Characteristics and traceability analysis of nitrate pollution in the Yellow River Delta, China

Hanyou Xie1,2, Jing Li1*, Deyao Liu1,2
1.Institute of Geographic Sciences and Natural Resources Research, CAS, Beijing 100101, China; 2.University of Chinese Academy of Sciences, Beijing 100049, China
Corresponding author’s E-mail: jingli@igsnrr.ac.cn

Abstract: The Yellow River Delta is one of the regions with the highest nitrogen application rate in China. Because of the high-intensity development and utilization of the Yellow River Delta, a large number of nitrate inorganic nitrogen pollutants have been transported offshore through rivers, which poses a threat to the ecological environment security of the region. The distribution characteristics of nitrate pollution, the source and transport characteristics of nitrate in surface water are unclear. In this study, we collected soil and surface water samples, determined stable isotopes of water (δ²H-H₂O and δ¹⁸O-H₂O) and nitrate (δ¹⁵N-NO₃ and δ¹⁸O-NO₃), and used the Isosource model to quantitatively analyze the distribution characteristics of soil nitrate-nitrogen and source characteristics of surface water nitrate. The results showed that:
(1) The average content of NO₃⁻-N in cultivated soil was 3.99 times higher than that in non-cultivated soil, in which cornfield > cotton field > soybean field > paddy field; (2) The nitrate flux of surface water increased from upstream to downstream, which was positively correlated with basin area; (3) In the middle and upper reaches of the study area, the surface water is mainly replenished from the Yellow River water and groundwater, while the lower reaches are affected by seawater intrusion; (4) The primary source of nitrate in the study area was dominated by human activities of agricultural production and residents’ lives, with a total contribution of 60.8%. This study will provide a scientific basis for the treatment of nitrate pollution in coastal areas.

1. Introduction
Nitrate pollution in soil and surface water has been widely concerned by scholars worldwide as it is hazardous to human health[1, 2]. Nitrogen fertilizer is the primary source of nitrate in the environment. China consumes about 30 million tons of pure nitrogen every year, accounting for nearly 1/3 of the global nitrogen fertilizer. About 50% of the nitrogen fertilizer applied to the soil remains in the soil or lost in other forms[3, 4]. According to statistics, nitrate storage in the thick vadose zone of North China Plain is 18.54 million tons. Nearly 80% comes from chemical fertilizer application in grain planting, which is 10.9-23.2 times that in Europe[5, 6]. The river is the primary channel to transport nitrate to the ocean[7, 8]. Inorganic nitrogen in more than half of China’s sea area exceeds the standard [9]. About 840,000 tons of pollutants enter the Bohai sea every year, and inorganic nitrate nitrogen is the dominant pollutant[10].

Nitrate pollution in the water body is affected by geographical location, landscape pattern, climate and hydrological characteristics[11]. The development and utilization of agriculture lead to the increase of nitrate concentration in water[12]. The Yellow River Delta is one of the regions with the highest nitrogen application rate in China[13]. Excessive nitrogen enters the water body through runoff or infiltration and participates in the water cycle process, posing a threat to the regional water environment.
security \cite{14}. It is speculated that the water quality in coastal areas will continue to deteriorate in the future, and the nitrate concentration in rivers will continue to increase\cite{15}.

Stable isotopes of water (δ²H-H₂O and δ¹⁸O-H₂O) and nitrate (δ¹⁵N-NO₃ and δ¹⁸O-NO₃) are powerful tools to identify their sources, which have been rapidly developed and applied in recent decades\cite{16}. ISOsource model is based on the principle of mass conservation of stable isotopes and multi-source linear mixing model, which is used to estimate the contribution ratio of different material sources. It has been widely used in D-¹⁸O and ¹⁵N-¹⁸O traceability analysis \cite{17, 18}. In this study, the dual stable isotopes of nitrate and water combined with ISOsource model were used: (1) to identify the land use types and the nitrate-nitrogen pollution characteristics of soil and surface water in the Yellow River Delta; (2) to trace the primary sources of surface water and nitrate; (3) to quantify the characteristics of nitrate flux into the sea. The results will provide a scientific basis for understanding the source, behavior process, flux into the sea, and emission reduction regulation of nitrate in the study area.

2. Materials and Methods

2.1. Study area

The study area is located at the estuary of the Yellow River, which spans from the south of the Yellow River to the north of the tributary river (37.26‒37.83 N, 118.21‒119.29 E) and covering an area of 2841 km². Combined with remote sensing images and DEM data, the hydrological analysis function of ArcGIS was used to obtain a watershed hydrological map. There are eight main rivers and 10 sub-watersheds in the study area, with water area accounting for 15.6%, cultivated land accounting for 32.5%, construction land and offshore aquaculture accounting for 19.8% and 24.8%, respectively.

2.2. Sample collection and analysis

Regional investigation and sample collection were carried out in the summer of 2019. A total of 218 soil samples were set up. And about 1 kg of topsoil 20 cm deep was taken from each soil sample site with a soil drill and stored in a sealed bag in the freezer layer of the refrigerator. 44 sampling points were set up at the confluences of main rivers. The water temperature (°C), pH, EC (ms cm⁻¹), DO (mg L⁻¹) and ORP (mv) were measured by Portable Multi-Parameter Water Quality Analyzer (HQ40D). The 500ml of the sample was collected into the plastic bottle, which was moistened with ultrapure water three times and dried in the air, and stored at -20 °C for the determination of nitrate-nitrogen, total N, total P, COD, δD-H₂O and δ¹⁸O-H₂O, δ¹⁵N-NO₃ and δ¹⁸O-NO₃.

Based on the shape of the river, width and depth of 1/6, 1/3 and 1/2 of the river surface width to calculate the river section area (S); The calculation equation of nitrate-nitrogen flux is as follows\cite{19}:

$$N_f = S \times V \times C$$  (1)

Where $N_f$ is the instantaneous flux of nitrate-nitrogen (g s⁻¹); $S$ is the sectional area (m²); $V$ is the average horizontal velocity (m s⁻¹); $C$ is nitrate N concentration (mg L⁻¹).

3. Results and discussions

3.1. The relationship between soil NO₃⁻N spatial distribution and land use

The soil nitrate-nitrogen content in the study area showed large variability. The maximum value was 505.14 mg kg⁻¹, the minimum value was 1.23 mg kg⁻¹, and the average value was 31.65 mg kg⁻¹. There were six samples and 16 samples with NO₃⁻N content exceeding 200, 100 mg kg⁻¹, respectively, mainly distributed in the Yellow River Farm Ditch and Zhimai river basins. The NO₃⁻N content of 84.7% of soil samples did not exceed 50 mg kg⁻¹, and soil nitrate-nitrogen concentration near urban areas, the natural reserve, and tidal flats is less than 20 mg kg⁻¹. The soil NO₃⁻N content under different land uses is shown in Table 1, and there is a big difference between cultivated land and non-cultivated land. The soil NO₃⁻N content in the nature reserve is between 3.51-14.37 mg·kg⁻¹, with an average value of 8.32 (±4.47) mg kg⁻¹. The average concentration of NO₃⁻N in grassland soil is 11.21 mg·kg⁻¹, and the highest value is 74.24 mg·kg⁻¹, which is the highest level of non-cultivated soil. The soil NO₃⁻N content of
forest land is between 1.23-43.31 mg·kg⁻¹, with an average value of 10.66 mg·kg⁻¹, which is higher than that of the natural reserve and lower than that of the grassland. On the one hand, it is because the grassland litter increases the total nitrogen content of the soil, and on the other hand, the microbial activity improves the availability of soil nitrogen.\(^{20}\) Whereas the soil in the nature reserve is often in a waterlogged state, and the soil NO₃⁻-N was runoff or leached with water, resulting in a low concentration.\(^{21}\) Due to nitrogen fertilizer application in cultivated land, the average soil NO₃⁻-N content is 3.99 times that of non-cultivated land. The average content of NO₃⁻-N in cornfield and cotton was 58.99 and 54.19 mg·kg⁻¹, which were 1.99 and 1.83 times the average content of NO₃⁻-N in soybean soil. This is related to the difference in nitrogen requirements of crops and the farming habits of farmers.\(^{22}\) The average nitrate-nitrogen content in paddy soil is 5.48 mg·kg⁻¹, which is relatively low. It shows that there is a higher risk of surface water pollution by runoff.\(^{23}\)

### Table 1. Soil NO₃⁻-N content in different land use

| Land use          | NO₃⁻-N /mg·kg⁻¹ |
|-------------------|-----------------|
|                   | Natural reserve | Grassland | Forestland | Soybean | Corn | Paddy field | Cotton |
| Maximum           | 14.37           | 74.24     | 43.31      | 110.77  | 505.14 | 19.94       | 242.25 |
| Minimum           | 3.51            | 2.36      | 1.23       | 9.08    | 3.70   | 2.35        | 4.59   |
| Average           | 8.32            | 11.21     | 10.66      | 29.57   | 58.99  | 5.48        | 54.19  |

### 3.2. The spatial distribution characteristics of surface water NO₃⁻-N

The pH value of surface water in this area is alkaline (7.16-10.3), with an average value of 8.85 (±0.81). The EC value varies between 0.80-53.30 ms·cm⁻¹, and the average value is 15.48 ms·cm⁻¹. The significant change in surface water of EC may be affected by the replenishment of the Yellow River and seawater. The average value of DO is 10.92 (±5.95) mg·L⁻¹ and the extreme value is 0.99 and 23.10 mg·L⁻¹. The water temperature during the sampling period was between 27.0-36.9 °C, with an average value of 31.5 °C. The total N concentration is 0.80-9.77 mg·L⁻¹, and the total P concentration is 0.06-4.63 mg·L⁻¹. The surface water of COD in the study area varied between 4.8-379.2 mg·L⁻¹, with an average value of 98.9 mg·L⁻¹.

The concentration of NO₃⁻-N in surface water of the study area ranges from 0.10-4.06 mg·L⁻¹, with an average value of 1.42 mg·L⁻¹ (Figure 1a). The concentration of NO₃⁻-N in the Yellow River water ranges from 0.95-2.96 mg·L⁻¹, with an average of 2.54 mg·L⁻¹. The concentration of NO₃⁻-N in water samples from estuaries was between 0.80-1.11 mg·L⁻¹, with an average value of 0.92 mg·L⁻¹. The concentration of NO₃⁻-N in the Yellow River Farm Ditch varies from 0.24 to 2.70 mg·L⁻¹, with an average of 0.96 mg·L⁻¹. The average values of NO₃⁻-N concentration in Xiaoda River and Zhangzhen River are 0.95 and 1.37 mg·L⁻¹, respectively. The concentration of NO₃⁻-N in the water samples of Yongfeng River range from 0.80-2.74 mg·L⁻¹, and the average value is 1.93 mg·L⁻¹. The average concentration of NO₃⁻-N in the mainstream of the Zhimai river in the study area varies from 2.47 to 4.06 mg·L⁻¹. The NO₃⁻-N concentration of the water sample from the Yihong river before it flows into the Guangli River is between 0.62 and 2.07 mg·L⁻¹. The average concentration in the Guangli River was 1.31 mg·L⁻¹.

The nitrate-nitrogen flux in surface water in the study area showed an increasing trend from upstream to downstream (Figure 1b). The nitrate-nitrogen flux at the estuaries of the Xiaoda River and the Yellow River Farm Ditch were 34.18 and 24.15 g·s⁻¹, respectively. At the same time, those of Yongfeng River nearly doubled from 1.96 g·s⁻¹, and the nitrate-nitrogen fluxes at the Zhimai River and Guangli River source were 60.12 and 0.65 g·s⁻¹, respectively. The Zhimai river and Guangli River had the highest flux into the sea (321.37 g·s⁻¹), followed by the Xiaoda River and Zhangzhen River estuary (21.45 g·s⁻¹),
the flux of nitrate-nitrogen into the sea from the Yellow River Farm Ditch and the Yongfeng River were 34.18 and 3.87 g·s⁻¹, respectively.

Figure 1: Spatial characteristics of surface water nitrate concentrations (a) and nitrate N fluxes (b) in the study area

3.3. Stable isotope traces the source of surface water nitrate

The range of surface water δD-H₂O in the study area is -9.09‰ ~ -68.48‰, the average is -42.12‰ (±18.91), the range of δ¹⁸O-H₂O is -10.26‰ ~ -0.24‰, the average is -5.33‰ (±3.08). The surface water supply in this area is affected by atmospheric precipitation, groundwater, and water diversion from the Yellow River. The range of δD-H₂O in water samples from estuary is -21.29‰ ~ -9.09‰, with an average value of -13.01‰ (±3.73), and the range of δ¹⁸O-H₂O is -2.81‰ ~ -0.24‰, with an average value of -1.09‰ (±0.75). The δ¹⁵N-NO₃⁻ value in the study area varies from -1.52 to 43.71, with an average value of -9.38‰ (±8.79); The range of δ¹⁸O-NO₃⁻ value is -7.57~63.70, and the average value is 24.51‰ (±18.11). Among them, the range of δ¹⁵N-NO₃⁻ and δ¹⁸O-NO₃⁻ in the water from the Yellow River is 8.44~9.87‰, -10.26~3.22‰, and the average value is 9.25‰ (±0.59) and 18.26‰ (±0.53) respectively. The maximum values of δ¹⁵N-NO₃⁻ and δ¹⁸O-NO₃⁻ in the samples of estuaries were 9.51‰ and 63.70‰ respectively; the minimum values were -1.52‰ and 12.21‰; the average values were 5.06‰ (±0.75) and 40.18‰ (±16.21).

The results of isotope analysis indicate the source and contribution ratio of surface water(Figure 2a). Among them, groundwater, Yellow River water, and seawater contributed more than 30% to surface water recharge. The replenishment relationship was affected by meteorological factors and irrigation measures, and the water sources of different rivers are quite different[24]. The Yellow River Farm Ditch and Xiaodao River’s seawater replenishment ratio exceeds 40%, and the groundwater contribution rate is greater than 30%. About one-third of the water in the Yongfeng River comes from seawater, nearly 25% is groundwater, and more than 40% comes from the Yellow River. The water sources of Zhimai River and the Guangli River and its tributaries were dominated by the Yellow River water and groundwater, with the sum of two sources exceeds 80%. The proportion of each river source receiving recharge from the Yellow River water was high, ranging from 48.5% to 99.0%, with an average of 85.6%. The ratio of Yellow River water, precipitation and groundwater replenishment in the estuaries of the sea was 3.7%~6.6%, and the proportion of seawater was 83.6%. From the source to the sea estuary, the Yellow River water recharge ratio decreases, and the percentage of groundwater and seawater recharge is increasing(Figure 2b). This was because the water diversion from the Yellow River is continuously consumed by surrounding farmland or replenishes groundwater from upstream to downstream[25]. The midstream was recharged by groundwater, and the downstream is affected by the intrusion of seawater, which accounts for a higher proportion of seawater[26].
IsoSource model data analysis shows that human activities such as agricultural fertilization, industrial and residential wastewater, and human and animal manure dominate the primary sources of nitrate in the study area, with a total contribution of 60.8% (Figure 3a). Irrigation from the Yellow River affected the source ratio of nitrate in surface water in the upper reaches of the study area [27, 28]. The analysis results show that the source of nitrate in the upstream surface water is stable, the proportion of fertilizer and sewage is 4.5%-7.2%, and 34.8%-48.0%, respectively. It is because the upstream water supply source is similar. The R^2 fit of the ratio of nitrate from sewage sources in Guangli River to that of water recharge from Yellow River is 0.90, which is noted by the results of previous study that the main contributors to nitrate in Yellow River are human, animal manure and sewage [29].

Nitrogen fertilizer is the primary source of surface water nitrate in concentrated agricultural areas. The contribution of chemical fertilizers to the surface water nitrate in the Yellow River Farm Ditch is 70.8% (Figure 3b), which may be due to the fertilizer application of the paddy fields in this area [30]. Livestock breeding and domestic sewage discharge have increased the release of nitrate nitrogen and the proportion of human and animal manure [31]. From upstream to downstream, the ratio of nitrate from precipitation in the surface water of Xiaodao and Zhangzhen River increased by 52.6% and 40.3%, respectively, which was similar to the proportion of nitrate in precipitation entering the sea at 54.0% (±11.0%). The fitting R^2 of the ratio for nitrate in rainwater and the ratio of seawater replenishment in the water samples at the estuary is 0.50, indicating that seawater replenishment increases the proportion of nitrate from rainfall.
4. Conclusion
As the youngest continent globally, the Yellow River Delta has received extensive attention from scholars in recent years for its environmental problems, especially inorganic nitrogen pollution. The study analyzed the source of nitrate-nitrogen through regional sampling and combined with isotopes, and reached the following main conclusions: (1) The average content of NO$_3^-$-N in cultivated soil is 3.99 times that of non-cultivated land, in which corn field > cotton > soybean > paddy field; (2) Surface water nitrate-nitrogen fluxes show a continuously increasing trend from upstream to downstream, which is positively correlated with the area of the basin; (3) In the middle and upper reaches of the study area, the surface water is mainly replenished from the Yellow River water and groundwater, while the lower reaches are affected by seawater intrusion; (4) The primary sources of nitrate in the study area are dominated by human activities in agricultural production and residents’ lives, and the total contribution rate is 60.8%. To reduce the risk of nitrate-nitrogen pollution, it is vital to optimizing the amount of nitrogen fertilizer and its application. In addition, promoting the resource utilization of human and animal manure is another critical way to reduce the output of non-point source pollutants.

Acknowledgments
This study was supported by the Strategic Priority Research Program of the Chinese Academy of Sciences (XDA23050101, XDA26050202) and the Youth Innovation Promotion Association of the Chinese Academy of Sciences (2017073).

Reference
[1] Bolinches A, De Stefano L, Paredes-Arquiola J. Designing river water quality policy interventions with scarce data: the case of the Middle Tagus Basin, Spain[J]. Hydrological Sciences Journal, 2020, 65(5):749-762.
[2] Górski J, Dragon K, Kaczmarek P M J. Nitrate pollution in the Warta River (Poland) between 1958 and 2016: trends and causes[J]. Environ Sci Pollut R, 2019, 26(3):2038-2046.
[3] Ju Xiaotang G B. Status-quo, problem and trend of nitrogen fertilization in China[J]. Journal of Plant Nutrition and Fertilizer, 2014, 20(04):783-795.
[4] Xina W, Zhaohui W, Hua L I, et al. Dynamics and Availability to Crops of Residual Fertilizer Nitrogen in Upland Soil[J]. Acta Pedologica Sinica, 2016, 53(5):1202-1212.
[5] Xiaoxin L I, Shiqin W, Xiaoru C, et al. Spatial distribution and changes of nitrate in the vadose zone and underground water in northern China[J]. Chinese Journal of Eco-Agriculture, 2021, 29(1):208-216.
[6] Ascott M J, Wang L, Stuart M E, et al. Quantification of nitrate storage in the vadose (unsaturated) zone: a missing component of terrestrial N budgets[J]. Hydrol Process, 2016, 30(12):1903-1915.
[7] Paerl H W. Controlling Eutrophication along the Freshwater–Marine Continuum: Dual Nutrient (N and P) Reductions are Essential[J]. Estuar Coast, 2009, 32(4):593-601.
[8] Pilotti M, Barone L, Balistrrochi M, et al. Nutrient delivery efficiency of a combined sewer along a lake challenged by incipient eutrophication[J]. Water Res, 2021, 190:116727.
[9] Guo Z, Yan C, Wang Z, et al. Quantitative identification of nitrate sources in a coastal peri-urban watershed using hydrogeochemical indicators and dual isotopes together with the statistical approaches[J]. Chemosphere, 2020, 243:125364.
[10] Zhou D, Yu M, Yu J, et al. Impacts of inland pollution input on coastal water quality of the Bohai Sea[J]. Sci Total Environ, 2021, 765:142691.
[11] Zhang Y, Shi P, Song J, et al. Application of Nitrogen and Oxygen Isotopes for Source and Fate Identification of Nitrate Pollution in Surface Water: A Review[J]. Applied sciences, 2018, 9(1):18.
[12] Richards G, Gilmore T E, Mittelstet A R, et al. Baseflow nitrate dynamics within nested watersheds of an agricultural stream in Nebraska, USA[J]. Agriculture, ecosystems & environment, 2021, 308.
[13] ZHANG H, LI Y, MENG Y, et al. The effects of soil moisture and salinity as functions of groundwater depth on wheat growth and yield in coastal saline soils[J]. J Integr Agr, 2019,18(11):2472-2482.

[14] Xu R, Cai Y, Wang X, et al. Agricultural nitrogen flow in a reservoir watershed and its implications for water pollution mitigation[J]. J Clean Prod, 2020,267:122034.

[15] Beusen A, Bouwman A, van Beek L P H, et al. Global riverine N and P transport to ocean increased during the 20th century despite increased retention along the aquatic continuum[J]. Biogeosciences, 2016,13(8):2441-2451.

[16] Denk T R A, Mohn J, Decock C, et al. The nitrogen cycle: A review of isotope effects and isotope modeling approaches[J]. Soil Biol Biochem, 2017,105:121-137.

[17] Shi Y, Jia W, Zhu G, et al. Hydrogen and Oxygen Isotope Characteristics of Water and the Recharge Sources in Subalpine Qilian Mountains, China[J]. Pol J Environ Stud, 2021.

[18] Xu L, Jiang Y J, Duan S H, et al. [Quantification of Nitrate Sources to Groundwater in Karst Trough-valley Areas Based on Dual Stable Isotopes of delta(15)N-NO3(-) and delta(18)O-NO3(-) and the IsoSource Model][J]. Huan Jing Ke Xue, 2020,41(8):3637-3645.

[19] Wang Z, Li S, Yue F, et al. Rainfall driven nitrate transport in agricultural karst surface river system: Insight from high resolution hydrochemistry and nitrate isotopes[J]. Agriculture, ecosystems & environment, 2020,291:106787.

[20] Sheng-xiang L, Yun-tao R, Xiao-bo Y, et al. Effects of fencing on contents of soil ammonium nitrogen and nitrate nitrogen in the Loess Plateau, northern China[J]. Pratacultural Science, 2016,33(6):1044-1053.

[21] Lu Qiongqing B, Z Q. Spatial and Temporal Distribution Characteristic of Nitrate Nitrogen in Soils of Tidal and Short-term Flooding Wetlands in Yellow River Delta[J]. Wetland Science, 2013,11(04):407-412.

[22] Zhang Peng Z R D S. Research advances in nitrate uptake and transport in plants[J]. Journal of Plant Nutrition and Fertilizer, 2015,21(03):752-762.

[23] Shi X, Hu K, Batchelor W D, et al. Exploring optimal nitrogen management strategies to mitigate nitrogen losses from paddy soil in the middle reaches of the Yangtze River[J]. Agr Water Manage, 2020,228:105877.

[24] Yin L, Feng X, Fu B, et al. A coupled human-natural system analysis of water yield in the Yellow River basin, China[J]. Sci Total Environ, 2021,762:143141.

[25] Chen Y, Fu B, Zhao Y, et al. Sustainable development in the Yellow River Basin: Issues and strategies[J]. J Clean Prod, 2020,263:121223.

[26] Chang Y, Hu B X, Xu Z, et al. Numerical simulation of seawater intrusion to coastal aquifers and brine water/freshwater interaction in south coast of Laizhou Bay, China[J]. J Contam Hydrol, 2018,215:1-10.

[27] Castaldo G, Visser A, Fogg G E, et al. Effect of Groundwater Age and Recharge Source on Nitrate Concentrations in Domestic Wells in the San Joaquin Valley[J]. Environ Sci Technol, 2021,55(4):2265-2275.

[28] Zhang X, Zhang Y, Shi P, et al. The deep challenge of nitrate pollution in river water of China[J]. Sci Total Environ, 2021,770:144674.

[29] Yue F, Waldron S, Li S, et al. Land use interacts with changes in catchment hydrology to generate chronic nitrate pollution in karst waters and strong seasonality in excess nitrate export[J]. The Science of the total environment, 2019,696:134062.

[30] Wang H, He P, Shen C, et al. Effect of irrigation amount and fertilization on agriculture non-point source pollution in the paddy field[J]. Environ Sci Pollut Res Int, 2019,26(10):10363-10373.

[31] Liu J, Shen Z, Yan T, et al. Source identification and impact of landscape pattern on riverine nitrogen pollution in a typical urbanized watershed, Beijing, China[J]. Sci Total Environ, 2018,628-629:1296-1307.