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Quantitative sources of nitrate in typical plain river network areas by a combined PMF and MixSIAR approach

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Nitrate nitrogen (NO_3^-) pollution has become a severe issue in the plain river network areas with the intensification of human activities, leading to environmental problems such as eutrophication. Therefore, it is imperative to trace the sources of NO_3^- in rivers. This study performed stable isotope sampling on samples collected from two main rivers of the Yubei Plain river network based on different land-use types, with sampling focused on aquaculture and industrial areas. A combination of positive matrix factorization models (PMF), isotope tracer and mixed stable isotope analysis in R (MixSIAR) was used to quantify the sources of NO_3^- in the typical plain river network in China. NO_3^- concentrations in the river network of the Yubei Plain ranged from 0.62 to 1.54 mg L^{-1} and showed an increasing trend downstream. NO_3^- accounted for over 70% of the total nitrogen (TN) concentration. PMF and MixSIAR results showed that industrial, agricultural, domestic and aquaculture wastewater were the main drivers of NO_3^- in the river network. The results from both the PMF and MixSIAR models were similar, confirming the validity of the analysis. The results showed that industrial wastewater contributed more than 40% of NO_3^-, which was the main driver affecting NO_3^- pollution in the river network. In addition, nitrification was significant in the plain river network, while denitrification was negligible. The results of this study provide valuable insights into the pollution control of nitrate nitrogen in plain river network areas.

Environmental significance

The theme of this study focused on quantifying the sources of NO_3^- in a typical plain river network in China using positive matrix factorization models (PMF), isotope tracing and mixed stable isotope analysis in R (MixSIAR). PMF and MixSIAR results showed that industrial, agricultural, domestic and aquaculture wastewater were the main drivers of NO_3^- in the river network. The results showed that industrial wastewater contributed more than 40% of NO_3^-, which was the main driver affecting NO_3^- pollution in the river network. Also, nitrification was significant in the plain river network, while denitrification was negligible. The results of this study provide valuable insights into the control of nitrate nitrogen pollution in the plain river network.

1. Introduction

Intensive production and subsistence activities in plains river networks have resulted in the discharge of large amounts of pollutants into the environment.[1] In recent years, economic development has caused nitrate nitrogen (NO_3^-) pollution, leading to a severe decline in the water quality of plain river networks and compromising water security.[2] NO_3^- has become the most common nitrogen pollutant in aquatic environments due to its stability, solubility and mobility.[3] NO_3^- pollution directly contributes to water acidification, eutrophication and algal blooms.[4] Long-term consumption of water with excessive NO_3^- will cause methemoglobinemia, hypertension and cardiovascular diseases, which seriously jeopardize human health.[5] In order to control NO_3^- pollution, it is critical to identify anthropogenic impacts and quantify NO_3^- sources.

NO_3^- pollution in the plain river network originates from various sources, such as agricultural cultivation, atmospheric deposition, domestic sewage, livestock farming and industrial wastewater.[6] Determining NO_3^- sources is the key to effectively controlling and managing NO_3^- pollution in plain river networks. For hidden emission pathways, sources are difficult to trace effectively by traditional methods such as emission inventories and comparisons of characteristic compounds.[7]

Source apportionment originally emerged from the study of atmospheric pollutants and has been extensively applied to water and soil systems in recent years.[8] Pollution sources in rivers include point and non-point sources.[9] The quantitative analysis of point sources often employs statistical methods based on survey data. In addition, quantitative analysis of non-point source pollution includes both statistical models and

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numerical simulation models. Currently, common pollutant source apportionment models include the chemical mass balance (CMB), positive matrix factorization (PMF) and multivariate statistical methods.[10] Stable isotopes are regarded as natural tracers and are extensively applied in pollutant source apportionment, integrated with pollutant source-tracking models, which enable precise and quantitative identification of pollution sources.[11]

Analyzing $\delta^{15}N/\delta^{18}O–NO_3^-$ combined with chemical composition, statistical methods and land use is one of the important ways to trace NO_3^- pollutants.[12] $\delta^{15}N$ and $\delta^{18}O$ are effective tracers for qualitatively assessing the fate of NO_3^- in plain rivers, although they may partially overlap in different pollution sources.[4] When the isotopic composition of sources is known, Bayesian-based mixed-mode methods, such as the stable isotope analysis in R (SIAR) model, assess NO_3^- source apportionments[6] and identify nitrification and denitrification. Other source apportionment methods, such as positive matrix factorization models (PMF), can elucidate and quantify source effects.[13] The above methods have been successfully applied in the field of NO_3^- pollution of surface water. According to the results of previous studies, the source and transformation of NO_3^- vary by region.[14] NO_3^- pollution sources are related to the intensity of human activities and land-use patterns.[12] Domestic wastewater is usually leached or discharged into rivers in towns and cities. In industrial areas, the main source of NO_3^- in rivers is industrial wastewater. In agricultural areas, fertilizers and livestock feed are the main sources of NO_3^- in rivers.[15] Nitrogen transformation processes are strongly influenced by environmental conditions. Specifically, nitrification is driven by neutral to slightly alkaline pH and high dissolved oxygen (DO) levels, whereas denitrification typically occurs under slightly acidic and anaerobic conditions.[16]

The Yubei Plain is located on the south coast of Hangzhou Bay. The river width of the river network in the Yubei Plain is 40–60 m. The normal water level of the river is 2.7 m, and the river network is mainly discharged to the Hangzhou Bay through the No. 2 and Dongjin lock. The water quality in the upper reaches of the river network in the Yubei Plain is basically stable at the Class III surface water standards of China. From north to south, water quality continues to deteriorate, and downstream water quality does not meet the Class V surface water standards of China. Previous studies have focused on water resource management and allocation, but little attention has been paid to the quantitative sources of NO_3^- in the plains river network water.[17] In this study, the physicochemical and isotopic characteristics of water quality in the river network of the Yubei Plain were investigated. Stable isotopes ($\delta^{15}N/\delta^{18}O–NO_3^-$) were introduced into the combination of PMF and Mixed SIAR (MixSIAR) models to assess the key factors affecting NO_3^- and to quantify the anthropogenic impacts and sources of NO_3^- in the plain river network.[13] The aim of this study was (1) to elucidate the distribution of nitrogen in the river network, (2) to analyze the main influencing factors of water quality, (3) to estimate the transformation of NO_3^-, and (4) quantify the contribution of NO_3^- as a source of pollution. The results of the study can provide a basis for NO_3^- pollution control in the river network of the Yubei Plain.

2. Study area and methodology

2.1. Study area

Yubei Plain is located in Shangyu County (the south coast), Zhejiang Province, and its location is shown in Fig. 1. The river network of the Yubei Plain consists of two main rivers, the Tuanjie River (west) and the Dongjin River (east). The location of sampling sites on the Yubei Plain river network was mainly distributed along the two mainstem rivers, and the information of the sampling sites is shown in Fig. S1. The main rivers in the Yubei Plain river network span a total length of 157 km, primarily including the Tuanjie River and the Dongjin River, with channel widths ranging from 40 m to 60 m. Industrial, agricultural, and aquaculture areas are distributed in clusters, while residential areas are relatively scattered. Among these, the aquaculture area is the largest, covering 103.93 km^2.

The industrial parks, agricultural plantation areas and aquaculture in the Yubei Plain are distributed in a continuous manner, while the distribution of residential areas is relatively scattered. According to the distribution characteristics, the survey area is subdivided into agricultural, shoal, aquaculture, greenhouse and industrial areas. The distribution is shown in Fig. S2. Along the Dongjin River, there are two distinct land-use patterns: greenhouse and industrial. The Tuanjie River is situated in the western area of the Yubei Plain, and there are paddy fields and shrimp farms.

2.2. Methodology

By analyzing the land use types and pollutant source classification in the Yubei Plain, the main influencing factors on water quality were identified. In addition, the relationship between the water quality indicators and the sources of NO_3^- contamination was explored using stable isotope statistical analysis using PMF. The potential sources are further assessed using MixSIAR for comparison with the PMF.

Water samples for detection of NH_4^+, TN, and $\delta^{15}N/\delta^{18}O–NO_3^-$ were filtered through a 0.22 μm Millipore organic phase filtration membrane. NH_4^+ and TN were analyzed according to the standard Chinese method (Standard Method for the Examination of Water and Wastewater Editorial Board, 2002). The $\delta^{15}N–NO_3^-$ and $\delta^{18}O–NO_3^-$ values were determined using the chemical conversion method. Specifically, 20 mL of a filtered water sample was placed in a headspace vial. Then, 0.1 mL of 20 g per L cadmium chloride, 0.8 mL of 250 g per L ammonium chloride, and a zinc plate were added sequentially. The vial was vigorously oscillated for 15 min to ensure complete reduction of NO_3^- to NO_2^-, after which the zinc plate was removed. Subsequently, 1 mL of azide buffer solution (2 M NaN_3 : 20% CH_3COOH, v/v = 1 : 1) was injected into the vial, followed by continuous oscillation for 30 min to allow full conversion of NO_2^- to N_2O. The $\delta^{15}N$ and $\delta^{18}O$ values of the produced N_2O were analyzed using an Isotope Ratio Mass Spectrometer (IRMS, Thermo Fisher MAT 253) coupled with a GasBench II device (Thermo Fisher). The reproducibility of the method was within ±0.2‰ for both $\delta^{15}N–NO_3^-$ and $\delta^{18}O–NO_3^-$.

Aliquots of 50 mL of all samples were used for $\delta^{15}N/\delta^{18}O–NO_3^-$ measurements. Water samples were pretreated in

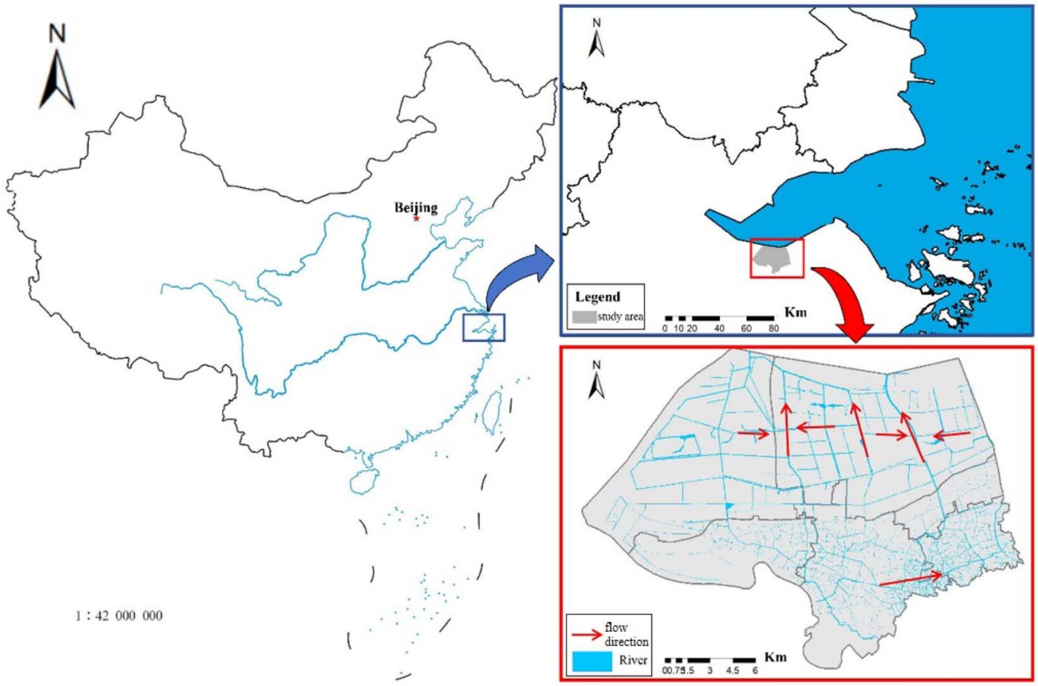

Fig. 1 Geographical location of the study area.

a weakly alkaline environment and then in a weakly acidic buffer system. An isotope mass spectrometer (MTA-253plus, Thermo Fisher Scientific Corp., US) was used to measure the $^{15}N/^{14}N$ and $^{18}O/^{16}O$ ratios of nitrous oxide. The $\delta^{15}N$ and $\delta^{18}O$ values of NO_3^- were calculated from eqn (1).

$$\delta(‰) = \frac{R_{\text{sample}} - R_{\text{reference}}}{R_{\text{reference}}} \times 1000 \quad (1)$$

R_{sample} and $R_{\text{reference}}$ are the ratios of $^{15}N/^{14}N$ and $^{18}O/^{16}O$ for the sample and references, respectively. The reference value for $^{15}N/^{14}N$ is atmospheric nitrogen and that for $^{18}O/^{16}O$ is Vienna Standard Mean Seawater.

2.3. Sampling and measurement

In this study, 15 water samples were collected from the Yubei Plain river network in April 2023 (Fig. S1). No. 1–7 samples were collected from the Dongjin river, No. 8–13 samples from the Tuanjie River, and No. 14–15 samples from the aquaculture area in the west of the Yubei Plain. Sampling sites were located as follows: sites 1, 2, 3 and 8 in the agricultural area; sites 4, 5 and 6 in the industrial area; site 7 in the shoal area; and sites 9–15 in the aquaculture area. A 500 mL water sample was collected at 0.5–1 m below the water surface using the glass sampler, and the samples were packed into brown glass bottles. The samples were transported to the laboratory and stored at 4 °C. In addition, a portable multiparameter detector was used to measure the temperature, pH and DO of water samples *in situ*.

2.4. Data analysis

Land-use types were analyzed using ArcGIS 10.4. The NO_3^- source contribution to the Yubei Plain was calculated using the PMF model constructed with the EPA PMF5.0 software. The MixSIAR model was used to quantify the sources of NO_3^- in the Yubei Plain.

The PMF model is a multivariate factor analysis class model, which decomposes the sample data into a factor contribution and a factor spectrum. The factor contribution of the sample is quantified by identifying its factor spectrum.

The MixSIAR model is a source apportionment model based on a Markov chain Monte Carlo fitting method. The model combines several previously proposed mixed models (IsoSource and SIAR) into a single framework for estimating the proportional contribution of the source.[18] Compared with previous mixed models, the MixSIAR model is able to account for variability in mixture proportions by including fixed and random effects as covariates.[19] The MixSIAR model calculates the proportion of potential sources contributing to the mixture based on the conservation of mass of the tracer, tracking the number of sources is greater than the number of tracers.

In this study, the MixSIAR model in R was employed to quantify the relative contribution proportions of NO_3^- sources in surface water. The model estimates the potential contribution of a source to a mixture based on tracers (typically stable isotopes) through mass conservation equations, as expressed below.

$$X_{ij} = \sum_{k=1}^{n_s} p_{ik} s_{kj} + \varepsilon_{ij} \quad (2)$$

X_{ij} is the value of the jth tracer in the ith sample; n_s is the number of potential sources; p_{ik} is the proportion of the mixture in the ith sample contributed by the kth source; s_{kj} is the value of the jth tracer in the kth source; and ε_{ij} denotes the residual error associated with the jth tracer in the ith sample.

3. Results and discussion

3.1. Physiochemical and isotopic characteristics of the Yubei Plain

3.1.1. Physiochemical characteristics. The TN concentration of water in the Yubei Plain river network varied between 1.31 and 3.31 mg L^{-1} (Fig. 2), and the TN concentration in the west of the Yubei Plain river network was significantly higher than that in the east of the Yubei Plain river network. The TN concentration was slightly higher downstream than upstream. The NO_3^- as a percentage of TN ranged from 19% to 81% (Fig. 2), and the percentage of NO_3^- in the east of the Yubei Plain was higher than 70%. According to the test results, NO_3^- is the main nitrogen pollutant. There were spatial differences in TP concentrations in the Yubei Plain, with mean values of 0.07 and 0.59 mg L^{-1} on the eastern and western sides, respectively. The COD_{Mn}, COD_{Cr} and BOD_5 spatial distributions all followed the same trend as TN.

3.1.2. Isotopic characteristics. In the eastern Yubei Plain river network, the $\delta^{15}N/\delta^{18}O–NO_3^-$ value varied from 3.89‰ to 9.08‰ and from 3.29‰ to 6.93‰, both showing decreasing and then rising trends along the Dongjin river (Fig. S3). In the western Yubei Plain river network, the $\delta^{15}N/\delta^{18}O–NO_3^-$ value ranged from 6.23‰ to 7.77‰ and from 5.76‰ to 7.18‰, and there were no significant changes in $\delta^{15}N/\delta^{18}O–NO_3^-$ along the Tuanjie River. The $\delta^{15}N/\delta^{18}O–NO_3^-$ mean values on the west of the Yubei Plain river network were higher than those on the east.

3.2. Main influencing components of water quality using PMF

Four major potential pollution sources affecting the water quality of the Yubei Plain river network were analyzed by principal component analysis (PCA). The percentage of each principal component and the proportional contribution to the variables were assessed by PMF (Fig. 3).

F1 accounts for 42.6% of the four components, contributing negligibly to a-ASS (anionic surface-active agent) and BOD_5 but contributes considerably to other variables such as F^-, TP and NH_4^+ (Fig. 3a and b). F^- in surface water usually comes from natural sources (weathering of fluoride minerals) and anthropogenic pollution (industrial wastewater).[20] According to the land-use type analysis, there is no mining activity for fluoride minerals in the study area, and there is a large-scale industrial park in the surrounding area. In addition, electroplating processing is an important component within the industrial park, according to the field survey. Therefore, F1 was concluded to be originating from industrial wastewater, contributing 42.6% of NO_3^- in the Yubei Plain river network.

F2 comprised 25.5% of the four components and contributed more (>20%) to all variables except F^- and TP, indicating the importance of agricultural pollution (Fig. 3). Frequent agricultural activities lead to widespread application of nitrogen fertilizers and sewage irrigation in the study area, resulting in NO_3^- pollution of surface water. The heavy use of fertilizers, such as nitrogen and phosphate fertilizers, causes surface water pollution through the spillage of irrigation water and runoff into nearby rivers.[21] Therefore, F2 may indicate the agricultural pollution contribution of 25.5% to NO_3^- in the Yubei Plain river network.

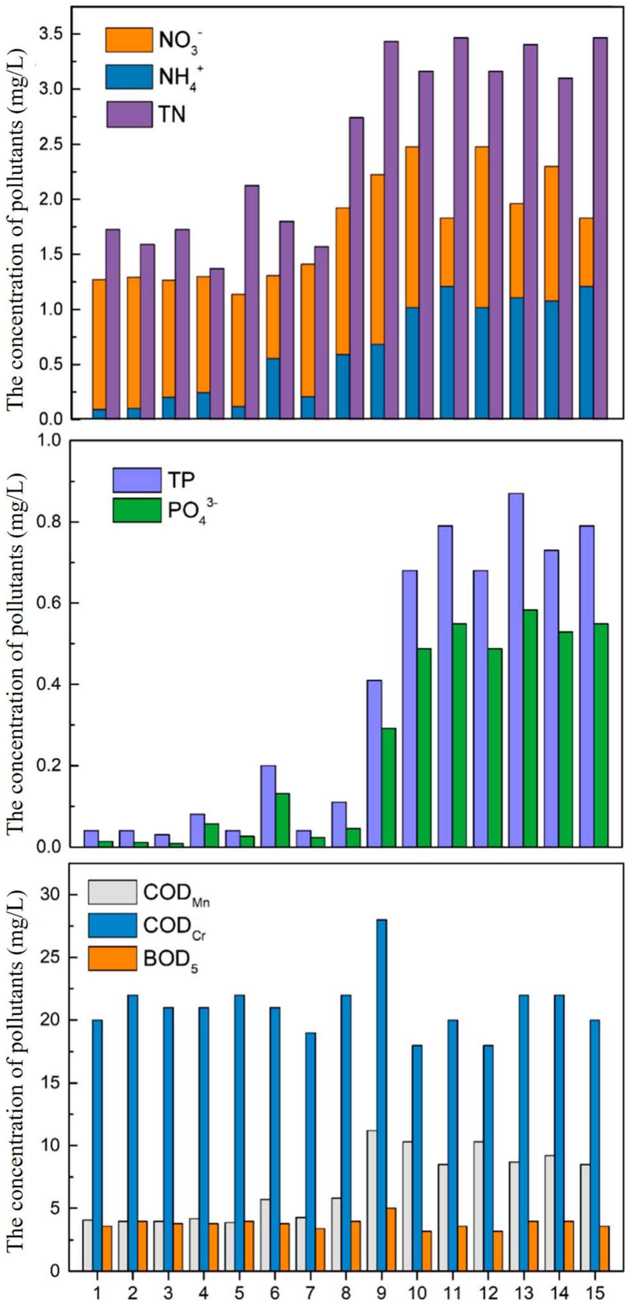

Fig. 2 Spatial variations of physiochemical variables in the Yubei Plain river network.

F3 comprised 20.3% of the four components, with a significant contribution (18% and 18%) to a-ASS and BOD_5 (Fig. 3b). The a-ASS occupies an important role in petrochemicals and also can be found in many products in use.[22] Furthermore, the domestic wastewater also exhibited a high BOD_5 concentration. Therefore, F3 may indicate that the domestic wastewater influx contributed 20.3% to NO_3^- in the Yubei Plain river network.

F4 accounts for 10.6% of the four components, and it contributed significantly (8%) to TN but negligibly to the other

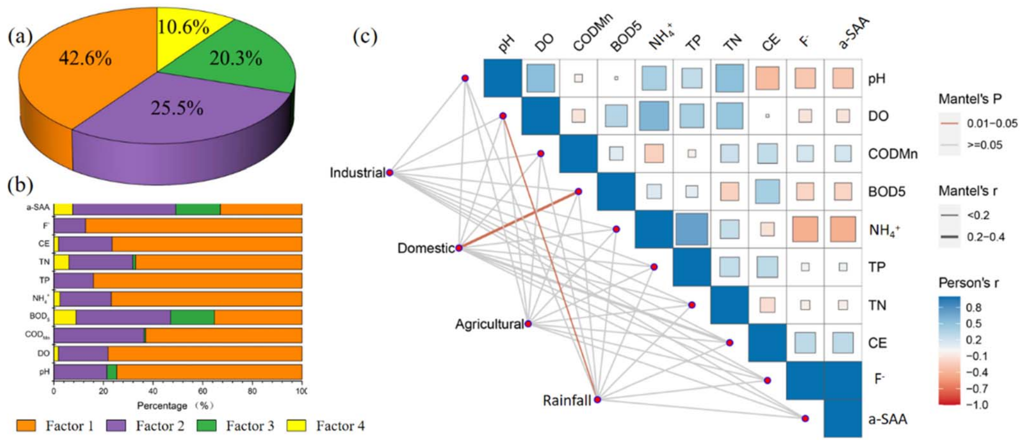

Fig. 3 The results of correlation analysis and PMF based on the physiochemical variables of the Yubei Plain river network. (a) The results of PMF analysis. (b) The contributions of factors (pollution sources) to different physiochemical variables. (c) Correlation analysis between physiochemical variables and pollution sources.

variables (Fig. 3a and b). TN was correlated with pH and DO, but not with a-ASS and F^- (Fig. 3c). pH and DO may be dependent on rainfall, as acid rainfall is frequent in the study region and rain promotes the dissolution of oxygen in surface water.[23] In addition, rainfall would promote surface runoff that carries pollutants into surface water.[24] Therefore, F4 should be associated with rainfall, which contributes only 10.6% of NO_3^- in the Yubei Plain river network (Fig. 3b).

According to the results of PMF analyses, the pollution sources in the river network of the Yubei Plain were mainly industrial wastewater. There are two industrial parks in the Yubei Plain, Hangzhou Bay Industrial Park and Lihai Industrial Park, with areas of 37.45 km^2 and 1.41 km^2, respectively. The concentration of NO_3^- in industrial wastewater (25.9 ± 7.6 mg L^{-1}) was higher than that of other wastewater.[25] The concentration of NO_3^- in the Yubei Plain river network is much lower than that in industrial wastewater. The leakage of industrial wastewater into the river has a significant effect on the NO_3^- concentration in the river network water quality.

3.3. Nitrogen transformation in the plain river network

Nitrification and denitrification are important parts of the nitrogen cycle, which can significantly change the concentration and type of nitrogen in water.[4,26] Nitrogen cycling has a significant impact on aquatic environments and ecosystems.[27]

Nitrification is the process of oxidation of NH_4^+ in water to NO_3^-, which usually occurs in an aerobic environment.[28] According to the results of a previous study, nitrification is easier to occur in an environment with DO concentrations of 4–9 mg L^{-1} and pH values of 6.5–8.[29] The test results showed that the DO concentration in the Yubei Plain river network was high, which favored the occurrence of nitrification (Fig. 4). DO was positively correlated with TN and NO_3^- (Fig. 4c), suggesting a strong nitrification reaction in the Yubei Plain river network. During nitrification, ^{16}O and ^{17}O of DO and ^{14}N of NH_4^+ are preferentially enriched in the NO_3^- formed, leading to an increase in NO_3^- concentration and a decrease in $\delta^{15}N/\delta^{18}O$–$NO_3^-$.[30] DO was positively correlated with $\delta^{15}N$–NO_3^- in the river network and only weakly positively correlated with $\delta^{18}O$–NO_3^- (Fig. 4a and b). Hydrological conditions also have an impact on nitrogen cycle processes. Due to the impact of sluices, there are significant differences in nitrogen transformation between the main and tributary rivers. Sluice opening accelerates river flow velocity and reduces denitrification. In contrast, rivers with poor hydrological connectivity exhibit stronger denitrification activity. Results indicate that nitrification in the main river is significantly stronger than that in the tributary. Previous studies have suggested that 2/3rd of the oxygen in NO_3^- originated from H_2O, while 1/3rd originated from O_2,[31] where the $\delta^{18}O$–O_2 is 23.5‰ during the nitrification and the $\delta^{18}O$–H_2O value of the river varies from −6.27‰ to −4.31‰.[32] The calculated theoretical values of $\delta^{18}O$–NO_3^- for each sample ranged from 3.65‰ to 4.96‰. The calculated results were significantly lower than the $\delta^{18}O$–NO_3^- values in the water of the Yubei Plain river network (Fig. S3). Therefore, the nitrification of the study area was stronger. The result was validated by the results in Fig. 2, in which the NO_3^- concentration as a percentage of TN was higher than NH_4^+.

Denitrification is the process of reducing NO_3^- to N_2 or nitrogen compounds under anaerobic conditions. The most suitable conditions for denitrification were a DO concentration of 0–2 mg L^{-1} and pH of 5.5–8; denitrification was negligible when the DO concentration exceeded 2 mg L^{-1}.[33] As can be seen in Fig. 4, the environment of the Yubei Plain river network did not provide optimal conditions for denitrification, and NO_3^- concentration showed a positive correlation with DO concentration, indicating that denitrification in the river was almost negligible. According to the results of previous studies, denitrification microorganisms preferentially consumed the light isotopes in NO_3^- and enriched the heavy isotopes, leading to a decrease in NO_3^- and an increase in $\delta^{15}N/\delta^{18}O$–$NO_3^-$ in water, with the $\delta^{15}N/\delta^{18}O$ ratio increasing from 1.3 : 1 to 2.1 : 1.[34] Therefore, $\delta^{15}N$–NO_3^- showed a significant positive correlation with $\delta^{18}O$–NO_3^- in the range of 0.48–0.77, which could be used as a basis for determining denitrification in water. As shown in Fig. S3, the $\delta^{15}N/\delta^{18}O$–$NO_3^-$ ratios ranged from 1.04 : 1 to 1.31 :

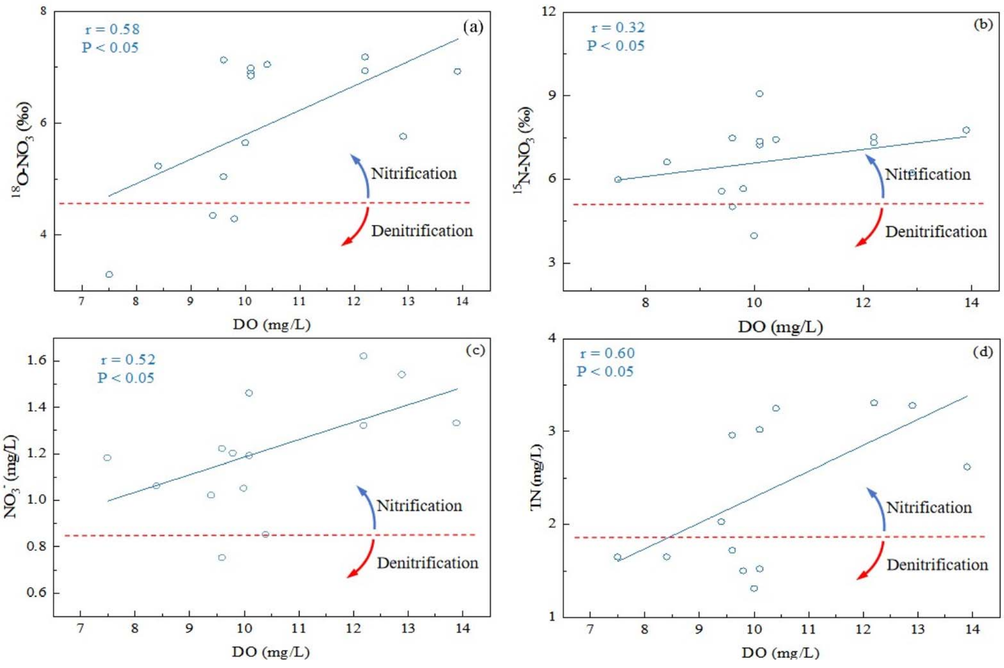

Fig. 4 The relationship between DO and isotopic variables in the Yubei Plain river network. (a) The relationship between $^{18}O-NO_3^-$ and DO. (b) The relationship between $^{15}N-NO_3^-$ and DO. (c) The relationship between NO_3^- and DO. (d) The relationship between TN and DO.

1 (consistently below 1.3 : 1), and the regression slope of the $\delta^{15}N$ *versus* $\delta^{18}O$ values (0.41) fell outside the range of 0.48–0.77. There was a positive correlation between TN and DO values (Fig. 4d), and the positive correlation between DO and $\delta^{15}N/\delta^{18}O$ supports this hypothesis (Fig. 4a and b). In summary, denitrification was not present in the Yubei Plain river network.

3.4. NO_3^- pollution sources of the plain river network using MixSIAR

As can be seen from Fig. 5, the stable isotopes in the Yubei Plain river network were similar to those in agricultural sources, domestic sources and pharmaceutical wastewater of industrial sources; however, the distances to aquaculture sources, chemical wastewater and dyeing wastewater of industrial sources were significantly farther away than the distances to agricultural sources. Because the aquaculture, agricultural, industrial and domestic samples were collected directly from the study area rather than from data in the previous study (Fig. S4), the stable isotope signatures of local potential pollution sources could be reliably represented. As shown in Fig. S4, in industrial wastewater, the $\delta^{18}O-NO_3^-$ values of chemical wastewater and dye wastewater are similar, while the $\delta^{18}O-NO_3^-$ value of pharmaceutical wastewater is closer to that of agricultural wastewater and domestic wastewater. Similar results were also found for the $\delta^{15}N-NO_3^-$ values. The single stable isotope indices of $\delta^{15}N$ or $\delta^{18}O$ still cannot effectively distinguish each potential pollution source. Therefore, it was necessary to analyze these types of pollution sources using the double isotope method, which can effectively reflect the characteristics of each source. As shown in Fig. 5, the double isotope method could effectively distinguish between individual pollution sources. Through the double isotope method of $\delta^{15}N$ and $\delta^{18}O$, six potential pollution sources could be effectively distinguished, and each pollution source was more specific. The specific calibration of potential sources of NO_3^- enabled further traceability of NO_3^- sources in the river network; the more significant the source specificity, the higher the traceability accuracy.

The isotopes of water samples from the plain river network were closer to those of industrial, agricultural and domestic wastewater, which was in agreement with the results of chemical analyses (Fig. 5). Therefore, industrial, agricultural and domestic wastewater were the main sources of NO_3^- in the Yubei Plain river network. The isotopes of the river network

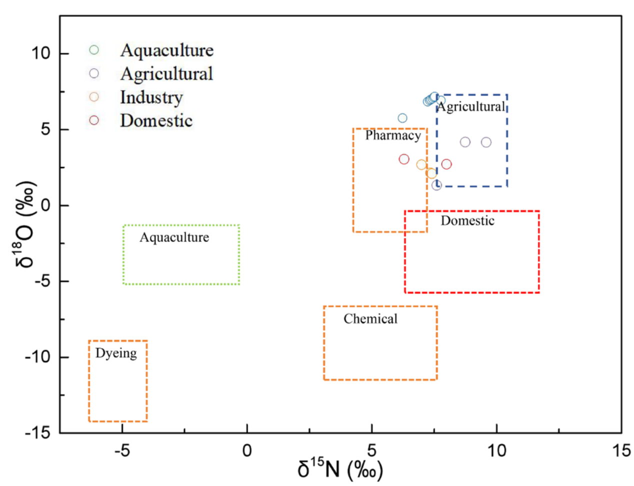

Fig. 5 Diagrams of $\delta^{15}N-NO_3^-$ and $\delta^{18}O-NO_3^-$ in the Yubei Plain river network.

water samples were on the upper side of the chemical wastewater range, indicating an important contribution of chemical wastewater to NO_3^- in the Yubei Plain river network. The contribution of NO_3^- from aquaculture and dyeing wastewater to the river network water was small because it was isotopically different from the river network water (Fig. 5). The results of the isotopic analyses were consistent with those of the PMF model. It was also found that the isotopic characteristics of the plain river network varied with land use patterns, reflecting changes in sources (Fig. 5). In order to determine the contribution of the plain river network to NO_3^- sources under different land use patterns, a quantitative assessment using the MixSIAR model was required.

In order to quantify NO_3^- sources in the Yubei Plain river network, industry, agriculture, domestic and aquaculture were used as pollution end-elements as these sources were identified by PMF as well as isotopic tracers (Fig. 3 and 5). To further quantify the NO_3^- sources in the plain river network in different land-use areas, industrial wastewater was also split into chemical, pharmacy and dyeing wastewater. As shown in Fig. S2 and Table S3, the southern part of the study area (river upstream) was dominated by agricultural activities according to the land-use type analysis, with a total agricultural area exceeding 100 km^2. Thus, pollution in the river upstream was primarily attributed to agricultural activities. In the river network downstream, the eastern side is predominantly occupied by industrial parks, with a total area of 37.45 km^2. Thus, pollution in the eastern river downstream was primarily influenced by industrial activities. On the western side, the area is mainly characterized by aquaculture areas, covering more than 100 km^2. Consequently, pollution in the river downstream of the western was primarily influenced by aquaculture-related emissions.

The contribution of potential sources to NO_3^- in the river network was estimated based on all the data (Fig. 6a). The MixSIAR results showed that the average contribution of NO_3^- in the river network was 45.92% from industrial wastewater, 22.97% from agricultural wastewater, 17.97% from domestic wastewater and 13.14% from aquaculture wastewater (Fig. 6a). Among these, the contribution of industrial wastewater to NO_3^- in the river network was subdivided into dyeing (14.72%), pharmacy (13.95%) and chemical (17.26%) wastewater. The MixSIAR and PMF results were consistent, proving the reliability of the model. It could be seen that the potential sources of aquaculture, pharmacy, chemical, dyeing, domestic and agricultural contributed 13%, 14%, 17%, 10%, 25% and 21% of NO_3^- pollution to the upper stream of the river, respectively. The results of the contribution indicate that NO_3^- pollution in the upper stream of the river was mainly due to agricultural and domestic sources, while the lower stream of the river was mainly affected by chemical wastewater (27%). Compared with upstream NO_3^- pollution, the contribution of chemical, pharmaceutical and dyeing sources to downstream NO_3^- pollution in the river increased (Fig. 6b).

The pollutant discharge survey was conducted in the river downstream impacted by industrial pollution. The spatial distribution of pollutant emissions across the study area was accurately identified and geographically localized by a combined approach of stable isotope source tracing and land-use pattern analysis. The results revealed the detection of pollutant discharge points as presented in Fig. S6 and S7. Among them, five points were located within the industrial area, with the remaining three points distributed individually across the aquaculture and agricultural area. The average concentration of NO_3^- at the discharge outlet was 22.17 mg L^{-1}, which far exceeded the standards for surface water.

The agricultural area was mainly located in the upper stream of the river in the Yubei Plain, and the contribution of agricultural wastewater to NO_3^- was higher in the upper stream than in the lower stream of the river. Nitrogen left in the paddy field was still lost to the river *via* surface runoff, and fertilizers were the main source of NO_3^- pollution, and vegetables grown along the river may also be major sources of NO_3^- pollution.[35] NO_3^- from crop fertilization, organic matter decomposition and other sources sinks into the river through surface runoff following rainfall, increasing the contribution of agricultural pollution to NO_3^- in the river.[35] In the upstream reaches, agricultural sources were the dominant contributor to nitrate pollution, a role which shifted to industrial wastewater in the downstream sections. According to the site survey, industrial activities become more intensive along the river and the

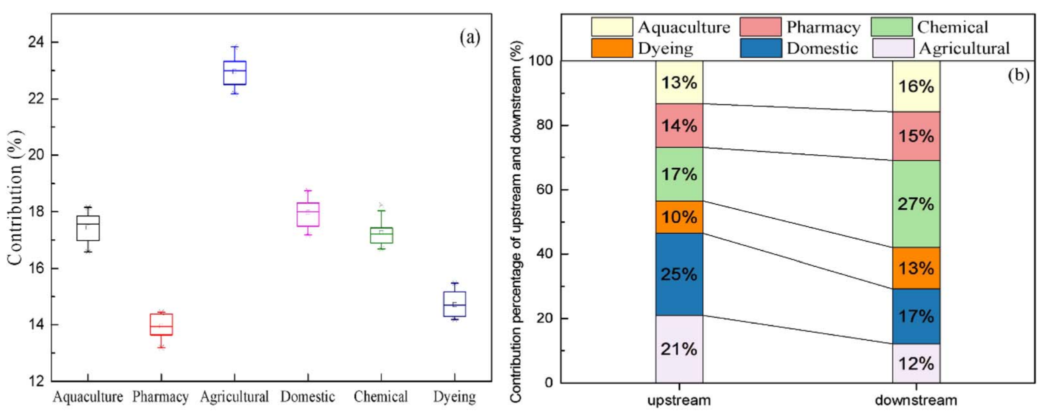

Fig. 6 The contribution of potential sources to NO_3^- based on the MixSIAR. (a) The contribution rates of different pollution sources to river pollution. (b) The changes in the contribution rates of different pollution sources to the pollution of upstream and downstream rivers.

farmland areas become smaller and smaller. Nitrogen compounds discharged from factories enter the river through precipitation runoff, increasing the nitrogen content of the river.

4. Conclusions

The anthropogenic influences and quantitative sources of NO_3^- in a typical plain river network were identified by integrating the PMF model, isotopic tracing and MixSIAR. The NO_3^- concentration of water in the Yubei Plain river network ranged from 0.62 to 1.54 mg L^{-1}, accounting for more than 70% of the TN concentration. The effects of industrial, agricultural, domestic and aquaculture activities were determined by multivariate statistical analysis. Strong nitrification and weak or no denitrification occur in the Yubei Plain river network based on water quality characteristics and isotope analyses. The results of the MixSIAR evaluation of NO_3^- sources in the river network were consistent with the PMF results, indicating that industrial wastewater contributes more than 40.1% to NO_3^-, while agricultural wastewater contributes more than 20%. In the upstream reaches, agricultural sources were the dominant contributor to nitrate pollution, a role which shifted to industrial wastewater in the downstream sections. This study has deepened the understanding of the river-scale nitrogen cycle and provided a scientific basis for NO_3^- pollution control.

Conflicts of interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

The data supporting this article have been included as part of the supplementary information (SI). Supplementary information: sampling points, land use types, stable isotope concentrations, conventional water quality data, information on pollution source discharge outlets, and the MixSIAR model. See DOI: https://doi.org/10.1039/d5va00273g.

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