sewage (32.9%) and soil N (29.4%), in Table 4. However, due to the biochemical reactions and interaction of multiple sources of pollution, it is impossible to accurately determine the sources of NO_3^- contamination in the study area.

Combination of PCA and SIAR

By comparing the analyzed results of PCA and SIAR, we can see that both methods have advantages and disadvantages. The PCA is superior to the SIAR in judging the sources of pollution, while the SIAR performs better in calculating the contribution rates. Therefore, the results of PCA are selected as the pollution sources in the study area. The sources of NO_3^- have sewage, inorganic fertilizer (NO_3^- fertilizer, NH_4^+ fertilizer), manure and soil N in the study area. Then, SIAR can be used to quantitatively estimate the contribution rate of the each potential source of NO_3^- in the study area. Since obvious denitrification did not occur in this region (except A29, in which may have a weak biochemical effect, but it will not have a significant impact on the isotopic composition), we assume the isotope fractionation coefficient (c_{jk}) is 0. The results of SIAR explain the differences of contribution rates of five pollution sources in the groundwater source of Dagu River (Fig. 7). The horizontal axis of the graph represents the contribution rates of all the pollution sources, and the vertical axis indicates

the occurrence frequencies of each pollution source contribution rate in the study area.

Combined with Table 5 and Fig. 7, it can be concluded that the contribution of manure, NO_3^- fertilizer and sewage is roughly normal distribution. Their posterior distribution ranges are 2.0–50.4%, 10.3–44.4%, 0–42.3% and their average values are 27.3, 27.7 and 21.8%, respectively. However, the distribution of soil N and NH_4^+ fertilizer & precipitation pollution sources is asymmetric. Their posterior distribution ranges are 0–30.9%, 0–26.3%, and their mean values are 13.0 and 10.2%. This may be due to different land use types or different fertilization conditions at various sampling points. Therefore, the contribution rate of NO_3^- fertilizer and manure are the highest 27.7 and 27.3%, respectively, followed by sewage (21.8%), soil N (13.0%), and NH_4^+ fertilizer & precipitation (10.2%). However, it is worth noticing that the contribution of NH_4^+ fertilizer & precipitation is lower than that of soil nitrogen, probably because ammonium ions are easily adsorbed and the sampling time is dry season (Yu et al., 2018).

In general, this mixed method is preferred clearing pollution sources and contribution rates. The result reveals that manure and fertilizer (NO_3^- fertilizer and NH_4^+ fertilizer & precipitation) are the main NO_3^- sources in the study area, with the contribution rate 27.3 and 37.9%. And this is consistent with the type of land use in the study area.

Conclusions

Through the analysis in this paper, we make conclusion as follows: (1) the pollution sources analyzed by PCA include manure, sewage, NO_3^- fertilizer, NH_4^+ fertilizer and soil N, while they only include manure, sewage and soil N according to SIAR. Due to the effects of

Figure 7. Distribution of the contribution rate of each pollution source.**Table 5. The mixed method result: contribution rates of nitrate pollution sources**

Source	Min	Max	Mode	Mean
Manure	0.020	0.504	0.280	0.272
Sewage	0	0.423	0.230	0.218
Soil N	0	0.310	0.03	0.130
NH_4^+ Fertilizer & Precipitation	0	0.263	0.022	0.102
NO_3^- Fertilizer	0.103	0.444	0.280	0.277

biochemical process and multiple pollution sources on the isotopic fraction, SIAR is not suitable to analyze the pollution source types in the study area; (2) the contribution rates determined by SIAR for manure, sewage and soil N are 37.7, 32.9 and 29.4%, respectively. However, PCA can only get the sum of contribution rates of related pollution sources so it is not able to accurately capture the contribution rate of each source; (3) according to the combination method of PCA and SIAR, the contribution rates of NO_3^- fertilizer, manure, sewage, soil N, NH_4^+ fertilizer & precipitation are 27.7, 27.3, 21.8, 13.0 and 10.2%, respectively. The results is in accord with the real hydro-geologic conditions in the study area. The results of the study provide clear evidence for a significant influence of different pollution sources on the groundwater in Shandong Peninsula Agricultural Area. Hence, to reduce the regional NO_3^- pollution, the usage of fertilizer should be decreased and the absorption rate is preferred increasing. Sewage pipes should be built in the countryside. Furthermore, changing crop cultivation methods can also make full use of mineral elements in different strata.

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Ruyi Yuan is a master student of college of Environmental Science and Engineering at Ocean University of China. Her research has been concerned with groundwater pollution control and remediation, with interest in pollution sources analysis.

Xilai Zheng is a Professor of Ocean University of China. He has published over 200 research papers in international and Chinese journals. His research interests involve groundwater pollution theory and remediation technology, development, utilization and protection of coastal water resources. He is in charge of the national natural science foundation of China, the joint key fund of the national foundation of China and Shandong province and so on

Tianyuan Zheng is a Postdoc of Ocean University of China. He did his ph.D in Helmholtz Centre for Environmental Research and Technical University of Dresden. He is specialized in the field of numerical modeling of multiphase flow, thermo-hydro-mechanical freezing process and density flow coupled with reactive transport. He was deeply involved in the development of open source finite element software OpenGeoSys (OGS). He has published over 20 research papers in international journals.

Dongsheng Liu is a postdoctor of Eco-Environmental Research Department, Nanjing Hydraulic Research Institute, China. His research interests involve Engineering Seepage and Groundwater Environment.

Jia Xin is an associate professor of Ocean University of China. Her research is focused on pollution mechanism and remediation technologies for soil and groundwater. Specific research interests include: 1) Environmental behaviors of emerging contaminant in porous media; 2) Nitrogen cycling in soil and groundwater. She has published nearly 30 research papers in international journals.

Guanqun Liu is a Professor of Ocean University of China. His research is focused on groundwater resource evaluation and management, water environmental protection and management. He has published nearly 100 research papers in international and Chinese journals.

Lu Yu is a ph.D. of college of Environmental Science and Engineering at Ocean University of China. Her research interests include groundwater pollution and control, environmental planning and management.