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Watershed-Scale Shallow Groundwater Anthropogenic Nitrate Source, Loading, and Contamination Assessment in a Typical Wheat Production Region: Case Study in Yiluo River Watershed, Middle of China

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Abstract: Nitrate pollution in groundwater has become a global concern for agriculture and regional ecology. However, tracing the spatiotemporal groundwater nitrate pollution sources, calculating the total nitrogen loading, and assessing contamination at the watershed scale have not been well documented. In this study, 20 groundwater samplings from 2020 to 2021 (in dry and wet seasons) on the Yiluo River watershed in middle China were collected. Tracing groundwater nitrate pollution sources, calculating total nitrogen loading, and assessing contamination using dual isotopes (18ONO3 and 15NNO3), conservation of mass, and the nitrate pollution index (NPI), respectively. The results indicated that there were three nitrate sources in groundwater: (1) manure and sewage waste input (MSWI), (2) sediment nitrogen input (SNI), and (3) agriculture chemical fertilizer input (ACFI) in the Yiluo River watershed. ACFI and SNI were the main groundwater nitrogen pollution sources. The average nitrogen loading percentages of ACFI, SNI, and MSWI in the whole watershed were 94.7%, 4.34%, and 0.96%, respectively. The total nitrogen loading in the Yiluo River watershed was 7,256,835.99 kg/year, 4,084,870.09 kg/year in downstream areas, 2,121,938.93 kg/year in midstream areas, and 1,050,026.95 kg/year in upstream areas. Sixty percent of groundwater in the Yiluo River watershed has been polluted by nitrate. Nitrate pollution in midstream areas is more severe. Nitrite pollution was more serious in the wet season than in the dry season. The results of this study can provide useful information for watershed-scale groundwater nitrogen pollution control and treatment.

Keywords: watershed-scale; groundwater nitrate pollution sources; total nitrogen loading; nitrate pollution index; Yiluo River

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1. Introduction

Groundwater, as an essential part of the water cycle, is an important water source for agriculture, industry, and drinking water and helps secure regional ecology and safety all over the world [1–4]. While groundwater nitrogen pollution has become more serious in recent decades [5–9], it is now the most serious threat to agriculture and industries that use water, particularly for human drinking water safety [8,10–14].

The Yiluo River watershed, located in the south of the Yellow River plain, is one of the most important wheat production regions in China [15]. The groundwater is the main irrigation source and one of the most important drinking water sources in the Yiluo River watershed. The farmers used groundwater for irrigation for years and used large amounts of nitrogen fertilizers in the past few years. The groundwater was polluted seriously. Meanwhile, Luoyang City, one of the biggest cities in the Yiluo River watershed, has many factories, such as fertilizer plants, that pour wastewater that contains high concentrations of nitrogen into the Yi and Luo Rivers and contribute to shallow groundwater nitrogen pollution.

However, faced with so many problems, previous studies about groundwater in the Yiluo River watershed only focused on the surface water, such as the impact of land use on hydrology [16,17], the impact of climate change on hydrology [18], ion transfer in the Yiluo River [15,19], ecohydrology [20], the impact of the environment on the runoff of the Yiluo River [21], and water pollution analysis [22]. However, no studies about the nitrogen sources and total nitrogen loading of groundwater in the Yiluo River watershed have been performed in the past. Nitrogen pollution sources frequently contain anthropogenic products (manure and sewage waste inputs, as well as agricultural chemical fertilizer inputs), fly ashes, and waste [23,24]. Until now, there are three serious problems that have not been well researched: (1) how many nitrogen pollution sources there are in groundwater in the different regions and different seasons; (2) what are the changing conditions of nitrate pollution among the whole Yiluo River watershed; and (3) how many total nitrogen loadings there are in groundwater in the different regions and different seasons. Unless these problems are solved, it is impossible to carry out targeted control of groundwater nitrogen pollution sources and subsequent treatment. The quality of water used for agriculture, industry, and drinking water for urban residents cannot be guaranteed.

Therefore, this paper will use the dual isotope and nitrate pollution index methods to study the temporal and spatial nitrogen sources of groundwater, calculate the total annual nitrogen loading input, conduct a nitrate pollution assessment, and provide an important reference and way for the effective control of groundwater nitrogen pollution in the future.

2. Study Area

The Yiluo River watershed is located in Henan and Shanxi provinces in the middle of China (34°30′00″–32°10′00″ N, 109°12′00″–113°10′00″ E; Figure 1), which covers an area of 1.92×10^4 km^2, and has two tributaries the Yi River and the Luo River.

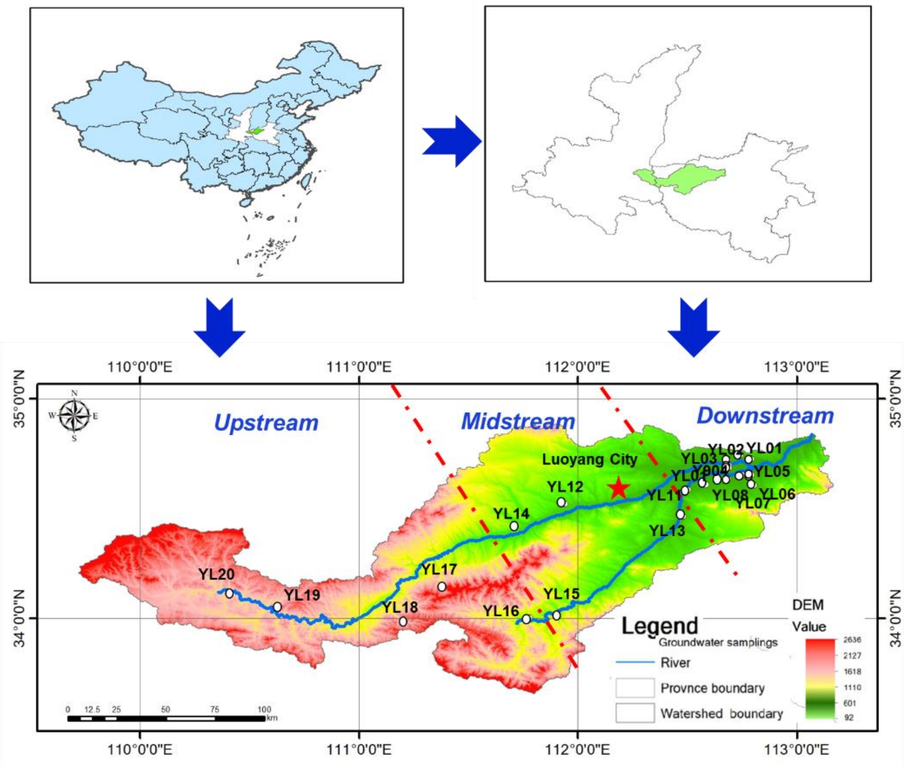


Figure 1. Location of the study area and groundwater sampling sites for the Yiluo River watershed in middle China.

The Yi River originates from the Xionger Mountain, in Henan Province. It is 264.8 km long; upstream and midstream are deep valleys and basins, respectively. The Luo River originates in Mupengou, Luannan City, Shanxi Province, with a total length of 453.0 km. The highest flow rates of the Yiluo River were 168 m/s, the annual average velocity was 0.67 m/s, and the highest water level was 106.25 m upstream. This region has a typical warm, temperate monsoon climate. The average annual temperature is 14.3 °C, and the annual average evaporation and average annual precipitation are 1451.7 mm and 545.9 mm, respectively. Maximum precipitation (>50%) occurs in July, August, and September [25].

The Yi and Luo Rivers form the lower reach of the watershed. Luoyang City, which is the most important city, gets its main water supply from shallow groundwater of the Luoyang Basin, which accounts for 97% of the total water supply. In addition, the aquifer of the Yiluo River contains silty sand, silt, and gravel; this is easy to pollute, and about 80% of the groundwater in the Yiluo River watershed was polluted [15].

3. Methodology

3.1. Water Sampling Collection

The field surveys were conducted during the dry season (10–17 July 2020 and 12–18 November 2021) and the wet season (6–14 July 2021). We collected 20 shallow groundwater samples for each field survey (total of 60 samples) (Figure 1).

3.2. Field Measurements and Laboratory Analysis

We collected the water samples after pumping for 10 min using the pump (Sample Pro, TM3/4 in., Manalapan, NJ, USA), then samples were filtered through a 1.45 µm filter [26,27], and stored in two precleaned 100 mL bottles for laboratory analysis of major ions. Additionally, the samples were brought to the laboratory and stored at a temperature of 4 °C.

Groundwater samples were collected, and field measurements were made on NO_3^-, NO_2^-, and NH_4^+ at each sampling location by a water quality analyzer (NOVER 400 and TR 320, MERCK Co., Potsdam, Brandenburg, Germany).

In groundwater samplings, the isotopes ($\delta^{15}N_{Nitrate}$(‰) and $\delta^{18}O_{Nitrate}$(‰)) were measured by a Finnigan MST253 mass spectrometer with an online Flash Elemental Analyzer and a Mircomass IsoPrime Mass Spectrometer coupled to an automated line in groundwater samplings, respectively. The ^{15}N results were shown as $\delta^{15}N_{Nitrate}$(‰) and $\delta^{18}O_{Nitrate}$(‰) relative to air in per mil (‰) data. The analytical precision of $\delta^{15}N_{Nitrate}$(‰) and $\delta^{18}O_{Nitrate}$(‰) were about 0.05‰ and 0.5‰, respectively [28]. The measurement uncertainty was expressed as a relative expanded uncertainty U (%), and its confidence level is 95% (uncertainty budget method calculated U). The measurement results are usually given as an average value.

3.3. Data Analysis

3.3.1. Total Nitrogen Loading

Three nitrogen pollution sources are primarily responsible for the Yiluo River's groundwater nitrogen loading. We used conservation of mass to select the calculation methods (Mclver et al. (2015) [29] and Nagel et al. (2018) [30]) for calculating the three nitrogen loadings. The application of fertilizer quantity to wheat and corn was based on data provided by the database (https://www.resdc.cn/Default.aspx, accessed on 1 February 2020).

Calculating nitrogen loading is always difficult due to the instability of nitrogen pollution. The main calculating nitrogen loading is the nitrogen remains in the soils of watershed, including nitrogen productions of crop growing, animals' production and transport, nitrification, denitrification, etc. [31,32]. In this study, we just discuss the relative stability of nitrogen (nitrate) in the Yiluo River watershed.

Agriculture chemical fertilizer input (ACFI)

$$\text{TN (kg year}^{-1}) = [(\text{area for wheat (ha)}) \times \text{quantity of nitrogen fertilizer (kg ha}^{-1}\text{ year}^{-1})] + [(\text{area for corn (ha)}) \times \text{quantity of nitrogen fertilizer (kg ha}^{-1}\text{ year}^{-1})] \times \text{length} \times \text{width} \times \text{infiltration coefficient} \times \text{hydraulic conductivity.} \quad (1)$$

Manure and sewage waste input (MSWI)

$$\text{TN (kg year}^{-1}) = [\text{manure and sewage waste nitrogen concentration (kg L}^{-1}\text{ year}^{-1}) \times \text{number} \times \text{the amount of runoff (m}^3\text{ year}^{-1}). \quad (2)$$

Sediment nitrogen input (SNI)

$$\text{TN (kg year}^{-1}) = [\text{the total nitrogen in the sediment (kg year}^{-1})] \times \text{length} \times \text{width} \times \text{infiltration coefficient.} \quad (3)$$

3.3.2. Nitrate Pollution Assessment

Here, we use the nitrate pollution index (NPI) to assess the anthropogenic nitrate contamination in the shallow groundwater at the watershed scale. The NPI is a very useful tool to indicate nitrate pollution and the influence of nitrates on humans and the environment; the specific calculation is as follows [33]:

$$\text{NPI} = \frac{C_S - HAV}{HAV} \quad (4)$$

where C_S is the concentration of groundwater nitrates and HAV is the groundwater nitrate threshold limit. In this study, the HAV was 10 mg/L (marked as N).

If NPI < 0 clean

$$\begin{array}{c} 0 < \text{NPI} < 1 \text{ Light pollution} \\ 1 < \text{NPI} < 2 \text{ Moderate pollution} \\ 2 < \text{NPI} < 3 \text{ Significant pollution} \\ 3 < \text{NPI Greater pollution} \end{array} \quad (5)$$

4. Results and Discussion

4.1. Nitrogen Pollution Sources and Tracing of Groundwater in the Yiluo River Watershed

The Keeling plot of $1/NO_3$ and $\delta^{15}N_{NO_3}$(‰) and the relationship of $\delta^{15}N_{Nitrate}$(‰) and $\delta^{18}O_{Nitrate}$(‰) in groundwater of the Yiluo River watershed can be used together to identify nitrogen pollution sources [34]. Firstly, the Keeling plot of $1/NO_3$ and $\delta^{15}N_{NO_3}$(‰) indicated that there were significantly three nitrogen groups (Figures 2 and 3). At the same time, the dual isotope ($\delta^{15}N_{Nitrate}$(‰) and $\delta^{18}O_{Nitrate}$(‰)) variation reflected that there were three nitrate sources: manure and sewage waste input (MSWI), sediment nitrogen input (SNI), and agriculture chemical fertilizer input (ACFI).

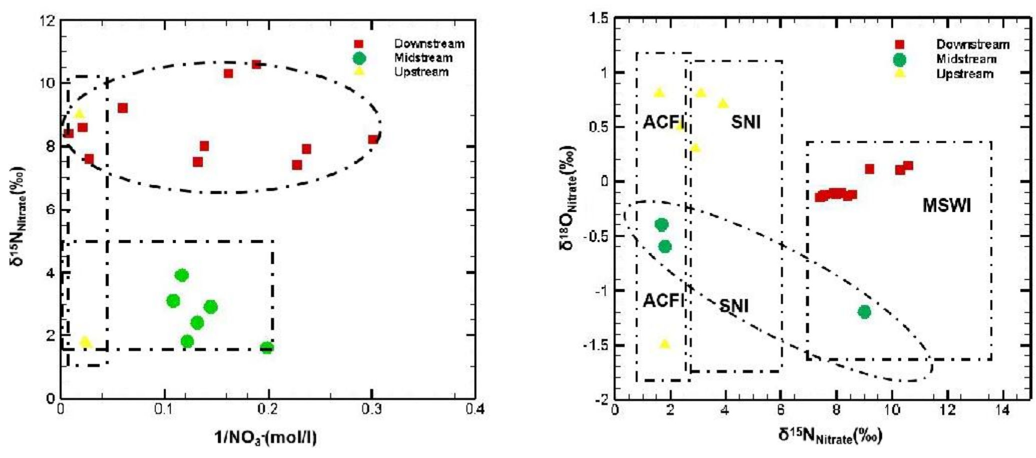


Figure 2. Keeling plot of $1/NO_3^-$ and $\delta^{15}N_{NO_3}$(‰) and the relationship of $\delta^{15}N_{Nitrate}$(‰) and $\delta^{18}O_{Ntrate}$(‰) [4] in groundwater of the Yiluo River watershed during the dry season. MSWI represents manure and sewage waste input. SNI represents sediment nitrogen input. ACFI represents agricultural chemical fertilizer input.

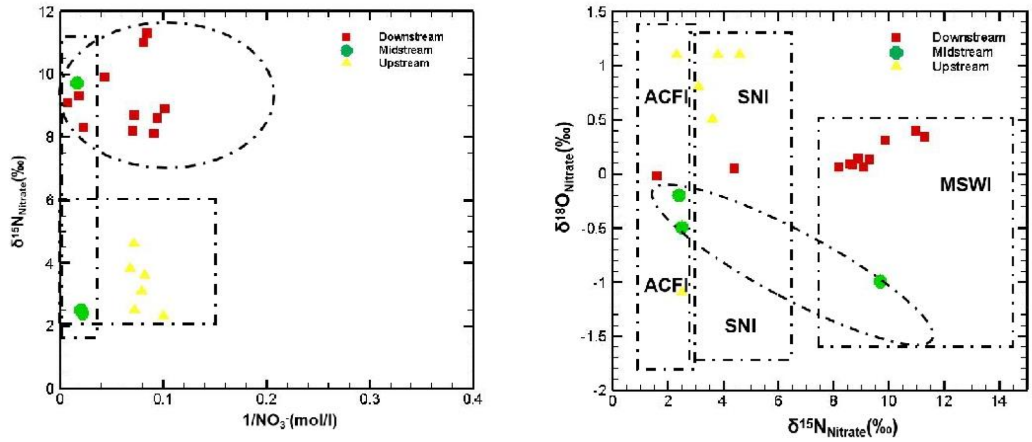


Figure 3. Keeling plot of $1/NO_3^-$ and $\delta^{15}N_{NO_3}$(‰) and the relationship of $\delta^{15}N_{Nitrate}$(‰) and $\delta^{18}O_{Nitrate}$(‰) [4] in groundwater of the Yiluo River watershed during the wet season. MSWI represents manure and sewage waste input. SNI represents sediment nitrogen input. ACFI represents agricultural chemical fertilizer input.

In the downstream and part of midstream, the NO_3^- concentration was low with high $\delta^{15}N_{Nitrate}$(‰) (7.40~10.9‰ in the dry season, 8.20~11.60‰ in the wet season) and $\delta^{18}O_{Nitrate}$(‰) (−0.2~0.2‰ in the dry season, −0.04~0.40‰ in the wet season) values, which suggested that the nitrates in the downstream were mainly derived from manure and sewage waste input (Figures 2 and 3). However, in the wet season, the results in the relationship of $\delta^{15}N_{Nitrate}$(‰) and $\delta^{18}O_{Nitrate}$(‰) also reveal that the groundwater nitrogen pollution source downstream partly came from sediment nitrogen input (SNI) and agriculture chemical fertilizer input (ACFI) (Figure 3). In the midstream, some samplings partly have high NO_3^- concentrations with low $\delta^{15}N_{Nitrate}$(‰) (1.7~9.40‰ in the dry season, 2.5~9.20‰ in the wet season) and $\delta^{18}O_{Nitrate}$(‰) (−1.2~−0.6‰ in the dry season, −1.10~−0.20‰ in the wet season), which indicates that the nitrates in this part were mainly derived from manure and sewage waste input and agricultural chemical fertilizer input (Figures 2 and 3). Partially high NO_3^- concentrations in the upstream were accompanied by low $\delta^{15}N_{Nitrate}$(‰) (1.90~4.20‰in the dry season, 2.20~4.50‰ in the wet season) and $\delta^{18}O_{Nitrate}$(‰) (−1.52~0.80‰ in the dry season, −1.10~1.20‰ in the wet season) values, indicating that the nitrate in the upstream was primarily derived from agricultural chemical fertilizer input and sediment nitrogen input (Figures 2 and 3). Zhang et al. (2014) [35] used the dual isotopes to identify the nitrogen sources of groundwater in the midstream and downstream of the Yellow River and found that the main nitrogen pollution sources were mineralization of soil organic N and sewage. Chen et al. (2007) [36] traced the sources of nitrogen in groundwater in the Yellow Delta and discovered that values ranging from 11.5 to 17.5‰ and $\delta^{18}O_{Nitrate}$(‰) values ranging from −9 to −7‰ indicated that nitrogen in groundwater was derived from irrigation and agricultural chemical fertilizer input (ACFI). The other source was the manure pits, with $\delta^{18}O_{Nitrate}$(‰) values ranging from 10 to 20‰. It is similar to the Yiluo River watershed, but the only difference is that the agricultural chemical fertilizer input (ACFI) was not the main nitrogen source in the mid- and downstream of the Yellow River. The main nitrogen source in groundwater in the Yellow Delta was not sediment nitrogen input. However, it is one of the most important wheat production regions and has many industries in the Yiluo River watershed, so the nitrogen sources of groundwater in the Yiljuo River watershed are greater than in other parts of the Yellow River.

4.2. Groundwater Nitrogen Loading of the Yiluo River Watershed

The nitrogen loading contains point pollution and nonpoint pollution [27,28]. There were three main sources of nitrogen pollution: agriculture chemical fertilizer input (ACFI), manure and sewage waste input (MSWI), and sediment nitrogen input (SNI). In the Yiluo River, pollution types include nonpoint pollution (agriculture chemical fertilizer input and sediment nitrogen input) and point pollution (manure and sewage waste input) (Figures 2 and 3).

Manure and sewage waste input (MSWI) were point nitrogen pollution sources for groundwater in the Yiluo River, while agriculture chemical fertilizer input (ACFI) and sediment nitrogen input (SNI) were nonpoint nitrogen sources. The nitrogen loading is mainly focused from 2021 to 2022. The total nitrogen loading in the Yiluo watershed was 7,256,835.99 kg/year; 4,084,870.09 kg/year in the downstream, 2,121,938.93 kg/year in the midstream, and 1,050,026.95 kg/year in the upstream (Table 1).

Table 1. The total nitrogen loading of groundwater in the Yiluo River watershed.

Pollution Types	TN (kg/year)	2021–2022		
		Downstream	Midstream	Upstream
Nonpoint pollution	Agriculture chemical fertilizers input	3,954,137.26	1,977,068.63	988,534.32
Point pollution	Manure and sewage waste input	21,168.60	35,306.07	7056.20
Nonpoint pollution	Sediment nitrogen input	109,564.23	109,564.23	54,436.43
Total		4,084,870.09	2,121,938.93	1,050,026.95
			7,256,835.99	

Specifically, the nitrogen loadings of ACFI in downstream, midstream, and upstream were 3,954,137.26 kg/year, 1,977,068.63 kg/year, and 988,534.31 kg/year, respectively. The nitrogen loadings of MSWI in downstream, midstream, and upstream were 21,168.60 kg/year, 35,306.07 kg/year, and 7056.20 kg/year, respectively. The nitrogen loadings of SNI in downstream, midstream, and upstream were 109,564.23 kg/year, 109,564.23 kg/year, and 54,436.44 kg/year, respectively (Table 1).

As a whole watershed, ACFI and SNI, as nonpoint pollution, were the main groundwater nitrogen pollution sources. The average nitrogen loading percentages of ACFI, SNI, and MSWI in the whole watershed were 94.7%, 4.34%, and 0.96%, respectively (Figure 4). The nitrogen loading percentages of ACFI in downstream, midstream, and upstream were 96.79%, 93.17%, and 94.14%, respectively. The nitrogen loading percentages of MSWI in downstream, midstream, and upstream were 0.53%, 1.67%, and 0.68%, respectively. The nitrogen loading percentages of SNI in downstream, midstream, and upstream were 2.68%, 5.16%, and 5.18%, respectively (Figure 4). There were 4552.64 km^2 of agriculture area (2015) and 313.13 km^2 of water body area (2015), and agricultural nitrogen fertilizer has been applied on a large scale for many years in the Yiluo River watershed, especially in the downstream and midstream. As a result, a significant amount of nitrogen entered the soil, the river, and finally infiltrated the shallow groundwater. As the manure and sewage waste input (MSWI) and the point pollution indicate, we found many industrial wastewater and livestock wastewater outlets beside the Yi River and Luo River (Figure 4). Despite the fact that the point pollution affected a small area, it had a high nitrogen concentration. Hobbie et al. (2017) [37] developed N mass balances for seven urban watersheds in Minneapolis and found that agriculture fertilizer, atmospheric deposition, and household pet waste accounted for the largest proportion (98%) of total nitrogen pollution sources.

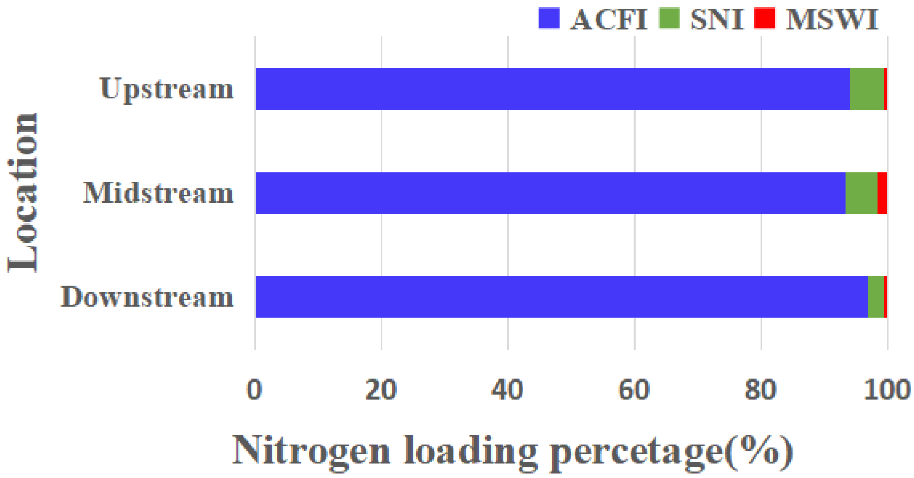


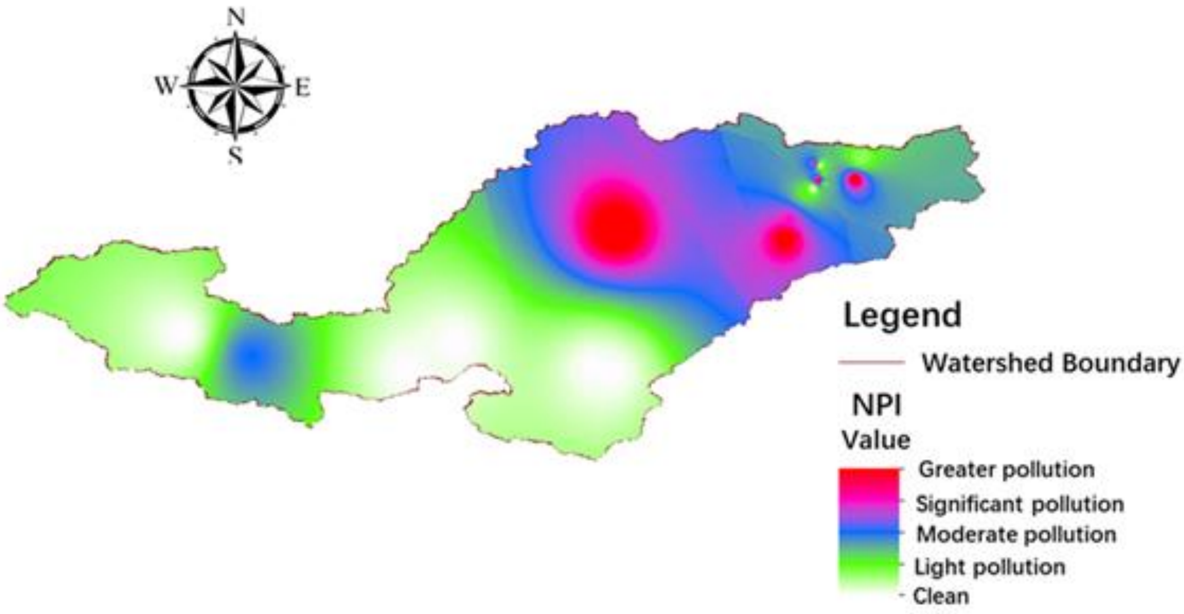
Figure 4. The total nitrogen loading percentage of groundwater in the Yiluo River watershed.

Compared with the results of Mclver et al. (2015) [29] and Hobbie et al. (2017) [37], it is found that atmospheric nitrogen deposition was the main source of pollution in these two research cases, which was directly related to the study of surface water in both cases and mainly caused by direct contact between the atmosphere and surface water. In addition, due to different land use types, the sources of nitrogen pollution were also different. Specifically, the former was near the bay, thus the seafood had become the main source of nitrogen, and the latter was in inland, so the atmospheric nitrogen deposition was the main source. Moreover, agricultural nitrogen fertilizer application has become the largest source of nitrogen pollution.

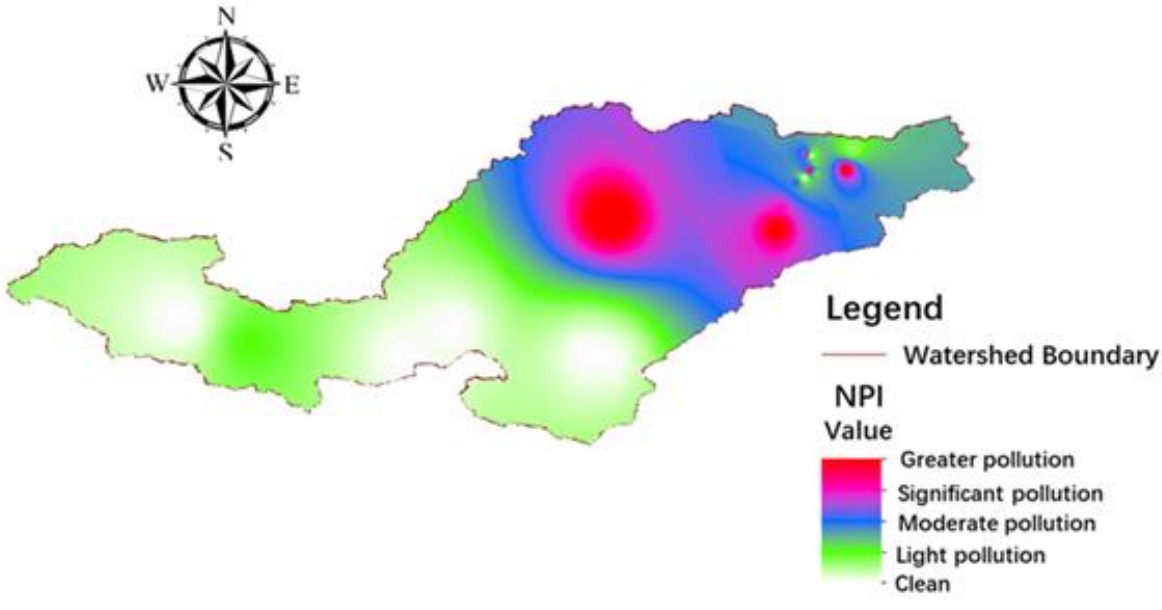
Similarly, compared with the groundwater nitrogen pollution loading in the Yiluo River Basin, the source of nitrogen pollution in the groundwater of the Yiluo River was very different from the surface water nitrogen pollution. Firstly, among the sources of nitrogen pollution in groundwater, atmospheric nitrogen deposition is no longer the main source of nitrogen pollution, mainly because groundwater cannot directly contact the atmosphere. In addition, the sources of groundwater nitrogen pollution in the Yiluo River Basin were mainly due to agricultural nitrogen fertilizer input and soil nitrogen release, while surface water was more from external sources and the release of soil sediment nitrogen had a greater impact on groundwater. At the same time, compared with the surface water nitrogen pollution sources, the groundwater nitrogen pollution sources of the Yiluo River were also mainly the same as manure and sewage polluted by surface nonpoint sources.

4.3. Nitrite Contamination Assessment of Groundwater in the Yiluo River Watershed

The nitrite contamination index showed a profound spatiotemporal change. Sixty percent of groundwater has been polluted by nitrate in the Yiluo River watershed. In terms of space, all the nitrate pollution in the middle reaches was light to moderate (Figure 5), both in the dry and wet seasons. Most sites have moderate-to-greater nitrate pollution except for a little light nitrate pollution upstream both in the dry and wet seasons. While in a section of the downstream, it was lightly polluted both in the dry and wet seasons (Figure 5). However, the most serious pollution point was in YL14, which reached 123 mg/L (Table 2). Timely, nitrite pollution was more severe in the wet season than in the dry season (Figure 5). Although rainfall increased in the wet season, the precipitation carried nitrate from nearby farmland and factories into rivers and deep into shallow groundwater. Wang et al. (2022) [4] also reported that the nitrate pollution in the Yiluo River was heavily affected by nitrate pollution. Similarly, nitrogen pollution of surface water in our study can also contaminate groundwater through the interaction between surface water and groundwater.



(**a**)



(**b**)

Figure 5. The nitrate pollution assessment of groundwater in the Yiluo River watershed. (**a**) Dry season and (**b**) wet season.

Table 2. The calculation process of the nitrate pollution index (NPI).

Location	Points	Dry Season					Wet Season				
		NO_3^- (mg/L)	Cs (mg/L)	HAV (mg/L)	NPI	Results	NO_3^- (mg/L)	Cs (mg/L)	HAV (mg/L)	NPI	Results
Down-stream	YL01	36.18 * ± 0.62	36.18 * ± 0.62	10	2.62	Significant pollution	37.18 * ± 0.62	37.18 * ± 0.62	10	2.72	Significant pollution
	YL02	4.21 * ± 0.06	14.21 * ± 0.20	10	0.42	Light pollution	5.21 * ± 0.06	15.21 * ± 0.20	10	0.52	Light pollution
	YL03	7.55 * ± 0.06	17.55 * ± 0.22	10	0.76	Light pollution	8.55 * ± 0.07	18.55 * ± 0.22	10	0.86	Light pollution
	YL04	4.38 * ± 0.06	4.38 * ± 0.06	10	−0.56	Clean	5.38 * ± 0.06	5.38 * ± 0.06	10	−0.46	Clean
	YL05	7.21 * ± 0.06	17.21 * ± 0.22	10	0.72	Light pollution	8.21 * ± 0.07	28.21 * ± 0.40	10	1.82	Moderate pollution
	YL06	3.32 * ± 0.05	3.32 * ± 0.05	10	−0.67	Clean	5.04 * ± 0.06	5.04 * ± 0.06	10	−0.5	Clean
	YL07	123.2 * ± 1.76	123.2 * ± 1.76	10	11.32	Greater pollution	126.8 * ± 1.76	126.8 * ± 1.76	10	11.68	Greater pollution
	YL08	47.3 * ± 0.70	47.3 * ± 0.70	10	3.73	Greater pollution	48.30 * ± 0.70	48.30 * ± 0.70	10	3.83	Greater pollution
	YL09	16.67 * ± 0.20	16.67 * ± 0.20	10	0.67	Light pollution	17.67 * ± 0.20	17.67 * ± 0.20	10	0.77	Light pollution
	YL10	6.18 * ± 0.06	6.18 * ± 0.06	10	−0.38	Clean	7.18 * ± 0.06	17.18 * ± 0.20	10	0.72	Clean
	YL11	5.29 * ± 0.06	15.29 * ± 0.20	10	0.53	Light pollution	6.29 * ± 0.06	16.29 * ± 0.20	10	0.63	Light pollution
Midstream	YL12	38.74 * ± 0.62	38.74 * ± 0.62	10	2.87	Significant pollution	40.2 * ± 0.63	40.2 * ± 0.63	10	3.02	Significant pollution
	YL13	42.61 * ± 0.65	42.61 * ± 0.65	10	3.26	Greater pollution	43.61 * ± 0.65	43.61 * ± 0.65	10	3.36	Greater pollution
	YL14	54.59 * ± 0.75	54.59 * ± 0.75	10	4.46	Greater pollution	60.21 * ± 0.80	60.21 * ± 0.80	10	5.02	Greater pollution
	YL15	8.22 * ± 0.07	8.22 * ± 0.07	10	−0.18	Clean	10.2 * ± 0.20	10.2 * ± 0.20	10	0.02	Clean

Table 2. *Cont.*

Location	Points	Dry Season					Wet Season				
		NO_3^- (mg/L)	Cs (mg/L)	HAV (mg/L)	NPI	Results	NO_3^- (mg/L)	Cs (mg/L)	HAV (mg/L)	NPI	Results
Upstream	YL16	5.02 * ± 0.06	5.02 * ± 0.06	10	−0.5	Clean	6.00 * ± 0.06	6.00 * ± 0.06	10	−0.4	Clean
	YL17	5.10 * ± 0.06	5.1 * ± 0.06	10	−0.49	Clean	6.2 * ± 0.06	6.2 * ± 0.06	10	−0.38	Clean
	YL18	9.68 * ± 0.20	9.68 * ± 0.20	10	−0.03	Clean	8.25 * ± 0.07	8.25 * ± 0.07	10	−0.18	Clean
	YL19	11.74 * ± 0.22	21.74 * ± 0.35	10	1.17	Moderate pollution	9.88 * ± 0.20	19.88 * ± 0.22	10	0.99	Light pollution
	YL20	8.27 * ± 0.07	8.27 * ± 0.07	10	−0.17	Clean	7.22 * ± 0.06	7.22 * ± 0.06	10	−0.28	Clean

Note: * There are significant differences between equivalent parameters vertically when $p < 0.05$.

In addition, ANOVA analysis is a useful method for showing the significantly different effects of many factors. In this study, significantly different among nitrogen (nitrate, ammonia, and nitrite) need to be identified. Although the ANOVA analysis is not the most robust, it is a quick and accurate method for identifying significant differences between different ions and has broad applications in environmental science, hydrochemistry, ecology, and agriculture [38,39].

5. Conclusions

Tracing the spatiotemporal groundwater nitrate pollution sources and calculating total nitrogen loading at the watershed scale can provide important information for watershed groundwater nitrate pollution treatment. This study is the first to research the watershed-scale spatiotemporal groundwater nitrogen pollution sources and total nitrogen loading in the Yiluo River watershed. The results and findings of this study suggest: (1) Agriculture chemical fertilizer input (ACFI) was the biggest groundwater nitrogen source in the Yiluo River watershed. To reduce the impact of agricultural nitrogen pollution on groundwater, farmers must control the amount of nitrogen fertilizer used, (2) in the downstream and midstream, manure and sewage waste input (MSWI) was another important nitrogen pollution source. As to the downstream and midstream, manure and sewage waste input (MSWI) was another important nitrogen pollution source. As the downstream and midstream are located in Luoyang City, a large amount of urban sewage and industrial and mining enterprise sewage were discharged into the river and the soil, resulting in serious groundwater pollution around the city. Therefore, it is necessary to strengthen the control of urban sewage wastewater gateways and increase sewage treatment plants, so that the sewage can only be discharged after reaching the standard, (3) the amount of agricultural nitrogen pollution from groundwater in the wet season had increased dramatically, so drinking groundwater during the rainy season requires more rigorous monitoring and treatment before it can be drunk; and (4) the groundwater among the whole Yiluo River watershed was severely polluted, and the midstream was the most nitrate polluted region and more measures are needed to control concentration and the trend of nitrate pollution in shallow groundwater. The limitations of this study are that: (1) well locations and numbers were limited, and (2) estimating nitrogen loading may be higher than actual loading in the watershed because nitrogen instability and temperature (cold or warm) were not fully considered. Further studies would consider the wells' number, location, and nitrogen instability. Those findings and suggestions can help in dealing with watershed-scale groundwater nitrogen pollution problems and human drinking water safety.

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