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Sources, Influencing Factors, and Pollution Process of Inorganic Nitrogen in Shallow Groundwater of a Typical Agricultural Area in Northeast China

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Abstract: As one of the largest agricultural areas, the Sanjiang Plain of Northeast China has faced serious inorganic nitrogen pollution of groundwater, but the sources and the formation mechanism of pollution in the regional shallow groundwater remain unclear, which constrains the progress of pollution control and agricultural development planning. An investigation on potential nitrogen sources, groundwater inorganic nitrogen compounds (NH_4^+, NO_3^-, NO_2^-), and topsoil total nitrogen concentration (TN) was conducted in a typical paddy irrigation area of Sanjiang Plain. Multivariate statistical analysis combined with geospatial-based assessment was applied to identify the sources, determine the governing influencing factors, and analyze the formation process of inorganic nitrogen compounds in shallow groundwater. The results show that the land use type, oxidation-reduction potential (Eh), groundwater depth, NO_2^- concentration, and electrical conductivity (EC) are highly correlated with the NO_3^- pollution in groundwater, while DO and Eh affected the distribution of NH_4^+ most; the high concentrations of NO_3^- in sampling wells are most likely to be found in the residential land and are distributed mainly in densely populated areas, whereas the NH_4^+ compounds are most likely to accumulate in the paddy field or the lands surrounded by paddy field and reach the highest level in the northwest of the area, where the fields were cultivated intensively with higher fertilization rates and highest values of topsoil TN. From the results, it can be concluded that that the NO_3^- compounds in groundwater originated from manure and domestic waste and accumulated in the oxidizing environment, while the NH_4^+ compounds were derived from N fertilization and remained steady in the reducing environment. NO_2^- compounds in groundwater were the immediate products of nitrification as a result of microorganism activities.

Keywords: inorganic nitrogen; shallow groundwater; multivariate statistical analysis

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1. Introduction

Nitrogen pollution in groundwater, especially in areas of intensive agriculture, has aroused widespread concern throughout the world [1]. It has been reported that the excess of the main inorganic nitrogen compounds in drinking water (NO_3^-, NH_4^+, NO_2^-) are detrimental to human health [2–4].

The mechanism of the formation process of inorganic nitrogen compounds in groundwater is complex due to the variety of nitrogen sources and the intricacy of influencing factors in the environment. Numerous studies have reported that the inorganic nitrogen compounds in groundwater could originate from nitrogen-based fertilizer, manure, as well as domestic and industrial pollution. Besides, the discharge from septic tanks, leaking sewers, and eutrophic surface water can all contribute [5]. In some cases, the atmospheric nitrogen deposition [6] and soil organic nitrogen mineralization [7] can also play important roles in nitrogen pollution in groundwater. In addition, some environmental factors such as pH, oxidation-reduction potential (Eh), soil organic matter, and bacterial activity [8–11] can greatly affect the species and amount of nitrogen in groundwater.

In previous research, several methods have been developed to identify nitrogen sources, among which the chemical analysis and stable isotope methods are the most traditional ones. Moreover, some new tracing methods and comprehensive methods have also been developed. As for chemical analysis, it has been widely used as an auxiliary identifying method because some characteristic ions (e.g., Ca^{2+}, Mg^{2+}, and SO_4^{2-}) in groundwater can carry information about their origins [12], and some halides (Cl^-, Br^- and I^-) usually have something to do with anthropogenic activities and remain relatively conserved in the subsurface environment [13–15]. The ratios of NO_3^-/Cl^-, Cl^-/Br^-, and I^-/Na^+ in groundwater are also key identifiers of the origin, by which Katz [16], Panno [17], and Pastén-Zapata [13] successfully identified the sources of nitrate coming from wastewater. Nevertheless, the types and concentrations of characteristic components vary widely in different pollution sources and change greatly during the physical and chemical reactions occurring in the subsurface environment, limiting the ability of chemical analyses to achieve accurate pollution source results.

In a similar manner, the stable isotope ratios of nitrogen (δ15N, δ18O) and boron (δ11B) are effective indicators of the pollution sources since different sources of nitrogen often share distinct isotopic compositions [18]. However, the use of single isotope tracers often cannot discriminate the sources correctly. This is because isotope ratios between sources have overlap values and the nitrification, denitrification, and other reactions that nitrogen may experience in the subsurface environment could cause the isotope values to deviate from theoretical ones, impacting the accuracy of the results. Hence, the nitrate-nitrogen and nitrate-oxygen dual-isotope methods have become a powerful tool in nitrate source identification since Kendall [19] reviewed the distribution of δ15N and δ18O values of various sources. The dual-isotope method can not only improve the accuracy of source differentiation but also make it possible to quantify the contribution of different sources to the pollution [20–22].

In recent years, some new types of tracers have been applied to identify sources of nitrogen pollution in groundwater. Nakagawa et al. [23] used coprostanol, which is produced by bacterial reduction of cholesterol in the gut of higher animals, as an indicator to investigate nitrate sources of pollution for an aquifer in Shimabara, Nagasaki, Japan, and verified that coprostanol had the potential for nitrate source identification by comparing the results with those obtained by the dual-isotope method. This indicates that it is essential to develop and adopt some new types of tracers as additional tools to support the dual-isotope method, which will make the identification process more efficient and accurate.

The single identification methods inevitably have some limitations in application due to the complexity of nitrogen formation processes, and some comprehensive methods have shown advantages in recent years, namely the adoption of multitracers and the integration of source appointment with the analysis of relevant factors (e.g., land use types). Moreover, some researchers have used geospatial-based assessment [24,25], groundwater age interpretation [26], and microbial community analysis [27] as auxiliaries to enhance the investigation of nitrogen sources. Multivariate statistics [28,29] is a powerful tool to integrate all the identification methods and relevant studies together, and thus the factor analysis [30], principal component analysis [31,32], clustering analysis [13,30], and factorial correspondence analysis [14] have been widely applied in hydrogeological research. Nevertheless, such studies have either focused on the origin and fate of the pollutants or the reactions experienced by nitrogen before or after leaching into groundwater, but both lines of study have seldom been combined in an analysis of the whole formation process of pollution systematically. As such deep insight into the essential nature of the pollution process is lacking.

There is no doubt that agricultural nonpoint source nitrogen pollution in groundwater is a serious worldwide problem since the pollution behaviors are intricate and disordered. Thus, to make clear the sources and pollution process of this kind of nitrogen pollution, it is necessary to investigate the potential pollution sources and relevant information such as the population density and amounts of fertilizer application at the early stage of source identification. Meanwhile, statistical analysis methods like multivariate statistics and geospatial statistics should be utilized to explore the intrinsic connection between nitrogen concentration and other factors that may contribute to pollution. Moreover, the tracing methods such as chemical analysis and stable isotope methods can provide more direct and powerful support to the analysis process.

The Sanjiang Plain in Northeast China (Figure 1), which is one of the most important national food production bases, has been intensively developed for agriculture since the 1950s. It has experienced four instances of large-scale reclamation, during which the large areas of wetland were adapted into paddy fields, and large amounts of fertilizers were applied to the soil every year. At the same time, the deterioration of groundwater quality in this area had become the key factor that limited the sustainable development of local water supply and agricultural planting. Recent studies reported that the Sanjiang Plain has faced the risk of serious inorganic nitrogen pollution of groundwater in some regions [33,34]. However, the information about nitrogen sources and behavior in this area is limited, and the formation process of nitrogen pollution in regional groundwater remains unclear, which will undoubtedly constrain the progress of its control and impact the large-scale plan of agricultural development.

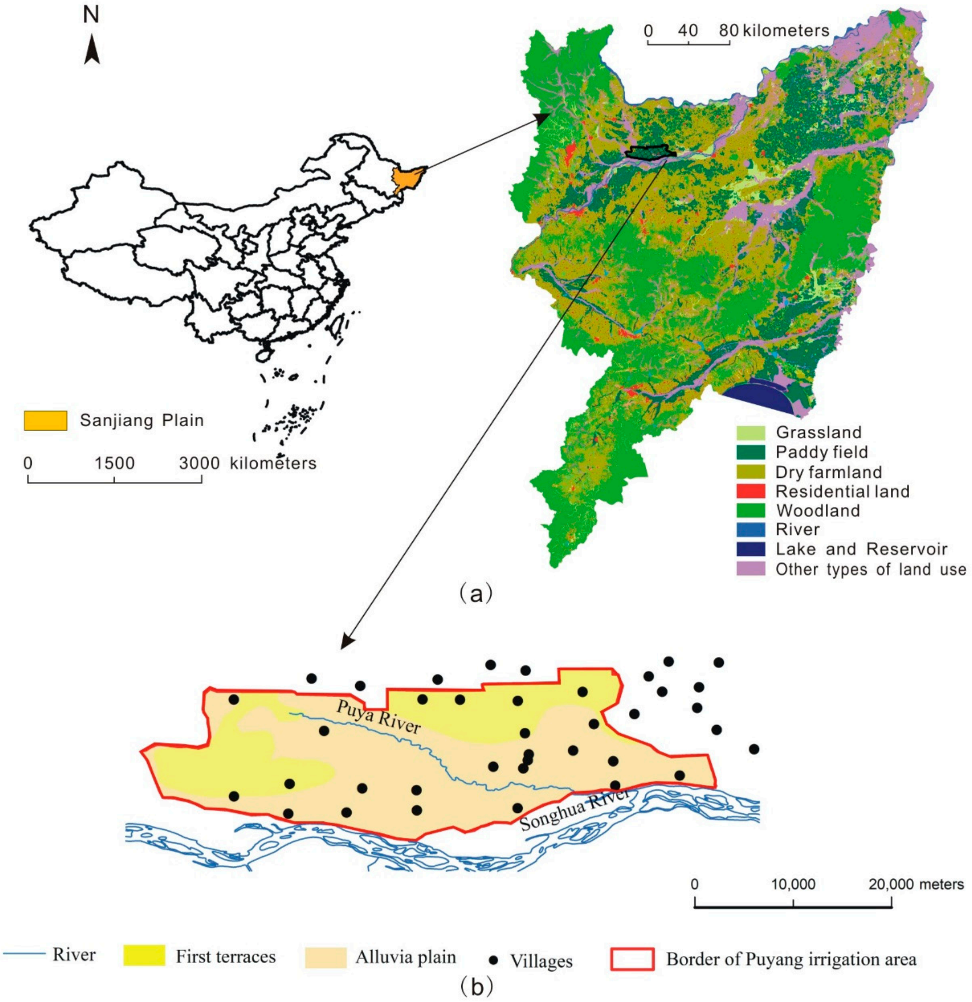


Figure 1. *Cont.*

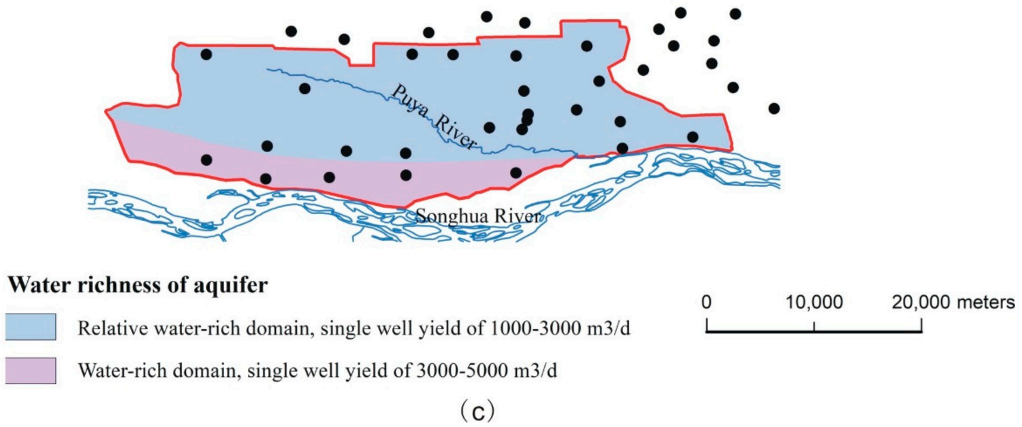


Figure 1. Location (**a**), water richness (**b**), and landform pattern (**c**) of Puyang irrigation area.

In this study, the survey was conducted in a typical paddy irrigation area of Songhua River watershed on the distribution of the potential nitrogen sources, groundwater inorganic nitrogen compounds (nitrate, ammonia, and nitrite), and topsoil total nitrogen concentration. Then, multivariate statistics and the geospatial-based assessment were combined to identify the nitrogen sources and the governing factors affecting pollution. After describing the methods and detailing the results, this paper discusses the formation process of inorganic nitrogen in groundwater. The results of this study provide a scientific basis for pollution control in the irrigation area and promote the future development of the agricultural security of the Sanjiang Plain.

2. Study Area

2.1. Geographic Location and Climate

Puyang irrigation area is located between Luobei and Suibin counties (47°12′54′′–47°22′04′′ N, 131°00′32′′–131°31′51′′ E) of the Sanjiang Plain and falls on the north bank of the lower reach of Songhua River (Figure 1). It has a cold temperate continental monsoon climate with a mean annual rainfall of 535.5 mm and a mean annual evaporation of 694.4 mm (E601). Most of the rainfall occurs from June to September, which accounts for about 70% of annual precipitation. The annual air temperature ranges from −19.3 °C (January) to 21.7 °C (July).

2.2. Geology and Hydrology Characteristics

Lying in the Songhua River alluvial plain, the characteristic landform pattern consists of first terraces and flood plains (Figure 1). The thickness of the quaternary strata ranges from 270 to 280 m, and the thickness of the aquifer is between 50 and 200 m. From top to bottom, the aquifer lithology can be separated as medium sand, medium-coarse sand, and a sand and gravel layer, which developed from the upper, middle, and lower Pleistocene respectively. There are no stable aquitard layers between aquifers, and the hydraulic conductivity ranges from 9.6 to 16.1 m/day. According to the embedment features and dynamic characteristic of groundwater, the regional groundwater can be divided into feeble confined water and phreatic water; the former is mainly distributed along the sides of the valley plain, which belong to the first terraces, and has a buried depth of 3–5 m, whereas the latter is mainly distributed in the flood plain area and shares a buried depth between 1 and 3 m (Figure 1).

The groundwater of the irrigation area is mainly recharged by precipitation and lateral groundwater runoff and is also recharged by surface water seepage, floodwaters, and irrigation water infiltration at some times and in some regions. Lateral groundwater runoff is also the main form of groundwater discharge. The irrigation area has flat terrain, and the groundwater flows slowly with the hydraulic gradient of 1/5000 to 1/10,000. In accordance with the terrain slope aspect, the groundwater flow direction is generally from southeast to northwest.

The groundwater table of a year meets the lowest level during the periods of March and April and then rises shortly after along the river bank due to the spring flood. It rises greatly during July and August as it is recharged by precipitation infiltration and reaches the peak level during August and September. From late October or early November to the end of April or early May, the ground surface is frozen and the groundwater table is in a state of decline.

3. Materials and Methods

3.1. Pollution Source Investigation

Due to the major activity of the area being rice farming and industrial pollution being absent, a field survey that focused on the domestic and agricultural situations was conducted to investigate the potential nitrogen sources in the Puyang irrigation area. The amount and distribution of towns, villages, population, livestock, fertilization, sewage systems, and landfills were all included in the survey.

3.2. Sampling and Analysis

A total of 78 groundwater samples and 19 soil samples were collected in August 2017. Most of the groundwater sampling points were evenly distributed within the domain of Puyang irrigation area, whereas some densely populated villages and previously monitored pollution areas were sampled much more intensively. Some outside wells adjacent to the irrigation area were also sampled to properly map the distribution of nitrogen pollution intensity. The types of sampling wells mainly consisted of domestic wells and irrigation wells. Because the depths of the two types of wells were significantly different (the depths of the domestic wells were generally less than 20 m, while those of the irrigation wells were about 30 m), the adjacent domestic and irrigation wells were both sampled in order to better understand how the well depth affected the nitrogen pollution of the groundwater. The pH, electrical conductivity (EC), dissolved oxygen (DO), and oxidation-reduction potential (Eh) of the groundwater were measured in situ using a portable multiparameter meter (HQ40d, Hach, Loveland, CO, USA), which was previously calibrated. All water samples for chemical analysis were filtered with a 0.45-µm filter before laboratory analysis. The inorganic nitrogen, including NH_4^+, NO_3^-, NO_2^-, was analyzed by ion chromatography. In addition, the use type of the land where the sampling wells were located, the well depth, and the potential pollution source conditions were recorded, and the water depth of the sampling wells was measured in situ.

Topsoil samples were collected to analyze the concentrations of the total organic and inorganic nitrogen (TN). The position of sampling points was close to the water sampling well, covering various land use types and geomorphic units. TN was analyzed by Jilin University Testing Center.

3.3. Statistical Methods and Graphical Representation

The average value, median value, and standard deviation of the pH, EC, DO, and Eh were evaluated to depict the results of the chemical analysis of groundwater. Nonparametric testing was used because inorganic nitrogen data in the study were not normally distributed. The concentrations of NH_4^+ and NO_3^- of water samples in this study were grouped by well depth and land use types. Mann–Whitney U test was used to determine whether there was a significant difference ($\alpha = 0.05$) between every two groups ($n > 10$) of data [35], which made the basis of the regrouping of the data.

To understand the spatial distribution characteristics of nitrogen pollution in groundwater, the pollution intensity of NH_4^+ and NO_3^- of the study area were mapped according to the ordinary kriging interpolation in ArcGIS (ESRI, Redlands, CA, USA) software.

3.4. Statistical Methods and Graphical Representation

Some indicators of nitrogen pollution sources in groundwater such as land use type and Eh, which also reflect the formation process that the nitrogen load experiences in the subsurface environment, are highly correlated among themselves. Multivariate statistical analysis could provide insight into the relationship between variables. In this study, factor analysis (FA) was conducted to highlight the main factors that determined the nitrogen concentration in groundwater. Then, the correspondence analysis (CA) was combined to further analyze and the conclusions drawn from FA. Both the FA and CA were performed in SPSS 20.0 software.

FA is widely applied for data reduction in hydrochemical and hydrogeological studies [31] and has also been used in nitrogen source appointment in recent years [14]. The main process of FA includes establishing an orthogonal factor model, selecting common factors, and performing factor rotation. In this study, eight quantitative variables (nitrogen concentration, Eh, EC, well depth, DO, water depth) and three qualitative variables (land use type, water richness of aquifer, landform pattern) were selected. Prior to FA, the qualitative variables were transformed into ordinal ones based on the practical situation and the regrouped results from the significance test, and all the variables were standardized to eliminate the effects of dimension.

CA is a multivariate analysis method that can reduce the original variables to a small number of orthogonal factors that by definition are independent [36]. It can not only study variables and samples simultaneously but also study both the qualitative and quantitative variables by dividing them into classes [36]. The correlation of variables can be depicted by a correspondence analysis plot, of which the vicinity of points could reflect the close level between variables. Due to the weakness of the analysis of the qualitative variables by FA, which could only distinguish between the effects of the two land use type groups on the nitrogen pollution in this study, CA was proposed to determine the qualitative variables, especially the land use type's effect on nitrogen pollution in the study area, and further analyze the correlation between the main influencing factors and identify the sources of nitrogen pollution. The variables of CA in this study include the concentrations of NH_4^+ and NO_3^-, land use type, well depth, and Eh. Among them, the concentrations of NH_4^+ and NO_3^- were divided into three classes, while Eh and the well depth were divided into two groups.

4. Results

4.1. Distribution of Potential Nitrogen Sources

According to the pollution source investigation, there was one densely populated town and 19 villages in the irrigation area. The main residential population in the villages had moved to the town in 2010, leaving all of the villages but four uninhabited most of the year except during the transplanting and harvesting periods. The northern suburb of the town had 70–80 households inhabited by farmers. Only the town and one village in the area had been equipped with operational sewage systems and centralized garbage disposal facilities. One hoggery and one cattle farm were operating in the area, and several heads of livestock were being raised in the inhabited villages.

Obviously, most of the irrigation area land surface was covered by paddy fields, which had an area of 273.5 km^2 according to the statistical data. The rate of fertilization of the farmland is shown in Figure 2.

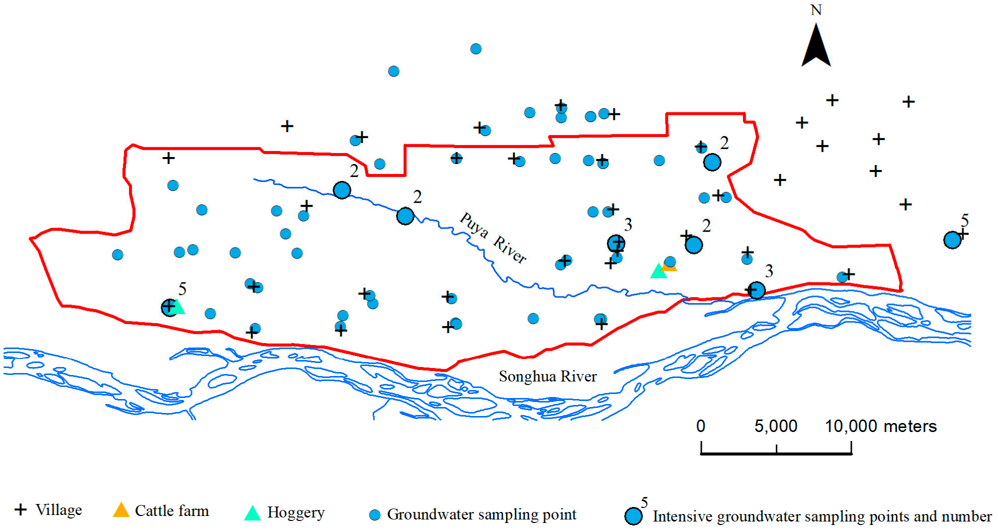


Figure 2. Location of groundwater and topsoil samples and distribution of potential nitrogen sources.

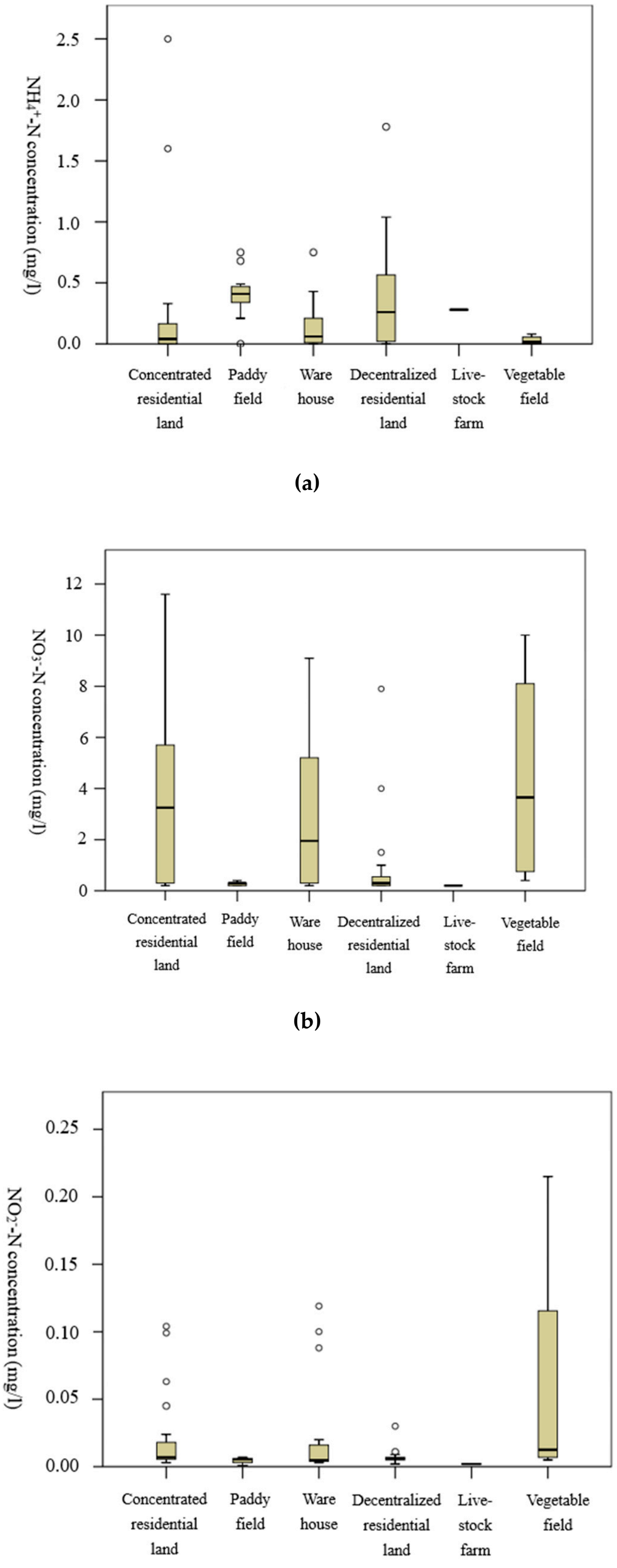
4.2. Distribution of NH_4^+ and NO_3^- in Different Well Depths and Land Use Types

The chemical analysis results of groundwater samples are shown in Table 1, and it can clearly be observed that the nitrogen concentrations under different well depths and land use types are significantly different (as shown in Figures 3 and 4). Considering that the nitrogen concentrations at different depths show a very obvious difference, the depth of sampling wells could be divided into two groups: greater than 20 m (WO_{20}), which is the depth of irrigation wells, and less than 20 m (WU_{20}), which is the depth of drinking water supply wells. The use type of the land where the sampling wells were located could be divided into six categories: concentrated residential land; paddy field; warehouse; and decentralized residential land surrounded by paddy fields, livestock farm, and vegetable field.

Table 1. Descriptive statistics of the chemical analysis of groundwater.

	Average Value	Median Value	Minimum Value	Maximum Value	Standard Deviation
NH_4^+-N (mg/L)	0.31	0.20	0.00	2.50	0.44
NO_3^--N (mg/L)	1.8	0.3	0.2	11.6	2.8
NO_3^--N (mg/L)	0.015	0.006	0.001	0.215	0.033
EC (µs/cm)	325.4	244.5	83.6	1296.0	223.3
DO (mg/L)	3.94	3.52	1.52	9.85	1.69
Eh (mv)	30.1	24.6	−108.6	162.6	76.1
pH	6.97	6.92	6.03	7.61	0.30

According to Mann-Whitney U test, the concentration of NH_4^+ in WO_{20} was significantly higher than that in WU_{20}; the opposite was found for NO_3^-. The significant differences in NH_4^+ concentration under different land use types can be summarized as follows: paddy field > concentrated residential land, decentralized residential land > concentrated residential land, and paddy field > warehouse. For NO_3^-, these differences were as follows: concentrated residential land > paddy field, concentrated residential land > decentralized residential land, warehouse > paddy field, and warehouse > decentralized residential land (Table 2). The water samples from livestock farm and vegetable field were not included in the test due to the small sample size. As seen in Figure 3, the distribution of NH_4^+ and NO_3^- in livestock farm is similar to that in decentralized residential land; the NH_4^+ concentration in vegetation field is lower than that in other land use types, and the distribution of NO_3^- in vegetation field is similar as that in concentrated residential land and warehouse.

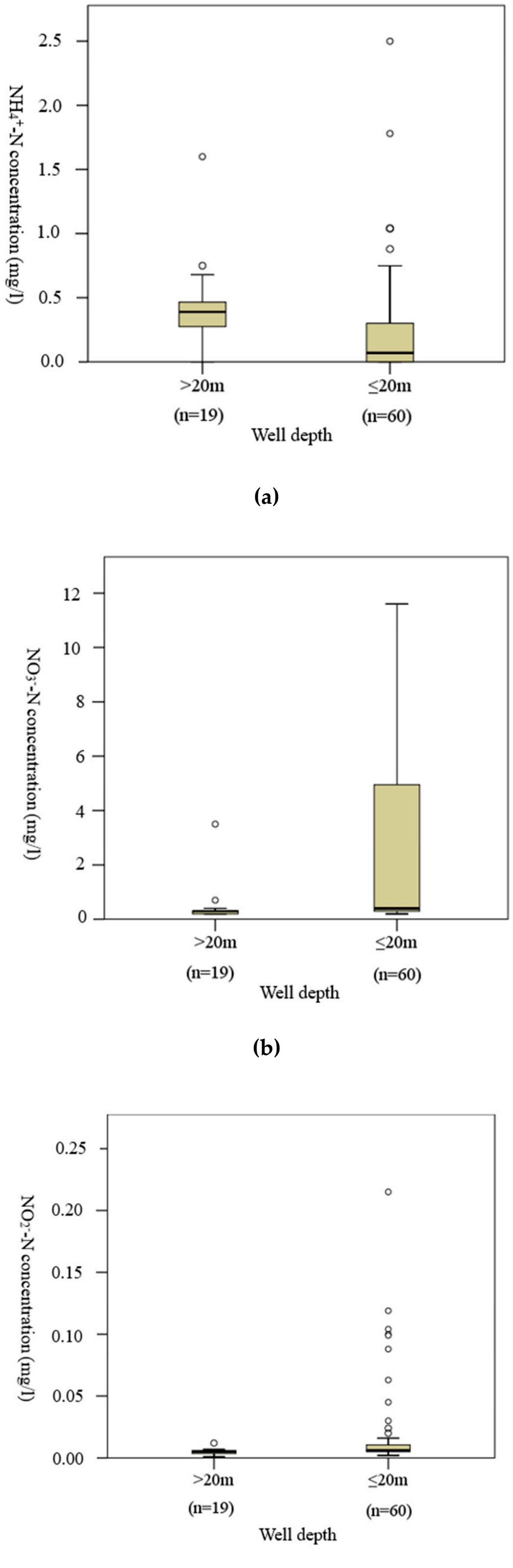


(a)

(b)

(c)

Figure 3. Box plot of NH_4^+ (**a**), NO_3^- (**b**) and NO_2^- (**c**) concentration in groundwater from different land use types.



(a)

(b)

(c)

Figure 4. Box plot of NH_4^+ (**a**), NO_3^- (**b**) and NO_2^- (**c**) concentration in groundwater from different well depths.

Table 2. The differences in NH_4^+ and NO_3^- concentrations under different categories of land use type and well depth.

		Categories	Significance Level (p)	Differences between Categories (Confidence Interval of 95%)
NH_4^+	Land use type	CR [a] vs. P [b]	0.001	P > CR
		CR vs. W [c]	0.421	not significantly different
		CR vs. DR [d]	0.044	DR > R
		P vs. W	0.002	P > W
		P vs. DR	0.302	not significantly different
		W vs. DR	0.108	not significantly different
	Well depth	WU_{20} vs. WO_{20}	0.004	$WO_{20} > WU_{20}$
NO_3^-	Land use type	CR vs. P	0.000	CR > P
		CR vs. W	0.508	not significantly different
		CR vs. DR	0.003	CR > DR
		P vs. W	0.004	W > P
		P vs. DR	0.134	not significantly different
		W vs. DR	0.037	W > DR
	Well depth	WU_{20} vs. WO_{20}	0.005	$WU_{20} > WO_{20}$

[a] Concentrated residential land; [b] paddy field; [c] warehouse; [d] decentralized residential land.

Based on the test results of the distribution of NH_4^+ and NO_3^- in different land use types, the land use type could be reclassified into two groups, with one including concentrated residential land, warehouse, and vegetation field and the other including paddy field, decentralized residential land, and livestock farm.

4.3. Multivariate Statistical Analysis

4.3.1. Factor Analysis

The values of the variables in FA are shown in Table 3. A correlation test of the standardized variables was conducted, and the correlation matrix and the correlation heat map are shown in Table 4 and Figure 5, respectively. The correlation coefficients between variables were not large due to the interactions between multiple variables, thus indicating that it is essential to highlight the common information in variables using FA. The KMO test statistic of variables was 0.655 (greater than 0.5), and the Sig value of Bartlett sphericity test statistic was less than 0.01, which indicated that the variables were significantly correlated and suitable for FA.

Table 3. Assigned values of the variables for factor analysis.

Quantitative Variables	Value	Qualitative Variables		Value
NH_4^+	The actual value of analysis	Land use type	Concentrated residential land, warehouse, vegetable field	2
NO_3^-			Paddy field, decentralized residential land, livestock farm	1
NO_2^-		Water richness of aquifer	Water-rich	2
Eh			Relatively water-rich	1
DO		Landform pattern	Alluvial plain	2
EC			First terrace	1

Table 4. Correlation matrix of variables in factor analysis.

	Well Depth	Water Depth	Eh	DO	EC	NH_4^+	NO_3^-	NO_2^-	Land Use Type	Water Richness	Landform Pattern
Well depth	1.000	0.296	−0.335	0.184	−0.354	0.143	−0.368	−0.212	−0.379	−0.037	−0.032
Water depth		1.000	−0.227	0.063	−0.267	0.191	−0.291	−0.157	−0.196	−0.572	−0.254
Eh			1.000	−0.030	0.384	−0.597	0.605	0.313	0.335	0.200	0.236
DO				1.000	0.025	−0.052	0.089	−0.063	0.010	−0.158	0.039
EC					1.000	−0.157	0.592	0.264	0.305	0.246	0.207
NH_4^+						1.000	−0.381	−0.193	−0.239	−0.111	−0.237
NO_3^-							1.000	0.572	0.479	0.169	0.001
NO_2^-								1.000	0.311	0.181	0.045
Land use type									1.000	0.299	−0.006
Water richness										1.000	0.353
Landform pattern											1.000

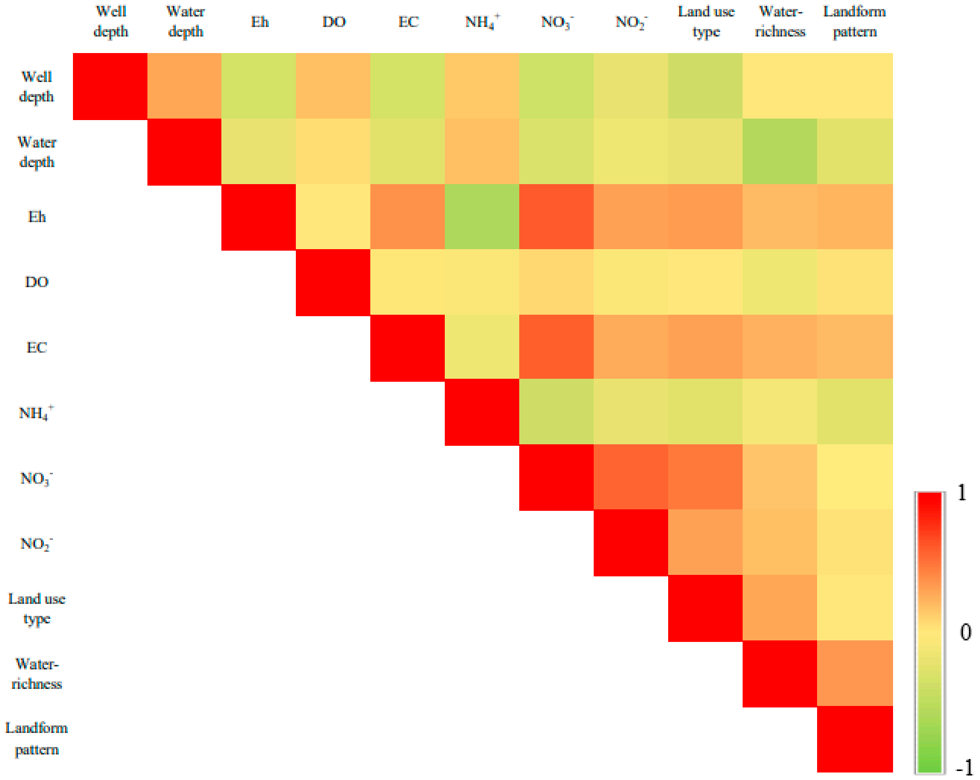


Figure 5. Correlation heat map of variables in factor analysis.

The first three factors (PC1, PC2, and PC3) contribute to 27.67%, 17.20%, and 12.38% of the variance, respectively, accounting for 57.24% of the total. From the load matrix and loading diagram of the rotation factor (Table 5 and Figure 6), the first factor (PC1) has a strong positive correlation with the concentration of NO_3^-, and this factor could be regarded as the NO_3^- pollution influencing index. The second factor (PC2) exhibits strong to moderate positive correlation with landform pattern and water richness of aquifer and negative correlation with water depth, and this factor could be considered as the groundwater cycling index. The last factor (PC3) shows the strongest negative correlation with the concentration of NH_4^+ and could be useful as a NH_4^+ pollution index.

Table 5. Load matrix of the rotation factor of the first three principal factors.

Variables	Principal Factors		
	PC1	PC2	PC3
NO_3^-	0.855	0.038	0.261
Land use type	0.671	0.104	−0.034
Well depth	−0.660	−0.073	0.254
NO_2^-	0.636	0.028	0.037
Eh	0.622	0.230	0.475
EC	0.609	0.248	0.103
Landform pattern	0.160	0.817	−0.137
Water richness	−0.112	0.712	0.370
Water depth	−0.288	−0.705	0.113
NH_4^+	−0.358	−0.214	−0.644
DO	−0.122	−0.200	0.638
Eigenvalue	3.043	1.892	1.362
Cumulative % of variance	27.667%	44.864%	57.244%

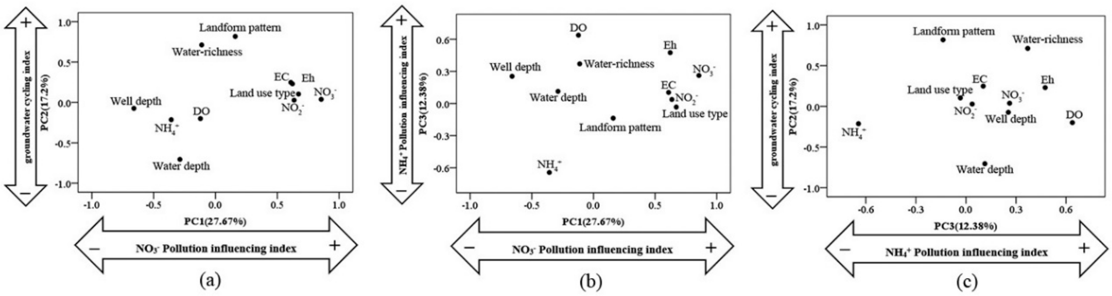


Figure 6. Loading diagram of the variables for principle factors. (**a**) Loading of the variables for PC1 and PC2. (**b**) Loading of the variables for PC1 and PC3. (**c**) Loading of the variables for PC3 and PC2.

The loading of variables for PC1 and PC3 depicted in Figure 6b reflects the variables' correlation with NO_3^- and NH_4^+ pollution and the distances between variables directly. From the x-axis (representing NO_3^- pollution index), it can be seen that PC1 has a strong to moderate correlation with land use type, well depth, the concentration of NO_2^-, Eh, and EC. The positive correlation with land use type means that greater NO_3^- pollution risks exist for groundwater in concentrated residential land, warehouse, and vegetation field than the others. EC has a moderate positive correlation with PC1 (0.609), indicating that the NO_3^- and EC may arise together in groundwater. In the meantime, the Eh, which represents the redox potential of groundwater, is positively correlated with PC1 (0.622), suggesting that an oxidizing environment is essential for NO_3^- in groundwater. The positive correlation with the concentration of NO_2^- reflects the transformation between NO_3^- and NO_2^-. On the other hand, PC1 shows a moderate negative correlation with well depth (−0.660), which means that the groundwater in shallow, oxidizing wells has more potential to accumulate NO_3^-. As for the y-axis (representing NH_4^+ pollution index), the concentration of NH_4^+ lies on the opposite end of the axis from DO and Eh, indicating that NH_4^+ exists in the anoxic and reducing groundwater environment. The weak positive correlation of PC3 with the water richness of aquifer demonstrates that the distribution of NH_4^+ in the regional aquifer is also affected by the dilution effect.

4.3.2. Correspondence Analysis (CA)

The values and categories of the variables are shown in Table 6, and the classes of nitrogen concentration (NO_3^-, NH_4^+), Eh, well depth, and land use type in the CA are projected on the primary plane in Figure 7. The first two factorial axes which explain 90.60% of the total data variance were retained in the primary plane. The first factor (x-axis) explained 58.74% of the total variance, where the reducing and oxidizing environments are oppositely located and could be divided into two parts, the left part representing the reducing environment and the right one representing the oxidizing environment. The WU_{20}, high to moderate concentration of NO_3^- (NN3, NN2), and the low concentration of NH_4^+ (AN1) are located on the right side, whereas the WO20, low concentration of NO_3^- (NN1), and high to moderate concentration of NH_4^+ (AN3, AN2) are on the left side, indicating that the deep aquifer is rich in reducing substances such as ferrous and organic matter, and the oxidizing groundwater has more potential to induce NO_3^-, while NH_4^+ is more likely to accumulate in the reducing environment, which is consistent with the FA explanation. Various land use types are distributed on the different sides of x-axis and reflect the well construction preference of local people. The wells in paddy field were constructed for irrigation, so the well depth is relatively deep to meet the need for water supply, and the groundwater is generally in a reducing condition. The wells situated in concentrated residential land mainly provide domestic water and were constructed with higher quality standards; the wells in such land are relatively shallow (the local deep aquifer is rich in iron), and the groundwater is in an oxidizing environment.

Table 6. Assigned values of the variables for correspondence analysis.

Variables	Categories	Value
NH_4^+-N	<0.20 mg/L	AN1
	≥0.20 and <0.50 mg/L	AN2
	≥0.5 mg/L	AN3
NO_3^--N	<1.0 mg/L	NN1
	≥1.0 and <5.0 mg/L	NN2
	≥5.0 mg/L	NN3
Eh	<0 mv	Reducing environment
	≥0 mv	Oxidizing environment
Well depth	≤20 m	WU_{20}
	>20 m	WO_{20}
Land use type	Concentrated residential land, paddy field, warehouse, decentralized residential land, vegetable field, livestock farm	

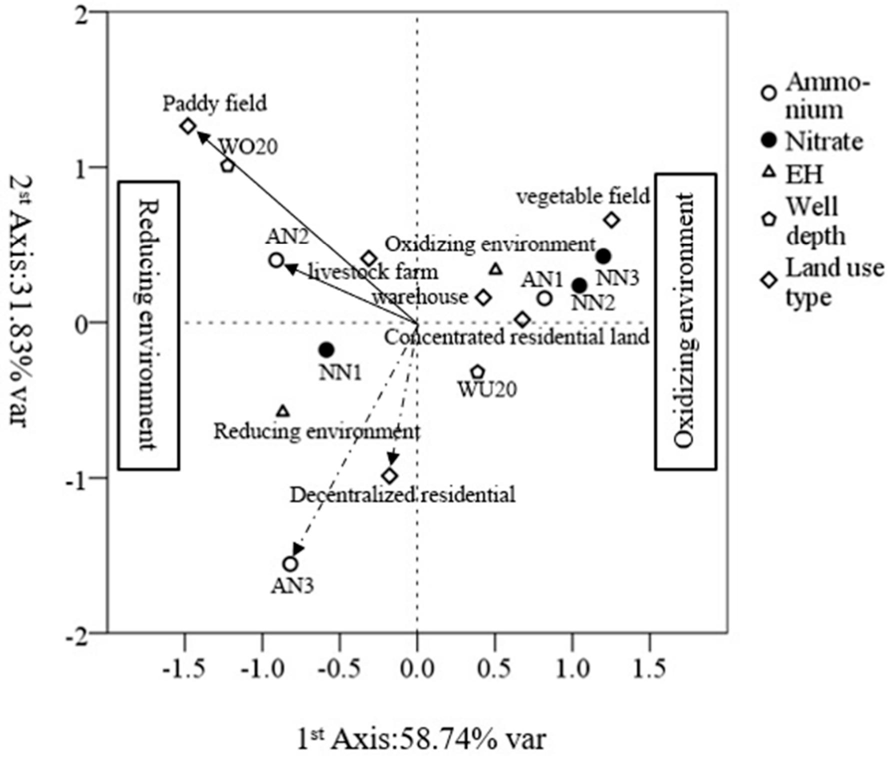


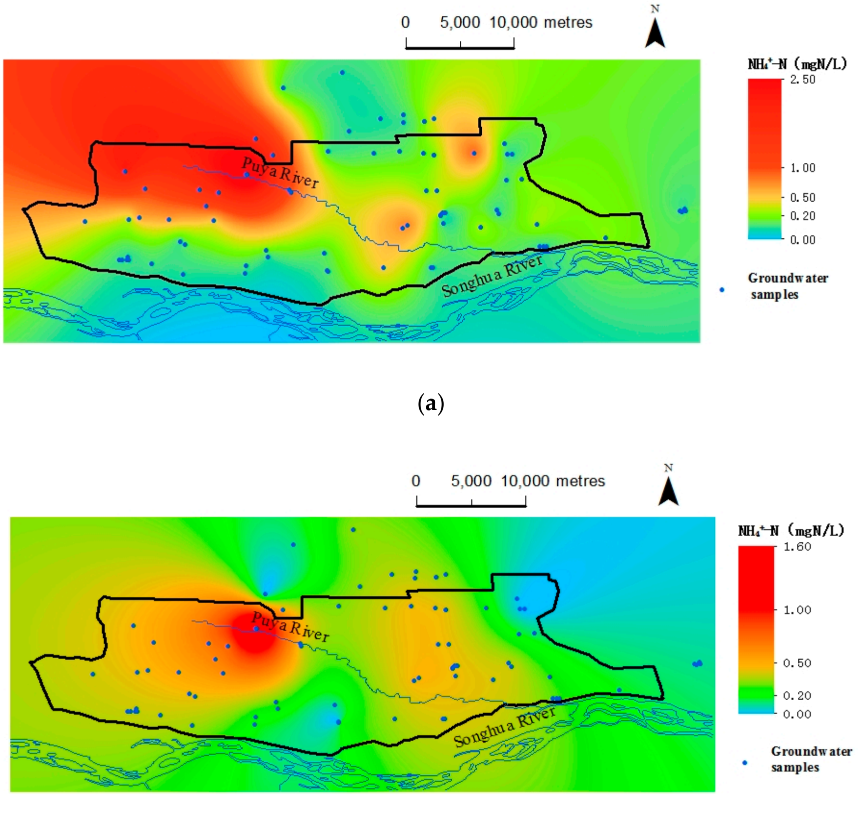
Figure 7. Primary factorial plane of correspondence analysis (CA) based on the variables of NH_4^+, NO_3^-, Eh, well depth, and land use type.

The distances between the variable classes in the plane can be used to interpret the essential relevance between each of them. The high to moderate concentration of NO_3^- is in the vicinity of vegetation field and concentrated residential land, which suggests that these two land use types are most likely to result in NO_3^- pollution in groundwater. Warehouses are closest to the oxidizing environment and are in the vicinity of NN3 and NN2, representing another place vulnerable to NO_3^- pollution.

Measuring the angle of the vector is another method to facilitate interpretation. Concerning the NH_4^+ classes, AN3 has the smallest angle with decentralized residential land which was surrounded by paddy field, and AN2 has the smallest angle with paddy field, suggesting that paddy field has the largest potential to impose NH_4^+ pollution.

4.4. Spatial Distribution of Nitrogen Concentration in Groundwater

The concentrations of NH_4^+ and NO_3^- in the wells of different depths were significantly different ($p < 0.01$); the spatial distribution of NH_4^+ and NO_3^- in the wells with the depths of ≤20 and >20 m was mapped using the method of ordinary kriging interpolation. Figure 8 shows that the concentrations of NH_4^+ in WU_{20} were generally smaller than those in WO_{20}, which was in accordance with the above-mentioned test ($p = 0.004$). The spatial area where NH_4^+-N concentrations exceeded the WHO criteria (0.5 mg/L) in the WO_{20} was larger than that of WU_{20}. However, the positions of the NH_4^+ excessive area were distributed similarly for both well depths. Generally, the highest concentration of NH_4^+ occurred in the northwest of the irrigation area, and the central part of the area also showed the risk of NH_4^+ pollution.

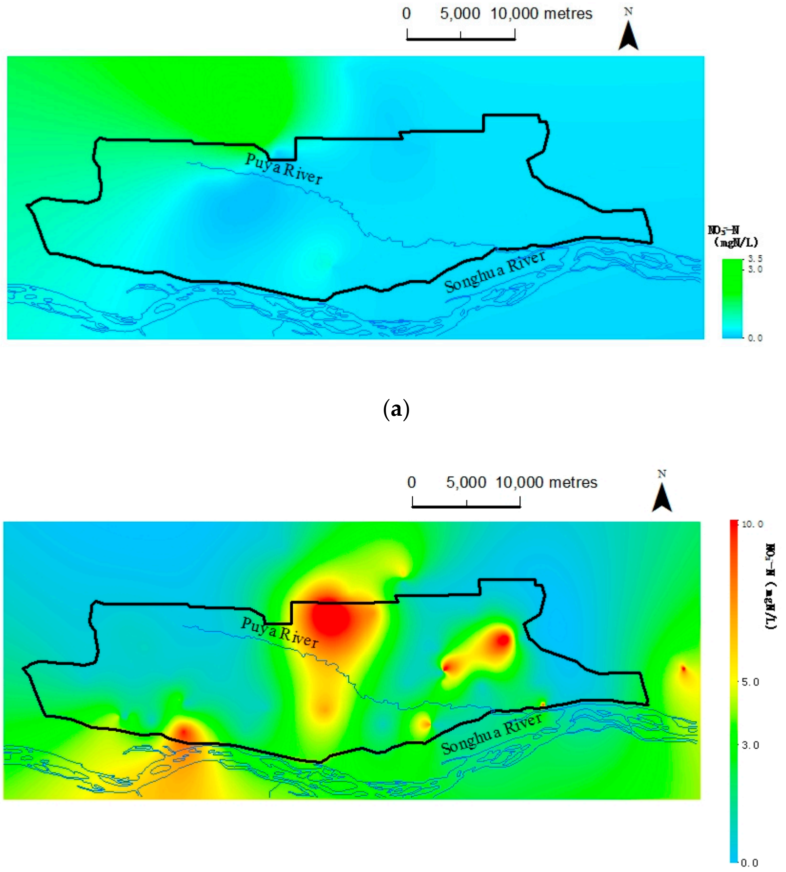


(**a**)

(**b**)

Figure 8. Spatial distribution of NH_4^+-N concentration in groundwater using ordinary kriging: (**a**) WO_{20}, (**b**) WU_{20}.

Figure 9 shows that the NO_3^- concentrations in WU_{20} were generally higher than those in WO_{20}, as verified by the above-mentioned test ($p = 0.005$). Large areas of the NO_3^- concentration in WU_{20} of the irrigation area exceeded 3 mg/L and were believed to be a result of anthropogenic sources as shown in previous studies, whereas NO_3^--N concentrations in WO_{20} were generally lower than 3 mg/L. The areas of excessive NO_3^- in WU_{20} were mostly distributed around the densely populated town and villages in a patchy shape or located in vegetation fields of places that were not densely populated.



(**a**)

(**b**)

Figure 9. Spatial distribution of NO_3^--N concentration in groundwater using ordinary kriging: (**a**) WO_{20}, (**b**) WU_{20}.

4.5. Distribution of TN Concentration in Topsoil

The distribution of TN concentration in topsoil is depicted in Figure 10, which shows that the average TN concentration of fields (dry land, paddy field, vegetation field) was higher than that of natural land. As for natural land, the TN concentration in forest land was higher than that in riverbank and wetland, due to the N deposition of plant litter.

Figure 11 shows that the TN concentration in topsoil was not significantly relevant to the NH_4^+-N concentration in the vicinity of groundwater sampling wells, while the location of the largest value of topsoil TN was in the vicinity of the highest NH_4^+-N concentration well; both were located in the northwest of the area. The TN values of topsoil located near the groundwater wells with low NO_3^--N concentrations were in random distribution, whereas the moderate to high concentrations of NO_3^--N in groundwater (>1.0 mg/L) appeared to be relevant to the TN value of nearby topsoil (Figure 11).

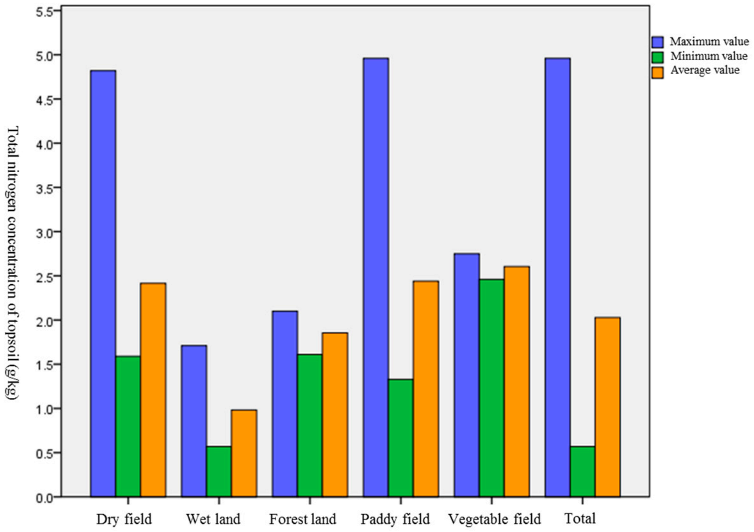
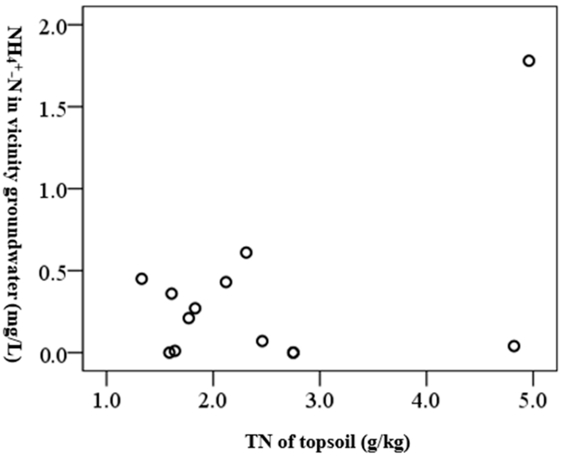
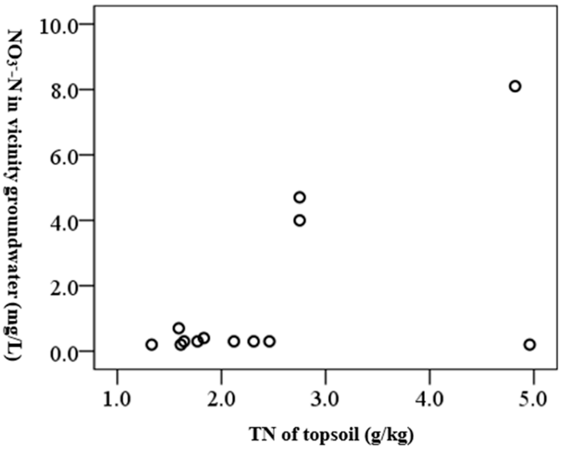


Figure 10. Descriptive statistics of total nitrogen (TN) concentration in topsoil of various land use types.



(**a**)



(**b**)

Figure 11. Scatter plot of topsoil TN and the $NH_4{}^+$-N (**a**) and $NO_3{}^-$-N (**b**) concentrations of groundwater in nearby sampling wells.

5. Discussion

5.1. Nitrogen Source Appointments

According to the results of the potential nitrogen source investigation in the study area, the dominating N sources include the excess N of fertilization (mainly composed of urea and ammonia), domestic sewage, and manure. Regarding the different land use types of paddy field, concentrated residential land, decentralized residential land, warehouse, and livestock farm, the N fertilization mainly contributed to the pollution in paddy fields and the land surrounded by paddy fields, such as decentralized residential land and warehouse, and the domestic sewage and manure pollution mainly occurred in residential land, vegetable field, and livestock farm, also occurring in decentralized residential land.

Figure 10 shows that the moderate to high concentrations of NO_3^--N in groundwater (>1.0 mg/L) appeared to be relevant to the TN value of nearby topsoil, proving that the NO_3^- pollution in groundwater was a result of the surface nitrogen infiltration. The FA results indicate that greater NO_3^- pollution risks exist for groundwater in concentrated residential land, warehouse, and vegetation field than groundwater in other land use types. It is expressed in detail by CA that the vegetation field and the concentrated residential land are most likely to result in NO_3^- pollution in groundwater. This indicates that the NO_3^- in groundwater of the irrigation area originated from domestic sewage and manure. This conclusion can be supported by FA results suggesting that the EC, which is regarded as an indicative index of wastewater, rises together with NO_3^-. Considering the spatial distribution of NO_3^- concentration in groundwater, the areas of excessive NO_3^- are mostly distributed around the densely populated town and villages or located in vegetation fields, which demonstrates again that it is the domestic sewage and manure that generate NO_3^- pollution in groundwater.

The CA results also indicate that paddy field has the greatest potential to impose NH_4^+ pollution, from which it can be concluded that the NH_4^+ in groundwater mainly came from the fertilizer N excess. Concerning the spatial distribution of NH_4^+ in groundwater, the highest concentration of NH_4^+ occurred in the northwest of the irrigation area. According to the fertilizer application investigation, the fertilizer rate in the north part of the irrigation area was larger than that in the south, and the northwest was the intensive agricultural district of the area; these findings are in accordance with the spatial distribution characteristics of NH_4^+ in groundwater and support the conclusion that NH_4^+ in groundwater originated from fertilizer. Meanwhile, the highest value of TN in topsoil also occurred in the northwest of the area, which was in the vicinity of the well with the highest concentration of NH_4^+. It is further suggesting that fertilizer was the main contributor to both the soil N and the NH_4^+ in groundwater.

5.2. Governing Factors Determining the Nitrogen Distribution in Groundwater

The nitrogen components in groundwater are a result of nitrogen emission and a series of physical, chemical, and biochemical reactions in the surface and subsurface environment. Besides the nitrogen sources, the specific characteristics of aquifers and vadose zones such as their permeability and thickness, the soil medium, and the environmental factors (e.g., dissolved oxygen and reducing matter, temperature, and soil water content) can all influence the distribution of nitrogen in groundwater. In this study, some comprehensive and accessible indexes (land use type, water richness of the aquifer, landform pattern, Eh, EC, DO, well depth, and water depth) were selected to facilitate the analysis of the influential elements and determine the governing factors. Among the selected indexes, the land use type and EC were indicative of the pollution sources; water richness of the aquifer, water depth, and landform pattern can represent the specific characteristics of aquifers and vadose zones; and the Eh, DO, and well depth reflect the oxidizing and reducing matter in the environment.

The FA results have highlighted the main factors that determine the nitrogen concentration in groundwater. The results show that the NO_3^- pollution influencing index (PC1) has a strong to moderate positive correlation with land use type, NO_2^- concentration, Eh, and EC and a negative correlation with the well depth, indicating that both the nitrogen sources and the redox environment are important for the development of NO_3^- pollution in groundwater of the study area. NO_3^- is stable in the oxidizing environment, but denitrification (the reduction of NO_3^- to N_2 and NO_2^-) happens as a result of microbial action when groundwater conditions become reducing; as such, Eh has a positive correlation with NO_3^- distribution. Moreover, in the results of CA, the high to moderate concentrations and low concentrations of NO_3^- belong to oxidizing and reducing environments, respectively, again proving that the redox environment is one of the main factors affecting NO_3^- distribution. The groundwater in shallow wells has a higher potential to accumulate NO_3^-. This is due to the mixing of the groundwater from different depths, which dilutes the polluting shallow water, and it is also due to the reducing matter in deeper aquifers making the denitrification possible and attenuating NO_3^-, which has been verified in the results of FA.

The results of FA also suggest that the DO and Eh are the most important factors that determine the NH_4^+ concentration. In an aerobic and oxidizing environment, NH_4^+ is easily oxidized, thus making it difficult to keep the NH_4^+ loading stable in the groundwater. Besides, the dilution effect is another factor affecting NH_4^+ distribution by diminishing the concentration of it. For the irrigation area, the NH_4^+ sources (mainly from fertilizer) are not highly variable in spatial distribution, and thus the variety of pollutants on the surface contribute little to the NH_4^+ difference in groundwater. The anoxic and reducing environment is the dominant factor that determines whether NH_4^+ can exist in a stable state and the concentration at which it exists in groundwater.

5.3. Formation Process of Inorganic Nitrogen in Groundwater

The inorganic nitrogen in groundwater is a result of surface nitrogen emission and the physical, chemical, and biochemical reactions that the nitrogen load experiences in the subsurface environment. According to the above-mentioned analysis, the nitrogen speciation and concentration are greatly affected by the redox environment of the aquifer, which is represented by the combination of Eh, DO, and well depth. When the groundwater was in the oxidizing condition, the NH_4^+ concentration was low, and the NO_3^- concentration was determined by nitrogen loading. When the groundwater was in a reducing environment, the NO_3^- concentration was fairly low, and the NH_4^+ concentration was determined by the amount of fertilizer application. The high levels of NO_2^- were accompanied by high concentrations of NO_3^-, as an immediate product of nitrification. The formation process of inorganic nitrogen pollution in groundwater can be summarized as follows:

(1) NH_4^+-N pollution: The paddy field, of which the soil was generally in a reducing environment due to the standing water, was mainly treated with ammonium fertilizer and urea, which easily transforms into ammonium; thus, the nitrogen loading was mostly in the form of NH_4^+-N. Previous studies have mentioned that NH_4^+ is apt to be assimilated by vegetation [37] and volatilization [38], and the excess NH_4^+ would be absorbed by soil materials to a great extent [39]. This greatly attenuates NH_4^+-N content before leaching into the groundwater. The NH_4^+-N that leaches into groundwater has two different fates: one is to remain stable as NH_4^+-N if the groundwater is in a reducing environment, while the other is to be transformed into NO_3^- or NO_2^- if the groundwater is in an oxidizing aquifer. The threshold concentration of NO_3^--N in groundwater is much greater than that of NH_4^+-N, so there will not be enough oxidized NO_3^- to lead to pollution, but the NH_4^+-N in a reducing environment has a large potential risk.

(2) NO_3^--N and NO_2^--N pollution: The soil of residential land is commonly in an oxidizing environment, and thus the nitrogen emission from manure and sewage water is mainly in the form of organic N and NO_3^--N. These kinds of nitrogen are not lessened as much as NH_4^+-N in the vadose zone, and most of them will leach into groundwater. Afterward, if the groundwater is in an oxidizing environment, NO_3^--N will remain stable, and organic nitrogen will be transformed into NO_3^--N or NO_2^--N by mineralization and nitrification with microorganisms, causing the NO_3^--N and NO_2^--N pollution of groundwater. If the groundwater is in a reducing environment, NO_3^--N will be transformed into N_2O and N_2 and attenuated to a large extent.

6. Conclusions

Groundwater inorganic nitrogen and topsoil total nitrogen were analyzed in the Puyang irrigation area of Sanjiang Plain, and a pollution source investigation was conducted to identify the sources, influencing factors, and formation process of inorganic nitrogen pollution in regional shallow groundwater. In the study area, the potential nitrogen sources are fertilizer, manure, rural domestic waste, and septic system leakage, while atmospheric nitrogen deposition was not considered in this study. For all of the land use types evaluated, the land use types could be reclassified into two groups, with one including concentrated residential land, warehouse, and vegetation field and the other including paddy field, decentralized residential land, and livestock farm. These groups were determined by the distribution characteristic of inorganic nitrogen, where the former might have higher NO_3^- and lower NH_4^+ concentration than the latter. As for the well depth, the concentration of NH_4^+ in WO_{20} was found to significantly higher than that in WU_{20} by Mann-Whitney U test. The opposite relationship was found for NO_3^-.

The results of multivariate statistical analysis showed that the land use type, well depth, NO_2^- concentration, Eh, and EC were highly related to the NO_3^- pollution, and the high concentration of NO_3^- was likely to be found in vegetation field and concentrated residential land and was associated with an oxidizing environment; the NH_4^+ pollution had the strongest correlation with DO and Eh, and the reducing environment, decentralized residential land, and paddy field had more potential to impose NH_4^+ pollution. These results highlight that the nitrogen sources and the redox environment determine the distribution of NO_3^- and the redox environment governs the distribution of NH_4^+ in the shallow groundwater of the irrigation area.

The NH_4^+ pollution area was mainly distributed in the northwest of the area, where the fertilizer application rate was much higher and the highest value of topsoil TN was found, supporting the conclusion drawn from multivariate statistical analysis that the NH_4^+ in groundwater originated from fertilizer. As for the high concentration of NO_3^- in groundwater, which was mainly situated around the densely populated villages and towns and was relevant to the TN value of nearby topsoil, this was thought to come from manure and domestic waste.

The formation process of inorganic nitrogen pollution in shallow groundwater of the area can be summarized as follows: (1) the NH_4^+ from fertilizer was greatly attenuated by volatilization, plant uptake, and soil matter absorption and then accumulated in a reducing aquifer or was transformed into NO_3^- and NO_2^- by nitrification in an oxidizing aquifer with microorganisms; (2) the organic nitrogen and NO_3^- in manure and domestic waste were leached, losing little on the surface, to the vadose zone, where they remained steady as NO_3^--N in the oxidizing groundwater or were attenuated by microorganism-caused denitrification in the reducing groundwater.

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