Evaluating Temporal and Spatial Variation in Nitrogen Sources along the Lower Reach of Fenhe River (Shanxi Province, China) Using Stable Isotope and Hydrochemical Tracers

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Abstract: Nitrate is one of the most common pollutants in river systems. This study takes the lower reach of Fenhe River as a case study, combined with a multi-isotope and hydrochemical as the tracers to identify nitrate sources in river system. The results show that all samples in the industrial region (IR) and urban region (UR) and 68.8% of the samples in the agriculture region (AR) suffer from nitrate pollution. NO_3^-–N is the main existing form of dissolved inorganic nitrogen (DIN), followed by NH_4^+–N, which account for 57.9% and 41.9% of the DIN, respectively. The temporal variation in nitrogenous species concentration is clear over the whole hydrological year. The spatial variation is smaller among different sampling sites in the same region but greater among different regions. The main source of nitrogenous species is from anthropogenic rather than natural effects. Multi-isotope analysis shows that denitrification is found in some water samples. Combined with the apportionment of nitrate sources by the IsoSource model and the analysis of the Cl^- content, the main source of nitrate in the IR, UR and AR are industrial sewage and manure, domestic sewage and manure, and chemical fertilizers, respectively. Atmospheric nitrogen deposition is also a source of nitrate in the study area.

Keywords: anthropogenic impact; nitrate isotope; quantitative analysis; river systems; temporal and spatial variation

1. Introduction

Nitrate pollution in river systems is a worldwide problem that has gained widespread attention in the field of aquatic ecology [1–3]. In recent years, economic development and anthropogenic activities have increased the concentration of nitrate in river systems, which has caused many environmental problems, such as the eutrophication of water, algal blooms, and low oxygen zones [4–6]. Excessive nitrates in drinking water and foodstuff can transform into nitrosamines with hydrochloric acid in gastric juice. The nitrosamines combine with hemoglobin and greatly reduce the function of hemoglobin to carry oxygen, endangering human and animal health; this disease is medically known as methemoglobinemia [7]. Accordingly, numerous independent countries and the World Health Organization (WHO) have stipulated that NO_3^-–N concentrations in drinking water should be limited to 10 mg/L.

A high load of nitrogen and other nutrients can cause eutrophication of water bodies. The study of the temporal and spatial distribution of nitrogenous species in watersheds can be used for watershed

management. It is also beneficial to reduce the loss of nitrogen in soil and improve the ecological environment of the watershed. Many studies show that industrial sewage and domestic sewage are the main sources of nitrogenous species, particularly in heavily polluted areas. The direct discharge of untreated industrial sewage and the overland flow of domestic sewage are the main sources of the nitrate pollution in the industrial and residential areas. The application of chemical fertilizers is the main source of nitrogen species in the highly agricultural areas [8–11].

Traditional methods to identify water pollutant sources are mainly by investigating the land use types and local hydrochemical characteristics in the polluted areas. However, the point-source and non-point-source pollutions generally overlap; the results are inaccurate [12]. Temporal and spatial variation in nitrogenous species are also studied in some catchment areas; the concentration of nitrogenous species shows characteristics of being higher in summer and lower in winter; the spatial distribution variability of nitrogenous species is complex [13–16]. However, the site-specific studies are not appropriate for the Fenhe River Basin, and there are few studies on the temporal and spatial variation in nitrate in the Fenhe River Basin.

The sources of nitrogen in nature include atmospheric deposition, industrial sewage, domestic sewage, municipal solid waste, chemical fertilizers, industrial synthetic nitrogenous substances, livestock manures and plant humic substances [17]. Many studies have shown that the multi-isotope tracer technique of $\delta^{15}N$ and $\delta^{18}O$ is an important way to study the nitrate pollution in groundwater and surface water [18,19]. Owing to that the ranges of stable isotopic compositions of different water bodies are not affected by the variation in water environmental factors, it is possible to trace the nitrate sources by using $\delta^{15}N–NO_3^-$ and $\delta^{18}O–NO_3^-$ multi-isotope and hydrochemical analysis data and field investigations [20–22].

At the same time, the multi-source mass balance (IsoSource model), based on the principle of stable isotope mass conservation, has been used to partition pollutant sources in wastewater, food sources in animal food, water sources for plant uptake, and nitrate sources in soil organic matter. The principle is to construct a conservation model for the nitrogen and oxygen isotopes by inputting the isotopic data of potential nitrate sources. The probability distribution of the different pollution sources' contribution rate in water samples is calculated by the model with the iterative method, and it gives the average values of all the sources [23,24].

In the past few decades, the Fenhe River Basin has suffered serious pollution. The amount of untreated sewage discharged into Fenhe River is 3.4×10^{10} kg year^{-1}. The main pollutants are volatile phenols, reducing substances and ammonia nitrogen, which form the main industrial waste of the coal mines, thermal power stations and coal preparation plants that exist in the area. These pollutants account for 42% of the sewage discharge; the reducing substances metered as chemical oxygen demand (COD) amount up to 5.8×10^7 kg year^{-1}; the amount of ammonia and nitrogen discharged into Fenhe River is up to 9.1×10^6 kg year^{-1} [25]. Fenhe River is the second major tributary of the Yellow River; there is an estimated 1.9×10^4 kg (N) km^{-2} year^{-1} of nitrate from nitrification of ammonium/urea-containing fertilizer discharged into the Yellow River annually [26]. The amount of nitrogen deposited from the atmosphere into the Yellow River is approximately 2000 kg (N) km^{-2} year^{-1} annually [27].

At present, the research on nitrate source identification and apportionment in Fenhe River Basin is fragmentary. There are some studies on water nitrate pollution in the Loess Plateau. However, the Fenhe River Basin is only considered as a subcatchment of the Yellow River Basin in these studies [28–31]. The common shortcoming is that there are too few sampling sites and data in the Fenhe River Basin, which has led to an incomplete analysis of the nitrate source identification and apportionment in the basin; systematic studies on the nitrogen cycle in this area are necessary. These would not only be beneficial to the sustainable utilization of local water resources but also provide a scientific basis for the management of water resources in the Yellow River Basin and Loess Plateau. In this study, the lower reach of the Fenhe River in Shanxi Province, China is taken as the case study, combined with $\delta^{15}N–NO_3^-$ and $\delta^{18}O–NO_3^-$ multi-isotope tracers, hydrochemical analysis, and the

IsoSource model to identify and apportion the nitrate sources in river systems. Our objectives are (1) to identify and verify the main existing forms of nitrogenous species, (2) to investigate the temporal and spatial variation in nitrogenous species, and (3) to trace and apportion the proportional contributions of each potential nitrate source in the river system. This study aims to provide scientific evidence and reference for an insight regarding water management and the safeguarding of water ecology in river systems.

2. Materials and Methods

2.1. Study Area

Fenhe River is the largest river in Shanxi Province, and it is also the second largest tributary of the Yellow River, China (Figure 1). Fenhe River is divided into upper, middle and lower reaches by Shanglan and Shitan as a result of the geologic and hydrologic characteristics [32]. The lower reach of the Fenhe River Basin is located between a latitude of $35°20'$ N and $36°57'$ N and a longitude of $110°30'$ E and $112°34'$ E, with a catchment area of 11,276 km^2. The total annual runoff of Fenhe River is 2.286 billion m^3, and the average annual runoff in the lower reach is 0.776 billion m^3. Loess and alluvial deposits constitute the hydrological underlying surface where the river flows through Linfen Basin and Yuncheng Basin.
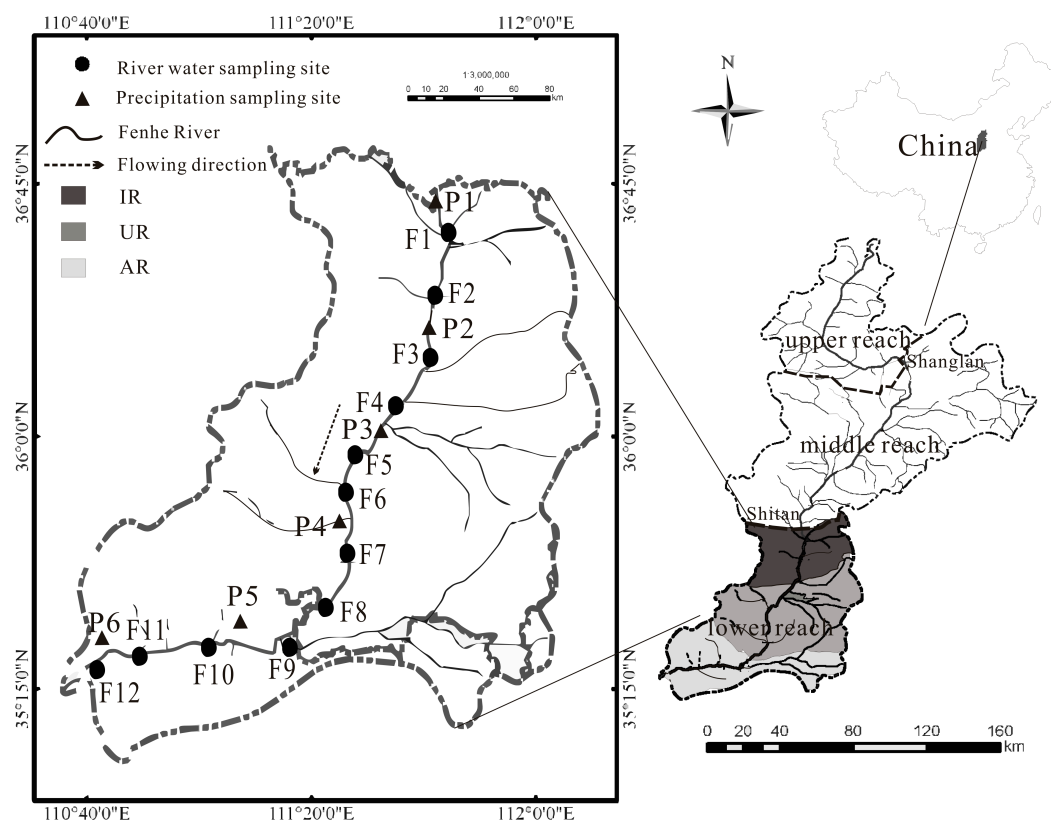

Figure 1. Location of lower reach of Fenhe River and sampling sites. IR: industrial region; UR: urban region; AR: agricultural region.

The lower reach of the Fenhe River Basin has a temperate continental monsoon climate; the climate is mild, and the sunshine is sufficient. The mean annual temperature ranges from 9 to 13 °C. The annual precipitation is 538.6 mm, and the evaporation is 1120 mm; 72% of the rainfall is concentrated in the rainy season (July to September) because of the uneven rainfall distribution. The per capita water resources constitute only 350 m^3, which belongs to the poor water resources area.

The study area is the main irrigation area of Shanxi Province, which is also the main industrial area and urban area. The study area can be divided into three categories by the different typical land use types along the river flow direction: the industrial region (IR), urban region (UR) and agricultural region (AR) (Figure 1). Many factories and enterprises are located in the IR, such as coal mines, thermal power stations, and coal preparation plants. Therefore, a large amount of industrial sewage discharges into the river; this tends to be the potential pollution source of the water bodies in this area. The UR is characterized by being densely populated and highly urbanized; the urban agglomeration in the lower reach of Fenhe River is located in this area, which has a population of 4.5 million. Domestic sewage and livestock manure tend to be potential pollution sources of the water bodies in this area. More than 83% of the land area in the AR is farmland; corn and winter wheat are planted as rotation crops. Ammonia fertilizer and nitrogen fertilizer are widely used in March and April in this area to improve the food production; these tend to be potential nitrate sources of the water bodies in this area [33].

2.2. Sample Collection and Field Experiment

Twelve sampling sites are situated in the lower reach of the Fenhe River according to the basin's topographic features and hydrological characteristics. F1, F2, F3, and F4 are in the IR; F5, F6, F7 and F8 are in the UR; and F9, F10, F11 and F12 are in the AR. The sampling sites were pinpointed with handheld GPS devices in the field (Figure 1). Six water samples were collected at each sampling site with a frequency of once every 2 months from July 2015 to June 2016. River water was collected at a depth of 50 cm in the central stream with an organic glass water collector (WB-PM, Beijing Purity Instrument CO., Ltd., Beijing, China). In order to determine the source of contaminants accurately, industrial sewage, domestic sewage, livestock manure, fertilizer and precipitation were collected in the study area. The industrial sewage was collected at the sewage outfalls of the main factories, domestic sewage was collected at the sewage outfalls of the urban residential area, livestock manure was collected at sheepfolds and pigsties, and fertilizer was collected in the farmland during the fertilization season; the main chemical compound of the fertilizer in the lower reach of Fenhe River was $CO(NH_2)_2$; NH_4Cl and NH_4NO_3 precipitations were collected at the hydrological stations of Fenhe River when it rained.

The liquid samples, which were measured for $\delta^{15}N–NO_3^-$ and $\delta^{18}O–NO_3^-$, were stored in 0.1 L polymethyl methacrylate (PMMA) organic glass bottles, and for water chemistry are stored in 1 L polyethylene terephthalate (PET) bottles, respectively. All the sampling bottles were washed with the collected water three times before storing the water samples to avoid contamination by impurities. The liquid samples were sealed with Parafilm to prevent water evaporation and isotopic fractionation and were stored at 4 °C. The solid samples were stored in a self-sealing bag at −20 °C in a refrigerator.

2.3. Laboratory Analyses

The hydrochemical was measured at Shanxi University within 24 h of sampling. The major cations were found by atomic absorption spectrometry (PE-2380, PE Company, Waltham, MA, USA) and the major anions were found by ion chromatography (Dionex-100, Dionex Company, Sunnyvale, CA, USA) after being filtered through a 0.45 μm cellulose acetate membrane to eliminate the interference of impurities. The charge balance calculation showed that the charge imbalance did not exceed ±5% for any of the samples. $NO_3^-–N$, $NO_2^-–N$, $NH_4^+–N$, and TN were analyzed by a flow-injection analyzer (HACH Quick chem 8500S2, Hach Company, Loveland, CO, USA). The solid samples were centrifugal oscillated and filtered (0.3 μm) before hydrochemical analysis [34]. The analytical precision was less than ±3%.

The measurements of $\delta^{15}N–NO_3^-$ and $\delta^{18}O–NO_3^-$ were taken with an isotope ratio mass spectrometer at the Institute of Environment and Sustainable Development in the Agricultural Chinese Academy of Agricultural Sciences (AESIL, CAAS) by the denitrifying bacteria method [35]. All the liquid samples were filtered through a 0.45 μm cellulose acetate membrane before determination and analysis. For solid samples, 2 mol/L KCl was added and the solution underwent centrifugal oscillation

for 1 h; the suspension was settled for 3–5 min to make the impurities precipitate completely and was then filtered. The denitrifying bacteria (*Pseudomonas aureofacien*) was added to the samples, which had a lack of the N_2O activating enzyme. All the NO_3^- and NO_2^- ions were transformed to N_2O gas before being delivered to a trace gas analyzer (Trace Gas) for automatic sampling to purify and trap N_2O; there was no isotopic fractionation in this process.

The per mil deviation values (δ) of the isotope ratio of the sample to the standard sample is used to indicate the isotopic content of the element; the isotope results are represented in δ units defined as follows:

$$\delta(‰) = [(R_{\text{sample}} - R_{\text{standard}})/R_{\text{standard}}] \times 1000 \tag{1}$$

where R_{sample} and R_{standard} are the ratio of heavy and light isotopes in the sample and standard sample, respectively.

The international isotope standards used were USGS-32, USGS-34 and USGS-35 (National Laboratory of the United States, USA). The test precision values of $\delta^{15}N–NO_3^-$ and $\delta^{18}O–NO_3^-$ of the water samples were 0.05‰ and 0.28‰, respectively. Duplicate analyses were within the σ of working standards, and the results were reproducible.

2.4. IsoSource Model Calculation

The IsoSource model is mainly used in the study of food web and plant water supply, and it provides a new means for quantitative research of nitrate point-source pollution. In order to quantify the proportion of different nitrate pollution sources, the data were calculated by the IsoSource model in this study [23]. The mass conservation model is constructed by inputting the nitrogen and oxygen isotopes in the water samples, as well as the sources of the determined nitrate (assuming there are three sources), as shown by the following formulas:

$$\delta^{15}N = \sum_{i=1}^{3} f_i \times \delta^{15}N_i \tag{2}$$

$$\delta^{18}O = \sum_{i=1}^{3} f_i \times \delta^{18}O_i \tag{3}$$

$$1 = \sum_{i=1}^{3} f_i \tag{4}$$

where i refers to the three kinds of nitrate pollution sources; $\delta^{15}N$ and $\delta^{18}O$ refer to nitrogen and oxygen isotope values in mixed waters, respectively; $\delta^{15}N_i$ and $\delta^{18}O_i$ refer to nitrogen and oxygen isotopes in different nitrate pollution sources, respectively; f_i refers to the proportion of different nitrate pollution sources.

The tolerance parameter and increment parameter are set up before the software runs. The probability distribution of the different sources in water samples is calculated by an iterative method [24]. All possible percentage combinations (the sum is 100%) from different sources are calculated by the following formula:

$$\text{No. Combinations} = \frac{[(100/i) + (s-1)]!}{(100/i)!(s-1)!} \tag{5}$$

where i refers to the increment parameter, and s refers to the number of nitrate sources. This model can test all possible combinations of potential contributions from each source. When the difference between the weighted average values of nitrogen and oxygen isotopes from different sources and the measured values of nitrogen and oxygen isotopes in the water samples is less than 0.1‰, it is considered to be a possible solution value [23].

3. Results and Discussion

3.1. Identification and Verification of Nitrogenous Species

The chemical compositions of river water samples collected in the lower reach of Fenhe River Basin are summarized in Table 1. $NO_3^- $–N, NH_4^+–N and NO_2^-–N were the main sources of dissolved inorganic nitrogen (DIN) in the study area.

Table 1. Mean concentration of hydrochemical parameters and the environmental isotopic ratios in water samples in the lower reach of Fenhe River.

Category	Site	NO_3^- (mg/L)	Cl^- (mg/L)	NO_3^-–N (mg/L)	NO_2^-–N (mg/L)	NH_4^+–N (mg/L)	TN (mg/L)	$\delta^{15}N$–NO_3^- (‰)	$\delta^{18}O$–NO_3^- (‰)
IR [1]	F1	42.0 ± 6.2	54.4 ± 7.3	9.5 ± 2.6	0.04 ± 0.02	5.2 ± 1.7	24.6 ± 4.8	12.3 ± 2.8	10.2 ± 2.1
	F2	44.9 ± 5.6	43.1 ± 6.1	10.1 ± 3.6	0.03 ± 0.01	5.1 ± 1.6	25.9 ± 6.4	12.7 ± 2.2	9.1 ± 2.0
	F3	43.5 ± 4.9	42.1 ± 4.1	9.8 ± 2.9	0.04 ± 0.01	4.8 ± 1.2	24.1 ± 7.8	12.7 ± 2.1	10.2 ± 1.8
	F4	42.7 ± 3.9	40.0 ± 3.9	9.6 ± 3.7	0.04 ± 0.01	5.6 ± 1.3	24.7 ± 5.9	12.7 ± 1.9	9.1 ± 1.7
UR	F5	39.5 ± 4.1	58.9 ± 4.5	8.9 ± 3.8	0.05 ± 0.02	7.7 ± 1.5	26.6 ± 4.9	16.7 ± 1.8	8.3 ± 2.0
	F6	40.5 ± 3.8	59.7 ± 4.2	9.1 ± 2.7	0.04 ± 0.01	8.5 ± 1.7	28.2 ± 7.4	16.3 ± 1.6	8.4 ± 1.7
	F7	40.1 ± 5.2	62.0 ± 4.9	9.01 ± 2.7	0.04 ± 0.02	8.1 ± 1.9	27.4 ± 8.1	16.7 ± 1.7	8.4 ± 1.5
	F8	37.6 ± 4.9	64.9 ± 7.8	8.5 ± 3.4	0.05 ± 0.02	7.6 ± 1.6	27.4 ± 7.1	16.5 ± 1.5	8.4 ± 1.8
AR	F9	29.9 ± 3.7	10.0 ± 3.1	6.8 ± 1.8	0.02 ± 0.01	5.1 ± 1.2	20.5 ± 3.1	0.7 ± 0.6	14.2 ± 2.1
	F10	28.2 ± 3.8	9.8 ± 4.9	6.4 ± 2.5	0.03 ± 0.01	5.6 ± 2.0	20.7 ± 5.9	−2.2 ± 1.1	18.1 ± 2.2
	F11	28.1 ± 3.4	10.3 ± 5.8	6.4 ± 3.7	0.02 ± 0.01	5.1 ± 1.3	19.7 ± 5.7	−1.4 ± 1.5	13.7 ± 1.7
	F12	30.0 ± 4.8	9.6 ± 4.7	6.8 ± 2.7	0.02 ± 0.01	5.2 ± 1.8	21.2 ± 4.5	−2.1 ± 0.9	17.7 ± 2.5

Notes: [1] IR: industrial region; UR: urban region; AR: agricultural region.

NO_3^-–N is the final product of oxidative decomposition of nitrogenous organic compounds. The NO_3^-–N concentration in the IR was the highest among the three regions, with mean values of 9.4 ± 1.4 mg/L in the rainy season and 9.9 ± 1.6 mg/L in the dry season. This is due to the industrial sewage discharge around the sampling sites. However, the NO_3^-–N concentration in the UR was lower than that of the IR, with mean values of 7.0 ± 0.8 mg/L in the rainy season and 9.5 ± 1.6 mg/L in the dry season. Although the AR is located in the lower reach of the IR and UR, the NO_3^-–N concentration in the AR was the lowest among the three regions, with mean values of 6.6 ± 0.5 mg/L in the rainy season and 6.5 ± 1.9 mg/L in the dry season.

The NH_4^+–N concentration in the UR was the highest among the three regions, with mean values of 6.1 ± 1 mg/L in the rainy season and 8.5 ± 1.6 mg/L in the dry season. This is due to the domestic sewage discharge and livestock manure around the sampling sites. The NH_4^+–N concentration in the IR was the lowest among the three regions, with mean values of 4.4 ± 0.6 mg/L in the rainy season and 5.4 ± 0.8 mg/L in the dry season. The NH_4^+–N concentration in the AR was higher than that in the IR, with mean values of 5.6 ± 0.6 mg/L in the rainy season and 5.1 ± 1.6 mg/L in the dry season. Related research shows that the NH_4^+–N concentration in river water would increase as a result of the discharge of domestic sewage and the application of nitrogen fertilizer along the riverbank [36].

NO_2^-–N is the intermediate product in the process of nitrogenous organic compounds oxidizing into nitrate. The presence of NO_2^-–N in water indicates that the decomposition of organic compounds is still in process. The high NO_2^-–N concentration illustrates a process of nitrogenous organic compounds oxidizing into nitrate in the river water. In this study, the NO_2^-–N concentration was relatively low, and the maximum concentration was 0.05 ± 0.03 mg/L in the UR in the dry season. This is due to the domestic sewage and livestock manure in the UR and the industrial sewage discharge from the IR, which is in the upper reach of the UR.

Total nitrogen (TN) is defined as the total amount of DIN and dissolved organic nitrogen (DON) in water. The TN concentration is one of the important indices to measure water quality [37]. In this study, the TN concentration in the IR was 26 ± 1.6 mg/L in the rainy season and 24.4 ± 3.0 mg/L in the dry season, while the TN concentration in the UR was the highest among the three regions, with mean values of 23.9 ± 3.1 mg/L in the rainy season and 28.6 ± 3.2 mg/L in the dry season, which means that the river water in this region is extremely polluted. The TN concentration in the AR was the lowest

among the three regions, with mean values of 21.5 ± 1.5 mg/L in the rainy season and 20.2 ± 4.9 mg/L in the dry season. The seasonal variations in the TN concentration were not obvious in the AR, while the seasonal variations among the three regions were clear, which was mainly due to the different land use types along the riverbanks. There was no clear variation in the nitrogenous species concentration between the rainy season and dry season in the AR. This is due to the insignificant change in the solute content buffered by the wide river channel and slow water flow in the AR.

Figure 2a shows the contrast between NO_3^--N, NO_2^--N, and NH_4^+-N concentrations. NO_3^--N is the main existing form of DIN in the lower reach of Fenhe River, particularly in the IR, and accounted for 65.2% of the DIN. The industrial wastewater discharge results in a higher NO_3^--N concentration in this area. The percentage of NH_4^+-N increased from 34.5% in the IR to 47.1% in the UR, which was relatively close to that of NO_3^--N (52.6%). This is due to the large amount of domestic sewage discharge from the urban residential area, which is typical of a higher ammonia nitrogen concentration. Figure 2b shows the contrast in NO_3^--N, NH_4^+-N and DON concentrations. The sampling sites that were situated in the IR showed characteristics of higher values of NO_3^--N and DON but a lower value of NH_4^+-N; the sampling sites that were situated in the UR showed characteristics of similar values of NO_3^--N, NH_4^+-N and DON, which indicates that the IR and UR are mainly polluted by anthropogenic sources, such as industrial sewage in the IR and domestic sewage and livestock manure in the UR. The sampling sites that were situated in the AR showed characteristics of lower values of NO_3^--N and NH_4^+-N but a higher value of DON, which indicates that the AR is mainly polluted by agricultural pollution, such as animal manure and nitrogenous fertilizer. The sampling site F9 was located near the water-source protection area, which is the main drinking water source of the residents. There are few industrial facilities and human activities around this area because of the protection policy of the local government. The hydrogeological conditions are the result of the Ordovician karst aquifer in this area; the groundwater is recharged by unsaturated vertical infiltration of the Fenhe River and its tributaries [38]. The TN in this area is mainly formed by soil organic nitrogen. The studies of Chanhe River in the Loess Plateau and the Songhua River in the Northeast China Plain show that the TN is mainly derived from soil organic nitrogen and the nitrate concentration is lower; these are rarely affected by human activities [39,40]. Compared with similar studies in Poland and Japan, the results also suggest that soil organic nitrogen is the main source of TN or nitrate in the less-anthropogenic-impacted river [6,13].
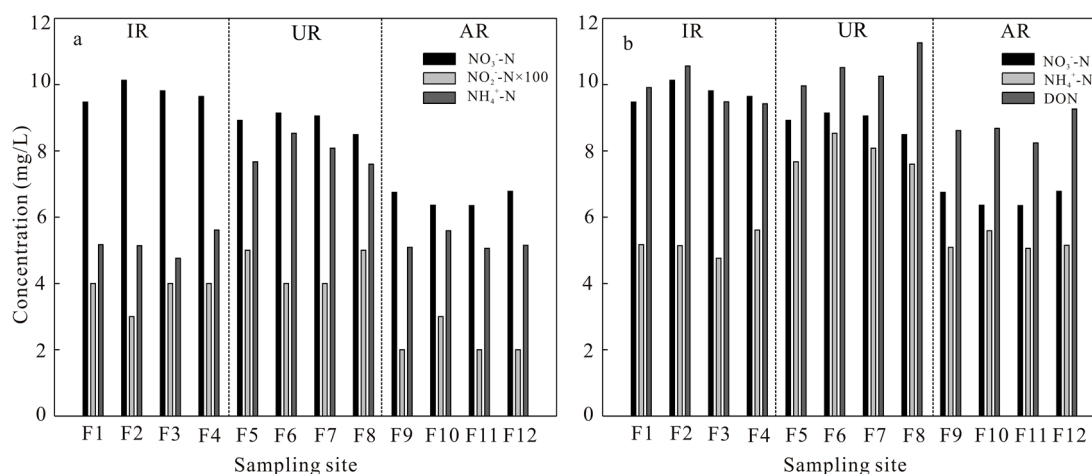

Figure 2. The contrast between nitrogenous species concentration in the lower reach of Fenhe River: (**a**) NO_3^--N, $NO_2^--N \times 100$, and NH_4^+-N; (**b**) NO_3^--N, NH_4^+-N, and dissolved organic nitrogen (DON).

3.2. Temporal and Spatial Variation in Nitrogenous Species

Figure 3a shows the temporal variation in the TN concentration in the lower reach of Fenhe River. The maximum concentrations of the TN were observed in the IR and AR in March, while the minimum concentrations were observed in the IR and AR in January and February. This could be attributed to the cyclical changes in the industrial production activities in the IR. Another reason is the application of nitrogen fertilizers to winter wheat from early March, and nitrogenous substances leaching into soil and flowing into the river water with the soil runoff. However, the TN concentration in the UR showed an opposite temporal variation trend; the maximum concentration was observed in January, and the minimum concentration was observed in September. This phenomenon could be explained by the TN concentration mainly being influenced by anthropogenic activities rather than natural effects. Although the seasonal variation in river water flow has an effect on the variation in the TN concentration, the influence of human-induced land use changes was more apparent in this study area. Industrial land and urban residential land will deteriorate water quality, whereas agricultural land has little influence on water quality change.
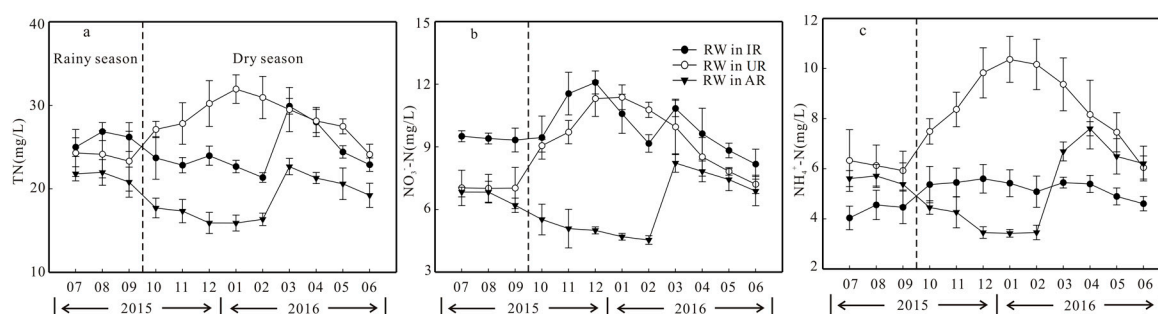

Figure 3. Temporal variation in (**a**) total nitrogen (TN), (**b**) NO_3^-–N, and (**c**) NH_4^+–N concentrations in the lower reach of Fenhe River. The error bars represent standard deviation. RW in IR: river water in industrial region; RW in UR: river water in urban region; RW in AR: river water in agricultural region.

The concentrations of NO_3^-–N and NH_4^+–N increased rapidly from March to May in the AR (Figure 3b,c); the maximum concentration of NO_3^-–N was observed in March, and the maximum concentration of NH_4^+–N was observed in April. This could be attributed to the agricultural activities in the AR, such as the application of fertilizers and aerial farming. March and April are the seeding period of most crops; large amounts of fertilizer are applied in this period. Nutrient nitrogen that is not absorbed by crops flows into the river with the surface runoff after a great deal of fertilization. The maximum concentrations of NO_3^-–N and NH_4^+–N were observed in the IR in December and in the UR in January, which was consistent with the land use investigation. This could be attributed to the IR being dominated by industrial and mining enterprises and the UR being dominated by urban residents' living and commercial areas. The maximum concentration of NO_3^-–N was found in the UR in February 2016. This is due to less upstream water from the IR, and the reduced denitrification process in the lower-temperature environment also makes the NO_3^- concentration increase.

The annual precipitation is 538.6 mm and the annual evaporation is 1120 mm in the study area. Related studies show that the lower reach of Fenhe River Basin is a semiarid region; a wide range of water shortages result because of the lower precipitation and higher evaporation in this area. The unreasonable development and excessive exploitation of the water resources has led to a serious decrease in the ground water storage. Precipitation is the main recharge source of surface water in this area [41,42]. Precipitation has a certain dilution effect on the concentration of river pollutants in the rainy season. Although surface water is recharged by groundwater in the dry season, the recharge is very small. Some river reaches have dried up in the dry season, and the interaction between groundwater and surface water has little influence on the nitrogen concentration of the surface water.

Additionally, many factors would affect the nitrogenous species concentration, such as the distribution of sampling sites, the topography of the study area, hydrogeological conditions, and regional precipitation, particularly in regions that are seriously influenced by anthropogenic activities. Figure 4 shows the spatial variation in the nitrogenous species concentration in the three regions. The results show that the variation was smaller among different sampling sites in the same region, while the variation was greater among different regions. This could be attributed to the different land use types along the riverbanks. Compared with the IR and UR, the nitrogenous species concentration was relatively low in the AR. The dissolved oxygen (DO) decreased as a result of the sluggish flow in the broad river channel; this environment is conducive to anaerobic microorganisms, and the NO_3^- ions are transformed into N_2 by the process of denitrification. At the same time, the Huihe River, which is one of the primary tributaries of Fenhe River, flows into the main stream of Fenhe River in the AR; the water quality of the Huihe Reservoir and Huihe Second Reservoir in the upper reach of the Huihe River is relatively good. Gudui Spring, which is a karstic spring with a 1.3 m^3/s natural resources quantity, is also in the AR. The recharge by Huihe River and Gudui Spring also reduce the nitrogen pollutant concentration. On the other hand, the sampling sites F9, F10, F11, and F12 were located at the Yumenkou irrigated area, not far away from the estuary of the Fenhe River and the Yellow River. The longitudinal gradient of the Fenhe River is slow, and the flow velocity is small. The Yellow River flowing backwards has caused a great deal of siltation in the Fenhe River. This is also an effective way to reduce nitrate concentrations in this region.
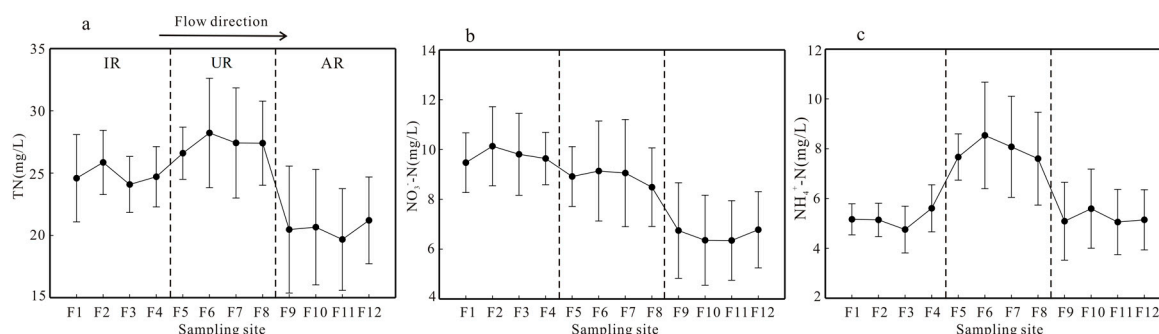

Figure 4. Spatial variation in (**a**) total nitrogen (TN), (**b**) NO_3^-–N, and (**c**) NH_4^+–N concentrations in the lower reach of Fenhe River. The error bars represent standard deviation. IR: industrial region; UR: urban region; AR: agricultural region.

On the whole, the mean concentrations of TN and NH_4^+–N increased with the flow direction in the IR and UR. The maximum concentrations of TN and NH_4^+–N were observed in the UR. This phenomenon could be explained by the urban domestic sewage discharged into the river water in this region; another reason is that the river water in this region is the influx of the upstream water from the IR. Land use types have changed the underlying surface characteristics and have a great impact on the water cycle and material transport. The nitrogen output of different land use types is different, and the output intensity of nutrients would increase as a result of the decrease in the forest land area and the increase in agricultural land area. Urbanization has increased the pollutants discharged into rivers by point-source pollution. Another main characteristic of urbanization is the increase in the impervious ground surface ratio; the natural infiltration process of soil will also weaken by the impervious ground surface. During the rainstorm period, the urban areas will lose the natural vegetation's interception and absorption of pollutants, and a large number of pollutants will flow into the river through the impervious ground surface in a short time [43]. Sampling sites F2 and F3 were nearby a coal preparation plant and a thermal power plant, and industrial sewage was the major factor of the increase in the NO_3^-–N concentration. Agricultural land will affect the degradation of water quality, which may depend on the farming methods and climatic characteristics in the study area [44]. Sampling site F10 was located in a typical intensive agricultural area, and the application

of nitrogenous fertilizer and ammonia fertilizer were the major factors for the increase in NH_4^+–N and NO_3^-–N concentrations. At the same time, the groundwater resources in the AR also reduced the nitrogen concentration by recharging the surface water [41]. The results of this study can be interpreted as the fact that the agricultural land is near the river channel, and the fluctuation of water quality is more sensitive with the changes in land use types or geological conditions, while the correlation between climatic conditions and water quality is offset or covered.

3.3. Nitrate Source Identification and Apportionment

Cl^- is a conservative element in natural water environments. Cl^- can be used as an indicator to trace the changes in the NO_3^- concentration in the process of water mixing and denitrification. The high Cl^- concentration in river water could signify a multi-anthropogenic source in the study area [1,45]. Cl^- in domestic sewage is high and it has the chemical property of stability. Comparing the concentrations of Cl^- and NO_3^- in river water can provide more evidence of nitrate sources [18].

The NO_3^- concentrations of sewage, manure and fertilizer collected in this study were 1.3 ± 0.2, 1.0 ± 0.12, and 0.2 ± 0.2 mmol/L, respectively. The Cl^- concentrations of sewage, manure and fertilizer were 1.3 ± 0.2, 2.2 ± 0.1, and 0.2 ± 0.1 mmol/L, respectively. There was no significant correlation between NO_3^- and Cl^- on account of the large variation in the Cl^- concentration in the study area (Figure 5). The IR had a relatively low Cl^- concentration but a high NO_3^- concentration. Most of the river water samples collected in this region are plotted in the triangle diagram and are close to the side of the sewage, which indicated that industrial sewage is the major factor controlling the hydrochemical composition in this region. At the same time, fertilizers and manure are also the potential sources of nitrate in water body in the region, while in the UR, the NO_3^- concentration was low and the Cl^- concentration was high. Most of the river water samples collected in this region are plotted around the line of sewage and manure, indicating that the domestic sewage discharge and livestock manures from local residents are the dominant sources in this region, because the domestic sewage and livestock manures were found to have the highest Cl^- concentrations and lowest NO_3^- concentrations. Both the NO_3^- and Cl^- concentrations of samples were low in the AR. All the river water samples collected in the AR are plotted around the lower left quarter of the triangle diagram, which suggests that fertilizer is the main source in this region. The Cl^- concentration in the AR decreased by a factor of 6 when compared with that in the UR; with no chloride leaving the water system and a decrease in concentration, the low-chloride water of tributaries and groundwater in the AR diluted the Cl^- concentration, which is a result that has also been found in low-gradient agricultural streams of Little Kickapoo Creek in Illinois State [46]. Similar studies in the large rivers of Bangladesh, India and Pakistan show that domestic sewage and manure are the main sources of nitrate in the urban regions [11]. The related study on the Yellow River of China also shows that the main source of nitrate in the agricultural region is chemical fertilizers [14].

The main sources of nitrate include manure, sewage, fertilizers, and atmospheric deposition; δ^{15}N–NO_3^- and δ^{18}O–NO_3^- are ideal geochemical tracers that can be used to identify the origin and transformation of nitrate [47,48]. For all samples in the IR, δ^{15}N–NO_3^- values ranged from 2.8‰ to 15.5‰ with a mean value of 12.5‰, and δ^{18}O–NO_3^- values ranged from 3.9‰ to 14.6‰ with a mean value of 9.6‰. For all samples in the UR, δ^{15}N–NO_3^- values ranged from 7.7‰ to 22.3‰ with a mean value of 16.5‰, and δ^{18}O–NO_3^- values ranged from -1.0‰ to 17.5‰ with a mean value of 8.3‰. For all samples in the AR, δ^{15}N–NO_3^- values ranged from -7.8‰ to 11.9‰ with a mean value of -1.3‰, and δ^{18}O–NO_3^- values ranged from 3.9‰ to 31.3‰ with a mean value of 15.7‰.
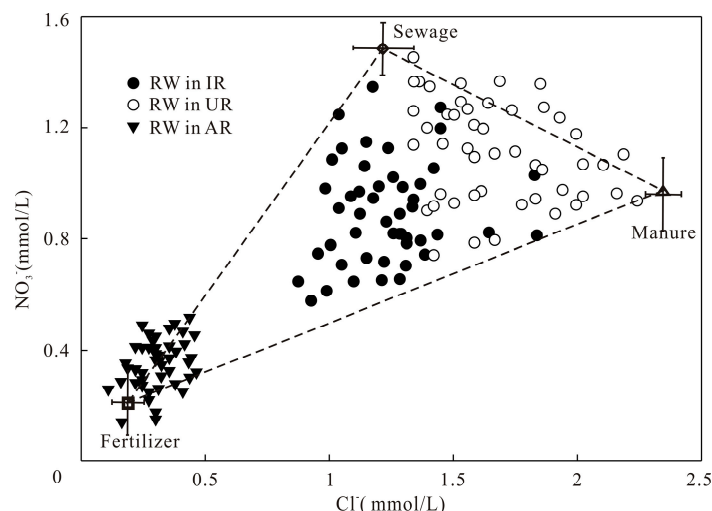
Figure 5. Mixing diagram of NO_3^- and Cl^- concentrations. The means and standard deviations are shown for sewage, fertilizer, and manure. RW in IR: river water in industrial region; RW in UR: river water in urban region; RW in AR: river water in agricultural region.

Nitrification and denitrification are the major controlling factors in the process of nitrogen cycling and nitrogen balance in ecological systems. Nitrification is the process of NH_4^+ oxidizing into NO_3^- by autotrophic microbes in soil and aquatic environments. Isotopic compositions of NO_3^-–N in water and soil are also greatly controlled by isotopic fractionation caused by nitrification. Theoretically, NO_3^- generated by nitrification derives one-third of its oxygen from DO, and two-thirds of its oxygen from water [49]. Denitrification is the process of reducing NO_3^-–N to N_2 and N_2O by anaerobic microorganisms [20]. The fractionation of nitrogen isotope is very significant in this process. Compared with the products of N_2 and N_2O, the residual nitrate is significantly enriched in ^{18}O and ^{15}N.

The $\delta^{15}N$–NO_3^- background value of shallow groundwater ($\leq +5‰$) under natural conditions is typically used to determine whether groundwater is polluted by nitrate [50]; 68.8% of the samples in the AR and all samples in the IR and UR exceeded the background value, which indicated varying degrees of nitrate pollution in the lower reach of Fenhe River, particularly in the IR and UR. At the same time, denitrification was also observed in the lower reach of Fenhe River. As Figure 6a shows, most of the samples are plotted in the fertilizer and soil organic nitrogen field, indicating that the fertilizer and soil organic nitrogen are the main sources of nitrate in the AR. The $\delta^{15}N$–NO_3^- and $\delta^{18}O$–NO_3^- in precipitation are affected by many complicated atmospheric processes, which leads to great spatial and temporal variability in the $\delta^{15}N$–NO_3^- and $\delta^{18}O$–NO_3^- in precipitation. The influence factors include isotope fractionation caused by heavy rain in the process of nitrification, and many other factors contribute to the reduction in $\delta^{15}N$–NO_3^- and $\delta^{18}O$–NO_3^- in atmospheric chemical reactions. Some of the samples are plotted within or close to the precipitation field, indicating that the nitrate in precipitation also plays the role of a nitrate source in the AR. In order to identify the sources accurately, we also determined the $\delta^{15}N$–NO_3^- and $\delta^{18}O$–NO_3^- values of industrial sewage, domestic sewage, manure, fertilizer and precipitation in the study area (Figure 6b). The results show that industrial sewage is the major source of nitrate in the IR. Domestic sewage and manure are the major sources of nitrate in the UR, and industrial sewage is also a potential source in this region.
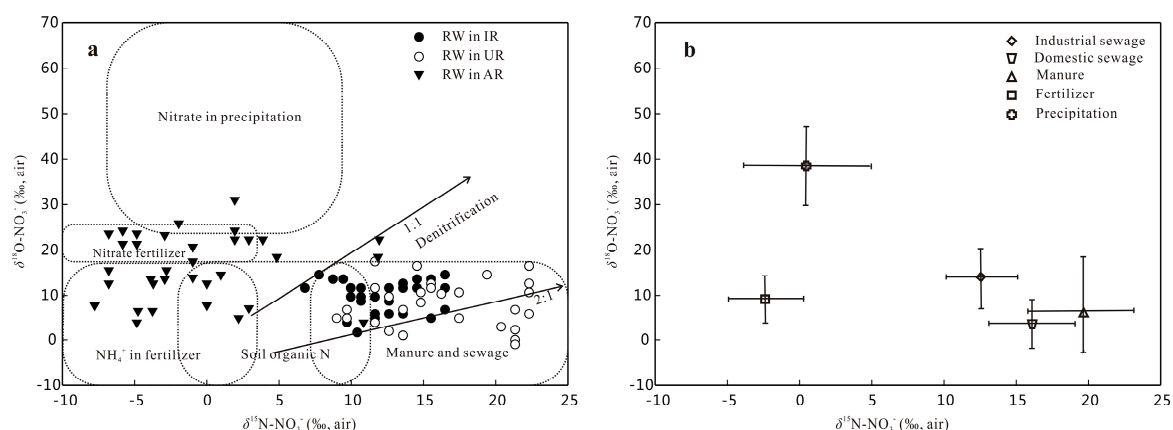
Figure 6. Relationship between $\delta^{15}N–NO_3^-$ and $\delta^{18}O–NO_3^-$ (**a**), and the end members of atmospheric N, chemical fertilizer, and sewage and manure in the lower reach of Fenhe River (**b**). The dotted contoured fields are based on those by Kendall [51,52]. RW in IR: river water in industrial region; RW in UR: river water in urban region; RW in AR: river water in agricultural region.

As Figure 6b shows, the ranges of stable isotopic compositions of nitrate for industrial sewage, domestic sewage, and manure overlap, which indicates that they cannot be considered as separate nitrogen sources in terms of stable isotopes of nitrate. In this regard, the three identified nitrogen sources were merged into one nitrogen source of sewage and manure for the apportionment of nitrate sources. In order to accurately identify the contribution of each source, the contribution rate of nitrate pollution sources in the study area were calculated by the IsoSource model. The $\delta^{15}N–NO_3^-$ and $\delta^{18}O–NO_3^-$ values of the chemical fertilizer, manure and sewage in the study area are shown in Figure 6b, and the $\delta^{15}N–NO_3^-$ and $\delta^{18}O–NO_3^-$ values of atmospheric nitrogen were −0.2‰ and 53.1‰, respectively [53]. Some water samples in the lower reach of Fenhe River were affected by denitrification (Figure 6a); thus, these water samples were excluded for the quantitative calculation of nitrate pollution sources by the IsoSource model.

As Table 2 shows, the mean contribution of sewage and manure was the highest (80.5%), followed by chemical fertilizers (14.2%) and then the atmospheric nitrogen (5.3%), for the river water in the IR. Significant differences were found among different sampling sites in this region. In fact, human activities were ubiquitous. For example, some residential areas are plotted in the IR for the industrial workers of coal mines, thermal power stations, and coal preparation plants. The domestic sewage and manure of the dependents also plays a role in the nitrate pollution in the local water. Furthermore, the sampling site F1 was located near a mixed rural and factory area; the agricultural activities also affect the water quality to a certain extent. Therefore, the results of the IsoSource model show that the atmospheric nitrogen, chemical fertilizers, and sewage and manure accounted for 5.3%, 26.4%, and 68.3% of the nitrate sources in the sampling site F1, respectively. The percentages of sewage and manure were high in sampling sites F2 (84.1%) and F3 (89.5%), respectively. This could be attributed to the sewage continuously discharged from the coal mine, thermal power station, and coal preparation plant around these two sampling sites, which would lead to the enrichment of heavy isotopes ^{15}N in the river water.

The mean contribution of sewage and manure was the highest (87.5%), followed by chemical fertilizers (6.7%) and then the atmospheric nitrogen (5.8%), for the river water in the UR. The results show that the percentages of sewage and manure were high in sampling sites F7 (88.1%) and F8 (89.3%), respectively. This is due to a large residential area near the sampling site F7 and a farm product market near the sampling site F8, according to our investigation. Cl^- in domestic sewage is high and has stable chemical properties. Comparing the concentration of Cl^- and NO_3^- in river water can provide more evidence of nitrate sources. The mean contributions of sewage and manure were 87.5% in the UR and 80.5% in the IR (Table 2). The mean values of Cl^- were 61.4 mg/L in the UR and 44.9 mg/L in

the IR (Table 1). Consequently, the main source of nitrate pollution in the UR is domestic sewage and manure; industrial sewage and manure are the main sources of nitrate pollution in the IR.

Table 2. Proportional contributions of three potential nitrate sources as estimated using IsoSource model in the lower reach of Fenhe River.

Category	Site	Atmospheric N (%)	Chemical Fertilizer (%)	Sewage and Manure (%)
IR	F1	5.3 ± 1.2	26.4 ± 4.8	68.3 ± 7.8
	F2	5.8 ± 1.0	10.1 ± 5.6	84.1 ± 10.1
	F3	4.7 ± 0.9	5.8 ± 2.4	89.5 ± 9.1
	F4	5.4 ± 1.1	14.5 ± 5.3	80.1 ± 11.2
UR	F5	5.6 ± 1.1	6.1 ± 2.4	88.3 ± 9.8
	F6	7.9 ± 3.2	7.9 ± 4.1	84.2 ± 12.3
	F7	4.7 ± 0.7	7.2 ± 3.1	88.1 ± 8.5
	F8	4.9 ± 0.9	5.8 ± 2.0	89.3 ± 10.2
AR	F9	4.8 ± 0.6	49.8 ± 5.4	45.4 ± 7.5
	F10	7.7 ± 2.3	53.7 ± 5.9	38.6 ± 5.7
	F11	7.6 ± 2.7	47.8 ± 7.1	44.6 ± 6.1
	F12	7.1 ± 1.6	60.2 ± 8.5	32.7 ± 5.9

The mean contribution of chemical fertilizers was the highest (52.9%), followed by sewage and manure (40.3%) and then the atmospheric nitrogen (6.8%), for the river water in the AR. This area is the main grain producing area of Shanxi Province. Nitrogen fertilizer and ammonia fertilizer are applied extensively in March and April in this region. The study area was located in the southeast of the Chinese Loess Plateau, where the soil and water loss is serious. The excessive fertilizers used are vulnerable to being lost and flowing into the river water by the surface runoff. This is the reason why fertilizer is the dominant pollution source in this region.

The contributions of each nitrate source in the lower reach of Fenhe River are similar to those of the Jinghe River in the Loess Plateau of China; the potential nitrate sources showed high variability between the different land use areas [39]. Compared with similar studies in other catchments, such as a river subcatchment in Germany and Baltic Sea catchments [54,55], the contributions of sewage and manure were much higher in the lower reach of Fenhe River. This phenomenon indicates that the nitrate pollution in the lower reaches of Fenhe River is serious because of the frequent industrial and anthropogenic activities.

4. Conclusions

The following conclusions can be drawn from this study:

(1) All samples in the IR and UR and 68.8% of the samples in the AR suffered from nitrate pollution. The nitrate pollution has already endangered the health of local residents in the lower reach of the Fenhe River. Denitrification was found in some water samples in the study area. Land use types were the major influencing factors of nitrate pollution sources. NO_3^-–N is the main existing form of DIN, followed by NH_4^+–N.

(2) Over the whole hydrological year, the temporal variation in the nitrogenous species concentration was clear in the study area. In the UR, the nitrogenous species concentration was high in winter and low in summer. In the IR and AR, the nitrogenous species concentrations were high in summer and low in winter. The major factor influencing the nitrogenous species concentration was anthropogenic rather than natural effects. The spatial variation was smaller among different sampling sites in the same region but greater among different regions. This distribution was not only affected by the seasonal changes of precipitation condition and runoff variation, but was also closely related to the seasonal changes in human activities. Compared with the IR and UR, the nitrogenous species concentration was relatively low in the AR.

(3) The apportionment of the nitrate pollution source by the IsoSource model showed that the atmospheric nitrogen, chemical fertilizers, sewage and manure are the main sources of nitrate in the study area. Combined with the analysis of Cl⁻, industrial sewage and manure are the main sources of nitrate in the IR, domestic sewage and manure are the main sources of nitrate in the UR, and chemical fertilizers are the main sources of nitrate in the AR. Atmospheric nitrogen deposition is also a source of nitrate in the study area. In order to control the pollution of the point-source pollution, we should establish a reasonable land use mode and scientific management measures for livestock manure. Environmental awareness and living environment management of urban and rural residents should also be strengthened.

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